THE VOLATILE OILS

BY

E. GILDEMEISTER AND FR. HOFFMANN.

SECOND EDITION

BY

E. GILDEMEISTER.

Written under the auspices of the firm of

SCHIMMEL & CO., MILTITZ NEAR LEIPZIG.

Authorized translation by

EDWARD KREMERS

MADISON, WIS.

FIRST VOLUME.

WITH TWO MAPS AND NUMEROUS ILLUSTRATIONS.

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PREFACE TO THE SECOND EDITION.

Eleven years have passed since the publication of the first edition. During this period enormous progress has been made, scientifically as well as practically, in the realm of the volatile oils. Numerous investigations have increased and broadened our knowledge of the volatile oils. The composition of a considerable number of volatile oils, heretofore unknown, has been revealed. New chemical compounds, the presence of which in volatile oils had, previously, not been established, have been found therein. The industry has not hesitated to utilize the results of these investigations. It has applied them to the methods of testing volatile oils and has improved these methods. The distillation of new volatile oils has greatly added to their number. All of these causes, as well as the circumstance that the first edition has been exhausted since several years, have induced me to begin work on a second edition.

Inasmuch as the material had grown too voluminous to be included within one volume, the book now appears in two volumes.

The first volume, now completed, contains the historical part, including the history of the several oils. This part had been written for the first edition by the late Dr. Friedrich Hoffmann. It remains almost unchanged and has received only occasional supplements. In addition, the first volume also contains the description of the principal constituents of the volatile oils, as well as the methods of testing them.

A new chapter has been added on the "Production of flower perfumes by extraction, *enfleurage* and maceration". During the past decade these methods have acquired considerable importance, more particularly in Southern France. The chapter devoted to the "Theoretical basis for obtaining volatile oils by

steam distillation" has been omitted. Being of the greatest industrial importance, it was carefully revised and amplified by Dr. C. v. Rechenberg, and, inasmuch as other matters, not pertaining directly to volatile oils, had to be included in the treatise, it became so bulky as to necessitate a separate volume. This has already made its appearance under the title: "Theorie der Gewinnung und Trennung der ätherischen Öle durch Destillation (Grundzüge der allgemeinen Destillationslehre)."

For their co-operation in the chapter: "The principal constituents of the volatile oils," which includes the principal artificial perfumes, I am indebted to Dr. O. Wiegand, Dr. A. Reclaire, Dr. H. Köhler, and Dr. W. Müller. The chapter on "The examination of volatile oils" was revised by Dr. O. Wiegand. All of these gentlemen, as well as Dr. F. Rochussen, have assisted in reading proof.

The tables contained in the first edition have been expanded and a new one has been added. Using 1,5 g. of oil and a half normal potassium hydroxide solution, this table enables the analyst to read off directly the ester value, also the percentage of ester and alcohol, without any computation. A second copy of these tables has been added to the book in such a manner that they can be used separately in the laboratory.

In the second volume, which is to appear later, the individual volatile oils are to be dealt with.

MILTITZ near Leipzig, July 1910.

E. GILDEMEISTER.

PREFACE.

It is only within the last few decades that the former empiric manufacture of volatile oils has been placed on a scientific basis, which has enabled it to develop into an independent branch of chemical industry. During the period of transition in which this branch still finds itself, those factories which have done pioneer work, both scientifically and technically, as well as those which use the oils in various manufactures, are often compelled to suffer from the competition of inferior and adulterated products. As a matter of fact, the proper understanding of the estimation and appreciation of quality and purity of the much used volatile oils is not as common as is desirable for industry, commerce and the trades. The principal cause for this condition is the fact that the recent chemical investigations and their application to the arts have not yet been generally offered in suitable form.

The want of a work which from a modern standpoint treats in an exhaustive and critical manner the entire subject of volatile oils, has induced the firm of Schimmel & Co. of Leipzig to commission the authors with the preparation of a treatise that would meet the present demands. The successful completion of this task has been greatly facilitated by having placed at their disposal the observation records of many years of manufacturing on a large scale.

Special stress has been laid on the description of properties and on tried methods of testing the commercially more important oils. Thus the consumer is placed in a position to distinguish pure from adulterated oils, good oils from those of inferior quality. Inasmuch as rational methods of examination are dependent on a knowledge of the physical properties and chemical composition of the oils, it became necessary to discuss thoroughly the results

of the scientific investigations of the subject. Those investigations, however, that cannot claim permanent value, as well as antiquated methods, such as color reactions, etc., have not been included.

Fully realizing the importance of a historical basis for such a work, this has received special attention. Detailed references to the original sources enable the reader to make further investigations in this direction.

Although the aim and object of this book is primarily of a practical nature, the authors venture to hope that it also offers to the scientific investigator a complete summary, with numerous references to original literature, of everything that has been accomplished in this line.

The authors acknowledge with thanks the co-operation of Dr. C. von Rechenberg who wrote the chapter "Theoretical foundation for the preparation of volatile oils by steam distillation;" also of Dr. J. Helle who contributed "The more common constituents of volatile oils;" finally that of Dr. J. Bertram who kindly assisted in reading proof and who repeatedly made valuable suggestions.

With regard to the share in the work by the two authors whose names appear on the title page: the "Historical introduction," also everything that pertains to the history of the volatile oils and the raw materials, as well as the description of the methods of production of the American products, and in part the statements regarding origin and production of the drugs, are from the pen of Dr. Friedrich Hoffmann; the entire chemical text and those parts not specially enumerated have been written by Dr. Eduard Gildemeister.

LEIPZIG and BERLIN, June 1899.

PREFACE TO THE AMERICAN EDITION.

In the work of Doctors Gildemeister and Hoffmann we find a happy blending of history with chemical science and technology that is quite unique in modern chemical literature. Moreover it covers a chapter of organic chemistry of which Professor Emil Fischer of Berlin recently remarked that it had undergone more rapid development within the past fifteen years than any other.

The translation of such a work should indeed prove of value. To make such a translation and to take cognizance of the numerous contributions on volatile oils and related subjects that have appeared since the original German edition was issued a year ago, has proved a severe task for one whose time was already divided between instructional duties and editorial labors. In judging the English edition, it is hoped that the limitations as to time and the difficulties encountered will be taken into consideration.

Owing to the impossibility of satisfactorily translating many of the numerous quotations in the historical introduction, chapters two and three have been condensed. Inasmuch as but very few if any readers are in a position to consult the numerous historical works quoted by Dr. Hoffmann, all bibliographic information has been placed in an appendix.

To the special part a few oils were added, and changes rendered necessary by recent investigations were made as far as time permitted.

The writer desires to acknowledge with thanks his indebtedness to Mr. Carl Fritzsche and to Dr. Hoffmann for suggestions, as to the scope of the translation and as to minor details. Mr. O. Schreiner has assisted in the translation and proof reading and Dr. C. Kleber of Garfield, N. J., has kindly read one proof. His long experience as chemical expert on the subject of volatile oils rendered his co-operation especially valuable.

MADISON, WIS., July 1900.

EDWARD KREMERS.

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ERRATA.

p. 25, line 1. Read Attafir for Attafin.
p. 76, line 13. Insert between "discovery" and "of" the following words: of the elementary composition of water by Cavendish about 1766 and
p. 111, line 13. Hyphenate the word Card-ammomum.
p. 115, after last line insert: Rheede also described pepper oil in 1688[7]).
p. 116, second last line, Read Masudi for Madusi.
p. 121, line 19. Read Redi for Redis.
p. 130, line 11. Read *medico-physica* for *medico-chymica.*
p. 134, line 7. Read Guibourt for Guibort.
p. 140, line 3. Read VII. for III.
p. 144, line 8. Read Charlard for Charland.
p. 146, line 15. Read Gerhardt for Gerhard.
p. 148, 3rd line from below. Read Edrisi for Idrisi.
p. 170, lines 4, 5 and 12. Read parsley for celery.
p. 171, line 1. Read parsley for celery.
p. 177, line 8. Read Engelbert for Adalbert.
p. 179, line 15. Read Uschak for Uschaq.
p. 188, line 7. Read Begninus for Begnini.
p. 249, line 26. Read lighter for ligther.
p. 474, The account under dihydrocuminic alcohol should be supplemented by the following statement: Its naphthyl urethane is a solid compound that melts between 140 and 174°. (Report of Schimmel & Co., Oct. 1906, 40.)
p. 412, line 15. Read pyroracemic acid for pyruvic acid.
p. 443, line 7. Read Beyer for Baeyer.
p. 457, 7th line from below. Read benzoate for succinate.
p. 521, line 17. For *imperialis* read *imperiale.*

HISTORICAL INTRODUCTION

I. THE SPICE-TRADE IN ANTIQUITY AND DURING THE MIDDLE AGES.

(With two maps.)

Parts of plants as well as natural plant products which have been used since antiquity on account of their agreeable odor, their pleasant taste, or their medicinal virtue, enter the world's commerce up to the present time in their original form, being either previously dried, or prepared in some other expedient manner. The essential constituents of these crude materials (drugs), the aromatic volatile oils, the resins, gum resins, bitter principles, alkaloids, and glucosides, have been recognized in the course of the development of the natural sciences. With the improvements in technology they have gradually been prepared in a purer and better condition.

Of these various products of the plant world, the spices and aromatics have from the very beginning ministered to the needs and welfare of man, and have, therefore, been appreciated by him in a special degree. As a result, they have always been a prominent and influential factor in the intercourse of nations as well as in the world's commerce. After several thousand years of knowledge and actual use of the spices in their original form, their essential constituents, the volatile oils, have since the middle ages and more particularly in modern times been successfully isolated and utilized.

In a treatise on volatile oils, a brief historical retrospect of the origin of and commerce in the bearers of these products, viz. the spices and aromatics, may be regarded as eminently proper. This all the more, since in this branch of knowledge as well as in others the historical element constitutes a valuable basis for a proper understanding and investigation.

All investigation in the realm of the history of civilization, that considers not merely a single people but mankind in general, and that goes back to the earliest historic documents, invariably leads to the wonderful orient so rich in legends—to central Asia, the traditional cradle of mankind. This is also true of the history of the trade of the oldest peoples, and especially of the source and distribution of the useful spices and aromatics.

Its geographical position and topographical configuration make Asia a very highly favored continent. Broad as it is, it extends from pole to equator. Favored by mighty mountain chains and rivers, its most beautiful and richest countries lie in latitudes where soil and climate afford all conditions favourable to luxuriant subtropical vegetation. The eastern and southern coastlands are cleft by large bays which penetrate far inland. Many navigable rivers which flow into these bays have their origin in distant highlands. The mainland is bordered by a wreath of islands extending from the Japanese island realm through the Malay archipelago to Ceylon. These islands abound in tropical vegetation. The entire continent, therefore, reveals a diversity and richness of plant life such as no other possesses.

These advantages have made southern Asia and the islands bordering on its coast the oldest and principal scene of international traffic and commerce, spices and aromatics constituting the main articles of exchange. They not only found general use on account of their agreeable odor and aromatic taste, but were employed by most peoples in religious rites and sacrificial customs, and thus acquired symbolic meaning. With the increase of prosperity and luxury, also with the development of the sense of cleanliness and of physical wellbeing, spices and aromatics not only became more valuable, but their consumption increased.

According to documents discovered in recent years, the territory between the Indus and the Oxus was the starting point of the early commerce between the oldest peoples of central and southern Asia. Attock, Cabura, Bactra, and Maracanda seem to have been the first larger centres for storage and exchange of oriental products. These consisted of spices and aromatics, the noble metals, silk, and jewelry. To Attock were brought the products of the eastern Chinese empire, which, at an early date, closed its markets to the rest of the world.

From Attock, at the junction of the Kabul river with the Indus, the caravan road led via Cabura (the present capital Kabul of Afghanistan) to the north via Bactra, Bochara, and Maracanda (Samarkand) to the countries of the Oxus and to the Scythian tribes. Also from Cabura southward to Kandahar, thence in a western direction through the realm of the Parthians to the *Pylæ Caspiæ* (Caspian gate), and to Ecbatana in Media. Thence the land route crossed the Tigris to Babylon on the Euphrates. In a later period, after the traffic along the water routes had developed, a round-about way via Susa to the mouth of the Tigris was taken and the caravan freight shipped up the Euphrates to Babylon. Between Attock and the ports on the Black and Mediterranean seas, Babylon—existing 3000 years B. C. — was in early antiquity the most important place of traffic and commerce for westward bound Chinese and Indian merchandise. To the northward the caravan roads led out of Babylon through Assyria and Armenia to the Black sea *(Pontus Euxinus)* and westward through Syria to the Mediterranean sea *(Mare Internum)*, thence through Palestine to Egypt. In spite of their highly developed industry the Egyptians, as is well known, closed their doors to foreign peoples as did the Chinese. As a result commercial centres were wanting in Egypt that were open to foreign merchants and to transitory commerce.

During the prime of the Babylonian empire, about 2000 to 1000 B. C., a lively caravan trade was developed which extended from China, India and Arabia to Egypt, Palestine, Syria, and the Black sea.

During this period, Arabia acquired special importance by means of the sea traffic of her southern coast, which was favored by the Persian gulf and the Red sea. At an early date, the Arabian population conducted a lively intermediate trade with Indian and Egyptian goods which were brought to the Arabian ports. By means of caravans these were carried northward to Babylonia, Syria, and other countries. The principal route from southwestern Arabia to Babylon, Damascus and Egypt led from Cane on the Arabian gulf (Erythraean sea) via Saba, Macoraba, Hippos, and Onne to Elath (the present Akabah) at the northeastern end of the Red sea. From this point the eastern route crossed the Jordan via Petra, Kir Moab, Ammonitis and Dan to

Damascus; the western route to Egypt via Azab, Axomis, and Meroë.

About 15 centuries before the Christian era, the world's commerce was gradually and, in the course of time, very greatly expanded by the Phoenicians, who lived on the narrow Syrian coast district. In the industrial and commercial field they acquired a prominent position; as mariners, however, a dominating position among the nations of their time. Besides having practical control of sea navigation, the Phoenicians were the first extensive and successful colonizing nation of antiquity. They established or extended commerce with the peoples living along the coast of the Mediterranean, they ventured through the "Pillars of Hercules" (Gibraltar) into the ocean and made accessible the products of the Madeira and Canary islands, the western coasts of Spain and France, the British islands, and the northland as far as the amber coasts of the Baltic sea.

For almost a thousand years, during which time they held their prominent position in marine traffic, the Phœnicians were the principal commercial agents between the nations of the orient and the occident. Sidon and, since the ninth century B. C., Tyre became prominent centres of the world's commerce of that time.[1])

The Phœnicians also extended their navigation to the Red sea and the Arabian gulf and from these to the Persian gulf. In the latter they established the colonies on Arados and Tylos, islands belonging to the present Bahrein group. From the twelfth century up to their decline in the fifth century B. C., these cities carried on a large transit-trade with goods from India and Ceylon to Babylon, Damascus, Tyre and Sidon, and to Egypt. A caravan route led from Gerra via Salma, Thæma and Madiana to Elath. From Elath the older routes to the north, to Damascus, Tyre and Sidon were followed, also westward to Egypt. To Babylon, on the other hand, the water route up the Euphrates or Tigris was taken from Arados and Tylos.

Carthage, a Phœnician colony established in 846 B. C., soon flourished and developed such power that it became the greatest rival of the mother country in the following century.

[1]) As is well known, the Phœnicians supplied King Solomon with the material for the building of the temple at Jerusalem about 1000 B. C. (1. Kings, 5, 9 and 10; also 2. Chron., 2 and 9).

THE HIGHWAYS OF COMMERCE IN ANCIENT TIMES.

(Spicery and Grocery Trades in Ancient Times and in the Middle Ages.)

Bearbeitet v. Dr. Fr. Hoffmann.

Druck v. Rud. Loës, Leipzig.

Owing to the rise of the Persian empire, the inland commerce of western Asia was somewhat shifted during the period from the sixth to the fourth century B. C. The old routes of traffic passing through countries controlled by the Persians were not only kept in good condition but extensions were also made. These old highways of transcontinental commerce underwent further changes at the time of the Greek conquests under Alexander the Great at the close of the fourth century B. C. Still greater, however, were the changes brought about by the migration of nations during the fourth and fifth centuries of the Christian era. Wars and other disturbances of the commercial intercourse along the old caravan routes frequently restricted traffic to the rivers and seas. Upon the re-establishment of peace, however, commerce always seems to have found its way back to the traditional caravan routes.

In the course of time, however, and especially during the sixth and seventh centuries still other changes took place. Thus, e. g. the products of the Chinese and Indian coast districts and of the Indian islands were brought in part by ship over the Bay of Bengal and by way of Ceylon to the commercial centres of the Persian gulf and the Red sea. From these they were distributed by coast-wise trade, by river navigation up the Tigris and Euphrates, or by caravans to the north and west. From the more northern Chinese and Indian districts the caravans passed through the present East-Turkestan following the older routes mentioned on p. 8 and 9 through the countries of the Oxus to the Araxes. The goods, instead of being carried by river to Phasis and the Black sea, were taken as far as Artaxata and then by caravan through Persia to the ports of Asia Minor. The old route from Kandahar along the northern border of the Iranian plateau, which likewise led through Persian territory, was also followed by caravans.

During the reign of the East Roman emperor Justinian, in the sixth century, when the world empire of the Romans was broken up by the migration of nations, Persia experienced a new rise to power under the Sassanidæ. The Persians ruled the entire territory from the Caspian to the Arabian seas and from Afghanistan of to-day to Syria and Armenia. They improved the old high-ways and caravansaries, kept them in repair and

promoted commerce and traffic, directing both over routes leading through their own territory. Owing to the wealth and luxury of the Roman empire, the commerce in oriental spices had risen to an unusual height. The East Roman empire which at that time was the principal western state with its capital at Constantinople, was forced by the Persians to procure such oriental goods as were not shipped by water, from and through Persia and to pay a heavy duty on them. The principal places of storage and for the collection of revenue at that time were Artaxata on the Araxes, Nisibis, south of the Tigris, and Callinicum (Rakka) on the Euphrates. To Artaxata were brought the goods from the countries of the Oxus over the Caspian sea. Those that were conveyed along the caravan routes south of the Caspian sea, and those that came from the coastlands of the Persian bay up the Tigris or Euphrates centered at Nisibis. For nearly five centuries, the aromatics of China and India, of the Malayan archipelago which came via Ceylon, and in part those of Arabia were transported over the two last-mentioned routes to the western countries. About this time also, the Levant commerce, which became so important in a future period, had its beginning.

During the life of the Persian empire (up to the middle of the seventh century A. D.) all attempts, made by Justinian and his successors, to divert the commerce from its course through Persian territory by means of marine transportation remained unsuccessful. They did not even succeed in opening up marine traffic between India and Ethiopia, because Persian merchants visited the Indian markets and persuaded the Indians and Chinese not to sell their goods to new customers. In the course of time, however, the Greeks succeeded in obtaining larger consignments by water from the ports of India and Ceylon and more particularly from the coastlands of the Arabian sea, which were rich in spices. These were delivered directly to their own ports, Kolsum, and Akabah and Berenice near the entrance to the Red sea.

About this time there existed three great caravan routes from China westward. They began in the territory of the Hoang Ho and the Yangtsekiang and passed through the Gobi desert. The northern route took its course through the oasis of Chami,

then northward along the Thian-Shan mountains through the present Dsungarai, past the Balkash sea, and via Talas. It then followed the Syr-Darya river to the Aral sea and the Caspian sea.

The middle route passed to the south of the Thian-Shan mountains through the northern part of East Turkestan via Chami, Turfan, Karashar, Kutsha, and Aksu to Kashgar; thence over the Terek pass to Ferghana via Samarkand, Buchara and Merv to Persia.

From the Gobi desert, the southern route passed through the southern part of East Turkestan via Chotan and Yarkand, then over the Pamir plateau and through Afghanistan to the Punjab (India) crossing the Bamian and Gazna passes to Multan. Goods intended for the west, coming via this route, were taken down the Indus river to Daybal. From this port they were shipped by sea with other goods from India and Ceylon.

During the seventh and eighth centuries A. D. the Arabs carried on an extensive marine commerce with India and China, especially in spices and aromatics. These were supplied in large quantities to the luxurious courts of the caliphs and the Byzantine emperors. The principal centres between China and Arabia were at that time on the Malay peninsula, to which were also brought the products of Java and other Sunda islands. Later on commerce concentrated itself in Kalah, a city on the east shore of the Malay peninsula. In the tenth century there existed between Kalah and Siraf, a city on the east coast of the Persian gulf, regular commercial intercourse between the Arabians and Chinese. From the northern point of Sumatra the Chinese crossed the bay of Bengal to Ceylon.

Arabian merchants also settled along the Malabar coast, in Ceylon and in the Indian sea ports. From the eighth to the tenth century, Daybal at the mouth of the Indus was the important commercial centre and seaport of India. It was the principal emporium for the products of the Indus valley and the Punjab on the one side and of Mesopotamia, Persia and Arabia on the other. For the products of northern India, Multan on the Djelam river in the Punjab, was the first larger rallying point. It was also a place of pilgrimage that was much revered and visited by the Hindoos.

From the eighth century on, Suhar and Muscat, near the entrance of the Persian bay, developed as rival ports for Indian and Chinese commerce with occidental countries. At the same time Aden, at the entrance to the Red sea, became the principal port and commercial entre for the products from Yemen, Hedsjaz, Ethiopia and Egypt.

In addition there were caravan routes: one from India to Persia through Seistan; the other via Gazna and Kabul to Afghanistan.

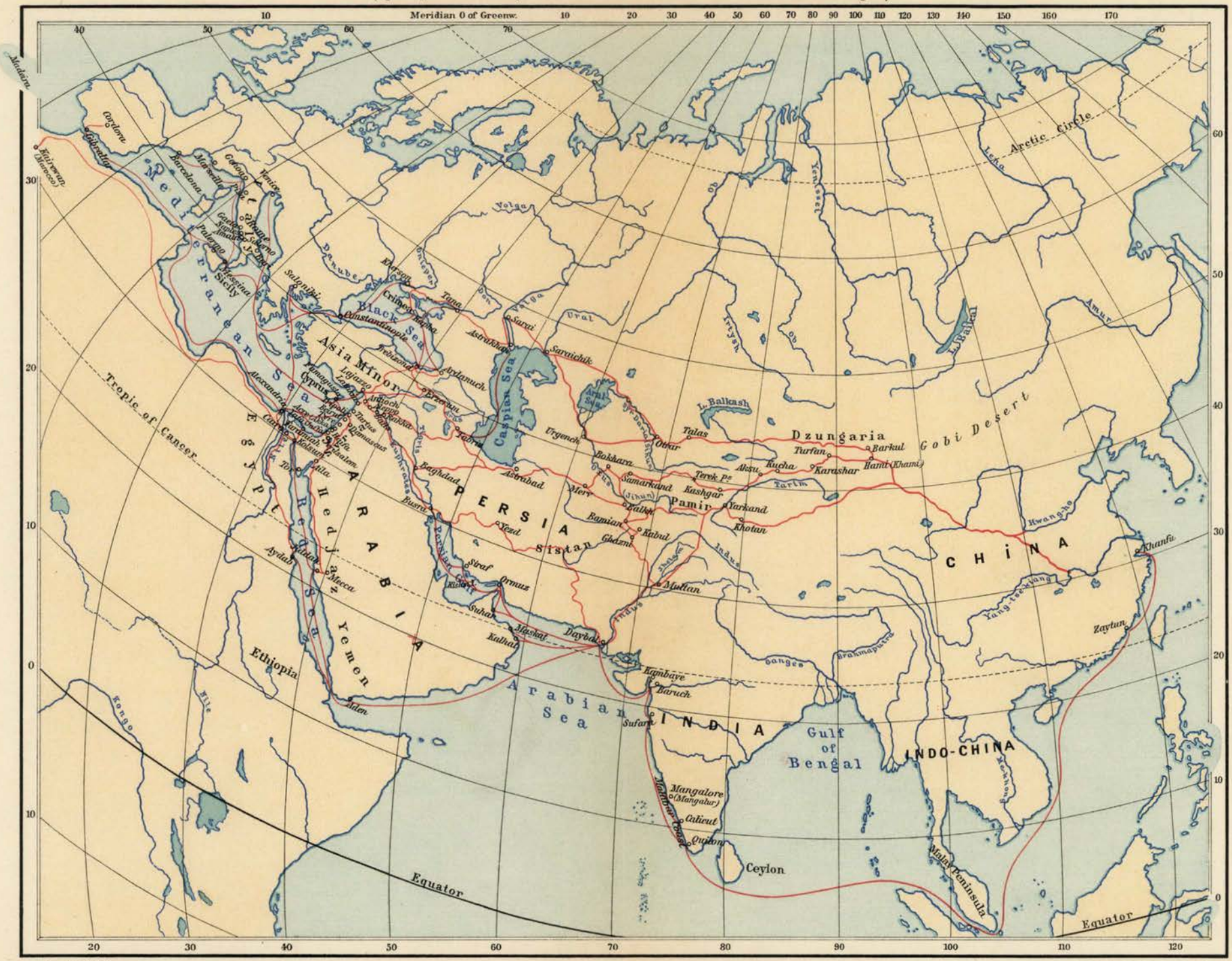
Seti I. and Rameses II., Egyptian pharaohs, had during the first quarter of the fourteenth century B. C. connected the Red sea with the Mediterranean sea. In order to re-establish this sea-route, Pharaoh Necho toward the end of the seventh century B. C. tried to have a new canal constructed from Bubastis on the Nile to Patumos on the Red sea. This was not completed, however, until 500 B. C. by Darius Hystaspes and was widened and improved by the Ptolemies. Before the beginning of the Christian era it was again choked up with sand. Under the caliph Omar in the seventh century A. D. the canal from Cairo to the Red sea was again restored, but did not exist longer than a century.

From the seventh to the twelfth century there also existed several land routes across the Suez isthmus. One of these followed the course of the old canal (choked up with sand) from the Red sea to Cairo, whence the goods were shipped down the Nile and then by sea. If the passage of the goods through Alexandria was not necessary, the shorter route over the isthmus from Kolsum to Pelusium (Faramiah), was preferred. At this time Damascus and Jerusalem were also important commercial centres. Here also oriental goods were exchanged by the merchants of Mecca on the one hand and those of Tripoli, Beirut, Tyre and Acre on the other.

From the seventh to the twelfth century there existed an active coastwise trade along the north African coast, having its centres in Syria and Egypt and extending as far as Morrocco and Spain. This commerce acquired a special importance for spices and aromatics although for a time it was limited by Mohammedan laws against intercourse with Christians. Commerce also soon flourished among the Greeks, who obtained spices and aromatics, possibly also rose water and aromatized fatty

THE HIGHWAYS OF COMMERCE IN THE MIDDLE AGES.

(Spicery and Grocery Trades in Ancient Times and in the Middle Ages.)



Dr. Fr. Hoffmann.

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oils from Antioch, Alexandria and Trapezunt and brought them to Constantinople, Thessalonica and Cherson. Already in the tenth century Trapezunt was an important emporium for the drugs of India and Arabia and for Persian perfumes. The Greeks, however, purchased these luxuries only for home consumption, which was large, without distributing them farther to other nations.

From the tenth to the fifteenth centuries, the commerce of the Mediterranean was conducted principally by Italian cities. In the tenth and eleventh centuries Bari, Salerno, Naples, Gaëta, and above all Amalfi, Pisa and Venice were the principal commercial centres. The Levant commerce, which was in its prime from the twelfth to the fifteenth century centered in Venice and Genoa. In the Levant itself, at the time of the crusades during the twelfth and thirteenth centuries, Acre on the Palestine coast was the most important commercial port. When this city, the last one held by the Christians, likewise fell into the hands of the Mohammedans in 1291, Famagusta on Cyprus, and, for a longer period, Lajazza on the bay of Alexandretta, became the commercial centres of the Levant up to the fifteenth century. The latter port was the junction for the western merchants with those coming from Asia.

Toward the end of the thirteenth century, the cities of Bagdad and Basra on the Euphrates, lost their commercial supremacy which they held for several centuries to Tebriz, the new rising capital of Persia near the Caspian sea. When Egypt in the thirteenth and fourteenth centuries began to levy a high toll on the finer Indian spices and aromatics, the land transportation was deviated more and more through Persia via Bagdad and Tebriz to Lajazzo and Trapezunt.

During the fourteenth century, the island port Ormuz in the Persian gulf became an emporium for the westward-bound goods from India and Ceylon. It maintained this position until its capture by the Portugese at the beginning of the sixteenth century. The more important ports along the western coast of India at that time were Mangalore, Calicut and Quilon. Ginger, cinnamon, cardamoms, pepper, cloves, nutmegs, sandalwood, lignaloes, indigo, etc., were brought to these ports from the interior. From the Chinese ports and the East Indian islands large importations of these and similar drugs were received.

Toward the close of the thirteenth and at the beginning of the fourteenth century the direct traffic between Europe and China became very active, more particularly over the land route. Under the protection of the Mongols the caravan routes through central Asia were generally safe. The greater part of the Chinese empire was also accessible to Europeans. About this time also Marco Polo, the first European world-traveler, visited China, India and the islands of the Indian ocean.

Owing to disturbances and invasions of central Asia, the overland traffic diminished after the middle of the fourteenth century. Up to the discovery of the sea route around Africa at the close of the fifteenth century, Tebriz, however, remained an important centre for transitory trade. The capture of Constantinople by the Turks in 1453 enabled them to interrupt the trade of the Italians via Trapezunt and the Crimea and soon to cut it off altogether. About this time Cyprus also lost its former importance for the Levant trade.

Egyptian commerce, however, once more increased considerably toward the close of the fourteenth and in the course of the fifteenth century. In place of Aden, Djidda, the sea-port of Mecca, became the principal junction of commerce between the Indian seas and the occident. The heavier goods were transported by water, the lighter by pilgrim caravans to Tor on the Sinai peninsula. The high toll levied by the Egyptians caused some of this trade to be deviated for the time being to Syria. Owing to the occupation of Lajazzo by the Turks in 1347, and the conquest of the Crimea in the fifteenth century, this traffic continued to develop for a short time.

Thus in the course of several thousand years, the commercial intercourse between the nations of Asia, later also those of Africa and of Europe underwent a variety of changes as did also the various routes of traffic. The circumnavigation of Africa by the Portugese in 1498, their conquest of Ormuz, the key to the Persian gulf, and their extended marine traffic brought about important changes in the traditional channels of traffic. The transport by means of caravans was gradually diminished; the highways, formerly well kept, got out of repair, the ocean ship displaced the "ship of the desert", the camel of the caravans.

From the sixteenth century on, the ocean became the preferred highway of international commerce. Hence the Levant commerce, which had flourished for several centuries and had enriched the commercial centres of Italy and of other Mediterranean countries, lost its importance.

Numerous ruins of magnificent buildings in cities and markets, well built high-ways covered with the sand of centuries, also caravansaries on the plateau and desert lands of western Asia and the Arabian peninsula reveal to these after-days the former greatness and the commercial prosperity of peoples who still live in history but principally in name only.

The spices and aromatics of southern Asia and the Asiatic islands, which constituted the first foundation of international commerce have retained their original value in spite of all changes in the world's history. The same spicy cinnamon, cloves, nutmegs and cardamoms, pepper and ginger and other spices used and highly appreciated since antiquity; frankincense and myrrh, benzoin and other incenses, camphor, sandalwood and lignaloes and other plant products acquiring use in ever increasing numbers thrive after thousands of years in the sunny countries and islands of the orient in primeval profusion.

However, they are no longer brought to the occident on the backs of camels over the plateaus and deserts of Asia, but in trim sailing vessels and speedy steamships crossing the ocean; or they are transported in freight cars that hasten over steel tracks encircling the continents. They are used up to this day, in the humble hut as well as in the palace of the rich, either in their original state, or in a concentrated form, purified by the giant stills of modern chemical industry.

II. GENERAL HISTORY OF THE VOLATILE OILS.

In the course of centuries various more or less independent branches have separated from the common trunk of natural science and have made a history of their own. This is true of the subject presented in this treatise. To be sure a fairly exact knowledge of those plant products, which are termed volatile oils, has been gained only in recent periods. Nevertheless the nature and value of these substances does not appear to have escaped the observation of the oldest peoples. It seems almost certain that not only the grace and vivid coloring of the flowers but also the fragrance of the vegetation in southern Asia must have aroused the curiosity of man, fully as much as did the utilization of the plants for the purpose of food and clothing. Indeed, those plants and plant products that were conspicuous on account of their aromatic odor and taste, seem to have attracted the attention of man in a special degree. These very properties seem to have induced him to use them and to seek proper methods for their cultivation and preservation.

It is true that the oldest documents pertaining to the history of the beginning of human industry have recorded only the most primitive methods for the preparation of implements that were used in the chase, the cultvation of the soil, and for the collection and preparation of foodstuffs and other useful products. Nevertheless it may not be amiss to suppose that the exigencies of self-preservation and of wellbeing at an early period caused man to utilize fire not only for the preparation of foodstuffs but for various other purposes. It may have required long periods of time before fire was used for the preservation of perishable foodstuffs, for the separation of pleasant substances from dis-

agreeable ones: so, e. g., the distillation of the "spirit of wine" from the wine itself; the separation of the "subtle principle", the aroma, from spices which were among the earliest articles of barter and commerce during antiquity; and which as products of nature agreeable to the gods, were offered as sacrifices in religious ceremonies, and were also used in the embalming of the dead.

It is especially this use of spices and of aromatic plant products by the priests, those promotors and supporters of natural science during antiquity, that renders it probable that their knowledge was early applied to the production, and preparation of the spices which were used in the sacrifices and in embalming. Whether a beginning in the preparation of the aromatic principles of plants, our modern volatile oils, was made previous to early Hindoo and Egyptian civilization, does not become apparent from the oldest documents. Even the Bible, which gives so much information concerning the customs of the Jews, makes no other statements than those pertaining to the spices and aromatics used in various countries. The early preparation and utilization of the more common metals would indicate that furnaces and other apparatus for heating were used in a variety of ways. One may suppose, therefore, that they were gradually used in primitive attempts to separate the spirit from wine, from other fermented fruit juices and honey; also the aromatic principles from spices, balsams and oleoresins. These crude experiments may be considered as constituting the first stages in the art of distillation.

The Egyptians, owing to the continuity of their early and highly developed civilization and to the preservation of their monuments and literary productions, are generally considered as standing at the portals of history. With reference to time, however, the Chinese and Aryans are probably the oldest peoples. These races, with whom civilization seems to have had its beginning, lived in central and southern Asia, a mountainous district favored with a mild climate and a luxuriant vegetation rich in useful and spicy products. Our knowledge of the peoples who first occupied this wide territory is but legendary. Concerning their industrial and technical accomplishments but little definite information has come down to us. These Chinese and

Indians may have developed considerable dexterity in industrial pursuits and may even have accomplished much in the scientific realm. Their attitude of exclusiveness, however, toward the outside world and their secrecy have prevented them from exerting a lasting influence on other nations. The oldest documents that throw light on their early scientific accomplishments are the Ayur-Veda (Book of the Science of Life) by Charaka and Susruta.[1]) As is the case with so many writings of early antiquity, nothing definite is known with regard to the age of these documents. It is possible that they are traditions reduced to writing at a rather late time.[2]) From this work it becomes apparent that the Indians were acquainted with primitive apparatus for distillation, with fermentation and the products obtained by distillation. Of "distilled oils", those of rose, schœnus (andropogon), and calamus are mentioned.[3]) Whether these oils are "distilled" in the modern sense of this term can not be ascertained.

From documents of the old Persians it would seem that they also were acquainted with the process of distillation and hence with distilling apparatus.[4])

With regard to the Egyptians, however, whose history goes back as far as 4000 B. C., we have definite information concerning the early development of industry, art, and science. Their commerce, which extended as far as India, Babylonia,

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[1]) Susruta's *Ayur-vedas, id est medicinæ systema a venerabili D'hanvantare demonstratum a* Susruta *discipulo compositum. Nunc primum ex Sanscrita in Latinum sermonem vertit, introductionem, annotationes et rerum indicem adjecit* Dr. Fr. Hessler, Erlangæ 1844.

The Susruta, or System of medicine, taught by *Dhanvantari* and composed by his disciple Susruta. Published by Sri Madhusudana-Gupta, Prof. fo medicine at the Sanscrit College at Calcutta. Calcutta 1835. 2 Vol.

[2]) Lassen, *Indische Altertumskunde.* 1. ed., vol. 2, 551.

J. F. Royle, An essay on the antiquity of Hindoo medicine. London 1837. Wallach and Heusinger, *Das Altertum der indischen Medizin.* Kassel 1839. p. 45.

Allan Webb, The historical relations of ancient Hindoo with Greek medicine. Calcutta 1850. p. 45.

Zeitschrift der Deutsch. Morgenländ. Gesellsch. **30** (1876), 617 and **31** (1877), 647.

[3]) Susruta's *Ayur-vedas.* Editio Hessler. Erlangæ 1844. p. 111 and 130.

[4]) Gebri *De alchemia libri tres.* Argentorati arte et impensa Io. Grieningeri anno 1529.

Chr. G. Schmieder, *Geschichte der Alchemie.* Halle 1832. p. 34.

Syria, Ethiopia and other countries, as well as their industry and art undoubtedly developed slowly before it reached that height which we now admire. Thus, they were acquainted with the preparation of the metals, with furnaces and distilling apparatus, with the distillation of wine, and of the oleoresin of cedar;[1]) with the preparation of soda, alum, vinegar,[2]) soap, leather; also with the preparation and use of colors and the manufacture of glass. The Egyptians used cedar (turpentine) oil[3]) and colophonium,[4]) and probably knew how to isolate plant aromas as distilled oils.

The height which Egyptian civilization reached is revealed better by their architectural monuments, mummies found in the pyramids, and by the products of artistic workmanship, than by the few written documents that have come down to us. Likewise in the building of ships and in their commerce with neighboring countries the Egyptians accomplished much.

Like their writings, many of their arts and crafts were lost at least in part to the civilized nations succeeding them and had to be rediscovered. In judging the relationship between their scientific knowledge and their accomplishments in the arts and crafts, it should be remembered that the manufacture of metals, of glass, and even dyeing were based on a rather crude empiricism and seem to have been almost wholly independent of the theoretical consideration of the age. Thus, with but little scientific knowledge of permanent value, these most ancient peoples, the Hindoos, Egyptians, Assyrians, Babylonians and Phœnicians, like the Chinese, who stand at the dawn of civilization, have in the

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[1]) Aetii medici græci *Ex veteribus medicinæ tetrabiblos.* Editio Aldina. Veneti 1547. fol. 10.

[2]) Numbers, 6 : 3.

[3]) Herodoti *Historiæ* II. 85.

Pedanii Dioscoridis Anazarbei *De materia medica libri quinque.* Editio Kühn-Sprengel. Lipsiæ 1829. Lib. 1, cap. 34, 39, 80, 95, 97.

Plinii Secundi *Naturalis historiæ libri 37.* Liber 15, cap. 6 and 7, and liber 16, cap. 22.

Scribonii Largi *Compositiones medicamentorum.* Editio Schneider. p. 323.

Theophrasti Eresii *Opera, quæ supersunt omnia. Historia plantarum.* Editio Wimmer. Parisii 1866. Liber 9, cap. 3.

[4]) Pedanii Dioscoridis Anazarbei *De materia medica libri quinque.* Editio Kühn-Sprengel. Lipsiæ 1829. Vol. 1, p. 660 and vol. 2, p. 639.

course of centuries of development accomplished much in a practical way. They, and among them the Egyptians more particularly, served as the teachers of the classical nations of Greece and Rome.

The scientific knowledge as well as the industrial and artistic accomplishments of the Hebrews and the Greeks, and indirectly also of the Romans, had their root in Egyptian civilization. However, the Greeks, like the Hebrews, tended toward the ideal rather than the practical in their conception of Nature. They did not experiment and were not bent on applying their scientific knowledge. The Greek philosophers and writers collected and systematized the information that had come down to them and thus aided in preserving it, without, however, putting it to practical use or adding anything new to it.

The Greeks, however, were well informed as to the Egyptian arts; they understood the preparation and working of the metals, the manufacture of glass, and other industrial arts. Their commerce, however, was mostly barter in natural products. The oriental spices were highly prized by them for incenses, cosmetic and sanitary purposes. Whether the primitive method of distillation practiced by the Egyptians and Persians was known to the Greeks does not appear from their literature. It is not improbable, however, for medicine and the use of cosmetics were hardly less thought of by the Greeks than by the Egyptians. Owing to the luxury of the later Greeks, perfumes and spices were extensively used. The much praised oriental perfumes, especially sandal wood (*ξύλα ἰνδικά*) were considered a necessity at all festivities. Hence the Greeks procured the aromatics known to them as articles of barter. In later periods, however, the procuring of these products like the sea traffic generally was left to other peoples.

At the time when Greek culture spread westward and became the basis of Roman civilization, Greek views concerning nature and Greek knowledge of it were likewise transmitted. In their numerous conquests, the Romans increased their knowledge of oriental natural products. These were brought by the old caravan routes and then by sea to Rome. Among them were the finest spices for the kitchen, perfumes and ointments for the toilet, balsams and incenses. Whether only aromatized fats, or distilled

oils as well, were used cannot be ascertained definitely from Roman literature. That the Romans themselves were adept in the preparation of toilet articles seems highly probable. That the natural sciences, including the science of drugs, were well cultivated is shown by the writings of Dioscorides,[1]) Pliny[2]) and Galen[3]).

[1]) Pedanius Dioscorides was the first important writer on the history of drugs during the Christian era. Born in Anazarbus, in the southeastern part of Asia minor, during the first century, he traveled in the capacity of a physician with the Roman armies through several countries. The Materia Medica, written by him in the second half of the first century, was the most thorough work of its kind during antiquity, and was regarded as authority far into the middle ages. Thus it was used for purpose of comment as late as the time of Luther, as is evidenced by the lectures of Melanchthon at the University of Wittenberg and by the writings of Valerius Cordus in the middle of the sixteenth century.

The principal works written by Dioscorides in the second half of the first century are the five books, of his *De materia medica,* also his *Alexipharmaca et theriaca* (Remedies against plant and animal poisons) which were edited as books 6 and 7. These and other more apocryphal writings have been republished frequently and in many languages. Among the oldest editions are the Arabic manuscript in the library at Leyden, which possibly was written about the year 940; a very rare Greek edition printed *apud* Aldum Manutium, Veneti 1499; also a Latin edition by J. Allemannum de Medemblich, printed in Colle 1503. Of the better translations and commentaries the following may be mentioned:

Pedanii Dioscoridis Anazarbensis *De materia medica libri quinque.* Jano Coronario medico physico interprete. Basiliae 1529.

Valerii Cordi Simesusii *Annotationes in* Pedanii Dioscoridis Anazarbei *De materia medica libros quinque, longe aliæ quam antea sunt hæc sunt emulgatæ. Ejusdem historia stirpium libri quatuor, et de artificiosis extractionibus liber* etc. Translatio Ruellii. Francofurti ad Mœnum 1549. Editio Gessnerii 1561.

Pedanii Dioscoridis Anazarbei *De medicinale materia medica libri sex,* Joanno Ruellio *Suessionensi interprete. Accesserunt priori editioni* Valerii Cordi Simesusii *Annotationes doctissimi* in Dioscoridis *de medica materia libros* Euricii Cordi *judicium de herbis et simplicibus medicinæ; ac eorum quæ apud medicos controverruntur explicatio.* Francofurti 1543.

Petri Andreæ Matthioli *Opera quæ extant omnia. Commentarii in sex libros* Pedacei Dioscoridis *de materia medica.* Veneti 1554.

Πεδανίου Διοσκορίδου Ἀναζαρβέως περὶ ὕλης ἰατρικῆς βιβλία, or: Pedacei Dioscoridis Anazarbei *Opera quæ extant omnia. Ex nova interpretatione.* Jani-Antonii Saraceni, Lugduni Medici, Francofurti 1578 und 1598.

A Latin translation of the *libri de materia medica* of Dioscorides had made its appearance as early as 1478 and a Greek edition appeared at about the same time in Cologne.

Although the Romans were good observers of natural objects and phenomena, and equally good compilers of the knowledge of their own period and of previous periods, they did not, in general, penetrate into the secrets of nature. Neither did they add much to the stock of knowledge handed down to them. The natural sciences and medicine were, therefore, but little advanced by them.

With the decay of Greek and Roman culture and the long night in the history of civilization that followed, many of the earlier achievements in the arts and crafts were lost. At the close of that period which we now designate as antiquity, birth was given to a new civilization. Strange as it may seem the Mohammedans were the forerunners of this new period although they are reported to have destroyed the transmitted treasures of art and literature in the belief that the Koran contained all human wisdom. The Arabians themselves, however, contributed but little to this Mohammedan period of civilization. This had its roots in the Alexandrian school, the spirit of which was imparted to the later conglomerate of Mohammedan peoples through the Syrians and Persians and their languages, also through the Greeks of Asia Minor. This Mohammedan empire, as it were, included practically all of the peoples subjugated during the eighth and ninth centuries. Westward it extended as far as the gates of Hercules, or Strait of Gibraltar; to the East as far as the sea of darkness, as the Arabs called the Indian Ocean. They succeeded in converting the subjugated peoples to the Mohammedan religion. In as much as the Koran was

A more recent edition of the Materia medica of Dioscorides, which was used in connection with this book, is the one edited by Professor Curtius Sprengel. It appeared in Leipzig in 1829 as a part of the Kuehn Collection, namely the *Medicorum græcorum Opera quæ extant,* of which it constitutes volume 25. Of the two parts the first contains the *De Materia medica libri quinque,* the second part *Liber de venenis eorumque precautione et medicamentione* (pp. 1—338) and *Commentarius in Dioscoridem* (pp. 340—675).

[2]) Plinii Secundi *Naturalis Historiæ libri* XXXVII. Recognovit atque indicibus instruxit Ludovicus Janus. Lipsiæ 1859.

Most of the references to Pliny made in this book refer to the two-volume-edition of Littré, Paris 1877.

[3]) Claudii Galeni *Opera omnia.* Editio Kuehn, in twenty volumes. Lipsiæ 1821—1833. Worthy of special mention among these are the *De simplicium medicamentorum temperaturis et facultatibus libri* XI.

not only the spiritual but also the legal codex, Arabic language and script passed from country to country. Hence it became the language, not only of the faithful, but of the intellectual world, occupying the position held later by the Latin language during the Christian middle age.

Permeated by the conceptions of the Alexandrian school, the Arabs revived the study of the natural sciences in the ninth century. Mathematics, astronomy and medicine were rapidly developed. With their tendency to faith in the miraculous, alchemy and magic developed with the natural sciences and played an important role in the theory of transmutation of the metals and in medicine. The philosopher's stone and a universal medicine, the faith in which permeated human society for centuries, were to banish all misery and disease from this world.

Above all it was Geber[1]) (Djabir), one of the most influential and prominent scholars of his time, who developed this theory and established a firm faith in it which lasted for centuries. During the period when Bagdad, Bassora and Damascus were the principal centres of commerce, no people was more skilled and more productive than the Arabians in the arts and trades and also in natural science. Their commercial relations extended to almost all known countries, and the use and knowledge of Eastern spices and aromatics was greatly fostered by them, as was also the practice of medicine.

With the development of the traditional knowledge, the Arabians also fostered the process of distillation in connection with the hermetic art[2]). As early as the fourth century, the

[1]) Gebri *Summa perfectionis magisterii.* Ex bibliotheca vaticana exemplari. Gedani 1682. Lib. IV. p. 156—178. — Alchemiæ Gebri Arabis libri excud. Joh. Petrius Nuerembergensis. Bernæ 1545. Lib. 2. cap. 12. — Torbert Bergmann, *De primordiis chemiæ.* Upsala 1779. § 3D and § 4C. Editio Hebenstreit. Lipsiæ 1787.

In addition to the works of Geber originally written in Arabian, a number of other works in Greek and Latin were until recently attributed to him. However, M. Berthelot has revealed the apocryphal character of these writings *(Introduction à l'étude de la chimie des anciens et du moyen-âge,* Paris 1889, also *Revue des deux mondes,* September 15. and October 1. 1893). Among these are the *Summa perfectionis magisterii* which appears not to have been written before the middle of the fourteenth century.

[2]) Hermannus Conringius, *De hermetica Aegyptiorum vetere et Paracelsiorum nova medicina libri duo.* Helmstedt 1648. Lib. II, cap. 4.

Greek scholars Synesios of Ptolomais [1]) and Zosimos of Panopolis [2]) had described the distilling apparatus and methods of the Egyptians. Aëtius of Amida, a physician and writer who lived in Constantinople during the beginning of the sixth century, also described the preparation of empyreumatic oils by downward distillation *(Destillatio per descensum)* [3]). This as well as the upward distillation *(Destillatio per ascensum)* are reported by Geber. According to Porta's *De destillatione* of 1567 [4]) and other writers of the sixteenth century the Arabian physicians and alchemists introduced the condensing tube *(Serpentina)* for the better cooling of the distillate, and a kind of fractionation for the distillation of wine [5]).

Through the Arabians the medical and alchemistic knowledge of their times, also the mysticism of the hermetic [6]) art were transmitted to southwestern Europe. They were most prominent in the establishment and advancement of the theory of the transmutation of the metals, a theory which held sway for many centuries; also of the preparation of a quintessence

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Torbert Bergmann, *Historiæ chemiæ medium seu obscurum ævum.* Editio Hebenstreit. Lipsiæ 1787. Vol. 4.

Schmieder, *Geschichte der Alchemie.* Halle 1832. p. 85 *et seq.*

[1]) Synesii *Tractatus chymicus* ad Dioscoridem. In Fabricii *Biblia græca.* Tom. 8.

[2]) "Et quid plura moramur? Unus Zosimos Panopolites libro *περὶ ὀργάνων καὶ καμίνων* loculente ad oculos nobis sistit antiquorum illa vasa destillationibus accommodata; postquam enim jussisset candidatos artis id agere ut ipsis ad manus esset *βίκος ὑέλικος σωλὴν ὀστράκινος λοπὰς καὶ ἄγγος στενόστομον*, mandassetque *ἐπὶ ἄκρα τῶν σωλήνων βίκους ὑέλου μεγάλους παχεῖς ἐπιθεῖναι, ἵνα μὴ ῥαγῶσιν ἀπὸ τῆς θέρμης τοῦ ὕδαος* tandem, ut clarius sese explicit, ipsas vasorum figuras appingit, quarum nonnullas licet rudiori manu exaratas ex bibliotheca regis christianissimi, et illa D. Marci Venetiis, libuit hic in gratiam curiosorum adjicere." (O. Borrichius, *Hermetis Aegyptiorum et chemicarum sapientia*, ab Hermanni Conringii *animadversionibus vindicata.* Hafniæ 1674. pag. 156.)

Detailed statements concerning Zosimos' account on distillation are also found in Höfers *Histoire de la chimie.* 2. Edit. 1866. Tom. 1. pp. 261—270.

[3]) Aetii *Βιβλία ἰατρικὰ ἑκκαίδεκα*, *Libri medicinales sedecim.* Editio Aldina 1533. fol. 10. — See also footnote 4, p. 68.

[4]) See p. 44, footnote 7.

[5]) See the illustration on p. 41.

[6]) The designation spagyric art, from *σπάω* and *ἀγείρω*, came into use during the time of Paracelsus, viz. in the first half of the 16. century.

from organic nature; and that of the much-sought *lapis philosophorum*. It was through this dogma that entered the medical and theosophic realm of the middle ages, and through the search for these imaginary phantoms that the Arabians laid the foundation for the acquisition, by empirical methods, of practical chemical knowledge, of numerous facts and products. These in turn served as building stones with which the later chemical structure was erected. In the course of the ninth and tenth centuries the Arabians also established the universities at Cordova, Seville and Toledo. As centers of learning and research, these institutions were visited by seekers of knowledge from all countries for the purpose of studying medicine, magic and necromancy.

Arabian medicine, and with it the art of distillation and the literature thereon, attained their greatest development during the period from the eighth to the eleventh centuries. However, but little definite information has come down to our own time concerning the numerous writers whose works have been perpetuated in their entirety or only in part. As a matter of fact, many of the works attributed to them are apocryphal and the real authors are not known with any degree of certainty. Not only is there a variation of one or more centuries in the dates attributed to them, but the opinions of historians concerning them is oftimes contradictory.

The Arabian writings which are of greatest importance in the documentary study of the history of distillation begin with the works of Geber about the ninth century. From the twelfth century on, the Arabian alchemists devoted themselves exclusively to the transmutation of the baser metals to the nobler ones, to the search for the *lapis philosophorum*.

It was during this earlier period of almost four centuries, devoted largely to medical research, that the Arabians acquired considerable skill in the art of distillation and the preparation of distilled waters, of several oils and of alcohol, a skill that was later lost in large part. Medical and alchemistic literature reveal this knowledge of distillation, distilling apparatus and distillates.

Since the time of the Egyptians it was Geber, whose fragmentary writings reveal for the first time a fair knowledge of distillation, both of the dry distillation and of the distillation

with water. He used apparatus made from glass, also from glazed earthenware. Next to Geber, Mesue the younger was probably the earliest of the more important medical writers. He lived somewhere between the eighth and tenth centuries. It is not improbable that there were several authors bearing this name, also that other writers published their works under this famous author's name, and that in later periods an exchange of names and writings may have taken place.

The most important work of Mesue is his *Antidotarium seu Grabaddin medicamentorum compositorum libri XII.* For many centuries it was a medical authority. In the twelfth chapter, *De oleis*[1]) the method of preparation of oils is described. Most of these are aromatized fatty oils. However, the oils from juniper wood and bitumen are directed to be prepared by dry distillation which process is described in detail. According to Bergmann, Mesue is supposed also to have known distilled oil of rose and amber oil.[2]).

Other medical authors of this period reveal a knowledge of distilled waters and oils and their uses. Thus Ibn Khaldun[3]), who lived during the ninth century, mentions that distilled rose water was an important article of Persian commerce during the eighth and ninth centuries. Nonus Theophanes,[4]) who during the tenth century was physician to emperor Michael VIII in Constantinople, recommended rosewater as a medicinal agent. The Syrian physician Serapion (Janus Damascenus) who lived in the ninth century, also Avenzoar[5]) who lived about a cen-

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[1]) Editio Veneti 1502. fol. 80.

[2]) "Mesue medicamentorum plurimorum inventione magnam famam et nomen evangelistæ pharmacopolarum consecutus est; durantque hodie nunc in officinis nostris compositiones nonnullæ, quæ ille primus descripsit." — "Mesue aquam destillatam rosarum, oleum ex succino et lateribus tamquam veteribus nota memorat". (Torbert Bergmann, *Historiæ chemiæ medium seu obscurum ævum.* Editio Hebenstreit. Lipsiæ 1787. p. 7).

[3]) *Notices et extraits des manuscripts de la bibliothèque impériale* à Paris 1862. Tom. 19, p. 364.

[4]) Nonus Theophanes, *Præfatio* ad Synesii *De febribus.* Editio Bernardi. Amstelodami 1749. Cap. 28, p. 112.

[5]) Liber Theizir Dahalmodana Vahaltadabir *Procemium* Averrhoi Cordubensis ab Jacobo Hebræo. Anno 1281. Colliget Veneti 1553. Liber 7. fol. 1. Lib. 5. cap. 9. fol. 44.

tury later and who was physician to the Caliph Ebn Attafin of Morocco, used rose water as an eye-remedy and rose oil sugar as an internal remedy. In the medical writings of Abn Dschafar Achmed, an Arabian physician of the eleventh century, which were translated into Greek by Synesius of Constantinople, rose water, rose oil and camphor are mentioned among the current remedies.[1])

While Geber was the first, and also the most important Arabian writer who was acquainted with distillation, the writings of Albucasis, who lived three centuries later, reveal such an exact knowledge of the subject, that the assumption seems justified that distillation was largely practiced by the Arabians. The *Liber servitoris*[2]) of Albucasis contains a very clear description of the process of distillation which Torbert Bergmann, the

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[1]) Synesius, *De febribus.* Editio Bernardi. Amstelodami 1749. p. 58 and 240.

[2]) A number of the works of the Arabian physicians and alchemists of this period have been preserved in a collective edition published in Venice in 1501. In addition to the principal work of Mesue and the *Antidotarium* of Nicolas and commentaries on the same, this folio contains several works of contemporaries. The titles of the individual works are herewith given: —

"Uni Joannis Mesue Liber de consolatione *medicinarum simplicium et correctione operationem ærum* canones universales: *cum expositione preclarissimi medici magistri* Bondini de lentiis *feliciter incipiunt.*" (fol. 2—31.)

"*Additiones* Petri Apponi medici clarissimi, *et* Francisci de Pedemontium." (fol. 31—90.)

"Joannis Nazareni filii Mesuë *Grabaddin medicinarum particularium incipit.*" (fol. 91—266.)

"*Antidotarium* Nicolai *cum expositionibus,* et *glossis clarissimi magistri* Platearii." (fol. 267—293.)

"*Expositio* Janis de Santo Amando *supra antidotarii* Nicolai *incipit feliciter.*" (fol. 294—330.)

"*Tractatus de synonymis quid pro quo.*" (fol. 331—334.)

"*Liber Servitoris seu libri* XXVIII Bulchasin Ben-aberazerin: *translatus* a Simone Januensi: *interprete* Abraamo Judeo Tortuosiensi." (fol. 334—345.)

"*Uni* Saladini *de esculo Servitati principis* Tarenti physici principalis *compendii aromatiorum opus feliciter incipit.*" (fol. 346—354.)

Quæ omnia supradicta hic finem habent ad laudem dei. Veneti impressa anno Domini 1502, die 23. Junii.

The oldest individual editions of some of these treatises date back as far as 1471, hence to the invention of the printing press.

Swedish chemical historian, regards as one of the first and best.[1])

The distillation of water, of acetic acid, and of alcohol is described in the following words in the writings of Albucasis.[2])

"Modus faciendi aquam rosatam. Operatio ejus est secundum quatuor modos . . . Sed modum operationis ejus, quæ fit cum aqua et inge lignorum, ego monstrabo secundum formam, quam faciunt reges Abarach. Et hic est modus ejus. Facias berchile parvum in domo ampla, cujus fundus et latera sint ex plumbo, adeo discreta simul solidata, ut aqua non possit egredi ab eo: et facias tibi coopertorium ex vitro cum sagacitate, vel ex terra vitreata, et in eo forma secundum formam vasorum destillationis, vel secundum quantitatem magnitudinis berchilis, vel parvitatem ejus, secundum voluntatem tuam faciendi multam, vel paucam aquam rosatam. Deinde pone ollam magnam ex ære vel cachabum post parietem, juxta quam posuisti berchile secundum formam ollæ balnei, et construe eam super furnum, et berchile sit constitutum super furnum, inferius ab olla, ita quod applicet de calore ignis berchilis ad ollam. Et facias caminam cum foraminibus, per quæ possit fumus extra domum egredi, ita quod fumus totus e domo egrediatur, et non noceat aquæ rosatæ. Deinde imple ollam ex aqua, quæ sit in puteo facto juxta ollam, sicut est puteus balnei, et accende ignem sub ea, quousque bulliat aqua bene. Deinde dimitte venire aquam per canale, quod fecisti per discretionem ad berchile, deinde pone aliam aquam frigidam in ollam ex puteo, sicut in olla balnei sit et constitue in berchile canale, per quod egrepone cucurbitas sive ventres, et sunt vasa destillatoria in foraminibus berchilis; et stringe cum panno lini discrete, ita quod bene sedeant in foraminibus suis, et vapor aquæ non egrediatur extra. Similiter, et capita eorum stringes cum panno lini . . . Et operatio ejus quæ sit in terra nostra est servior et brevior, quam illa, quam dixi. Et est, quod accipias ollam ex ære sicut est illa tinctorum, et pone post parietem, et pone super eam coopertorium discrete factum, cum foraminibus in quibus ventres ponuntur, et pone in eo ventres cum sagacitate, et postea imple ollam aqua . . . . Operatio ejus sine aqua et cum igne carbonum est, quod facias furnum quadrum, aut rotundum, et habeat coopertorium superius, super quod stabunt ventres ex terra vitreata, ut possint sustinere ignem, et quando accendentur carbones, et incipiet aqua rosata destillare, claude os furni, et dimitte foramina aperta, per quæ fumus egrediatur."

[1]) "Describuntur in hoc libro præter alia, destillationis modus triplex, aquæ, aceti et vini destillatio, alembici et cucurbitæ quatuor generum, vitrei, fictiles vitro incrustati, plumbei et ærei commemorantur." — Torbert Bergmann, *Historiæ chemiæ medium seu obscurum ævum.* Editio Hebenstreit. Lipsiæ 1787.

[2]) *Liber Servitoris seu libri* XXVIII Bulchasin Ben-aberazerin: *translatus* a Simone Januensi: *interprete* Abraamo Judeo Tortuosiensi 1471. — Editio Veneti 1502. fol. 339b, 341b und 342.

"Modus alius cui vult destillare paucam aquam. Accipe ollam ex ære, et imple eam aqua, et pone super lanem ignem, et pond super os ejus coopertorium perforatum foraminibus duobus vel tribus vel pluribus aut paucioribus ventribus, secundum quod poterit capere coopertorium ollæ, et sint ventres ex vitro . . ."

"Modus albificandi acetum . . . Construe athanor simile illi, in quo destillatur aqua rosacea, at superpone ei vas destillatorium ex vitro, vel ex terra vitreata et imple tres partes ex aceto bono, et quarta pars vasis superius sit vacua, ne cum ebullierit acetum, effundatur extra; deinde operi vas cum vase aliquo superius, sicut novisti habente nasum, sicut sit in aqua rosacea; et fac ignem levem non fortem, nam si esset fortis, non fieret acetum album tantæ albedinis, et est necesse, ut acetum, quod distillatur, sit ex uvis albis, clarum, et acre, in fine acredinis, quia tunc distillatur album et purum."

"Secundum hanc disciplinam potest destillari vinum, quod vult ipsum destillare."

During the period from the eighth to the twelfth centuries medicine and materia medica were greatly advanced by the Arabian scientists. The method of preparation of medicaments by subjecting vegetable and animal substances to distillation was in common vogue at this time. Hence the art of distillation was one of the principal methods of technique described in medical as well as in alchemistic treatises. It is not likely, therefore, that the separation of oils from the distillates of plants and plant products rich in oil, should have escaped the observation of the eager experimenter. Inasmuch, however, as the distilled waters were regarded as the bearers of the "subtle" ingredients of the drugs, any oil separating from the aqueous distillate may have been regarded as a more gross product and hence may have received but little attention. Moreover, little was known concerning the character of oils, whether fatty or aromatic. So much is certain, that the literature of the period reveals the fact that but few volatile oils found application.

From the eleventh century on, the desire for gain and the search for the *lapis philosophorum*, i. e. the conversion of the baser metals into nobler ones predominated more and more. Hence Arabic science went astray and pursued the illusory speculations of the hermetic art. After the middle of the 12. century there do not appear to have been any great Arabian physicians and scientists. With the conquest of Bagdad by the Mongols in 1258, Arabic dominance ceased and with it its spiritual leadership. For a time Arabian culture lingered in

Spain and was re-echoed from the school of Salerno, which had been founded in the 9. century on the Tyrrhenian Sea, to the south of of Naples.

During the crusades, i. e. from the close of the eleventh to the close of the thirteenth century, there were times when extensive friendly intercourse took place between the crusaders and their followers on the one hand and the peoples of the Orient on the other hand, such as had not occurred before. It may well be supposed that the crusaders thus became acquainted not only with the products of the Levant, among them the citrus fruits, but also with the customs, the trades, and the arts and crafts of the Mohammedans; indeed, that they acquired them in order to practice them at home. Thus, much was introduced and cultivated in western Europe that was lost even to the Arabians when shortly afterward they were overrun by barbarian nomadic tribes. It is probably in this manner that the art of distillation, and a knowledge of the conventional distilling apparatus were spread in western Europe.

It was in the thirteenth century that the onward movement of nations, that had been incited by the Islam and had progressed under the auspices of Arabic civilization, came to a halt. The conglomerate of peoples united loosely under Arabic rule went to pieces under the onslaughts of the Mongols and later of the Turks. It was then that general scientific and medical research turned more and more toward theosophy and sought refuge in monasteries and remote dwellings. The chemical study of Nature, having fallen a prey to mysticism and miracular faith, went astray. For centuries chemistry was bound up with theosophy, with the search for the *lapis philosophorum*, with the endeavor to transmute the baser metals into gold, and with the search for a "quintessence" as a panacea for health and the prolongation of life. With these changes the art of distillation had strayed from its original tendency.

It was Paracelsus (born 1493, died 1541) who, at the time of the Reformation, revived medical research and who caused the transferrence of chemical endeavors from the laboratories of dilettantes, magicians, monks and necromancers to those of physicians, and thus became the founder of iatrochemistry with new scientific ideals. In the benefits of this productive period,

pharmacy shared as well as chemistry. However, this phase in the process of the evolution was a very gradual one, accompanied by ups and downs in the course of four centuries.

As has already been pointed out (p. 17) the distillation of wine was probably known to the Indians and Egyptians. The oldest, definite, documentary evidence, however, is to be found in the *Liber ignium ad comburendos hostes*, an apocryphal treatise of the eighth century attributed to a mythical author, viz. Marcus Græcus. The directions for making a "water that will burn" are as follows: "Take black wine, add finely powdered sulphur, tartar and common salt and place all into a distilling vessel. Upon distillation you will obtain a water that will burn". The texts of this treatise found in the library at Paris and in the University Library at Munich contain the following additional statement. "The peculiar property of this burning water can be demonstrated in the following manner: Dip a strip of linen into this water. When you ignite it a large flame will result. If you moisten a finger with this water and approach the fire with it, the finger will burn like a candle without being injured."

In the same treatise Marcus Græcus also describes the distillation of turpentine oil from turpentine in an alembic.[1]) Supposing it to closely resemble the spirit of wine, he likewise designates it as *aqua ardens*. The synonymous designation of both distillates was maintained for a long time. A distinct difference between the two was possibly not recognized before the beginning of the seventeenth century. The designation "*Spiritus*" *terpentini*, however, is still in use at the present time.

Further mention of the distillation of the spirit of wine is found in treatise of the twelfth century. One of these references, viz. the one found in the "Key to Dyeing" may here be mentioned. The treatise itself is a collection of technical formulæ, in part of Greek, in part of Roman origin, with Arabic addenda. The reference pertaining to spirit of wine reads as follows: "When strong wine is heated with salt in a suitable vessel, a combustible water results, which burns without destroying the substance on which it burns."

[1]) "Recipe terebinthinam et destilla per alembicum aquam ardentem quam impones in vino cui applicatur candela et ardebit ipsa." *(E libro ignium ad comburendos hostes.)*

With the downfall of Arabian civilization, the art of distillation as practiced by the Arabians appears largely to have been restricted to the distillation of alcohol. The better kinds of distilling apparatus that had been made by the Arabians, the cooling vat and the spiral tube *(serpentina)* which had been introduced by them, had been preserved and were revived for the production of the spirit of the wine, the "burnt" water.

Among the "burnt" waters it was the "spirit of wine" which was early appreciated because of its animating effect. Being regarded as representing the highest potency of the wine, it found ready application in medicine. Thus the Cardinal Vitalis de Furno of Basel, and Bishop of Albano, in the beginning of the fourteenth century declared that spirit of wine was a panacea.[1]) Bishop Albertus Magnus of Regensburg (Albert von Bollstaedt, born 1193, died 1280) occupied himself with the distillation of wine, which process he described carefully in his writings. It was possibly Arnoldus Villanovus (Arnold de Bachuone, born 1235, died 1312) who first introduced the Arabic term "alcohol" into German nomenclature. In his treatise *De conservanda juventute* he describes its preparation in the following words: "Burnt water also known as *aqua vitæ*, is obtained by the distillation of wine or wine yeast. It is the subtlest portion of the wine. Some say that it is "the everlasting water", also that, because of its sublime method of preparation, it is the "gold water" of the alchemists. Its advantages are well known. It cures many diseases, prolongs life and hence deserves to be known as *aqua vitæ.*[2])"

With the distillation of turpentine oil[3]) and rosemary oil,[4]) Villanovus was well acquainted. His *oleum mirabile* consisted essentially of an alcoholic solution of rosemary and turpentine oils. This mixture was sold by him or his disciples as an external remedy and later, with the omission of the turpentine oil, as a perfume. Under the designation "Hungarian water" it remained for centuries a much used specialty.

[1]) Vitalis de Furno, *Pro conservanda sanitate liber utilissimus.* Editio Manget. Geneva 1531. Cap. 2, p. 12.

[2]) Arnoldi Villanovi *Opera omnia.* Veneti 1505. *Liber de vinis.* p. 558.

[3]) Arnoldi Villanovi *Breviarium practicæ, procemium in operis omnibus cum* N. Taurelli *in quosdam libros annotationibus.* Basiliæ 1587, p. 1055.

[4]) Arnoldi Villanovi *Opera omnia.* Veneti 1505. *Liber de vinis.* p. 589—590.

Raymundus Lullus (born 1234, died 1315) the most famous of the disciples of Villanovus, in the second half of the thirteenth century, described the distillation of the *aqua vitæ ardens* from wine and its refining. In order to obtain a liquid which would burn without leaving a moist residue, this rectification had to be repeated four times with the addition of burnt potash as dehydrating agent[1]). Of the alcohol he says: "*Est consolatio ultima corporis humani*[2])."

According to the alchemistic nomenclature of that period, the spirit of wine repeatedly rectified was designated as *Mercurium vegetabile*, *Argentum vivum vegetabile* and *Cœlum philosophorum*[3]). It was regarded as possessing certain powers in the transmutation of the elements and as representing a first step in the preparation of the *lapis philosophorum* and the *magisterium magnum*[4]).

That "burnt wine" was a common article of commerce as early as the middle of the fourteenth century, also a beverage subject to abuse, becomes apparent from a collection of municipal ordinances of 1360 of the city of Frankfurt on the Main[5]). The municipal council of Nuernberg, in the year 1496, prohibited the sale of "gebranndt weynes" on Sundays and holidays[6]). In other German cities similar ordinances were issued: e. g. in Hessia in 1523, viz. under the Margrave Philipp[7]), in Frank-

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[1]) "Accipe vinum rubrum vel album, et sït de meliore quod poterit reperiri, vel saltem capias vinum, quod non sit acetosum quo vis modo, neque parum, neque minimum, et destilla aquam ardentem, sicut consuetum est per cannas brachiales æris et postea rectificata illam quater ad majorem rectificationem." (Raimundi Lulli *Majoricæ, Philosophi acutissimi, de secretis naturæ vire Quinta essentia libri duo.* Anno 1541.)

[2]) Raymundi Lulli *Testamentum novissimum.* In Mangets *Bibliotheca chemica curiosa.* Basiliæ 1572. Vol. 11, p. 792.

[3]) Euonymi Philiatri *Kostbarer theurer Schatz.* Vol. 1, p. 99.

[4]) Raimundi Lulli *Testamentum novissimum.* In Mangets *Bibliotheca chemica curiosa.* Basiliæ 1572. Vol. 1, p. 792 and 808.

[5]) Henrici Christiani Senckenberg *Selecta juris et historiarum.* Francofurti 1734. Tom. 1, p. 44.

[6]) J. Baader, *Nürnberger Polizeiordnungen aus dem 13. bis 15. Jahrhundert.* p. 264.

[7]) Joh. Beckmann, *Beiträge zur Geschichte der Erfindungen.* Leipzig 1786—1795.

furt a. M. in 1582 also in 1605[1]); likewise in Spain[2]). Indeed the production of whiskey from cereals was regarded as an act displaying want of piety. Moreover, the adulteration of brandy with whiskey was punishable[3]). On the other hand, brandy was introduced into Sweden in 1565, in the reign of Erich XIV, as an antidote against the plague[4]).

About the middle of the sixteenth century a distinction was made in German apothecary shops between the stronger *Spiritus vini rectificatissimus* and the weaker *Spiritus vini rectificatus simplex*, also between both and brandy *(aqua ardens)*[5]). During the second half of the sixteenth century Italy, more particularly Modena and Venice, appear to have supplied the more northern countries with spirit of wine[6]).

The familiarity with which spirit of wine was used as early as the first half of the sixteenth century, becomes apparent from the "*Cœlum philosophorum*"[7]), by Philipp Ulstad, professor of medicine in Nuernberg. It was used for the preservation of meat, for the improvement of stale wine, for the extraction of spices and other parts of plants, hence for the preparation and utilization of alcoholic solutions of volatile oils, aromatic resins, and balsams.

From the thirteenth century on distilled aromatic waters were used more extensively as medicaments. The separation

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[1]) Joh. F. Gmelin, *Geschichte der Chemie.* Göttingen 1797. vol. 1, p. 360.

[2]) Christophoro a Vega, *De arte medendi.* Lugduni 1564. Pars 2. Cap. 2, p. 237.

[3]) Joh. Beckmann, *Beiträge zur Geschichte der Erfindungen.* Leipzig 1786—1795.

[4]) P. J. Bergius, *Tal om Stockholm för ar sedan och Stockholm nu förtiden.* p. 100—101. B. Bergius, *Tal om läkerheter.* T. 1, p. 32—33.

Joh. Beckmann, *Beiträge zur Geschichte der Erfindungen.* Leipzig 1786—1795.

[5]) Möhsen, *Geschichte der Wissenschaften.* 1810. p. 488—498.

[6]) Alex. Tassoni *Pensieri diversi.* Venezia 1676. pp. 317 and 352.

A. Baccius, *De naturali vinorum historia et vinis Italiæ et conviviis antiquorum.* l. vii. *acc. de facticiis vinis et cerevisiis, de omni vinorum usu.* Roma 1596 and 1598.

[7]) Philippi Ulstadii *Cœlum philosophorum, seu liber de secretis naturæ, id est, quomodo ex rebus omnibus quinta essentia paretur.* Argentorati 1528 et 1562 — Augustæ Trebocorum 1530 — Lugduni 1540 and 1553 — Parisii 1543 — Francofurti 1600.

of oils both at the surface and beneath the aqueous distillate was observed, but apparently received but little attention. Owing to the practice of using alcohol in the preparation of many of these aromatic waters, the oil must frequently have remained in solution wholly or in part. Thus, e. g. the plants or plant products to be distilled were moistened with wine or *aqua vitæ* before distillation; or, steeped in water, they were first allowed to undergo fermentation. Moreover, both alcohol and volatile oil were lost, in part at least, by submitting the plant products to a process known as circulation, a preliminary operation consisting of more or less prolonged digestion. In this manner inferior distilled or burnt waters were obtained.

Nevertheless, several of the more important experimenters and writers of that period knew and described volatile oils. In addition to the oils of turpentine and rosemary already mentioned, Arnoldus Villanovus[1]) and Raymundus Lullus[2]) describe the distillation of oil of sage; Sancto Amando[3]) that of bitter almond oil, oil of rue and oil of cinnamon; Saladinus of Aesculo[4]) that of oil of rose and oil of sandalwood. The writings of their contemporaries also reveal a knowledge of these and other distilled oils without, however, making mention of their use in medicine or the arts.

The epoch-making inventions and discoveries of the fourteenth and fifteenth centuries wrought great changes in the natural sciences and their application. The discovery of the new world, made possible by the rediscovery of the compass, and the circumnavigation of Africa to the East Indies widened the horizon of the people. The period of the Renaissance and the Reformation assisted in doing away with the blind faith in authority, not only

[1]) Arnoldi Villanovi *Opera omnia.* Veneti 1505. *Liber de vinis.* fol. 589—590.

[2]) Raimundi Lulli *Experimenta nova.* In Manget's *Bibliotheca chemica curiosa.* Geneva 1702. Vol. 5, fol. 829.

[3]) *Expositio* Joannis de Sancto Amando *Supra Antidotarium* Nicolai *incipit feliciter.* In the same edition with the works of Mesue. Veneti 1502. fol. 228 and *Additiones* fol. 85, 86, 87.

[4]) *Compendium aromatiorum* Saladini, principis Tarenti dignissimi, medici diligentis, correctum et emendatum. Bononæ 1488. Editio Veneti 1471, 1488 and 1502. fol. 349b.

in theology but in the natural sciences as well, more particularly in medicine and alchemy. The founding of universities to the nord of the Alps during the fourteenth and fifteenth centuries, and the invention of printing with type toward the close of the fifteenth century, which followed wood engraving invented in the previous century, assisted largely in revealing anew the literary treasures of the past.

Up to this time all treatises had to be multiplied in manuscript form. Presumably, therefore, many discoveries were known only to small circles and by no means to all scientists and investigators. No doubt, much disconnected work was done by some that was long known to others. As a result, the first discovery *e. g.* of a process or product, has never been traced. Moreover, as a result of tradition from one generation to another, from one country to another, much was lost[1]) even though recorded in manuscripts. Or, if inadequately recorded, it was not understood. Furthermore, it was the practice among alchemists, to use an allegorical language for the purpose of surrounding their treatises with a mysticism suited to their spagyric art and science. Hence these treatises were comprehensible only to the initiated. There was still another reason why the seeking for the *lapis philosophorum* was surrounded by a mystic language. It was done partly to cover up the alchemist's own uncertainties, partly to render it more difficult for others to find the much coveted solution to the secret. At the same time each adept, experimenting in his own secluded laboratory, supposed that the others already possessed the secret.

It was with the gradual introduction of printed books during the beginning of the sixteenth century, that the treatises of the past became more and more the common property of those versed in science and reading. Up to this time, and even in later times, much that had been known to and practiced by individuals, was lost and had to be rediscovered.

This is true of the methods of distillation and of the apparatus used. Thus the apocryphal treatises of antiquity seem to show that the early method of primitive distillation was discovered by peoples widely separated both as to locality and time. Frequently

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[1]) Compare *e. g.* the quotation from Adam Lonicer on p. 49.

there is no record of the direct transmittance of the art from one people to another. Wherever such transmittance may have taken place, it appears to have led less to a technical accomplishment than to a general stimulus.

In the history of special peoples, cultural stages are found, in the evolution of their trades as well as in their literary productions, which are fundamentally related both to their material development and their political changes. Hence, the former can be fully understood only when considered in connection with the latter. Material and national welfare appear in history as a rule contemporaneously with intellectual and industrial achievement.

As to the discovery of natural products, the knowledge and separation of their components, and the utilization of these discoveries in materia medica and medicine, a new epoch was inaugurated, at the time of the reformation, by Paracelsus and others. With it the practice of the art of distillation was again conducted into proper channels. Thus it was made serviceable to materia medica and later to the trades. As a result there were produced in the course of time, an ever increasing number of important products. In addition to the production of alcohol, there should be mentioned the distilled aromatic waters which were highly prized and used in medicine for nearly three centuries. These were followed later by the distilled oils.

In the course of the twelfth and thirteenth centuries the art of distillation, which had been developed first by the Egyptians and later by the Arabians, was practiced but little.[1]) Hence, the methods and apparatus had been forgotten and had to be rediscovered. This reintroduction and rediscovery was furthered toward the end of the thirteenth and the beginning of the fourteenth centuries by the principal alchemists and physicians of that period, viz. by the Cardinal Vitalis de Furno of Basel (died 1327), the Bolognese teacher Thaddeus (Taddeo Alderotti, born 1215, died 1303), Arnoldus Villanovus (Arnold de Bachuone of Villeneuve or Villanova, born 1235, died 1312) and Raymondus Lullus (born 1235, died 1315). With this period, the distilling

[1]) Compare pp. 17, 24 and 26.

apparatus again found their way into the work shops of physicians and alchemists, became increasingly important and were accordingly improved. As the art of pharmacy was separated more and more from that of medicine, and as apothecary shops were established in larger numbers, the art of distillation gained admission to the laboratories attached to these shops. Carefully nursed, the art of distillation here developed into an important industry viz. that of the production of volatile oils.

As a result, the progress made by the art of distillation henceforth is primarily to be sought in the literature on materia medica, as this had already been the case in the earlier Arabian medical treatises, viz. the antidotaries, e. g. the Grabaddin and other treatises. With the printing of books the number of medical treatises increased. Although they afford information concerning the time of introduction of drugs and distilled waters, and hence are of permanent interest to the student of materia medica, they are less satisfactory as sources of information concerning the production and introduction of distilled oils. Nevertheless, even for this purpose they constitute almost the only available literary sources.

The numerous works that came under consideration may be classed into three groups of equal importance: the antidotaries and the later dispensatories; the treatises on distillation which occupied a prominent position from the close of the fifteenth century to the close of the sixteenth century; and the price ordinances of various cities for spices and drugs which had come into use about the same time.

As already pointed out, the term "distilled" oils should not necessarily be interpreted in the same sense as we use it to-day The ancients had already known how to obtain fragrant oils by boiling seeds, fruits and other parts of plants with water also by cold and warm expression. These were used in the preparation of aromatic oils and ointments. However, all exact knowledge concerning the nature of these oils was wanting. Up to the seventeenth century this was equally true of the oils, obtained in all probability by the process of distillation, by the Indians, the Egyptians and later peoples. Neither was there any clear conception as to the distinction between fatty, expressed oils and distilled, aromatic oils.

Far into the middle ages, the designation "distillation" was used as a collective term for the preparation, according to the rules of the art, of plant and animal extracts and their supposed refinement. For this process of rectification, various methods and sources of heat also diverse utensils were used. The general term included such processes as maceration, digestion, straining, filtration, expression and sometimes even the processes of fermentation and decay.[1]) With the exception of turpentine or cedar oil those products mentioned in older literature as oils, or even as distilled oils, are to be regarded as fatty oils which have been aromatized and which were used for medicinal purposes and as unguents.

Whether the oils of rose, andropogon, and calamus, mentioned in the Ayur-Veda as distilled oils, were such in the modern sense of the term, can not be decided. The same doubt exists as to the oils of spike, rosemary and sage, as well as of other oils of later writers. As has already been pointed out, the art of distillation, known at an early period, may have fallen into disuse and have been forgotten.

Although, in all probability, the Indians, the Babylonians, and especially the Egyptians were acquainted with the art of distillation, also with volatile oils, a sharp distinction between true distilled oils and aromatized fatty oils does not seem to have existed at the beginning of the Christian era. The latter were used principally for the purposes of cleanliness and well-being, also in religious rites, such as anointing and embalming. Hence the simpler process of aromatizing fatty oils may have been preferred by the priests. In accordance with this assumption are the directions for the preparation of rose oil, a supposedly "distilled oil" by Dioscorides,[2]) copied by Pliny[3]) during the first century.

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[1]) Compare p. 33.

[2]) Petri Andreæ Matthioli *Opera quæ extant omnia: hoc est Commentarii in sex libris* Pedacei Dioscoridis Anazarbei *de materia medica. Post diversarum editionum collationem infinitis locis aucti. De ratione destillandi aquas ex omnibus plantis; et quomodo genuini odores in ipsis aquis conservari possint.* Veneti 1544 — Basiliæ 1565. Liber I, cap. 53.

[3]) Plinii Secundi *Naturalis historiæ libri.* Liber XIII, cap. 2.

"Five and one-half pounds of bruised *Juncus odoratus* (probably *Andropogon Schœnanthus*, L.) are boiled with 20 1/2 pounds of oil with constant stirring. Into the strained liquid the floral leaves of 1000 roses free from moisture are pressed with hands that have been anointed with fragrant honey. After standing over night the oil is expressed. After all impurities have subsided the oil is decanted into another vessel and the expressed rose petals are treated with a second quantity of 8 1/2 pounds of fresh oil. After standing for a day the oil is again expressed. This is the *Oleum secundarium.* If a third and fourth maceration are to be made, oil is again poured on the roses and as often expressed. Thus the *Unguentum primarium, secundarium, tertiarium and quartarium* are prepared.

The vessel, however, must each time be covered with a film of honey. If the maceration is to be repeated a second time, a like quantity of fresh rose petals free from moisture is immersed into the oil first expressed. The mixture is kneaded with hands anointed with honey. In like manner the oil is expressed a second, third and fourth time, and each time rose leaves free from the calix are added. In this way the oil becomes much stronger. Up to a seventh infusion the same oil can be used but no farther. Furthermore, the oil should be carefully separated from the aqueous juice, for the oil will spoil if any of this juice remains with the oil."[1])

A single distilled oil, however, was known as early as the first century, viz. turpentine oil. Its peculiar method of preparation, as well as the apparatus used, are described in the chapter on the "History of the methods of distillation and distilling apparatus."

Taking into consideration the early acquaintance of distilled oils by ancient peoples and later by the Arabians, it can scarcely be doubted that the oils which must have separated on the surface of "burnt waters" during the process of distillation of aromatic plants and spices, practiced so diligently during the fifteenth century, could have escaped attention. Being regarded as coarser particles they probably received little attention and hence found no application, for the therapeutically active waters alone were the only object of the distillation. Thus, while it is known from other sources that a number of distilled oils were known, one of the oldest price lists of drugs and spices, viz. the one of the city of Frankfurt-on-the-Main of 1450 does not mention a single distilled oil.[2]) However, a similar list of the same city

[1]) From the German translation of the works of Dioscorides in *Trommsdorffs Journ. der Pharm.* 11 (1803), 112.

[2]) *Ita sunt nomina medicinarum simplicium sive materialium quæ ad apothecam requirentur, In genere et in specie.* Published as a separate by Prof. F. A. Flückiger in 1873 with the title *"Die Frankfurter Liste."*

for the year 1582 mentions forty-two volatile oils,[1]) and a further list of 1587 fifty-nine such oils.[2])

At the close of the fifteenth century the art of distillation and the distillation of aromatic waters were greatly advanced by the first larger treatise on distillation, viz. the *Destillirbuch* of the Strassburg physician Hieronymus Brunschwig (born abt. 1450, died abt. 1534) which was published in the year 1500. The book is illustrated by numerous cuts of stills and utensils, likewise of the plants used in the preparation of "burnt waters." In some editions, these cuts were colored. The title pages of the two voluminous folios, which were printed in 1500 and 1507, are of special interest in the history of distillation. Reduced facsimile reproductions will be found on pages 40 and 41.

The first volume contains 212 paged leaves (424 pages), the second volume 344 leaves (688 pages). The work is devoted mainly to a description of the methods of preparation of the much lauded[3]) "burnt waters," accompanied by directions for their use and an explanation of their action. In addition it contains directions for the preparation of numerous "burnt

[1]) *Register aller Apothekischen Simplicien und Compositen, so in den beiden Messen zu Frankfurt am Main durch Materialisten, Kauffleut, Wurzelträger, Kräutler und durch die Apotheker daselbst verkauft werden.* Frankfurt-on-the-M. 1582.

[2]) *Reformatio oder erneute Ordnung der heilig Reichstadt Frankfurt a. M., die Pflege der Gesundheit betreffend. Den Medicis, Apothekern und Materialisten zur Nachrichtigung gegeben. Darneben den Tax und Werth der Arzneien, welche in den Apotheken allda zu finden.* 1587.

[3]) The praises of the "burnt waters" were sung in prose and verse. Of the more prominent writings the following may be mentioned: *Loblied vom branntewein. Wem der geprant wein nutz sey oder schad. un wie er gerecht oder falschlich gemacht sey. getruckt zu Bambergk von marxen Ayrer. Unnd Hannsen Pernecker in dem Zinkenwerd. in 1493 jar.* Reprinted in: Joh. Beckmann, *Beiträge zur Geschichte der Erfindungen.* Leipzig 1786 — 1795. Bd. II, Abt. 2, S. 277 — 288.

Michael Schrick, *Nützlich Büchlein von Kunst und Tugend der geprenten Wassern. getruckt am 28. Mai zu Nürnberg 1517.* New editions appeared in 1529 and 1601.

By Hubertus Barlandius in Namur: *Epistola medica de aquarum destillatarum facultatibus.* Antwerpiæ 1536.

By the Canon Remaclius Fuchsius in Liège: *Historia omnium aquarum, quæ in commune hodie practicantium sunt usu, vires et recta destillandi ratio.* Parisii 1542 — Veneti 1542.

Liber de arte distillandi. de Simplicibus.

Das buch der rechten kunst zů distilieren die eintzigē ding

von Hieronymo Brunschwygk/Bürtig vñ wund artzot der keiserlichē frye statt straßburg.

un getruckt durch den wohlgeachte Johannem grueninger zu Strassburg in den achte tag des meyen als man zelt von der geburt Christi funfzehnhundert. Lob sy got. Anno 1500.

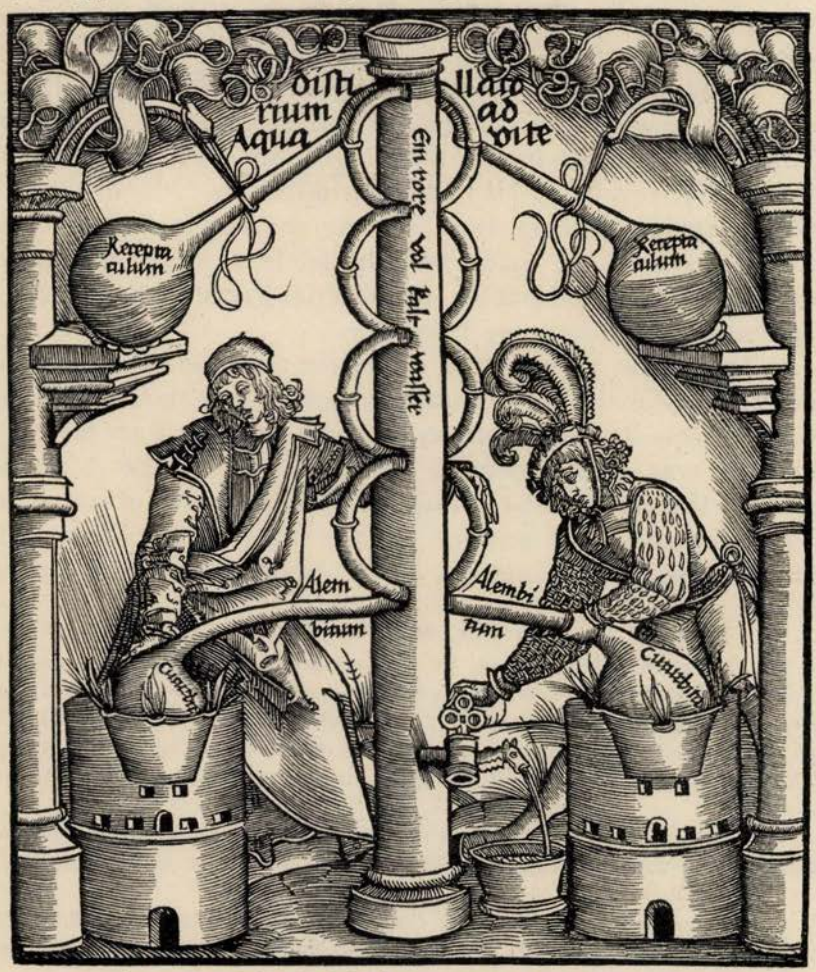
Fig. 1.

Liber de arte Distil

landi de Compositis.

Das buch der waren kunst zů distillieren die

Composita vñ simplicia/vnd dz Büch thesaurus pauperū/Ein schatz d armē gey nār/Vicariū/die bösamlin gefallen vō dē büchern d Artzny/vnd durch Experimēt vō mir Jheronimo brūschwick vff geclubt vñ geoffenbart zů trost denē die es begerē.



getruckt un gendigt in die keisserliche frye statt Strassburg uff sanct Mathis abent in dem jar 1507.

Fig. 2.

wines," elixirs of life, and simple and complex oils and balsams.

The lesser significance of the volatile oils becomes apparent from the fact that, in spite of the thorough knowledge and even practical experience of the author, but a single volatile oil, viz., the *oleum spicæ*,[1]) is mentioned and described in the first volume; and in the second volume only three additional ones, viz. *oleum terebinthinæ*,[2]) *oleum ligni juniperi*[3]) and *oleum rosmarini*.[4])

In harmony with the knowledge of his times, are Brunschwig's views as to the nature and products of distillation. These are recorded in the following words in the introduction to the first volume of his treatise on distillation: "By distillation we understand nothing else than the separation of the subtle from the coarse, the coarse from the subtle, to render the fragile or destructible indestructible, the material immaterial, the bodily spiritual, the unhandsome handsome."

Ambiguous as were the conceptions of the nature of the constituents of the distilled parts of plants and their distillates, the technique of distillation, as becomes apparent from the next chapter, was well developed. For this very reason it seems strange that no mention is made of the observation of oils when such aromatic plant products as the umbelliferous fruits, the labiate leaves, juniper berries, cloves, cinnamon and other spices

[1]) Vol. I, fol. 72. *„Das krut von de lateinischen lavendula und in tütscher zungen lavender genannt, ist ein krut gemeiniglich yederman bekant, doch so ist syn zweingestalt, das ein von den lateinischen spicula und von den tütschen spic genant, des vyl wachsen ist in dem lant provinz. Zu dyser zyt ouch in tütscher nation glich dem gemeinen lavender, von des blumen ein öl wird gemachet mit putrisieren un dystillieren genant oleum de spica."*

[2]) Vol. I, fol. 33, cap. 25. The rectification of turpentine oil by repeated shaking with water, rosewater or wine and final distillation is also described.

[3]) Vol. II, fol. 289.

[4]) Vol. II, fol. 52, also *oleum benedictum compositum* (fol. 53). Both are distillates from rosemary, turpentine, frankincense, mastix, ammoniacum, galbanum, oppopanax, cloves and cinnamon.

In Vol. I, liber 4, fol. 271—272 are likewise found descriptions for the preparation of a number of aromatic balsams (mixtures of volatile oils) by the distillation of mixtures of resins and spices to which turpentine oil has been added.

were subjected to distillation with water. Some of these non-aqueous "subtle" parts must have risen to the surface of the aqueous distillate, others must have collected at the bottom of the receiver, still others must have congealed. This silence is all the more remarkable since the specific object of distillation consisted in the separation and isolation of the volatile, the subtle, the *quinta essentia* from crude plant products and other natural objects; and since such oily separations had been known much earlier and had been mentioned in the literature of earlier periods.

The explanation for this lack of correct observation and the ambiguity of views as to the nature of the products of distillation is possibly to be sought in the change which the concept *quinta essentia* underwent in the course of time. Originally applied to the spirit of wine only,[1]) it was later applied to aromatic and empyreumatic oils, even to acetic acid[2]) and other products of distillation.

The treatise of Brunschwig, which had received general recognition became the precursor of numerous other treatises on distillation which appeared in the course of the sixteenth century. They reflect the height of the faith which the medicine of that period had in the "burnt waters" and in the miraculous powers of the "most subtle" powers obtained from natural objects by distillation. Of the numerous treatises that made their appearance during the sixteenth century, the following are particularly worth mentioning, not only because of the fame of their authors, but also because of the influence which they exerted on the development of the art of distillation, and on a better understanding of the distilled oils, viz. those of

Philipp Ulstad,[3]) physician and professor of medicine in Nuern-

[1]) *Liber de arte destillandi.* Vol. I, vol. 18 and 19. Brunschwig was well acquainted with the preparation of spirit of wine, not only by the distillation of wine, but also by that of fermented honey (vol. II, liber 1, cap. 14 and 28), of fermented fruit juices (vol. II, cap. 18), also by the fermentation and distillation of herbs, roots and flowers (vol. II, cap. 19).

[2]) *Ibidem.* Vol. II, cap. 26.

[3]) Philippi Ulstadii *Cœlum Philosophorum, seu liber de secretis naturæ tractatus, id est, quomodo ex rebus omnibus Quinta essentia paretur.* Argentorati 1543 u. 1528 — Augustæ Treboc. 1530 — Lugduni 1540 u. 1553 — Parisii 1543 — Francofurti 1600.

berg (at the beginning of the 16. century), Walter Hermann Reiff (Ryff),[1]) surgeon in Strassburg (in the first half of the 16. century), Pierandrea Matthioli[2]) (born 1501 in Siena, died 1577 in Trient), Remaclius Fuchs[3]) (born 1510 in Limburg, died 1587 in Brussels), Valerius Cordus[4]) (born 1515 in Simshausen in Hessia, died 1544 in Rome), Conrad Gesner[5]) (Euonymus Philiatrus, born 1516, died 1565 in Zuerich), Adam Lonicer[6]) (born 1528, died 1586), Giovanni Baptista della Porta[7]) (born 1537, died 1615

[1]) H. Gualtherus Ryff, *Neu gross Destillirbuch wohl gegründeter künstlicher Destillation.* Francofurti 1556. (See p. 46.)

[2]) Petri Andreæ Matthioli Medici Cæsarii et Fernandi Archiducis Austriæ *Opera quæ extant omnia: hoc est Commentarii in sex libris* Pedacei Dioscoridis Anazarbei *de materia medica. Post diversarum editionum collationem infinitis locis aucti: De ratione destillandi aquas ex omnibus plantis; et quomodo genuini odores in ipsis aquis conservari possint.* Veneti 1544 — Basiliæ 1565.

[3]) Remaclii Fuchsii *Historia omnium aquarum, quæ in commune hodie practicantium sunt usu, vires et recta destillandi ratio.* Veneti 1542—Parisii 1542.

[4]) Valerii Cordi Simesusii *Annotationes in* Pedacei Dioscoridis Anazarbei *de materia medica libros quinque, longe aliæ quam ante hac sunt emulgatæ. Ejusdem historiæ stirpium libri quatuor, et de artificiosis extractionibus liber.* Tiguri 1540.

After the death of Cordus this work was published with additions *(Horti Germaniæ)* and comments by Conrad Gesner in Zuerich. Several editions appeared in 1557, 1561 and 1583.

[5]) Thesaurus Euonymi Philiatri *de remediis secretis; liber physicus, medicus et partim etiam chymicus et œconomicus in vinorum diversi sapores apparatur, medicis et pharmacopolis omnibus præcipue necessarius.* Tiguri 1552. Liber I. *De destillatione ejusque differentiis in genere. Auctor est* Conradus Gesnerus. Tiguri.

The German edition bears the following title: *Ein kostlicher Schatz* Euonymi Philiatri *darinn enthalten sind viel heimlicher guter stuck der artzney, verteutscht durch* Joh. Rud. Landenberger. Zürich 1555.

[6]) Adami Loniceri, *Der Arzney Doctor und weiland Ordinarii Primarii Physici zu Francfurt am Meyn, Kräuterbuch und künstliche Conterfeyungen der Bäumen, Stauden, Hecken, Kräutern, Getrayde, Gewürzen und nützlichen Kunst zu destilliren. . . . . — Auf das allerfleissigste übersehen, corrigirt und verbessert durch Petrum Uffenbachium, Ordin. Physicus in Francfurt am Meyn.* Ulm, anno dei 1551, 1573 und 1589.

[7]) Joh. Baptistæ Portæ Neapolitani, *Magiæ Naturalis libri viginti, in quibus scientiarum naturalium divitiæ et deliciæ demonstrantur. Jam de novo, ab omnibus mendis repurgati, in lucem prodierunt. Liber decimus: Destillat, destillata ad fastigia virium sustollit.* Ravennæ 1565 — Antwerpiæ 1567 — Neapoli 1589 — Hanoviæ 1619.

in Rome), Geronimo Rossi[1]) (Hieronymus Rubeus, born 1539 in Ravenna, died 1607 in Rome), C. C. Kunrath[2]) (about the middle of the 16. century) and Jacob Besson[3]) (about the middle of the 16. century).

Next to Brunschwig's treatise on distillation, those of Ulstad and Ryff are given priority. Not only were they frequently quoted by the later authors but the illustrations were invariably copied from the two volumes of Brunschwig and the next oldest treatise by Ulstad. Possibly Brunschwig and Ulstad obtained their illustrative material from Arabian sources.

About twenty-five years after the appearance of Brunschwig's treatise, the above mentioned smaller treatise on distillation by the Nuernberg physician Philipp Ulstad was used almost equally extensively.[4])

It was published in Strassburg in 1526 and was shortly thereafter reprinted in Paris, Leyden, Frankfurt and elsewhere.

In 57 chapters the book supplies direction for the preparation of the supposed *Quinta essentia* by means of curious methods of circulation and distillation, which will be found mentioned in a subsequent chapter. The detailed explanations of the nature of the "fifth being" are merely a circumscription of the conventional ideas about distillation and the products of distillation already mentioned in connection with Brunschwig (p. 41). In

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[1]) Hieronymi Rubei Ravennatis *De destillatione liber, in quo stillatitiorum liquorum, qui ad medicinam faciuntur, methodus ac vires explicantur.* Ravennæ 1580 and 1582, Basiliæ 1581 and 1585.

[2]) C. C. Cunrathii *Medulla destillatoria et medica, oder Bericht, wie man den Spiritus vini zur Exultation bringen soll.* Leipzig 1549.

[3]) Jacobi Bessonii *De absoluta ratione extrahendi aquas et olea ex medicamentis simplicibus a quodam empirico accepta et a* Bessonio *locupletata, experimentis confirmata.* Tiguri 1559. — A French edition appeared in Paris 1573.

[4]) Philippi Ulstadii, patris nobilis *Cœlum Philosophorum seu liber de secretis naturæ, id est: quomodo non solum e vino, sed etiam ex omnibus metallis, fructibus, radicibus, herbis etc. Quinta essentia, sive aqua vitæ, ad conservationem humani corporis educi debeat.* Argentor. 1526 and 1528 — Lugduni 1540 and 1553 — Parisii 1543 — August. Treboc. 1553 — Francofurti 1600.

The German edition bears the following title: *Dess Edlen und Hocherfahrenen Herrn Philippi Ulstadii von Nürmberg Büchlein von Heimligkeiten der Natur, jetzund verdeutischt.* Frankfurt am Mayn 1551.

The French translation which appeared in Paris in 1547 bears the title: *Le Ciel des philosophes ou secrets de la nature.* Paris 1547.

general, the aim of all of the cumbersome processes described by Ulstad, is the separation of the spirit of all substances from their earthy body. This *quinta essentia* in turn practically resolves itself either into a spirit of wine, more or less strong and aromatised by means of plant or animal products, or into a spirituous solution of metallic acetates *(aurum potabile)*. All plant products, even apples, pears, cherries etc. further human blood, urine and other "subtle animal products" are subjected to cumbersome "digestion" and "circulation, i. e. to prolonged fermentation and putrefaction. Finally, "the spirit" is distilled and repeatedly rectified.

For the preparation of this "spirit" and that of a number of farfamed *aquæ vitæ* the book provides exact directions.

Inasmuch as all of these distillates *(Quintæ essentiæ)* are strongly alcoholic, Ulstad had no knowledge of distilled oils and hence does not mention them in his treatise. This is true in spite of the fact that his *aquæ vitæ* are distilled from strongly aromatic spices and other plant products with wine.

The value which the works of Brunschwig and Ulstad have today in the history of distillation lies in the detailed and careful description of the apparatus and methods of distillation and the illustrations thereof.

About 56 years after the appearance of Brunschwig's "Destillirbuch" and 28 years after that of the first edition of Ulstad's *Cœlum Philosophorum*, Walter Reiff (Gualtherus Ryff),[1]) a surgeon in Strassburg during the first half of the sixteenth century, published a third treatise on distillation which was held in high repute for a long time. It has the following title:

New gross Destillirbuch, wohl gegründeter künstlicher Destillation, sampt underweisung und bericht, künstlich abzuziehen oder Separiren die fürnembste destillirte Wasser, köstliche aquæ vitæ, Quintam essentiam, heilsame oel, Balsam und dergleychen vielgüter Abzüge. Recht künstlich und viel auff bequeme art dann bisher, auch mit bequemerem Zeug der Gefäss und Instrument, des ganzen Destillirzeugs von Kreutern, Blümen, Wurzeln, Früchten, Gethier unnd anderen stucken, darinnen natürliche feuchte unnd Elementische krafft, einfach oder mancherley gestalt vermischt und componirt; durch H. Gualtherum Ryff, Medicum & chirurgum, Agentinensem, getruckt zu Frankfurt a./m. bei Christian Egenolff's seligen Erben im jar 1556.

This treatise is supplied with numerous colored illustrations of plants, also with cuts of furnaces and utensils used in distillation. Its succinct text reveals technical knowledge, as a result

[1]) He lived during the middle of the 16. century.

of which the book demanded considerable respect, was widely distributed, and repeatedly imitated. The personality of the author finds expression even in the preface in which he fearlessly criticises contemporary authors, more particularly Theophrastus Paracelsus,[1]) the reformer of medicine. The folio of 197 leaves (394 pages) is divided into four parts. The first part of 52 pages is devoted to the explanation and description of the art of distillation and of the utensils used, in parts two and three the preparation and action of the distilled waters are described, and in the fourth part the preparation of the *Aquæ vitæ*, of oils and balsams.

Distillation is explained in a manner similar to that of Brunschwig given 56 years before, but it is more explicit (fol. 45):

"Die rechte gründliche Distillation an ir selbs ist nichts anders, dann ein abzug der natürlichen feuchten von gewechs, oder andere irdischen materi, durch gewalt der hitz abgezoge oder abgetriebe. Solche herrliche kunst ist den alten Griechischen ärzten und Philosophen unbekannt gewesen und ein neuer fundt und aufbringens der nachkommenden, zum theyl erdacht und nützlich erfunden von wegen der zartigkeit der menschen diser zeit, so allein, was in auch wohlschmecket, für nützlich achten, ... dann zu dem dass solche künstliche Abstractiones, oder gedestillierte wasser, öl, aquæ vitæ, und andere dergleichen stuck sehr nützlich und künstlich, also, dass sie ir gewaltige Wirkung, welche sie vermögen in menschlichem cörper zu erzeygen, ganz augenscheinlich darthun und wirken. . . . .

Es haben aber die natürlichen Philosophi solche Kunst des Destillierens erstlich abgenommen in nachfolgung der natur, welche natur in der grössern welt durch krafft und macht der Sonnen und hitz die dämpff in der erden

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[1]) The following bit of criticism by Ryff may here be quoted: *"Es wird die hochlöbliche Artznei nit aus Kräutterbüchern oder aus schlechtem teutschen schreiben gelernet, wie leyder jetzo solche kunst nit in geringen missbrauch kompt viles teutsches unformiges schreibens halber, welches auch von etlichen die grossen name in medicina haben wöllen geschicht. Aus solchem schreiben will dann jeder artzniren unn geschicht dardurch, dass der gemein man und etliche geachte leut iren leib anvertrawen einem Zanbrecher, Juden, Moench und alten vetteln. Dann bei diesen gilt mehr das geschwetz und der rhüm, dann die ware kunst. Wie da sagt das carmen:*

Sæpe rudes tantum facit ostentatio doctos,
Sæpius hæc rudibus nomina magna dedit.

Das ist:

Kannst du dich dapffer geben aus,
Mit rhüm und schwatz hoch prangen raus,
So wirst du haben rhüm und gunst,
Ob du gleich seist ein esel sunst."

verborgen, fürnemlich von wasser und feuchtigkeyt auffzeuchet, oder auffttreibet bis in die mitler region des luffts, von welcher sie zusammen getriben werden in einn nebel und wolken, so sich dann der selbig zerspreytet und schmelzet in Regen, Schnee oder Hagel, fallet er widerum herab zur erden. . . . .

Solche natürliche abziehung der feuchte von eim ding und gewechs haben unsere vorfahren abgenommen aus obgemelter wirkung. Haben also die materi, von welcher sie solche feuchte haben abziehen wollen, in ein grösser Geschire, so unden in die runde weit mit einem Bauch zusammen gethon, welches Instrument sich in der proportion der Spheren, darinnen wasser und erdreich versammelt, vergleicht wirt. So nun solche feuchte von der underlegten hitz verdünnert und gesubtiliert, wird sie obersich getriben, wo sich solche aufsteigende vapores wider erkületen unnd von der kelte gedensiert, sich dann in wasser zerlassende oder zerschmelzend, welcher durch solchs obergefess bequemlicher aussgeführt, gesammelt und zu mancherley nutzbarkeyt behalten und gebraucht werde." (New gross Destillirbuch, fol. 175—189.)

In the last part of the book he also describes "the correct method of preparing by distillation, according to the rules of art, several precious oils". These are distilled, some of them with wine, from myrrh, liquid storax, sagapenum, opopanax, ammoniac, styrax calamita, sacocolla, benzoin, labdanum, galbanum, turpentine, mastic, sandarac, guaiac wood, rosemary, spike, anise, cloves, cinnamon, mace, safron, and from various mixtures of spices (balsams).

Under spike and lavender oils (fol. 186) he mentions that these oils are commonly imported from France in small bottles and sold at a high price.[1])

How little Ryff knew about the nature of volatile oils and how primitive were his methods of preparation, becomes apparent from fol. 187 and 188 of his "Destillirbuch" where he describes "how from several strong and good spices precious oils can be distilled." To prepare specially good oils from cloves, nutmeg,

[1]) In the "Reformirte Apothek" published by Gualtherus Ryff in 1563 the following interesting statement is found (fol. 191): "When lavender flowers are distilled, a very fragrant oil usually floats on the surface. In the French Provence, about Narbona, where this plant grows abundantly, a specialty is made of the distillation of this oil. Oils are likewise distilled there from other useful and fragrant herbs, flowers, fruits and roots."

This statement is of historical interest since it is probably the earliest reference in German literature to the volatile oil industry which apparently existed in France as early as the 16. century.

mace and safron these spices are to be comminuted and distilled with rectified spirit. When the "spirits" have been distilled off and oil begins to come over, the mass is to be taken out and pressed between warm metal plates. The oil thus obtained is to be rectified by "circulation" until it is clear.

Among the other larger works of the sixteenth century which treat of medicinal plants and the preparation of distilled waters, also of the methods of distillation and of the utensils employed, those of Matthiolus and Lonicer are worthy of special mention.

In his comprehensive treatise on distillation,[1]) the former devotes a highly illustrated chapter to *De ratio destillandi aquas ex omnibus plantis.* Volatile oils, however, are mentioned only incidentally.

In his herbal of 1551,[2]) Adam Lonicer, however, describes in part the distillation of oils. Moreover, he reveals a better understanding of the same, as indicated in the following quotation from the preface (pp. 1 and 2).

"Dieweil der Gebrauch der gebrannten Wasser so von allerhand Kräutern und Gewächsen durch die Kunst der Destillirung abgezogen werden, an allen Orten so gar gemein ist, dass auch die geringsten Leute sich der Destillirung befleissigen, deswegen habe ich es vor gut angesehen, eine kurze Einleitung und Bericht des Destillirens zu beschreiben. Zudem werden viel herrliche und kräfftige Öhle von Gewürzen und Samen, als von Zimmet, Nägelin, Anis und dergleichen anderen vielen mit merklichem Nutzen der Kranken durch das Destilliren zu Wege gebracht.[3]) *. . . . Diese Kunst des Destillirens ist fast eine neue, und nicht gar alte Erfindung, den alten griechischen und lateinischen Medicis unbekannt und gar nicht in Gebrauch gewesen."*

Thus at the beginning of the sixteenth century Brunschwig's treatise on distillation gave the impetus not only for the more general introduction into medicine, of distilled waters and of spirituous aromatic distillates, but also for the perfection of the method of distillation. Indeed, it would seem that during the first half of the sixteenth century the herbals and treatises on distillation largely replaced the older antidotaries. As already

[1]) See p. 44, footnote 2.

[2]) See p. 44, footnote 6.

[3]) Aside from the use of rose oil and several other volatile oils as *oleosacchara,* already referred to, this statement is possibly the first reference to the medicinal use of volatile oils.

pointed out, the treatises mentioned above were not only reprinted but imitated in Germany as well as outside of Germany.

The professional scholars of this period who were most prominent because of their comprehensive knowledge and literary activity were Valerius Cordus and Conrad Gesner. Their works appeared about the middle of the sixteenth century and somewhat later. They were not only modeled after the earlier treatises but excelled them by a more thorough knowledge, by clearer exposition, and by greater wealth of material. Hence they were generally appreciated and recognized by municipal authorities.

Valerius Cordus (born 1515 in Simshausen, Upper Hessia; died 1544 in Rome), whose father was Professor of Medicine in Marburg, studied medicine at his home receiving the academic baccalaureate in 1531. In the same year he went to Wittenberg to attend the lectures by Melanchthon. Having soon obtained the *venia docendi,* he lectured on the *Materia medica* of Dioscorides.

These lectures of Cordus appears to have put down in writing. Five years after his death the German translation of these lectures was published in Frankfurt-on-the-Main by Ruellius. The commentaries on Dioscorides, also other scientific writings by Cordus were published in 1561 (possibly as early as 1557) by Conrad Gesner of Zuerich (born 1516, died 1565), who was a many sided scholar and a profuse medical writer. To the commentaries of Cordus were added not only additions by Gesner but an entire treatise by the latter.[1]) Only a single treatise

[1]) This folio bears the following title: *In hoc volumine continentur Valerii Cordi Simesusii Annotationes in Pedaceii Dioscoridis Anazarbei de medica materia libros quinque longe aliæ quam antea sunt hac sunt evulgatæ.*

Ejusdem Val. Cordi Historiæ stirpium libri quatuor posthumi nunc primum in lucem editi, adjectis etiam stirpium iconibus et brevissimis Annotatiunculis. Sylva qua rerum fossilium in Germania plurimarum. Metallorum, Lapidum et Stirpium aliquot rariorum noticiam brevissime persequitur, nunc hactenus visa.

De artificiosis extractionibus liber. — Compositiones medicinales aliquot non vulgares. — Hic accedunt Stockhornii et Nessi in Bernatium Helvetiorum ditione montium, et nascentium in eis stirpium, descriptio Benedicti Aretii Græcæ et Hebraicæ linguarum in schola Bernensi professoris clarissimi. Item Conradi Gesneri De Hortis Germaniæ liber recens una cum descriptione Tulipæ Turcarum, Chamæcerasi montani, Chamæopiti, Chamæenrii et Conizoidis. — Omnia summo studio atque industria doctissima atque excellentis viri Conr. Gesneri medici Tigurini collecta et præfationibus illustrata. — 1561 *Argentorati excudebat Josias Rihelius.*

appears to have been published by Cordus himself, viz. a botanical work, the *Historia plantarum,* a description of plants used in medicine. It is a folio of 224 pages with numerous illustrations and appeared 1540.

These "Annotationes" of Cordus are of special importance in the history of volatile oils, partly on account of the reputation of the author, partly because of his knowledge of the subject and also because they appeared in a century that was so productive of literature. Whereas Brunschwig's book reveals a retrogression in the technique of distillation as compared with the Arabian period, Ulstad, Ryff, Matthiolus, Lonicer and others advanced the art during the period of distilled waters and *aquæ vitæ* in several ways: they not only made known many of the older pieces of apparatus that had been forgotten, but they also improved them and invented new ones.

The ground thus prepared was further cultivated by Cordus and Gesner. Owing to the short life time of the former, it was the latter who continued their common labors and realized better results.

In the chapter *de destillatione oleorum* (fol. 226) of the *Liber de artificiosis extractionibus* of his *Annotationes,* Cordus discusses the nature of the plant extracts obtained by expression and distillation. Concerning the oily plant constituents, Cordus distinguishes between the viscid, fatty oils *(Oleum crassum, viscosum, terrestre)* obtained by expression, e. g. of seeds, and those of a spirituous nature *(ærea)* which can be separated from the "terrestrial" substances by distillation. As illustrations of the first class, he mentions a number of the common fatty oils, as illustrations of the second class the oils of carpobalsam,[1]) cardamom, cubeb, pepper, cloves, cinnamon, mace, nutmeg, lignaloes and those of some of the common umbelliferous fruits, such as anise, fennel, caraway, cumin, angelica, Ligustrum, Libanotus, Pastinaca, Apium, Petroselinum, Pimpinella and Anethum.

In his description of the properties of volatile oils, Cordus makes mention of the remarkable property of the oils of anise

[1]) Carpobalsamum is the name applied to the fruits of *Balsamea meccanensis,* Gleditsch (*Balsamodendron Opobalsamum,* Kunth), which were formerly used medicinally.

and fennel to congeal to a butyraceous or spermaceti-like mass; also of the property of the oils of cinnamon and cloves to sink under water.

The method of distillation of volatile oils has been carefully described by Cordus, (fol. 229)[1]) the description being accompanied by a cut of a glass still, consisting of body and helmet, constructed by himself.

Of still greater value than the *Annotationes* of Cordus is the *Thesaurus Euonymi Philiatri* of Conrad Gesner, the Latin edition of which was possibly published as early as 1550:

"De remediis secretis. Liber physicus, medicus et partim etiam chymicus et œconomicus in vinorum diversi saporis apparatu, medicis et pharmacopolis omnibus præcipue necessarius. Quem præter hæc qua antea prelo commissa fuere, quam plurimis fornacum figuris et auximus et illustravimus." Tiguri 1552 — Lugduni 1557—1566 — Francof. 1578.

As early as 1555 a German edition made its appearance which bears the following title:

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[1]) *"Eliciuntur hæc olea per destillationem in arena, ita ut tusa aromata aut semina injiciantur in cucurbitam vitream luto intectam optime, una autem vice ad unc. iii injiciantur, et sint trita secundum capacitatem cuburbitæ, infundatur deinde ad vi lib. aquæ clarissimæ, ac misceto diligenter. Pone deinde cucurbitam in capellam aptam fornaci et arena imple, et non attingat fundum, sed intersit arena. Cucurbitæ impone alembicum vitreum, cujus rostrum desinat in stanneam vel ferream fistulam (stanno forte addentum) intus et foris illitam; ea fistula transeat in obliquum per vas quod habet in se aquam frigidam, ut inter destillandum egrediens cum oleo liquorum refrigeretur, claude juncturas accurate, madefacto papyro vel linteo et suppone exceptorium. Postea accende ignem lentum et vide ne nimium surgat et ebulliat in alembicum, quod in cucurbita continetur. Semina enim quædam ut anisum propter raritatem substantiæ suæ, simulque viscosum largiter ebulliunt, ideo non statim alembicum imponere debemus, sed posteaquam bullas excitari videris et vaporem sursum ferri. Quod cum fiet depone alembicum et immisso bacillo agita, ita resolvetur in vaporem spuma, quæ postea, mediocri igne moderari, compesci et excitari potest. Quo facto impone rursus alembicum, et circumlutatio satis, ac destillari sine cessatione, donec conjeceris nullum amplius intus contineri oleum: quod visu et gustu statim percipies: nam cum gustu destillantes guttæ non amplius resipient injecti aromatis saporem, desistendum est ne aroma fundo cucurbitæ inhæreat et exuratur. Deinde segrega contentum in destillata aqua oleum optimum, quo potes artificio. Porro notandum est, quædam ex his oleis aquæ innatare, quædam fundum petere." (De artificiosis extractionibus, vol. 2, fol. 226.)*

"Ein kostlicher theurer Schatz des Euonymus Philiatrus, darinnen behalten sind vil heymlicher gütter stuck der arzney, fürnemmlich aber die art und eygenschafften der gebrannten wasseren und ölen, wie man dieselbigen bereiten sölle: desgleychen yeder wasseren und ölen art und eygenschafft, nutz und brauch. Item alles mit schönen lieblichen figürlinen angezeigt unnd Item wie man mancherley weyn bereiten sölle, auch den abgestandenen durch hilff der gebrannten wasseren, gewürtzen unnd anderley materi widerumb helffen möge für die augen gestellt, ganz lustig, nutzlich, und güt allen Alchemisten, haushalten: inbesonders den Balbiererern, Apothekern und allen liebhaberen der Arztney. — Erstlich in Latin beschrieben durch Euonymum Philiatrum, unn newlich verteutscht durch Johannem Rudolphum Landenberger zu Zürich: vormals in Teutsche sprach niemals gesähen. Getruckt in Zürich bei Andrea und Jacobo den Gessneren gebrüder im jar als man zalt von Christi unseres Heylands geburt 1555."[1])

Later there appeared a second part also written by Gesner, but the original Latin text of which was not published until after his death, which occurred in 1565, by Caspar Wolf. A German translation by Jacob Nueschler was published in 1583, likewise in Zuerich, under the following title:

Ander Theil des Schatzes Euonymi von allerhand künstlichen und bewerten ölen, wasseren und heymlichen Arzneyen, sampt ihrer ordentlichen bereytung und dienstlichen Figuren. Erstlich zusammen getragen durch Herrn Doctor Cunrat Gesner, Demnach von Caspar Wollfen der Arzneyen Doctor. Zürich; in Latin beschrieben und in Truck gefertiget, jetzt aber newlich von Johann Jacobo Nüscheler Doctoren, in Tütsche Sprach vertolmetschet. 1583.

Compared with Brunschwig's treatise which had appeared 50 to 65 years earlier, Gesner's treatises reveal a decided advance in the technique of distillation, also in his knowledge of volatile oils. The first German edition of 1555 contains several chapters "on distilled oils" (pp. 212—249) and on "balsams" and other mixed oils[2]) (pp. 249—273). The distillation of a

[1]) This famous book went through a considerable number of editions in the course of a century or more and was evidently very widely read. The English translation, by Morvyng, appeared in 1559 under the title: New book of distillation called the treasure of Euonymus. London 1559, 1564—1565. A French translation appeared at Lyons in 1555.

The nom-de-plume chosen by Gesner was most likely derived from evonymus = Spindle tree (prik-wood) and philiatros, φίλος ἰατρος = friend of science of medicine.

[2]) Literally: *"Balsamen und anderen kostlichen krefftigen und artig zusammen gesetzten Oelen."*

number of oils, viz.: of the oils of lavender, rosemary, rue, cinnamon, cloves, nutmeg and others, is described, and the description accompanied with cuts of the apparatus to be used; also the distillation of juniper berries and juniper wood by *destillatio per ascensum* and *destillatio per descensum.* (pp. 217 and 247). Of the oils of gum resins, oleoresins and resins, those of ammoniac, benzoes, galbanum, labdanum, myrrh, opopanax, liquid storax and styrax calamita, mastic and turpentine are described. The oils from guaiac wood and sandal wood and from several other woods and barks are mentioned (pp. 244—247) and their distillation described.

The second part published in 1583, which may be regarded as a new edition brought up to date, contains much the same material and illustrations.

To what extent Gesner's conception of the nature of the products of distillation was influenced by tradition, becomes apparent from the preface of the first German edition in which he praises the art of distillation as a means to obtain from medicaments

"Die aller reinest, edlest, krefftigst und durchtringest substanz, so die arzet nennen das fuenfft waesen (quinta essentia), von der unreinen, groben, yrdischen, unnuetzen und untaugliche substanz abgesuenderet und ausgezogen werden."

And further on he says:

"Demnach so findest du in diesem buche vergriffen die fuertraefflichen und tugendreychen stuck und arznyen, so die kuenstler, arzet und Alchymisten als sundere geheimnuessen und secret der natur, mit grossem fleyss verborgen und verhalten habend: als da sind die wohlriechenden wasser, die oel die aus kreueteren, gewaechsen, bluemen, fruechten und wurzeln gezogen und separirt werden."

A better understanding of the volatile oils themselves is revealed in the following passage from the first volume (p. 103):

"Lass ordentlich destillieren in waermer aeschen, von der absuenderung und scheidung des oels vom erdreych, so wirst du saehen von den selbigen materi, so auf diese art destillirt wirdt, ein feyn lauter, schoen und klaar wasser und oel herabfliessen, welches in im hatt de lufft oder des luffts eigenschafft, und das wasser, das ist die substanz unn das waesen, so das Element lufft und wasser in im hatt."

However, the confusion of ideas concerning distilled oils on the one hand and aromatized fatty oils on the other still manifests itself repeatedely in the writings of Gesner and Cordus.

Thus in the chapter on "distilled oils" three and even four methods for the preparation of one and the same oil are described. Among these are found not only the method of distillation proper, but that of infusion and digestion (circulation) with fatty oils, *e. g.* rose oil (pp. 224 and 236), lavender oil (p. 337), marjoram, myrrh and other oils (p. 332).

According to Gesner's directions a preliminary moistening of the material to be distilled with spirit of wine *(aqua vitæ)* is recommended. The oils are designated as a „feiste Feuchtigkeit" which is inherent in the herbs, flowers and roots. Flowers which have a delicate odor, such as roses, jasmine, etc, are packed in layers into the still, each layer being separated from the next by a similar layer of perfectly odorless flowers or leaves. The latter are to take up the aroma and to transfer it to the distillate.

In addition to many admirable directions, Gesner's writings contain descriptions of methods of distillation which reveal a complete absence of a clear distinction between aromatized fatty and distilled oils.

Thus among other descriptions, Euonymus Philiatrus gives the following directions for the preparation of distilled oils of several spices, viz. from cloves, nutmeg, mace, benzoes, storax, myrrh, safran etc.

"Die Specerei wird grob gepulvert, dann mit aqua vitæ durchfeuchtet und in den gläsine retorte gethan, und bei gelinder Wärme destillirt. Wenn das öl anfahrt zu fliessen, so nimm die materi der specereyen aus dem kolben und thus in ein säcklin, welches wohl verbunde sye mit einem faden, und trucks aus under einer prässen. Also dass du beide bläch der prässen wohl heiss machest. Und also gebürt es sich das ausgetruckt öl destilliren, rectificiren und circuliren, damit auff diese weis das rein lauter öl werde geschieden von der groben yrdischen materi. Demnach mag man wohl widerumb die häpffen putrificiren und digeriren mit dem vorgemeltem aqua vitæ, so von anderem abgesünderet worden. Unn zum letzten widerumb destilliren."

Thus the distillation was interrupted at the beginning, the fatty oil aromatised with the volatile oil was expressed, and the volatile oil separated from the aromatised fatty oil by distillation.[1])

For the distillation of the ethereal oil of flowers Philiatrus gives the following directions:

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[1]) *Ein köstlicher theurer Schatz etc.* Edition of 1555, fol. 215—217.

„Die Blümen der Spicken oder des Lavender solt du eine kurze Zeyt lang sonnen in einer grossen gläsinen retorte und darnach ein wasser in einem alembik darvonnen destilliren und abziehen. Dieses Wasser durch den ganzen Sommer gesetzt an ein warme statt an die Sonnen, so treybt es für und für öl über sich, welches öl du allwägen solt von dem wasser separiren und absündern mit einem fäderlich und dasselbe fleyssig behalten in einem gläsinen guttern[1]) *wohl vermacht und verstopfet."*[2])

As the last of the important practitioner-scientists and authors during the period in which the treatises on distillation dominated, the many sided Neapolitan noble man, Giovanni Battista della Porta (born 1537, died 1615) should be mentioned. Of his works,[3]) published in twenty books, two, viz. his *liber de destillatione* and his *liber de vinis* are of special importance to the history of distillation. Of all his contemporaries, all of whom, it is true, preceded him, he had the clearest conceptions of distillation and of the products of distillation. Both of the two books, which appeared about 1563 distinguish themselves from their precursors by a more comprehensive knowledge not only of the subject matter and literature, but also by means of originality in research and mode of presentation.

Porta makes a clear cut distinction between fatty expressed and distilled oils, describes their method of preparation, also the distillation of aromatic waters and the separation of the volatile oils from the water and the apparatus used for this purpose. However, even with this clear thinking and enlightened practitioner the term distillation conveys the traditional concept of various methods of separation and extraction of parts of plants. In like manner Porta adheres to the general use of the designation oil for certain hygroscopic preparations, *e. g. oleum ex salibus, oleum ex tartaro, oleum ex soda,* etc.

To what extent Porta's views concerning the nature of the distillation process and the changes produced by heat in general coincide with those of contemporaries, becomes apparent from

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[1]) Flask.

[2]) *Ein köstlicher theurer Schatz etc.* Edition of 1555, fol. 222.

[3]) Jo. Baptistæ Portæ, Neapolitani, *Magiæ naturalis libri viginti, in quibus scientiarum naturalium divitiæ et deliciæ demonstrantur. Iam de novo, ab omnibus mendis repurgati, in lucem prodierunt.* Romæ 1563 — Antwerp. 1564 — Hanoviæ 1619.

the preface (p. 367) to *De destillatone*, which constitutes book ten of his *Magiæ naturalis libri.*[1])

These sixteenth century treatises on herbs and their distillation, as well as a number of less important ones, were the principal handbooks for the preparation of medicaments, especially of distilled waters, oils, and vinous distillates. At first they supplemented the older antidotaries, later they replaced them. The gradual change from these treatises on distillation to the so-called dispensatories is marked by the appearance of several works classed with the latter. Those of Ortolff Meydenberger,[2]) and the later ones of Otto Brunfels[3]) (born 1488, died 1534), Leonhard Fuchs[4]) (born 1501, died 1566) and of W. H. Ryff[5]) (first half of sixteenth century) may here be mentioned.

With the appearance of Paracelsus (1493—1541) and the spread of his iatrochemical ideas in medicine, vegetable remedies lost their former importance, their place being taken more or less by chemical products. Thus the distilled waters had to surrender their supremacy and with it the herbals and treatises on

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[1]) "*Iam ad artes deventum est, et a distillatione duximus sumendum initium neotericorum inventum, res mira ultra mortalem sortem laudanda, non quæ a sciolis et vulgaribus usurpari solet, nam verum esse corrumpunt, destruuntque sed ad causarum gnaris pertractata. Docet enim hæc ars admirabilis, ut gravia corpora fiant spiritus et subliment et spiritus crascescant ac corpora evadant. Rerum vires, quæ mole obrutæ concultatæ, suis veluti in loculis delitescentes puriores, tenuioris et absque ulla impurioris materiæ accessione e plantis, metallicis, lapidibus et gemmis elicere, easque veluti non sua forte contentas, nobiliores in sublime educere, ac veluti in cœlum sustollere, poterimus chymisticis organis plantarum virtutes investigare et melius quam veteres gustu. Quid igitur majus poterit excogitari. Natura est res producere, ac viribus dotare, artis est productas nobilitare, ac multiplicibus viribus ditare. Accedat lector φιλομαθής, a natura secretorum perscrutator, nam distillationes haudquaquam inglorius tractabit. Primo aquas et olea extrahemus, mox esse tincturas, elixires, sales et ejusmodi similia. Mistum quodammodo in elementa dissolvere, ac singula puriora reddere, varias et adversantes, suas facultates separare et elicere, ut ex voto uti possimus, aliaque, quæ scisse et novisse non pænitebit.*"

[2]) Ortolff von Bayrland. *Arzneibuch. Hie fahet an eyn büchelin von manigerley Artzeney.* Mainz 1485.

[3]) *Spiegel der Arznei.* Strassburg 1532. — *Reformation der Apotheken.* Strassburg 1536.

[4]) *De componendorum miscendorumque medicamentorum ratione.* 1549.

[5]) *Reformirte deutsche Apothek.* Frankfurt a. M. 1563.

distillation lost in importance. The volatile oils, however, gradually taking the place of the distilled waters, gained in importance. This change was contemporaneous with the transition from the *Destillirbücher* to the dispensatories. Although this change was brought about gradually, it is usually identified historically with the appearance of the *Dispensatorium Noricum* of Valerius Cordus in the year 1546.

While in Wittenberg, Cordus (born 1515, died 1544) was in the habit of visiting with his uncle, the apothecary Ralla, who from 1532 to 1560 was proprietor of the *Salomo-Apotheke* in Leipzig. Here he seems to have taken an active interest in the art of distillation and in making chemico-pharmaceutical preparations. At Ralla's instigation and with his assistance, Cordus collected tried formulas for the preparation of distilled waters and other pharmaceutical preparations. These were published by Ralla.

This compilation, and still more his lectures on the *materia medica* of Dioscorides as well as his *Historia Plantarum* published in 1540, had established the fame of the young scholar. On one of his botanical excursions, Cordus appears to have stopped at Nürnberg where he received due attention in medical circles. In 1542 the council of that city charged him with the preparation of a dispensatory for the guidance of physicians and apothecaries of that municipality. This task Cordus accomplished with the aid of his uncle Ralla and of Caspar Pfreund, a friend and able apothecary at Torgau. The book was favorably received by the council of Nürnberg and was published in 1546, two years after the death of its author.[1]) Several editions appeared in rapid succession without date of publication, the third Nürnberg edition bearing the date 1548. As an authoritative treatise, the book seems to have found general recognition. It was frequently re-

[1]) *Pharmacorum omnium, quæ quidem in usu sunt, conficiendorum ratio. Vulgo vocant Dispensatorium pharmacopolarum. Ex omni genere bonorum authorum, cum veterum tum recentium collectum, et scholiis utilissimis illustratum. in quibus obiter, plurium simplicium, hactenus non cognitorum vera noticia traditur. Authore Valerio Cordo. Item de collectione repositione et duratione simplicium. De adulterationibus quorundam simplicium. Simplici aliquo absolute scripto, quid sid accipiendum, Ἀντιβαλλόμενα, id est, Succedanea, sive Quid, pro Quo. Qualem virum Pharmacopolam esse conveniat. Cum indice copioso.* Norimbergæ, apud Joh. Petreium.

Die Richtig-
ſte Ordnung/iſt
ein jedes an ſeinen
Orth/
Verhüttet viel
Schaden/vnd giebt
gute Förderung.
Ubi non ordo.
Ibi confuſio.
M.DC.XXIX.
LABOR ET VIGILANTIA MVLTVM
L. Kilian. Schalpsit.
IB. Invent. 1629.

Fig. 3.

printed, both in its original form and with the additions made by Conrad Gesner.

The long title of this work was abbreviated to *Dispensatorium Noricum* and it is commonly regarded as the first German pharmacopœia, though this is not quite true.[1]) It was recognized as standard up to the close of the seventeenth century, although twenty years later it had to share honors with the Augsburg Pharmacopœia of Adolph Occo.[2])

Notwithstanding the want of a clear understanding of the nature of the distilled oils during the whole of the sixteenth and part of the seventeenth centuries, their preparation was fostered and their use in medicine, the arts and in the household increased. Among the medical experimenters and writers of this period, Johann Winther,[3]) who was born 1487 in Andernach and who died 1574 as professor of medicine in Strassburg, seems to have distilled a large number of the more common volatile oils with great care.

Moreover, the distillation of aromatic waters and volatile oils was now being conducted principally in the pharmaceutical laboratories where both the process and the utensils were variously improved in the course of time.[4])

In addition to the Nürnberg and Augsburg pharmacopœias

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[1]) See p. 58.

[2]) *Pharmacopœa seu Medicamentarium pro Republica Augustana.* Author Adolphus Occo. *Augusta Vindelicorum* 1564.

Of this pharmacopœia there also appeared numerous reprints and editions as late as 1734. The titles of many of these are often modified by such terms as *reformata, renovata et aucta.*

The great demand for both of these pharmacopœias, which lasted a century and a half, is largely due to two reasons. First, these new pharmacopœias satisfied the practical demand better thenn did the older *Antidotaria* and the more recent treatises on distillation. Secondly, it was due to the rapidly increasing number of apothecary shops that were established during the 16. and 17. centuries.

[3]) Guintheri Andernacei *Liber de veteri et nova medicina tum cognoscenda tum facienda.* Basiliæ 1571.

[4]) On p. 59 will be found the title page of such a pharmacopœia of the *Res publica Gorlicensis* of 1629. It is characterized not only by the predominance of illustrations pertaining to the art of distillation, but also by the expression given to the sense of order prevailing in all laboratories of apothecary shops.

and similar authoritative works, the municipal price ordinances, which since the sixteenth century were issued in various cities to regulate the sale of drugs and spices, are reliable sources of information concerning the introduction of distilled oils into medicine and the arts. As documents they are of similar importance to the price lists of modern wholesale merchants and manufacturers.

The following list has been prepared with the aid of the previously discussed historical documents.[1]) It should, however, be definitely understood that the dates given are not necessarily those of the first introduction or use, but those of their legal recognition as articles of commerce.

DISTILLED OILS KNOWN AND IN USE:[2])

Up to the beginning of the sixteenth century:

The oils of benzoin, calamus, cedarwood, costus root, mastix, rose, rosemary, sage, spike, turpentine, juniperwood, frankincense, cinnamon.

TO THESE WERE ADDED:

From 1500 to 1540:

The oils of lignaloes, angelica, anise, cardamom, carpobalsam,[3]) cubeb, wild caraway, fennel, caraway, libanotis, lovage, mace, nutmeg,

[1]) In addition to the *Destillirbücher* previously mentioned, the following pharmacopœial works have been used in the compilation of this list: Of the *Dispensatorium Noricum* the editions of 1546, 1552, 1559, 1563, 1580, 1589, 1592 and 1612; of the *Pharmacopœa Augustana* the editions of 1580, 1597 and 1640; and the *Dispensatorium Brandenburgicum* of 1698.

Of the large number of municipal price ordinances the following were consulted: Frankfort-on-the-Main, for 1582, 1587, 1668, 1710; Nürnberg, for 1552, 1613, 1624, 1644, 1652; Worms, 1582; Strassburg, 1586; Wittenberg, 1599, 1632; Halberstadt, 1607, 1697; Halle 1643, 1700; Ulm, 1649; Bremen, 1644, 1664; Dresden, 1652; Leipzig, 1669, 1689, 1694; Berlin, 1574.

[2]) Bitter almond oil and several other poisonous oils, such as cherry laurel oil were excluded from general commerce on account of their poisonous properties. Hence they do not appear in the price ordinances. Inasmuch as they were not used medicinally when they first became known, they do not appear in the pharmacopœias. Both of the above mentioned oils were known before the middle of the sixteenth century, bitter almond oil even during the middle ages. Oils of animal origin are not mentioned in the above list.

[3]) *Carpobalsamum* is the name applied in the fruits of *Balsamea meccanensis,* Gleditsch *(Balsamodendron Opobalsamum,* Kunth) which were formerly used for medicinal purposes.

Pastinaca savita, L., pimpinella, pepper (from *Piper nigrum*), celery, sandal wood, juniper berries, juniper tar *(Oleum cadinum)*, mastix.

From 1540 to 1589:

The oils of elecampane, ammoniac, horehound, anime, asafetida, basilicum, bdellium, mountain melissa *(Calamintha montana)*, mountain thyme *(Thymus acinos)*, amber, citrus, coriander, "costiver", dill, origanum, sweet marjoram, elemi, galbanum, galangal, guaiac, chamomile, Roman chamomile, spearmint, labdanum, lavender, lemon, spoonwort, laurel, *marum verum,* marjoram, balm, mints, carrot seeds, feverfew, cumin, myrrh, cloves, opopanax, parsley, pepper (from *Piper longum*), summer savoy *(Satureja hortensis)*, European penny-royal, orange peel, tansy, wild thyme, rue, rhodium, saffron, sagapenum, sandarac, sassafras, false cumin, storax, tacamahac, thyme, iris, wormwood, hyssop, zedoary (root).

From 1589 to 1607:

The oils of *Chærophyllum bulbosum*, peppermint, savin, white mustard, seseli, zedoary (flowers).

From 1607 to 1652:

The oils of ginger, arbor vitæ, costmary *(Tanacetum Balsamita)*.

From 1652 to 1672:

The oil of cow-parsnip *(Heracleum sphondylium)*, cascarilla, cypress, *Anthriscus cerefolium, Eupatorium cannabinum,* black mustard.

From 1672 to 1708:

The oils of valerian, bergamot, mugwort, box-tree, masterwort, neroli, *Oleum templinum* (from *Pinus Pumilio*).

From 1708 to 1730:

Bitter almond oil and oil of cajeput.

At the beginning of the seventeenth century a change took place in the tendencies underlying alchemistic activities. These were accompanied by the transition of the practice of the art of distillation to the laboratories of apothecary shops. They were due also, in part, to the revival of the desire for the transmutation of the metals and for the discovery of the *lapis philosophorum* that had been sought for many centuries. The place of distilling apparatus was resumed by furnaces and subliming apparatus. Having failed to find the panacea for all ills and the fount of youth in organized nature, attention was again directed to mineral and metallic substances.

Chemical science was continuously driven to false conclusions, not only by its experiments to convert base metals into gold, but also by its search for a *quinta essentia* by means of a separation of the "subtle and spirituous" from the "coarse and earthy" by means of distillation and sublimation. False doctrines frequently guided both the plan and execution of alchemistic research, and thus influenced the object of the experiment as well as the interpretation of the phenomena observed. Consequently, the results were correspondingly uncertain and often a matter of accident. Thus chemical knowledge proved a false structure without internal coherence. Considerable as was the sum total of empirical progress made during the sixteenth and seventeenth centuries, it served merely the purpose of supplying building material for a later period. Included in this progress was the discovery of numerous useful chemical preparations and volatile oils. In like manner as the *lapis philosophorum*, the highest and final power of (inanimate) nature was being sought in the former, so the *quinta essentia*, the true panacea for the restoration of health and the prolongation of life, was sought in the latter. Thus Philipp Ulstad and other enlightened investigators of the sixteenth century thought they had discovered this *quinta essentia* in the spirit of wine. Each success, true or only apparent, stimulated the disciples of spagyric and alchemistic art to renewed activity and strengthened their belief in the imaginary powers of the coveted products. To this class belonged the majority of medical and pharmaceutical laboratory experimenters.

Although the diligent practice of the art of distillation brought about considerable progress in the technique, the conception of the nature of the products remained under the bann of the traditional theosophic doctrines. This was also the time when the thirty years war produced such disastrous effects upon the cultural and spiritual life of Germany. This religious war, in which Germany fared worse than any other country, destroyed wealth and well being, and for nearly a century crippled the scientific and commercial life of the nation. Traditional knowledge and practice in the arts and crafts was largely lost. Superstition and the spagyric art were revived and abstract alchemy flourished once more in Christian Europe as it had done in the Arabic world.

Whereas during the period described above, aromatic waters were used for medicinal purposes in Europe and more particularly in Germany, in Asia fragrant drugs of vegetable and animal origin, also the aromatic waters and aromatized fatty oils prepared from them were used extensively in religious ceremonies and in perfumery. Interesting accounts concerning these perfumes are found in the "Ain-i-Akbari", the annals of the emperor Akbar (1542—1605) written in the Persian language by his historian Abul Fazl toward the close of the 16. century.[1])

Lignaloes, which formerly played an important role, was comminuted and buried, thus causing the inferior portion to decay whereas the portion richer in resin, the pure lignaloes, remained. It was used for a variety of purposes: as a medicine, in perfumery and fumigation, as insecticide, etc. The oil of lignaloes, the Chuwah, is distilled by covering the comminuted wood with water in an earthenware flask, the neck of which is connected with a dish containing water. With the aid of a moderate fire the oil is driven over into the receiver. In order to remove the smoky odor, the oil is washed with water, the oftener the better. Concerning the history of rose oil, which was introduced into India by way of Persia, the following statement is made. In the imperial garden the bride of the emperor Jehanger observed a film on the surface of the canals which were supplied with rose water. This film she had collected and the oil thus obtained she named after her husband *Atr-i-Jehángiri.* Other fragrant waters, e. g. those prepared from orange and jasmine flowers, were known by the collective name of *Araq.* The fragrant grasses *Andropogon Schœnanthus, A. muricatus* and *A. laniger* are met with under the names *Rus* and *Abir Izkhir.* Of resins storax, benzoes, frankincense and labdanum are mentioned as being known. The last mentioned is described correctly as a substance obtained from *Cistus,* "a Cyprian and Chiotic tree". It is also obtained from the beards of goats who have eaten Cistus leaves. This second quality is regarded as the better.

Of camphor it is said that it was first found in a country not far from Ceylon. A substitute perfumed with camphor was

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[1]) David Hooper, The perfumes of the Moguls. Calcutta Review, October 1904. — Report of Schimmel & Co., October 1905, 83.

also known. By means of it "people without a conscience tried to enrich themselves at the expense of others." Borneo camphor was also highly prized.

Of minor importance are perfumes obtained outside of India, such as orris root, wormseed and patchouli leaves.

Of animal perfumes ambra, civet and musk are mentioned.

During the period under consideration all endeavors were directed toward the artificial preparation of gold. As a result there were more adepts during the 17. century than during the two previous centuries. Many courts, suffering from want of money, became the fruitful fields cultivated by the adepts of the spagyric art. Of these, only very few attained practical results of any kind, as did, *e. g.*, the alchemist Bœttger (born 1685, died 1719) who discovered the art of making porcelain. Chemically this poverty stricken century accomplished but little. Princes, scholars, physicians, indeed members of all classes of educated society were open or secret adherents and believers in the transmutation of the metals.

These endeavors which forced into the background all true chemical research, appear likewise to have caused a prolonged stagnation in the art of distillation. During the 17. century it was practiced only by a few experimenters far away from the turmoil of war that raged on German soil. Among these should be mentioned in particular Joh. Baptista van Helmont in Brussels (born 1577, died 1644), Johann Rudolf Glauber in Amsterdam (born 1604, died 1668), Nicolas Lemery in Paris (born 1645, died 1715), and Wilhelm Homberg in Paris (born 1652, died 1715).

During this period the practice was introduced of adding salts, such as common salt, potash, alum, and tartar to the water in the still. The object sought was to increase the gravity of the water so that the parts of plants might not so readily adhere to the bottom of the still and become empyreumatic. Presumably it was also observed in certain instances that an increased yield of oil resulted. The addition of hydrochloric acid, however, as recommended by Glauber must be characterized as going astray.

Even with these assumed improvements, the art of distillation at the close of the 17. century still rested on the basis of

empirical experimentation. Neither was it advanced by the phlogistic theory, proposed toward the end of the century by J. J. Becher (born 1635, died 1681) and more firmly established by G. E. Stahl (born 1660, died 1734), which theory permeated all chemical speculation for more than a century. Even if this theory, that characterized the last transition period of theoretical chemistry, was ingenious and productive, and prepared the way for the chemical reformation that occurred toward the close of the 18. century, it failed utterly to throw light on the composition of the volatile oils. Moreover the elemental components of air and the constituents of water, also the elements of which minerals and rocks are composed were known only in part up to the middle of the 18. century.

Renewed progress, however, in the manufacture and use of volatile oils is to be recorded during the eighteenth century. The technique of distillation was improved in the laboratories of the apothecary shops where the oils were largely distilled and a better product was prepared. The distilled oils were not only prepared on a larger scale and of better quality, but they found extended application not only in medicine, but also in the arts and in the household. The number of oils mentioned in municipal price ordinances and other literature up to 1500 had been only thirteen; in 1540 the number had increased to thirty-four and in 1589 to one hundred and eight oils. The *Dispensatorium Noricum* of Cordus mentions only three oils in 1543; the edition of 1552 mentions five; that of 1563 six; and that of 1589 fifty-six distilled oils. In 1708 one hundred and twenty oils are mentioned in the price ordinances of that time.

The distillation of pure volatile oils and the skill to mix them so as to produce agreeably fragrant mixtures, not only stimulated the improvement of methods of preparation, but also their extended use. With the distillation of the oils of lavender and rosemary, a volatile oil industry, as has already been indicated,[1]) seems to have developed from small beginnings in southern France during the fifteenth and sixteenth centuries. In like manner, the perfume industry seems to have had its origin. The preparation of "Hungarian water" in the sixteenth century by making

[1]) See p. 48.

an alcoholic distillate from fresh rosemary has already been referred to.[1]) During the seventeenth century, a *Karmeliter Geist,* an alcoholic distillate from balm and lavender,[2]) was introduced. In 1725 Johann Maria Farina of Cologne introduced his famous *Eau de Cologne.* The successful mixture of several odors and the prime quality of the oils used proved an important stimulus to the manufacture of these oils.[3]) From these small beginnings the perfume industry gradually developed into the important position it has held since the middle of the past century.

With the increased importance of the volatile oils, more attention was bestowed upon their nature and composition. Boerhaave (born 1668, died 1738), who at the beginning of the eighteenth century was professor of medicine, botany and chemistry at the University of Leyden, in his treatise on chemistry[4]) states that volatile oils consist of two elements: the one cruder and resinous, insoluble in water *(mater)*; the other more subtle, ethereal, which can scarcely be weighed and which by itself is possibly gaseous *(spiritus rector).* The first part he considered to be common to all oils and a unit by itself. The characteristic odor and taste, however, of the various oils were due to the *spiritus rector* which was peculiar to each oil. It was water soluble and therefore gave to the distilled waters their odor, taste and medicinal virtue. The changes produced in volatile oils upon exposure to air and light were attributed, in harmony with this theory, to the escape of the *spiritus rector.*[5])

This conception was perfectly in harmony with the belief, current during the middle ages and up to the 17. century, in

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[1]) See p. 30.

[2]) See the history of the oils of lavender and spike.

[3]) See the history of oil of balm.

[4]) *Elementa chemiæ, quæ anniversario labore docuit in publicis privatisque scholis,* Hermannus Boerhaave. *Tomus primus, qui continet historiam et artis theoriam. Tomus secundus, qui continet operationes chemicas.* Lugduni Batavorum 1732 — Londini 1732, 1735 — Parisii 1732, 1733, 1753 — Lipsiæ 1732 — Basiliæ 1745 — Veneti 1745, 1759.

[5]) *In hoc autem oleo essentiali rursus subtilissimus, volatilis, paucus, acerrimus, vix ponderandus, spiritus iterum complecticur illud omne, quod huic toti oleo dabat hanc vim; eoque ablato nihil in oleo. . . . Inquisivi in pondus spirituum, invenire non potui est.* (Boerhaave's *Elementa chemiæ,* Tom. 2, p. 124—131.)

the subtle properties and medicinal virtues of aromatic plant substances and their aqueous distillates. With the assumption of the water solubility of the *spiritus rector* the distilled waters were naturally regarded as being charged in the highest degree with the medicinal properties of the crude drugs. Boerhaave's dualistic theory concerning the composition of the volatile oils was therefore received as the most rational explanation of the firmly established belief in the efficacy of distilled waters, and was also accepted as a further argument for their retention in medicine. Even after the antiphlogistic nomenclature came into vogue after 1787, the *spiritus rector* was not discarded, being rebaptized as *arôme*.

The first chemists who discarded the dualistic theory of the volatile oils in their writings, and claimed that odor and taste are due to the oil as such, are F. A. C. Gren,[1]) Professor of Medicine in Halle, and the French chemist Ant. François de Fourcroy[2]) of Paris. The former exposed the untenability of Boerhaave's theory in 1796, the latter in 1798. Indeed Fr. Hoffmann (born 1660, died 1743), a contemporary of Boerhaave and professor at Halle, had not accepted the latter's theory without reserve. A many-sided investigator and writer, he had prepared and studied the volatile oils with great care.[3]) Yet he had no clearer conception concerning the nature and composition of the oils than his contemporaries. He distinguished between oils obtained by expression, by *destillatio per ascensum* and *per descensum*.[4]) He regarded sulphur as a fundamental principle of all oils, the bituminous and empyreumatic oils containing a

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[1]) Grens *Grundriß der Chemie nach den neuesten Entdeckungen entworfen und zum Gebrauch akademischer Vorlesungen eingerichtet.* Halle 1796. Vol. 2, p. 217.

[2]) Annal. de Chim. **25** (1798), 232 and Fourcroy, *Système des connaissances chimiques.* Paris 1801.

[3]) Frederici Hoffmannii *Opera omnia physico-medica. Denuo revisa correcta et aucta. In sex tomos distributa.* Genevæ 1740—1761 — Veneti 1745, 17 Volumina — Neapel 1753, 25 Volumina.

[4]) The *destillatio per ascensum* corresponds to the method now generally used, allowing the vapors to pass upwards in the still and removing them from above. In the *destillatio per descensum* the vapors were forced downward through the material and collected in a receptacle underneath the still. An incomplete extraction was thus effected. (Comp. chapter IV.)

relatively large amount of sulphur.[1]) He also believed that the color and odor of oils was influenced by their larger or lesser sulphur content.

It should be of interest to note that camphor which had been regarded as a volatile organic salt, was pronounced by Hoffmann to be a congealed volatile oil.[2]) He also made the observation that most of the commercial oils of his time were adulterated with turpentine oil, *oleum vini*, alcohol and fatty oils.[3]) Further he determined the yield[4]) and specific gravity[5]) of many oils. At the beginning of the 18. century, distillation was regarded as a well known and universally practiced method of laboratory technique. Hence the special interest of that period was directed mainly toward the determination of the yield of oils and the study of their properties. This interest was, no doubt, stimulated by Glauber's suggestion to rectify by distillation with dilute muriatic acid oils that had become colored by age.

Glauber's views[6]) and those of his contemporaries were opposed by Hoffmann. He declared the employment of *spiritus salis*,[7]) dilute sulphuric acid,[8]) potash, tartar and alum[9]) in the distillation of volatile oils as useless, but consented to the use of common salt. He argued that the addition of salt facilitated the separation of the oil particles and prevented decay; that

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[1]) Frederici Hoffmannii *Opera omnia physico-medica. Denuo revisa correcta et aucta. In sex tomos distributa.* Genevæ 1740—1761 — Veneti 1745. Tom. 4, Liber 1, p. 449—451.

[2]) *Ibidem.* Liber 72. *Observatio* 13, p. 44—50.

[3]) *Ibidem.* Liber 67. *Observatio* 2, p. 9—11.

[4]) *Ibidem.* Liber 65. *Observatio* 1, p. 1—9. *"De oleis destillatis inque eorum destillatione observanda."*

[5]) *Ibidem.* Liber 72. *Observatio* 8, p. 27—30. *"Gravitas specific oleorum."*

[6]) Johanni Rudolphi Glauberii *Furni novi philosophici.* Lugduni Batavorum 1648 — Amstelodami 1648 — Prag 1700. Pars 1, p. 35, 36 et 41, et pars 3, p. 30.

[7]) *Ibidem.* Pars 1, p. 36. This was crude hydrochloric acid prepared by the distillation of common salt and alum or sulphuric acid.

[8]) Crell's Chem. Journ. **3** (1780), 30. — Pfaff's *System der Materia medica.* 1815. Vol. 4, p. 50.

[9]) Glauberii *Furni novi philosophici.* Lugduni Batavorum 1648 — Prag 1700. Pars 1, p. 38 et pars 3, p. 31.

it made the water "heavier" and thus prevented the settling and burning of the plant material; that it also purified the distillate.[1])

In some instances recourse was again taken to the process of fermentation before distillation which was in vogue during the fifteenth and sixteenth centuries. This was done *e. g.* with juniper berries, wormwood, sage and other herbs, honey and yeast[2]) occasionally being added. The old practice of previously moistening the plant material with alcohol[3]) was also resorted to. In this manner a larger yield of oil was obtained but it would seem that the dilution of the oil with alcohol was not recognized.

Downward distillation *(destillatio per descensum)* was applied by Hoffmann[4]) in the preparation of oils with high specific gravity such as the oils of cinnamon and cloves. This method was evidently regarded as being better because the dark colored oils thus obtained were supposed to contain more sulphur.

With the increased use of volatile oils during the first half of the eighteenth century it became more and more desirable not only to prepare oils of good quality but to obtain the largest possible yield as well. As guides there appeared new treatises on distillation[5]) which had little more than the title in common with the older *Destillirbücher.* They treated not only of distilled

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[1]) Fr. Hoffmannii *Opera omnia physico-medica. Supplementum secundum.* Geneva 1760. Pars 1, p. 730.

[2]) *Berlinisches Jahrbuch für Pharmacie* 1804, 380.

[3]) Demachy, *Laborant im Großen, oder die Kunst die chemischen Produkte fabrikmäßig zu verfertigen. Aus dem Französischen übersetzt, mit Zusätzen versehen von* Samuel Hahnemann, *der Arzneikunde Doctor und Physikus des Amtes Gommern.* Leipzig 1784, p. 238.

[4]) Fr. Hoffmannii *Opera omnia physico-medica.* Tom. 4. *Observationum selectiorum libri.* 1717. Liber 1, p. 449—451. — *Supplementum secundum.* 1760. Pars 1, p. 730.

[5]) Of these the following are the more important:

Die zum allgemeinen Gebrauch wohl eingerichtete Destillirkunst. Auch die Bereitung verschiedener destillierter Wässer und Öle. Von C. H. Burghart. Breslau 1736. *Neue Auflage mit vielen Zusätzen von* J. Christian Wiegleb. 1754.

Das Brennen der Wasser, Öle und Geister. Wohleingerichtete Destillierkunst und neue Zusätze. Von G. H. Burghart. Breslau 1748.

waters, but also of volatile oils and spirit of wine. Coupled with the scientific problem of the distillation of the volatile oils was the commercial problem of the largest possible yield.

Following the lead of Winther,[1]) Boerhaave and Hoffmann, a number of investigators of the eighteenth century ascertained the yield of oil obtainable from the more common aromatic plant products. Of these the following deserve special mention: Joh. Fr. Cartheuser[2]) (born 1704, died 1769), Professor of Medicine, Botany and Chemistry at the University of Frankfurt-on-the-Oder; Caspar Neumann[3]) (born 1683, died 1737), a Berlin apothecary; Claude Joseph Geoffroy (born 1685, died 1752), a Parisian apothecary; and Guillaume François Rouelle[4]) (born 1703, died 1770).

Their experiments were conducted on a small scale and with simple apparatus. Their results, however, published in their

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Traité raisonné de la distillation, ou la distillation réduite en principes avec un traité des odeurs. Par *Dejean.* Paris 1753. — Deutsche Ausgabe, Altenburg 1754.

Traité des odeurs, Suite du traité de la distillation. Par *Dejean.* Paris 1764.

[1]) See p. 60.

[2]) Cartheuser's researches on the volatile oils are contained in the following of his treatises:

Fundamenta materiæ medicæ. Francofurt. ad Viadr. 1738 and edition of Paris 1752.

Elementa Chymiæ dogmatico-experimentalis, una cum synopsi Materiæ medicæ selectioris. Hallæ 1736. *Editio secunda priore longe emendatior.*

Dissertatio chymico-physica de genericis quibusdam plantarum principiis hactenus neglectis. Francof. ad Viadr. 1754. *Editio secunda* 1764.

Dissertatio physico-chemica medica de quibusdam Materiæ medicæ subjectis exarat. ac publice habet nunc iter. resus. Francof. ad Viadr. 1774.

Dissertationes nonnullæ selectiores physico-chemicæ ac medicæ, varii argumenti post novam lustrationem ad prelum revocat. Francof. ad Viadr. 1778.

Pharmacologia theoretico-practica prælectionibus academicis accommodata. Berolini 1745.

[3]) Caspar Neumann's researches on volatile oils can be found in the second volume of his *Chymia medica dogmatico-experimentalis, oder Gründliche mit Experimenten bewiesene Medizinsche Chemie.* Published by Christ. Heinr. Kessel. 4 vols. Züllichau 1749—1755.

[4]) Geoffroy's and Rouelle's work on volatile oils was published in the *Mémoires de l'académie royale des sciences de Paris* for the years 1730 to 1760.

works and in journals,[1]) were regarded as standard and were quite generally introduced into the literature on the subject. Through the dispensatory of the English physician and chemist, William Lewis,[2]) the results of the above mentioned and of other continental investigators found their way into English literature.

Aside from the publications already mentioned, the interest shown in the study of volatile oils toward the close of the seventeenth and during the course of the eighteenth century is possibly best shown by the number of dissertations on the subject which were written at German universities under the stimulus of a number of university teachers.[3])

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[1]) In 1789, Remler of Erfurt collected and tabulated the observations relative to the yield and properties of volatile oils published up to that year.

A similar tabular compilation taking into consideration also the origin of the oils was published in the *Journal de pharmacie* for August 1834 by Raybaud of Paris in connection with the industrial exposition of the previous year. A German translation appeared in Buchner's *Repert. der Pharm.* for 1835, vol. 51, p. 54. Two further treatises on this subject appeared by G. H. Zeller in 1850 and 1855 respectively in the *Jahrbuch für praktische Pharmacie und verwandte Fächer.* The former appeared also as a separate under the title of *Studien über ätherische Oele,* Landau, 1850; the latter under the title *Ausbeute und Darstellung der ätherischen Oele.* Stuttgart, 1855.

[2]) The new Dispensatory: Containing the theory and practice of pharmacy, a description of medicinal simples, according to their virtues and medicinal qualities, the description, use and dose of each article etc. Intended as a correction and improvement of Quincy. London 1753.

[3]) The more important ones are herewith enumerated:

1670. *De oleorum destillatiorum natura et usu in genere. Dissertatio ab* David Kellner. Helmstadii.
1696. *De oleis destillatis. Dissertatio ab* Henrico Rosenberg. Jenæ.
1744. *De oleis destillatis empyreumaticis. Dissertatio ab* Christian Lindner. Francofurti ad Viadrum.
1744. *De sale volatili oleoso solido in oleis æthereis nonnunquam reperto. Dissertatio ab* Fr. Günther. Francofurti ad Viadrum.
1745. *De oleis vegetabilium essentialibus. Dissertatio ab* A. Fr. Walther. Lipsiæ.
1746. *De spiritu rectore in regno animali, vegetabili et fossili, atmosphærico. Dissertatio ab* Gottfried de Xhora. Leydæ.
1747. *De oleorum destillatorum usu multiplice principue in castris. Dissertatio ab* Joh. Paul Ziegler. Altorfii.
1748. *Dissertatio chemica inauguralis sistens Dosimasiam concretionum in nonnullis oleis æthereis observatum ab* F. Hagen. Regiomontanæ.

The investigations reported in these dissertations, however, rest on false premises and, therefore, produced no valuable results. Research based on the phlogistic theory and the doctrines of Boerhaave and Hoffmann concerning the constitution of volatile oils, could hardly be expected to yield results of any importance. As is well known, water was resolved into its elements as late as 1766, the elements composing the atmosphere were discovered in 1774, and the phlogiston theory was disposed of in 1785.

How crude the notions concerning the chemical nature of volatile oils were even at the time of Scheele, is shown in a dissertation[1]) of the year 1765 accepted by the University of Jena. From it the following propositions or conclusions are quoted:

"The essential constituents of volatile oils are of two kinds, solid and liquid. To the first class belong sulphur, phlogiston, earth and salts; to the second class air, fire and water. The presence of the first is revealed by the inflammability of the oils, for every object that burns with a flame contains much sulphur or phlogiston. The color as well as the coloration of the oil likewise argue in favor of their presence. Some oils are yellow, others green or blue; with age, the colors become darker. As is known, all coloration is due to particles of sulphur or phlogiston. Such oils have a penetrating odor, which is caused by their content of volatile saline sulphur particles. They, therefore, contain sulphur or phlogiston in sufficiently large quantities.

"In the course of time these oils are converted into a resinous mass, a change that is not conceivable without phlogiston.

"Volatile oils always burn with a smoking flame. All soot, however, consists of earth, salt, water and phlogiston. When the oils are treated with nitric acid, a residue of earth and carbon remains.

"Some volatile oils have a higher specific gravity than water. This is due to their larger content of earthy constituents and salts."

1752. *De oleis essentialibus æthereis eorumque modo operandi et usu. Dissertatio ab* Johann Friedr. Vangerow. Hallæ.

1759. *De oleis destillatis æthereis. Dissertatio ab* Fr. W. Eiken. Helmstadii.

1765. *De partibus oleorum æthereorum constitutivis. Dissertatio ab* Johannes Christ. Schmidtius. Jenæ.

1765. *De partibus oleorum æthereorum constitutivis. Dissertatio ab* J. Fr. Faselius. Jenæ.

1765. *De oleis vegetabilium essentialibus, eorumque partibus constitutivis. Dissertatio ab* W. B. Trommsdorff. Erfurti.

1778. *De adulterationibus oleum æthereorum. Dissertatio ab* K. W. Chr. Müller. Gœttingen.

[1]) *De partibus oleorum æthereorum constitutivis. Dissertatio inauguralis per* Johannes Christianus Schmidtius. Jenæ *d. 30. Mærz 1765.*

Only a superficial insight into the nature of the volatile oils was obtained through the study of their properties and their behaviour toward strong chemical reagents, a study that was taken up at the beginning of the 18. century. Indeed, many of these experiments yielded no results whatever. This is true *e. g.* of the repeated distillations of volatile oils with chalk[1]) and burned lime, such as were undertaken by the otherwise excellent chemist Wilhelm Homberg (born 1652, died 1715) about the year 1700.

A better knowledge was attained by careful observation. Thus the crystalline deposits formed in some oils upon standing, also the congealing of certain oils at lower temperatures, which had been observed by Valerius Cordus in 1539, by Joh. Kunkel in 1685, by J. H. Link in 1717, by Friedr. Hoffmann in 1701, by Caspar Neumann in 1719 and by others, were studied. The crystalline parts were regarded as a volatile salt, later as a camphor peculiar to each oil, at times also as benzoic acid.[2]) Fr. Hoffmann explained the congealing of oils of rose, anise and fennel by assuming the formation of a curdled modification of the oil. Caspar Neumann in 1719 and Cl. J. Geoffroy in 1726 regarded the crystals formed upon standing as camphor.[3]) The formation of such crystals was observed by Caspar Neumann[4]) in the oils of thyme, cardamom and marjoram; in peppermint oil by H. D. Gaubius[5]) of Leyden in 1770; in oil of mace by J. G. Wiegleb[6]) in 1774; in the oils of lavender, rosemary, sage and marjoram by Arezula[7]) in 1785. They regarded these

[1]) *Mémoires de l'académie royale des sciences de Paris.* 1700, p. 298 and 1701, p. 129, also *Chem. u. botan. Abhandlungen der Acad. d. Wissensch. zu Paris.* Translated by Steinwehr. Vol. 3, pp. 155—157.

[2]) Hagen, *Dissertatio chemica inauguralis sistens dosimasiam, concretionum in nonnullis oleis æthereis observatarum.* Regiomontanæ 1748.

P. J. Macquer's *Dictionnaire de Chymie.* Paris 1766. *Deutsche Übersetzung von* J. G. Leonhardi. Leipzig 1781. Vol. 4, p. 465, footnote 9.

[3]) *Mémoires de l'académie royale des sciences de Paris.* 1726. p. 95.

[4]) *De salibus alcalino fixis camphora.* Berolini 1727. p. 105.

[5]) *Adversariorum varii argumenti liber unus.* Leidæ 1771. Sectio 7, p. 99—112.

[6]) Vogel's *Lehrsätze der Chemie. Mit Anmerkungen herausgegeben von* J. G. Wiegleb. Weimar 1775. § 342.

[7]) *Resultato de las experiencas hachas sobre alcanfor de Murcia con licencia.* En Segovia 1789.

separations as varieties of camphor, only J. G. Wiegleb thought them to be peculiar combustible salts.[1])

The action of strong acids had been observed by Glauber[2]) as early as 1663. The effect of strong nitric acid on a number of distilled oils was studied by Olaus Borrichius[3]) in 1671, by J. P. Tournefort[4]) in 1698, by Hasse[5]) in 1783; that of sulphuric acid by Joh. Kunkel[6]) in 1700 and by W. Homberg[7]) in 1701. A more detailed study of the action of strong acids on volatile oils was made by Friedrich Hoffmann[8]) and by Cl. J. Geoffroy[9]) in 1726 and by Rouelle[10]) in 1747. Upon distillation of oils with strong hydrochloric acid, especially if the acid was generated in an almost anhydrous condition in the experiment, it was supposed that compounds of the oil with the acid were obtained. Such a supposed compound was known to Homberg[11]) as early as 1709. The preparation, however, of such a compound of definite chemical composition was first accomplished by Kindt[12]) an apothecary in Eutin, in 1803 by the action of gaseous hydrogen chloride on turpentine oil.

The solubility and color of distilled oils also received atttention during the eighteenth century. Thus Macquer in 1745 published his investigations on the solubility of distilled oils in alcohol, which were the most extensive on this subject.[13]) The color of oils and the changes in color were studied by Wilh. Homberg[14]) in

[1]) See p. 74, footnote 6.

[2]) R. Glauberii *Prosperitas Germaniæ.* Amstelod. 1656.

[3]) *Acta medica et philosophica Haffnienses.* 1671. p. 133.

[4]) *Historia regiæ scientiarum academiæ. Autore du* Hamel. Parisii 1701. p. 495.

[5]) Crell's *Neueste Entdeckungen in der Chemie* **9** (1783), 38. — Crell's Chem. Annalen **1** (1785), 417.

[6]) *Laboratorium chymicum.* Hamburg 1716. p. 347.

[7]) *Chem. botan. Abhandlungen der königl. Acad. d. Wissensch. in Paris.* Translated by Steinwehr. **1**, 720.

[8]) *Observatorium physico-chimicarum selectiorum.* 1712. Liber III, p. 123.

[9]) *Mémoires de l'académie royale des sciences de Paris.* **1726**, 95.

[10]) *Ibidem.* **1747**, 45.

[11]) *Chem. botan. Abhandl. d. königl. Acad. d. Wissensch. in Paris.* Translated by Steinwehr. **3**, 155—167.

[12]) Trommsdorff's Journ. d. Pharmacie **11**, II. (1803), 132.

[13]) *Mémoires de l'académie royale des sciences de Paris.* **1745**, 4.

[14]) *Chem. botan. Abhandl. d. königl. Acad. d. Wissensch. in Paris.* Translated by Steinwehr. **3**, 155—167.

1707 and by Jacob J. Bindheim[1]) of Moscow in 1788. The latter arrived at the conclusion that the color depends on a larger or lesser amount of resin carried over in the process of distillation, hence the darker colored oils are apt to contain considerable resin. Bindheim also determined the yield of oils, especially of those of chamomile and peppermint, by distilling larger amounts of these herbs.

In 1793 and 1794 Margueron studied the action of frost on volatile oils and observed the formation of crystals and congealing in connection with a number of the more common oils.[2])

As has already been pointed out, the phlogistic theory afforded no satisfactory basis for the study of organic substances and consequently of volatile oils. With the discovery of oxygen by Scheele and Priestley during the years 1771[3]) to 1774 and the ingenious interpretation of this and other discoveries by Lavoisier with the aid of the balance, a reaction against the phlogistic theory set in which resulted in the inauguration of the present chemical period. The study of the chemical constitution of substances was placed on a rational scientific basis. Inorganic chemistry, having to deal with the simpler substances, profited first by the new theories of the opponents of the phlogistic school. Organic chemisty, and with it the study of the volatile oils, were benefited somewhat later.

Though of little consequence, the experience of the Dutch chemists Deimann, Troostwyck, Bond and Lauwerenburg[4]) should here be mentioned. They passed the vapors of volatile oils through red hot iron tubes and examined the resulting gases. At the same time they made the bold attempt to synthesize oils by the action of gaseous hydrogen chloride on olefiant gas.

The first investigation suggested by the new theories that was of positive value, was the elementary analysis of turpentine oil

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[1]) Crell's Chem. Annalen. **1788**, II. 219 and 488.

[2]) Journ. de Chim. et de Phys. **2** (1794) 178. — Crell's Chem. Annalen. **1795**, II. 195, 310 and 430.

[3]) A. E. von Nordenskiöld, Scheele's *nachgelassene Briefe und Aufzeichnungen*. Stockholm 1892. pp. XXI, 86, 408, 458 and 466. — Pharm. Rundschau (New York) **11** (1893), 28 and 48.

[4]) Journ. de Chim. et de Phys. **1794**, II. 178. — Crell's Chem. Annalen. **1795**, II. 195, 310 and 430.

made by Houtton-Labilliardière.[1]) He found the ratio of carbon to hydrogen to be five to eight, the same that was later established for all hemiterpenes, terpenes, sesquiterpenes and polyterpenes.

Attention has already been called to the crystalline deposits that had been observed in the course of several centuries. These were mostly considered as identical with ordinary camphor because like it they were volatile, soluble in alcohol and fatty oils, and burned with a smoky flame. Only in a few instances, however, had these deposits been proven to be identical with camphor. Berzelius,[2]) therefore, argued against the indiscriminate generic use of the term camphor.

"Several writers have applied the term camphor to all solid volatile oils. Thus a well known term of a commonly used substance has been given a different meaning from the one of long standing. Because of this disadvantage I felt myself constrained to disregard entirely this use of the word camphor."

In its place he suggested the use of the term stearoptene (from στέαρ, tallow, and πτήνον, volatile). He pointed out the analogy existing between volatile and fatty oils in so far as they can be a mixture of several oils having different congealing points. Thus oils may, under favorable circumstances, be separated into an oil which is solid at ordinary temperature, the stearoptene, and one which is liquid at low temperatures, the elaoptene (from ἔλαιον, oil, and πτήνον, volatile.[3])

The result of this was that the solid deposits from volatile oils were thereafter designated alternately stearoptene as well as camphor. Up to this day the misuse of the term camphor has not ceased as becomes apparent from such words as cedar camphor, cubeb camphor, juniper camphor, etc.

Soubeiran and Capitaine[4]) made matters even worse by applying the term "liquid camphor" to the liquid hydrogen-chloride addition products of the terpenes. After it had been shown that true camphor contained oxygen, the term camphor in its generic sense was also applied to other oxygenated constituents of volatile oils though they were liquid.

[1]) Journ. de Pharm. 4 (1818), 5.
[2]) Berzelius, *Lehrbuch der Chemie.* 3. ed. 1837. vol. 6, p. 580.
[3]) Berzelius, *Lehrbuch der Chemie.* 3. ed. 1837. vol. 6, p. 580.
[4]) Liebig's Annalen **34** (1840), 311.

In 1833 Dumas published an article entitled *Über die vegetabilischen Substanzen, welche sich dem Campher nähern und über einige ätherische Öle.*[1]) Although a number of important observations of rather striking properties of individual oils had been made, the systematic study of the volatile oils may be said to have begun with the analysis of a number of stearoptenes by Dumas. He suggested the following classification of volatile oils:

1. Those that consist of carbon and hydrogen only, like turpentine oil and oil of lemon;
2. Those that contain oxygen, like camphor and anise oil;
3. Those that contain sulphur,[2]) like mustard oil, or nitrogen, like oil of bitter almonds.

The elementary analysis of solid peppermint oil, camphor and solid anise oil revealed the composition $C_5H_{10}{}^1/_2O$, $C_5H_8{}^1/_2O$ and $C_5H_6{}^1/_2O$. By doubling these formulas of Dumas the modern formulas for the respective substances are obtained.

Of the oxygen-free oils, he analyzed turpentine oil and the hydrocarbons of lemon oil, verifying the earlier results of Houtton-Labilliardière. During the years 1833—1835, Dumas published further contributions on the subject of volatile oils, several jointly with Pelouze and Peligot. They pertain to artificial camphor (pinene hydrochloride), mustard oil, cinnamon oil, terpin hydrate, orris oil, pepper oil, oil of juniper berries and others.

Almost simultaneously with the first publications by Dumas, Blanchet and Sell[3]) published the results of their investigation which had been carried out in Liebig's laboratory and which involved in large part the same substances studied by Dumas. The most noteworthy result of these investigations is the recognition of the identity of the stearoptene from fennel oil with that from anise oil.

Several years later, in 1837, the highly important and very

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[1]) Liebig's Annalen **6** (1833), 245.

[2]) The fact that mustard oil contains sulphur was recognized by Thibierge in 1819 (Journ. de pharm. **5**, pp. 20, 439 and 446; Trommsdorff's Neues Journ. d. Pharm. **4**, II. p. 250). That sulphuretted hydrogen is given off during the distillation of several umbelliferous fruits, such as caraway, dill, fennel, etc., was pointed out by L. A. Planche of Paris in 1820. (Trommsdorff's Neues Journ. d. Pharm. **7**, I. p. 356.)

[3]) Liebig's Annalen **7** (1833), 154.

interesting results of Liebig and Woehler's work on bitter almond oil were published.[1]) As early as 1802 Schrader and Vauquelin had discovered hydrocyanic acid in the distillate of bitter almonds. In 1822 Robiquet showed that no volatile oil preexisted in the almonds, and with Boutron-Charlard he had prepared amygdalin in 1830. They had not succeeded, however, in preparing bitter almond oil from amygdalin. That amygdalin is decomposed by emulsin into benzaldehyde, hydrocyanic acid and sugar was demonstrated by Liebig and Woehler. They also point out that the manner of formation of mustard oil must be closely related to that of bitter almond oil, for the mustard seeds deprived of their fatty oil possess no odor, this being produced only when water is present. The investigation of mustard oil by Will[2]) in 1844 substantiated this supposition.

Chemists now became especially interested in the action of hydrogen chloride on various terpenes and in the resulting hydrochlorides, some of which were solid, others liquid; also in the study of terpin hydrate and its decomposition products. The study of the literature pertaining to these subjects is rendered difficult by the error of regarding mixtures of several substances as chemical individuals and describing them as such;[3]) further by the fact that almost every author, irrespective of the work of others, coined a nomenclature of his own.[4])

Crystalline pinene monohydrochloride had been discovered by Kindt,[5]) an apothecary, in 1803. He regarded it as artificial camphor, a view shared by Trommsdorff.[6]) The true composition of this compound was ascertained by Dumas in 1833.

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[1]) Liebig's Annalen **22** (1837), 1.

[2]) Liebig's Annalen **52** (1844), 1. A more complete insight into the mechanism of the reaction by which mustard oil is produced was supplied by the later investigations of Will and Koerner in 1863. Liebig's Annalen **125** (1863), 257.

[3]) This confusion continued until Wallach cleared up the situation.

[4]) The historical development of this chapter of the chemistry of the terpenes is described in *Terpene und Terpenderivate, ein Beitrag zur Geschichte der ätherischen Oele* by E. Kremer's (Pharm. Rundschau **9** (1891), 55, 110, 159, 217, 237; and **10** (1892), 10, 31, 60; also Proc. Wisc. Acad. Sc. Arts and Letters, 8, pp. 312—262).

[5]) Trommsdorff's Journ. d. Pharm. **11**, II. 132.

[6]) *Ibidem*, p. 135.

Crystalline dipentene dihydrochloride was discovered by Thenard in 1807. It is the *salzsaures Citronenöl*, muriate of lemon oil, of Blanchet and Sell, the artificial lemon camphor of Dumas. These and similar substances were investigated by Soubeiran and Capitaine (turpentine oil), Deville (turpentine oil and elemi oil), Schweizer (carvene) and Berthelot (turpentine oil).[1]) The formation of terpin hydrate and the action of acids on this substance was studied principally by Wiggers, List, Deville and Berthelot.[2])

A paper published about this time (1841) by Gerhardt and Cahours[3]) is of special interest in so far as it contains a definition of a volatile oil which in a general way holds good to-day. It also makes known new methods of investigation. About oils in general the authors state:

"There are, indeed, but very few oils which can be crystallized; most oils are liquid and consist of a mixture of two and even three peculiar substances, which rarely are obtained by themselves when distilled at different temperatures."

The separation of the individual substances is effected by first allowing any solid constituent to crystallize out, then the lower boiling hydrocarbon is isolated by distillation at a temperature 20—30° below the boiling point of the crude oil.[4]) Inasmuch, however, as the hydrocarbon cannot be completely freed from oxygenated constituents in this manner it is treated with fused alkali. The oxygenated constituents also are subjected to like

[1]) Of later investigators of this subject Oppenheim (1864), Hell and Ritter (1884), Bouchardat and Lafont (1886), and finally Wallach (1884—1887) may be mentioned.

[2]) The same subject was later investigated by Oppenheim (1864), Flawitzky (1879), Tilden (1878—79), Bouchardat and Voiry (1887). Here also Wallach's exact investigations revealed the fact that different acids, as well as the same acid in different degrees of concentration, produce different results.

[3]) Liebig's Annalen **38** (1841), 67.

[4]) Fractional distillation, however, had been previously employed in the examination of volatile oils. As early as 1838 Walter had subjected peppermint oil to interrupted distillation, *gebrochene Destillation* (Gmelin, *Handbuch d. Chem.* [4], vol. 7a, p. 404). In 1840 Völckel (Liebig's Annalen **35**, 306) speaks of "fractional distillation." Already Blanchet and Sell in 1833 had applied fractionation with water vapor as a means of separation and had found that the first fraction of lemon oil boiled at 167°, the last fraction at 173°.

treatment with fused alkali, and cumin oil is thus made to yield cuminic acid, oil of valerian valeric acid.

Strong reagents were also employed by Rochleder, Persoz, Laurent and Gerhardt in order to obtain an insight into the nature of volatile oils. They oxidized either the entire oil or fractions thereof with chromic acid or nitric acid. Their investigations included the oils of valerian, sage, anise, staranise, fennel, cumin, cinnamon, tansy and estragon. The conclusions drawn from these oxidation experiments were in part correct, in part wrong. Thus e. g. Gerhardt pointed out the identity of dragonic acid, obtained from estragon oil, with anisic acid, and claimed that estragon oil and anise oil were absolutely identical. This conclusion was wrong, for the anethol of anise oil is paramethoxypropenylbenzene, whereas the formation of anisic acid from estragon oil is due to the presence of paramethoxyallylbenzene.[1])

Moreover, this method rendered it impossible to decide whether a substance obtained after the oxidation preexisted in the oil or not. Thus camphor was found in several oxidized oils and was regarded as an original constituent although, as was the case in the oils of valerian and sage, it had resulted from borneol. Persoz, however, seems to have had doubts as to the reliability of these conclusions, for he leaves it undecided whether the camphor obtained from oil of tansy was contained in the oil or not. As a matter of fact, tansy oil contains camphor as an original constituent,[2]) this being less readily attacked by the oxidizing agents than the other constituents of the oil.

Of considerable importance in the further development of the chemistry of volatile oils are the investigations of Berthelot from 1852 to 1863, which involve principally the hydrocarbons contained in these oils. He studied first of all the hydrocarbon of turpentine oil[3]) and its isomers and polymers obtained from its hydrochloride. By heating pinene hydrochloride with barium stearate or sodium benzoate he obtained a new hydrocarbon which he

[1]) This difference was first ascertained in the laboratory of Schimmel & Co. (Report of Schimmel & Co. April **1892**, 30) and verified by Grimaux in 1893 (Compt. rend. **117**, 1189).

[2]) Report of Schimmel & Co. October **1895**, 46.

[3]) Compt. rend. **55** (1862), 496 and 544; also Liebig's Annalen, Suppl. II. (1862—63), 226.

regarded as "camphene proper"[1]) and which is identical with the camphene of to-day. This new camphene was either dextrogyrate, lævogyrate or optically inactive according to the turpentine oil employed. Berthelot, therefore, distinguished between the following hydrocarbons:

1. *Terebentene* (*l*-pinene) from French turpentine oil, lævogyrate[2]) b. p. 161°. It yields a lævogyrate monohydrochloride, also under proper conditions an inactive dihydrochloride (dipentene dihydrochloride).
2. *Terecamphene* (*l*-camphene) from terebentene hydrochloride, lævogyrate, m. p. 45°, b. p. 160°. With hydrogen chloride it forms a dextrogyrate hydrochloride.
3. *Australene* (*d*-pinene) from American turpentine oil, b. p. 161°, dextrogyrate like its hydrochloride. Its behavior to hydrogen chloride is analogous to that of terebentene.
4. *Austracamphene* (*d*-camphene) from australene hydrochloride. It corresponds to terecamphene.
5. *Inactive camphene* (*i*-camphene) can be obtained by proper treatment from the hydrochloride of terebentene as well as that of australene.
6. *Terebene*,[3]) b. p. 160°.

These six hydrocarbons are isomeric and have the formula $C_{10}H_{16}$. With these the following are polymeric:

1. A liquid hydrocarbon boiling at 250° which is probably a sesquiterebene, $C_{15}H_{24}$.
2. Diterebene (Deville's colophene) $C_{20}H_{32}$, an inactive liquid boiling at about 300°.
3. Several polyterebenes $C_{10n}H_{16n}$, optically inactive liquids becoming more and more viscid, which boil between 360° and a dark red heat.

After a discussion of the methods of formation of the individual hydrocarbons, Berthelot continues:

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[1]) Soubeiran and Capitaine in 1840 had applied the term camphene to all hydrocarbons C_5H_8 (Liebig's Annalen **34**, 311).

[2]) The rotatory power of volatile oils was first observed by Biot in 1817 in connection with French oil of turpentine (Mémoires de l'Acad. des Sc. **13**), later also with oil of lemon. The turpentine oil was shown to be lævogyrate, the oil of lemon dextrogyrate. In 1843, Leeson of London found that American turpentine oil possessed a rotatory power opposite to that of the French oil. This observation was soon after verified by Pereira and Guibourt. Pereira introduced the terms lævo-gyrate and dextro-gyrate (Pharm. Journ. **5** [1845], 70).

[3]) This substance which was considered a chemical unit by Berthelot was shown by Riban to be a mixture of a terpene, cymene and camphor. Power and Kleber in 1894 found camphene, dipentene, terpinene and cymene in terebene. (Pharm. Rundsch. **12** [1894], 16.)

In accordance with the known facts, the hydrocarbon $C_{10}H_{16}$ — *e. g.* terebentene — may be regarded as the starting point of two series:

1. Of a monatomic or camphol[1]) series (monohydrochlorides or chlorine esters of camphol, $C_{10}H_{17}Cl$; camphene, $C_{10}H_{16}$; camphol alcohols, $C_{10}H_{18}O$);
2. Of a diatomic or terpil series (dihydrochlorides, $C_{10}H_{18}Cl_2$; terpilene, $C_{10}H_{16}$; hydrate $C_{10}H_{20}O_2$).

Each of these two series constitutes a larger group, which can be divided into secondary series (australene, terebentene, etc.) the parallel and isomeric members of which occur in twos; each has as type an inactive hydrocarbon, namely camphene in the first group, terpilene in the second.

A similar, but much less detailed classification was attempted by Gladstone[2]) in 1864, after having determined the specific gravity, the index of refraction and the optical rotation of a number of oils. By means of fractional distillation he isolated the hydrocarbons of various oils, rectified them by distillation over sodium and arranged them into three large groups:

1. Hydrocarbons of the formula $C_{10}H_{16}$ which boil between 160—170°;
2. Hydrocarbons of the formula $C_{15}H_{24}$ which boil between 249—260°;
3. Colophene, $C_{20}H_{32}$, b. p. 315°, representing the third group.

About this time the word terpene was introduced, evidently by Kekulé. In his *Lehrbuch der organischen Chemie* (1866) vol. 2, p. 437, the following statement occurs:

". . . . andrerseits das Terpentinöl und die zahlreichen mit ihm isomeren Kohlenwasserstoffe, welche im allgemeinen als Terpene bezeichnet werden mögen."

His investigations, preceded by those of Barbier and Oppenheim were of considerable importance, inasmuch as by revealing the relations between the terpenes and cymene, they threw new light on the molecular structure of these hydrocarbons.

Almost simultaneously Barbier[3]) and Oppenheim[4]) obtained cymene by heating the dibromide of terpin either by itself or with aniline. By the action of iodine on turpentine oil, Kekulé[5]) obtained the same hydrocarbon. He, therefore, thought himself

[1]) Berthelot changed the name borneol to camphol. Liebig's Annalen **110** (1859), 368; from Compt. rend. **47** (1858), 266.

[2]) Journ. chem. Soc. **17** (1864), 1. A second contribution appeared eight years later. *Ibidem,* **25** (1872), 1.

[3]) Compt. rend. **74** (1872), 194.

[4]) Berl. Berichte **5** (1872), 94.

[5]) Berl. Berichte **6** (1873), 437.

justified in supposing six atoms of the turpentine oil to be arranged in similar manner as in benzene. Further, that the methyl and propyl groups in the turpentine oil occupy the same relative positions as in cymene.[1])

This view of the constitution of the terpenes was the predominant one for a long time. It is only recently that researches have revealed facts not in harmony with this view. With this the question of the constitution of the terpenes had its origin. Important in this direction was also the synthesis of a terpene — the polymerization of isoprene to dipentene — by Bouchardat[2]) in 1875.

In the same year, Tilden[3]) found that the hydrocarbon of turpentine oil combines with nitrosylchloride to form a well crystallizing compound. Together with Stenhouse, he applied this reaction to the terpenes from the oils of sage, orange, lemon and bergamot. On the behavior of these hydrocarbons to nitrosylchloride he based a new classification, concerning which he makes the following statement:

"The natural terpenes are colorless limpid liquids which vary in specific gravity from about 0.84 to about 0.86. They are divisible into two groups as follows: —

1. Turpentine group: b. p. 156° to 160°; m. p. of nitroso-derivative 129°; form solid crystalline hydrated terpin $C_{10}H_{20}O_2H_2O$.
2. Orange group: b. p. 174° to 176°; m. p. of nitroso-derivative 71°; form (by Wigger's process) no solid crystalline terpin hydrate.[4])

The liquids included in each group are allotropic modifications of the same hydrocarbon distinguished one from another by their various rotatory action on the polarized ray. It will, however, be found I believe that the terpenes from several different plants will on further examination be conclusively proved to be really identical and not simply isomeric. This, I believe, to be the case with the terpenes from French turpentine and sage, also with the terpenes from orange peel, bergamot and lemon."

Tilden's prediction, that the number of terpenes would be shown to be much smaller than assumed in his days, has proven

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[1]) Kekulé's formula for camphor was based on the same consideration.

[2]) Compt. rend. **80** (1875), 1446.

[3]) Journ. chem. Soc. **28** (1875), 514; *Ibidem,* **31** (1877), 554; Pharm. Journ. III. **8** (1877), 191.

[4]) This statement is incorrect, for dipentene and limonene likewise produce terpin hydrate. Comp. Flückiger, Arch. der Pharm. **222** (1884), 362; also Kremers, Americ. chem. Journ. **17**, 695.

itself true. His classification, however, was insufficient, for it included only a small number of terpenes. Indeed the material at hand was not sufficiently sifted for an attempt of that kind. It consisted of a large number of disconnected observations, the study of which was rendered difficult by an arbitrary nomenclature. Only by a systematic exploration of this disorderly realm could a clear insight into the subject be gained.

That we are able to-day to distinguish sharply between so many terpenes and their derivatives is due primarily to the excellent experimental researches of Otto Wallach, the founder of modern terpene chemistry.

Inasmuch as it was impossible to isolate the numerous terpenes boiling between 155 and 185° by fractional distillation, methods had to be sought which enabled the characterization of these hydrocarbons, even in mixtures, by means of crystalline derivatives. Only after the characterization of the numerous isomers was accomplished was it possible to study successfully the relation of one terpene to another, the relation of the terpenes to their oxygenated derivatives, and the problem of their constitution.

These problems have been solved in so far that it is now possible to identify many if not most terpenes without great difficulty. The inversions, or changes from one to the other, are also better understood. The problem of their constitution, however, is still far from a satisfactory solution, though structural formulas have been proposed for a number of the terpenes.

In 1884 Wallach[1]) began his researches on this subject with the investigation of the oil of wormseed *(Oleum cinæ)*. Three years later he was in a position to characterize eight terpenes by means of crystalline derivatives (tetrabromides, hydrochlorides, hydrobromides, nitrosites etc.), viz. pinene, camphene, limonene, dipentene, sylvestrene, terpinolene, terpinene and phellandrene.

[1]) Wallach's contributions are to be found in the following volumes of Liebig's Annalen: 225, 227, 230, 238, 239, 241, 245, 246, 252, 253, 258, 259, 263, 264, 268, 269, 270, 271, 272, 275, 276, 277, 278, 279, 281, 284, 286, 287, 289, 291, 296, 300, 302, 305, 306, 809, 312, 313, 314, 315, 319, 323, 324, 327, 329, 331, 332, 336, 339, 340, 343, 345, 346, 347, 350, 353, 356, 357, 359, 360. — Several papers from his pen are to be found in the Berl. Berichte **23** (1890) to **40** (1907).

To these fenchene was added later. The sesquiterpenes were also included in his investigations. Three of these were well characterized, *viz.*, cadinene, caryophyllene and clovene. The reactions that were applied were for the most part first studied in connection with simpler substances. Thus a series of contributions resulted including amylene, indene, methylindene, anethol, isosafrol etc.

Hand in hand with these investigations, researches were conducted with the oxygen derivatives of the terpenes which have a greater capacity for reaction. Of these even less was known. Like the terpenes, they were characterized by crystalline derivatives.

The genetic relationship between the terpenes themselves and also that existing between the terpenes and the oxygenated constituents of the volatile oils was revealed by transforming the one into the other. These changes were of the greatest importance in the study of the chemical constitution of these compounds. Moreover, this study yielded numerous new compounds, among them such as methylheptenone, which are found in volatile oils. Mention may here be made of the relation existing between the terpenes, terpin hydrate and the terpineols; between the members of the carvone group; of cineol; and of the first synthetic oxide of a terpene, the pinol and its hydrate. Mention may also be made of the more recent work on terpinene, the terpinenol, terpinene terpin and terpinene cineol and their relation to sabinene and thujene. As a chapter by itself, mention should be made of the study of the camphor and fenchone groups, which were made possible by the discovery of the latter ketone and its optical isomers. These studies led to the preparation of numerous new derivatives as did also those connected with the discovery of thujone.

When the cleavage of pulegone made 1,3-methylheptenone a readily accessible substance, the study of alicyclic compounds resulted in a considerable number of papers. These substances are mostly closely related to the terpenes and their derivatives. Hence many a reaction was first studied in connection with these simpler substances in order to be applied later to the more complicated terpenes. These simpler substances, *e. g.* isopropyl hexenone, nopinone, sabinaketone having been obtained from other terpene derivatives, were in turn used for synthetic pur-

poses. In this connection methods of condensation were studied, especially those with brom substitution products of the fatty acids. Thus were accomplished the syntheses of menthene, phellandrene, terpinene, β-pinene, fenchene, and of homologues of the terpenes.

An important place in Wallach's researches is occupied by the successful efforts to unravel the isomeric complications so prevalent in the terpene group. Thus special investigations dealt with the study of optical isomerism, molecular refraction, cleavage of cycles as well as their formation, hydration and other physical and chemical problems.

After Wallach had removed the principal difficulties in the investigation of volatile oils, other chemists also developed a successful activity. A. v. Baeyer's valuable investigations into the constitution of the terpenes and related compounds appeared in the *Berichte der deutschen chemischen Gesellschaft* since 1893.

Whereas Wallach and v. Baeyer investigated primarily the cyclic compounds, Semmler paid special attention to chain compounds. He showed that the alcohols geraniol and linalool and the aldehydes citral and citronellal, which occur frequently in volatile oils, are chain compounds; also that they, like the more or less closely related cyclic compounds, can be converted into cymene. Later, Semmler's activity extended to practically all fields of volatile oil and terpene chemistry. Of the terpenes he examined sabinene, camphene, phellandrene, camphenilone. Among other problems, Semmler cleared up the constitution of buchu camphor, of santalol and of myrtenol. To him we are also indebted for our knowledge of the constituents of the oils of asarum, of East Indian sandalwood, of pilea oil, ayapana oil, etc. Practically all of his results have been published in the *Berichte der deutschen chemischen Gesellschaft.*[1])

In this connection the work of Tiemann and his colaborers, which began with the nineties of the past century, should be mentioned. This included the isolation of irone, the principal constituent of orris oil; later this led to the synthesis of ionone, which possesses the aroma of the violet. In this connection he published numerous articles on the chemistry of citral.

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[1]) Berl. Berichte **23** (1890) to **41** (1908).

In addition to these, numerous other chemists have investigated the composition of volatile oils and the constitution of the terpenes and their oxygenated derivatives. In so far as their results pertain to the composition of volatile oils, these are included in the special part of this treatise.

The constitutional problems involved in the study of the terpenes and their derivatives are among the most difficult of organic chemistry because of the readiness with which rearrangements within the molecule take place under the influence of ordinary physical and chemical reagents. A typical example of some of the difficulties involved may be had in the ordinary camphor. Of this substance investigators had an almost unlimited supply at their disposal. Moreover, many chemists have been incessantly investigating this compound for several decades, during which period no less than thirty structural formulas received consideration. And yet it was but recently that Bredt found in his formula a generally satisfactory expression,[1]) a formula that finally led to the synthesis of camphor by Komppas.[2])

This brief history of volatile oils would not be complete without some reference to the literature on the subject since the beginning of the past century. So long as the volatile oils were principally prepared in the laboratories of apothecary shops, the description of the oils and of the methods of their preparation was found in pharmaceutical reference works and pharmacopœial commentaries. Likewise the results of scientific and technical studies were published in pharmaceutical rather than in purely chemical journals. With the early forties, the preparation of volatile oils was taken out of the pharmaceutical laboratories and a separate literature was created. Yet Zeller's publications, already referred to, appeared first in the *Jahrbuch für praktische Pharmacie* before they were published as separates.

Zeller's[3]) publications contain a compilation of the yield,

[1]) Bredt, *Versammlung D. Naturf. u. Ärzte,* Braunschweig 1907. Liebig's Annalen **314** (1901), 388.

[2]) Komppa and Hirn, Berl. Berichte **36** (1903), 4332.

[3]) G. H. Zeller, *Studien über die ätherischen Öle. I. Heft. Des chemischen Teils erster Abschnitt.* Landau 1850. — *II. Heft. Die physischen und chemischen Eigenschaften der officinellen ätherischen Öle.* Stuttgart 1855. — *III. Heft. Die Ausbeute und Darstellung der ätherischen Öle aus officinellen Pflanzen.* Stuttgart 1855.

also a very meagre description of the physical properties of the oils and their behavior toward reagents. Maier's[1]) later treatise also takes into consideration the scientific investigations. The methods of preparation and the subject of distillation are described in detail by Mierżinski.[2]) A similar work was written by Askinson.[3]) *Die Toiletten-Chemie* of Hirzel,[4]) which passed through four editions, also "The art of perfumery" by Piesse,[5]) which was translated into several languages, may here be mentioned.

The results of the earlier papers by Wallach are contained in the excellent work of Bornemann,[6]) whereas the *Odorographia* of Sawer[7]) emphasizes the botanical side of the subject.

Indispensable to scientific work on the chemistry of the terpenes was the monograph of F. Heusler[8]) which comprises the otherwise scattered literature up to the close of the last century. Translated into English by F. J. Pond[9]) and supplemented, it was published in the U. S. in 1892. Restricted to the sesquiterpenes is the smaller monograph by O. Schreiner.[10])

Shortly after the appearance of *Die ätherischen Öle* by E. Gildemeister and Fr. Hoffmann, a similar work in French was published by Charabot, Dupont and Pillet,[11]) another in English by E. J. Parry.[12])

[1]) Dr. Julius Maier, *Die ätherischen Öle, ihre Gewinnung, chemischen und physikalischen Eigenschaften, Zusammensetzung u. Anwendung.* Stuttgart 1867.

[2]) Dr. Stanislaus Mierżinski, *Die Fabrikation der ätherischen Öle und Riechstoffe.* Berlin 1872.

[3]) Dr. George William Askinson, *Die Fabrikation der ätherischen Öle.* Wien 1876.

[4]) Dr. Heinrich Hirzel, *Die Toiletten-Chemie.* Leipzig 1864 and subsequent editions.

[5]) S. Piesse, The Art of Perfumery. London 1862 and subsequent editions.

[6]) Dr. Georg Bornemann, *Die flüchtigen Öle des Pflanzenreichs, ihr Vorkommen, ihre Gewinnung und Eigenschaften, ihre Untersuchung und Verwendung.* Weimar 1891.

[7]) J. Ch. Sawer, Odorographia. London 1892—1894.

[8]) Dr. Fr. Heusler, *Die Terpene.* Braunschweig 1896.

[9]) The Chemistry of the Terpenes by F. Heusler. Authorized Translation by Francis J. Pond. Carefully revised, enlarged and corrected. Philadelphia 1902.

[10]) O. Schreiner, The Sesquiterpenes. A Monograph. Milwaukee 1904.

[11]) E. Charabot, J. Dupont et L. Pillet, *Les huiles essentielles et leurs principaux constituants.* Paris 1899.

[12]) Ernest J. Parry, The Chemistry of Essential Oils and Perfumes. London 1899 and 1910.

Dealing primarily with artificial perfume materials, but also with natural products, the smaller works by J. M. Klimont,[1]) E. Charabot,[2]) P. Jeancard and C. Satie,[3]) G. Cohn[4]) and R. Knoll[5]) should be mentioned. O. Simon's[6]) book deals exclusively with analysis.

Also indispensable to the terpene chemist working along scientific lines are the excellent treatises on related subjects by C. Harries[7]) and O. Aschan.[8])

Die ätherischen Öle is the title of a large four volume work by Semmler[9]) published between 1905 and 1907. It is replete with references to original literature and treats of all substances found in volatile oils and might well have been labled "Chemistry of the constituents of the volatile oils." Finally, there should be mentioned the recent French book on volatile oils by Durvelle.[10])

This extraordinary growth of our knowledge of the volatile oils during the past twenty-five years has had a very stimulating effect on the practical development. Hence, parallel with the scientific development, the industry of volatile oils and artificial perfumes has to record a vigorous growth. Older factories, having outgrown their former quarters, had to be enlarged, and a number of new factories, both foreign and domestic were established.

The progress made in the investigation of the composition and properties of the volatile oils has resulted in a similar

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[1]) J. M. Klimont, *Die synthetischen und isolierten Aromatica.* Leipzig 1899.

[2]) E. Charabot, *Les Parfums artificiels.* Paris 1900.

[3]) P. Jeancard et C. Satie, *Abrégé de la Chimie des Parfums.* Paris 1904.

[4]) G. Cohn, *Die Riechstoffe.* Braunschweig 1904.

[5]) R. Knoll, *Synthetische und isolierte Riechstoffe und deren Darstellung.* Halle 1908.

[6]) O. Simon, *Laboratoriumsbuch für die Industrie der Riechstoffe.* Halle 1908.

[7]) C. Harries, *Einkernige hydroaromatische Verbindungen einschließlich der Terpene und Campherarten. Erschienen im Lehrbuch der organischen Chemie* of Victor Meyer and Paul Jacobson. Leipzig 1902.

[8]) O. Aschan, *Chemie der alicyclischen Verbindungen.* Braunschweig 1905.

[9]) F. W. Semmler, *Die ätherischen Öle nach ihren chemischen Bestandteilen unter Berücksichtigung der geschichtlichen Entwicklung.* Leipzig 1906—1907.

[10]) J. P. Durvelle, *Fabrication des Essences et des Parfums.* Paris 1908.

development of the analysis of these oils. Hence the pharmacopœial requirements concerning the volatile oils have become more specific and exacting. Not only are pure oils demanded, but such that are rich in active constituents. However, the great variation existing in the requirements of the several pharmacopœias, merely reveals the fact that the composition of these natural products as well as the variation to which they are subject, has not yet been sufficiently investigated. Hence the methods of testing still leave much to be desired. If this is true of the oils used medicinally, which as a rule are among the better known oils, this lack of knowledge is felt even more among the non official and lesser used oils. The recent rapid scientific and technical development of this field, however, justifies the hope that the present defects will be removed in the not distant future, and that problems still to arise will also be solved in a satisfactory manner.

III. HISTORY OF INDIVIDUAL VOLATILE OILS.

TURPENTINE OIL.

The oils obtained by the distillation of the oleoresins of various *Abietineæ* were known to the ancients as cedar oil (πισσέλαιον)[1]) and later became known as turpentine oil. The oil as well as the resin, the colophonium, were used by seafaring people. The preparation of turpentine oil, as recorded by Dioscorides, is described in the next chapter. Taking into consideration the perfection of varnishes and lacquers employed by the Chinese, it may be supposed that coniferous oils were distilled and used by them. However this may be, the oils of the *Abietineæ* obtained in a crude manner have evidently been the first volatile oils that found commercial use and technical application.

The name turpentine oil seems to have been introduced during the period of Greek civilization. Like the older synonyms (cedar oil, etc.) it apparently was used as a collective term. It is of Persian origin,[2]) and may have been derived from the name of the resinous exudation of the Cyprian species *Pistacia terebinthus,* L.

As far as is known to history, the preparation of turpentine oil probably had its origin in the Caucausus and its south-western spurs. In central Europe it became known during the middle ages, somewhat later also in northern Europe. The North American industry had its origin in the dense and extensive pine

[1]) Herodoti *Historiæ.* Lib. II. 85. — Dioscorides, *De materia medica,* Lib. I. 34, 39, 80. Editio Kühn-Sprengel 1829. 1, 93. — Plinius, *Naturalis historiæ libri,* Lib. XV, cap. 6—7 and Lib. XVI, cap. 22.

[2]) Flückiger, *Pharmakognosie,* 3nd ed., p. 77.

forests of the South Atlantic States and developed in the beginning of the eighteenth century especially in Virginia and Carolina.[1])

Inasmuch as the crude turpentine oil found little or no use in either household economy or in religious rites, it is but seldom mentioned in early literature. Attention has already been called on pp. 17, 29, 30, and 38 to mentionings by the older writers. Since its introduction into medicine, the mediaeval works on distillation and materia medica make mention of the oil. In addition to the references by A. Villanovus and R. Lullus, who lived in the thirteenth century, to which attention has been called on pp. 31 and 33, mention is made of oil of turpentine by the following writers of the fifteenth century: Saladinus of Asculo[2]) and the canon Johann of Santo Amando of Doornyk[3]); during the sixteenth century by Walter Ryff,[4]) Conrad Gesner,[5]) Joh. Baptista Porta,[6]) Valerius Cordus[7]) and Adolphus Occo.[8])

Attention has already been called to the synonymous usage during the seventeenth century of the designations of alcohol and turpentine as *aqua ardens* and *spiritus*. The name *Spiritus*

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[1]) Prof. Peter Kalm's *Reise nach dem nördlichen Nordamerika im Jahre 1748—1749. Göttinger Sammlung neuer und merkwürdiger Reisen zu Wasser und zu Lande.* 3 vol. Göttingen 1754. Vol. 2, pp. 418, 556; vol. 3, pp. 293, 305, 523.

Johann David Schöpf, *Reise durch einige der mittleren und südlichen Staaten von Nordamerika in den Jahren 1783—1784.* 2 vol. Erlangen 1787. Vol. 2, pp. 220, 223, 273.

F. A. Michaux, *Histoire des arbres forestiers de l'Amérique septentrionale.* Paris 1810.

[2]) Saladini Asculani *Compendium aromatariorum.* Venetii 1488. Index.

[3]) *Expositio* Janis de Santo Amando *supra antidotarii* Nicolai *incipit feliciter. "Oleum de terebinthina fit similiter per sublimationem, et est clarum ut aqua fontis . . . et ardet ut ignis græcus cum oleo benedicto etc."* Turpentine oil is mentioned fol. 228b of the edition of 1589 already referred to on p. 25, footnote 2.

[4]) Gualtherius Ryff, *New groß Destillirbuch wohl gegründeter künstlicher Destillation.* Francofurti 1556, fol. 180.

[5]) *Ein köstlicher theurer Schatz* Euonymi Philiatri *darinnen enthalten sind vil heymlicher guter stück der artzney.* Editio 1555. Vol. 1, p. 238.

[6]) Gio. Batt. Portæ *Magiæ naturalis libri viginti.* Editio 1589.

[7]) *Dispensatorium Noricum.* 1546.

[8]) *Pharmacopœa pro Republica Augustana.* 1564.

terebinthinæ has maintained itself as a popular term up to this time. As *huile ætherée* it seems to have been first designated in the year 1700.

The early observations made in connection with oil of turpentine concerned its behavior at low temperatures. As early as 1794 Margueron[1]) claims to have observed that the oil, when reduced to a temperature of —22° R. solidifies to a crystalline mass. Crystals had already been observed by Cl. Jos. Geoffroy in 1727 in the neck of the retort while distilling the oil. In conformity with the practice of designating as camphor all solid substances separating from volatile oils, these needle-like crystals, presumably pinol hydrate, were called turpentine camphor.

While making the socalled *Liquor antarthriticus Pottii,* in the preparation of which hydrogen chloride is passed into turpentine oil, the apothecary Kindt[2]) of Eutin, in 1803 obtained a solid crystalline mass[3]) which he considered to be artificially prepared camphor. This compound was examined by Gehlen[4]) and by Dumas.[5]) The first elementary analysis of the oil was made by Houton-Labilliardière[6]) in 1817. In the same year this oil served as the first volatile oil of which the angle of rotation was ascertained.

AMERICAN TURPENTINE OIL.

The enormous turpentine industry of the United States had its origin in the large pine forests of North and South Carolina, Georgia, and Alabama. Up to the middle of the last century the products of this industry were tar and pitch which were used principally in ship building and as naval supplies and hence were termed "naval stores".[7]) The distillation of turpentine oil

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[1]) Journ. de Chim. et de Phys. 2 (1794), 178. — Crell's Chem. Annalen 1795. II. 195, 310 and 430.

[2]) Trommsdorff's Journ. der Pharm. 11, II. (1803), 132.

[3]) Pinenemonochlorhydrate $C_{10}H_{17}Cl$.

[4]) Gehlen's Allgem. Journ. für die Chemie 6 (1819), 462—469.

[5]) Annal. de Chim. et Phys. II. 52 (1833), 400. — Liebig's Annalen 9 (1834), 56.

[6]) Journ. de Pharm. II. 4 (1818), 5.

[7]) The oldest mention concerning tar and pitch, and the preparation of turpentine in Virginia is to be found in vol. 1 of the "Calendar of State Papers. Colonial Series" for the year 1574 to 1660 in the Public Record

seems to have begun as late as the middle of the eighteenth century in North Carolina and Virginia. Professor Kalm, the Swedish traveler, who is known as a careful observer, and who explored the Atlantic provinces of the then British colonies from Quebec to Virginia during the years 1749 and 1750, reports concerning the preparation of tar and pitch only.[1]) Later travelers and reports first make mention of the preparation of turpentine, turpentine oil and colophony in Carolina. Among these are Dr. Johann David Schoepf, who traversed the Atlantic States from Canada to Florida[2]) in 1783 and 1784; also François André Michaux, who about twenty years after the longer stay of his father, the well known botanist André Michaux, traveled in North America at the beginning of the nineteenth century.[3])

Up to the year 1820 the consumption of turpentine, turpentine oil and colophony was restricted to the limited demands of the home industries. The exportation of oil and rosin to England was unimportant. Up to 1830 the manufacture of turpentine was restricted to the coast: between the Tar river in the north, and Cape Fair river in the south; while the ports New Bern, Wilmington and Washington in North Carolina served as collective points. The distillation of turpentine was conducted in cast iron stills.

At the beginning of the thirties the application of turpentine in the industries experienced considerable extension. This was caused primarily by the increased use of paints accompanying the increase in wealth; by the development of the varnish,

Office in London. Of the year 1610 this volume contains "Instructions for suche thinges as are to be sente from Virginia," also a printed pamphlet: "The Booke of the Commodities of Virginia." Both mention pitch, tar, rosin and turpentine among the products of Virginia. The former also contains brief directions for the method of preparation of turpentine which is still in vogue. (Dan. Hanbury, in Proceed. Americ. pharm. Ass. **19** [1871], 491.)

[1]) *Reise nach dem nördlichen Nordamerika im Jahre 1748 bis 1750 von* Prof. Peter Kalm in *Göttingsche Sammlung neuer und merkwürdiger Reisen zu Wasser und zu Lande.* Göttingen 1754—1764. Vol. 2, pp. 418, 474; vol. 3, pp. 305, 523.

[2]) *Reise durch einige der mittleren und südlichen Vereinigten Nordamerikanischen Staaten in den Jahren 1783 und 1784 von* Dr. Johann David Schöpf. Erlangen 1788. Vol. 2, pp. 141, 247—252.

[3]) *Histoire des arbres forestiers de l'Amérique septentrionale, par* F. André Michaux. Paris 1810. Vol. 1, p. 73.

lacquer and caoutchouc industries; and, finally, by the use of a mixture of turpentine oil and alcohol as an illuminating agent, which had been introduced since 1839 as camphine and under other fanciful names. Up to the introduction of petroleum products (kerosene) about 1860, this was the cheapest illuminating material. The improvements, made in the course of the thirties, by Comstock, Hancock, Macintosh, Chaffee and especially by Luedersdorff in the processes employed in the caoutchouc industry did much to bring about a larger consumption of turpentine oil.

This increase in the consumption brought about an increase in the turpentine industry in 1834, and caused the introduction of better distilling apparatus such as copper stills which insured not only a larger yield of turpentine oil but also a better quality of resin.[1]) The exportation of American turpentine oil and colophony to England and other countries asumed large proportions only after the removal of the import duty in England in 1846. It was interrupted, however, during the years 1861 to 1865 of the civil war, the period of industrial and commercial stagnation.

Up to the year 1837, the opinion prevailed in Carolina that the pine forests farther to the south were not adapted to the production of turpentine on account of differences in climate and soil. In the year mentioned, experiments conducted on a large scale showed this opinion to be erroneous. As a result of the great demand and of increasing speculation, the industry spread rapidly to South Carolina and Georgia, and later to Alabama and Mississippi.[2]) With the introduction of the more readily transportable copper stills, the distillation was more and more conducted at the place of production, so that the turpentine farms began to supply the finished though crude products of distillation, oil and rosin, in place of turpentine, to the ports along the coast. With the increased consumption of turpentine oil a corresponding overproduction of rosin resulted. This could

[1]) The forests, forest lands and forest products of Eastern North Carolina. By W. W. Ashe. Raleigh N. C. 1894.

[2]) Carl Mohr, The timber pines of the Southern United States. Washington 1897. p. 69. — *Die Gewinnung und Verarbeitung des Terpentins im Süden der Ver. Staaten.* Pharm. Rundschau (New York) 2 (1884), 187.

not be disposed of and consequently suffered a corresponding depreciation in value.

This disparity was equalized toward the end of the sixties. The opening up of new territories of production brought about an overproduction in turpentine oil as well, which was felt all the more because petroleum products took its place as an illuminating agent and also superseded it in various branches of the arts and industries. On the other hand, colophony found new and large application.

The turpentine industry in the Southern states thus developed more and more. With the establishment of cheap means of transportation by rail and by water, all the conditions were given for a prosperous growth to the enormous dimensions on which this industry is being conducted at present.

FRENCH TURPENTINE OIL.

The production of turpentine in southwestern France, from *Pinus pinaster,* Solander, must have been in progress at a very early period.[1]) At least this is the inference drawn from petrified trunks of trees, found along the coast, which reveal the wounds characteristic of the resin production. Later on, historic documents of 1382 and 1383 reveal that Richard II. of England gave permission to the Captal de Buch Archambault de Grailly to conduct resin markets within his territory. Probably the maritime pine was first planted as a protection to the dunes. After numerous failures, this plan proved a success only toward the end of the 18. century. The experiment to sow the seeds in the sand successfully tried by the engineer Brémontier is followed up to the present time by the government.

The method, still in use, to collect the resinous exudation in earthenware pots is attributed to Serres (1836) and Hugues (1840).

The distillation of turpentine oil is being conducted in France since 1783.[2])

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[1]) O. A. Oesterle, *Die Harzindustrie im Südwesten von Frankreich.* Berichte d. deutsch. pharm. Ges. **11** (1901), 217.

[2]) Corps gras industriels **34** (1908), 179.

TURPENTINE OIL FROM VENETIAN (LARCH) TURPENTINE.

Larch turpentine was known to the Romans. It is mentioned in the writings of Vitruvius,[1]) a contemporary of Cæsar, also in those of Dioscorides,[2]) Pliny,[3]) and Galen. During the middle ages, larch turpentine was one of the most highly prized balsams. The name Venetian turpentine was applied to it during the fifteenth century,[4]) because it was brought into the market from Venice, at that time the center of the drug commerce.

The first mention of larch oil *(Oleum laricis)* in medical treatises is found in the works of Matthiolus[5]) and Conrad Gesner.[6])

TURPENTINE OIL FROM CANADA BALSAM.

Canada balsam, which was probably long known to the American Indians and employed by them, is first mentioned in European reports of travel by Marc Lescarbot[7]) who traveled in Canada during the years 1606 and 1607. He declares the balsam equal in value to the Venetian. In the European market, however, it is not found before the eighteenth century (Flückiger).[8])

OIL OF CYPRESS.

Oil of cypress was known as early as 1672 (comp. p. 62). In 1892 it was recommended as a remedy against whooping cough by J. M. Bravo[9]) and since 1894 it has been distilled by Schimmel & Co. on a commercial scale.[10]) The experiences of Professor Dr. Soltmann in connection with a large number of patients of the chil-

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[1]) Marcus V. P. Vitruvius, *De architectura.* Vol. 2, p. 9.

[2]) Dioscorides, *De materia medica libri quinque.* Editio Kühn-Sprengel 1829, vol. 1, p. 95.

[3]) Plinius, *Naturalis historiæ libri 39.* Littré's edition. Cap. XVI, 575.

[4]) Flückiger, *Pharmakognosie.* 3rd edition, p. 80.

[5]) Petri Andreæ Matthioli *Opera quæ extant omnia,* edit. 1598, vol. I, p. 103.

[6]) Euonymi Philiatri *Ein köstlicher Schatz.* Zürich 1555. p. 289.

[7]) M. Lescarbot, *Histoire de la Nouvelle-France.* 1612. Edit. Ed. Tross. Paris 1866. pp. 805, 811, 820.

[8]) Flückiger, *Dokumente zur Geschichte der Pharmazie,* p. 92.

[9]) Deutsche Medizinal-Zeitung **13** (1892), 45. No. 4.

[10]) Report of Schimmel & Co. October **1894**, 68 and April **1895**, 29.

dren's hospital in Leipzig substantiate the claims made for a remarkable efficiency of the oil in the treatment of whooping cough.[1])

OIL OF JUNIPER BERRIES.

As *Oleum de granis Juniperi,* oil of juniper berries was kept in stock in the *Rathsapotheke* of Braunschweig in 1521[2].) Its preparation is described by Valerius Cordus[3]) in 1546.

The oil yield from the juniper berries was determined by Cartheuser[4]) and Spielmann.[5])

The oil distilled from juniper wood is mentioned repeatedly in the treatises on distillation. In the pharmacopœias and price ordinances of the 16. century it is mentioned together with the oil distilled from the fruit.[6])

The juniper tar oil or cade oil, *Oleum Cadinum,* obtained by the process of destructive distillation is but rarely distilled from the wood of *Juniperus communis,* but mostly from *J. Oxycedrus.* It was known to the Romans.[7]) Its method of preparation is described by Mesue the younger[8]) who died in 1015.

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[1]) O. Soltmann, *Keuchhusten und Cypressenöl.* Therapie der Gegenwart. March 1904.

[2]) Flückiger, *Pharmakognosie,* 3rd ed., p. 898.

[3]) Valerii Cordi *Dispensatorium Noricum,* p. 404.

[4]) *Fundamenta materiæ medicæ 1738.* Vol. 2, p. 346.

[5]) *Ibidem.* Vol. 2, p. 272.

[6]) Saladini *Compendium aromatariorum.* 1488. *Index.* — H. Gualther. Ryff, *New gross Destillirbuch wohl gegründeter künstlicher Destillation.* Francof. 1556, fol. 181. — Val. Cordi *Dispensatorium Noricum.* 1546. — *Ein köstlicher Schatz* Euonymi Philiatri. Editio 1555, pp. 228, 232, 306. — Van Helmont, *Ortus medicinæ vel opera et opuscula omnia.* Editio Lugdunensis 1648. *De febribus.* Cap. IV, p. 33. — Schnellenberg, *Artzneybuch.* Königsberg 1556. p. 35. — *Estimatio materiæ medicæ in usum publicum civitatum Marchiæ Brandenburgensis.* Autore Matthæo Flacco. Berolini 1574. Frankfurter Taxe. 1582.

[7]) Dioscorides, *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, p. 102. — Plinii *Naturalis historiæ libri.* Cap. XXIV, 36. Editio Littré 1877. Vol. 1, p. 142. — Scribonius Largus, *Compositiones medicamentorum.* Editio Helmreich 1887, pp. 47, 55, 56. — Joannes Actuarius, *De medicamentorum compositione,* J. Ruellio *interprete.* Basiliæ 1540, fol. 30. — Matthæus Platearius in *Circa instans,* in Choulant's *Handbuch der Bücherkunde für die ältere Medizin zur Kenntnis der griechischen, lateinischen und arabischen Schriften.* 2nd ed. Leipzig 1841. p. 299.

[8]) Mesue, *Antidotarium seu Grabbadin medicamentorum libri XII.* Caput 12. *De oleis.* Comp. p. 24.

OIL OF SAVIN.

Savin was used medicinally and in veterinary practice by the Romans.[1]) It seems probable that the name *Sabina* has been derived from the mountainous country of the Sabines lying to the northeast of Rome. Dioscorides[2]) and Pliny[3]) mention the plant among those being used medicinally. Charlemagne in the ninth century mentioned it in his *Capitulare* and thus caused its cultivation in the northern Alps.[4]) The abbess Hildegard of Bingen mentions savin as a remedy in her writings;[5]) it is also one of the 77 remedies praised by Otto of Meudon (Macer Floridus).[6]) In England the tree seems to have been cultivated and used before the Norman conquest.[7])

During the period in which distilled waters were in general use, *Aqua sabinæ* was also officinal and is enumerated in the treatises on distillation mentioned on pp. 39 *et seq.*

The distilled oil is first mentioned in the price ordinance of Frankfurt-on-the-Main for 1587 and was described by Joh. Begninus at the close of the seventeenth century.[8]) Concerning the yield of the oil Friedrich Hoffmann seems to have made the first experiments about 1715.[9]) G. W. Wedel examined the oil in 1707 according to the methods in vogue at his time.[10]) The first chemical examination was made by Dumas in 1835.[11])

[1]) Marcus Porcius Cato, *De re rustica*, p. 70. — Editio Nisard, p. 25, Meyers *Geschichte der Botanik.* Vol. 1, p. 344.

[2]) Pedanii Dioscoridis Anazarbei *De Materia medica libri quinque.* — Editio Kühn-Sprengel 1829, vol. 1, p. 104.

[3]) Plinii *Naturalis historiæ libri.* Cap. XVII, 21 and cap. XXIV, 61. — Editio Littré 1877, vol. 1, p. 623 and vol. 2, p. 149.

[4]) *Capitulare de villis et cortis imperialibus.*

[5]) Hildegardis Abbatissæ *Subtilitatum diversarum naturarum creaturarum libri novem.* — Editio Migne 1885, p. 1145.

[6]) Macer Floridus, *De viribus herbarum una cum Walafridi Strabonis, Ottonis Cremonensis et Joannis Folcz carminibus similis argumenti.* Neapoli 1487. — Editio Choulant, Lipsiæ 1832.

[7]) Cockayne, Leechdoms, wortcunning and Starcraft of early England. 1865. Vol. 2, p. 12.

[8]) Johannis Begnini *Tyroceynium chymicum*, in Joh. Hartmannii *Opera omnia medico-chymica congesta atque pluribus aucta a Conrado Johrenio.* Francofurti ad Mœnum 1690. Vol. 3, p. 27.

[9]) Fr. Hoffmannii *Opera omnia-physico-medica.* Liber 65. *Observatio 1. De oleis destillatis inque eorum distillatione observanda.*

[10]) G. W. Wedel, *Dissertatio de Sabina.* Jenæ 1707.

[11]) Liebig's Annalen 15 (1835), 159.

LEBANON CEDAR OIL.

According to Herodotus and Diodor the Egyptians used cedar oil in the embalming of the dead. Pliny also mentions an *oleum cedrinum* and its use in the preservation of dead bodies.[1]) The method of preparation of this oil according to Herodotus, Dioscorides and Pliny will be found at the beginning of the next chapter. Whether this oil is that of the Lebanon cedar (*Cedrus Libani,* Barr.) can only be surmised, but not established with any degree of certainty.

On account of the durability of its wood, this tree is frequently mentioned in the old testament.[2])

ANDROPOGON (CYMBOPOGON) OILS.

The aromatic grasses which at the present time yield a number of valuable volatile oils, such as palmarosa oil, gingergrass oil, citronella oil, lemongrass oil and vetiver oil, have been used on account of their fragrance during antiquity: for the aromatization of wine; also of earthenware wine cups, the so-called Rhodian cups;[3]) in the preparation of fragrant ointments[4]) and oils; as incense in religious rites; and as couches during festivities. In Sanskrit writings, in the Old Testament,[5]) and in other documents of antiquity, these grasses are referred to under

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[1]) Herodotus II. 85. — Diodor, lib. I, 91. According to R. Sigismund, *Die Aromata.* Leipzig 1884. p. 5.

[2]) In the books of the Old Testament coniferous woods are frequently referred to. The names used in the translations presumably do not always indicate the proper source of these words. Wherever the words cedar and pine are used, Lebanon cedar probably is meant. Such references are: — Leviticus, 14 : 4. — 1. Kings, 4 : 33; 5 : 6, 8 and 10; 6 : 9, 15, 18, 20 and 26; 7 : 2, 3, 7, 12 and 14; 10 : 27. — 2. Chronicles, 2 : 8; 3 : 5 and 9. — Isaiah, 14 : 8; 37 : 24, 60 and 61. — Hesekiah, 27 : 2. — 2. Samuel, 6 : 5. — Zechariah, 11 : 1 and 2. — Revelations, 18 : 12.

[3]) Athenæi Naucratitæ *Deipnosophistarum.* Lib. XV, p. 472. — Plinii *Naturalis historiæ libri.* Lib. V, pp. 64, 65 and lib. XIV, p. 15. — Horatii *Carmina.* XII, 16—17:

"Nardo vina merebere
Nardi parvus onyx eliciet cadum."

[4]) Dioscorides, *De materia medica libri quinque.* Lib. 1, p. 52. — Plinii *Naturalis historiæ libri.* Lib. XIII, p. 2.

[5]) Exodus, 30 : 34. — Song of Solomon, 4 : 13 and 14.

various names. The names used in the translations of the Bible and other ancient writings for spices and annointing oils[1]) such as *narde, stakte, schönos,* etc., apparently have also been used synonomously for the fragrant andropogon grasses and their roots. Of these, it may be supposed that *Andropogon laniger,* Desf. was the best known and most used during antiquity, inasmuch as it was more widely distributed throughout northern India, Thibet, Persia and Arabia as far as Egypt, Nubia and Ethiopia than the other species. Originally,[2]) however, and again in more modern times, the term narde was applied only to the aromatic root of the valerianaceous *Nardostachys jatamansi,* D. C., indigenous to the Himalayas of northern India, perhaps also to *Valeriana celtica,* L. indigenous to the European Alps.

The Greek and Roman writers possibly referred to the same aromatic andropogon species when they used the words ξοῖνος or σχοῖνος, also *juncus.*[3]) In the occident they apparently have never been cultivated nor introduced in the dried condition.

The first mention of andropogon grasses[4]) by European travelers is to be found in the works of Garcia da Orta,[5]) van Rheede tot Draakenstein,[6]) — who was governor of the Dutch East-India company on the Malabar coast about the middle of the seventeenth century, — and of G. E. Rumpf[7]) (Rumphius, also Plinius indicus), Dutch governor in Amboyna during the second half of the seventeenth century. The first sample of a distilled andropogon oil, a lemon-grass oil, is said to have been

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[1]) Wilhelm Nowack, *Lehrbuch der hebräischen Archäologie.* Freiburg 1894. Vol. 1, p. 133.

[2]) Dioscorides, *De materia medica libri quinque.* Lib. I, 6 and 77.

[3]) Dioscorides, *De materia medica libri quinque.* Lib. I, pp. 2, 16, 17. Editio Kühn-Sprengel 1829. Vol. 1, p. 30. — Plinii *Naturalis historiæ libri.* Lib. XII, pp. 26, 59, 62 and lib. XIII, p. 2.

[4]) A detailed account of the individual grasses is given by Otto Stapf. *The Oil-Grasses of India and Ceylon.* Bulletin of Miscellaneous Information Royal Botanic Gardens, Kew. 1906. No. 8, p. 297.

[5]) Garcias ab Horto, *Colloquios dos simples e drogas he cousas medicinais da Intia, e assi dalguas frutas achadas nella ande se tratam.* 1563.

[6]) Van Rheede, *Hortus indicus malabaricus.* Amstelodami 1678—1703.

[7]) Rumphius, *Herbarium amboinense.* Amstelodami 1741—1755.

brought to Europe from the Moluccas in 1717.[1]) However, the distillation of these oils on a large scale and their introduction into the commerce of the world and into industry apparently first began in 1820. In this year the botanist William Roxburgh, who was Director of the Botanical Garden at Calcutta for a long time, mentions lemon-grass oil as coming from the Moluccas.[2]) In 1832 the first large assignment was received in London. Since then, it, as well as the palmarosa oil and somewhat later citronella oil, have been finding increased application in perfumery and especially in the soap industry. As a result of the ever increasing demand, the cultivation of these aromatic grasses, has increased considerably especially that of the citronella grasses in Ceylon, and during the last decade of the 19. century also in Java, so that these oils are now exported in large quantities.

CALAMUS OIL.

Both as spice and as medicament, calamus root is mentioned in the writings of antiquity. Thus it is mentioned in the *Ayur-Vedas,*[3]) in the Old Testament[4]) and in other of the earliest written documents. In the scientific treatises of the Greeks and Romans[5]) it is likewise recorded. During the middle ages a distinction between Asiatic and European calamus was maintained. Still later a distinction was made between the commercial varieties from the several countries from which it was obtained. As one of the spices introduced into Portugal from India,

[1]) *Ephemerides naturæ curiosorum.* 5—6 cent. London (1717). Appendix p. 157. — Medical and Physical Transactions. London. Vol. 1 (1825), p. 367 und Vol. 3 (1827), p. 231.

[2]) Roxburgh, Flora indica, edited by Carey and Wallich. 1820—1824. Calcutta. Vol. 1, p. 280.

[3]) Page 16, footnote 1. — Royle, Essay on the antiquity of Hindoo Medicine. London 1837. p. 28 and 34.

[4]) Exodus, 30:23. — Isaiah, 43:24. — Hesekiah, 27:19. — Song of Solomon, 4:14.

[5]) Agatharchides, *De mari Erythræo,* p. 97. — Theophrasti *Historia plantarum* Lib. 9. 7. — Dioscorides, *De materia medica.* Lib. 1. 17 and 52. Editio Kühn-Sprengel, p. 11. — Plinii *Naturalis historiæ libri.* Lib. XII. 12, 48. Lib. XXV. 100. — Plutarchi *Moralia. Isis et Osiris.* — Strabonis, *Geographia XVI.* 4.

Odoardo Barbosa[1]) mentions calamus in 1511. Matthias Lobelius of Flanders,[2]) in the second half of the 16. century, claims that the calamus imported into Antwerp via Venice is better than that imported from Siebenbuergen and Russia. Rheede supplied the first good illustration of the plant.[3])

Calamus is reported to have been cultivated in the thirteenth century in Poland;[4]) in Germany first during the sixteenth century;[5]) whence it became more widely distributed.[6]) Calamus is also indigenous to North America, being found from Nova Scotia south to Florida and westward to Minnesota, Iowa and Kansas. Of botanists Schöpf first observerd it in 1783 in Pennsylvania and New Jersey.[7])

The distilled oil of calamus is first mentioned in the price ordinance of Frankfurt of 1582 and in the Dispensatorium Noricum of 1589. The yield of oil obtainable upon distillation of the rhizome was determined at the beginning of the eighteenth century by Fr. Hoffmann[8]) and Caspar Neumann;[9]) and about the middle of the eighteenth century by Joh. Fr. Cartheuser.[10]) The first investigations of the oil appear to have been made by

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[1]) Ramusio, *Della navigationi et viaggi.* Venetia 1554. fol. 413—417. — Flückiger, *Dokumente zur Geschichte der Pharmazie.* 1876. p. 15.

[2]) Mathiæ de Lobel et Petri Penæ *Nova stirpium adversaria.* London 1576. p. 29.

[3]) *Hortus indicus malabaricus.* Amstelodamo. 1678—1703. Vol. XI. (1692), Tab. 48 and 49.

[4]) Rostafinski, *Floræ Poloniæ Prodromus* 1873. p. 12. — Clusius, *Rariorum plantarum historia.* Antwerpiæ 1601. fol. 230 and 232.

[5]) Bock, *Teutsche Speiskammer.* Strassburg 1550. p. 104. — Matthioli *Commentarii in Dioscoridem.* 1544. Editio 1565, p. 20. — Joach. Camerarius, *Hortus medicus et philosophicus.* Francofurti 1588. p. 5.

[6]) The assumption that calamus was spread since 1574 from Vienna through botanical gardens as a result of the efforts of Charles de l'Escluse (Clusius) who lived in Vienna from 1573—1588 (Luerrsen, *Handbuch der systematischen Botanik,* vol. 2, p. 320) can scarcely be accepted as a full explanation of its wide distribution. (Engler und Prantl, *Natürliche Pflanzenfamilien.* T. II. Abt. III. p. 118.)

[7]) Schöpf, *Materia medica americana.* Erlangæ 1787.

[8]) Fr. Hoffmannii *Opera omnia physico-medica.* 1740. Liber 65. *Observatio* 1.: *De oleis destillatis atque eorum destillatione observanda.* p. 8.

[9]) Casp. Neumann, *Chymia medica dogmatico-experimentalis.* Editio Kessel. 1749. Vol. 2, p. 272.

[10]) See p. 71, footnote 2.

Joh. Ad. Wedel[1]) in 1718 and by Joh. Barth. Trommsdorff in 1808.[2]) Later examinations are by Martius[3]) in 1832, Schnedermann[4]) in 1842, J. H. Gladstone[5]) in 1863, and A. Kurbatow[6]) in 1873.

SAFFRON OIL.

In the literature of antiquity saffron is frequently mentioned among the spices, also as medicament and dyestuff.[7]) During the Arabian period it was cultivated, especially in Persia[8]) and Spain.[9]) Its introduction into western Europe as far as England was no doubt assisted by the crusades.[10]) In the commerce with the Levante, saffron was one of the most costly spices and played an important role. As an object subjected to heavy duties, it frequently became the subject of rigid legislation,[11]) also

[1]) Joh. Adolf Wedel, *De Calamo aromatico.* Dissertatio. Jenæ 1718.

[2]) Trommsdorff's Journal der Pharmazie **18**, II. (1809), 122.

[3]) Liebig's Annalen **4** (1832), 264 and 266.

[4]) *Ibidem* **41** (1842), 374.

[5]) Journ. chem. Soc. **17** (1864), 1.; Ref. Jahresber. d. Chem. **1863**, 546 and 547.

[6]) Liebig's Annalen **173** (1874), 4.

[7]) Song of Solomon, 4: 14. — Homeri Ilias, 14, 348. — Dioscorides, *De Materia medica libri quinque.* Editio Kühn-Sprengel. Vol. 1, 39. — Plinii *Naturalis historiæ libri.* Lib. XXI, 17 and 18. — Virgilii *Georgica.* Lib. IV, 109. — Alex. Tralliani *medici libri duodecim, græce et latine.* Basiliæ 1556. German edition by Th. Puschmann. Vienna 1878. — Matthæus Platearius, *Circa instans* in Choulant's *Handbuch der Bücherkunde für die ältere Medizin zur Kenntnis der griechischen, lateinischen und arabischen Schriften.* 2nd ed. Leipzig 1841. p. 299. — Hehn, *Kulturpflanzen und Haustiere in ihrem Übergange aus Asien nach Griechenland und Italien.* 3rd ed. 1877. pp. 225—231. — *Liber pontificalis.* Editio Duchesne. Paris 1886. Vol. 1, p. 177.

[8]) Istachri, *Buch der Länder.* German translation by Mordtmann. pp. 87, 93, 124 and 126. — Edrisi, *Géographie, traduite par* Amédée Jaubert. 1836. pp. 168 and 192. — Meyer, *Geschichte der Botanik.* Vol. 3, pp. 282, 284, 299. — Bretschneider, Chinese Botanical Works. Foochow 1870. p. 15. — Ibn Baitar, *Traité des Simples.* Edit. Leclerc. 1881. Vol. 2, p. 209.

[9]) *Le Calendrier de Cordoue de l'année 961.* Leyde 1873. pp. 33, 109.

[10]) Conrad et Waldmann, *Traité du Safran du Gâtinais.* Paris 1846. p. 20. — Morant, History and Antiquities of Essex. 1768. Vol. 2, p. 545. — *Revue pharmaceutique.* 1858. p. 58. — Douglass, Philosophical Transactions. November 1728. p. 566.

[11]) Simonsfeld, *Der Fondaco dei Tedeschi in Venedig und die deutsch-venetianischen Handelsbeziehungen.* Stuttgart 1887. p. 35. — Mone, Zeit-

because it was excessively adulterated with the florets of *Carthamus tinctorius* and parts of other plants. So important did the commerce in saffron become during the middle ages that the traders in spices of some of the larger German cities united under the name of *Safranzünfte* to special corporations.[1])

Into the United States of North America, saffron appears to have been introducd by German immigrants during the first half of the 18. century. In 1748 Peter Kalm found saffron gardens near Philadelphia and in New Jersey,[2]) and in 1787 Joh. David Schœpf found them near Lancaster, Pa.[3])

The distilled oil of saffron is first mentioned by Walter Ryff[4]) and Conrad Gesner,[5]) and is enumerated in the municipal price ordinance of Nürnberg of 1613. The older medical treatises do not mention it. The yield was apparently first determined in 1670.[6]) Saffron and its constituents were further examined by Bouillon Lagrange and Vogel in 1810.[7]) In 1821 Henry examined the coloring matter of saffron and arrived at the conclusion that the yield of oil was almost doubled if for every ounce of saffron 8 oz. of common salt and 4 oz. of potassa are added to the water in the still.[8])

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schrift für die Geschichte des Oberrheins **5** (1854), 28. — Warnkönig, *Histoire de la Flandre.* Vol. 4 (1851), p. 449. — Flückiger, Schweiz. Wochenschr. f. Chem. u. Pharm. **19** (1881), 109. — Falke, *Geschichte des deutschen Handels.* 1859. Vol. 1, p. 267. — Elben, *Zur Lehre von der Warenfälschung.* Dissertatio. Tübingen 1881. p. 37. — Flückiger, *Beiträge zur älteren Geschichte der Pharmazie in Bern.* 1862. p. 6. — Roth, *Geschichte des Nürnbergischen Handels.* 1802. Vol. 4, p. 221. — Beckmann, *Beiträge zur Geschichte der Erfindungen.* 1784. Vol. 2, pp. 88 and 91. — Peters, *Aus pharmazeutischer Vorzeit.* 1899. Vol. 2, pp. 225—229.

[1]) Flückiger, *Dokumente zur Geschichte der Pharmazie.* 1876. pp. 46 and 66.

[2]) Prof. Peter Kalm's *Reise nach dem nördlichen Nordamerika im Jahre 1748—1749.* Göttingen 1754. Vol. 3, p. 135.

[3]) Joh. David Schöpf, *Materia medica Americana potissimum regni vegetabilis.* Erlangæ 1787.

[4]) Gualtherus Ryff, *New gross Destillirbuch.* 1556. fol. 188.

[5]) Euonymus Philiatrus, *Ein köstlicher Schatz.* Zürich 1555. fol. 222.

[6]) Joh. Ferd. Hertodt, *Crocologia.* Dissertatio. Jenæ 1671.

[7]) Annales de Chimie **80** (1811), 185. — Trommsdorff's Journ. der Pharm. **21**, I. (1812), 206.

[8]) Trommsdorff's Neues Journ. der Pharm. **6** (1822), 65. — Berliner Jahrbuch f. Pharm. **24**, I. (1822), 160.

OIL OF ZEDOARY.

During the 6. and 7. centuries, zedoary is mentioned by Aetius, Paulus Aegineta and other writers as coming from India where it had been in use for a long time. In western Europe it became known toward the beginning of the 8. century.[1]) From that time on, zedoary is frequently referred to, under various names,[2]) among the spices,[3]) in the formulas of pharmacopœias,[4]) and by travellers.

During the middle ages zedoary appears to have been introduced into commerce principally from the Malabar coast.[5])

The distilled oil of zedoary is first mentioned in the price ordinance of Berlin of 1574,[6]) in those of Worms and Frankfurt-on-the-Main of 1582, also in the *Dispensatorium Noricum* of 1589. Examinations as to yield and properties of the oil were later made by Neumann[7]) (1785), Dehne[8]) (1779) and E. F. Geoffroy[9]) (1757).

OIL OF GALANGAL.

Galangal appears to have been used in China during antiquity. It is mentioned in the *Ayur-Vedas* of Susrutas,[10]) also by Plutarch.[11]) The Arabian physicians used it for medicinal

[1]) Niccolò de Conti. In Kunstmann's *Kenntnis Indiens im 15. Jahrhundert.* Munich 1863. p. 48. — Odoardo Barbosa, *Delle navigationi et viaggi.* Venetia 1554. pp. 413 and 417. — Meyer, *Geschichte der Botanik.* Vol. 2, p. 421.

[2]) Zituar. Zodear. Zitewar. Citowart. Citoal. Cytoal. Zerumbet.

[3]) Guérard, *Polyptique de l'abbé* Irminon II, *Statuta antiqua abbatiæ* St. Petri Corbeinensis. Paris 1844. — W. Heyd, *Geschichte des Levantehandels.* 1879. Vol. 1, p. 104.

[4]) I. G. Eckhart, *Commentarii de rebus Franciæ orientalis et episcopatus Wirceburgensis.* Wirceburgi 1729. Tom. II, p. 980. — F. A. Reuss, Walafridi Strabi *Hortulus.* Wirceburgi 1834. p. 73.

[5]) Kunstmann's *Kenntniss Indiens im 15. Jahrhundert.* 1863. p. 48. — Flückiger, *Dokumente zur Geschichte der Pharmazie.* 1876. p. 15.

[6]) *Estimatio materiæ medicæ . . . in gratiam et usum publicum civitatum Marchiæ Brandenburgensis.* Autore Matthæo Flacco. Berolini 1574.

[7]) J. F. A. Göttling's Almanach für Scheidekünstler 1785, 118.

[8]) Lorenz Crell's Chemisches Journal 3 (1779), 20.

[9]) E. F. Geoffroy, *Tractatus de materia medica.* Paris 1757. Vol. 3, p. 265.

[10]) See p. 16, footnote 1.

[11]) Plutarchi *Moralia. Isis et Osiris.* The use of galangal for fumigating purposes by the ancient Egyptians is referred to.

purposes and thus, no doubt, assisted in its introduction into western Europe. Thus Rhazes, Avicenna, Alkindi[1]) and other physicians who lived during the 9. and 10. centuries, mention galangal in their writings as an esteemed remedy. Its importation is reported in the 9. century by the Arabian geographer Ibn Kurdadbah,[2]) and in the beginning of the 12. century by the Sicilian geographer Edrisi.[3]) In the *Della decima* etc., a commercial treatise of the first half of the 14. century by the Florentine merchant Pegolotti, galangal is described as occuring in two varieties, *viz.*, the light and the heavy.[4]) Marco Polo reports on the cultivation of the plant in China and Java.[5]) In 1563 Garcia da Orta, a physician in Goa, describes two varieties of galangal, a smaller variety coming from China, and a larger one from Java.[6]) The first good illustration was published by Rumpf in 1754.[7])

In German literature the rhizome is found as early as the 8. century and is mentioned as a medicinal drug. Galangal also occurs as one of the ingredients of a prescription found in a medical manuscript of the 8. century in the library of the University of Würzburg.[8]) It is also mentioned in a formulary of

[1]) Macer Floridus, *De viribus herbarum.* Naples 1487. Editio Choulant. 1832. Cap. 70. — Ibn Baitar, *Traité des Simples.* Editio Leclerc. Vol. 2, p. 61.

[2]) *Le livre des routes et des provinces, par* Ibn Khordadbeh, *traduite par* B. de Meynard; *en Journal asiatique,* Ser. VI, Tom. 5 (1865), p. 294.

[3]) *Géographie* d'Edrisi, *traduite par* A. Jaubert. 1836. Tom. 1, p. 51.

[4]) Francesco Balducci Pegolotti, *La pratica della mercatura scritta.* In Pagnini's *Della decima e delle altre gravezze, della moneta* etc. Lisboa e Lucca. 1766. pp. 296 and 375.

[5]) Pauthier, *Le livre de Marco Polo.* 1865. pp. 522 and 561.

[6]) Garcias ab Horto, *Colloquios dos simples e drogas he cousas medicinais da India.* Goa 1563. *Colloquio 24.* — Whereas at the present time only the smaller root, the *Radix galangæ minoris* obtained from *Alpinia officinarum,* Hance is in use and obtainable commercially the *Radix galangæ majoris* obtained from *Alpina Galanga,* Willd. was formerly also current. The latter came from Java. See also Daniel Hanbury, *Science papers.* 1876. p. 370.

[7]) G. E. Rumphius, *Herbarium amboinense* etc. Amstelodami 1741—1754. Vol. 5, Tab. 63.

[8]) *Würzburger Universitätsbibliothek Manuscriptes* Mp. th. fol. 146. — Printed in F. A. Reuss, Walafridi Strabi *Hortulus.* Wirceburgi 1834. p. 37. D. G. ab Eckhart, *Commentarii de rebus Franciæ orientalis et episcopatus Wirceburgensis.* Wirceburgi 1729. Vol. 2, p. 980, *Glossæ Theotiscæ.*

the 9. century by Bishop Salomo III of Constance.[1]) Its medicinal virtues are praised by Matthæus Platearius,[2]) a Salernitan scientist of the 12. century, and by Hildegard,[3]) abbess of Bingen.

Galangal found a place in the *Dispensatorium Noricum,* but its volatile oil appears to have been distilled later. It is first mentioned in the municipal price ordinance of Frankfurt-on-the-Main in 1587.

OIL OF GINGER.

Ginger appears to have been used as a spice by the Chinese and the Indians. It is mentioned repeatedly in Chinese medical treatises, in the *Ayur-Vedas* of Susruta, also in Sanscrit literature and later in the Talmud. The Greeks and Romans[4]) obtained ginger via the Red Sea and hence regarded Arabia as its geographic source. In the 3. century, however, it was counted among the Indian products brought via the Red Sea and Alexandria.[5]) Ginger was one of the favorite spices of the Romans.[6]) Apparently it was introduced into Germany[7]) and France[8]) during the 9. century and into England[9]) during the 10. century. A better understanding

[1]) Dümmler, *Formelbuch des Bischofs Salomo von Constanz.* In *St. Gallische Denkmäler aus der Karolingischen Zeit.* Zürich 1859. p. 37.

[2]) *Circa instans. Liber de simplice medicina.* In Choulant's *Handbuch der Bücherkunde für die ältere Medicin.* 2nd ed. Leipzig 1841. p. 229.

[3]) Hildegardis Abbatissæ *Subtilitatum diversarum naturarum creaturarum libri novem.* In Migne, *Patrologiæ Cursus completus.* Tom. 197. *Lutetia Parisiorum.* 1855. pp. 1134 and 1158.

[4]) Dioscorides, *De Materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 2, p. 300.

[5]) Vincent, Commerce and Navigation of the Ancients in the Indian Ocean. 1807. Vol. 2, p. 695. — Meyer, *Geschichte der Botanik.* Vol. 2, p. 167.

[6]) Apicius Cælius, *De re coquinaria libri decem.* Editio Schuch. Heidelberg 1867. pp. 36, 45, 68, 98, 105, 138, 139, 142, 165.

[7]) Cless, *Landes- und Kulturgeschichte von Württemberg.* 1807. Vol. 2, p. 260. — In the preface of a Codex of the 8. century of the Würzburg Library (Mp. th. f. 146) it is mentioned together with cinnamon, costus, cloves, pepper and gentian. The title of this manuscript is J. G. ab Eckhardt, *Commentarii de rebus Franciæ orientalis et episcopatus Wirceburgensis, Glossæ Theotiscæ.* — The preface referred to is printed in F. A. Reuss, *Walafridi Strabi Hortulus.* Wirceburgi 1834. p. 73.

[8]) W. Heydt, *Levantehandel im Mittelalter.* 1879. Vol. 1, p. 103, footnote 3.

[9]) *Pharmacographia.* p. 635. — Rogers, History of Agriculture and Prices in England. 1866. Vol. 1, p. 629.

as to the geographical source of ginger was obtained by Marco Polo, Pegolotti, Barbosa and Niccolo Conti on their voyages along the coast and among the islands of southwestern Asia.[1]) As early as the 13. century ginger entered the market either fresh *(zenzeri verdi)*, preserved with sugar *(giengiaro confetto)* or dried. For a long time Alexandria was the principal port for the purchase of this delicacy.[2]).

As a dutiable article of commerce, ginger is mentioned repeatedly: thus, in 1173 in Acre in Palestine,[3]) in 1221 in Barcelona,[4]) in 1228 in Marseilles,[5]) and in 1296 in Paris.[6]) In an old apocryphal German pharmacopœia of the 12. century, ginger occurs in several formulas.[7])

Into the West Indies and Mexico, the ginger plant was introduced by the Spaniards during the middle of the 16. century;[8]) and as early as 1547 ginger was exported from Jamaica[9]) to Spain, in 1585 from St. Domingo and in 1654 from Barbadœs.[10])

The first mention of a distilled oil of ginger is found in a municipal spice ordinance of Copenhagen of the year 1672. The yield was determined in the course of the 18. century first by

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[1]) *Le livre de* Marco Polo, *publié par* Pauthier. 1865. Vol. 2, pp. 381, 488. — Pegolotti, in Pagnini's *Della decima e delle altre gravezze, della moneta e della mercatura de' Fiorentini fino al secolo XVI.* Lisboa e Lucca 1766, p. 360. — Od. Barbosa. Editio Ramusio, *Delle navigationi et viaggi.* Venetiæ 1554. pp. 311 and 323. — Niccolò Conti, India in the 15. century. Edition Major, London 1857. — Kunstmann, *Kenntnis Indiens im 15. Jahrhundert.* Munich 1863.

[2]) Pegolotti, Editio Pagnini. *Della decima* etc. pp. 298 and 317.

[3]) *Recueil des Historiens des Croisades.* Lois 1843. Tom. 2, p. 176.

[4]) Capmany, *Memorias historicas sobre la Marina Commercio y Artes de la Ciudad de Barcelona.* Madrid 1779. Vol. 2, p. 3.

[5]) Méry et Guindon, *Histoire des Actes de la Municipalité de Marseille.* 1841. Tom. 1, p. 372.

[6]) *Revue archéologique.* Paris 1852. Tom. 9, p. 213.

[7]) Pfeiffer, *Zwei deutsche Arzneibücher aus dem 12. und 13. Jahrhundert, in* Sitzungsberichte der Wiener Akademie d. Wissenschaften 42 (1863), 124, 138, 159. — Haeser, *Geschichte der Medicin.* 1875. Vol. 1, p. 663.

[8]) Monardes, *Historia medicinal de las cosas que se traen de nuestras Indias occidentales que sirven en medicina.* Sevilla 1574. p. 99. — Editio Clusius. Antverpiæ 1593. p. 309.

[9]) Renny, History of Jamaica. London 1807. p. 154.

[10]) Calendar of State Papers. Colonial series 1574—1660. London 1860. p. 4.

Caspar Neumann,[1]) and then by J. A. Gesner,[2]) E. F. Geoffroy[3]) and Friedrich Cartheuser.[4])

The first illustration of *Zingiber officinale,* Roscoe was published by H. A. van Rheede in 1670.[5])

OIL OF CARDAMOM.

Cardamom, i. e. the capsular fruit of several species of *Elettaria* and *Ammomum,* (N. O. *Zingiberaceæ*), indigenous in the islands of the East Indian archipelago, appears, to have been used during antiquity. In the *Ayur-Vedas* of Susrutas[6]) they are mentioned as *Ela.* According to Plutarch[7]) the Egyptians used cardamom together with other spices in religious incense.

Later writers use as synonyms the terms *Amomis, Amomum* and *Cardamomum.*[8]) Although a number of spices were imported during antiquity from southern India, it is highly probable that these designations were applied only to cardamom. Dioscorides,[9]) Theophrastus,[10]) Pliny,[11]) Scribonius Largus and Alex. Trallianus,[12]) mention cardamom as well as Amom, mostly together with pepper, cloves and nutmeg. During the 3. and 4. centuries, when Roman luxury had reached its climax, cardamom was one of the favorite

[1]) *Chymia medica dogmatico-experimentalis.* Editio Kessel. 1749. Vol. 2, p. 638.

[2]) Joh. Alb. Gesneri *Dissertatio de Zingibere.* Altdorf 1723. p. 18.

[3]) *Tractatus de materia medica.* Paris 1757. Vol. 2, p. 265.

[4]) *Elementa Chymiæ dogmatico-experimentalis una cum synopsi Materiæ medicæ selectioris.* Halæ 1736. Vol. 2, p. 62.

[5]) *Hortus indicus malabaricus.* Amstelodami 1678—1703. Vol. 2, p. 24, Tab. 12.

[6]) See p. 16, footnote 1.

[7]) Plutarchi *Moralia. Isis et Osiris.*

[8]) The usage of these synonyms continued up to the close of the 18. century. Thus in Murray's *Apparatus Medicamentorum* (Göttingen 1790) and in similar works the designation *Amomum Cardamomum* still occurs.

[9]) Dioscorides, *De materia medica libri quinque.* Editio Kühn-Sprengel. Leipzig 1829. Vol. 1, p. 14.

[10]) Theophrasti Eresii *opera, quæ supersunt omnia. Historia plantarum.* Editio Wimmer. Parisiis 1866. p. 147.

[11]) Plinii *Naturalis historiæ libri.* Lib. XII. 28, 29. — Editio Littré. Paris 1877. Vol. 1, pp. 482, 483.

[12]) Alexandri Tralliani *medici libri XII.* Basiliæ 1556. Editio Puschmann. 1878. Vol. 2, p. 354.

spices.[1]) As products of farther India, the Arabian traveler Masudi[2]) in 912 mentions cardamom, cubebs, nutmegs, cloves, camphor, sandelwood and linaloes. In the middle of the 12. century, the Sicilian geographer Edrisi[3]) makes a distinction between Ceylon and Chinese cardamom. Like Barbosa[4]) and Pegolotti,[5]) he also mentions that at that time the spices entered the European market via Aden and Alexandria, also via Accon[6]) during the existence of the Kingdom of Jerusalem.

Even at that time, a distinction was made between wild and cultivated cardamom.[7]) Garcia da Orta[8]) distinguished between a larger but less aromatic cardamom from Ceylon and a smaller but more spicy variety. Finally, at the time of Valerius Cordus the Malabar *Cardamomum minus* was given preference over the larger kind.[9])

The first good illustration of *Eletteria cardamomum* was published by Henry van Rheede,[10]) governor of the Dutch East

[1]) Apicius Cælius, *De re coquinaria libri X.* Editio Schuch. Heidelberg 1867. pp. 36, 45, 64, 98, 105, 139, 142, 165. — Hieronymi *Opera omnia.* Editio Migne *Patrologiæ cursus completus.* Vol. 2, p. 297.

[2]) Ali el-Masudi, *Prairies d'Or.* Editio Meynard et Courteille. Paris 1861—1877. Vol. 1, p. 341.

[3]) *Géographie* d'Edrisi, *traduite par* Amédée Jaubert. 1836—1840. Vol. 1, pp. 51, 341.

[4]) Libro di Odoardo Barbosa. In Ramusio's *Delle navigationi et viaggi.* Venetia 1554. fol. 413—417. — Editio Hakluyt Society in London: Description of the Coasts of East Africa and Malabar. 1866. pp. 59, 64, 147, 154.

[5]) Francesco Balducci Pegolotti, *La pratica della mercatura.* In Pagnini's *Della decima e delle altre gravezze, della moneta e della mercatura de' Fiorentini fino al seculo XVI.* Lisboa e Lucca 1766. p. 57.

[6]) Beugnot, *Assies de Jérusalem.* Paris. Vol. 2, p. 175.

[7]) Pegolotti, *Cardamomi salvatichi, domestici.* l. c. (see footnote 5) p. 211 and 296.

[8]) Garcias ab Horto, *Colloquios dos simples e drogas he cousas medicinais da India, e assai dalguas frutas achadas nella ande se tratam.* 1563. Edited by Carolus Clusius in 1567 with the title: *Aromatum et Simplicium aliquot medicamentorum apud Indus nascentium historia: primum quidem Lusitanica lingua διαλογικῶς conscripta,* a D. Garcia ab Horto, Proregis Indiæ Medico: *Deinde latino illustrata* a Carolo Clusio Atrebate. Antverpiæ p. 98. The original Portuguese was reprinted in 1872 by F. A. von Varnhagen. See p. 51 of this edition.

[9]) Valerius Cordus, *Dispensatorium Noricum.* Editio Paris. pp. 40, 76, 77, 115, 157, 158.

[10]) Van Rheede, *Hortus indicus malabaricus, cum notis et commentariis* Johanni Commelini. Amstelodami 1678—1703. Vol. XI (1692), Tab. 4—5: *Elettari.*

India Company on the Malabar coast, and by Georg Eberhard Rumpf,[1]) who, born in Hanau, lived as merchant and botanist in Amboina.

Cardamom oil was distilled as early as 1540 by Valerius Cordus.[2]) The yield was determined by Caspar Neumann,[3]) C. Ph. Martius,[4]) Joh. Friedr. Cartheuser and J. R. Spielmann.[5])

OIL OF PARADISE GRAINS.

The Grains of Paradise were formerly used extensively as a spice. In the apothecary shops they were known as *Grana Paradisi, Semina Cardamomi majoris,* and as *Piper Melegueta.*

Oil of paradise grains was distilled by Porta[6]) at the beginning of the 17. century and used medicinally.

OIL OF PEPPER.

Pepper is one of the oldest known spices mentioned in Sanskrit and ancient Indian literature. In the 4. century B. C. it is mentioned by Theophrastus.[7]) Dioscorides,[8]) and Pliny[9]) already distinguished between black, white and long pepper and counted the first among the most important spices of their time. Toward the end of the 1. century, we already find special warehouses *(horreæ piperatariæ)* for this precious ware. As ports of exports for pepper, places on the west Indian coast, between

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[1]) Rumphius, *Herbarium Amboinense (Het Amboinische Kruidboek).* Editio Johanni Burmanni. Amstelod. 1741—1755. Vol. 5, p. 152 also plate 65. *Amomum Cardamomum.* (This work had been completed by Georg Eberhard Rumpf in 1690, but was not published until after his death viz. in 1741.)

[2]) Valer. Cordus, *De artificiosis extractionibus.* 1561. fol. 226.

[3]) Caspar Neumann, *Chymia medica dogmatico-experimentalis.* Editio Kessel. 1749. Vol. 1, p. 328.

[4]) J. C. S. Schweigger's Journal für Chemie u. Physik 3 (1811), 311.

[5]) Jacob R. Spielmann, *Cardamomi historia et vindiciæ.* Argentor. 1762.

[6]) Porta, *De destillatione.* Romæ 1608. Lib. IV. Cap. 4.

[7]) Theophrasti Eresii *opera quæ supersunt omnia.* IX. 20. — Editio Wimmer. Vol. 1, p. 162; vol. 2, p. 476.

[8]) Dioscorides, *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, p. 298.

[9]) Plinii *Naturalis historiæ libri.* Lib. XII, 14. — Editio Littré. Vol. 1, p. 478.

Mangalose and Cochin, are enumerated in the *Periplus* of the Erythrean sea, a commercial catalogue that was presumably written in A. D. 76, in Alexandria.[1])

Into western Europe pepper was likewise introduced at an early date. The quantities in which it was imported, in spite of its high price at the beginning of the 5. century, become apparent from the statement that the west Roman Emperor, Honorius paid a tribute of 3000 lbs. pepper to Alaric, King of the Vesigoths in 408, while the latter was besieging Rome.[2]) Pepper retained its high price late into the middle ages. Hence, it was used in place of the noble metals in the payment of tribute, taxes, rent, duty and ransom; as gifts and as objects of bequest.[3]) Among the presents made to the popes by the East and West Roman emperors, pepper is usually enumerated first among the costly spices. According to a privilege granted 716 by the Merovingian king, Chilperich II, the monastery at Corbie in southern France obtained among other objects pepper, cloves, cinnamon and spike as annual revenue.[4]) Boniface, the apostle of the Germans, repeatedly obtained from Roman prelates,[5]) presents of aromatics for incense purposes, among which pepper is enumerated.

In 1290 Marco Polo found pepper in abundance in the islands of the Malay Archipelago and on the Indian coast. It constituted an important article of commerce with China.[6])

The increasing demand for pepper and the high price paid therefor constituted not the least of the motives for the search of an all water route to the East Indies. This was accomplished

[1]) Fabricius, *Der Periplus des Erythräischen Meeres von einem Unbekannten.* Greek and German. Leipzig 1883. p. 188. — Vincent, Commerce and Navigation of the Ancients in the Indian Ocean. London 1807. Vol. 2, pp. 458 and 754.

[2]) Zosimi *Comitis et exadvocati fisci Historiæ novæ libri septem.* Basiliæ. Lib. V, cap. 41. — Gregorovius, *Geschichte der Stadt Rom im Mittelalter.* — Hodgkin, Italy and her Invaders. London 1880. p. 347.

[3]) Wilh. Heyd, *Geschichte des Levantehandels im Mittelalter.* 1879. Vol. 1, p. 99; vol. 2, pp. 458 and 754.

[4]) Pardessus, *Diplomata, chartæ* etc. Paris 1849. Tom. 2, p. 309. — W. Heyd, *Geschichte des Levantehandels im Mittelalter.* 1879. Vol. 1, p. 99.

[5]) Jaffé, *Bibliotheca rerum germanicarum.* Berlin 1866. Vol. 3, pp. 156, 157, 199, 218 and 231.

[6]) W. Heyd, *Geschichte des Levantehandels im Mittelalter.* 1879. Vol. 1, p. 634.

by the Portugese under the leadership of Vasco da Gama in 1498. The cultivation of the pepper plant having been spread over several islands of the Malay archipelago, the production of pepper was greatly increased. This resulted in a larger export with the consequent reduction in price and increased consumption. The discovery of an all water route naturally deviated the spice trade from Venice which then was a commercial republic at its prime. In 1504, Portugese vessels laden with pepper sailed up the Thames and embarked at London and in 1522 they also entered the harbor of Antwerp. In spite of all the endeavors of the Venetian captains of commerce, the trade in pepper became a Portuguese monopoly[1]) from that time on, and remained such nearly up to the 18. century.

The estimate in which pepper was held during the middle ages is indicated by the fact that it was symbolic for the entire spice trade. Already in Rome the spice peddlers were known as *Piperrarii.* Later in France they were called *Pebriers,* and in England *Pepperers.*[2])

In all probability, oil of pepper was known during the middle ages. It is first mentioned, however, by Saladin.[3]) It was first described by Valerius Cordus[4]) and later by Giov. Batt. Porta.[5]) The method of distillation of the oil is first described by Winther[6]) of Andernach, who, about 1550, distilled the oils of pepper, cinnamon, cloves, etc. The *Dispensatorium Noricum* of 1589 was the first of the pharmacopœias to include the oil. It is also enumerated in the municipal pharmaceutical price ordinance of Berlin of 1574, also in that of Frankfurt of 1688.[7])

[1]) W. Heyd, *Geschichte des Levantehandels im Mittelalter.* 1879. Vol. 2, pp. 502—527.

[2]) *Ibidem,* vol. 2, pp. 634—640.

[3]) Saladini Asculani *Compendium aromatariorum.* Venetii 1488. Index.

[4]) Val. Cordi *Annotationes* in Pedacei Dioscoridis Anazarbei *de materia medica libros quinque. De artificiosis extractionibus.* Editio Gesner. Argentorati. 1561. fol. 226.

[5]) Portæ *Magiæ naturalis libri viginti. Liber de destillatione.* 1567. p. 379. Editio 1589, p. 184.

[6]) Guintheri Andernacensi *de medicina veteri et nova.* Basil. 1571. pp. 630—635.

[7]) H. A. van Rheede tot Draakestein. *Hortus indicus malabaricus.* Vol. 7, p. 14. *"Oleum ex pipere destillatum levem piperis odorem spirans, saporis parum acris."*

The first chemical investigations of pepper were conducted by Caspar Neumann[1]) and H. D. Gaubius,[2]) later ones by Willert,[3]) Oerstedt,[4]) and Pelletier.[5])

PEPPER OIL FROM LONG PEPPER.

Long pepper was used in antiquity both as spice and as medicament. It is mentioned in a number of mediaeval drug lists.[6]) Presumably, however, it never was in general use and in recent times it has come into disuse.

Distilled oil of long pepper is first mentioned in pharmaceutical price ordinances in 1589. It was included in the 1589 edition of the *Dispensatorium Noricum*. The first chemical examination of long pepper was made by Winkler[7]) in 1827.

OIL OF CUBEBS.

Apparently cubebs were used as spice in China and in India during antiquity.[8]) As medicament they appear to have first been used by the Arabians.[9]) Kurdabah[10]) of Mesopotamia and Madusi[11]) of Bagdad, travelers living in the 9. and 10. centuries, mention cubebs among the more important spices. Edrisi,[12]) a

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[1]) C. Neumann, *Gründliche mit Experimenten erwiesene Chymie*. Editio C. H. Kessel. 1749. Vol. 2, Prt. 4, p. 9.

[2]) Gaubii *Adversariorum varii argumenti liber unus*. 1771. Cap. 5, p. 55.

[3]) Trommsdorff's Journ. der Pharm. **20**, II. (1811), 44.

[4]) Schweigger's Journ. für Chemie und Physik **29** (1819), 80.

[5]) Trommsdorff's Neues Journ. der Pharm. **6**, II. (1822), 233.

[6]) Macer Floridus, *De viribus herbarum una cum* Walafridi Strabonis, Othonis Cremonensis et Joannis Folcz *carminibus similis argumenti*. Editio Choulant. Lipsiæ 1832. p. 114. — Simon Januensis. *Synonyma medicinæ seu Clavis sanationis*. Veneti 1510. — Bonaini *Statuti inediti della città* de Pisa. 1857. Vol. 3, p. 492. — Kunstmann, *Kenntnis Indiens im 15. Jahrhundert*. Munich 1863. p. 40. — Saladini *Compendium aromatariorum*, Bononiensi 1488. Index.

[7]) Arch. der Pharm. **26** (1828), 89.

[8]) Alexandri Tralliani *Opera*. Edit. Puschmann. Vol. 2, p. 396.

[9]) Paulus Aegineta. — Editio Fr. Adams. London 1847, Vol. 3, p. 455.

[10]) Khordadbeh, *Le livre des routes et des provinces par* Barbier de Meynard in the Journal asiatique **5** (1865), 294.

[11]) Meynard and de Courteille, *Prairies d'Or*. Paris 1861—1877. Tom. I. p. 367 and Tom. IV, p. 78.

[12]) Amédée Jaubert, *Géographie d'Edrisi* 1836. Tom. 1, p. 51 and 89.

Sicilian geographer of the 12. century mentions cubebs among the spices imported via Aden. The abbess Hildegard[1]) and the Danish cannon Henrik Harpestreng[2]) describe cubebs as a valuable remedy. During the 13. century cubebs were used generally in Europe both as spice and as medicament. As such they are mentioned from the 14. century on in medical writings and municipal price ordinances.[3])

Later the use of cubebs as spice declined. Indeed they had almost been forgotten when at the beginning of the past century their use was again urged by English physicians.[4])

Cubebs were examined chemically by G. Wedel[5]) in 1704, soon therafter by Caspar Neumann,[6]) in 1810 by Trommsdorff[7]) and in 1821 by Vauquelin.[8])

The volatile oil of cubebs was known to Valerius Cordus[9]) in 1540. In price ordinances it first occurs in that of Frankfort-on-the-Main of 1582.

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[1]) Hildegardis Abbatissæ *Subtilitatum diversarum naturarum creaturarum Libri novem.* Editio Migne. *Patrologiæ cursus completus.* Tom. 197 (1855), p. 1147. — Meyer, *Geschichte der Botanik.* Vol. 3, p. 537.

[2]) Harpestreng, *danske Laegebog fra det trettende Aarhundrede, foerste Gang utgivet efter et Pergamenthaandskrift.* Copenhagen. 1826. p. 62.

[3]) *Monumenta Gildhallæ Londoniensis. Liber albus 1,* p. 230. — Capmany, *Memorias historicas sobre la Marina, Commercio y Artes de la Ciudad de* Barcelona. 1779. p. 44. — Bourquelot, *Etudes sur les foires de la Champagne.* Mémoires de l'Institut. Tom. 5 (1865), p. 288. — Saladini *Compendium aromatariorum.* 1488. — Hans Folcz, *Confectbuch vom Jahre 1480.* In Choulant's *Handbuch der Bücherkunde für die ältere Medicin.* 1832. p. 188. — Rogers, History of Agriculture and Prices in England. Vol. 1, p. 627; vol. 2, p. 544. — *Liber niger Scaccarii.* London 1771. Vol. 1, p. 478. Val. Cordus, *Dispensatorium Noricum.* Edit. 1548. pp. 76, 77 and 327. — Flückiger, *Dokumente zur Geschichte der Pharmazie.* 1876, 15, and *Die Frankfurter Liste* in the Arch. der Pharm. **201** (1872), 441 and **211** (1877), 101.

[4]) Dictionary of the Indian Islands. London 1856. p. 117. — Edinburgh Medical and Surgical Journal 14 (1818), 32. — Mérat et de Lens, *Dictionnaire universel de materia medica.* Tom. 5 (1833), p. 331.

[5]) G. Wedel, *De cubebis.* Dissertatio. Jenæ 1705.

[6]) Caspar Neumann, *Lectiones chymici de salibus alkalinofixis et de camphora.* Berlin. 1727.

[7]) Trommsdorff's Journ. der Pharm. **20**, I. (1811), 69.

[8]) Trommsdorff's *Taschenbuch für Chemiker und Pharmazeuten* **1822**, 195.

[9]) Valerii Cordi *Annotationes* in Pedacei Dioscoridis *de medica materia libros quinque longe aliæ quam antea sunt hac sunt evulgatæ.* 1561. fol. 226.

OIL OF BETEL.

When and by whom betel oil was first distilled is not known: it is highly probable that the preparation of the oil by Kemp[1]) in 1885 was not the first. A superficial examination of Siam betel oil in the laboratory of Schimmel & Co.[2]) in 1887 revealed the presence of a phenol in fraction 250—260°, which seemed to correspond with eugenol. Eykman,[3]) who in 1888 examined an oil distilled by himself in Java, found no eugenol, but a new phenol which he called chavicol. A second examination in the laboratory of Schimmel & Co. revealed the fact that Siam betel oil contains neither eugenol nor chavicol, but a third phenol, a previously unknown isomer of eugenol, which Bertram and Gildemeister[4]) in 1889 termed betel phenol.

OIL OF SWEET BIRCH.

Next to turpentine oil, the oils of sassafras, wintergreen and birch bark are among the first oils obtained by distillation in the United States. The similarity in odor and taste of birch bark oil with true oil of wintergreen from *Gaultheria procumbens* was known before 1818.[5]) The chemical identity of the principal constituent of both, however, was demonstrated by Wm. Procter Jr.[6]) of Philadelphia in 1843. As the demand for wintergreen oil increased and since wintergreen leaves were not as readily collected, sweet birch bark was distilled indiscriminatly with wintergreen leaves or even distilled alone as substitute[7]) so that the commercial natural oil is at present obtained almost exclusively from the bark of *Betula lenta*, L.

[1]) Dymock, Warden and Hooper, *Pharmacographia indica*. Part. VI, p. 188.

[2]) Schimmel's Bericht October 1887, 34.

[3]) Chem. Ztg. 12 (1888), 1338.

[4]) Journ. f. prakt. Chem. II. 39 (1889), 349.

[5]) Bigelow, American Medical Botany. Boston 1818. Vol. 2, pp. 28 and 241.

[6]) Americ. Journ. Pharm. 15 (1843), 241.

[7]) *Betula lenta* and *Gaultheria procumbens* grow together in the wooded mountainous regions of the North Atlantic states. In a report on the wintergreen oil industry, Kennedy of Pottsville, Pa. (Americ. Journ. Pharm. 54 [1882], p. 49) called attention to the fact that the cost of collection of birch bark was but 1/7 of that of wintergreen leaves; also that the yield of oil from the bark was about 0.25 p. c., whereas that from wintergreen was 0.80 p. c. According to these figures the cost of production of the oil from birch bark is but half as great as that of wintergreen leaves.

OIL OF HOPS.

As early as the middle ages hops were used for the aromatization of beer, being mentioned in literature since the 8. century.[1]) For medicinal purposes hops and their glands have been used only in more recent times. The medicinal use of lupulin was first suggested in 1820 by Ives,[2]) a New York physician.

Apparently the volatile oil of hops was first distilled from the glands in 1821 by Payen and Chevallier.[3])

OIL OF SANDALWOOD.

Because of its peculiar odor sandalwood from *Santalum album* was highly prized during antiquity in India and China. Of the useful woods it was the most durable because it is avoided by the white ant that destroys most other kinds of wood. In India it was therefore used for carving images of the dieties, and temple decorations. Both in China and India it is used as incense in the cult of the dead and other religious worship.

Sandalwood is mentioned in the earliest Sanscrit literature and probably also in that of China. Yet it does not appear to have been an article of barter between India and China and the occident. To the Egyptians, however, it was known as early as the 17. century B. C. They obtained it from the countries lying between the gulf of Aden and the Persian bay, then known as the Punt or Phun.[4])

The first mention of sandalwood during the Christian era occurs about the middle of the first century in the Periplus of the Red Sea;[5]) somewhat later in the 5. century in the writings

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[1]) Flückiger and Hanbury, *Pharmacographia*. 1879. p. 551.

[2]) Silliman's Journal of Sciences and Arts **1820**, 302.

[3]) Journ. de Pharm. **8** (1822), 214 and 533.

[4]) Dümichen, *Die Flotte einer ägyptischen Königin*. Leipzig 1868. — Dümichen, *Historische Inschriften*. 1869. — Dümichen, *Aegypten*. 1880. p. 100. In Oncken's *Allgem. Weltgeschichte*. — Lieblein, *Handel und Schifffahrt auf dem roten Meere in alten Zeiten*. Christiania 1886. pp. 21 and 31. — Quatremère, *Mémoires géographiques et historiques sur l'Egypte*. 1811. Vol. 2, pp. 366—375.

[5]) *Periplus maris Erythræi*. Editio Fabricius. Leipzig 1883. p. 75. — Vincent, Commerce and Navigation of the Ancients in the Indian Ocean. London 1807. Vol. 2, p. 378.

of Kosmas Indikopleustes.[1]) From that time on, sandalwood is mentioned by a number of writers and travelers: in the 9. century by Avicenna,[2]) in the 10. century of Serapion[3]) and by Masudi,[4]) in the 11. century by Constantinus Africanus of Salerno[5]) and in the 13. century by Marco Polo.[6]) Saladin of Ascoli[7]) in the 15. century distinguished between white, yellow and red sandalwood.[8]) Barbosa[9]) in 1511 makes a like distinction and adds that the white and yellow wood are obtained from the Malabar coast and cost ten times as much as the red. Rumpf[10]) in 1741 was the first to give a good illustration of the tree.

Inasmuch as the volatile oil of sandal-wood has come into use medicinally only in recent times, it is mentioned but seldom in mediaeval works and in the later treatises on distillation.

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[1]) *Christiana topographia*, in Mignes *Patrologiæ cursus completus. Series græca.* Vol. 88, pp. 574 and 446. — Lassen, *Indische Altertumskunde.* Vol. 3, p. 40. — Meyer, *Geschichte der Botanik.* Vol. 2, p. 388.

[2]) Avicennæ *libri in re medica omnes; latine redditi ab* I. Paulo Mongio *et* I. Costæo *recogniti.* 2 Vol. Venetis 1564. *Canon medicinæ.* Lib. II. *tractat.* II. Cap. 656.

[3]) *Liber* Serapionis *aggregatus in medicinis simplicibus.* Mediolani 1473.

[4]) Ali el Masudi, *Les Prairies d'Or, texte et traduite par* Meynard *et* P. de Courteille. 9 Vol. (the original Arabian text was completed in 984). Paris 1861—1877. Vol. 1, p. 222.

[5]) Constantini Africani *Opera omnia.* Basiliæ 1536. *Liber de gradibus.* p. 369.

[6]) Pauthier, *Le Livre de Marco Polo.* Paris 1865. Tom. 2, p. 580.

[7]) *Compendium aromatariorum* Saladini *principis tarenti dignissimi medici diligenter correctum et emendatum.* 1488.

[8]) It is not at all improbable that even during premediaeval times the wood of the *Pterocarpus santalinus*, L., N. O. *Leguminosæ*, which tree is indigenous to the Southern parts of the East Indies and to the Philippines, was used on account of its red pigment. Inasmuch as it was imported from the same countries that yielded the fragrant sandalwood it was at first regarded as related to sandalwood and hence so designated. This error and with it the false designation has remained. In consequence many an author has placed them together, e. g. in the list of Frankfurt of 1450. Garcia da Orto recognised the mistake and called attention to it though in vain. (Ab Horto, *Colloquios dos simples e drogas he cousas medicinais da India, e assi dalgũãs frutas achadas nella ande se tratam.* 1563. Varnhagen's reprint 1872, p. 188. — Editio Carolus Clusius 1539, p. 68.)

[9]) Ramusio, *Delle navigationi et viaggi.* Venetia 1554. fol. 357, 6.

[10]) Rumphii *Herbarium Amboinense.* Amstelodami 1741. Vol. 2, p. 42.

Its distillation is recorded by Saladin,[1]) by Conrad Gesner[2]) and by Friedrich Hoffmann.[3]) The yield was first ascertained by Caspar Neumann and Dehne.[4]) It was first examined by P. Chapoteaut.[5])

It is reported that in Ceylon distilled oil of sandal-wood was used for the embalming of the dead bodies of princes as early as the 9. century.[6])

OIL OF STARANISE.

Owing to its peculiarly shaped and aromatic fruits, the star-anise tree has no doubt been known since antiquity and has received attention. However, Chinese literature appears to contain little concerning its use. Under the Sung dynasty, between 970 and 1127, several of the southern Chinese provinces had to furnish star anise as tribute.[7]) Into European commerce it was apparently introduced by the circumnavigator Thomas Cavendish, who in 1578 brought it to London from the Philippines. It was in London that the Leyden Professor Carolus Clusius first became acquainted with the fruit and described it as *Anisum philippinarum insularum.*[8]) According to a statement by Redis, star-anise is supposed to have been known to the Italian drug trade as early as the middle of the 16. century under the name *Fœniculum sinense,*[9]) but apparently was not used until the middle of the 17. century.

The volatile oil of staranise was distilled some time during the 18. century but was not used to any extent until the 19. century.

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[1]) *Compendium aromatariorum* Saladini. 1488. fol. 349.

[2]) *Ein köstlicher Schatz* Euonymi Philiatri. 1555. p. 246.

[3]) Frederici Hoffmannii *Observatorium physico-chemicarum selectiorum.* Halæ 1722. Lib. III. Observ. I, p. 69.

[4]) Crell's Chemisches Journal **3** (1780), 18.

[5]) Bull. Soc. chim. II. **37** (1882), 303.

[6]) Flückiger and Hanbury, *Pharmacographia.* II. edit., 599.

[7]) Bretschneider, Study and value of Chinese botanical works. Foochow 1870. p. 14.

[8]) Clusii *Rariorum plantarum historia.* Antwerp. 1601. p. 202.

[9]) Redi, *Experienze naturali.* Firenze 1671. p. 119. *Tavola 2.* — Latin edition: Redi, *Experimenta circa res diversas naturales, speciatim illas, quæ ex India adferuntur.* Amstelodami 1675. p. 172.

The chemical composition of staranise and the yield of oil were studied about the time by Caspar Neumann and Friedr. Cartheuser;[1]) somewhat later, *i. e.* in 1818, by W. Meissner.[2])

OIL OF YLANG YLANG.

It is only since the beginning of the sixties of the past century that ylang-ylang oil is being distilled in the island of Luzon, P. I. The first to take up this distillation was F. Steck[3]) a German apothecary in Manila, and the uncle of Pablo Sartorius, whose name is still associated with the firm that makes a speciality of this oil. Of the larger distillers of that early period, J. Witte and von Westernhagen should be mentioned.

In Europe it was the Parisian apothecary F. Rigand[4]) who contributed to make known this oil. However, ylang-ylang oil did not become widely known until the world's fair in 1878, when it was exhibited in Paris by Oskar Reymann and Adolf Roensch of Manila.

OILS OF MACE AND NUTMEG.

Older literature contains no definite information pertaining to knowledge of or use made of nutmegs during antiquity. Statements, such as occur in the writings of Plautus, Scribonius Largus, Dioscorides, Pliny, Galen etc. that seem referrable to mace, may as well be referred to the bark of *Ailanthus malabarica,* D. C., an East Indian tree.[5]) Into western Europe the fruits were probably introduced by Arabian physicians.

About the year 1180 nutmegs are enumerated among the spices imported into Accon, the port of southern Syria.[6]) In

[1]) F. A. Cartheuser, *Elementa chymiæ-medicæ dogmatico-experimentalis; una cum synopsi materiæ medicæ selectioris.* Halæ 1736. Vol. 2, p. 327.

[2]) *Chemische Untersuchung des Sternanis.* Buchholz, *Taschenbuch für Scheidekünstler und Apotheker auf das Jahr 1818 und 1819,* 1.

[3]) Pharm. Zentralh. **9** (1868), 46.

[4]) *Ibidem* **7** (1866), 478.

[5]) Acosta, *Tractato de las drogas y medicinas de las India orientales.* Burgos 1578. p. 40. — Mérat et De Leus, *Dict. de Materia medica.* 1832. Vol. 4, p. 173.

[6]) *Recueil des Historiens des Croisades.* Lois. 1843. p. 173. — W. Heyd, *Geschichte des Levantehandels im Mittelalter.* 1879. Vol. 2, p. 624.

1158 *nuces muscatarum* from Alexandria were articles of commerce in Genoa.[1]) At that time they were evidently prized for fumigating purposes.[2]) From that time on, nutmegs were found in all of the larger marts and soon became one of the most precious spices. Their geographic source, however, apparently first became known through the travelers Lodovico Barthema and Pigafetta[3]) in the beginning of the 16. century.

It was about this time that the Portuguese, having taken possession of the Spice Islands, made a monopoly of nutmegs and other indigenous spices. A century later, when in 1605 the Portuguese were driven out by the Dutch, the latter attempted to concentrate the production and commerce of nutmeg to a few islands, notably on Banda and Amboina. With this in view they destroyed the spice-producing trees and shrubs on the most productive islands and forbade their cultivation.[4]) This interdiction was not removed until 1863. In 1769 the French succeeded in transplanting the nutmeg tree to Mauritius and at the beginning of the 19. century the English began its cultivation in Benkulen (Sumatra) and Penanz.

Until recently nutmeg and mace belonged to the most expensive spices. With the cultivation of the nutmeg tree in Dutch, English and French colonies, nutmegs became more plentiful and hence cheaper.

The distilled oils of nutmeg and mace were well known to the authors of the treatises on distillation that appeared during the middle of the 16. century and later. Valer. Cordus,[5]) Walter Ryff,[6]) Conrad Gesner,[7]) Porta,[8]) Winther[9]) and others make repeated mention of both oils.

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[1]) *Historia Patriæ monument.* Chartæ II. Torino 1853. fol. 514.

[2]) Petrus de Ebulo, *Carmen da motibus siculis.* Basiliæ 1746. p. 23.

[3]) Ramusio, *Delle navigationi et viaggi.* Venetia 1554. fol. 183 and fol. 389b.

[4]) Hasskarl, *Neuer Schlüssel zu Rumpfs Herbarium amboinense.* Halle 1866. Vol. 2, p. 17.

[5]) Valer. Cordi *Annotationes* in Pedanii Dioscoridis *de Materia medica libri V. De artificiosis extractionibus liber.* 1540. fol. 226.

[6]) Gualtherius Ryff. *New gross Destillirbuch.* Editio Frankfurt a. Main 1556. fol. 181. 1888.

[7]) Euonymi Philiatri *Ein köstlicher Schatz* etc. 1555. p. 215.

[8]) Portæ *Magiæ naturalis libri 20. Libri de destillatione.* Pars 1, p. 378.

[9]) Guintheri Andernacei *de medicina veteri et nova.* Basiliæ 1571. p. 630—635.

Both oils are first mentioned in pharmaceutical price ordinances of Berlin of 1574, of Frankfurt and of Worms of 1582, and in the 1589 editions of the *Dispensatorium Noricum.*

These oils were first examined by Caspar Neumann,[1]) Conrad Mich. Valentine[2]) and Bonastre.[3])

OIL OF CAMPHOR.

In China, camphor has been prepared and used in early antiquity. The first documental reference to it is found in the writings of the Arabian prince Imru-l-Kais of the sixth century;[4]) also in the Koran, in which it is mentioned as a refrigerant in connection with the beverages of the blessed in paradise.[5]) Aetius of Amida, also in the sixth century, mentions camphor as a remedy.[6]) When the palace in Madain of Choroës II. king of the Sassanidæ was pillaged in 636, much camphor was taken in addition to musk, ambra, sandalwood and other oriental aromatics.[7]) Later, when Arabian sailors and merchants sailed to India and China, they became acquainted not only with the principal ports via which the camphor was shipped from south-eastern Asia to the Mediterranean countries, but also with the sources of supply. Thus the Arabian merchants and physicians became acquainted with the different varieties which entered the world's market in part from China, in part from Sumatra. Marco Polo, in the 13. century, also became acquainted with the camphor in Sumatra and Borneo.[8])

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[1]) Neumann, *Chymia medica dogmatico-experimentalis.* Züllichau 1749. Vol. 2, Part 3, p. 437.

[2]) *Macis vulgo sed perperam, Muskatenblume dicta.* Dissertatio. Giessen 1719.

[3]) Trommsdorff's Neues Journ. der Pharm. 8, II. (1824), 231.

[4]) In Ibn Hagik al Hamdany's manuscript on the description of Arabia, p. 170, and Flückiger's *Pharmacognosie.* p. 159.

[5]) *Le Koran, traduit par Kasimirski.* Cap. 76. V. 5 and 6.

[6]) Aetii ab Amida *medici græci ex veteribus medicinæ Tetrabiblos.* Editio Froben. Basiliæ 1542. p. 926.

[7]) Weil, *Geschichte der Chalifen.* Mannheim 1846. p. 75.

[8]) Yule, Book of Ser Marco Polo. London 1871. Vol. 2, p. 185. — Pauthier, *Le livre de Marco Polo.* Paris 1865. Vol. 2, p. 577. — Masudi, *Prairies d'Or.* Editio Meynard et de Courteille. Paris 1861. Vol. 1, p. 367. — Ritter's *Erdkunde von Asien.* 1834. Vol. 3, pp. 858—881.

The preparation of camphor in Japan was first described by Engelbert Kaempfer.[1]) Probably the Japanese learned the method of preparation from the Coreans. It is said to have first been introduced into the province Satsuma on Kiuschiu and later spread over the rest of Kiuschiu and over Schikoku and other parts of Japan.[2]) The age of the production of camphor in Formosa is unknown. Klaproth[3]) who visited the island at the beginning of the past century refers to the production of camphor as one of the principal industries of Formosa. Since the occupation of the island by the Japanese, the distillation of camphor has been increased materially.

In medical practice camphor was known to the Arabians. In Italy it was used during the 11. century and in Germany during the 12. century.

Camphor oil was first brought to Europe in 1884. As principal constituent of the oil, Schimmel & Co. discovered safrol and isolated it on large scale.

OILS OF CASSIA AND CEYLON CINNAMON.

The cassia bark of China and the cinnamon bark of the Indian archipelago are among the longest known and used spices. Cassia is mentioned in the earliest herbals and medical treatises of China,[4]) about 2500 B. C., and as early as the 17. century B. C., it appears to have been used by the Egyptians.[5]) It is also mentioned in most of the writings of antiquity. Thus in addition to other spices it is mentioned in Sanskrit literature and in the Old Testament.[6])

[1]) E. Kämpfer, *Amœnitates exoticæ.* Lemgo 1712. p. 772. (With an illustration of the tree.)

[2]) James W. Davidson, The Island of Formosa. London and New York 1903.

[3]) Klaproth, *Memoires relatifs à l'Asie.* Paris 1824.

[4]) Bretschneider, On the study and value of Chinese botanical works, with notes on the history of plants and geographical botany from Chinese sources. Foochow 1870.

[5]) Dümichen, *Die Flotte einer ägyptischen Königin.* Leipzig 1868. — Schumann's *Kritische Untersuchungen über die Zimtländer. Ergänzungsheft No. 73 zu Petermann's Mitteilungen.* Gotha 1883. p. 11.

[6]) Exodus, 30: 23 and 24. — Psalms, 45: 9. — Jeremiah, 6: 20. — Hesekiah, 27: 19. — Proverbs, 7: 17. — Song of Solomon, 4: 14. — Jesus Sirach, 24: 20 and 21. — Apocalypse, 18: 13.

As its geographical source, mythical countries are mentioned; also and this, no doubt, because of the customary commercial routes[1]) Arabia and Ethiopia.[2]) At the time of the Hebrews the commerce in cinnamon was largely in the hands of the Phœnicians.[3]) In order to guard their own interests, the Phœnician merchants did not correct these erroneous surmises and statements. Hence for centuries the real source of cassia remained undecided.

Both Greeks and Romans knew and used cinnamon. The Arabians introduced it into western Europe. From the 8. century on, it was a well known though costly spice. As such it is frequently mentioned among the presents given by princes to each other or to the pope.[4]) During the 12. and 13. centuries both Chinese and Ceylon cinnamon were common articles of the Levant trade[5]) and in the eastern ports of the Mediterranean. From the 15. century on, both were current articles in apothecary shops.[6])

Later when the more expensive Ceylon cinnamon was also brought into the European market, the two kinds were frequently

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[1]) Historical introduction, p. 5.

[2]) Dümichen, *Die Flotte einer ägyptischen Königin.* 1868. — Dümichen, *Historische Inschriften.* 1869. — Dümichen, *Ägypten* in *Onchens Allgemeiner Weltgeschichte.* 1880. p. 100. — Herodoti *Historiarum libri.* Lib. 1, 107 and 110. Lib. 3, 110—112. — Theophrasti *Historia plantarum.* Lib. 9, 4—5. — Arriani *Anabasis.* Lib. 7, 20 and 21. — *Fragmenta historicorum græcorum. De mari Erythræo.* p. 97. — Dioscoridis, *De medica materia libri quinque.* Lib. 1, 12 and 13. Editio Kühn-Sprengel 1829. Vol. 1, p. 23. — Plinii *Naturalis historiæ libri.* Lib. 12, 41—43 and 46. — *Periplus maris Erythræi.* Editio Fabricius. 1883. pp. 47 and 51. — A. H. L. Heeren, *Ideen über die Politik, den Verkehr und den Handel der vornehmsten Völker der alten Welt.* Göttingen 1796. Vol. 2, pp. 611—613. — Meyer, *Geschichte der Botanik.* Vol. 2, p. 86.

[3]) See pp. 5 and 6. — Lassen, *Indische Altertumskunde.* Bonn 1847. Vol. 1, p. 280.

[4]) *Liber pontificus.* Editio Duchesne. Paris 1886. Vol. 1, p. 177. — *Pardessus, Diplomata chartæ* etc. Paris 1849. Vol. 2, p. 309. — Jaffé, *Bibliotheca rerum Germanicarum.* 1886. Vol. 3, p. 218.

[5]) See p. 11.

[6]) Fr. Bald. Pegolotti, *La pratica della mercatura.* In Pagnini *Della decima e delle altre gravezze* etc. Lisboa e Lucca. 1766. pp. 27, 44, 49, 64. — Joh. de Garlandia, *Dictionnaire.* Editio Schéler in *Lexigraphie latine du 12. et 13. siècle.* p. 28.

confounded. Garcia ab Orta in 1536 was the first to distinguish definitely between the two kinds.[1]) In the accounts of the Portuguese, who under Vasco da Gama touched at Ceylon in 1498, mention is made of cinnamon as one of the products of the island, without, however, regarding it as better than the Chinese cinnamon previously known to them.[2]) Even later most of the cinnamon that was imported over the water route via Ceylon into the ports of the Erythræan and Red seas, appears to have been Chinese cinnamon. Ceylon cinnamon was originally collected in the forests of the interior of the island. This product was in no way the equivalent of the present-day bark, obtained by rational pealing from improved plants. These improved methods of production appear to have been introduced toward the close of the 16. century.[3]) After the occupation of Ceylon by the Dutch in 1556, one of the governors greatly improved the cultivation of cinnamon. As a result they soon were in a position to supply the European market with a bark that was superior to the wild product.[4]) After the occupation of the island by the British in 1796, the cultivation of and commerce in cinnamon became the monopoly of the British East India Company. The monopoly lasted until 1833.[5]) This company levied an export duty and thus injured the Ceylon trade causing the Dutch to cultivate cinnamon in Java and Sumatra.

When in the course of the fifteenth century the distillation of aromatic waters for medicinal purposes became a common practice,[6]) cinnamon bark was undoubtedly distilled for the preparation of its water. The Canon St. Amando of Doornyk living

[1]) Garcias ab Horto, *Colloquios dos simples e drogas he cousas medicinais da India* etc. 1563. Editio F. A. von Varnhagen. 1872. p. 63. — Editio Clusius, *Aromatum et simplicium aliquot medicamentoriorum apud Indos nascentium historia.* Antverpiæ 1593. p. 60.

[2]) Odoardo Barbosa in Ramusios *Delle navigationi et viaggi.* 1554. Editio Hakluyt Society, London 1866. "East Indies."

[3]) *Lettera* di Filippo Sassetti a Francesco I. di Medici, *Storia dei viaggiatori italiani.* Leghorn 1875. p. 367.

[4]) J. A. Murray, *Apparatus medicaminum tam simplicium quam præparatorum et compositorum.* 1787. Vol. 4, p. 421. — Nees von Esenbeck, *Amœnitates botanicæ Bonnenses.* 1823. Fasc. 1.

[5]) Sir James Emerson Tennent, Ceylon, an account of the island, physical, historical and topographical. 5th edit. London 1860. Vol. 2, p. 164.

[6]) See p. 39.

toward the end of the 15. century seems to have been the first to isolate oil of cinnamon[1]) in addition to bitter almond oil and oil of rue, and several other volatile oils. Valerius Cordus had prepared the oil about 1540.[2]) At that time it may already have found application in medicine, so that it was included in the first edition of the *Dispensatorium Noricum*. Lonicer soon afterward distilled the oils from the spices, among them cinnamon oil, in a new peculiar apparatus.[3]) In the price ordinances cinnamon oil is first mentioned in that of Berlin of 1574, also in that of Frankfurt-o.-M. of 1582.

Winther of Andernach[4]) distilled and described the oil in 1570, and G. B. Porta in 1589.[5])

The early observations made on cinnamon oil were restricted mainly to the crystalline deposit formed upon prolonged standing. Such crystal formations were observed (among others) by Ludovici[6]) about 1670, later by Slare in England,[7]) by Boerhaave[8]) and Gaubius[9]) in Holland. The latter regarded them as camphor; Du Menil[10]) and Stockmann[11]) supposed them to be benzoic acid, Dumas and Péligot[12]) in 1831 recognized them to be cinnamic acid. C. Bertagnini prepared pure cinnamic aldehyde in 1852.[13])

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[1]) See p. 33.

[2]) Valerius Cordus, *De artificiosis extractionibus liber.* Edit. Gesner. Argentator. 1561. fol. 226.

[3]) See the next chapter.

[4]) Guintheri Andernacei *Liber de veteri et nova medicina.* Basiliæ 1571. pp. 630—635.

[5]) G. B. della Porta, *Liber de destillatione.* Romæ 1563. fol. 75.

[6]) *Ephemerides medico-physicæ Academiæ naturalis, Curiosorum observationes 145.* p. 378.

[7]) Philosophical Transactions of the Royal Society of London. Vol. 3 (1686), p. 362.

[8]) Boerhaave, *Elementa chemiæ* etc. Lugduni Batavorum 1732. Vol. 1, p. 106. — Vol. 2, pp. 114 and 121.

[9]) Gaubii *Adversariorum varii argumenti liber unus.* Leydæ 1771. p. 29.

[10]) Buchner's Repertor. der Pharmacie 5 (1819), 1. — Schweigger's Journal für Chemie und Physik 21 (1819), 224.

[11]) Trommsdorff's Neues Journ. der Pharm. 14 (1827), 237.

[12]) Annal. de Chim. et Phys. II. 57 (1834), 305. — Liebig's Annalen 14 (1835), 50.

[13]) Liebig's Annalen 85 (1853), 271.

The yield of volatile oil from cassia and cinnamon barks was determined by the following observers: G. W. Wedel[1]) in 1707; Friedr. Cartheuser,[2]) Caspar Neumann[3]) and Phil. F. Gmelin[4]) in 1763; J. F. A. Goettling[5]) about 1803; by Dehne[6]) about the same time; also by Buchholz[7]) in 1813.

OIL OF SASSAFRAS.

As already mentioned under the oils of sweet birch and wintergreen,[8]) next to turpentine oil, the oil of sassafras was the first volatile oil distilled in North America. On account of the pleasant aroma, the root bark known as *Pavame* was chewed by the natives. It was also mixed with smoking tobacco[9]) and added as aromatic to refreshing beverages and was used as a remedy. On account of its peculiarity, the sassafras tree is said to have attracted the attention of the Spaniards at their first landing in Florida under Ponce de Leon in 1512, also under de Soto in 1538. They are said to have regarded it as a kind of cinnamon tree. Afterward the sassafras tree soon came to be regarded as a valuable medicinal plant[10]) and article of luxury of the new world. In Mexico it had long been regarded as such.[11]) As late as the first half of the 19. century the bark, leaves and

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[1]) Wedel, *De cinnamomo.* Dissertatio. Jenæ 1707.

[2]) Cartheuseri *Elementa chymiæ dogmatico-experimentalis.* Halæ 1736. Vol. 1, p. 127; vol. 2, pp. 109 and 187.

[3]) Neumannii *Chymia medica dogmatico-experimentalis.* Editio Kessel. Züllichau 1750. Vol. 2, pars 2, p. 20.

[4]) Philipp F. Gmelin, *De analepticis quibusdam nobilioribus et cinnamomo.* Dissertatio. Tübingen 1763.

[5]) J. F. A. Göttling, *Analyse der Cassienzimtrinde. — Buchholz Taschenbuch für Scheidekünstler und Apotheker* **1804**, 1.

[6]) Neues Berl. Jahrbuch für Pharmacie **1805**, 289.

[7]) *Buchholz Taschenbuch für Scheidekünstler und Apotheker* **1814**, 1.

[8]) See p. 118.

[9]) C. S. Rafinesque, Medicinal Flora or Manual of the Medical Botany of the United States of North America. 1830. Vol. 2, p. 235.

[10]) Monardes, *Historia medicinal de las cosas que se traen de nuestras Indias occidentales qui sirven en medicina.* Sevilla 1574. p. 51. *Editio latina* Clusii. Antverpiæ 1593. pp. 355—359.

[11]) Joannis de Laet, *Americæ utriusque descriptio, Novus Orbis, seu descriptionis Indiæ occidentalis libri 18* Lugduni Batav. 1633. p. 215.

buds were used in the middle and central states as a substitute for Chinese tea.[1])

As early as 1582 sassafras wood and bark became known in Germany as a new American drug and were used under the name of *Lignum pavanum, Lignum floridum, Lignum xylo-marathrum (Fenchelholz).*[2]) In 1610 young plants were brought to England and cultivated.[3]) Bark and wood were apparently first distilled in 1620 by Angelus Sala of Vicenza, who as body physician to the Duke of Mecklenburg, lived in Schwerin from 1610—1639, and who mentions that the oil is heavier than water.[4]) Schrœder's *Pharmacopœa medico-chymica,* published in Frankfurt-on-the-Main in 1641, is the first pharmacopœia that gives directions for the distillation of the oil, whereas the municipal price ordinance of Frankfurt-on-the-Main of 1587 already enumerates *Oleum ligni sassafras.* Friedrich Hoffmann in Halle distilled the oil in 1715 and describes it as being colorless and specifically heavy.[5]) In 1738, John Maud, an Englishman, observed the formation of large crystals of sassafras camphor.[6]) Early examinations of the oil were made by Muschenbroeck, by Caspar Neumann,[7]) and by Dehne.[8]) The first thorough investigation was made by Grimaux and Ruotte[9]) in 1869.

Detailed and definite statements concerning the medicinal use of sassafras bark and wood appear to be wanting in American literature. This is also true of the early distillation of the oil. Aside from the communications by Monardes, De Laet and others, one of the first references to these drugs is found in the list of drugs mentioned on p. 94 (footnote 7), as having been im-

[1]) J. U. Lloyd, Historical study of Sassafras. Pharmac. Era (New York), **20** (1898), 608.

[2]) Flückiger, *Dokumente zur Geschichte der Pharmacie.* Halle 1876. pp. 30—31.

[3]) Flückiger and Hanbury, Pharmacographia. 1879. p. 537.

[4]) Sala, *Opera physico-medica. Hydrelæologia.* Rostock 1639. p. 84.

[5]) Fr. Hoffmannii *Observationes physico-chymicæ. Observatio 1. De oleis destillatis inque eorum destillatione observanda.* pp. 13—14.

[6]) Philosophical Transactions of the Royal Society. London, 8 (1809), 243.

[7]) Caspar Neumann, *Chymia medica dogmatico-experimentalis.* 1749. Vol. 2, pars 3, p. 248.

[8]) Pfaff, *System der Materia medica.* 1815. Vol. 4, p. 242.

[9]) Compt. rend. **68** (1869), 928.

ported from the "Province of Virginia" into England in 1610. More than a century later it is again mentioned in the reports on his travels made by the Swedish botanist Peter Kalm, who in 1748—1749 traveled through the north Atlantic provinces of the then English colony as far as Montreal and Quebec. He found the sassafras tree widely distributed in Pennsylvania, New Jersey and New York.[1]) Kalm also mentions that the bark and wood are used for flavoring rootbeer and brandy, also universally as medicament. In the distillation of brandy, bark and root are distilled with the brandy.[2])

With the Indians, sassafras was highly reputed as blood purifyer.[3]) Later the colonists used it in the preparation of their domestic remedies.

It is unknown when the distillation of sassafras oil had its beginning, though this was probably at the beginning of the 19. century. This much at least is true that Joh. David Schœpf, an experienced physician and careful observer, who in 1783 and 1784 traveled through the Atlantic states of the Union alludes on several occassions in his reports to the wide distribution of the sassafras tree, but apparently has not heard of the distillation of sassafras.[4])

OIL OF BAYBERRY.

In classical antiquity the laurel, *Laurus nobilis,* L., was utilized as symbol of victory and fame[5]) but found no other use than that of a decorative plant. During the middle ages its bark and leaves were used medicinally.

The mixture of fatty and volatile oil, or butter, the *oleum laurinum* obtained by boiling the fruits with water was used

[1]) Peter Kalm, *Beschreibung der Reise nach dem nördlichen Nordamerika im Jahre 1748—1749.* German translation. Göttingen 1754. Vol. 3, p. 355.

[2]) *Ibidem* vol. 2, p. 482.

[3]) C. S. Rafinesque, Medicinal Flora or Manual of the Medical Botany of the United States of North America. 1830. Vol. 2, p. 235.

[4]) Johann David Schöpf, *Reise durch die mittleren und südlichen Vereinigten nordamerikanischen Staaten, nach Ost-Florida und den Bahama-Inseln in den Jahren 1783—1784.* Erlangen 1788. Vol. 1, p. 415.

[5]) Hehn, *Kulturpflanzen und Haustiere in ihrem Übergang aus Indien nach Griechenland und Italien.* 3rd ed. 1877. pp. 196—201.

during antiquity. In the older literature it is enumerated among the substances used for anointing and for medicinal purposes,[1]) also among the aromatics.[2]) It found a place in the first edition of the *Dispensatorium Noricum* of 1543.

The volatile oil of the fruits appears to have been used formerly for medicinal purposes. At least it is included in the price ordinance of Frankfurt of 1582 and in others of a later date.

OIL OF SPOONWORT.

During the middle ages spoonwort was regarded as a remedy against scurvy. As such it is mentioned in older treatises on medicine and distillation. It was pictured in Joh. Wier's[3]) treatise on scrofula in 1567. The distilled oil of spoonwort seems to have been known and to have been used medicinally since the middle of the sixteenth century. This use, however, does not appear to have been general, for the oil is not mentioned in any edition of the *Dispensatorium Noricum,* neither in the *Pharmacopœa Augustana* nor in Schrœder's *Pharmacopœa medico-physica* of Frankfurt-on-the-Main. It occurs, however, in the municipal ordinance of Frankfurt of 1587. Later it occurs also in inventories of apothecary shops of Braunschweig and Dresden of 1640 and 1683 respectively.[4]) At the beginning of the eighteenth century it was distilled by Friedr. Hoffmann in Halle and described by him.

OIL OF MUSTARD.

Mustard seed was known during antiquity and was esteemed for one reason or another as becomes evident from the symbolic references made to it in the New Testament.[5]) It appears to

[1]) Dioscorides, *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, p. 53. — Palladius, *De re rustica.* II. 7. Editio Nisard. p. 554. — Plinii *Naturalis historiæ libri.* Lib. 7. — Editio Littré. Vol. 1, p. 548. — Hildegardis Abbatissæ *Physica.* Editio Migne. *Patrologiæ Cursus completus.* Vol. 197. 15, p. 1228.

[2]) Douët-d'Arcq, *Comptes de l'Argenterie des rois de France au* XIV^me^ *siècle.* 1851. Vol. 1, p. 207.

[3]) Joh. Wier (Piscinarius), *Medicarum observationum rararum liber.* Basiliæ 1567. pp. 32—34.

[4]) Flückiger, *Dokumente zur Geschichte der Pharmacie.* 1876.

[5]) Matth., 13:31. — Luke, 13:18 and 19.

have been utilized first as spice,[1]) and later also as external remedy. As the latter it is referred to by Theophrastus,[2]) Dioscorides,[3]) Pliny,[4]) Scribonius Largus[5]) and Alexander Trallianus. In the writings of Columella are found the oldest directions for the preparation of table mustard.[6]) About the year 800 mustard was cultivated in the neighborhood of Paris.[7]) Its cultivation was directed by Charlemagne in his *Capitulare* of 812.[8]) In Spain it was cultivated by the Arabians.[9]) From here its cultivation spread to Germany and France in the 10. century and thence to England[10]) during the 12. century.

The first statement which indicates a knowledge of the fact that mustard oil can be obtained by distillation with water, is found in the writings of Porta;[11]) another in the writings of the Parisian apothecary Nic. le Febvre.[12]) Boerhaave, however, seems to have been the first to prepare the volatile mustard oil in 1732 and to have called attention to its properties.[13]) That it contains sulphur was observed by Thibierge of Paris in 1819.[14]) Boerhaave and Murray[15]) observed the great density of the oil;

[1]) Mommsen, Berichte der Sächsischen Gesellschaft der Wissenschaften. Leipzig 1851, 1—80.

[2]) Theophrasti Eresii *opera, quæ supersunt, omnia.* Editio Wimmer. 1866. p. 109.

[3]) Dioscoridis *de materia medica libri quinque* in Kühn-Sprengel. *Medicorum græcorum opera quæ extant.* 1829. Vol. 1, p. 52, 191 and 293.

[4]) Plinii *Naturalis historiæ libri.* Lib. 19, p. 54 and Lib. 20, p. 87.

[5]) Scribonii Largi *Compositiones medicamentorum.* Editio Helmreich. 1887. 9, p. 56.

[6]) Columellæ *De re rustica et de arboribus.* Editio Nisard. 1877. p. 493.

[7]) Guérard, *Polyptique de l'abbé* Irminon. Paris 1844. p. 716.

[8]) *Capitulare de villis et cortis imperialibus.* Explained by A. Thaer in Fühling's Landwirtschaftliche Zeitung. Berlin 1878, 241—260.

[9]) Dozy, *Le Calendrier de Cordue de l'année* 961. Leyde 1873.

[10]) Rogers' History of agriculture and prices in England. 1866. p. 223. — Pharmaceutical Journ. III. 8 (1878), 852.

[11]) Portæ *Magiæ naturalis libri viginti. Liber de destillatione.* Romæ 1608. p. 153.

[12]) N. le Febvre, *Traité de la Chymie.* Paris 1660. Tom. 1.

[13]) Boerhaave, *Elementa chemiæ, quæ anniversario labore docuit in publicis privatisque scholis.* Lugduni Batavorum 1732. Editio Londini. 1732. Pars 2, p. 38.

[14]) Journ. de Pharm. 5 (1819), 20, 439 and 446. — Trommsdorff's Neues Journ. d. Pharm. 4, II. (1820), 250.

[15]) J. A. Murray, *Apparatus medicaminum tam simplicium quam præparatorum et compositorum.* Göttingen 1794. Vol. 2, p. 399.

Jul. Fontenelle determined the specific gravity in 1824, also its solubility in water.[1])

Undoubtedly those who prepared mustard oil knew that the volatile oil does not preexist in the seed but is produced by the action of water. Yet the first to call attention to this fact were Glaser[2]) in 1825, Boutron and Robiquet[3]) in 1831, and independently of these Fauré[4]) as well as Guibort,[5]) both in 1831. Shortly after (1833), Dumas and Pelouze[6]) made the first elementary analysis of the oil and discovered the thiosinamine, which mustard oil forms with ammonia. That mustard oil is produced by the action of a ferment was noticed by Boutron and Fremy.[7]) They isolated myrosin by extracting the seed with alcohol and obtained mustard oil by allowing this substance to act on the aqueous extract of the seed which had previously been extracted with alcohol. Sinigrin or myronate of potassium, was first prepared by Bussy.[8]) He termed the underlying acid *acide myronique* and with Robiquet[9]) determined its physical constants and its behavior toward reagents. The knowledge of the chemical composition of the oil was advanced materially by Will[10]) and simultaneously by Wertheim[11]) who regarded the mustard oil as allyl sulphocyanate.

Ludwig and Lange[12]) confirmed the existence of sinigrin and its decomposition by ferment action into mustard oil, sugar and potassium acid sulphate. This reaction was made more clear by the detailed studies of Will and Kœrner.[13])

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[1]) Journ. de Chim. médicale **1** (1825), 130. — Trommsdorff's Neues Journ. der Pharm. **15**, II. (1827), 210.

[2]) Repert. f. d. Pharm. I. **22** (1825), 102.

[3]) Journ. de Pharm. II. **17** (1831), 294. — Geiger's Magazin f. Pharm. und Exper. Kritik **36** (1831), 64 and 67.

[4]) Journ. de Pharm. II. **17** (1831), 299 and **21** (1835), 464.

[5]) *Ibidem* **17** (1831), 360.

[6]) Ann. de Chim. et Phys. II. **53** (1833) 181. — Liebig's Annalen **10** (1834), 324.

[7]) Journ. de Pharm. II. **26** (1840), 48 and 112. — Liebig's Annalen **34** (1840), 230.

[8]) Journ. de Pharm. II. **26** (1840), 39. — Liebig's Annalen **34** (1840), 223.

[9]) Journ. de Pharm. II. **26** (1840), 110.

[10]) Liebig's Annalen **52** (1844), 1.

[11]) *Ibidem* **52** (1844), 54.

[12]) Zeitschr. f. Chemie und Pharm. **3** (1860), 430, 577.

[13]) Liebig's Annalen **125** (1863), 257.

Artificial mustard oil had been prepared by the action of allyl iodide on potassium sulphocyanate by Zinin[1]) and by Berthelot and de Luca.[2]) The natural oil was therefore regarded as an ester of thiocyanic acid. Oeser,[3]) however, showed that allyl thiocyanate and natural mustard oil possess different properties.

The true constitution of mustard oil as the ester of the iso-thiocyanic acid was recognized by Billeter[4]) also by Gerlich.[5]) They showed that by the interaction of allyl iodide and potassium sulphocyanate, allyl sulphocyanate is first formed and that upon heating this is converted into its isomer, the allyl *iso*sulphocyanate.

As an explanation of this form of isomerism, A. W. Hofmann[6]) had suggested that in the true thiocyanates the carbon is directly united with the sulphur, but in the *iso*compounds with the nitrogen.

Inasmuch as the possibility was not excluded that by the ferment action on sinigrin allyl sulphocyanate may first by formed, E. Schmidt[7]) allowed this action to take place at low temperature. He ascertained that even at 0° allyl *iso*sulphocyanate is formed and only traces of the normal isomer.

The last uncertainty in connection with the hydrolysis of sinigrin was removed by Gadamer.[8]) He showed that the formula of sinigrin is $C_{10}H_{16}NS_2KO_9$ and not $C_{10}H_{18}NS_2KO_{10}$ as was supposed by Will and Kœrner, also that the hydrolysis takes place by the addition of the elements of one molecule of water.

OIL OF STORAX.

Storax was known as a spice during antiquity and as such is mentioned by Herodotus,[9]) Theophrastus[10]) and Dioscorides.[11])

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[1]) Journ. f. prakt. Chem. **64** (1855), 504. — Liebig's Annalen **95** (1855), 128.
[2]) Compt. rend. **41** (1855), 21.
[3]) Liebig's Annalen **134** (1865), 7.
[4]) Berl. Berichte **8** (1875), 464 and 820.
[5]) *Ibidem* 650. — Liebig's Annalen **178** (1875), 89.
[6]) Berl. Berichte **1** (1868), 28.
[7]) *Ibidem* **10** (1877), 187.
[8]) Arch. der Pharm. **235** (1897), 44.
[9]) Herodoti *Historiarum libri.* Lib. 3, 97 and 107.
[10]) Hehn, *Kulturpflanzen und Hausthiere in ihrem Uebergang aus Asien nach Griechenland und Italien.* Berlin 1877. p. 370.
[11]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, p. 82; II, p. 375.

In mediaeval literature storax from several sources is mentioned. At times it was used medicinally.

The volatile oil of storax was distilled by Walter Ryff[1]) and Conrad Gesner.[2]) Storax moistened with *aqua vitæ* (spirits) was distilled by Porta.[3])

OIL OF AMERICAN STORAX.

Among the drugs from the new world, which received consideration in Europe after the discovery of America, there was an aromatic balsam derived from a tree named *Ocosotl* which was found in Mexico and Central America. In nearly all of its properties this balsam resembled the Levante storax *(Styrax liquidus)* which had been known since antiquity. As in the case of the other American balsams (tolu, Peru, copaiba etc.) little was known about the botanical source and mode of production of this balsam. As a result balsams of different origin were frequently confounded.

The best descriptions of American storax are found in the 16. century treatises of Monardes,[4]) Garcia da Orta[5]) and Petrus Andr. Matthiolus.[6])

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[1]) Gualtherius Ryff, *New gross Destillirbuch.* 1556. fol. 176.

[2]) Euonymi Philiatri *Ein köstlicher theurer Schatz.* 1555. Vol. 1, p. 176.

[3]) Giov. Battistæ Portæ *Magiæ naturalis libri viginti.* 1563. *Liber de destillatione,* p. 378.

[4]) Monardes, *Historia medicinal de las cosas que se traen de nuestras Indias occidentales qui sirven en medicina.* Sevilla 1574. pp. 121—123. *Editio latina* Caroli Clusii. Antverpiæ 1539. p. 44.

[5]) Garcias ab Horto, *Aromatum et simplicium aliquot medicamentorum apud Indos nascentium historia. Deinde latino sermone in epitomen contracta . . . locupletioribus ab annotatiunculis illustrata a* Carolo Clusio *Atrobate. Quarta Editio, castigator et aliquot locis auctior,* Justus Bertramus. Antverpiæ 1593. — *Advehitur Hispalim, totius, non dicam Bæticæ, sed etiam Hispaniæ celeberrimum emporium, olei quoddam genus ex America, subrusi coloris, cujus mirabiles prædicant effectus in omnibus uteri morbis. Id oleum de Liquidambar nuncupant, ejus sane odoris fere, qui Styracis odorem æmuletur. Id vero ex eo liquore exprimitur, quem de Ocosotl arbore destillare Mexicana historia tradit in hunc modum: Inter arbores Mexicanas memoratur et Ocosotl arbor prægrandis et venusta, foliis hederæ similibus. Hujus liquor quem Liquidambar nuncupant, vulnera curat, atque cum corticis ipsius pollim permixtus, elegans odoratumque suffimentum præbet.*

[6]) Petri Andreæ Matthioli *Opera quæ extant omnia.* Veneti 1554. German edition. 1598. Lib. 1, fol. 90. *"Zu den Styraxarten gehört auch ein*

The first chemical investigation of American storax was carried out by Bonastre.[1]) Upon distillation of a relatively fresh balsam he obtained the high yield of 7 p. c. oil. Further investigations were made toward the end of the fifties by Wm. Procter,[2]) and in 1874 by W. L. Harrison.[3])

OIL OF ROSE.

Since the earliest periods the charm and fragrance of the rose have led to its appreciation and use. This is shown by the entire older literature, and of all the flower perfumes that from the rose has always received preference. In Chinese and Sanskrit writings the fragrance of the rose is much praised. Fats and oils saturated with the rose perfume have been used since earliest antiquity in perfumery and religious cults.[4]) Thus Aphrodite anointed the dead body of Hector with rose oil.[5]) The Greeks and Romans celebrated annually a rose festival, at which the graves of the dead were decorated with roses and their tombstones were anointed with rose oil.[6]) Of the various flower cults that of the roses has been the most eminent since antiquity.[7])

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aus Neu-Spanien und Westindien kommendes flüssiges Harz, welches bei Einschnitten aus der Rinde großer Bäume mit epheuartigen Blättern ausfließt. Diese Bäume heißen "Ocosotl". Die Eingeborenen kauen die Rinde mit dem exsudierten Harze. Dieselbe ist angenehm wohlriechend und gibt beim Auspressen ein dickes, ebenso riechendes Öl, Oleum liquidambar."

[1]) Journ. de Pharm. II. **16** (1830), 88; *Ibidem* II. **17** (1831), 338. — Trommsdorff's Neues Journ. de Pharm. **21**, II. (1830), 242 and **24**, II. (1832), 236.

[2]) Americ. Journ. Pharm. **29** (1857), 261; *Ibidem* **38** (1866), 33. — Proceed. Americ. pharm. Ass. **13** (1865), 160.

[3]) Americ. Journ. Pharm. **46** (1874), 161—165. — Arch. der Pharm. **206** (1875), 541.

[4]) Apparently the rose was not cultivated in Palestine. It is mentioned only a few times in the Bible. The "rose of Jericho," which is repeatedly mentioned, is the cruciferous *Anastatica hierochuntica*, L., a small plant growing in the desert which, upon drying, rolls up like a ball (Wisdom of Solomon, 2: 8. — Song of Solomon, 2: 1. — Jesus Sirach, 24: 18; 50: 8. — Acts, 2: 8.)

[5]) Homeri *Ilias*, chap. 23, V. 186.

[6]) Friedländer, *Sittengeschichte der römischen Kaiserzeit.* 5th ed. 1881. p. 254.

[7]) Ferd. Cohn, *Die Pflanze.* Breslau 1882. pp. 326—335. — Flückiger Pharm. Rundschau (New York) **12** (1894), 43, 91.

The earliest description of the method of preparation of the oil of rose of the ancients is found in the writings of Dioscorides.[1]) It was an aromatised fatty oil as were the majority of the rose oils of the middle ages, such as *Oleum rosarum, O. rosatum* or *O. rosaceum,* etc.

Aside from apocryphal Persian and other oriental traditions, the earliest definite directions for the preparation of roses and the use of the distillate are found in the writings of the Arabian historian Ibn Chaldun. He mentions that during the eighth and ninth centuries rose water was an important article of commerce, being carried as far as China and India.[2]) In a codex of ceremonies of 946 by the East Roman emperor Constantine VII., Persian rosewater is mentioned as a toilet water.[3]) At the beginning of the 10. century, Nonus Theophanes,[4]) the physician to emperor Michael VIII., recommended and used rose water as a medicament. Avenzoar,[5]) the physician to the calif Ebn Attafir of Morocco, who lived at the beginning of the 12. century; also his contemporaries Joannes Actuarius,[6]) a physician of Constantinople, used rose water as an ophthalmic, and rose sugar as an internal remedy.

During this period, Persia seems to have supplied most of the rose water. During the fourteenth century it was also exported from Mesopotamia.[7]) After the prime of the levant commerce, the Portuguese and Dutch were the principal carriers of goods between Aden, the ports of the Persian bay, India and the occident. Rose water constituted one of their

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[1]) See p. 38 — Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, pp. 56 and 123; Vol. 2, pp. 399—404.

[2]) *Notices et extraits des manuscrits de la bibliothèque impériale* à Paris. Tom. 19 (1862), p. 364. — Istachri, *Das Buch der Länder.* Editio Mordmann. Hamburg 1754. p. 73.

[3]) Constantinus Porphyrogenitus, *De ceremonibus antiquis byzant.* Editio Reiske. Lipsiæ 1751. Lib. II. cap. 15, p. 338.

[4]) Nonus Theophanes. Editio Bernardi. Præfatio ad Synesium: *de febribus.* Amstelodami 1749. Cap. 28, p. 112.

[5]) See p. 24.

[6]) Actuarius, *De medicamentorum compositione.* Joanne Ruellio interprete. Basiliæ 1540. pp. 18, 19, 22, 31.

[7]) *Voyage* d'Ibn Batontah. 1854. Tom. 2, p. 140. *Traduite par* Defrémery.

principal articles of merchandise.[1]) During the 10. century the distillation of roses was introduced into Spain by the Arabs.[2])

Throughout the middle ages, the distillation of rose water seems to have been an important industry of Persia. Unless strongly alcoholic wine was used in the process,[3]) one would expect that in the distillation of large amounts of rose water[4]) the separation of oil of rose at low temperatures in the form of a butyraceous mass had been noticed at an early date and probably used to perfume fats and fatty oils.

The first statement concerning rose oil, which possibly refers to the distilled oil, is found in the writings of Mesuë,[5]) and in the almanac of Harib for the year 961, which mentions the time suitable for the preparation of rose water and a rose preserve.[6]) In his *Compendium aromatariorum* written about the middle of the fifteenth century, Saladin of Asculi,[7]) the body physician of a prince of Tarentum, describes the distillation of roses for the preparation of rose water and rose oil.

According to a statement by Langles,[8]) distilled rose oil is twice definitely mentioned in Mohammed Achem's history of the great moguls of 1525 to 1667; also in the annals of the Mongolian empire written by Manucci,[9]) a Venetian physician who lived 40 years in India.

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[1]) Carl Ritter, *Erdkunde von Westasien.* Vol. 8, p. 745 and Vol. 9, p. 1010.

[2]) *Calendrier rural* d'Harib in Duran de la Malle, *Climatologie comparée.* Paris 1849. p. 65. — Dozy, *Le Calendrier de Cordoue de l'année 961.* Leyden 1873.

[3]) The above supposition is not supported by specific statements in literature. However, it seems reasonable since Persian rose water could be shipped without detriment to its quality to distant lands with tropical climate such as India, China and Egypt.

[4]) See p. 64.

[5]) See p. 24.

[6]) Dozy, *le Calendrier de Cordoue de l'année 961.* Leyden 1873.

[7]) Saladini Asculani *Compendium aromatariorum.* Venetii 1488. fol. 349.

[8]) L. Langles, *Recherches sur la découverte de l'essence de roses.* Paris 1804.

[9]) Manucci, *Histoire générale de l'Empire Monghol depuis sa formation jusqu'à present. Traduite par* Catron. 2. edit. pp. 326—327.

Unquestioned mention of the butyraceous oil of rose is made in 1574 by Hieronymus Rubeus,[1]) body physician to Pope Clemens III.; also in the writings of Porta[2]) of the year 1563 and again in 1604.

In the apothecary ordinances of Worms of 1582 and of Frankfurt-on-the-Main of 1587 *Oleum rosarum verum* is mentioned in the list of distilled oils.[3]) About the same time Angelus Sala[4]) describes the distillation of rose oil and characterizes it as *candiscente pinguidine, instar spermatis ceti.* In his Pharmacopœia of 1641, J. C. Schröder[5]) enumerates the oil under the *Olea destillata usitatoria.*

Up to the 17. century and beyond Persia seems to have supplied the market with rose water and rose oil.[6]) In the course of the century, however, the cultivation of the rose and the oil industry spread to India,[7]) also westward, in its southerly course to Arabia, Tunis, Algiers, and Morocco and in its more northerly

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[1]) Hieronymi Rubei *De destillatione liber, in quo stillatitiorum liquorum, qui ad medicinam faciuntur, methodus ac vires explicantur.* Ravennæ 1582. Sect. 2. Cap. 16, p. 102 and cap. 5, p. 132.

[2]) Portæ *Magiæ naturalis libri viginti. — De destillatione Libri.* Romæ 1563. Liber XX. — *Omnium difficillime extractionis est rosarum oleum atque in minima quantitate, sed suavissimi odoris.*

[3]) Flückiger, *Dokumente zur Geschichte der Pharmacie.* Halle 1876. pp. 37—41, 45, 47, 48, 49, 65.

[4]) Angelus Sala, *Opera medico-chymica, quæ extant omnia* Francofurti 1647. p. 63, 79.

[5]) J. C. Schröder, *Pharmacopœa medico-physica.* Ulm 1649. Lib. II. Cap. 70, p. 241.

[6]) Chardin, *Voyages en Perse* Amsterdam 1711.. Vol. III, p. 178 and 349. — Kämpfer, *Amœnitatum exoticarum politico-physico medicarum fasciculi quinque, quibus continentur variæ relationes, observationes et descriptiones rerum Persicarum et ulterioris Asiæ, multa attentione, in peregrinationibus per universum Orientem, collectæ ab auctore.* Lemgoviæ 1712. p. 373. — Olivier, *Voyage dans l'Empire Othoman* etc. Paris 1807. Tom. 5, p. 367.

[7]) Concerning the production of rose oil in India there are two reports written in 1782 by European scientists who lived at that time in Calcutta: the one under the title of "Asiatic Researches" in the Transactions of the Society instituted in Bengal etc., Calcutta 1788, vol. 1, paper 17; the other by Don Monro in the Transactions of the Society of Edinburg, vol. 2, Physical section. An abstract of the latter may be found in Tromsdorff's Journ. der Pharm. 1, II. (1794), 195.

course to Asia Minor, Turkey and Bulgaria.[1]) On the island of Chios also considerable rose oil was distilled at the beginning of the past century, which entered commerce via Smyrna.[2])

The cultivation of roses in Bulgaria, which became of such importance in later years, was begun about the beginning of the 17. century. It seems to coincide approximately with the founding of Kezanlyk, a city on the southern slope of the Balkan mountains in East Roumelia.[3]) It was not until the 19. century, however, that the rose industry of Bulgaria became a dangerous competitor of the Persian rose distillation. In recent years Bulgaria, in turn, has found successful competitors in Germany and France.

Since the 14. century, rose water and with it small quantities of rose oil, have been distilled for popular and medicinal use, also for perfumery, in the north European countries, especially in France, Germany and England. The amount of congealing oil obtained, however, was so small that rose oil was mostly bought from the orient and later from the Balkan states. The cultivation of roses for the purpose of distilling rose oil on a large scale was begun in France about the middle of this century, in Germany in 1883.[4])

The high price of rose oil and the ease with which it can be adulterated seems to have brought about adulteration in Persia in the course of the 17. century. Engelbert Kämpfer[5]) from Lemgo, who traveled in Persia in the years 1682 to 1684, mentions that rasped sandalwood is added for the sake of improvement to the roses in the process of distillation. This observation was verified in 1787 by Archibald Keir[6]) in Chatra in the Ramgur, whereas Polier[7]) observed in Cashmere during the same year

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[1]) Forbes Watson, Catalogue of the Indian Department. Vienna Exhibition 1873, p. 94. — Douglas, Pharmaceutical Journ. III. 8 (1878), 811. — H. v. Schlagintweit in Buchner's Neues Repert. d. Pharm. 24 (1875), 129—143.

[2]) Olivier, *Voyage dans l'Empire Othoman* etc. Paris 1807. Tom. 5, p. 367.

[3]) Kanitz, *Donau-Bulgarien.* Leipzig 1877—1879. Vol, 2, p. 111.

[4]) Flückiger, Pharm. Rundschau (New York) 12 (1894), 92.

[5]) Engelbert Kämpfer, *Amœnitatum exoticarum fasciculi* etc. Lemgoviæ 1712. p. 373.

[6]) Archibald Keir, "Asiatic Researches" in Transactions of the Society instituted in Bengal, for inquiring into the history and antiquites, the arts, sciences and literature of Asia. Calcutta 1788. Vol. 1, p. 309.

[7]) *Ibidem* Vol. 1, p. 332.

that in this country not sandalwood, but the fragrant Indian grass *(Andropogon)* is added to the roses for distillation.

Aside from its similar use during antiquity,[1]) the utilization of *Andropogon Schœnanthus,* L. for the purpose of adulteration of rose distillates, dates back more than a century. As a more convenient adulterant, palmarosa oil is more recently used in place of the grass from which it is distilled in India.

At an early period oil of rose was used as a perfume and, filled in fancy flasks, became a much sought for article in the bazaars of Constantinople, Smyrna, the levant and the entire orient. The demand being greater than the supply, both, manufacturers as well as dealers, early learned to increase the supply in a manner profitable to themselves. The former added palmarosa oil to the roses in the process of distillation, the latter still further diluted it with indifferent oils and spermaceti, the latter being necessary to maintain the proper congealing point.

OIL OF BITTER ALMONDS.

Almonds were known during antiquity. They are mentioned several times in the Old Testament,[2]) also by Egyptian and by later Greek and Roman authors. Of the latter Theophrastus,[3]) Dioscorides,[4]) Scribonius Largus,[5]) Pliny,[6]) Palladius,[7]) Celsus,[8]) Alexander Trallianus,[9]) Platearius[10]) and others distinguished the

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[1]) See p. 38.

[2]) Genesis, 43:11. — Numbers, 17:8. — Ecclesiastes, 12:5. — Rosenmüller, *Handbuch der biblischen Altertumskunde.* Leipzig 1831. Vol. 4, p. 263.

[3]) Theophrasti *Historia plantarum.* Lib. I, cap. 11, 18.

[4]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. Vol. 1, p. 155.

[5]) Scribonii Largi *Compositiones medicamentorum.* Editio Helmreich. 1887. p. 8.

[6]) Plinii *Naturalis historiæ libri.* Lib. XVI, cap. 22; lib. XXXIII, cap. 75. — Editio Littré. Vol. 2, p. 127.

[7]) Palladii *De re rustica,* in Nisards *Les agronomes latins.* Paris 1877. p. 552.

[8]) Celsi *De medicina libri* VIII. Editio Védrènes. *Traité de médecine.* de A. C. Celse. Paris 1876. p. 274.

[9]) Alexandri Tralliani *Medici libri* XII. Editio Puschmann. Wien 1878. Vol. 2, p. 445.

[10]) Platearii *Liber de simplice medicina.* "*Circa instans.*" Editio Choulant.

bitter almond from the sweet. During the middle ages, both kinds of almonds were in use.

Bitter almond oil is first mentioned in the writings of Saladin[1]) in 1488 and those of Sancto Amando[2]) in the 16. century. The distillates from bitter almonds and of other *Prunoideæ*, seem to have received but little attention during the period of general use of distilled waters. It is also uncertain whether the poisonous character of bitter almond oil was generally known. Even Scheele,[3]) when he discovered hydrocyanic acid in 1782 does not seem to have fully realized its poisonous properties. He did not even recognize the similarity in odor between this acid and the distillates from the bitter almond and the cherry laurel.

It was not until the eighties of the 18. century that bitter almond oil again received more attention. In spite of earlier observations,[4]) it was not regarded decidedly poisonous until so pronounced in 1784 by Joh. Andr. Murray[5]) of Gœttingen. Following him, other contemporaries made the same statement.[6])

The hydrocyanic acid content of bitter almond oil was first suspected in 1785 by the Erfurt apothecary Joh. Christ. Wil-

[1]) Saladini *Compendium aromatariorum.* Bononæ 1488. Index.

[2]) *Expositio* Joannis de Sancto Amando *supra Antidotarium* Nicolai *incipit feliciter.* In the edition with Mesue's works. Veneti 1502. fol. 228, and *Additiones* fol. 85—87.

[3]) Carl W. Scheele's *Physische und chemische Werke.* Translation by Hermstædt. Vol. 2, p. 331. — Flückiger, Arch. der Pharm. **224** (1886), 388. — Pharm. Rundschau (New York), 4 (1886), 211.

[4]) According to the statement made by A. Wynter Blyth in his treatise on "Poisons", London 1895, the poisonous character of the peach and almond kernels was known to the Egyptians. — Mortimer in Philosophical Transactions (London) **37** (1731), 84 and 166. — Vater, *Dissertatio de laurocerasi indole venenata.* Wittenbergæ 1737. — Langrish, *Expériences de médecine sur des animaux.* Paris 1750. — Fontane, *Traité sur le venin de la vipère, le laurier cerise etc.* Fiorenze 1781 and Philosophical Transactions (London) **70** (1781), I. 210.

[5]) J. A. Murray, *Apparatus medicaminum tam simplicium quam præparatorum et compositorum in praxeos adjumentum consideratus.* Göttingen 1784. Vol. 3, p. 215, 220 and 259.

[6]) Heyer, Crell's Chem. Annalen, *Beiträge* 1 (1793), 414, 415. — Gilbert's Annal. der Physik. *Neue Folge* **23**, 220.

helm Reinder[1]) and in 1797 by Lucas[2]) of Armstadt. Its presence, however, was not proven until 1803 when Bohm,[3]) apothecary in Berlin, identified it. From that time on, bitter almond oil and its hydrocyanic acid content became the subjects of numerous investigations. Of these the reports of Schaub,[4]) Schrader[5]) and Ittner[6]) advanced our knowledge, but a clear understanding of the formation and composition of the oil was gained only through those of Gay-Lussac,[7]) Robiquet and Vogel,[8]) Boutron-Charland[9]) and finally those of Liebig and Wœhler,[10]) and C. Winkler.[11])

The separation of the hydrocyanic acid from the benzaldehyde was first accomplished by Vogel in 1822 by treating the oil with baryta water. Liebig and Wœhler[12]) introduced the method still in use involving ferrous sulphate, ferric chloride and milk of lime, which yielded pure benzaldehyde. Bertagnini[13]) proposed sodium acid sulphite.

The separation of benzoic acid from bitter almond oil which has been exposed to the air was observed as early as 1823 by Stange[14]) in Pegau.

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[1]) Crell's Chem. Annalen **1785**, II. 443. — Göttling's Almanach für Scheidekünstler und Apotheker 8 (1787), 136.

[2]) *Ibidem* **18** (1797), 101.

[3]) Scherer's Allgem. Journ. der Chem. **10** (1803), 126. — Gilbert's Annal. der Physik **13** (1803), 503.

[4]) Schaub, *Dissertatio medico-chymica sistens Laurocerasi qualitates medicas ac venenatas etc.* Marpurgi 1802.

[5]) Trommsdorff's Journ. der Pharm. **11**, I. (1803), 259 and 262.

[6]) *Über das Vorkommen der Blausäure im Öle der bittern Mandeln.* Schweigger's Journ. f. Chem. u. Phys. **24**, 395. — F. v. Ittner, *Beiträge zur Geschichte der Blausäure, mit Versuchen über ihre Verbindungen und Wirkungen auf den tierischen Organismus.* Freiburg and Constanz 1809.

[7]) Poggendorff's Annal. der Phys. *Neue Folge* **23** (1831), 1 and 138. — Schweigger's Journ. f. Chem. u. Phys. **16** (1831), 1.

[8]) Journ. de Pharm. II. 8 (1822), 293. — Annal. de Chim. et Phys. **15** (1810), 29 and **21** (1822), 250. — Trommsdorff's Neues Journ. der Pharm. **7**, I. (1823), 217.

[9]) Annal. de Chim. et Phys. **44** (1837), 352. — Liebig's Annalen **25** (1838), 175.

[10]) Liebig's Annalen **22** (1837), 1.

[11]) Repert. f. d. Pharm. II. **17** (1839), 156. — Pharm. Zentralbl. **1839**, 634.

[12]) Liebig's Annalen **3** (1832), 252.

[13]) *Ibidem* **85** (1853), 183.

[14]) Repert. f. d. Pharm. I. **14** (1823), 329, 361 and **16** (1824), 80.

OIL OF CHERRY-LAUREL.

Cherry-laurel (*Prunus laurocerasus,* L.), appears to have become known in Europe toward the beginning of the 16. century. The aqueous distillate from the leaves has been used medicinally since the first half of the 18. century and its poisonous properties were repeatedly observed.[1]) The distilled oil is included in pharmacopœias since 1780.[2]) The precence of hydrocyanic acid in the oil was observed simultaneously by Schaub[3]) and by Schrader[4]) at the beginning of 19. century.

OIL OF ROSE GERANIUM.

The pelargoniums which are indigenous to South Africa and which are now largely cultivated as decorative plants were introduced into Europe in 1690.[5]) Recluz[6]) of Lyon in 1819 first obtained a volatile oil[7]) from the leaves. However, Demarson of Paris, in 1847 was the first to cultivate pelargoniums for the distillation of the oil. Since then their cultivation throughout France has been largely extended and was introduced into Algiers by Chiris and Monk.

In Spain pelargoniums were cultivated in the vicinity of Valencia by Robillard. Later they were also cultivated in the province of Almeria.

The island of Réunion has entered upon the cultivation of these plants since the eighties of the past century. Of much less importance are the plantations in Corsica.

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[1]) Philosoph. Transact. (London) **37** (1731—1732), 84. — Abr. Vater, *Dissertatio de Laurocerasi indole venenata.* Wittenbergæ 1737. — Bergius, *Materia medica.* Stockholm 1778, p. 401.

[2]) J. A. Murray, *Apparatus medicaminum tam simplicium quam præparatorum et compositorum* etc. Göttingen 1784. Vol. 3, p. 213.

[3]) D. Schaub, *Dissertatio medico-chymica, sistens Laurocerasi qualitates medicas ac venenatas* etc. Marpurgi 1802.

[4]) Trommsdorff's Journ. der Pharm. **11**, I (1803), 259 and 262.

[5]) Piesse, *The Art of Perfumery.* IV. Edition, London 1879, p. 124.

[6]) Pharmaceutical Journal I. **11** (1852), 325.

[7]) This oil is not to be confounded with the so called Indian geranium oil, the palmarosa oil from *Andropogon Schœnanthus,* L.

OIL OF RUE.

Rue is mentioned in the Bible.[1]) As medicinal plant useful in the treatment of diseases of the eye, it is mentioned by Dioscorides,[2]) Pliny, Columella[3]) and Ovid.[4]) For like purposes the plant was used during the middle ages.[5])

The first mention of oil of rue (although possibly of the fatty oil) is found in Saladin's writings.[6]) Gesner[7]) distilled the oil about the middle of the 16. century. It is mentioned in the price ordinances of the cities of Berlin for the year 1574 and of Frankfurt for the year 1582, and in the *Dispensatorium Noricum* of the year 1589.

The yield of volatile oil from rue was first determined by Cartheuser[8]) in the beginning of the 18. century. The oil was investigated by Caspar Neumann[9]) and by G. S. P. Mähl[10]) in Rostock in the year 1811, by Will[11]) in the year 1840, by Cahours[12]) in 1845, by Gerhard[13]) in 1848, by C. G. Williams[14]) in 1858, by W. Hallwachs[15]) in 1859, by C. Harbordt[16]) in 1862, by Giesecke[17]) in 1870, and by E. von Gorup-Besanez and Grimm[18]) in 1871.

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[1]) St. Luke, 11 : 42.

[2]) Dioscoridis *De materia medica libri quinque.* Lib. III, cap. 45 and 52. — Editio Kühn-Sprengel. 1829. Vol. 1, p. 391.

[3]) Columellæ, *De re rustica et de arboribus.* Lib. XII, 7.

[4]) Ovidii *Remedia amoris.*

[5]) Pfeiffer, *Zwei deutsche Arzneibücher aus d. 12. u. 13. Jahrh. Sitzungsberichte d. kais. Akad. der Wissensch. in Wien* **42** (1863), 137 and 142. (Haeser, *Geschichte d. Medizin.* 1875. Vol. 1, p. 663.) — Milton's Paradise Lost. XI. line 414:

"— then purg'd with Euphrasy and *Rue*
The visual nerve, for he had much to see."

[6]) Saladini *Compendium aromatariorum.* Bononæ 1488. Index.

[7]) Euonymi Philiatri *Ein köstlicher Schatz.* 1555. Fol. 226.

[8]). Joh. Friedr. Cartheuser, *Fundamenta materiæ medicæ.* Francof. ad Viadr. 1738. Vol. 2, p. 129.

[9]) Casp. Neumann's *Medic. Chemie.* Ed. C. H. Kessel 1749. Vol. 2, p. 292.

[10]) Trommsdorff's Journ. der Pharm. **20**, II. (1811), 29.

[11]) Liebig's Annalen **35** (1840), 235.

[12]) *Thèse présentée à la Faculté des sciences le 15. janv.* 1845. Compt. rend. **26** (1848), 262.

[13]) Liebig's Annalen **67** (1848), 242.

[14]) *Ibidem* **107** (1858), 374.

[15]) *Ibidem* **113** (1860), 107.

[16]) *Ibidem* **123** (1862), 293.

[17]) Zeitschr. für Chemie **13** (1870), 428.

[18]) Liebig's Annalen **157** (1871), 275.

OIL OF BUCHU LEAVES.

Buchu leaves indigenous to southern Africa appear to have long been used for medicinal purposes. In 1820 they were introduced into European commerce,[1]) having been brought from Cape Town to London. Since the later twenties of the past century they have been included in most pharmacopœias.

The volatile oil was first prepared by R. Brandes[2]) in 1827.

THE OILS OF THE AGRUMEN FRUITS.

The genus *Citrus,* belonging to the subfamily *Aurantieæ* of the *Rutaceæ,* is indigenous to Central Asia. The large number of varieties of the citrus fruits, known by the collective term of agrumen fruits, is indicative of a very long period of cultivation. The citrus tree, having spread from southern China to Cochinchina and India,[3]) became known to occidental peoples through the wars of Alexander the Great. Gradually its cultivation spread over Persia and Media to the westward.[4]) Later, the Romans, and more particularly the Arabians, contributed to the spread of the citrus tree along the coast of the Mediterranean as far as Spain and Morocco. In the course of the crusades the tree and its fruit were spread among the peoples living to the north of the Mediterranean countries. Thus citrus culture has been spread over all countries with a warm or temperate climate so that at present the citrus tree is among the most cosmopolitan of all cultivated plants.

Whether the number of citrus species was limited during antiquity and whether the numerous varieties were gradually

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[1]) R. Reece, Monthly Gazette of Health. London. Febr. 1821, p. 799.

[2]) Arch. der Pharm. 22 (1827), 229.

[3]) Bretschneider, On the study and value of Chinese botanical works with notes on the history of plants and geographical botany from Chinese sources. Foochow 1870, pp. 11 and 12. — E. Bonavia, The cultivated Oranges and Lemons of India and Ceylon with researches into their origin and the derivation of their names etc. London 1890.

[4]) Brandis, Forest Flora of Northwestern and Central India. 1874, p. 50. — Hehn, *Die Kulturpflanzen und Haustiere in ihrem Übergang aus Asien nach Griechenland und Italien.* Berlin. 3rd ed. 1877. — Alphonse de Candolle, Origin of cultivated plants. 1885. p. 176.

developed with changed conditions in soil, climate and method of cultivation, does not become apparent from literature. The several names of the agrumen fruits appear to have passed from the Sanskrit to the languages of later peoples of antiquity. Thus the Greeks and Romans knew the lemon but not the orange, bergamot and limette.[1]) The lemon they named *Malum persicum, Malum citratum* or *citreum.* The supposition that the odor of the lemon, like that of the juniper and of the cedar (χέδρος) of the Greek forests, kept away insects, caused the Greeks to apply this name to the "Persian" or "Median" apple, calling it *Malum cedreum, Malum citreum.* Hence developed the names *Citrus, Citrus medica* and *Citrus persica.*[2])

During the period from the 8. to the 10. centuries, the Arabians spread the cultivation of the bitter orange (*Citrus Bigaradia,* Risso) and of the lemon (*Citrus Limonum,* Risso) from Omân and Mesopotamia to Syria and Arabia. Thence the cultivation of these trees spread during the crusades along the coast of the Mediterranean to Spain and Morocco.[3]) In Sicily the tree was cultivated as early as 1002.[4])

The writings of the 12. to the 14. centuries frequently reveal the gradual spread of the agrumen fruits and the esteem in which they were held. Idrisi,[5]) an Arabian geographer of the 12. century describes the lemon, in his travalogues of the African coast lands of the Mediterranean, but apparently did not find other

[1]) Scribonius Largus, *Compositiones medicamentorum.* Editio Helmreich. 1887. p. 65. — Oribasius, *Medicinalia collecta.* Lib. I, cap. 64. — Palladii *De re rustica.* In Nisard's *Les agronomes latins.* Paris 1877. p. 585.

[2]) Theophrasti *Historia plantarum.* Editio Wimmer. Vol. 1, lib. IV. — Dioscoridis *De materia medica libri quinque.* I. 166. — Virgilii *Georgica.* 2, 126:

Media fert tristis succos tardumque saporem
Felicis mali: quo non præsentius ullum,
Pocula si quando sævæ infecere novercæ.

Hehn, *Kulturpflanzen und Hausthiere in ihrem Uebergang aus Asien nach Griechenland und Italien.* Berlin 1877, p. 359.

[3]) Ibn Baithar, *Heil- und Nahrungsmittel.* Translated by Sontheimer. 1842. Vol. 2, p. 452.

[4]) Risso et Poiteau, *Histoire et culture des Orangers.* Edition Du Breuil. Paris 1872. — Hehn, *Kulturpflanzen und Hausthiere in ihrem Uebergang aus Asien nach Griechenland und Italien.* 1877, pp. 380—394. — Götze, *Beitrag zur Kenntnis der Orangengewächse.* Hamburg 1874, pp. 26—29.

[5]) *Géographie* d'Edrisi *traduite par* Amédée Jaubert. 1836. Vol. 1, p. 162.

agrumen fruits, although such were cultivated in Spain at that time.[1]) Jacques de Vitri[2]) who traveled through Palestine about 1225 found several varieties.

The sweet orange tree (*Citrus Aurantium,* Risso) was cultivated for decorative purposes in Nizza in 1336. In 1340 sweet oranges[3]) *(Arancio)* were well known in Venice.[4]) In 1369 *Arbores citronum* were cultivated in Genoa and along the Ligurian coast. Among the articles of export from Alexandria the lemon is mentioned in a treatise of 1420. In 1486 lemon trees were cultvated along the Riviera[5]) and in 1494 in the Azores.[6]) In 1546 the sweet orange was brought by the Portuguese Juan de Castro (viceroy of India from 1545 to 1548) from China to Portugal and cultivated there.[7]) Although the sweet orange has been cultivated occasionally in northern Italy, its general culture in southern Europe appears to have spread from Portugal. The name *Portugallo* for oranges has maintained itself in Italy up to the present time. In 1516 Barbosa,[8]) a Portuguese traveller mentions the lemons as fruits being introduced from the Malabar coast and Ceylon.

Into Germany the citrus fruits appear to have been introduced in the course of the 15. century. According to Conrad Gesner[9])

[1]) Ibn-al-Acram il Ishbilis during the second half of the 12. century wrote an agricultural treatise which was translated into French *„Livre d'Agriculture"* edited by Clément Mullet. Paris 1864.

[2]) *Limones, Citri et alia poma citrina . . . acidi seu pontici saporis quæ poma orenges ab indigenis nuncupantur.* Bongars, *Gesta Dei per Francos.* Hanoviæ 1611, fol. 1099.

[3]) For the etymology of the name orange see De Candolle, Origin of the cultivated plants. 1885. p. 184. — W. Roxburgh, *Flora Indica.* Vol. 2 (1839), p. 392.

[4]) Cecchetti, *Archivio Veneto.* Vol. 30 (1885), p. 63.

[5]) Gallesio, *Traité du Citrus.* Paris 1811, pp. 89, 103 and 321.

[6]) Kunstmann, *D. Hieronymus Münzers Bericht über die Entdeckung der Guinea. Abhandlungen der histor. Klasse der bayerischen Akademie.* 1855, p. 362.

[7]) Le Comte, *Nouveaux mémoires sur l'état de la Chine.* 2. Edition. Paris 1679. Tom. 1, p. 173. — Ferrari *Hesperides seu de malorum aureorum cultura et usu.* Romæ 1646, p. 425. — E. Bretschneider, History of European botanical discoveries in China. London 1898, Vol. 1, p. 6.

[8]) *Libro* di Odoardo Barbosa, in Ramusios *Delle navigationi et viaggi.* Venetia 1554, fol. 347b. — Götze, *Beitrag zur Kenntnis der Orangengewächse.* Hamburg 1874, p. 24.

[9]) Conrad Gesner, *De hortis Germaniæ liber recens.* Argentorati 1561. Lib. III.

they were cultivated during the middle of the 16. century for decorative purposes in hot houses and gardens.

Lemon juice, which is again being used for medicinal purposes in recent times, was esteemed as such by Roman physicians. Alexander Trallianus[1]) prescribed it during the middle of the 6. century. Lemon syrup was introduced as medicament by the Arabian physician Mesue through his *Antidotarium.*[2]) The method for its preparation was included in his *Dispensatorium Noricum* of 1543 by Valerius Cordus.[3])

The oil which is secreted in the cell tissues of the outer fruit rind of the agrumen fruits flows out when these oil cells are ruptured by pressure or friction. It is in this way that the oil is actually obtained. With the introduction and utilization of the agrumen trees, this oil must have been known at an early period, without, however, finding any application.

The earliest statements concerning distilled lemon and orange oils were made by Conrad Gesner[4]) in 1555. Jaques Besson[5]) followed in 1571, and Porta[6]) in 1589. The latter described the preparation of the two oils by distillation of the fresh grated rinds. During the sixties of the 18. century Gaubius[7]) recommended the same process.

The mechanical method of preparation of the agrumen oils by rupturing the oil cells of the fruit rinds by means of a grate was described by Cl. Joh. Geoffroy[8]) in the beginning of the 18. century. In all probability, however, this method was practiced before this date.

The variety *Citrus Bergamia,* Risso, appears to be a cultural variety of much later date. The earliest information concerning oil of bergamot dates back as far only as the close of the 17. century. Thus *e. g.* it is mentioned in an inventory of an

[1]) Alexandri Tralliani *medici libri XII græce et latine multo quam antea auctiores et integriores* etc. Basiliæ 1556. Editio Puschmann. Vienna 1878.

[2]) See p. 24. — Gallesia, *Traité du Citrus.* Paris 1811. pp. 122, 247, 248.

[3]) *Dispensatorium Noricum.* Editio 1548, pp. 179, 273.

[4]) Euonymi Philiatri *Ein köstlicher, teurer Schatz* etc. Zürich 1555.

[5]) Besson, *L'art et moyen parfait de tirer huyles et eaux de tous medicaments simples et oléagineux.* Paris 1571.

[6]) Portæ *Magiæ naturalis libri viginti.* Romæ 1563. Edit. Napoli 1589. p. 188.

[7]) H. D. Gaubii *Adversariorum varii argumenti liber unus.* Leidæ 1771. p. 31.

[8]) *Mémoires de l'Académie des sciences de Paris.* **1721**, 159.

apothecary shop of Giessen of 1688,[1]) also in the treatise *Le parfumeur François, par le Sieur Barbe,* published in Lyon in 1693. In the latter the bergamot fruit is described as a pear, from the fruit rind of which the fragrant oil is obtained by trituration and expression. The further statement is made that the name bergamot is derived from the Turkish *Beg-âr mû dî*, the "prince of pears". This statement would seem to indicate that the bergamot had its geographic source in the eastern coast lands of the Mediterranean. In his *Hesperides Norimbergensis* of 1713, the Nuernberg physician and botanist, I. G. Volkamer, described the *Limon bergamotta* as *gloria limonum et fructus inter omnes noblissimus.*[2]) He mentions that the Italians prepare an extremely fine essence from the fruit rind; that the name bergamot is in no way associated with Bergamo, a city in Lombardy; also that no agrumen varieties are cultivated in that region.

In some of the West Indian islands, agrumens have been cultivated since the beginning of the past century. Aside from the island Montserrat, they did not prosper, either because they did not receive proper care, or because the soil was not favorable. Proper care as well as soil they, however, found in the southern part of United States since about 1815. They are now being cultivated extensively in Florida, Louisiana, and, since the forties, in southern California.

In the municipal price ordinances concerning the wares of the apothecary and spices, oils of lemon and orange are enumerated among the distilled oils for the first time in that of Frankfurt-on-the-Main of 1582. Both oils had been introduced into the *Dispensatorium Noricum* of 1589 and into the *Pharmacopœia Augustana* of 1613. As indicated above, bergamot oil appears to have come into use in 1690.

In 1786 Remmler[3]) tried to prepare rosin from oil of lemon. About the same time Liphard[4]) mentions that the yield of lemon oil is larger when the fruit is allowed to stand until decay sets in.

In 1789 the apothecary Heyer[5]) of Braunschweig, upon cooling bergamot oil, obtained crystals which he termed bergamot camphor.

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[1]) Flückiger, *Dokumente zur Geschichte der Pharmazie.* Halle 1876, p. 72.
[2]) *Hesperides Norimbergenses,* 1713. *Liber* III, cap. 26, p. 156, b.
[3]) Göttling's Taschenbuch für Scheidekünstler **1786.**
[4]) Crell's Chem. Annalen **1787,** II. 250.
[5]) *Ibidem* **1789,** I. 320.

OIL OF ORANGE FLOWERS.

Oil of orange flowers was known as early as the sixteenth century. Its distillation was described for the first time by Porta.[1]) About a century later, in the year 1680, it appears to have been made the fashionable perfume by the Duchess Flavio Orsini, Princess of Neroli, hence the name of essence of neroli.[2]) On account of its delicate pleasant odor, the oil has been able to hold its reputation as one of the finest flower perfumes. This is also true of the distilled orange flower water, or *Aqua naphæ*,[3]) which is used extensively for the aromatizing of food, confections and beverages, also for toilet purposes. The distillation of orange flower oil was described by Benatius[4]) in 1806. The oil was investigated in 1825 by Bonastre[5]) and in 1828 by Boullay.[6])

OIL OF MYRRH.

The history of myrrh is inseparable from that of frankincense. Both come from the same countries. From early antiquity on, both have found like application in religious cults. In the commerce of the spices, both have played an important role. Hence myrrh and frankincense are almost invariably mentioned together in the oldest writings. As their geographic source, mythical Arabia and the coast lands along the south end of the Red Sea, the *Punt* or *Phun* of Egyptian documents, are

[1]) Jo. Batt. Portæ, *Neapolitanæ Magiæ naturalis libri viginti etc.* Romæ 1563. fol. 118.

[2]) Menagio, *Origini della lingua Italiana.* 1685. — *Dictionnaire de Trévoux.* — Paris 1771. Vol. 6, p. 178.

[3]) The names *Naphé* and *Naphore* probably had their origin in Languedoc. (Risso and Poiteau, *Histoire naturelle des Orangers.* Paris 1818. Edition Du Breuil 1872. p. 211.) — Orange flower water was distilled in the laboratories of German apothecary shops as early as the middle of the 17. century. (Simonis Paulli *Quadripartitum botanicum de simplicium medicamentorum facultatibus etc.* Argentorati 1667. p. 385.)

[4]) Berl. Jahrbuch der Pharm. **1806**, 256.

[5]) Journ. de Pharm. II. **11** (1825), 529.

[6]) Journ. de Pharm. II. **14** (1828), 496. — Trommsdorff's Neues Journ. der Pharm. **19**, I. (1829), 226.

mentioned.[1]) As precious spices for burnt offerings, for the purpose of embalming and anointing,[2]) both resins are frequently mentioned in Sanskrit writings, in the Vedas, in the Bible,[3]) in the Koran, in the Papyrus Ebers and in the writings of Greek, Roman and Arabian authors. Moreover, they are frequently confounded with each other.[4])

[1]) Agatharchides. In *Geographi Græci minores. — De mari Erythræo.* p. 87. — Arrianos, *Anabasis.* Lib. VII, 20 and 22. — Diodori *Bibliotheca historica.* Lib. 19, cap. 24. — Kosmas *Indopleustes, Topographia Christiana* in Migne's *Patrologiæ cursus completus. Series Græca.* 1860. Vol. 88, p. 374. — G. A. Haggenmacher, *Ergänzungsheft zu Petermanns Geographischen Mitteilungen.* 1876, 19. — I. M. Hildebrandt *Sitzungsberichte der Gesellschaft naturforschender Freunde zu Berlin.* 19. November 1878. p. 195. — K. Niebuhr, *Beschreibung von Arabien.* Copenhagen 1772. pp. 282 and 286. — H. Brugsch-Bey, *Geschichte Aegyptens unter den Pharaonen.* 1877. pp. 109, 110, 113, 281, 314. — Revoil, *Voyages au Cap des Aromates.* Paris 1880. pp. 136, 184, 227, 255, 259, 276, 283.

[2]) For the preparation of the sacred oil, used according to Jewish ritual for the anointing of the high priests, the "pure myrrh" (Exodus 30:23) was prescribed. It was the exudation that flowed naturally (Song of Solomon, 5:5 and 13), hence it was also called tears or flowing myrrh (Stakte) (Exodus, 30:34). The wives of the Persian kings and the garbs of the kings were perfumed with myrrh. (Esther, 2:12. — Psalms, 45:9. — Proverbs, 7:17). As a precious spice, myrrh was brought by the magi from the Orient to the new born King of the Jews (Matth, 2:11). Roman soldiers refreshed Christ, while on the cross, with wine and myrrh (Mark 15:23), and Nicodemus brought myrrh for the embalming of his body (John, 19:39).

[3]) Exodus, 30:23; 37:25. — Psalms, 45:9. — Proverbs, 7:17. — Song of Solomon, 1:13; 3:6; 4:14; and 5:5 and 13. — Mark, 15:23. — Matthew, 2:11. — John, 19:39.

[4]) Statements concerning the origin and history of myrrh and frankincense may be found in the following treatises: Papyrus Ebers of the University Library at Leipzig and of the Royal Library at Berlin. — Herodoti *Historiarum libri* IX. Lib. III. 107. — Theophrasti *Historia plantarum* Lib. IX, cap. 4. — Plutarchi *Moralia Isis et Osiris.* V. 383. — Diodori *Bibliotheca historica* Lib. V, cap. 41 and Lib. XIX, cap. 94. — Luciani *Opera, Drapetui* p. 1. — Athenæi *Dipnosophistarum libri* XV, pp. 101 and 464. — Apulei *Metamorphoseon* Lib. 8 and 10. — Dioscoridis *De materia medica libri* V. Lib. 1, cap. 24, 78 and 81. Editio Kühn-Sprengel 1829. Vol. 1, p. 78. — Plinii *Naturalis historiæ libri.* Lib. XII, 15, 16, 30—35 and Lib. XIV, 15. — Dümichen, *Geschichte des alten Aegyptens.* In Oncken's *Allgemeiner Weltgeschichte. Grabpal. d. Petam.* Vol. 2, pp. 12—34 — *Periplus maris Erythræi.* Lib. IX, cap. 4. — Vincent, Commerce and Navigation of the Ancients in the Indian Ocean. London 1807. Vol. 2, pp. 316 and 698. — Chishull, *Antiquitates asiaticæ.* London 1728, p. 71. D. Hanbury, Science Papers 1876. pp. 378—382. — Comp. also Sigismund, *Die Aromata.* Leipzig 1884. pp. 6—13.

Upon the disappearance of sacrifical customs, the consumption of both resins decreased. The Roman Catholic and the Greek Catholic chruches, however, continued to use them, even in the ordeals of the inquisition.[1])

With the cessation of the use of myrrh for incense purposes in antiquity, its use was restricted more and more to medicine, perfumery and cosmetics and hence gained in importance in the treatises on distillation and medical treatises of the middle ages.

Distilled oil of myrrh was well known to Walter Ryff,[2]) Valerius Cordus[3]) and Conrad Gesner[4]). In the price ordinances of medicines and spices it first occurs in that of Frankfurt-on-the-Main of 1587, and in pharmacopœias first in the *Dispensatorium Noricum* of 1589.

Observations on the method of preparation and yield of oil of myrrh were made in the course of the 18. century by Fr. Hoffmann,[5]) Caspar Neumann,[6]) J. R. Spielmann,[7]) Thielebein,[8]) and later by Braconnot,[9]) Pelletier[10]) and Rudolf Brandes.[11])

OIL OF FRANKINCENSE.

Like its geographic source, so the history of frankincense coincides very nearly with that of myrrh. However, as a spice gum, it was chewed and for incense purposes it appears to

[1]) Runge, *Adjurationen, Exorcismen, Benedictionen bei Gottesgerichten.* In *Mittheilungen der antiquarischen Gesellschaft in Zürich.* Vol. 12 (1859), fascicle 5, p. 187.

[2]) H. Gualtherus Ryff, *New gross Destillirbuch.* 1545. fol. 275b.

[3]) Valerii Cordi *De artificiosis extractionibus. De destillatione oleorum.* Tiguri 1540. p. 216.

[4]) Euonymi Philiatri *Ein köstlicher theurer Schatz.* Zürich 1555. p. 237.

[5]) Frederici Hoffmannii *Observationes physico-chemicarum selectiores.* Halæ 1722. Vol. 1, p. 20.

[6]) Caspar Neumann, *Medizinische Chemie.* Editio Kessel. 1749—1755. Vol. 2, p. 375.

[7]) J. R. Spielmann, *Institutiones chemiæ prælectionibus academicis accommodatæ.* Argentorat. 1763. p. 221.

[8]) Crell's Neueste Entdeckungen in der Chemie 2 (1781), 118.

[9]) Trommsdorff's Journ. der Pharm. 18, I. (1809), 149.

[10]) *Examen chimiques de quelques gommes-résines.* Annal. de Chim. 80 (1811). — Bull. de Pharm. 4 (1812), 54. Schweigger's Journ. f. Chem. u. Phys. 5 (1812), 245.

[11]) Buchholz, Taschenbuch für Scheidekünstler und Apotheker. 1819, 125.

have been used earlier than myrrh. In addition to the literary sources mentioned under myrrh,[1]) the age of such uses is indicated by recent investigations.[2]) Its most common application and largest use, frankincense found as incense in the religious cults of most of the peoples of antiquity. As such it was adopted by the Roman and Greek Catholic churches. Its use as incense, either by itself[3]) or with myrrh[4]) and other spices was especially esteemed in the temple service of the Hebrews, who obtained these spices through the Phœnicians.[5]) Frankincense was also transported by caravan to Persia and Babylonia.[6]) Indeed, the trafic in frankincense and myrrh exerted a great influence on the commerce of the coastlands of the Red Sea.

Among other writers Herodotus,[7]) Plutarch,[8]) Theophrastus,[9]) and Athenæos,[10]) later Strabon,[11]) Dioscorides[12]) and Pliny,[13]) also Arrian[14]) make mention of the importance of frankincense.[15])

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[1]) See pp. 153 and 154.

[2]) Cruttendon, in Transactions of the Bombay Geographical Society. Vol. 7 (1846), p. 121. — Chishull, *Antiquitates Asiaticæ*. London 1728. pp. 65—72. — Harris, The Highlands of Abyssinia. Description of the Frankincense tree in Guardafui. London 1844.

[3]) Exodus, 30:34. — Leviticus, 2:1, 2, 15, 16; 5:11; 6:15. — 1. Chronicles, 10:29. — Song of Solomon, 4:14. — Isaiah, 43:23; 60:6. — Jeremiah, 6:20. — Matthew, 2:11.

[4]) See p. 153, footnote 3 and 4.

[5]) p. 6. — Movers, *Das phönicische Alterthum*. 1856. Vol. 3, pp. 99 and 299.

[6]) Sprenger, *Die alte Geographie Arabiens*. Bern 1875. pp. 212, 218, 219, 230, 264, 282, 284, 299, 308.

[7]) Herodoti *Historiarum libri* IX. Editio Rawlinson. 1858. Vol. 2, p. 488.

[8]) Flückiger, *Pharmakognosie*. 1891. p. 50.

[9]) Theophrasti *Eresii Opera quæ supersunt omnia. Historia plantarum* Liber IV, cap. 4 and Liber IX, cap. 4. — Editio Wimmer. Vol. 1, pp. 66 and 143.

[10]) Athenæi *Dipnosophistarum libri* XV. pp. 253, 289 and 309.

[11]) Strabonis *Geographica*. Lib. XVI, cap. 4. — Meyer, *Botanische Erläuterungen zu Strabo*. Königsberg 1852. pp. 137—139. — Meyers *Geschichte der Botanik*. Königsberg 1855. Vol. 2, p. 88.

[12]) Dioscoridis *De materia medica libri quinque*. Editio Kühn-Sprengel. Vol. 1, p. 24.

[13]) Plinii *Naturalis historiæ libri*. Lib. XII, p. 41. Editio Littré. p. 489.

[14]) *Periplus maris erythræi*. In Caroli Mülleri *Geographi Græci minores*. Paris 1855. Vol. 1, pp. 264—265.

[15]) Hebrew *Lebonah*, Latin. *Thus* (from θύειν, to sacrifice).

The distilled oil of frankincense was known to Valerius Cordus, but it is seldom mentioned in literature. In the treatises on distillation of the 16. century frankincense is mentioned as one of the many substances used in the distillation of the complex balsams *e. g.* by Gesner.[1]) Oil of frankincense is first found as *Oleum thuris* in the drug ordinances of the city of Berlin for 1574, and of Frankfurt-on-the-Main for 1587; further in the *Dispensatorium Noricum* of the year 1589.

The older investigations of frankincense as to content of volatile oil as well as the properties of the oil were mostly made in connection with like investigations of oil of myrrh of which the more important have been mentioned on p. 153.

Special observations concerning the oil and its constituents were made by Joh. E. Bær[2]) in 1787 and by Johnston[3]) in 1839. The first investigation of the oil was made by Stenhouse[4]) in 1840.

OIL OF ELEMI.

Statements supposed to pertain to elemi made during the period of the Romans are based largely on surmise.[5]) In Europe, elemi became known in the course of the 15. century,[6]) being used as an external remedy.[7]) However, its use was anything but general and at the time of Valerius Cordus, little was known concerning the *resina elemnia*.[8]) The regular introduction into Europe of Philippine elemi does not date back farther than about 1820.[9])

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[1]) Euonymi Philiatri *Ein köstlicher theurer Schatz.* 1555. p. 163.

[2]) *Dissertatio.* Erlangæ 1787.

[3]) Philosoph. Transact. London **1839**, 301.

[4]) Liebig's Annalen **35** (1840), 306.

[5]) Flückiger, *Pharmakognosie.* III. ed., p. 88. — Flückiger and Hanbury, Pharmacographia. p. 147.

[6]) Monardes, *Historia medicinal de las cosas que se traen de nuestras Indias occidentales qui sirven en medicina.* Sevilla 1574. — Editio Clusii 1593, p. 315. — W. Piso, *Historia naturalis et medica occidentalis* 1658, p. 122. — Ray, *Historia plantarum* 1704. Vol. 3. *Appendix* p. 60 and 67. — B. Pomet, *Histoire des drogues.* Paris 1694. p. 261.

[7]) Winkelmann, *Urkundenbuch der Universität Heidelberg* 1886, I. 125, 32. — Flückiger, *Dokumente zur Geschichte der Pharmazie.* 1876. p. 26. — Flückiger, *Die Frankfurter Liste* 1872. p. 16.

[8]) Valerii Cordii *Historia stirpium.* Lib. IV, cap. 97, p. 208.

[9]) Arch. der Pharm. **17** (1826), 72.

Distilled oil of elemi is first mentioned in the price ordinance of Frankfurt-on-the-Main of 1587. It was admitted to the *Pharmacopœa Augustana* of 1613 and the Frankfurt Pharmacopœia of 1649.[1])

The first determination of the yield of oil was made by Caspar Neumann[2]) about 1730. Redeterminations were made later by Manjeau[3]) and Bonastre.[4])

OIL OF LIGNALOES.

Fragrant woods from Mexico and French Guyana have been articles of commerce since the 18. century. They were named aloe wood because at first they were regarded as being identical with the older aloe wood.[5]) Mexican lignaloes was first

[1]) Schröder, *Pharmacopœa medico-physica.* Ulm 1649. p. 194.

[2]) Caspar Neumann, *Chymia medica dogmatico-experimentalis.* Editio Kessel. 1749. Vol. 2, p. 403—405.

[3]) Journ. de Pharm. **10** (1824), 199.

[4]) Journ. de Pharm. **9** (1823), 45—49. Trommsdorff's Neues Journ. der Pharm. **7**, I. (1823), 368.

[5]) During antiquity the name aloe wood or *Adlerholz* was used as a collective term for fragrant woods obtained from different sources (Comp. J. Möller, *Lignum Aloes und Linaloeholz.* II. Mitteil., Pharm. Post. 1898.) However, it appears to have been applied primarily to the resinous wood of *Aquilaria Agallocha,* Roxb. (N. O. *Thymeleaceæ*). Like sandalwood, it belongs to the spices used during antiquity. The East Indians called it *Ahalia* or *Ahaloth,* the Greeks ἀλόης also ἀγάλλοχον. The Arabians designated it *al-oed,* meaning the wood, also *agaluchin.* The latter word gave rise to the Portuguese designation *pao de aquila,* this in turn to the Latin *lignum aquilæ.* (Boorsma, *Ueber Aloeholz und andere Riechhölzer. Bull. du Départ. de l'Agriculture aux Indes Néerlandaises.* No. VII. [Pharmacologie III] Buitenzorg 1907, p. 1, footnote 4.) — Proverbs, 7 : 17. In Luther's translation (Psalms, 45 : 9. — Song of Solomon, 4 : 14. — St. John, 19 : 39, &c.). In the English version it is translated as aloe wood. During antiquity it was prized so very highly that it was regarded as a most precious gift. From Egyptian documents from the 17. century B. C. it becomes apparent that lignaloes, sandalwood and cassia were highly esteemed spices by the Egyptians and that these were imported via the Red Sea route. (Lieblein, *Handel und Schiffahrt auf dem Roten Meere in alten Zeiten.* Christiania 1886. p. 31). Not until the crusades did lignaloes enter the Mediterranean commerce. During the reign of the East Roman and later of the Greek emperors in Constantinople, and during the prime of the Levant commerce, lignaloes was one of the common spices of the Orient. (W. Heyd, *Geschichte des Levantehandels im Mittelalter.* 1879. Vol. 1, pp. 181, 191, 256, 418, 423; vol. 2, pp. 9, 153, 559.) About 1290

introduced into France in 1866. Guyana lignaloes was first brought to Marseille in the seventies and was there used for the distillation of the oil. In Cayenne the oil was first distilled in 1893.

CASCARILLA OIL.

It appears to have been in the first half of the 17. century that cascarilla bark was imported into Europe from the Bahama islands where the *Croton Elutaria,* Bennett is indigenous.[1]) The aborigines of these islands used the bark for fumigating purposes and as admixture to tobacco. Toward the end of the same century, cascarilla bark was used medicinally in Germany. In the pharmaceutical price ordinance of Minden of 1691, it is enumerated as *Cortex Chinæ de China nova,* and in that of 1694 as *Cortex Chinæ novæ seu Schacorillæ.*[2])

Cascarilla oil is first mentioned in the *Taxa universalis,* Nuernberg 1747, as *Oleum Schaquerillæ.*[3]) Statements concerning the yield and its specific gravity are made by Trommsdorff[4]) in 1838.

OIL OF MASTIC.

During antiquity mastic was used for fumigation, embalming and as a taste corrective for wine. With other spices used for

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Marco Polo found it to be one of the most precious perfumes used in China and India. (*Le livre de Marco Polo.* Edition Pauthier. Paris 1865. p. 532). Since the 16. century a lignaloes is brought into the market from Cochinchina and Siam under the Malayan name *Kalambak.* It is obtained from the leguminous tree *Aloexylon Agallochum,* D. C. The wood of this tree resembles that of *Aquillaria Agallocha,* Roxb. and for a long time it was used medicinally and for perfume purposes under the name *Lignum aloes* or *Lignum agalli veri.* According to Möller the genuine lignaloes is odorless and hence contains no volatile oil. Hence the *oleum ligni aloes* of the spice ordinance of Ulm of 1596 (Reichard, *Beiträge zur Geschichte der Apotheken.* Ulm 1825. p. 208) must have been distilled from a different wood.

The wood of *Gonystylus Miquelianus,* T. and B. (N. O. *Thymelaceæ*) is likewise to be regarded as a genuine lignaloes. In European countries the *lignum aloes* is no longer in use. In British India, China and the Dutch archipelago it finds extended use even to-day. (Boorsma, l. c. p. 2.)

[1]) Flückiger and Hanbury, Pharmacographia. II. ed., p. 561.

[2]) Flückiger, *Pharmakognosie.* III. ed., p. 612.

[3]) G. Fendler, *Inaug. Dissertat.* Rostock 1900. p. 2.

[4]) Trommsdorff's Neues Journ. der Pharm. **26**, II. (1833), 136.

like purposes, it is frequently mentioned in literature.[1]) During the middle ages, mastic from Chios, Cyprus[2]) and Samos[3]) was one of the highly prized condiments. It was chewed and much used in the preparation of compound balsams. Hence it is referred to in Arabian medical treatises and later treatises on distillation as *Granomastice.*[4]) Occasionally it is mentioned in connection with and at times confounded with frankincense as *Thus.*

Distilled oil of mastic, probably obtained by dry distillation, is first mentioned about the middle of the 15. century.[5]) Such an empyreumatic oil of mastic is also mentioned in the inventory of the *Rathsapotheke* in Braunschweig of the year 1518.[6]) Ryff[7]) and Gesner[8]) distilled mastic with wine. In the drug ordinances oil of mastic is first mentioned in that of Berlin of 1574, in books on medicine in the *Pharmacopœa Augustana* of 1480 and in the *Dispensatorium Noricum* of 1589. Later the oil went out of use almost altogether. Recently it is being used in Turkey for the preparation of a liquor.

GURJUN BALSAM OIL.

In India, gurjun balsam has been in use for a long time. The attention of Europeans was first directed to gurjun balsam

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[1]) Esekiel, 27:17. — Herodoti *Historiarum libri.* Lib. IV, 177. — Theophrasti *Historia plantarum,* Lib. IX, cap. 1 and 4. — Plinii *Naturalis historiæ libri.* Lib. XII, cap. 36. Editio Littré, vol. 1, p. 487. — Plutarchii *Moralia, Isis et Osiris.* Editio Parthey. 1850. p. 143 and 276. — Avicennæ *Libri in re medica omnes.* Venetiis. 1546. Lib. XI, cap. 462. — Palladii *De re rustica.* Editio Nisard. 1877. p. 626.

[2]) W. Heyd, *Geschichte des Levantehandels im Mittelalter.* 1879. Vol. 2, p. 617.

[3]) *Geographie d'Edrisi, traduite par* Amédée Jaubert. 1836. Vol. 2, p. 27. — Meyer, *Geschichte der Botanik.* 1856. Vol. 3, p. 299.

[4]) Guérard, *Polyptique de l'abbé* Irminon. Paris 1844. Vol. 2, p. 336. — Pfeiffer, *Zwei deutsche Arzneibücher aus dem 12. und 13. Jahrhundert.* In *Sitzungsberichte der kaiserl. Akademie der Wissensch. zu Wien.* 42 (1863), 110—162. (Hæser, *Geschichte der Medizin.* 1875. Vol. 3, p. 663.)

[5]) Saladini *Compendium aromatariorum.* Venetii 1488. Index.

[6]) Flückiger, *Pharmakognosie.* 1891. p. 119.

[7]) Gualtherus Ryff, *New gross Destillirbuch.* 1545. Fol. 181.

[8]) Euonymi Philiatri *Ein köstlicher theurer Schatz.* 1555. p. 237.

by Franklin[1]) in 1811 and by Wm. Ainslie[2]) in 1813. Its source and method of preparation, however, were first described by Wm. Roxburgh[3]) in 1827.

Its similar action to copaiba balsam was made known in India by the physician O'Shaughnessy[4]) as early as 1812. It acquired a considerable reputation in India as a remedy against lepra, later also in England in dermatological[5]) practice.

OIL OF LADANUM.

The ladanum resin, used since antiquity[6]) as incense and embalming agent, is an exudation of the bush-like plants *Cistus creticus,* L., *C. ladaniferus,* L. and other species of the N. O. *Cistaceæ* indigenous to Asia Minor, Crete, Cyprus and a few other islands off the coast of Asia Minor. Up to the beginning of the 19. century it was an officinal drug, valued for its pleasant odor. It is often mentioned in literature[7]) along with the ancient aromatics, storax, myrrh and frankincense. Not infrequently, especially in the translations of the Bible, it has been confounded with galbanum.[8]) Lately it has gone almost completely out of use.

Ladanum oil, distilled at first with wine or spirits of wine *(aqua vitæ),* was already known to Walter Ryff,[9]) Conrad Gesner,[10])

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[1]) Franklin, Tracts on the dominions of Ava. London 1811. p. 26.

[2]) Wm. Ainslie, *Materia medica* of Hindoostan. Madras 1813. p. 186.

[3]) Roxburgh, Plants of the coast of Coromandel. 1828. Vol. 3, p. 10 and plate 113.

[4]) Bengal Dispensatory, Calcutta. 1842. p. 22.

[5]) Pharmaceutical Journ. III. 5 (1875), 729.

[6]) Herodoti *Historiarum libri novem.* Lib. III, 107, 112.

[7]) Plinii *Naturalis historiæ libri.* Lib. XII, cap. 37 and 44. — Dioscoridis *De materia medica libri quinque.* Lib. I, cap. 23. Edit. Kühn-Sprengel 1829. p. 120. — Doüet d'Arcq, *Comptes de l'Argenterie des rois de France.* 1851, p. 19. — Heyd, *Geschichte des Levantehandels im Mittelalter.* 1879. vol. 2, p. 614. — Schrader, *Monatsberichte der Berliner Akademie der Wissenschaften,* 1881, 413. — Thiselton Dyer, Pharmaceutical Journ. III. 15 (1884), 301 and 16 (1885), 386 and 779.

[8]) W. Smith, Dictionary of the Bible. London. Vol. 2 (1863), p. 450. — Rosenmüller, *Handbuch der biblischen Altertumskunde.* Vol. 4 (1830), p. 156.

[9]) Gualtheri Ryff, *New gross Destillirbuch.* 1545. fol. 179.

[10]) Euonymi Philiatri *Ein köstlicher theurer Schatz.* 1555. p. 237.

Hieronymus Rubeus,[1]) and to Porta.[2]) It was taken up in medical books, first in the *Dispensatorium Noricum* of the year 1589 and in the *Pharmacopœa Augustana* of the year 1613.

CANELLA OIL.

When first introduced into Europe from the new world, canella bark, from *Canella alba,* Murray, was regarded as a kind of cinnamon bark. Later is was confounded with other barks, more particularly with Winter's bark, from *Drimys Winteri,* Forst. Canella bark was described as early as 1605 by Clusius[3]) of Leyden. In 1690 Dale[4]) called attention to its being mistaken for Winter's bark. In 1694 Pomet[5]) confounded canella bark with that of *Cinnamodendron corticosum,* Miers[6]) of St. Thomas. The latter was also repeatedly confounded with Winter's bark, even as late as the Paris Exposition of 1855.

In all probability canella oil was first distilled in 1707 by Sloane in England, later by Henry[7]) in 1820. However, it appears to have found no application. It was examined by Meyer and von Reiche[8]) in 1843, later by Bruun[9]) and by Williams.[10])

OIL OF CLOVES.

With cinnamon, nutmeg and pepper, cloves belong to the oldest known spices. As such they are mentioned in Chinese,

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[1]) Hieronymi Rubei Ravennatis *De destillatione liber, in quo stillatitiorum liquorum, qui ad medicinam faciuntur, methodus ac vires explicantur.* Basiliæ 1581. cap. 5, fol. 146.

[2]) Portæ *Magiæ naturalis libri viginti.* 1564. p. 387.

[3]) Caroli Clusii *Exoticorum libri decem.* Antverpiæ 1605. p. 78.

[4]) Dale, *Pharmacologia seu manuductio ad Materiam medicam.* London 1693. p. 432.

[5]) Pierre Pomet, *Histoire générale des Drogues.* Paris 1694. Tom. 1, p. 130.

[6]) Annals and Magazine of Natural History, May 1858. — Miers, Contributions to Botany. Vol. 1, p. 121. — Grisebach, Flora of the British West Indian Islands. Vol. 1, p. 109.

[7]) Trommsdorff's Taschenbuch f. Chemiker und Pharmazeuten **24** (1821), 101. — Berliner Jahrbuch d. Pharm. **24** (1821), I. 166.

[8]) Liebig's Annalen **47** (1843), 224.

[9]) Proceed. Wisc. Pharm. Assoc. **1893**, 36.

[10]) Pharm. Rundschau (New York) **12** (1894), 183.

Indian and Sanscrit literature.[1]) Strange as it seems, they are, however, not referred to in Egyptian and Hebrew literature. The earliest reference to cloves in European literature appears to be found in that of Rome.[2])

Among the presents sent in 315 by the Emperor Constantine to the Bishop Silvester, "Cariophylæ"[3]) are mentioned. In the *Christiana topographia* compiled by Kosmos Indiopleustes about the year 545, cloves are mentioned as coming from China and Ceylon.[4])

Cloves being used extensively in Rome, the Roman physican Alexander Trallianus, who lived in the 6. century, employed them as medicament.[5]) A century later, Paulus Æginatus, a Greek physician, described them as spice and as medicament.[6]) Cloves are repeatedly mentioned in the literature of the 8., 9. and 10. centuries,[7]) but, in the European countries their origin was not definitely known. The Moluccas and their products, however, became better known after the discovery of the direct sea route by the Portuguese toward the close of the 15. century; more particularly through the travelogues of Ludowicio de Barthema of Bologna[8])

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[1]) Heyd, *Geschichte des Levantehandels im Mittelalter.* 1879. Vol. 1, pp. 90 and 99; Vol. 2, p. 593. — Schumann, *Beiträge zur Kenntniss der Etymologie und Geschichte der Gewürznelke. Jahrbuch des botanischen Gartens und Museums in Berlin.* Vol. 3 (1881—1884), pp. 119—140.

[2]) Plinii *Naturalis historiæ libri.* Lib. XII, cap. 15. "*Est etiam nunc in India piperis grani simile quod vocatur garyophyllon, grandius fragiliusque. Tradunt in Indico luco id gigni. Advehitur odoris gratia.*"

[3]) *Liber pontificalis, seu de gestis Romanorum Pontificum.* Romæ 1724. Vol. 1, p. 94. — Editio Duchesne. Paris 1886. Vol. 1, p. 177.

[4]) *Christiana topographia.* Editio Migne, *Patrologiæ cursus completus. Series Græca* 1850. Vol. 88, p. 446.

[5]) Alexandri Tralliani *Opera.* Editio Puschmann. Vol. 1, pp. 430 and 613; Vol. 2, pp. 290 and 545.

[6]) "*Caryophyllum quasi dicas nucifolium, . . . ex India veluti flores cujusdam arboris festucacei et nigri sunt . . . odorati acres.*" Pauli Æginati *Opera, a* Joanne Guintero Andernaco *conversa.* Lib. VII: *De re medica,* cap. 3, p. 299b. — *Compendii medici septem.* Editio Paris 1532.

[7]) Benedictus Crispus, *Poematicum medicum.* Editio Migne, *Patrologiæ cursus.* 1850. Vol. 89. — Pardessus, *Diplomata, Chartæ* etc. Paris 1849. Vol. 2, p. 309. — W. Heyd, *Geschichte des Levantehandels.* 1879. Vol. 1, p. 99. — *Recueil des historiens des croisades.* Lois 1843, p. 173.

[8]) W. Heyd, *Geschichte des Levantehandels im Mittelalter.* 1879. Vol. 2, p. 296.

and those of Pigafetta,[1]) the companion of Magellan. Both described from their own observations not only the clovetree, but also the collection of the cloves, the former in 1504, the latter in 1521.

From the beginning of the 16. century to the close of the 17. century the commerce in cloves was almost exclusively in the hands of the Portuguese. Having crowded out the Portuguese, the Dutch in 1605 attempted to make a monopoly of the trade in cloves. With this end in view they destroyed the clove plantations in the Moluccas with the exception of those in the island of Amboina.[2])

However in 1769 Poivre, the French governor of Bourbon and Mauritius, succeeded in transplanting clove and nutmeg trees from Amboina to his islands.[3]) From here, in 1793, cultivated specimens were transplanted to French Guiana (Cayenne), Martinique, St. Vincent, Domingo and Trinidad; also about the same time to Zanzibar.[4])

As ornamental plants, clove trees were introduced into Europe, more particularly into Venice, about the beginning of the 16. century.[5])

On account of the high price of cloves, the aromatic stems remaining after the picking of the blossoms were introduced into commerce as early as the beginning of the 15. century.[6]) However, they appear to have been used primarily for the

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[1]) Ramusio, *Raccolta delle navigationi et viaggi.* Venetia 1554, fol. 404b. Edit. Hakluyt Society, London 1874, p. 134.

[2]) Hasskarl, *Neuer Schlüssel zu Rumpfs Herbarium amboinense.* 1866. Vol. 2, p. 17.

[3]) Tessier, *Sur l'importation du giroflier des Moluques aux Isles de France, de Bourbon et de Sechelles, et de ces isles à Cayenne. Observations sur la physique.* Paris. juillet 1779.

[4]) *Las Colonias espanoles, Islas Filipinas.* Madrid 1880, pp. 72 and 122. — Guillain, *Documents sur l'histoire, la géographie et le commerce de l'Afrique orientale.* Paris 1856. Tom. 3, p. 318. — Annales de Chim. et Phys. I, 7 (1790), 1—21.

[5]) Conrad Gesner, *Horti Germaniæ.* 1562. fol. 288.

[6]) Pegolotti, *Della decima e delle altre gravezze imposte dal comune di Firenze.* 1766. Vol. 3, p. 98. — Luciano Banchi, *I porti della maremma Senese durante la republica.* Archivio storico italiano. XII. parte 2 (1880), p. 90. — Bonaini, *Statuti inediti della città di Pisa.* Firenze 1857. Vol. 3, p. 106. — Henschel, *Janus.* Breslau 1846. Vol. 1, p. 40.

adulteration of clove powder.[1]) Nevertheless Porta in his writings about the middle of the 16. century, mentions that he had obtained an oil distilled from the stems.[2])

Oil of cloves appears to have been distilled for the first time in the 15. century, but probably, like other aromatics, with wine or the addition of spirits of wine. This method of distillation was described by Walter Ryff,[3]) Conrad Gesner,[4]) Adam Lonicer[5]) and others. Gesner also mentions the distillation of the oil, *per descensum.*[6]) The pure oil however was, shortly afterwards distilled by Valerius Cordus,[7]) by Winther of Andernach[8]) and by Porta.[9]) In the *Dispensatorium Noricum,* oil of cloves was admitted with a number of other oils in the edition of 1589. In drug ordinances it was first mentioned in that of the city of Berlin in 1574.[10])

The yield of volatile oil from cloves was determined by Boerhaave,[11]) Fr. Hoffmann,[12]) Caspar Neumann[13]) and H. Tromms-

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[1]) Baader, *Nürnberger Polizeiverordnungen aus dem 13. bis 15. Jahrhundert.* 1861. pp. 19 and 139. — Flückiger, *Zur älteren Geschichte der Pharmazie in Bern.* Schaffhausen 1862, p. 21.

[2]) Baptistæ Portæ *Magiæ naturalis libri viginti. Liber de destillatione.* Edit. Romæ. 1608. p. 75.

[3]) Gualtherus Ryff, *New gross Destillirbuch.* 1545. fol. 88.

[4]) Euonymi Philiatri *Ein köstlicher theurer Schatz.* Zürich 1555. pp. 227, 232. Editio 1557, p. 288.

[5]) Adami Loniceri *Kräuterbuch und künstliche Conterfeyungen.* Editio Peter Uffenbach. 1551. p. 546.

[6]) Euonymi Philiatri *Ein köstlicher theurer Schatz.* Editio 1557. p. 288.

[7]) Val. Cordus, *De artificiosis extractionibus liber.* Argentorati 1561. pag. 226.

[8]) Guintheri Andernaci *Liber de veteri et nova medicina.* Basiliæ 1571. fol. 630—635.

[9]) Jo. Baptistæ Portæ *Magiæ naturalis libri viginti. Liber de destillatione.* Antverpiæ 1567. pp. 184 and 379.

[10]) *Estimatio materiæ medicæ utriusque genus . . . in gratiam et usum publicum civitatum Marchiæ Brandenburgensis. Autore* Matthæo Flacco. Berolini anno 1574.

[11]) Hermannus Boerhaave, *Elementa chemiæ, quæ anniversario labore docuit in publicis privatisque scholis.* 1732. Vol. 2, p. 114.

[12]) Frederici Hoffmannii *Observationum physico-chemicarum selectiorum.* 1722. Vol. 1, p. 11. — *De caryophyllis aromaticis.* Halæ 1701.

[13]) Caspar Neumann, *Chymia medica dogmatico-experimentalis.* Editio Kessel. 1749.

dorff.[1]) Boerhaave remarked that the variation in yield obtained on distillation was somethimes due to the adulteration with cloves which had been exhausted of their oil by distillation and then dried again.[2])

Bonastre[3]) in 1827 recognized the acid nature of clove oil and investigated the salt-like compounds of eugenol that were formed with alkalies. Ettling and Liebig[4]) first showed that besides *"Nelkensäure"*, eugenic acid, there is also present in the oil an indifferent body. Of the older investigations which were restricted mostly to eugenol, those of Dumas[5]) (1833), Böckmann[6]) (1838), Calvi[7]) (1856), Brüning[8]) (1857), Williams[9]) (1858), Hlasiwetz and Grabowski[10]) (1866) and Erlenmeyer[11]) (1866) may be mentioned.

OIL OF CAJEPUT.

Oil of cajeput appears not to have been brought to Europe until the beginning of the 17. century, when the Dutch took possession of the Moluccas. The first accurate account of the source of this oil was given by the missionary Valentyn,[12]) and the merchant Georg Eberhard Rumpf of Hanau, both living in Amboina. The latter was an enthusiastic plant collector, and author of the first flora of the island Amboina.[13]) According to

[1]) Trommsdorff's Journ. der Pharm. **23**, II (1814), 23.

[2]) Pfaff, *System der Materia medica*, **6** (1821), 433.

[3]) Journ. de Pharm. II. **13** (1827), 464 and 513; Poggendorff's Annalen **10** (1827), 609 and 611.

[4]) Liebig's Annalen **9** (1834), 68.

[5]) Ann. de Chim. et de Phys. II. **53** (1833), 165. — Liebig's Annalen **9** (1834), 68.

[6]) Liebig's Annalen **27** (1838), 155.

[7]) *Ibidem* **99** (1856), 242.

[8]) *Ibidem* **104** (1857), 202.

[9]) *Ibidem* **107** (1858), 238.

[10]) *Ibidem* **139** (1866), 95.

[11]) Zeitschr. f. Chemie **9** (1866), 95.

[12]) *Verhandl. van der Geschiedenissen en Zaaken in Amboina.* Vol. 3, p. 193.

[13]) G. E. Rumphii *Herbarium amboinense, plurimas complectens arbores frutices, herbas, plantas terrestres et aquaticas, quæ in Amboina et adjacentibus reperiuntur insulis . . . (Het Amboinsche Kruid boek).* It was not until forty years after the death of Rumpf that this work was published by Johann Burmann, Professor of Botany in Amsterdam. It appeared during the years 1741—1755 in six folios with 587 plates. The reference to cajeput oil will be found in vol. 2, p. 72.

Rumpf's[1]) statement, the Malays and Javanese were acquainted with oil of cajeput long before the Moluccas, the Banda and the Sunda islands were taken possession of, and used it as a diaphoretic. In Europe, the oil at first appears to have found no application. The first notice of such is by the physician J. M. Lochner in Nürnberg, and by the apothecary Joh. Heinr. Link in Leipzig. The former mentioned the oil in 1717,[2]) the latter had bought the oil about the same time as a novelty from the physician of a ship which had just returned from the East Indies.[3]) From this time on cajeput oil was used medicinally in Germany and was introduced into the apothecary shops[4]) and mentioned in price ordinances and in medical works. For some time, however, it remained rare and expensive[5]) and not until 1730 did larger quantities of the oil come into the European market via Amsterdam.[6]) In Germany, it was at first called *Oleum Wittnebianum* after a merchant E. H. Wittneben of Wolfenbüttel, who had lived several years in Batavia, and who, in German essays,[7]) had recommended the oil as a valuable remedial agent.

In France and in England oil of cajeput was not used until the beginning of the past century.

The first detailed account of the simple methods of distillation of cajeput oil used on the Moluccas, was given by the French traveler Labillardière,[8]) who had visited the island of Buru in 1792. The use of copper stills and condensers gave rise to a green

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[1]) Rumphii *Herbarium amboinense* Vol. 2, chapt. 26.

[2]) *Academiæ Natural. Curiosor. Ephemerides Centuri* V, VI. Nürnberg 1717. p. 157.

[3]) *Sammlung von Natur und Medizin, wie auch von Kunst- und Literaturgeschichten.* Leipzig and Budissin. 1719. p. 257.

[4]) Flückiger, *Dokumente zur Geschichte der Pharmazie.* 1876. pp. 88 and 90.

[5]) Abraham Vater, *Catalogus variorum exoticorum rarissimorum.* Wittenbergæ 1726.

[6]) Schendus van der Beck, *De Indiæ rarioribus. Acta natural. Curiosor.* Vol. 1. *Appendix* 1725. p. 123.

[7]) This designation was largely due to an erroneous statement in the *Commercium litterarium* published by I. C. Götz in 1731 in Nürnberg. In it Wittneben is mentioned as discoverer of the oil of cajeput. This misstatement was not corrected until twenty years later in the dissertation of Martini, p. 178, footnote 4.

[8]) Travels in the East Indian Archipelago. London 1868. p. 282.

color due to a small amount of copper in the oil. The cause of this coloration was first detected by the apothecaries Hellwig[1]) in Stralsund in 1786, Joh. Friedr. Westrumb[2]) in Hameln in 1788, and Trommsdorff[3]) in Erfurt in 1795.[4])

EUCALYPTUS OIL.

The oil of *Eucalyptus piperita,* Sm., is the oldest oil of eucalyptus leaves, being mentioned as early as 1790.[5]) In 1853 the botanist Ferdinand von Müller recommended to the Province of Victoria the distillation of the leaves of the eucalyptus species.[6]) Bosisto,[7]) who had distilled experimentally the dried leaves in London, established in 1854 the first factory in Australia,[8]) and is, therefore, to be considered as the founder of this extensive industry.

Australian eucalyptus oil came into the German market about 1866 without any botanical reference as to its source. Probably it was principally the distillate from *Eucalyptus amygdalina.*

Eucalyptus Globulus was discovered in Tasmania in 1792 by Labillardière and introduced into Europe in 1856 by Ramel.[9]) The oil of this species was obtained on a large scale, first in southern France, Algiers and California, and has become a staple article of commerce only since the early eighties of the past century.

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[1]) Crell's Chem. Annalen **1786**, II. 141.

[2]) Joh. F. Westrumb, *Kleine physikalisch-chemische Abhandlungen.* Leipzig 1788. Vol. 2, No. 1.

[3]) Trommsdorff's Journ. der Pharm. **2**, I. (1795), 115.

[4]) Earlier contributions on cajeput oil are: D. Martini, *Dissertatio epistolaris, qua de oleo Wittnebiano seu Kajeput ejusque saluberrimis effectibus exponit.* Guelpherb. 1751. — Joh. Fr. Cartheuser, *De oleo cajeputi. Dissertatio physico-chemica.* Erfurt 1754.

[5]) Journal of a Voyage to New South Wales by John White. Surgeon-General to the Settlement, published 1790.

[6]) Ferd. v. Müller, Eucalyptographia. Melbourne 1879. — Ferd. v. Müller, Select Extra-Tropical Plants. IX. Edit. Melbourne 1895. p. 184.

[7]) Bosisto, Transact. Royal Soc. Victoria **1861—64**.

[8]) Bericht von Schimmel & Co. October **1886**, 13.

[9]) Bentley, On the characters, properties and uses of *Eucalyptus Globulus.* London 1854. — Sawer, *Odorographia.* London 1894. Vol. 2, p. 241.

OIL OF CORIANDER.

The coriander plant, *Coriandrum sativum,* L., cultivated in many countries and in nearly all climates, was used as a kitchen spice even before the Christian Era.[1]) As such, coriander fruit is mentioned repeatedly in Sanscrit writings, in the Bible[2]) and in later Roman writings.[3]) Together with other offerings,[4]) coriander fruit has also been found in old Egyptian monuments of the 10. century B. C.

Coriander is also mentioned among the useful plants recommended for cultivation by Charlemagne,[5]) but it appears to have received, as with the Arabians so also with the Germans in the middle ages, only slight consideration. The fruit is again mentioned in the medical[6]) and distilling books of the 16. century, although it had been employed now and again as a kitchen spice.[7])

The distilled oil of coriander appears to have been first obtained by Porta[8]) in the 16. century who prepared it after moistening the fruit with *aqua vitæ*. In the price ordinances of spices, the oil is first included in that of Berlin of 1574 and that of Frankfurt-on-the-Main of 1587; also in the 1589 edition of the *Dispensatorium Noricum.*

Coriander oil was investigated in 1785 by Hasse,[9]) in 1835

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[1]) Prosper Alpinus, *De plantis Ægypti liber.* Venetii 1591. Cap. 42, p. 61.

[2]) Exodus, 16 : 31. — Numbers 11 : 7.

[3]) Theophrasti *Opera quæ supersunt omnia. Historia plantarum.* Lib. VI. 4. Editio Wimmer. 1866, p. 117. — Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829, p. 410. — Plinii *Naturalis historiæ.* Lib. XIX. 35 and XX. 82. Editio Littré. Vol. 1, p. 729 and Vol. 2, p. 33. — Catonis *De re rustica* Libri XII. Cap. 119 and 157, Edit. Nisard, p. 34 and 54. — Columellæ *De re rustica.* Cap. 10 and 11. Edit. Nisard, pp. 414, 442. — Palladii *De re rustica.* Lib III. 24. Lib. IV. 9. Editio Nisard, p. 567 and 583.

[4]) G. Schweinfurth, in the *Berichte der deutsch. botan. Gesellschaft,* 2 (1884), 359.

[5]) See footnote 8, p. 133.

[6]) K. Regel, *Das mittelhochdeutsche Gothaer Arzneibuch.* 1873. p. 13.

[7]) Hirsch, *Danzigs Handels- und Gewerbe-Geschichte.* Leipzig 1858. p. 243.

[8]) Jo. Bapt. Portæ *Magiæ naturalis libri viginti.* Lib. X. *"De destillatione."* Romæ 1608, p. 379.

[9]) Crell's Chemische Annalen 1785, I. 422.

by Trommsdorff,[1]) in 1852 by A. Kawalier[2]) and in 1881 by B. Grosser.[3]) A true insight into its composition, however, was brought about by the investigations of Semmler (1891) and of Barbier (1893).

OIL OF CUMIN.

During antiquity both the Roman or mother caraway of the Orient, *Cuminum Cyminum,* L., and the common caraway were used as spices. In literature, *e. g.* in the translations of the Bible, both have been confused, not only the one with the other, but both with the seeds of the black caraway, the *Nigella.*[4]) According to statements in the Papyrus Ebers, cumin and caraway seeds have been found in Egyptian graves. Dioscorides[5]) describes both. In Spain both cumin and caraway were cultivated by the Arabians during the 12. century.[6]) Both are enumerated in the market ordinances of Brugge in Flandria of 1307,[7]) and of Danzig in the beginning of the 15. century.[8]) In 716 cumin seed is mentioned among the objects of tribute to be paid to the Norman monastery Corbie.[9]) During the early part of the 13. century, Edrisi, the geographer, mentions both fruits as products of Morocco and Algiers.[10]) Both were used in England toward the beginning of the 13. century,[11]) and in Germany in the 15. century.[12])

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[1]) Arch. der Pharm. **52** (1835), 114.

[2]) Liebig's Annalen **84** (1852), 351; Journ. f. prakt. Chem. **58** (1853), 226.

[3]) Berl. Berichte **14** (1881), 2485.

[4]) Isaiah, 28 : 25 to 27. — Rosenmüller, *Handbuch der biblischen Altertumskunde.* Leipzig 1830. Vol. 4, p. 100. — Plinii *Naturalis historiæ libri.* Lib. XIX, cap. 8.

[5]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel 1829. Vol. 1, 407.

[6]) Ibn-al-Awam, *Livre d'agriculture, traduit par* Clément-Mullet. 1864. Vol. 2, p. 242 and 244.

[7]) Warnkönig, *Histoire de la Flandre.* 1836. Vol. 2, p. 512 and vol. 4, p. 449.

[8]) Hirsch, *Danzigs Handels- und Gewerbegeschichte.* Leipzig 1858, p. 243.

[9]) Pardessus, *Diplomata, Chartæ,* etc. Paris 1849, p. 307.

[10]) Edrisi, *Description de l'Afrique et de l'Espagne, traduit par* Dozy *et* De Goeje. Leyden 1866. pp. 75, 97, 150.

[11]) Rogers, History of Agriculture and Prices in England. 1876. Vol. 1, p. 631 and vol. 2, pp. 543—547. — Riley, *Monumenta Guildhalli Londoniensis.* 1859. p. 224.

[12]) Thomas, *Fontego dei Tedeschi in Venezia.* 1874. p. 252.

The volatile oil of cumin is included in the price ordinances of Berlin of 1574, and of Frankfurt of 1582, also in the 1589 edition of the *Dispensatorium Noricum.*

OIL OF CELERY SEED.

Celery was known at the beginning of the Christian era.[1]) As a kitchen spice it is recommended in the *Capitulare* of Charlemagne 812,[2]) as a medicament by the abbess Hildegard[3]) in the early part of the 12. century.

During the period of the distilled waters, celery water was used as a domestic remedy and is repeatidly described in the treatises on distillation of the 15. and 16. centuries.[4])

Distilled oil of celery appears to have come into use during the middle of the 16. century. In the spice and drug ordinances it is first mentioned in that of Frankfurt-on-the-Main of 1587, also in the 1589 edition of the *Dispensatorium Noricum.*

The apiol which crystallizes from the oil at lower temperatures was observed as early as 1715 by the apothecary Christian Link[5]) of Leipzig, again in 1745 by A. Fr. Walther.[6])

The oils from the fresh herb and seeds was distilled by Pabitzky[7]) in 1754. Both the oils and the crystals separating therefrom are further mentioned by Dehne,[8]) Bolle,[9]) and

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[1]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, p. 413. — Plinii *Naturalis historiæ libri.* Lib. XX, cap. 47. Editio Littré. Vol. 2, p. 18. — Apicius Cælius in Meyer's *Geschichte der Botanik.* Vol. 2, p. 242. — Dierbach, *Flora Apiciana.* 1831. p. 52.

[2]) *Capitulare de villis et cortis imperialibus.* Anno 812. Comments by A. Thær in Fühling's Landwirtschaftliche Zeitung. Berlin 1878. 241—260.

[3]) Hildegardis *Abbatissæ Subtilitatum diversarum naturarum creaturarum libri novem.* Editio Migne. *Patrologiæ cursus completus.* Paris 1855. p. 1158.

[4]) Hieronymus Brunschwig, *Liber de arte destillandi.* 1500. fol. 87.

[5]) *Sammlung von Natur und Medicin, wie auch von Kunst- und Literaturgeschichten.* Leipzig and Budissin 1716.

[6]) A. Fr. Walther, *De oleis vegetabilium essentialibus. Dissertatio.* Leipzig 1745. p. 17.

[7]) Braunschweiger Anzeiger 1754, 1205.

[8]) Crell's Chem. Journ. 1778, I. 40.

[9]) Arch. der Pharm. 29 (1829), 168.

Bley.[1]) The first elementary analysis of the "celery camphor" was made by Blanchet and Sell.[2]) It was further investigated by Lœwig and Weidmann.[3])

OIL OF CARAWAY.

Like other related umbelliferous plants, caraway or *Carum Carvi,* L., has been cultivated in Europe and Asia since antiquity and used as a kitchen spice.[4]) With these other umbelliferous plants, and at times confounded with the one or the other, it is frequently mentioned in ancient literature,[5]) also in midæval medical books and in the treatises on distillation. During the beginning of the 12. century caraway was cultivated by the Arabians in Morocco[6]) and Spain.[7]) About the same time caraway was praised as a medical agent by the abbess Hildegard.[8]) As such it was introduced into the German medical treatises of the 12. and 13. centuries.[9]) In England caraway was cultivated during the 13. century and used as a kitchen spice.[10])

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[1]) Trommsdorff's Neues Journ. der Pharm. 14, II. (1827), 134.

[2]) Liebig's Annalen 6 (1833), 301.

[3]) Liebig's Annalen 32 (1839), 283.

[4]) See also oil of cumin on p. 169. Plinii *Naturalis historiæ libri.* Lib. XIX, cap. 8. *Condimentorum omnium stomachi fastidiis cuminum amicissimum.*

[5]) Isaiah, 28:25 and 27. — Matth., 23:23. — Dioscoridis, *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, p. 406. — Plinii *Naturalis historiæ libri.* Lib. XIX, 49. Editio Littré. Vol. 1, p. 736. — Palladii *De re rustica.* Lib. XII, p. 51. — Editio Nisard, *Les agronomes latins.* Paris 1877. p. 486.

[6]) Edrisi, *Description de l'Afrique et de l'Espagne. Texte arabe avec une traduction, par* Dozy and De Goeje. Leyden 1866. pp. 75, 97, 150.

[7]) Ibn-el-Baitar, *Djâmi el-mufridât.* Translated by Sontheimer. 1840. Vol. 2, p. 368. — Leclerc's translation. Vol. 3, pp. 164, 197, 198. — Ibn-al-Awam, *Livre d'agriculture.* Translated by Clément-Mullet. 1864. Vol. 2, pp. 242 and 244.

[8]) Hildegardis *Abbatissæ Subtilitatum diversarum naturarum creaturarum libri novem.* Editio Migne. 1855. p. 1158.

[9]) Pfeiffer, *Zwei deutsche Arzneibücher aus dem 12. und 13. Jahrhundert. Sitzungsberichte der kais. Akad. der Wissenschaften in Wien.* 1863. p. 14. (Häser, *Geschichte der Medizin.* 1875. Vol. 1, p. 663.)

[10]) Meddygon Myddfai. Published at Llandovery. 1861. pp. 158, 354. — Rogers, History of Agriculture and Prices in England. 1876. Vol. 1, p. 631 and Vol. 2, p. 543—547.

In municipal spice ordinances, caraway is first mentioned in that of Brugge[1]) of 1304. It is also enumerated in that of Danzig[2]) of the middle of the 15. century.

Distilled oil of caraway is first mentioned in the price ordinance of Berlin of 1574, and that of Frankfurt of 1589, also in the 1589 edition of the *Dispensatorium Noricum.*

OIL OF AJOWAN.

Apparently ajowan[3]) was first brought to Europe in 1549.[4]) In 1693 it was used for medical purposes in London.[5]) In 1773 it is mentioned by Percival[6]) of England.

OIL OF ANISE.

Anise is one of the spice plants known to, and used during, antiquity. It is mentioned in the Vedas and in the Bible.[7]) The cultivation of anise in Egypt and in the Island of Crete is recorded in the writings of Dioscorides, Columella and Pliny;[8]) its medicinal use in those of Scribonius Largus, Marcellus Empiricus, and Alexander Trallianus. In the 4. century Palladius[9]) gave directions for its cultivation. In 970 Asia Minor and the mediterranean countries[10]) supplied anise, during the 12. century Spain also.[11]) Trough his *Capitulare* of 812 Charlemagne stimulated

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[1]) Warnkönig, *Histoire de la Flandre.* 1836. Vol. 2, p. 512 and vol. 4, p. 449.

[2]) Hirsch, *Danzigs Handels- und Gewerbsgeschichte.* Leipzig 1858. p. 243.

[3]) Flückiger and Hanbury, Pharmacographia. London 1879. p. 303.

[4]) Anguillara, *Semplici Vinegia.* 1561. p. 130.

[5]) S. Dale, *Pharmacologia seu manuductio ad Materiam medicam.* London 1693. p. 211.

[6]) Essays, Medical and Experimental II. (1773), p. 226.

[7]) Matth., 23:23. In the English version the original is translated as anise, whereas Luther translates it with dill. Comp. p. 180, footnote 2.

[8]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, p. 405. — Columellæ *De re rustica* in Nisard's *Les agronomes latins.* Paris 1877. — Plinii *Naturalis historiæ libri.* Lib. XX, 72—73.

[9]) Palladii *De re rustica libri* XIV. Lib. III, 14 and lib. IV, 9 In Nisard's *Les agronomes latins.* Paris 1877. pp. 569 and 583.

[10]) *Codex Vindobonensis, sive* Abn Mansur Mowafic (Alherri) *Heratensis liber fundamentarum Pharmacologiæ.* Editio F. R. Seligmann. Wien 1859. p. 21.

[11]) Ibn-al-Awam, *Livre d'agriculture,* translated by Clément-Mullet. 1864. Vol. 2, p. 249.

the cultivation of anise north of the Alps.[1]) In 1305 anise is enumerated among the dutiable spices in London,[2]) and toward the beginning of the 16. century anise and fennel were cultivated in England.[3])

On account of its property to solidify, distilled oil of anise has, no doubt, been noticed as long as anise has been used for the preparation of anise water. The distillation of the oil was, however, first described in the works of Hieronymus Brunschwig,[4]) Ad. Lonicer,[5]) Walter Ryff,[6]) Conrad Gesner,[7]) Hieronymus Rubeus[8]) and Porta.[9]) Valerius Cordus[10]) in 1540 called attention to the ready solidification of the oil. Nearly a century later Robert Boyle again described the "butter-like" solidification of anise oil.[11])

In medical books and ordinances anise oil is first mentioned in the *Pharmacopœa Augustana* of 1580, the *Dispensatorium Noricum* of 1589, and the Berlin ordinance of Matthæous Flacco of 1574.

The first accurate investigations of anise oil were undertaken by Th. de Saussure[12]) in 1820, by Dumas[13]) in 1833, by Blanchet and Sell[14]) in 1833, by A. Cahours[15]) in 1841, by

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[1]) A. Thær, *Übersetzung und Erläuterung des "Capitulare".* In Fühling's Landwirtschaftliche Zeitung. Berlin. April number 1878, pp. 241—260.

[2]) R. Thomson, Chronicles of London Bridge. 1827. p. 156.

[3]) Boorde, Dyetary of helth. 1542. — Reprinted for the Early English Text Society. London 1870. p. 284.

[4]) Hieronymus Brunschwig, *Liber de arte destillandi. De simplicibus.* Anno 1500. fol. 45.

[5]) See p. 49.

[6]) Gualtherus Ryff, *New gross Destillirbuch.* Frankfurt-on-the-Main 1567. fol. 186.

[7]) Euonymi Philiatri *Ein köstl. theurer Schatz.* Zürich 1555 pp. 227 and 301.

[8]) Hieronymi Rubei *Liber de destillatione, in quo stillatitiorum liquorum, qui ad medicinam faciuntur, methodus ac vires explicantur.* Basiliæ 1581. Cap. 5, pp. 113 and 143.

[9]) Giov. Bapt. Portæ *Magiæ naturalis libri viginti.* Romæ 1563. p. 379.

[10]) Valerii Cordi *De artificiosis extractionibus liber.* Editio Gesner. Argentorati 1561. fol. 226.

[11]) R. Boyle, *Historia fluiditatis.* London 1661. p. 15.

[12]) Annal. de Chim. et Phys. II. **13** (1820), 280; Schweigger's Journ. f. Chem. u. Phys. **29** (1820), 165.

[13]) Liebig's Annalen **6** (1833), 245.

[14]) *Ibidem* **6** (1833), 287.

[15]) *Ibidem* **41** (1842), 56; and **56** (1845), 177.

A. Laurent[1]) and Gerhardt[2]) in 1842. Gerhardt called the stearoptene of anise oil anethol and Cahours again pointed out the identity of the stearoptenes of anise and fennel oils, previously recognized by Blanchet.[3])

OIL OF FENNEL.

Fennel was known to the ancient Chinese, Indians and Egyptians who used it principally as kitchen spice. No mention is made of it in the translations of the Bible. It is frequently mentioned, however, as a garden and medical plant in Roman literature at the beginning of the Christian era,[4]) also in the treatises on medicine and distillation of the later middle ages.[5]) During the latter period fennel appears to have been cultivated and used more extensively than anise.

The oil of fennel has no doubt been known since the time of the preparation of the distilled waters. In the 16. century it appears to have been introduced along with fennel water as a remedy. Its preparation is described by Brunschwig[6]) and by

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[1]) Liebig's Annalen 44 (1842), 313.

[2]) *Ibidem* 44 (1842), 318; and 48 (1843), 234. — Journ. f. prakt. Chem. 36 (1845), 267.

[3]) Liebig's Annalen 41 (1842), 74.

[4]) Theophrasti, *Eresii Opera quæ supersunt omnia. De causis plantarum.* Edit. Wimmer. Vol. VI, 10, 3, pp. 16, 18, 99, 101, 310. — Dioscoridis, *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, pp. 406, 417. — Columella, *De re rustica* in Nisard's *Les agronomes latins.* Paris 1877. Lib. V, cap. 10, p. 303. — Plinii *Naturalis historiæ libri* XXXVII. *Lib.* XX. 95, 96. Editio Littré. Vol. 1, p. 334 and vol. 11, p. 39. — Palladii *De re rustica,* Editio Nisard, *Les agronomes latins.* 1877. Lib. III, 14, p. 568 and lib. XII, p. 486.

[5]) *Capitulare de villis et cortis imperialibus 812.* Translated and explained by A. Thær in Fühling's Landwirtschaftliche Zeitung. April number 1878, pp. 241—260. — Walafridi Strabonis *Hortulus.* In Choulant's *Macer Floridus, De viribus herbarum.* 1832. p. 148. — Ibn-al-Awam, *Livre d'agriculture,* translated by Clément Mullet. 1864. — Ibn-Baitar, *Sammlung der Rohstoffe.* Editio Leclerc, *Traité des Simples.* Paris 1881. Vol. II, p. 164. — Hildegardis *Abbatissæ Subtilitatum diversarum naturarum creaturarum libri novem.* Editio Migne. 1855. Fol. 1154 and 1156. — Pfeiffer, *Zwei deutsche Arzneibücher aus dem 12. und 13. Jahrhundert. Sitzungsber. der kais. Akademie der Wissensch. in Wien.* 42 (1863), 142. (Hæsers *Geschichte der Medicin.* 1875. Vol. 1, p. 663.)

[6]) Hieronymus Brunschwig, *Liber de arte destillandi. De simplicibus.* 1500. fol. 47.

Porta.[1]) In the municipal ordinances of drugs and spices it is first mentioned in that of Berlin of 1574 and of Frankfurt-on-the-Main of 1582; also in the *Pharmacopœa Augustana* of 1580 and the *Dispensatorium Noricum* of 1589.

Early investigations of fennel oil were made in 1779 by Heyer[2]) of Braunschweig, in 1792 by Gertinger[3]) of Eperies in Hungary, and in 1793 by Göttling of Jena and by Giese of Dorpat. Further observations, which like the above deal mainly with anethol, were made by Buchner[4]) and by Gœbel. Blanchet and Sell[5]) recognized in 1833 the identity of the stearoptenes from fennel and anise oils. This observation was corroborated in 1842 by Cahours.[6]) Wallach investigated fenchone, a body characteristic of fennel oil, and which possesses considerable theoretical interest on account of its similarity to camphor.

OIL OF LOVAGE.

As a kitchen spice, and possibly also for medicinal purposes, lovage was cultivated and used by the Romans.[7]) Its cultivation north of the Alps was no doubt caused by Charlemagne's *Capitulare* of 812. About the same time, the utility of the plant was praised by Walafried Strabo and Macer Floridus.[8]) The German medical treatises of the middle ages, beginning with that of the abbess Hildegard of the 12. century, make mention of lovage under various, partly corrupted names. In the treatises on distillation, the distillates of lovage are likewise mentioned.[9])

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[1]) Giov. Baptistæ Portæ *De destillatione libri* IX. Romæ 1563. p. 379.

[2]) Crell's Chem. Journ. **3** (1780), 102.

[3]) Göttling's Almanach für Scheidekünstler und Apotheker **14** (1793), 149.

[4]) Buchner's Repert. f. die Pharm. **15** (1823), 163.

[5]) Liebig's Annalen **6** (1833), 287.

[6]) Liebig's Annalen **41** (1842), 74; and Journ. für prakt. Chem. **24** (1841), 359.

[7]) Dioscoridis, *De materia medica libri quinque*. Editio Kühn-Sprengel. 1829. Vol. 1, p. 400. — Columellæ *De re rustica libri* XII. Lib. XII. 51. — Meyer, *Geschichte der Botanik*. 1855. Vol. 2, p. 74.

[8]) Walafridi Strabonis *Hortulus*. In Choulant's Macer Floridus, *De viribus herbarum una cum* Walafridi Strabonis, Othonis Cremonensis et Joannis Folcz *carminibus similis argumenti*. Lipsiæ 1832. pp. 141—156. — Meyer, *Geschichte der Botanik*. 1855. Vol. 3, p. 425.

[9]) Hieron. Brunschwig, *Liber de arte destillandi. De simplicibus*. 1500. fol. 70.

The oil distilled from the root appears to have come into use about the middle of the 16. century. It is mentioned as *Oleum Levistici* in the price ordinance of Frankfurt-on-the-Main of 1587, and as *Oleum Ligustici* in the 1589 edition of the *Dispensatorium Noricum.*

OIL OF ANGELICA.

Angelica appears to have first come into use as a spice plant during the 15. century,[1]) and was no doubt first used for the preparation of the distilled angelica water, the preparation of which is described in Brunschwig's[2]) and in later treatises on distillation.

The distilled oil of the roots was not prepared until the second half of the 16. century and is first mentioned in the price ordinance of Frankfurt in 1582 and in the *Dispensatorium Noricum* of 1589.

Oil of angelica root was investigated by L. A. Buchner[3]) in 1842, by F. Beilstein and E. Wiegand in 1882,[4]) by L. Naudin in 1883,[5]) and by G. Ciamician and P. Silber in 1896.[6])

OIL OF ASA FŒTIDA.

Asant or *asa fœtida* was used during antiquity as a spice and as a medicament. As such it is mentioned in Sanskrit and other writings, *e. g.* in the *Susruta* (Comp. p. 16). The Egyptians and Hebrews do not appear to have used it. According to Garcia *(De aromatibus),* the *silphion* of the Greeks, and the *laserpitium* of the Romans, are identical with *asa fœtida.*[7]) Among the later references it is first found in the writings of the Persian

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[1]) Valerii Cordi *Historia de plantis.* Lib. XI, cap. 135, fol. 158. — Flückiger, *Dokumente zur Geschichte der Pharmazie.* 1876. pp. 23, 46, 54, 63, 72, 83, 85. — Petri Andreæ Matthioli *Commentarii in sex libros* Ped. Dioscoridis, *De materia medica.* Veneti 1554. fol. 1169.

[2]) Hieronymus Brunschwig, *Liber de arte destillandi. De simplicibus.* 1500. fol. 20.

[3]) Buchner's Repert. f. d. Pharm. **76** (1842), 167.

[4]) Berl. Berichte **15** (1882), 1741.

[5]) Bull. Soc. chim. II. **39** (1883), 114.

[6]) Berl. Berichte **29** (1896), 1181.

[7]) Sigismund, *Die Aromata.* Leipzig 1884. p. 45.

geographer Istachri[1]) of the 10. century, and those of the Sicilian geographer Edrisi[2]) of the 12. century. It is also mentioned as medicament in the writings of Ibn Baitar[3]) of the 11. century, and of Platearius[4]) of the 12. century. In a tariff list of Pisa of 1305 *asa fœtida* is mentioned as an article that is imported from Aden via the Red Sea and Meditteranean route.[5]) Its geographic source and botanical origin were first ascertained in 1684—1685 by Adalbert Kæmpfer[6]) of Lemgo.

In the mediæval treatises on distillation, *asa fœtida* is not used by itself, but as an ingredient in the distillation of spirituous balsams.[7]) The volatile oil of *asa fœtida* is apparently first mentioned in the price ordinance of Strassburg of 1685.

OIL OF GALBANUM.

Oriential people, among them the Israelitis, first used galbanum in incense offerings and for fumigations.[8]) It was known to Theophrastus[9]) and Virgil.[10]) Dioscorides[11]) and Pliny[12])

[1]) Istachri, *Buch der Länder.* Translated by Mordtmann. Hamburg 1745. p. 111.

[2]) *Géographie* d'Edrisi, translated by A. Jaubert. Vol. 1 (1836), p. 450. — Meyer, *Geschichte der Botanik,* 1856. Vol. 3, p. 298.

[3]) Ibn Baitar, *Traité des Simples.* In *Notices et extraits des Manuscripts de la Bibliothèque nationale.* Paris. Vol. 1, p. 447. — Leclerc, *Histoire de la médecine arabe.* Paris 1874. Vol. 1, p. 553.

[4]) Matth. Platearius, *Liber de simpli medicina. (Circa instans.)* In L. Choulant, *Handbuch der Bücherkunde für die ältere Medizin.* Leipzig 1841. p. 299.

[5]) Bonaini, *Statuti inediti della città di Pisa.* 1857. Vol. 3, p. 106.

[6]) Kæmpfer, *Amœnitatum exoticarum fasciculi* etc. Lemgoviæ 1712. p. 535—552.

[7]) Conrad Gesner, *Anderer Theil des Schatzes Euonymi von allerhand künstlichen und bewerten Ölen* etc. Published by Caspar Wolff. Zürich 1583. fol. 163.

[8]) Exodus, 30 : 34. — Ecclesiasticus, 24 : 21.

[9]) Theophrasti *Historia plantarum.* Lib. IX. Cap. 1 and 2.

[10]) Virgilii *Georgica.* Lib. III. p. 415.

Disce et odoratam stabulis accendere cedrum,
Galbaneoque agitare gravi nidore chelydros.

[11]) Dioscoridis *De Materia medica libri.* Lib. III, 87. Editio Kühn-Sprengel. 1829. Vol. 1, p. 437.

[12]) Plinii *Naturalis historiæ libri.* Lib. XII. Cap. 25 and 56; and Lib. XXIV. Cap. 5 and 13.

mention Syria as its source. In 176 A. D. galbanum was one of the dutiable Indian spices passing through Alexandria.[1])

During the middle ages galbanum is enumerated but sparingly in literature. It is one of the spices enumerated as being in possession of King James of France while a prisoner in England.[2]) In 1503 it is mentioned as one of the articles of commerce between Venice and London,[3]) and again in 1581 in one of the French tariff lists.[4]) However, in medical literature of the early middle ages, also in Arabian literature, galbanum is frequently mentioned both as spice and as medicament.

Distilled oil of galbanum was prepared by Walter Ryff,[5]) by Conrad Gesner,[6]) and by Hieronymus Rubeus.[7]) It was included in the 1589 edition of the *Dispensatorium Noricum* and in the *Pharmacopœa Augustana* of 1580, and was mentioned in apothecary and spice ordinances about 1560. Early cursory investigations of the oil were made by Caspar Neumann[8]) about 1728, by Walter[9]) in Leipzig about 1744, by Fiddichow[10]) in 1815, and by W. Meissner[11]) in 1816.

OIL OF GUM AMMONIAC.

The air-hardened gumresin of *Dorema ammoniacum,* Don. (*Peucedanum ammoniacum,* H. Baillon) and of several species of *Ferula,* produced by the puncture of insects, was used during antiquity for incense, for embalming and, in all probability, for

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[1]) Vincent, *Commerce and Navigation of the Ancients in the Indian Ocean.* London 1807. p. 692. — Meyer, *Geschichte der Botanik.* 1855. Vol. 2, p. 167.

[2]) Doüet d'Arcq, *Comptes de l'Argenterie des rois de France.* 1851. p. 236.

[3]) Pasi, *Tariffa de Pesi e Misure.* Venetiæ 1503. fol. 204.

[4]) Fontanon, *Edicts et Ordonnances des rois de France.* 1585. Vol. 2, p. 388.

[5]) Gualtherus Ryff, *New gross Destillirbuch.* 1545. fol. 179. — See also p. 48.

[6]) See p. 53. — Euonymus Philiatrus, *Ein köstlicher theurer Schatz.* 1555. p. 237.

[7]) Hieronymi Rubei, *Liber de destillatione.* Basiliæ 1581. Cap. 5, p. 148.

[8]) Caspar Neumann, *Chymia medica dogmatico-experimentalis.* Editio Kessel. 1749. p. 422. — Zimmermann, *Prælectiones chemicæ.* Berlin 1740. p. 853.

[9]) A. F. Walther, *De oleis vegetabilium essentialibus. Dissertatio.* Lipsiæ 1745.

[10]) Berl. Jahrbuch der Pharm. **1816**, 230.

[11]) Trommsdorff's Neues Journ. der Pharm. **1**, I. (1817), 3.

medicinal purposes as well. In ancient literature both the plant and the gumresin are mentioned repeatedly. Both Dioscorides[1]) and Pliny[2]) mention that the gumresin was named after that of the temple of Jupiter Ammon in the Libyan desert in the neighborhood of which it was produced. Dioscorides' description seems to harmonize with that of *Ferula marmarica,* Aschers et Taub., found in Barka (Cyrenaica). Later the African gumresin was replaced by that from *Dorema ammoniacum,* Don. Hence the translators of Dioscorides into Arabian, some of whom were Persians, erroneously applied the Persian name *Uschaq* also to the African gumresin.[3]) One of the earliest mentions of ammoniac is to be found in an Alexandrian tariff list for Indian goods, which was compiled during the years 176 to 180 A. D. under the emperors Marcus Aurelius and Commodorus.[4]) Persian ammoniac is mentioned as medicament under the Persian name *Uschaq* during the 10. and 11. centuries in the writings of the physicians Isaac Judæus[5]) and Alhervi in Bochara.[6]) Other ancient medical treatises, among them those of Scribonus Largus, Alexander Trallianus, and others, mention the gumresin as a current drug.

The oil of gum ammoniac was distilled by Walter Ryff,[7]) Val. Cordus, and Conrad Gesner.[8]) It is included in the Frankfurt tax for the year 1587, and in the *Dispensatorium Noricum* of 1589.

The earlier investigations were made by Buchholz[9]) of Erfurt in 1808, by Calmeyer[10]) of Hamburg in 1808, by H. Braconnot[11]) in 1809, and by Hagen[12]) of Königsberg in 1814.

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[1]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, p. 439.

[2]) Plinii *Naturalis historiæ libri.* Liber XII, cap. 25.

[3]) O. Stapf, Kew Bull. **1907** (No. 10), 375. Report of Schimmel & Co., April **1908**, 14.

[4]) Meyer, *Geschichte der Botanik.* 1855. Vol. 2, p. 167.

[5]) Isaaci Judæi *Opera omnia.* Lugduni 1515. Lib. II. Cap. 44. In Choulant's *Handbuch der Bücherkunde für die ältere Medicin.* Leipzig 1841.

[6]) F. R. Seligmann, *Codex Vindobonensis. Liber fundamentorum Pharmacologiæ.* 1830. p. 35.

[7]) Gualtherus Ryff, *New gross Destillirbuch.* 1567. fol. 177b. – See also p. 46.

[8]) See p. 53. – Euonymi Philiatri *Ein köstlicher theurer Schatz.* 1555. p. 237.

[9]) Buchholz, Taschenbuch für Scheidekünstler und Apotheker **1809**, 170.

[10]) Trommsdorff's Journ. der Pharm. **17**, II. (1808), 82.

[11]) Ann. de Chim. **68** (1808). – Trommsdorff's Journ. d. Pharm. **18**, I. (1809), 202.

[12]) Berl. Jahrbuch der Pharm. **1815**, 95.

OIL OF DILL.

Dill was known during antiquity.[1]) With other kitchen spices the dill plant is mentioned in Sanskrit literature, and in the Bible.[2]) Like that of fennel, anise, and caraway, its cultivation was early extended over the countries of Europe. It was cultivated in England as early as the 10. century.[3])

In the treatises on distillation of the 15. and 16. centuries the distillation of dill is mentioned frequently.[4]) In German drug and spice ordinances dill oil is first mentioned in that of Frankfurt-on-the-Main of 1587.

OIL OF WINTERGREEN.

The distillation of oil of wintergreen[5]) was probably begun in the first decades of last century along with that of sassafras bark (p. 129) and birch bark (p. 118) in the states of Pennsylvania, New Jersey and New York. At first these aromatics were used for chewing, later for the preparation of refreshing beverages and home remedies, and especially for the much used, socalled blood purifiers. After the production of these volatile oils had been made a success they were often used instead of the aqueous extracts of the drugs. This use is of considerable importance to the history of the introduction of wintergreen and

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[1]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, p. 405.

[2]) Matth., 23 : 23. In English translations of the Bible, since the days of Wycklif [1380], the Greek ἄνηθον has been translated as anise. Luther translates it more correctly as dill, which is always meant in Greece when ἄνηθον is used. (Langkavel, *Botanik der späteren Griechen.* Berlin 1866. p. 39.)

[3]) *Herbarium Apuleii.* In Leechdoms, Wortcunning and Starcraft of early England, edited by Cockayne. London 1864. Vol. 1, pp. 219, 235, 237, 281, 293. — Popular Names of British plants. London 1870.

[4]) Hieronymus Brunschwig, *Liber de arte destillandi.* 1500. Fol. 40.

[5]) Upon the suggestion of Kalm, after his return to Sweden, Linné named the plant *Gaultheria procumbens* in honor of Dr. Gaulthier, a French physician and botanist in Quebec, whom Kalm had met in 1749. Kalm, who had obtained herbarium specimens of the plant from John Bartram of Philadelphia, with the latter regarded it as a species of *Trientalis.* (Peter Kalms *Reise nach dem nördlichen Nordamerika im Jahre 1748—1749.* Göttingen 1754. Vol. 3, pp. 283, 421, 477, 515 and 533.)

sassafras oils, in as much as both of these were used as popular remedies (socalled patent medicines) in the United States since the beginning of last century. The preparation and use of these remedies soon became general, and with it came a greater demand for these oils. Wintergreen oil was especially in demand for the preparation of one of the oldest popular remedies in the United States, namely Swaim's *Panacea,*[1]) introduced in 1815, which at that time had an enormous sale and in the efficiency of which great confidence was placed.

Wintergreen oil does not appear to have been used for other purposes at that time. The first mention of it in literature is found in a botanical work published in 1818 by Bigelow,[2]) a physician of Boston. In it, gaultheria oil is mentioned as a staple article of the drug stores. He further states that this oil occurs also in *Spiræa ulmaria,* the root of *Spiræa lobata,* and especially in the bark of *Betula lenta.* In pharmacopœias, the oil was first taken up in that of the United States of 1820. The medicinal use of the oil, however, did not become general until 1827, when the New York Medical Society made known its use in the preparation of the popular specific mentioned above.[3])

Although the similarity of the volatile oil from *Gaultheria procumbens,* L., to that from the bark of *Betula lenta,* L., was known before 1818,[2]) the identity of their principal constituent was shown scientifically in 1842 by Wm. Procter jr.[4]) of Philadelphia and in 1844 by A. A. Th. Cahours[5]) of Paris. From that time on the oil was no longer distilled exclusively from wintergreen, but often from this together with birch bark, or only from the latter. The oil came more and more into use as an aromatic for pharmaceutical and cosmetic preparations, for beverages and

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[1]) This remedy was an imitation of the *Rob de Laffecteur,* a secret remedy exploited with great success by the Parisian apothecary Boiveau at the beginning of the last century. Swaim, a bookdealer in Philadelphia, had been cured by this remedy. He succeeded in securing the formula, and after substituting gaultheria oil for sassafras oil, he introduced it into commerce. (Pharm. Review **16** [1898], 179.)

[2]) Jacob Bigelow, American Medical Botany. Boston 1818. Vol. 2, p. 28.

[3]) Pharm. Review **16** (1898), 179. — Americ. Journ. Pharm. **3** (1831), 199.

[4]) Americ. Journ. Pharm. **14** (1842), 211. — Liebig's Annalen **48** (1843), 66.

[5]) Annal. de Chim. et Phys. III. **10** (1844), 327—358 and Liebig's Annalen **48** (1843), 60; **52** (1844), 327.

medicinal remedies,[1]) and thus became an important article of commerce.

As artificial oil of wintergreen, methyl salicylate has been produced on a commercial scale by Schimmel & Co. since 1886. It was made officinal in the 1890 edition of the U. S. Pharmacopœia.

OIL OF ROSEMARY.

Rosemary was greatly esteemed by the Greeks and Romans,[2]) and also by the Arabians.[3]) Like the laurel, rosemary was employed by the former as a decorative plant in religious rites and in hero cult. In as much as the plant was not used for medicinal or other practical purposes, rosemary was given but little attention in midæval literature. However, it received prominent mention in the *Capitulare* of Charlemagne of 812; among the seventy-three economic plants recommended therein also in the drug inventory of Platearius[4]) of the 12. century.

The first mention of the distillation of rosemary is found in the writings of Arnoldus Villanovus[5]) of the 13. century. He distilled, probably for medicinal purposes, turpentine oil and rosemary oil. An alcoholic distillate of both oils or of rosemary only was in use for centuries as the first popular perfume under the name of Hungarian water.[6]) The distillation of the oil is described more fully by Raimund Lullus,[7]) a disciple of Villanovus.

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[1]) New York Medical Record **22** (1882), 505. — Squibb's *Ephemeris* (New York) **3** (1892), 950.

[2]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829, p. 424.

[3]) Ibn el Baitar, *Liber magnæ collectionis simplicium alimentorum et medicamentorum.* Translated by Jos. Sontheimer. Stuttgart 1840. Vol. 1, p. 73.

[4]) Matthæi Platearii *Liber de simplici medicina.* In Choulant's *Handbuch der Bücherkunde für die ältere Medizin* etc. Leipzig 1841. p. 229.

[5]) Arnoldi Villanovi *Opera omnia.* Cap. *De vinis.* Veneti 1595. p. 589 to 590.

[6]) Pp. 30 and 66. — Sapata, *Mirabilia seu secreta medico-chirurgi per* D. Spleissium. Ulm 1696. p. 49.

[7]) *Postquam singulorum individuorum dictorum lentissimo igne aquæ destillatæ fuerit, amoto priori recipiente aquam destillatam optime occlusam servabis et annexo altero recipiente augebis ignem ut deinde destillet oleum cujusque, quod proiicias, quia nihil valet, excepto eo quod e rore marino extraxeris, quod servabis, cum in se aliquid virtutis contineat.* — Raimundi Lulli *Experimenta novissima.* In Magnet's *Bibliotheca chemica curiosa.* Genevæ 1702. Vol. 1, fol. 829.

Oil of rosemary was a much used oil in the middle ages, and is often mentioned in the writings of that period. It is described in the index of the Compendium of Saladin[1]) at the end of the 15. century and in the works of Brunschwig,[2]) Ryff,[3]) Gesner,[4]) Porta,[5]) and others, and is mentioned in drug and spice ordinances of the 15. century. In several of the treatises on distillation, and in medical works of the 14. and 15. centuries, an empyreumatic oil of rosemary is also mentioned.[6])

One of the first investigations of rosemary oil was made in 1720 by the Parisian apothecary Cl. J. Geoffroy.[7]) A century later it was more fully investigated by Th. de Saussure,[8]) and in 1837 by Kane.[9]) In 1734 Cartheuser[10]) determined the yield of oil.

The so-called rosemary camphor was first noticed in 1685 by Joh. Kunkel[11]) of Berlin, and a century later (1785) by Arezula[12]) of Cadiz. Proust[13]) prepared it in 1800.

OILS OF LAVENDER AND SPIKE.

Originally the oily distillates from the several species of lavender were all designated spike oil. It was not until the close

[1]) Saladini Asculani *Compendium aromatariorum.* Venet. 1488. Index.

[2]) See p. 39 and 47.

[3]) Gualtherus Ryff, *New gross Destillirbuch.* 1545. p. 186.

[4]) Page 52. — Euonymi Philiatri *Ein köstlicher theurer Schatz.* 1555. pp. 226, 249, 273.

[5]) Joh. Bapt. Portæ *Magiæ naturalis lib. viginti. Liber de destillatione.* p. 385.

[6]) Christ. Lindner, *De oleis destillatis empyreumaticis.* Dissertatio, Francofurti ad Viadrum. 1744.

[7]) *Mémoires de l'Académie des sciences de Paris.* 1721. p. 163.

[8]) Annales de Chim. et de Phys. II. **13** (1820), 278.

[9]) Transact. of the Royal Irish Acad. **18**, 135. — Journ. f. prakt. Chem. **15** (1838), 156.

[10]) Fr. Cartheuser, *Elementa Chymiæ dogmatico-experimentalis, una cum synopsi Materiæ medicæ selectioris.* Halæ 1736. II. p. 83 and 106.

[11]) Joh. Kunkel, *Probierstein. Fünf curiose chymische Tractatlein nebst einer Vorrede.* Frankfurt-on-the-Oder and Leipzig 1721. p. 397. *"Mein gnädigster Kurfürst hat mir einsten des alten verstorbenen Thurnhäusers Apothek geschenkt, darinne noch viele Olea destillata seynd, die noch so frisch, als wenn sie diese Stund destilliret wären. Darunter ist ein Gläslein mit oleo Anthos, darinne ein Sal angeschossen ist."*

[12]) Page 74. — Arezula, *Resultado de las experiencias hechas sobre el alcanfor de Murcia con licencia.* Segovia 1789. p. 8.

[13]) Trommsdorff's Journ. der Pharm. **8**, II. (1800), 221.

of the 16. century that a distinction was made between spike oil and lavender oil.[1])

In all probability, *Lavandula Stœchas,* L., which is indigenus to the Mediterranean coast lands, and which is characterized by its aromatic violet-red inflorescence, was first used in the distillation of spike oil.

The spike or stœchas oil[2]) mentioned in the writings of Dioscoridis,[3]) Pliny,[4]) Scribonius Largus,[5]) and their contemporaries was, in all probability, only an aromatized fatty oil, like rose, spikenard and other aromatic oils used during antiquity.[6])

It is not at all improbable that the Phoceans, Greek colonists from Asia Minor, who about 600 B. C. colonized the coast of the Bay of Lyons and founded Marseille, brought with them *Lavandula Stœchas* as well as other native plants and introduced them into southern France, whence they soon spread over Spain. Apparently the *L. Stœchas* was used together with the spike *(L. Spica)* during the middle ages, whereas *Lavendula vera* and *Lavendula latifolia*[7]) were used later. Indeed, the name *Lavandula* had its origin in Italy during the later middle ages.

Spike, occasionally designated narde, was used during the early middle ages by the physicians of the Alexandrian School. In European medical treatises we find it recommended by the

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[1]) F. de Gingins-Lassaraz, *Histoire des Lavandes.* Geneva and Paris 1826.

[2]) Because of the supposed similarity in odor, *Lavandula Stœchas,* which was used during antiquity, was confounded with *Nardostachys jatamansi,* D. C., the rhizome of which was likewise prized as a spice and as an incense. The latter was named *Nardus indica,* the former *Spica Nardi.* During the middle ages, the former was also designated *Nardus italica* and *Nardus celtica.* In the pharmacopœias the flowers of this plant were known as *Flores stœchados arabicæ.* (Camerarius, *Hortus medicus et philosophicus.* Francofurti 1588. p. 164.) See also Nardostachys.

[3]) Dioscoridis, *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, pp. 15, 17, 35, 40, 62, 508, 542.

[4]) Plinii *Naturalis historiæ libri* XXXVII.

[5]) Scribonii Largi *Compositiones medicamentorum.* Editio Helmreich. Leipzig 1887. p. 72. — Meyer, *Geschichte der Botanik.* 1855. Vol. 1, p. 33.

[6]) See p. 37, 137 and 195.

[7]) M. Platearius, *Liber de simplici medicina. (Circa instans.)* In Choulant, *Handbuch der Bücherkunde für die ältere Medizin.* 2. ed. Leipzig 1841. p. 299.

Abbess Hildegard[1]) for the preparation of an eye remedy. As early as the 14. century, spike as well as narde flowers were used for filling pillows for healthy persons as well as the sick.[2]) Brunschwig refers to spike as to a universally known plant.[3])

The distilled spike or spikenard oil was probably known in the 15. century. As *Oleum de Spica* from the Provence,[4]) it is the only distilled oil, besides cedar (turpentine) oil, mentioned by Hieronymus Brunschwig in his *Destillirbuch* of 1500. Saladin also mentioned spikenard oil at the end of the 15. century.[5])

In his *Dispensatorium Noricum* of 1543 Valerius Cordus mentioned only three distilled oils: turpentine oil, juniper oil and spike oil.[6]) Ryff described in his treatise on distillation, published somewhat earlier, the distillation of *"Spik und anderen fürnemen Olen"*, and added the statement that, *"das Spiken- oder Lavendelöl gemeygklich aus der Provinz Frankreich gebracht wird in kleinen glässlin eingefasst und theuer verkaufft"*.[7]) In the 16. century the several species of lavender were cultivated in Germany[8]) and in England.[9])

Conrad Gesner used the name spike oil only and described the distillation of the spike blossoms,[10]) whereas Giovanni

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[1]) Hildegardis Abbatissæ *Subtilitatum diversarum naturarum, creaturarum libri novem.* Editio Migne. 1855. pp. 1140 and 1143.

[2]) Doüet d'Arcq, *Comptes de l'Argenterie des rois de France.* 1874. Vol. 2, p. 148.

[3]) Hieronymus Brunschwig, *Liber de arte destillandi. De simplicibus.* 1500. fol. 72.

[4]) *Ibidem* fol. 72. — See p. 39.

[5]) Saladini *Compendium aromatariorum.* Venet. 1488. Index.

[6]) *Dispensatorium Noricum.* Autore Valerio Cordo. Editio Paris 1548. p. 439. *Ex majori lavendula quæ spica vocatur, apud nos majoribus sumptibus fit quam in Gallia Narbonensi, ideo potius emendum est a mercatoribus qui illud e Gallia afferunt.*

[7]) Gualtherus Ryff, *New gross Destillirbuch.* fol. 186. — Compare also p. 46.

[8]) Conrad Gesner, *De hortis Germaniæ liber recens.* Argentorati 1561. fol. 264.

[9]) Meddygon Myddfai. Edit. John Pughe. Llandovery 1861. p. 287.

[10]) *„Die Blümlein der Spiken oder des Lavanders solt du eine kurze zeyt lang sonnen in einer grossen gläsinen retorte und darnach ein wasser in einem Alembik darvonnen destilliren und abziehen. Dieses Wasser durch den ganzen Sommer gesetzt an eine warme statt an die Sonnen so treybt für und für öl über sich, welches öl du allwägen solt von dem wasser*

Baptista Porta,[1]) at the end of the 16. century, described also the distillation of lavender blossoms and especially emphasized the superiority of the oil from the French lavender.

An interesting description of the preparation of the French spike or lavender oil is contained in a treatise published in 1773 by Joh. Frances Demachy,[2]) who was director of the laboratories of the Paris municipal hospitals. In its essential features this description corresponds with that quoted an p. 48.

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separieren und absündern mit einem fäderlin und dasselbe fleiyssig behal im einer gläsinen gutteren (Flasche) wohl vermachet und verstopfet." *Thesaurus* Euonymi Philiatri *Ein köstlicher theurer Schatz.* Zürich 1555. p. 222.

[1]) G. B. della Porta, *Magiæ naturalis libri viginti. Liber de destillatione.* Romæ 1567. fol. 87. "*. . . e spica fragrantior excipitur, est illud quod ex Gallia provenit.*" — *Ibidem* p. 54 and 78: "*tanta odoris fragrantia ut omnes flores odoris jucunditate provocet.*"

[2]) „*Dieses Öl, welches fast ebenso gemein ist, als das Terpentinöl, mit dem es fast alle Schriftsteller verwechseln, oder in Verdacht gestanden haben, es werde damit verfälscht, wird auf freiem Felde von Schäfern und anderen Hirten in Languedoc und Provence verfertigt.*"

„*Wenn die Gattung Lavendel, wilder Lavendel oder Aspic genannt, welcher auf Hügeln und Wiesen dieser Provinzen häufig wächst, in Blüte ist, gehen die Schäfer zur Stadt um bei den Kaufleuten, die mit dem Öle handeln, eine grosse kupferne Blase und verzinntem Hute, und einem etwas hohen Dreifuß zu holen. Sie lagern sich in einer Wiese neben einem Bache und destilliren das Spiköl folgender Gestalt. Sie schneiden die blühenden Spitzen der Spike ab, füllen die Blase damit, gießen Wasser hinzu, setzen den Hut dicht auf, zünden mit trockenen Kräutern ein gutes Feuer unter dem Dreifuss, und fangen in einer grossen gläsernen Flasche dasjenige auf, was strählings herüber läuft. Wenn sie herüber gezogen haben, was die Erfahrung ihnen gelehrt hat, wieviel die Ladung einer Blase giebt, so leeren sie sie aus, füllen mit frischen Blumen und fangen wieder an zu destillieren. Sie tun dies von Ort zu Ort bis die Blütezeit vorüber ist. Sie füllen das abgesonderte Öl in lederne Schläuche. Wenn der Sommer vorüber ist, kommen die Destillateure zu Stadt, überliefern ihren Apparat dem Eigentümer und verkaufen ihm zu sehr mässigem Preise die Frucht ihrer Nebenstunden, welcher reiner Profit für sie ist. Sie lassen zuweilen absichtlich Wasser im Öle, was man ihnen für Öl bezahlen würde, wenn man nicht die Vorsicht brauchte, die Schläuche einige Tage aufgerichtet liegen zu lassen, ehe man das Öl ausfüllt; öffnet man nun, so kommt das Wasser zuerst heraus.*"

„*Dieses Öl ist im Geruche nicht eins der feinsten, dennoch aber vom Terpentinöle durch eine gelbliche Farbe und seinen Lavendelgeruch verschieden. Die Firnißmaler brauchen viel davon.*"

J. F. Demachy, *L'art du destillateur des eaux fortes.* Paris 1773. German edition *Laborant im Grossen* by Sam. Hahnemann. Leipzig 1784. Vol. 1, p. 250.

In medical works *Oleum spicæ* was mentioned as early as the 14. century.[1]) In was included in the first edition of the *Dispensatorium Noricum* of 1543. *Oleum lavandulæ* is also mentioned, together with spike and other essential oils, in the 1589 edition. The *Pharmacopœa Augustana* of Occo, contains up to 1613 only *Oleum spicæ;* from that date on also *Oleum lavandulæ.*

Spike oil is mentioned in the oldest drug and price ordinances of German cities; *Oleum lavandulæ,* however, is not found until 1582 in the Frankfurt ordinance.[2])

The statements of Demachy and other writers of his time agree with the assertions of later authors, that the spike oil found in commerce in the 18. century was probably only a distillate or mixture of turpentine and lavender oils.[3])

The yield of oil from the distillation of spike and lavender blossoms appears to have been first mentioned by W. Lewis,[4]) also by Friedr. Cartheuser.[5]) The so-called "lavender camphor" was observed in 1785 by Arezula,[6]) and in 1800 by Proust. The first investigations of lavender oil were made by Saussure.[7])

OIL OF SAGE.

Sage appears to have been used as a medicinal herb at the time of the Romans[8]) and was one of the plants recommended by Charlemagne for cultivation.[9]) In the "Destillirbuch" by Brunschwig of 1500 a distinction is made between large and small sage[10])

[1]) Pfeiffer, *Zwei deutsche Arzneibücher des 12. und 13. Jahrhunderts.* In *Sitzungsberichte der Wiener Akad. der Wissensch.* **1863.** Vol. 42, p. 124.

[2]) *Register aller apothekischen Simplicien und Compositen, so in den beiden Messen zu Frankfurt a. M. durch die Materialisten, Kauffleut, Wurzelträger, Kräutler, auch durch die Apotheker daselbst verkaufft werden.* 1582.

[3]) Dulk, *Commentar zur Pharmacopœa Borussica.* 3. ed. 1833. Vol. 1, p. 643.

[4]) Wm. Lewis, The new Dispensatory. London 1746.

[5]) F. Cartheuser, *Elementa chymicæ dogmatico-experimentalis.* Halæ 1736. Vol. 2, pp. 133 and 149.

[6]) Arezula, *Resultado de las experiencias hechas sobre alcanfor de Murcia non licencia.* Segovia 1789.

[7]) Annal. de Chim. et Phys. **4** (1790), 318; **13** (1792), 273; **49** (1804), 159.

[8]) Theophrasti *Historia plantarum.* Lib.VI, cap. 2. — Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel 1829. Vol. 1, p. 381. Vol. 2, p. 510.

[9]) *Capitulare de villis et cortis imperialibus.* Anno 812. Translated and explained in Fühling's Landwirtschaftl. Zeitung. April number 1878. pp. 241 to 260.

[10]) Brunschwig, *Liber de arte destillandi. De simplicibus.* 1500. fol. 103.

for the distillation of sage water. Furthermore a species of *Eupatorium,* the *Kunigundenkraut,* is referred to as wild sage and directed to be distilled.[1])

The distilled oil of sage[2]) is first mentioned in the price ordinances of Worms of 1582, and of Frankfurt of 1587. It is also included in the 1589 edition of the *Dispensatorium Noricum.* In 1688, the distillation of the oil was described by Begnini.[3]) The yield of oil from the leaves was determined by Wedel[4]) in 1715 also by Friedr. Cartheuser[5]) about 1732. In 1720 Cl. J. Geoffroy observed a stearoptene which had crystallized from the oil, and which he termed sage camphor.[6]) The same substance was again observed by Arezula[7]) of Cadiz in 1789 and described by him.

The first examination of the leaves appears to have been made by Illisch[8]) of Riga in 1810; whereas the oil was investigated by Herberger[9]) in 1829 and by Fr. Rochleder[10]) in 1841.

OIL OF BALM.

On account of its fragrance, balm was cultivated by the Greeks, Romans, and Arabs,[11]) and during the middle ages in Italy, Germany[12]) and Scandinavia.[13])

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[1]) Brunschwig, *Liber de arte destillandi. De simplicibus.* 1500. fol. 117.

[2]) See p. 33.

[3]) Johannis Begnini *Tyrocynium chymicum.* In Joh. Hartmannii *Opera omnia medico-chymica congesta atque pluribus aucta* a Conrado Johrenio. Francofurti ad Mœnum. 1690. Vol. III, p. 27.

[4]) Wedel, *Dissertatio de Salvia.* Jenæ 1715.

[5]) Cartheuser, *Elementa chymiæ dogmatico-experimentalis, una cum synopsi Materiæ medicæ selectioris.* Halæ 1736. Vol. 2, p. 87.

[6]) *Mémoires de l'Académie royale des sciences de Paris.* 1721. p. 163.

[7]) Arezula, *Resultado de las experiencias hechas sobre el alcanfor de Murcia con licencia.* Segovia 1789, p. 8.

[8]) Trommsdorff's Journ. der Pharm. **20**, II. (1811), 7.

[9]) Buchner's Repert. f. d. Pharm. **34** (1830), 131.

[10]) Liebig's Annalen **44** (1842), 4.

[11]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829, p. 453. — Platearius, *Circa instans.* Editio Choulant. 1841. Vol. 1, p. 299. — Macer Floridus, *De viribus herbarum* etc. 1832. Editio Choulant, p. 64. — Plinii *Naturalis historiæ libri* 37. Lib. XX, 45; Lib. XXI, 86. Editio Littré, 1877. Vol. 2, p. 18 and 66. — Varro, *De agricultura,* Lib. III, 16. Editio Nisard, p. 149. — Meyer, *Geschichte der Botanik.* Vol. 1, p. 362.

[12]) Conradi Gesneri *De Hortis Germaniæ liber recens.* 1561. Fol. 267 b.

[13]) Henrik Harpestreng, *Danske Lægebok.* Copenhagen 1826, p. 118.

During the period of distilled waters, from the 15. to the 17. centuries, balm water was a current article. Oil of balm appears to have come into use about the middle of the 16. century. It is first mentioned in the ordinance of Frankfurt-on-the-Main for 1582 and in the *Dispensatorium Noricum* of 1589.

Comparable to the distillate from rosemary of the 16. century, which was the precursor of the *Eau de Cologne* of the 18. and 19. centuries, the fragrant distillate from balm, lemon peel and lavender of the 17. century developed later into a very popular perfume. It was first prepared by the Carmelite monks of Paris in 1611 and became famous as *Eau des Carmes* (Ger. *Karmelitergeist*).[1]) Later the alcoholic distillate was made officinal as *Spiritus Melissæ compositus.*

The earlier investigations of the oil were made by Schultz[2]) in 1739, by Friedr. Hoffmann[3]) about the same time, and by Dehne[4]) in 1779.

OIL OF HYSSOP.

In antiquity hyssop was already included among the spice plants.[5]) The word "Ysop", used by Luther in his translation of the Bible, did not apply to hyssop but to *Origanum.*[6]) The volatile oil thereof was used during the late middle ages and is mentioned in the German price ordinances of the 16. century.

OIL OF THYME.

As a kitchen spice thyme was used during antiquity.[7]) Theophrastus, Dioscorides, Pliny and Columella[8]) mention thyme and

[1]) See p. 67.

[2]) Schultz, *Dissertatio de Melissa.* Halæ 1739.

[3]) Friedr. Hoffmanii *Observationum physico-chemicarum selectiorum.* Halæ 1722—1736. Lib. III, p. 19.

[4]) Crell's Chemische Annalen 3 (1780), 29.

[5]) Prosper Alpinus, *De plantis Ægypti liber.* Veneti 1591. Cap. 20. — Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel 1829. Vol. 1, p. 374. — 1. Kings, 4 : 33. — Exodus, 12 : 22. — Lev. 14 : 4; Numbers, 19 : 6 and 18.

[6]) Rosenmüller, *Handbuch der bibl. Altertumskunde.* 1830. Vol. 4, p. 108.

[7]) Apocalypse, 18 : 13.

[8]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, p. 385. — Plinii *Naturalis historiæ libri* 37. Lib. XXI, 31. — Columellæ *De re rustica.* Editio Nisard. 1877, p. 446.

distinguish it from wild thyme or *Thymus Serpyllum,* whereas the two were not always kept separate by writers during the middle ages. It is probably for this reason that Valerius Cordus[1]) refers to thyme as *Thymus nostras.*

Although it never played an important role in medical practice, it, as well as the oil distilled therefrom, has been officinal in the medical treatises since the 16. century, also in the drug and spice ordinances. The oil was introduced into the 1589 edition of the *Dispensatorium Noricum.*

Thyme camphor (thymol) was first observed by Caspar Neumann[2]) in 1719, then by Friedr. Cartheuser[3]) in 1754. It was examined by Lallemand[4]) in 1853 who named it thymol.

MENTHA OILS.

Several mints, the botanical identity of which it may be impossible to establish, were known during antiquity, being used as kitchen spice,[5]) possibly also as medicament by the Egyptians,[6]) Hebrews[7]) and Romans.[8]) A similar use the mints seem to have found with the Germanic tribes. Among the 73 economic plants recommended for cultivation in his *Capitulare* of 812 by

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[1]) Val. Cordi *Historiæ plantarum.* Editio C. Gesneri. Argentorati, 1561. p. 136.

[2]) Philosophic. Transactions of the Royal Soc. of London. 1724, 1725, 1733, 1734. — *Chymia medica dogmatico-experimentalis* 2, 282, and *Lectiones chymiæ de salibus alcalinofixis et de camphora.* Berlin 1727. pp. 135—137.

[3]) Cartheuser, *De sale volatile oleoso solido in oleis athereis nonnunquam reperto.* Dissertatio. Francofurto 1774. — Cartheuser, *Materia medica.* Vol. 2, p. 115.

[4]) Journ. de Pharm. et Chim. III. **24** (1853), 274; Compt. rend. **37** (1853), 498.

[5]) Prosper Alpinus, *De plantis Ægypti liber.* Veneti 1591. Cap. 42, p. 61.

[6]) G. Schweinfurth, *Ueber Pflanzenreste aus altägyptischen Gräbern,* in Berichte der deutsch. botan. Gesellschaft **2** (1884), 366.

[7]) Matth., 23 : 23. — Luk., 11 : 42.

[8]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. p. 383. — Plinii *Naturalis historiæ libri.* Lib. XIX, cap. 8: *"Grato mentha mensas odore percurrit in rusticis dapibus."* Lib. XX, cap. 14: *"Menthæ ipsius odor animum excitat, et sapor aviditatem in cibis; ideo embammatum misturæ familiaris."* — Columellæ *De re rustica,* Lib. XI, 3. Editio Nisard, *"Les agronomes Latins."* Paris 1877. p. 445.

Charlemagne,[1]) three mints are mentioned. Two of these belonged to what is now regarded as the genus *Mentha, viz.*, the *Mentha Menthastrum* and *Sisymbrium (Mentha crispa).*[2]) In the writings of the abbess Hildegard[3]) of 1160, *Bachmyntza, Myntza major, Rossmyntza,* and *Römische Myntza* are mentioned. In the Pharmacopœia of Gotha[4]) of the beginning of the 15. century *Cruseminte* is also mentioned.

In like manner the treatises on distillation of the 15. and 16. centuries give directions for the preparation of distilled waters from mints without further characterization of the plants.[5]) The mint oils mentioned in the older pharmacopœias and drug ordinances, likewise, reveal an uncertainty concerning the origin of the different kinds. Thus the Berlin ordinance of 1574 mentions only *Oleum menthæ.* The Frankfurt list of 1582 mentions *Oleum menthæ, Oleum polemii* and *Oleum pulegii.*

OIL OF PEPPERMINT.

Whether or not peppermint was among the mints used during the middle ages can no longer be determined. In the oldest German treatise on distillation the *Liber de arte distillandi*[6]) of the year 1500, the following mints are mentioned as being used in the preparation of distilled waters: *Mentha aquatica, Mentha rubra, Mentha balsamica, Mentha sarracenica* and *Mentha crispa,* but no distinguishing characteristics are given. Neither is it definitely known whether the kinds of mint used formerly agree with those now in use. As far as known, the only spe-

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[1]) *Capitulare de villis et cortis imperialibus.* Translated and explained by A. Thaer. In Fühling's Landwirtschaftliche Zeitung. April number 1878. p. 241—260.

[2]) Meyer, *Geschichte der Botanik.* 1856. Vol. 3, p. 406.

[3]) Hildegardis Abbatissæ *Subtilitatum diversarum naturarum creaturarum libri novem.* Editio Migne. 1855. p. 1161.

[4]) Karl Regel, *Das mittelhochdeutsche Gothaer Arzneibuch.* Gotha 1873. p. 21.

[5]) Hieronymus Brunschwig, *Liber de arte destillandi. De simplicibus.* 1500. fol. 75b. — Val. Cordus, *Dispensatorium Noricum.* Editio Parisiis. 1548. pp. 77, 284, 285, 378, 381, 418, 419, 432. — Gesner, *De Hortis Germaniæ liber recens.* 1561.

[6]) Brunschwig, *Liber de arte destillandi. De simplicibus.* 1500. fol. 75.

cimens of *Mentha piperita* which are several hundred years old, are found in the herbarium of the British Museum in London. John Ray,[1]) the English naturalist, had obtained them from the county of Hertfordshire of southern England in 1696 and described them as *Mentha palustris*, "peper mint". The well preserved specimens correspond in all essential characteristics with the peppermint which is to-day cultivated in Mitcham, county of Surrey, near London.[2]) The cultivation of peppermint in Mitcham seems to have begun about the middle of the 18. century and was of some importance toward the end of that century. Up to 1805, however, the distillation of peppermint oil was not conducted in Mitcham but in London.[3])

The English peppermint industry reached its height about 1850. From that time on American competition caused a decided setback in the production.[4]) For purposes of distillation, peppermint was evidently not cultivated earlier on the continent than in England. According to the Leyden botanist David Gaubius, it was cultivated for this purpose near Utrecht in 1770. He also mentions the menthol, the *camphora europæa menthæ piperitidis.*[5]) Meanwhile Linnæus had named the plant *Mentha piperita.*

About the same time peppermint was cultivated in Germany. Following the example of the London Pharmacopœia, in which peppermint was officinal since 1721 as *Mentha piperitis sapore,* it was mentioned in medical and botanical treatises. The treatise by Knigge[6]) seems to have made it better known in professional circles.

In Japan, hower, the cultivation of peppermint appears to antedate that of any other country. It is reported to have begun before the Christian period. According to Flueckiger, even menthol *(Hakuku, Hakka)* has been separated since that time and used

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[1]) John Ray, *Historia plantarum.* London 1704. Vol. 3, p. 284.

[2]) Flückiger, *Pharmakognosie.* 3. edition. 1891. p. 726.

[3]) Lysons, Environs of London. 1800. p. 254.

[4]) Chemist and Druggist 1891, 405.

[5]) Hieronymi Davidii Gaubii *Adversariorum varii argumenti liber unus.* Leidæ 1771. pp. 99—112.

[6]) Knigge, *De mentha piperitide commentatio. Dissertatio.* Erlangæ 1780.

as a remedy.[1]) According to Naojiro Inouye,[2]) the words *Hakuku* and *Hakka* do not mean menthol, but peppermint. In the oldest medical treatise of Japan, the *Daiso-Rui-Shu-Ho* (806—809), peppermint is not mentioned. However, in the *Shin-J-Ho,* compiled by Tamba Yasuyori in 984, the plant is mentioned as *Megusa* (*Me* = eye, *gusa* = herb), of which an eyewater was made. When peppermint oil was first distilled in Japan is not known. The export of this oil began in 1873.

OIL OF EUROPEAN PENNYROYAL.

European pennyroyal (Ger. *Polei*) is derived from *Mentha pulegium,* L., (*Pulegium vulgare,* Mill.) or its hybrid varieties, and has been used medicinally since the middle ages[3]) and possibly earlier.[4]) The distilled *Oleum pulegii* is mentioned in the price ordinance of Frankfurt for 1582 and appears to have been used medicinally, like the plant and its distilled water, in the 16. and 17. centuries.

OIL OF SWEET BASIL.

Oil of sweet basil appears to have been in use during the middle of the 16. century. It is enumerated among the oils of the Frankfurt price ordinance for 1582 and in the *Dispensatorium Noricum* of 1589. The distilled water was used as early as the 15. century.[5])

OIL OF VALERIAN.

During antiquity valerian was known as *Phu.* It is described in the writings of Dioscorides[6]) and Pliny. Later it is mentioned

[1]) Flückiger, *Pharmakognosie.* 1891. p. 726.

[2]) Bericht von Schimmel & Co., October 1908, Supplement.

[3]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. p. 377.

[4]) Pfeiffer, *Zwei deutsche Arzneibücher des 12. und 13. Jahrhunderts.* In *Sitzungsberichte der Wiener Akad. d. Wissensch.* Vol. 42 (1863), II, p. 137. (However, the possibility is not excluded that the *Poleiöl* mentioned here and in earlier treatises pertains to the oil of *Thymus Serpyllum.*)

[5]) Hieron. Brunschwig, *Liber de arte destillandi. De simplicibus.* fol. 27.

[6]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, pp. 20 and 348.

as a remedy by Isaac Judæus[1]) and Constantinus Africanus,[2]) who are the first to use the term *Valeriana.* In a drug list of the Medical School of Solerno, *Phu, Amantilla* and *Valeriana* are mentioned as being identical.[3]) In the 11. century, however, the name *Valeriana* appears to have been in use,[4]) though the name *Phu* continued in literature as late as the 15. century.[5])

During the middle ages the odor of valerian must have been a favorite for it was used for perfuming rooms, clothing and linen,[6]) in like manner as the roots of *Valeriana celtica,* L., and those of *Nardostachys Jatamansi,* D. C., *(Nardus indica)* were used during antiquity.[7])

How common the use of valerian root was in Germany becomes apparent from the large number of popular names and synonyms of which lists are given by the abbess Hildegard[8]) in the 12. century, and by Hieronymus Brunschwig[9]) toward the end of the 15. century.

The treatises on distillation of the 16. century provide directions for distillates of valerian with either water or wine.

The distilled oil was obtained by Hoffmann, Boerhaave, and Geoffroy, in part from the dry, in part from the fresh root.[10]) Later Graberg (1782) described the oil,[11]) and Trommsdorff investigated the root in 1808.[12]) In 1830 he named the acid obtained from the aqueous distillate valerianic acid.[13])

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[1]) Isaac Judæus, *Opera omnia.* Lugduni 1545. Cap. 45. *"Fu, id est valeriana, melior rubra et tenuis".*

[2]) Steinschneider, in *Rohlf's Archiv für Geschichte der Medizin.* 1879. p. 96. *"Fu, id est valeriana; naturam habet sicut Spica Nardi".*

[3]) S. de Renzi, *Collectio Salernitana. Alphita.* 1854. III. pp. 271—322.

[4]) Cockayne, Leechdoms, Wordcunning and Starcraft of Early England. 1866. III. 6, 136.

[5]) Saladini *Compendium aromatariorum.* Bononæ 1488. Index.

[6]) Turner, *New Herball.* 1568. Part. 3, p. 76. — Langham, Garden of Health. 1633. p. 598.

[7]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, p. 7; and vol. 2, p. 348. — Brunschwig, *Liber de arte destillandi. De simplicibus.* 1500. fol. 39 and 107.

[8]) Hildegardis Abbatissæ *Subtilitatum diversarum naturarum creaturarum libri novem.* Editio Migne. p. 1187.

[9]) Brunschwig, *Liber de arte destillandi. De simplicibus.* 1500. fol. 39.

[10]) Pfaff, *System der Materia medica.* Vol. 4 (1815), p. 172.

[11]) Lorenz Crell, *Die neuesten Entdeckungen in der Chemie* **6** (1782), 123.

[12]) Trommsdorff's Journ. der Pharm. **18**, I. (1809), 3.

[13]) Trommsdorff's Neues Journ. der Pharm. **24**, I. (1832), 134.

OIL OF NARDOSTACHYS JATAMANSI.

The rhizomes of *Nardostachys Jatamansi*, D. C., (*Patrinia Jatamansi*, Wallich) and of *N. grandiflora*, D. C., (N. O. *Valerianaceæ*) which are indigenous to the Himalaya mountains of northern India have an odor reminding faintly of musk but more strongly of patchouly. On account of its fragrance this root was highly prized during antiquity, being esteemed all the more because of its limited supply. It was used for perfuming ointments and fatty oils which were employed in anointing ceremonies. It was evidently regarded as one of the most precious aromatics.[1]) Later, especially out side of India, other roots were used as substitutes for the Indian narde (spikenarde), and frequently confounded with it, notably that of *Ferula sumbul*, Hook. fil., and still later that of *Valeriana celtica*, L.[2])

The original Hebrew name was *Nerd;* in Greek (derived from the Sanskrit) it was termed *νάρδος*, *ναρδόσταχυς*; in Latin, *Nardus indica, Nardus spica, Spica Nardus;* in Arabic *Senubol* (ear). Later this name was applied by different peoples to similar and even to different aromatic plants. Moreover, these were confounded with narde. In the first century of the Christian era, Dioscorides[3]) already distinguished between *Nardus indica, syrica* and *celtica.* As *Phu*[4]) he probably regarded partly narde, partly valerian.

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[1]) Song of Solomon, 1:12; 4:13 and 14. — St. Mark., 14:3—5. — St. John., 12:3—5. — Horatii *Carmina.* Lib. IV, carm. 13, verses 16—17. — During festive meals it was a Roman custom, not only to decorate guests with flowers, but to anoint them as well with narde.

Cur non sub alta vel platano, vel hac
Pinu jacentes sic temere, et rosa
Canos odorati capillos,
Dum licet, Assyriaque Nardo
Potamus uncti.

(Horatii *Carmina.* Lib. II. carm. 11.)

[2]) Sir Wm. Jones, On the Spikenard of the ancients in "Asiatic Researches" in Transactions of the Society instituted in Bengal, for inquiring into the history and antiquities, the arts, sciences and literature of Asia. Calcutta 1789. Vol. 2. (London edition p. 416.) — Roxburgh, Additional remarks on the Spikenard of the ancients. *Ibidem* vol. 4, p. 97.

[3]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, pp. 15—17.

[4]) *Ibidem* p. 20.

As having a similar odor, Scribonius Largus[1]) enumerates *Nardus indica, Nardus celtica, Stœchas, Nardus italica, Spica Nardi* (also used to designate species of *Lavandula*), and Indian grass (species of *Andropogon*).[2])

In midæval literature the original narde is mentioned but once, namely as one of the precious incense materials used during the entrance of emperor Henry IV. in to Rome.[3]) In midæval treatises on distillation and in pharmacopœias, Indian narde no longer is mentioned, but *spica* and spikenard are.[4])

OIL OF ELECAMPANE.

Aqueous distillates of elecampane were used medicinally during the middle ages.[5]) *Oleum radicis helenii* is first mentioned in the Frankfurt ordinance of 1582.

OIL OF ROMAN CHAMOMILE.

Owing to the similarity of some of the species of *Anthemis, Chrysanthemum* and *Matricaria,* it can not longer be determined which were cultivated by the Greeks and Romans and used by them. Nor is it possible to ascertain which species of the above genera is implied whenever *Anthemis* is used in the writings of Dioscorides,[6]) Pliny, Tragus,[7]) and other authors. According to Gesner,[8]) Roman chamomile was introduced into France and Germany from Spain. *Anthemis nobilis,* L., however, received more consideration, in England, in the southern part of which

[1]) Scribonii Largi *Compositiones medicamentorum.* Editio Helmreich. Leipzig 1887. p. 72.

[2]) See pp. 101, 184.

[3]) Petrus d'Ebulo, *Carmen de motibus siculis.* Basiliæ 1746. p. 23. — Flückiger and Hanbury, Pharmacographia. 1879. p. 503.

[4]) Hieronymus Brunschwig, *Liber de arte destillandi. De simplicibus.* 1500. fol. 72. — See p. 195, footnote 2.

[5]) *Ibidem* fol. 19.

[6]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. p. 482.

[7]) Hieronymus Tragus, *De stirpium maxime earum quæ in Germania nostra nascuntur commentarium libri tres.* Argent. 1552. fol. 149.

[8]) Conradi Gesneri *De Hortis Germaniæ liber recens.* 1561. Fol. 253.

it was cultivated and used medicinally. Even during the 16. and 17. centuries the several chamomiles were not kept separate in literature, a condition that apparently also prevailed in practice.

Hieronymus Bock (Tragus),[1]) who lived during the first half of the 16. century, called the plant *Chamomilla nobilis;* whereas Joachim Camerarius, who lived during the second half of the same century called it Roman chamomile.[2]) In the treatises on distillation of the 16. century the common chamomile seems to have been greatly preferred to the Roman chamomile.

On the continent, the latter was little used or not at all for medicial purposes, whereas in England it was used almost exclusively as chamomile flower.

Side by side with *Oleum chamomillæ,* distilled oil of Roman chamomile was first mentioned in the drug ordinance of Frankfurt of 1587.

OIL OF GERMAN CHAMOMILE.

The common chamomile, *Matricaria Chamomilla,* L., was used medicinally by the Greeks and Romans, and is repeatedly referred to in classical literature.[3]) It was also highly valued during the middle ages. Brunschwig[4]) describes the distillation of the flowers.

The oil, which attracted attention on account of its blue color, seems to have been known since the middle of the 15. century. Saladin[5]) mentions it in his list of medicaments of 1488, and the Nürnberg physician Joachim Camerarius[6]) prepared it in 1588. Conrad Gesner[7]) and Porta[8]) distilled the oil after moistening the flowers with *aqua vitæ.*

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[1]) See footnote 7, p. 196.

[2]) Flückiger and Hanbury, Pharmacographia. 1879. p. 384. — Camerarii *Hortus medicus et philosophicus.* Francofurti 1588. p. 39.

[3]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. p. 482—483. — Plinii *Naturalis historiæ libri.* Lib. XXII, 26. Editio Littré. Vol. 11, p. 82. — Palladii *De re rustica.* Editio Nisard. 1877. p. 608.

[4]) Hieronymus Brunschwig, *De arte destillandi.* 1500. Fol. 38.

[5]) Saladini Asculi *Compendium aromatariorum.* Venetii 1488. Index.

[6]) Camerarii *Hortus medicus et philosophicus.* Francofurti 1588. p. 39.

[7]) Euonymi Philiatri *Ein köstlicher theurer Schatz.* 1555. p. 222.

[8]) Gio. Battistæ Portæ *De destillatione.* Romæ 1608. p. 83.

In the price ordinances it is first mentioned in that of Berlin for 1574 under the title of *Oleum matricariæ,* and of Frankfurt-on-the-Main for 1587. In the *Dispensatorium Noricum* of 1589 it is mentioned as *Oleum chamomillæ vulgaris* besides *Oleum matricariæ.*

The blue color of the oil was attributed to a copper content due to the distilling vessels, until Pauli and Herford of Copenhagen showed in 1664 that the oil distilled from glass vessels likewise possessed a blue color.[1]) On a large scale, by steam distillation, chamomile oil was first distilled in 1822 by the apothecary Franz Steer[2]) of Kaschau in Hungary. The oil was first examined by Zeller[3]) in 1827.

OIL OF TANSY.

The distilled water from the flowers and leaves of tansy was a common remedy during the 16. and 17. centuries.[4]) The oil is first mentioned in the price ordinance of Frankfurt-on-the-Main for 1582 and in the *Dispensatorium Noricum* of 1589.

The oil was first examined by J. Persoz[5]) in 1841.

OIL OF WORMWOOD.

Wormwood is supposed to have been known to the Egyptians as early as the 16. century B. C.[6]) In the Old Testament the plant is referred to repeatedly.[7]) Whether the plant known to the ancients and later referred to as wormwood was the present *Artemisia absinthium,* L., or not can no longer be determined.

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[1]) Simonis Paulli *Quadripartitum botanicum de simplicium medicamentorum facultatibus* etc. Argent. 1667. p. 425.

[2]) Buchner's Repert. f. d. Pharm. **61** (1837), 85.

[3]) *Ibidem* **25** (1827), 467.

[4]) Hieronymus Brunschwig, *Liber de arte destillandi. De simplicibus.* 1500. Fol. 94.

[5]) Compt. rend. **13** (1841), 436; Journ. f. prakt. Chem. **25** (1842), 55, 60.

[6]) Papyrus Ebers, Jahresbericht f. Pharm. **1880**. 26. — Flückiger, *Pharmakognosie.* 1891. p. 686.

[7]) Deut., 29 : 18. — Proverbs, 5 : 4. — Amos, 5 : 7 and 6 : 12. — Jeremiah, 9 : 15; 23 : 15. — Lamentations, 3 : 15 and 19.

In Greek and Roman literature wormwood received but little consideration; however, it is mentioned in the writings of Dioscorides.[1]) As a remedy, wormwood is praised by Walafried Strabus[2]) in the 9. century and by the abbess Hildegard[3]) in the 12. century. From that time on it received occasional mention in pharmacopœias, but is wanting in most of the treatises on distillation of the 16. century, although known to their authors,[4]) and even distilled by Brunschwig.[5])

The distilled oil of wormwood was known to Porta,[6]) who directed attention to its blue color. It was first examined by Fr. Hoffmann of Halle and recommended by him for medicinal purposes.[7]) Later the oil was examined by Cl. J. Geoffroy,[8]) by Fr. Kunzemüller,[9]) by Buchholz,[10]) and by Margueron.[11]) In price ordinances it is first mentioned in that of Frankfurt-on-the-Main of 1587, also in the 1589 edition of the *Dispensatorium Noricum.*

OIL OF COSTUS ROOT.

Costus root from *Saussurea Lappa,* Clarke, was known to the Greeks as κόστος. During antiquity it was used as a spice, also in the preparation of a fragrant oil, for purposes of anoint-

[1]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, p. 367.

[2]) Walafridi Strabi *Hortulus. De viribus herbarum.* Editio Choulant. 1832. p. 147.

[3]) Hildegardis Abbatissæ *Subtilitatum diversarum naturarum creaturarum libri novem.* Editio Migne, *Patrologiæ cursus completus.* 1855. p. 1172.

[4]) Conradi Gesneri *De Hortus Germaniæ liber recens.* 1561. Fol. 243.

[5]) Hieronymus Brunschwig, *Liber de arte destillandi. De simplicibus.* 1500, fol. 112. — Brunschwig distinguished between the following species, *viz., Absynthium ponticum, Absynthium cretensis, Absynthium marinum,* used in the distillation of wormwood water .— See also Murray's *Apparatus Medicaminum* Göttingiæ 1766. Vol. 1, p. 118.

[6]) Portæ *De destillatione libri IX.* Romæ 1608. p. 79.

[7]) Friedr. Hoffmannii *Observationum physico-chemicarum selectiorum libri.* Halæ 1722. Lib. III. Observ. I, p. 9 and 355.

[8]) *Mémoires de l'Académie des sciences de Paris.* 1721.

[9]) Crell's Chem. Annalen 1784, 206.

[10]) Göttling's Almanach für Scheidekünstler und Apotheker 1785, 101.

[11]) Trommsdorff's Journ. der Pharm. 5, II. (1798), 202.

ment,[1]) similar to nard oil. It was also highly esteemed as remedy. Dioscorides[2]) distinguishes between the white Arabian or Indian, and the black Syrian costus. Garcia[3]) mentions that costus was used in Asia Minor, Syria, Arabia and Persia, but that it grows only in India. Costus root should not be confounded with *Costus dulcis,* a synonym for the bark of *canella alba.*

[1]) p. 195. — W. Heyd, *Geschichte des Levantehandels im Mittelalter.* 1879. Vol. 1, p. 90; and Vol. 2, p. 580. — Dymock, *Materia medica of Western India.* 1885. p. 449.

[2]) Dioscoridis *De materia medica libri quinque.* Editio Kühn-Sprengel. 1829. Vol. 1, pp. 15 and 29.

[3]) R. Sigismund, *Die Aromata.* Leipzig 1884. p. 34.

IV. HISTORY OF THE METHODS OF DISTILLATION AND OF DISTILLING APPARATUS.

The literary documents considered in the previous chapter reveal the slow process of evolution leading up to a better understanding of the subject of volatile oils. In like manner, a short historical retrospect of the methods of distillation and distilling apparatus may result in an insight into the gradual development of the art of distillation and of the methods of preparation of distilled oils. The history of the evolution from the primitive *Cucurbita,* the *Alembic* and the *Berchile* to the steam and vacuum apparatus of our own time reveals a long and varied course which had to be traversed by this apparently modern branch of industry in order to bring it to its present technical and scientific perfection.

As is well known, primitive man regarded fire as something supernatural. Thus the Greeks believed it to the gift of Prometheus and used it accordingly in their religious rites. The oldest tribes of the Persians worshiped it as a divine element. A more practical use was made of it by the Chinese, who in the remotest antiquity utilized it in the development of a most remarkable, though primitive industry. The oldest books of the Bible report that Tubal-Kain was "an instructor of every artificer in brass and iron";[1]) they also state that bricks were burnt[2]) for the construction of the tower of Babel. According to the apocryphal document, the *Ayur-Vedas,*[3]) the Indians at an early date not

[1]) Genesis, 4:22.
[2]) Genesis, 11:3.
[3]) See p. 16.

only used furnaces for melting and firing, but also for distillation. They were used extensively by the Egyptians during their long and highly developed period of civilization.

For more than ten centuries, from the time of the Arabians to the end of the middle ages, the solution of minerals, of vegetable and animal drugs with the aid of furnaces was regarded as a noble and "subtle" activity in the search for the philosopher's stone. This philosopher's stone was not only to serve the purpose of converting baser metals into gold, but also of preparing a *quinta essentia* for the maintenance and reestablishment of health and the prolongation of life. Hence the furnaces, apparatus, and implements constructed for the practice of the hermetic art and for alchemistic purposes are important, not only for their own sake, but as essential aids to technology. They afford an interesting illustration of the desire to solve the problems of a better knowledge of natural objects in so far as it can be gained by the direct or indirect action of heat as generated in the several types of furnaces used since antiquity. Thus the furnaces constructed for melting and sublimation were used in the search for the *lapis philosophorum,* the latter together with the furnaces used for distillation in the search for the *quinta essentia* of organic nature. As a final hypothesis, the doctrine of phlogiston was developed in the long epoch of practical endeavor and theoretic speculation. With its overthrow there were also abandoned at the close of the 18. century the beliefs in the miraculous, and the prevailing doctrines of the elementary nature of natural objects.

The first definite statement found in ancient writings which indicates a kind of primitive distillation, although probably not illustrated until the middle ages, is the mention of the method for obtaining oil of cedar, πισσέλαιον (turpentine oil?), which occurs in the writings of Herodotus, Dioscorides and Pliny.[1]) This oil is said to have been obtained from the oleoresin by boiling with water in an open earthen kettle. The oil either collected at the surface of the liquid and was removed, or its vapors were con-

[1]) Herodoti *Historiæ.* Lib. II, 85. — Dioscorides, *De materia medica.* Lib. I, 34, 39, 80. — Plinii *Historia naturalis.* Lib. XV, cap. 6—7; and Lib. XVI, cap. 22. *E pice fit, quod pissinum appellant, quum coquitur, velleribus supra habitum ejus expansis, atque ita expressis . . . . color oleo fulvus.*

densed in layers of wool spread over sticks of wood laid crosswise on the kettle as illustrated in figure 4. The wool when saturated was replaced from time to time by fresh portions and the oil expressed with the hands.

Authentic representations of the distilling vessels used by the Egyptians do not exist.[1]) Some of their forms of apparatus were undoubtedly adopted by the Arabians and improved by them. To the oldest known writings which give information on methods of distillation and distilling apparatus belong those of the Greek physician Dioscorides[2]) who lived during the first century of our era in Anazarbus, Sicily, and those of the Greek philosopher Zosimos[3]) of Panopolis. In a Arabian manuscript translation of Dioscorides' *Liber de materia medica* in the library at Leyden, distilling furnaces and apparatus are mentioned and described. These descriptions probably occur in the original Greek text. Among them are found the *cucurbita* and the *alembic*.[4])

Fig. 4.

Just as pictures of animals have served as symbols in the oldest mythology of and as characters in writing by the earliest peoples, the forms of animals were used by the ancients as prototypes in the making of jewelry, and of all kinds of useful articles and apparatus. The same practice appears to have obtained in the making of

[1]) Egyptian and Greek distilling apparatus of the 3. and 4. centuries, which served primarily for the distillation of mercury, have been reproduced in Dujardin's *L'art de la Distillation.* Paris 1900. These illustrations were found in a manuscript of the end of the 10. century in the Marcus library in Venice and are copied from Berthelot's *Introduct. à l'Etude de la Chimie des Anciens et du Moyen-âge.* 1889.

[2]) See p. 19.

[3]) *Περὶ ὀργάνων καὶ καμίνων* (of apparatus and furnaces). See p. 22.

[4]) Extracts from this as well as from the later Arabic texts of Rhases, also an unimportant illustration of an Arabic distilling apparatus, have been published by Prof. E. Wiedemann in vol. 32 (1878), p. 575 of the *Zeitschrift der deutschen morgenländischen Gesellschaft.*

primitive digestion and distilling vessels. Such pictorial representations have been carried over from the writings of Zosimos, and probably of others into the writings of the Arabians and from these into other alchemical works of the middle ages.[1])

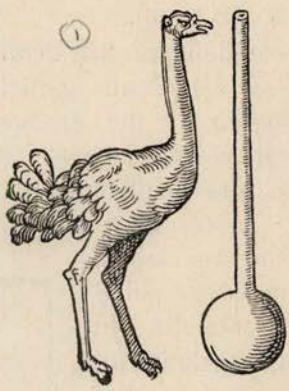

Fig. 5.

As the prototype of a common flask, the figure of an ostrich[2]) is given (fig. 5); as that of a retort a goose (fig. 6) or a pelican[3]) (fig. 7). The shape of a bear served for a still *(cucurbita)*[4]) and head *(alembicus)* (fig. 8). An improved form of this simple distilling apparatus is found in the writings of Geber,[5]) and of Albucasis.[6]) The latter not only described glass distilling vessels, but also those

Fig. 6.

Fig. 7.

prepared of glazed earthenware (fig. 9). He also described a kind of fractional distillation for the purpose of a "better con-

[1]) Joannis Rhenani, Medici, *Solis e puteo emergentis: sive dissertationis chymia technice practica, materia lapidis philosophici et clavis operum Paracelsi, qua abstrusa implicantur deficientia supplentur.* Francofurti 1613. Pars 1. *Theoremata chymio technica.*

[2]) *Phiala est vas vitreum ex ventre in modum sphæræ rotundo gracilem canàlem in proceritatem emittens.*

[3]) *Pelicanus est vas circulatorium e figura pelicani pectus suum rostro fodientis, pullosque suos refarcientis nuncupatum, amplo ventre sensim in angustiis collum vergente, quod retortum et curvatum os rursus in ventrem immittit.*

[4]) *Cucurbita est vas plerumque turbinatum, in cucurbitæ vel pyri formam utero turgescens. Cucurbita cum suo alembico juncta ejusmodi est.*

[5]) Gebri *Summa perfectionis magisterii. Gedani* 1682.

[6]) See p. 25.

densation and separation of subtle spirits" by placing several *alembices*[1]) on top of one another (fig. 10).

From the writings of Geber and Albucasis, also from those of the excellent physician and writer Rhases *(El Râzi)* who lived in Bagdad during the 9. century, it becomes apparent that the Arabians distinguished as early as the 8. century between

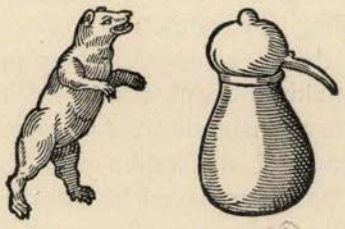

Fig. 8.

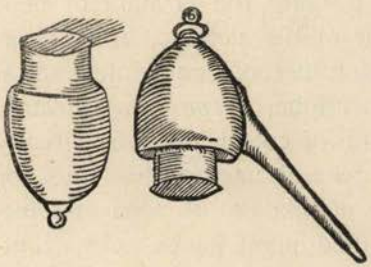

Fig. 9.

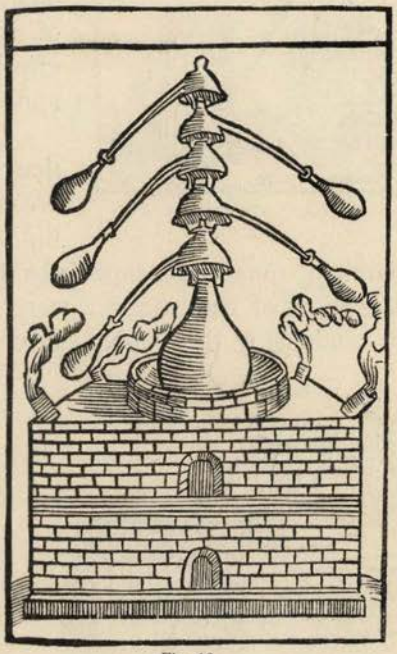

Fig. 10.

distillation over an open fire and from a water bath and an ash bath.[2]) Geber described both methods in detail.[3])

For the purpose of better condensation, Costæus of Lodi,[4]) a physician and alchemist of Bologna, recommended that the

[1]) *Liber servitoris* Bulchasin-Ben-aberazerin. Venetiæ 1471. Lib. XXVII, p. 247. *Modus alius cui vult destillare paucam aquam. Accipe ollam ex ære, et imple eam aqua, et pone super lanem ignis, et pone os ejus coopertorium perforatum foraminibus duobus vel tribus vel pluribus, aut paucioribus ventribus secundum quod poterit capere coopertorium ollæ, et sint ventres ex vitro . . .*

[2]) *Das Buch der Geheimnisse des* Abû Bekr Ben Zakarîjâ Er-Râzî. Fleischer's *Katalog* No. 266. *Leipziger Stadtbibliothek.* Codex K. 25.

[3]) Gebri *Summa perfectionis magisterii.* Cap. 50. *Ex bibliotheca vaticana exemplari.* Gedani 1682.

[4]) Mesue, *Simplicia et composita, et antidotarii novem posteriores sectiones adnotationes.* Venetiæ 1602.

beak of the alembic be cooled by water (figs. 11 and 12), also that the distillate be improved by the use of the water bath *(balneum Mariæ)* (fig. 13) and the sand bath *(balneum arenæ)* (fig. 14).

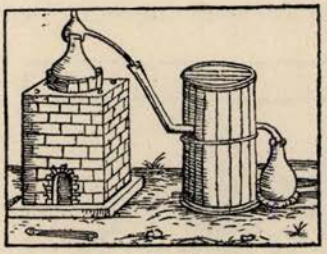

Fig. 11.

Among the writings left by the Arabians, the work of Albucasis previously mentioned probably contains one of the first and most striking descriptions of the manner of distillation and distilling apparatus.[1])

From the 14. century on the practice of making distilled liquors increased very considerably. As a result the methods of distillation and the distilling apparatus, especially those parts employed for the condensation of the vapors, were greatly improved. The method of condensing the vapors, already well known to the Arabians, by passing the straight or bent tube of the alembic, or an elongation thereof wound into a spiral (wormtube, *serpentina*) through a tub of cold water was already in general use at that time for the distillation of wine and fermented plant juices. As examples of such distilling apparatus and methods, *"die mancherley Kühlungen der Teutschen und Welschen Weinbrenner"*, are described and illustrated in treatises on distillation of the first half of the 16. century, namely in those of Brunschwig, Ulstad, Ryff, and Lonicer. In these a distilling apparatus constructed with considerable skill is described. The helmet of the still and the outer condenser jacket were made of sheet copper. The head-like form of the expansion of the helm with the outer jacket, the lower open rim of which was tightly

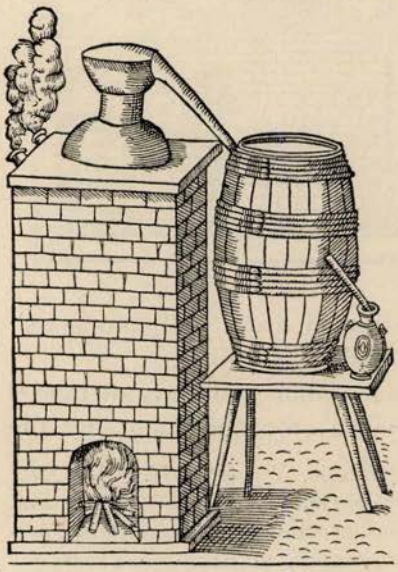

Fig. 12.

[1]) See p. 26.

luted to the still, gave rise to the name of *Mohrenkopf*. The condensation was effected by a continuous flow of cold water through the outer jacket (fig. 15).

The method of condensation derived from the Arabians was considered the most perfect for the distillation of spirit of wine *(aqua vitæ)*. The illustration of this apparatus was selected for the title page of the second volume of Brunschwig's Destillirbuch published in the year 1507 and is reproduced on page 41. Where the two upright serpentine connecting tubes *(serpentinæ)* between the retorts *(cucurbitæ)* and the receivers *(receptacula)* cross each other they pass through a condensing tube filled with cold water. The cooling effect thus produced is not sufficient for the condensation of all the vapor. The worm acts therefore, as a dephlegmator and increases the alcoholic strength of the distillate. This is correctly emphasized by Brunschwig.

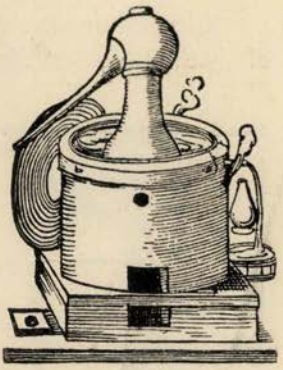

Fig. 13.

diweil die Geister, so über sich getrieben werden, vil reyner und subtiler seind, denn in solchem aufsteigen alles, so schwer, irdisch oder flegmatisch ist, nit hinauf kommen mag. Darumb die Geyster des weins am flüchtigsten über sich, aber anderer materi, so mehr mit flegmatischer feucht behafft, under sich getrieben werden.[1])

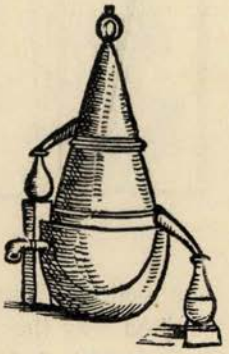

Fig. 14.

The perfection of the apparatus for the preparation of distilled waters and oils, which up to that time had received but little attention, seems to have progressed much more slowly and with greater difficulty. In comparison with the readily volatile alcohol, water was considered as that product of distillation most closely related to it, whereas the oil was regarded as the "obese and fatty substance that had to be driven over with a stronger and more violent heat." This had led to the firmly established belief that in the process of purification the volatile and

[1]) Hieronymus Brunschwig's *De arte destillandi*. Vol. 2, liber 1.

subtle part must penetrate and exhaust the material as much as possible (resolving). As a result all sorts of queer apparatus and sources of heat were invented for producing the so-called circulation. They all resulted in a prolonged digestion and an unintentional loss of the alcohol, ofttimes formed by fermentation, and of the aroma.

Circulation was therefore considered not only as the essence of distillation, but also as an important preparatory part of it. It

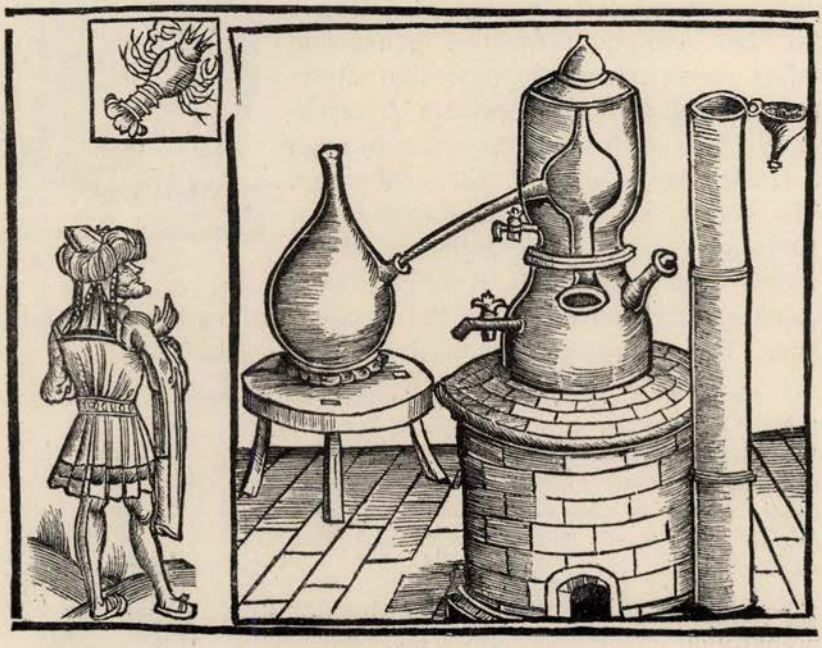

Fig. 15.

was believed that the plant and animal material finally to be distilled was thereby prepared for the refinement and purification of the spirit beings ("geistige Wesen") contained in them, and for their better and easier separation and purification. A large variety of vessels, usually constructed after some symbolic prototype, was used for this purpose. The simple *Circulatoria* were ordinary glass flasks, retorts the tubes of which were bent in a variety of ways, also so-called urine glasses used by physicians for diagnosis.

The operations performed in the pelican (fig. 16) and double or twin *Circulatoria*[1]) (fig. 17) provided with reflux tubes were considered as the most perfect kinds of circulation, especially for refining the "spirits."

Still more peculiar than the form of the *Circulatoria* was the source of heat used for the purpose of circulation, which was usually accompanied by fermentation, and even decomposition processes. Not only was the water bath *(balneum Mariæ)* (fig. 18) and the ash bath *(balneum per cinerem)* (fig. 19) employed, but also the sun bath *(destillatio solis)* (fig. 20). The circulation vessels were also immersed in fermenting dough, and heated with this in an oven *(destillatio panis);* or they were

Fig. 16.

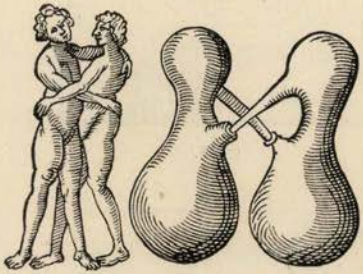

Fig. 17.

imbedded in decomposing, well wetted horse manure which was placed in a layer above unslaked lime in pits *(destillatio per ventrem equinum)* (fig. 21).

With the introduction of aromatic waters as one of the principal forms of medication, the condensation of the vapors gave rise to difficulties, because a greater degree of heat was necessary for their distillation. Plant material lying on the bottom of the still was also easily burnt, and the distillate received therefrom an empyreumatic odor and taste. With a strong heat a serious overheating of the helm and tube, which were usually constructed of lead or tin, took place, while with the employment

[1]) *duota est vas circulatorium a duabus auribus, vel viro utrumque brachium lateribus applicatum habente, dictum, hujus inferior pars est in modum cucurbitæ, cui impositus est alembicus in summo canalem habens; in loco autem conveniente duobus rostris incurnatus et in cucurbitam a capitello humorem, condensatum ducentibus præditum.*

of a moderate heat the yield of the distillate remained unsatisfactory. In order to overcome these disadvantages, and to prevent the flowing back of the distillate condensed in the helmet, as well as to increase the cooling effect of the air, the helmet known as the "Rosenhut" (fig. 1, p. 40 and fig. 22) was constructed as early as the 15. century. Near its base, at about the height of the

Fig. 18.

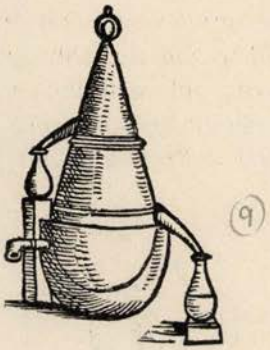

Fig. 19.

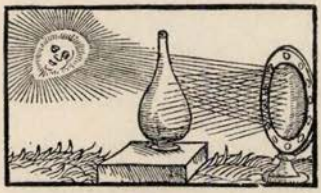

Fig. 20.

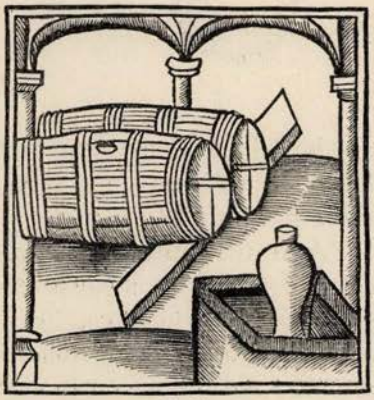

Fig. 21.

outlet tube, a groove extended around the inside of the helmet. Through this the water, condensing on the upper inner wall of the helmet and running down, was conducted into the outlet tube and from there into the receiver. The "Rosenhut" was therefore in itself an inefficient air condenser, which served its purpose with much less efficiency than did the "Mohrenkopf" in the distillation of alcohol (fig. 15, p. 208).

In the preparation of the distilled waters, the first step toward a better condensation with cold water, consisted in surrounding the head of the helmet *(alembic)* with an oxbladder.

It was securely fastened and provided with a wooden stop-cock. The hood-like basin thus formed (fig. 23) was kept cold by means of flowing water. In a similar manner the helmet was also surrounded by a basin-like metallic addition which was either fastened by luting or soldering. Thus the helmet could be well cooled by running water (fig. 24). By means of an inner horizontal groove like that in the "Rosenhut" (fig. 22) the distillate

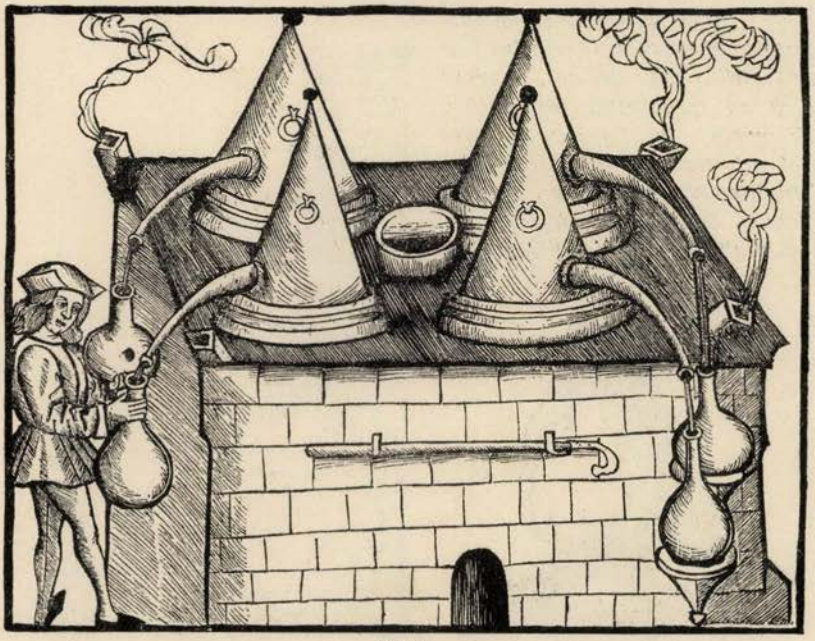

Fig. 22.

which condensed on the inner walls of the helmet was conducted into the receiver.

About the middle of the 16. century, Walter Ryff in his treatise on distillation[1]) describes and illustrates distilling apparatus with condensing tubes which are passed through vessels of cold water. The first apparatus has two tubes, connected with the helmet (fig. 25), which are passed through a barrel of water. However, Ryff declares this method of condensation as insufficient and recommends a worm tube, for the shape of which

[1]) See p. 46.

he gives two forms (figs. 26 and 27), and concerning the use of which he gives the following account.

Die Spiritus sollen durch sonderliche Instrument recht digerirt oder gekult, und von der unmessigen hitz und erbrennung solcher geyster abgezogen werden, als nemlich mit den rören so mit vilen krümmen durch ein wasser geht, von irer seltsamen krümme wegen Serpentina genannt, das ist Schlangenrör. Solcher rören empfahen die erhitzigten geyster, so von der werme aufgetrieben werden, und füret sie durch die vile krumb lini, und wider durch das wasser damit sie genügsamlichen gekület werden . . . . Zu einem Destillationsgeräthe nit allein in der Abstraction der spiritus oder geyster, sondern auch zu mancherley Destillation, als nemlich der Emacerirten oder wol erhitzigten, Purificirten oder Dirigirten Weckholderbeer, Stichasblumen, Spic, Lawendel, und anderer dergleychen öliger, hitziger und

Fig. 23.

Fig. 24.

feyster gewechs und Wurzeln, von welcher wir das oel abziehen wöllen, darumb schaff die ein küpfferin oder irdin kessel zu Destilliren durch den dampff des hitzigen Wassers. Auf diesen kessel lass dir einen helm . . . . . bereiten von guter erden, innerhalb und ausserhalb wol verglasurt. Dieser helm sol sich auf den kessel wohl schliessen, also dass es nit möge ausriechen. . . . . Dieser helm sol oben ein loch haben, darin du die rören oder Serpentine stecken, und auch auf das best vermachen mögest, welches Serpentin durch ein wasser gericht sol werden, das allezeit kalt sei, damit die geyster, so fast rein und subtil, ganz leichtlich zu verhitzigt und verbrennt werden, on underlass külung und erquickung empfahen. Solch Serpentin magstu nach mancherley art und

manier bereyte, also dass die geyster under sich oder ober sich getrieben werden.[1])

A peculiarly constructed apparatus for the distillation of aromatic waters and oils was recommended by Adam Lonicer in his *Kräuter- und Destillirbuch* published in 1573. Uffenbach's translation of the description is as follows:

Von Gewürzen und allerhand Saamen, als von Nägelein, Zimmet, Muskatnuss, Anissamen, Römisch Kümmel, Wisskümmel, Fenchelsaamen und dergleichen, kann man mancherley edle und köstliche Öle abziehen. Und dieweil solche Öle nun sehr gemein im Gebrauch seien habe ich die Form und Weise der gemeinen Instrument und Ofens, sammt der Destillation,

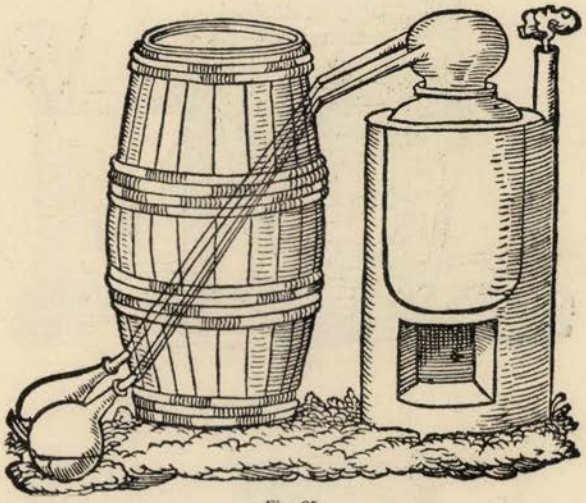

Fig. 25.

hiebei gesetzt (fig. 28). *Man bereitet einen gemeinen Destillierofen, wie zu einem einfachen balneo Mariæ pflegt gemacht werden, darin setze man ein kupffern Blase so ziemlich grosz ist, dasz sie eine gemeine Masz oder sechs haltet. Solcher Blasen Hals oder Mund sol oben handbreit weit sein, und über den Ofen herausgehen. Darauff stürtzet oder decket man ein kupffern Hut, so wol darin einschliesset. Solcher Hut soll oben ein Rörlin haben so eines Fingers dick weit ist und eines halben Fingers lang über sich gehet. Daran steckt man die blechen Rören, so uff die art, wie folgende Figur aussweiset, bereitet sein, dass sie gehet in ein andern kupffern Kolben, so auch einen Hut mit einem Rörlin oben hat. Darauff setzet man ein andere auch dergleichen blechen Rören oder Serpena in welche durch ein Vasz, in ein Fürlegerglasz, darin die destillirte Materie fliesset, ausgehet.*

[1]) W. Ryff, *New gross Destillirbuch, wohlbegründeter Destillation.* Frankfurt a. M. 1567. Fol. 21.

So man nun von Gewürtze oder von Samen die Olea distillirn will, sol man die kupffern Blase so in dem Brennofen stehet halb vol Brunnenwasser füllen, und darnach die Gewürtze oder Samen, darvon man die Olea abziehen will, wol zerstoszen, derselben ein Pfund oder zwei darin thun. Die Instrument oder Rören an allen Orten, da sie zusammen gesteckt werden, wol gehab mit Ochsenblasen und Meel verwaren, und das Feuer under-

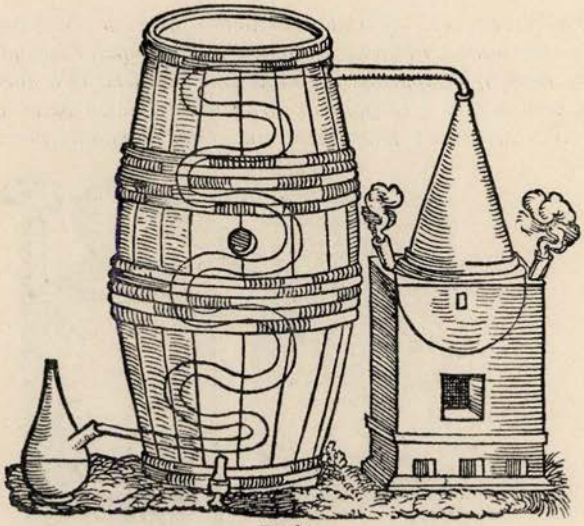

Fig. 26.

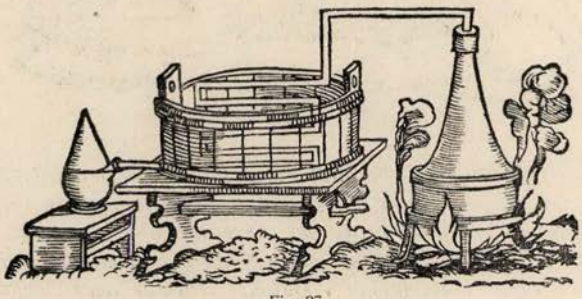

Fig. 27.

machen. Erstlich sanfft und darnach je lenger je hefftiger regieren. Solche Distillation gehet geschwind naher, in drei oder vier Stunden. Wann nun die beste Spiritus also herausz gefliesen und abgelauffen sein, sol man das Oleum so oben in dem Glasz schwimmet, sauber darvon in ein besonder Gläszlin geschicklich absondern.[1])

[1]) Adami Loniceri *Kräuter Buch und künstliche Conterfeyungen sammt der schönen und nützlichen Kunst zu destilliren. Von* Petrus Uffenbach *in's Teutsche übertragen.* Ulm 1703. pp. 18—19.

Finally, the Arabians and probably others before them practiced "downward distillation" which corresponds on the whole to our modern dry or destructive distillation for obtaining empyreumatic or tar oils. At the time of the revival of the distilling art, this method was also applied to the preparation of the oils of certain woods, barks and spices. Juniper wood in particular had been submitted to this *destillatio per descensum* since

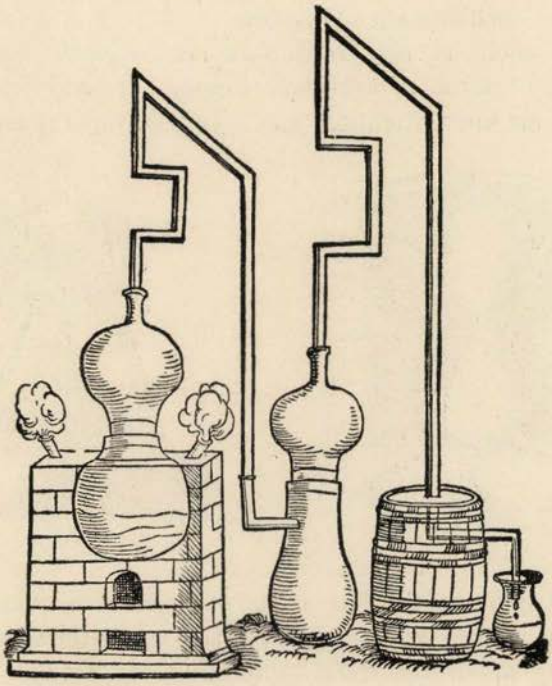

Fig. 28.

antiquity, later also guaiac wood, cinnamon, cloves, mace and other spices were distilled in this manner. The furnace contained a division in the middle, with a central opening into which a pot, provided with a beak-like opening at the bottom, was either hung or plastered in. On top of the opening extending into the upper part of the furnace was placed a wire gauze and a second pot filled with the dry substance to be distilled was luted with its opening on the top of the lower pot. The heating was then effected by building a fire around the upper pot (fig. 29). Some-

times the lower pot was buried in the earth and a fire built about the upper pot fastened on top of this one in the same manner.

For the *destillatio per descensum* on a small scale, glass vessels heated from the side (fig. 30) were also employed, and for some easily distilled substances even the heat of the sun *(destillatio solis)* (fig. 31) was used. At present the preparation of empyreumatic oils as well as of the finer tars is effected in cast iron or earthenware cylinders.

Titles, such as *de furnacibus construendis,* as well as illustrations of some of the older treatises, already enumerated, reveal that no little attention was given during the middle ages

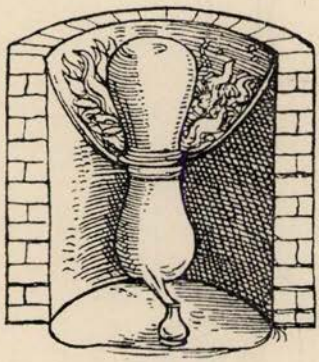

Fig. 29.

Fig. 30.

to the construction of distilling furnaces. Abundant evidence thereof is found in the 16. century treatises on distillation. Besides the distilling apparatus most generally used at that time, and reproduced in figs. 11, 12, 15, 18, 22, 24, 25 and 26, the socalled *faule Heinz* or *Athanor* (from ἀθάνατος, imperishable), called *furnus Acediæ* by Ulstadt (fig. 32), was much in favor and was used to a great extent for the distillation of waters and oils. Above a common fireplace were placed three or more distilling retorts with *Rosenhuthelm* (p. 211, fig. 22). The fireplace ended in a central iron, copper or earthenware pipe, the opening of which could be closed by a cover. By means of slides at the sides of the fireplace the heat could be conducted under any one of the stills or retorts as desired, and the distillation was thus regulated.

For the distillation of large quantities in a large number of individual retorts or stills, larger cupil furnaces after the manner of the so-called "galley furnaces" appear also to have been in use. The illustrations and descriptions of these in some of the treatises on distillation of the 16. century represent no doubt

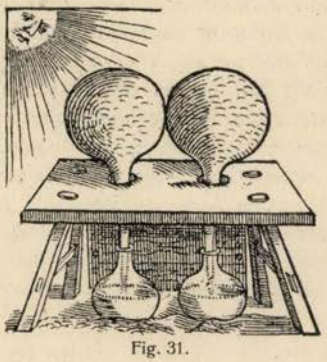

Fig. 31.

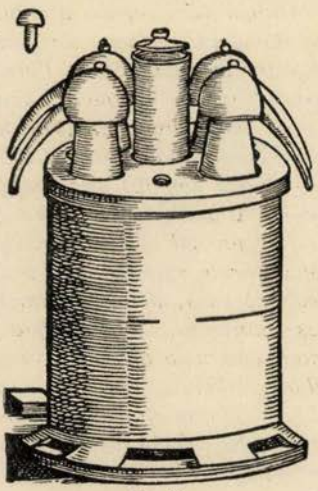

Fig. 32.

more the possibility than the realization of perfection. The illustrations of these furnaces were transferred from one distilling

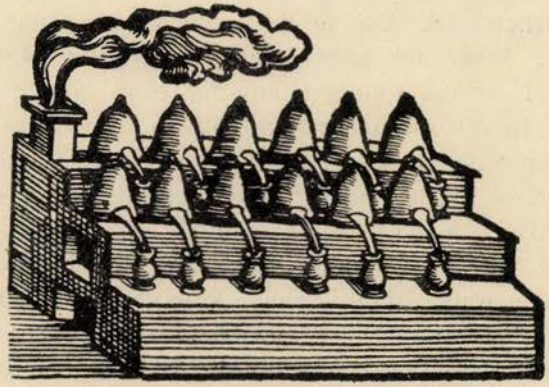

Fig. 33.

book to another, but the furnaces themselves probably have not been generally used in practice. Among others they are thoroughly described in the text and reproduced by illustrations in the works of Matthiolus and of Lonicer previously mentioned. They are built either in the shape of a terrace (fig. 33), or of a

bee hive (fig. 34). Matthiolus describes one of the latter type, in which the retorts are placed between the tiles, and its mode of operation in the following words:[1])

Ultima hac fornace utuntur Veneti ac Neapolitani, qui vitreis alembicis abundant. In aqua una tantum die et nocte, sicco ignis calore, eliciunt quæ ultra centum libras. Fornax rotunda est, ut ex imagine hic appicta apparet, fornacibus, quæ in Genuanorum visuntur vaporariis, omnino similis. Continet hæc circumcirca numerosa fictilia, intrinsecus vitro incrustata, urinalis forman referentia et diligente sane artificio argillaceo luto agglutinata, quibus singulis per rotum fornacis ambitum singuli adduntur vitrei alembici, e quorum vertice ex globulo ad hoc parato, recipientia crassiusculo funiculo ad alligata, pendent. Calefit hæc fornax eodem modo, quo Germanicorum vaporariorum fornacis. Atquedum ignis vehemens est, vacua relinquunt vasa, donec parumper remittatur, ne violente calore plantæ et flores exurantur. Tunc itaque plures ministri, qui hoc tantum artificio aluntur, obstructo undique fornacis ostio, ne conclusus expiret calor, herbas fictilibus injiciunt, et simul vitreos applicant alembicos. Atque in hunc modum copiosas eliciunt aquas et olea, quæ longe meliores habentur, quam quæ plumbeis conficiuntur instrumentis, quod nullam metallorum contrahunt infectionem.

Although the compilers of the distilling books of the 16. century have successively followed the pioneer work of Brunschwig, especially in regard to illustrations, their writings nevertheless quite often show considerable differences in views, practical skill, and experience, and also in the originality of their knowledge and ability. With but little public intercourse these secluded workers and writers toiled mostly far from one another, each in his own sphere and manner, often with but a slight knowledge of the older writings and of the work of his contemporaries. With regard to the manner of distillation of the aromatic waters and oils, this is shown in an unmistakable manner in works compiled in the course of the first half of the 16. century by Philipp Ulstad, Walter Ryff, Adam Lonicer, Valerius Cordus, and Conrad Gesner. All of these were mainly based on the writings of Hieronymus Brunschwig. Their views, however, as to the nature of distillation itself and of the distilling methods and apparatus are neither in accord with those of Brunschwig, nor with those of their contemporaries.

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[1]) Petri Andreæ Matthioli *Opera quæ extant omnia. Supplementum: De ratione destillandi aquas ex omnibus plantis: et quomodo genuini odores in ipsis aquis conservari possint.* Basiliæ 1565. p. 5.

How little personal skill, practical experience and familiarity with the literature on the subject may be found in the writings and methods of working of the most prominent experimenters of that time becomes apparent *e. g.* from the construction of

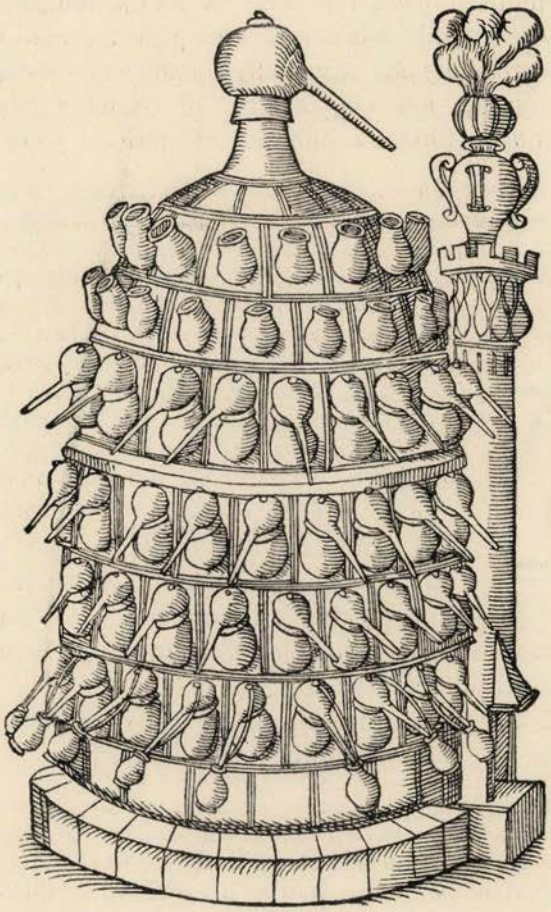

Fig. 34.

and preference for the distilling vessels employed. Thus for instance, Valerius Cordus,[1]) profound in theoretical science, but ignoring the rationally constructed distilling apparatus then well known, used and recommended *ein Kolb mit einem ange-*

[1]) Valerii Cordi *Annotationes in* Pedacei Dioscoridis *de Materia medica libros quinque. Liber de artificiosis extractionibus.* Liber II. *De destillatione oleorum.* Anno dei 1540. p. 229.

schmelztem Helm (fig. 35) as an efficient apparatus meeting all the requirements of the art. At the same time Conrad Gesner,[1]) his contemporary, used for the same purpose a distilling furnace (fig. 36), which had long been in use.

How confused were the ideas as to the nature of the distillation of the volatile oils even on the part of a man like Gesner who was theoretically and practically equally well trained, becomes apparent from the following extract of Gesner's description of the preparation of distilled oils and of spirit of wine from wine.

Die Specerey (Nelken, Muscatnuss, Safran, Macis, Benzœ, Myrrha, Storax etc.) wird grob gepulvert, dann mit aqua vitæ durchfeuchtet und bei gelinder Wärme destillirt . . . . wenn das Öl anfahrt zu fliessen, so nimm die materi der specereyen aus dem Kolben und thus in ein säcklin, welches wohl verbunde sye mit einem faden, und trucks aus under einer prässen. Also dass der beide bläch der pressen wohl heiss machest. Und also gebührt es sich das ausgetruckt öl zu destilliren, rectificiren und circuliren, damit auff diese weis das rein lauter öl werde geschieden von der groben yrdischen materi. Demnach mag man wol wiederumb die häpffen putrificiren und digeriren mit dem vorgemelten aqua vitæ, so von anderem abgesünderet worden. Unn zum letzten wiederumb destilliren.[2])

Fig. 35.

The operation was interrupted at the beginning, the fatty oil saturated with ethereal oil expressed, and the volatile oil remaining in the residue separated by distillation.

For the distillation of the volatile oils from flowers, Conrad Gesner gives the following directions:

Die Blümen der Spiken oder des Lavander solt du eine kurze Zeit lang sonnen in einer grossen gläsinen retorte und darnach ein Wasser in einem alembik darvonnen destilliren und abziehen. Dieses Wasser durch den ganzen Sommer gesetzt an eine warme statt an die Sonnen, so treybt es für und für öl über sich, welches öl du allwägen solt von dem wasser separiren und absündern mit einem fäderlich (feathervane) *und dasselbe fleyssig behalten in einem gläsinen guttern* (flash) *wohl vermacht und verstopfet.*[3])

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[1]) *Thesaurus* Euonymi Philiatri, *Ein köstlicher Schatz etc.* Zürich 1555. Fol. 216. *"Wie man möge Oel separiren und abziehen von den Specereyen, Blümen und Samen".* Edition of 1583. p. 206.

[2]) *Thesaurus* Euonymi Philiatri, *Ein köstlicher Schatz etc.* Zürich 1555. Fol. 215—237.

[3]) *Ibidem* fol. 222.

According to Gesner, anise and other umbelliferous fruits are to be bruised and macerated with wine (fol. 227) before being distilled. Juniper berries are distilled *per descensum*, and the empyreumatic oil thus obtained rectified by *destillatio per ascensum* (fol. 231).

As an illustration of the crude views held as to the nature of distillation, and as to the products of distillation, the directions for the rectification of spirit of wine given by Ulstad[1]) and followed by Gesner[2]) may here be quoted:

Wann weyn zwey oder drey mal fleyssig und ordentlich destillirt sein wird, so nimm einen reinen und dunnen Schwamm und zerhauwe denselbigen in so grosse stuck, welche in der grösse sygend, dass sy oben für an allen orten inwendig der kolbensmogind anrüren. Der selbig schwamm sol angebunden werde und mit zweyen oder dreye schnürlinen, welche für den kolbe härausreichind, damit so du demnach einen helm darauf setzest, die schwämm nit mögind an boden des destilliergefesses fallen, und dieselbigen schwämm söllend vorhin in baumöl gesetzt werden, und demnach wiederum ein wenig ausgetruckt, damit nicht etwan das baumöl in den kolben herabtrieffe, und der materi so man zum destilliere genomme hat, vermischt werde und wann du jm also thon hast, so setz ei helm darauff welcher allenthalben verstriche seyge, damit kein dampff nirgends heraus gan möge. Unnd durch diesen schwamm werdend die aufgetriebenen geyster des aquæ vitæ simplicis seer wäsentlich und feyn destilliert. Also was grober unreiner, yrdischer und ungedöuwter materi und substanz ist, mag von wägen dess öls nicht durch den schwamm gan und durchtringen. Und so du den gebrannten weyn auff diese weys und art zu destillieren zu hand nimbst, so wirst du mer in einem abzug schaffen, dann sunst in dreyen.

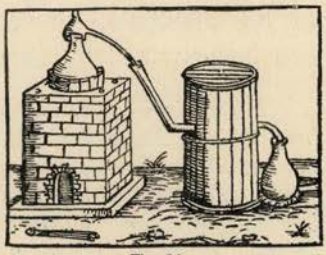

Fig. 36.

As has already been mentioned, the 17. century, crippled as it was by the destructive storms of the Thirty Years war, added but little to the further development of the art of distillation and other technical scientific industries. The few active experimenters, however, favored with a better understanding, endeavored to perfect not only the apparatus used, but the processes as well. As the *Destillirbuch* of Brunschwig and similar treatises of his successors reflect the practical and theoretical knowledge

[1]) *Cœlum Philosophorum seu liber de secretis naturæ.* Argentor. 1528.

[2]) *Thesaurus de remediis secretis.* Vol. 1, fol. 68. Tiguri 1552.

of the 16. century with its mistakes and imperfections, so Rudolph Glauber's[1]) treatise on distillation reflects the condition of the art and science of distillation during the second half of the 17. century. Although Glauber's laboratory work and the character of his writings was of a wider scope than that covered by the older treatises on distillation, yet he also paid special attention to the distillation of aromatic plants and spices. In this, he and his contemporaries seem to have paid special attention to the improvement of the methods of distillation for the purpose of relatively increasing the products of distillation. For this purpose, as has already been mentioned on page 65, a very rational expedient of increasing the specific gravity and thus raising the boiling point of the water used for the distillation, was resorted to. It was effected by the addition of salts. A peculiar method for the distillation of volatile oils with the addition of muriatic acid is described by Glauber in the following words.

Fülle einen gläsernen Kolben voll mit Cinnamomum oder anderem Holz, Samen, Macis etc. und giesse darauf so viel Spiritus salis,[2]) *dass es das lignum bedecke, setze solchen mit einem alembic in das Sandbad, gieb Feuer, dass der Spiritus salis koche, so steigt mit wenig phlegmate alles Öl über, denn der Spiritus salis durchdringet wegen seiner Schärfe das lignum, macht das Öl ledig, dass es desto lieber übersteiget. Also wird auff solche Weise das Öl nicht wegen grosser Menge des Wassers verschmieret und verlohren sondern in kleinen Gläsern mit wenig Wasser aufgefangen und separiret . . . . Auf solche Weise mit dem Spiritus salis kann man aus allen theuerbaren Vegetabilibus ihr liebliches Öl mit Nutzen machen. Desgleichen können auch alle Gummi und Harze, wie Mastix, Olibanum etc. in klare Olea durch Hülff des Spiritus salis destillirt werden.*[3])

For the decoloration of distilled oils, also for the improvement of oils that have darkened with age, such as the oils of cinnamon, cloves and nutmeg, Glauber describes their rectification *per retortam* with *Spiritus salis.*[4])

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[1]) Johanni Rudolph Glauberi *Furni novi philosophici oder Beschreibung der neu erfundenen Destillirkunst.* Amsterdam 1648 — Leiden 1648 — Prague 1700.

[2]) An impure muriatic acid obtained by the distillation of common salt with sulphuric acid or alum.

[3]) Glauberi *Furni novi philosophici.* Editio Prague 1700. Part. 1, pp. 35—36.

[4]) *Ibidem* Part. 1, pp. 39—43.

For the distillation of plant materials with salt and dilute muriatic acid, Glauber gives the following directions:

Die olea aromatum seminum, florum, herbarum, radicum, lignorum etc. werden gemacht, indem die Samen gemahlen, die Blumen, Kräuter und Wurzeln kleingehackt, die Hölzer geraspelt und mit soviel Wasser angefüllt werden, dass dieselben wohl darinnen schwimmen und maceriren können und noch feuchtigkeit genug bleibe, damit dieselben bei der Destillation nicht anbrennen und statt eines lieblichen ein brenzliches Öl erhalten werde. Trockene Samen, Blumen, Kräuter, Wurzeln und Hölzer müssen zuvor etliche Tage in dem Wasser stehen und sich erhitzen, ehe sie können destillirt werden, und muss auch das Wasser zu den trockenen Species gut gesalzen werden, dadurch dieselben erweichen und ihre olea desto lieber von sich geben. Zu denen noch grünen Gewächsen ist es nicht nöthig; doch kann es auch nichts schaden, denn das Wasser kann durch Hülfe des Salzes desto heisser werden, dadurch die Olea desto lieber steigen, und hilfft auch viel dazu dass man Weinstein und Alaun zuthut, welche der Destillation nicht wenig Beförderniss thun. Wenn dann die Species ihre Zeit in dem gesalzenen Wasser gestanden und wohl durchbissen seyn, thut man dieselbe in das Destillirfass etc., so gehet mit dem Wasser, wenn es kochet, des Kraut's, Samen's oder Holzes Öl herüber, und wiewohl auf diese Weise durch Hülff des Salzes vielmehr übergehet, als mit süssem Wasser allein, so bleibt doch noch viel zurück, welches vom Wasser nicht hat ledig gemacht und übergetrieben werden können. Dieserhalben der beste Weg ist, solche olea mit Nutzen zu machen, durch den Spiritum salis zu destillire, wie im ersten Buch gelehrt.[1])

Glauber's authority was recognized until the middle of the 18. century, and the methods of distillation recommended by him in his several writings were employed by his contemporaries and their successors. Therefore, Boerhaave, Hoffmann, their contemporaries, and later investigators prepared the volatile oils by using common and other salts, or hydrochloric acid.

It is perhaps due to the observation that metal was present in an oil or a distilled water, especially if an acid had been used in its preparation, that in the course of the 18. century more attention was again bestowed upon the material of which the still was constructed. In consequence glass and glazed earthenware were substituted for metal. As a matter of fact it seems that as early as the 15. century the presence of metals in the distillates obtained from metallic stills did not escape the notice of some of the experimenters. Among others Joh. Krafft[2])

[1]) Glauberi *Furni novi philosophici.* Editio Prague 1700. Part. 3, p. 30.

[2]) Crato von Kraftheim, *Conciliorum et epistolarum libri* VII. Francofurti 1589. Vol. 1, fol. 190.

(Crato von Kaftheim, born 1519, died 1585) cautions against the use of copper distilling vessels. The famous Parisian physician Ambroise Paré[1]) (born 1510, died 1590) warns against the use of lead helmets and condenser tubes "which ofttimes cause the distilled water to be milky". The Bologna physician and professor, Benedetto Vettori[2]) of Faenza (Victorius Faventius, born 1481, died 1561) declared about the year 1555, that water, when conducted through lead pipes, dissolves lead and thus becomes poisonous.

However, these observations, like so many others made in the art of distillation, appear either to have been known to but a few, or else were unheeded and again forgotten, for even during the 17. and 18. centuries when oils were distilled with acids, lead and tin heads and condensers were in general use in connection with copper stills or glass and earthenware retorts.

As already mentioned in the preceding chapter, the distillation of the volatile oils and the construction of the distilling apparatus received more attention and underwent a more rapid development with their general introduction into the laboratories of apothecaries. In these the volatile oils used in medicine and the arts were prepared up to the first decades of the 19. century. Only a few oils, such as the oils of lavender, rosemary and rose, which could be produced readily in some countries and which were largely used in the perfume and soap industries, have been obtained since the 16. century in larger quantities by means of primitive portable distilling apparatus.[3]) The distilling vessels used in the apothecary laboratories and the intinerant stills *(Wanderdestillirgeräte* or *alambics voyageants)* used in France, Spain, Italy and Bulgaria, consisted of copper stills with a copper or tin head and tin condensing tubes of various shapes.

One of the better distilling apparatus used for the distillation of volatile oils in the 18. century consisted of a tin or copper body suspended in a water bath, and provided with a *Mohrenkopf* (fig. 15, p. 208), a *Rosenhut* (fig. 22, p. 211) and a spiral tube

[1]) *Les Œuvres de* M. Ambroise Paré, *conseiller et premier chirurgien du roy.* Paris 1575. *Editio latina par* Jean Haultin. Parisii 1582. p. 746.

[2]) Victorii Faventini *Practicæ magnæ de morbis curandis ad tirones, tomi duo.* Veneti 1562. Tom. 1, cap. 21, fol. 144.

[3]) See pp. 48, 137, 182 and 183.

for condensation. An illustration (fig. 37) and description of this distilling apparatus was published in 1784 by François Demachy[1]) (born 1728, died 1803), director of the apothecary laboratories of the civic hospitals of Paris.

The copper kettle *v* serves as a waterbath, which can be turned by the handles *s s* and refilled with a fresh supply of water through the side tube *m*. The tin still *d* rests with the upper ring *n* on the rim *h* of the kettle. The lower neck *q* of the head of the still *b* rests at *n* on the upper rim of the still. Around the lower edge of the head runs the trough *c* in which the distillate that has been condensed in the cone collects and passes with uncondensed vapors through the tube *c—u* into the spiral condenser.

The *Mohrenkopf a*, serving as a cooler for the *Rosenhut b*, is soldered to the neck *k* of the condensing cone. The water in the cooler warmed during the process of distillation, runs off through the upper tube *e* as fast as cold water is added.

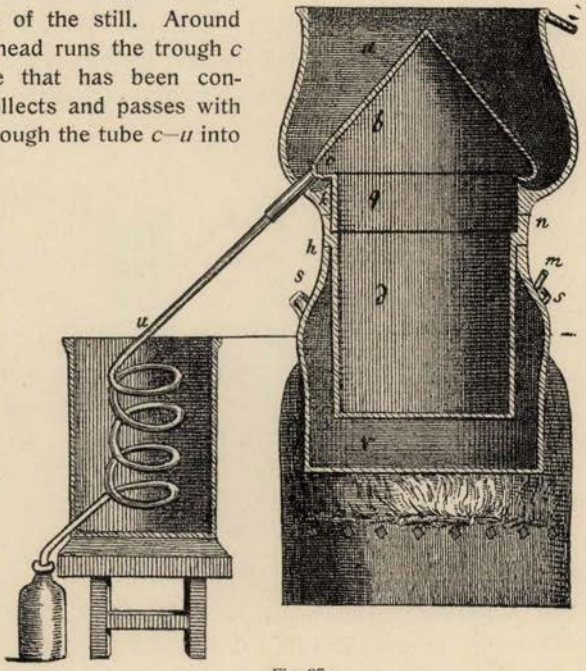

Fig. 37.

Since the beginning of the 19. century attemps have been made to simplify and to improve the construction of the distilling apparatus, more especially of the cooler, also to prevent the burning of the plants on the bottom of the still caused by the application of direct heat. Such improvements were made

[1]) J. F. Demachy, *L'art du destillateur des eaux fortes.* Paris 1773. — The German edition bears the following title: *Herrn Demachy's Laborant im Grossen, oder die Kunst, die chemischen Produkte fabrikmässig zu verfertigen. In 3 Theilen. Mit Dr. Struves Anmerkungen und einem Anhange einiger Abhandlungen des Apothekers Wiegleb.* Translated from the French and supplied with additions by Samuel Hahnemann, *der Arzneikunde Doctor und Physicus des Amts Gommern.* 3 Vols. Leipzig 1784. Vol. 1, pp. 192—198 and plate 2, Fig. 1.

especially by Joh. Gottfr. Dingler,[1]) apothecary in Augsburg, during the years 1815—1820, by Smithson Tennant[2]) in 1815 and by Henry Tritton[3]) in 1818, both of England. The latter attempted to carry on the distillation at a lower temperature by connecting the apparatus with an air pump. The distilling apparatus more commonly in use at that time for the distillation of volatile oils was the one shown in the accompanying cut (fig. 38).

Steam distillation was recommended in 1826 by H. Zeise[4]) and especially for volatile oils by van Dijk in Utrecht,[5]) who thereby materially aided in its introduction. He demonstrated that "the volatile oils which were obtained by steam alone from

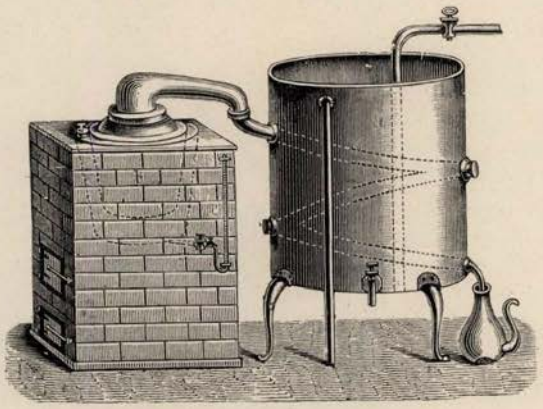

Fig. 38.

the vegetable material, distinguished themselves from those obtained by distillation over open fire, by a lighter color and purer odor. Clove oil distilled with steam is nearly colorless, cinnamon oil light straw yellow and orange peel oil completely colorless."[6])

[1]) Trommsdorff's Journ. der Pharm. **11**, I. (1803), 241; also Buchner's Repert. für die Pharm. **3** (1817), 137; and **6** (1819), 142.

[2]) Philosoph. Transact. of the Royal Soc. of London. **1815**. — Repertory of Arts. London. Sept. 1815.

[3]) Annals of Philosophy. June 1818. — Buchner's Repert. für die Pharm. **6** (1819), 98.

[4]) H. Zeise, *Beiträge zur Nutzanwendung der Wasserdämpfe*. Pamphlet. Altona 1826. — Arch. der Pharm. **16** (1828), 69.

[5]) Buchner's Repert. für die Pharm. **29** (1828), 94.

[6]) *Ibidem* **29** (1828), 110.

The first steam distillation on a larger scale in a pharmaceutical laboratory appears to have been that in the old Apothecary's Hall in London.[1])

In Germany steam distillation for the preparation of volatile oils in apothecary laboratories was also made possible by the introduction of a steam distilling apparatus, constructed about the year 1826 by Johann Beindorff,[2]) mechanic and tin founder

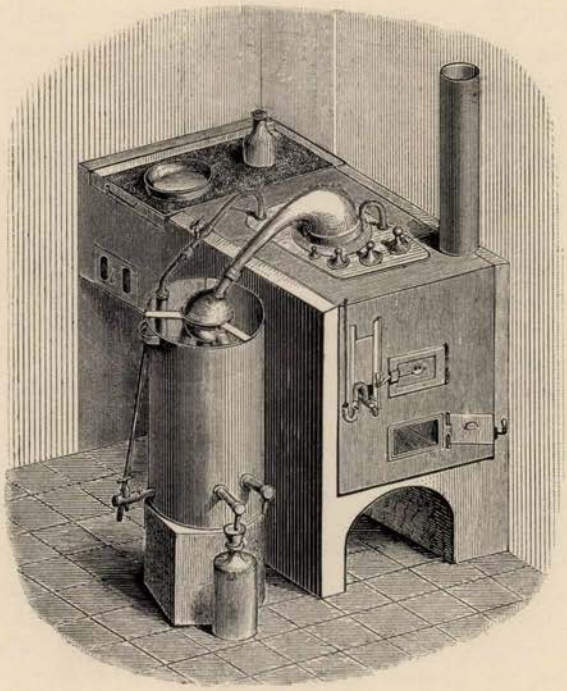

Fig. 39.

in Frankfurt-on-the-Main (fig. 39). With this apparatus, soon perfected in many ways, the distillation of volatile oils with steam under pressure was possible. The condensing arrangement also had the advantage over the spiral tube by being made up of separate parts, and thus allowing it to be readily cleaned even on the inside.

[1]) Buchner's Repert. für die Pharm. **29** (1828), pp. 112 and 113.

[2]) Geiger's Magazin für Pharmazie etc. **11** (1829), 174 and 291. — Buchner's Repert. für die Pharm. **33** (1830), 436.

For the preparation of volatile oils on a small scale, the arrangements based on the original steam distilling apparatus of Beindorff remained, until the industry conducted on a large scale became dominant also in this field and prepared products of a quality and at prices with which the preparation on a small scale could not compete.

Of the arrangements used for a long time for the separation and removal of the oils from the water, the Florentine flask in various forms and sizes has shown its utility and has been in continual use. It probably came into use in the middle ages. A method of separation of oil and water, which in its principles corresponds to those of the Florentine flask, was apparently described for the first time by Porta[1]) in the latter half of the 16. century.

"When oils are extracted from plants, those substances which with the water pass over into the receiver must be separated carefully, in order that the oil, which contains on excess of phlegm, may not be weakened. Hence the oil must be rectified in order that it may retain its full strength. This is accomplished by distillation and separation. For this purpose the first distillates are mixed, poured into a retort placed into a water bath *(in balneo Mariæ)* and slowly distilled over. The pure oil will float on the surface of the aqueous distillate. The separation of the oil from the water demands painstaking labor. For this purpose, however, ingenious vessels have been devised which admit of the ready separation of water and phlegm from the oil. The glass vessel serving this purpose is open at the top and widens out funnel-like toward the bottom. The water, phlegm and oil are transferred slowly, drop by drop, into this flask, whereby the oil rises to the surface. A lateral tubular opening is closed with the finger. By effecting a partial opening the lower layer of water is allowed to flow out, whereas the oil collects above the opening closed by the finger. Thus the oil is separated from the water that has been allowed to flow out. Finally the oil is transferred to another container.

"Still another separating vessel has been devised for this same purpose. The bulging flask contracts to a narrow neck, to the middle of which is attached a bill-like tube. The oil mixed with water is poured into this flask, the water remains below, the oil rises to the surface and into the neck. Water is then added drop by drop so that the pure oil flows drop by drop out of

[1]) Joh. Baptistæ Portæ, Neapolitani *Magiæ naturalis libri viginti, in quibus scientiarum naturalium divitiæ et deliciæ demonstrantur. Iam de novo, ab omnibus mendis repurgati, in lucem prodierunt.* Romæ 1565. Antwerp. 1567. Editio Hanoviæ 1619. *Liber decimus: Destillat, destillata ad fastigia virium sustollit.* p. 367—412.

the bill. In the case of other oils which sink to the bottom, the water is allowed to flow out above. Any water remaining at the surface is removed by cotton (a lamp wick) whereby the purest oil remains behind."[1])

The Florentine flask, like many other improvements pertaining to the art of distillation which were not generally known, was soon forgotten. As a result it was rediscovered several times from the beginning of the 17. century to the year 1823. Thus the flask was again described and introduced by Homberg[2]) at the end of the 17. century, about one hundred years after Porta's description — only, however, again to be forgotten for a considerable period of time. A century later, in the year 1803, the Florentine flask was again recommended for the distillation of volatile oils by the Augsburg apothecary Johann Gottfried Dingler[3]) and later in 1823 once more introduced as something new by the apothecary Samuel Peetz[4]) in Pesth.

The Florentine flask of older construction, as described by Porta, has been in use for a long time. The oil was siphoned off by means of a porous siphon consisting of a lamp wick into small bottles (fig. 40). Later the Florentine flask shown in fig. 41 was also used. The flask used at the present time in the large factories is not only larger, but contains in the upper part on a level with the oily layer a glass stopcock through which the oil can be drawn off from time to time (fig. 43), or an overflow tube through which the oil when it reaches a certain level runs into a receiver (fig. 42).

In the course of time a number of differently constructed receivers for the separation of the volatile oils have been proposed,

[1]) ". . . . *Quomodo oleum ex aquis separemus — aliud separatorium vas ad idem ingenuosissime excogitatum est, tenuet venter vasis, collum angustum est, cujus medio rostellum affixum est. Transfundatur in vas oleum aqua remistum, occupat aqua fundum, oleum supra collum: guttatim aquam addes, donec oleum ascendat ad rostellum, ex pernento, inclinato vase, descendet purissimum oleum et purgatum, ubi aliquid evacuasti, sensim aquam addendo, ascendit oleum ad canaliculam coq.; iterum inclinato, reliquum transfundas. Si vero oleum subsidet, aqua super adlatur, ut multories eveniet, in latam fideliam vel quodcunq.; vas impositum, gossipino licineo adaptato, aqua foras transmeabit, oleum purissimum quod superest, in fundo residebit*".

[2]) Philippe and Ludwig, *Geschichte der Apotheker.* 1858. p. 513.

[3]) Trommsdorff's Journ. der Pharm. 11, II. (1803) 242.

[4]) Buchner's Repert. für die Pharm. 14, III. (1823), 481.

without however, causing the Florentine flask to be discarded. The first of these was proposed by Amblard of Paris[1]) in 1825. It consisted of a conical glass tube, open at both ends and drawn out to a taper. This tube was suspended by means of a cork ring at its upper end in a high glass mixing cylinder. This cylinder was provided at the top with an overflow tube. The oil collects in the glass tube and can be removed from this after closing the small lower opening, by pouring out as often as desired.

The more salable volatile oils which were used in larger quantities in the perfume industry that had developed in France in the course of the 18. century were still prepared during the first quarter of the 19. century in the traditional primitive distilling

Fig. 40.

Fig. 41.

vessels, and were improved by rectification. In Germany the apparatus shown in figs. 38 and 39 were principally used. While the oils of lavender, rosemary, orange flower, and other fragrant oils *(essences)* were manufactured in France, and rose-oil in Turkey, Germany and Hungary supplied the market with the oils of caraway, fennel, anise, coriander, calamus, peppermint, spearmint, valerian, chamomile, and others used in medicine and in the fine arts. In southern France, especially on the sunny slopes of the Alps near the Mediterranean coast, the industry of the aromatic oils developed considerable proportions in the early part of the past century. The oils principally used for medicinal purposes, however, were still prepared in apothecary labor-

[1]) Bulletin des travaux de la Société de Pharm. Paris, May 1825, p. 247.

atories. In the course of time certain apothecaries and druggists, having made a beginning on a small scale, erected much larger establishments for the preparation of volatile oils. This was done especially in regions suited to the cultivation of medicinal plants, for instance, in Thuringia on the Saale and the Elbe, in Saxony, Bohemia, Franconia, and also in Hungary. Only a few of these, however, remained in existence for any appreciable length of time. As in other branches of chemical industry, these originally small distilling operations were replaced everywhere by a larger, more rational and efficient industry. Since the middle of the past century this new industry has worked hand in hand with science and technology. It has not only enlarged, but also improved the conventional methods and apparatus

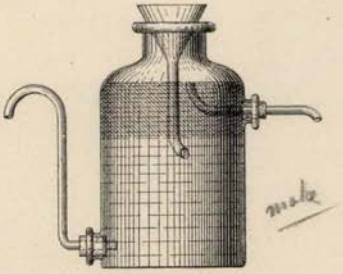

Fig. 42.
Receiver for oils lighter than water.

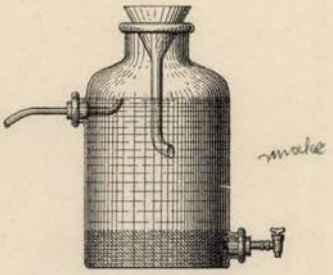

Fig. 43.
Receiver for oils heavier than water.

for distillation. Whereas on the one hand it utilized the results of science, on the other it not only stimulated science, but gave direct assistance.

Beginning about the middle of the past century the earlier, simple apparatus took on a different shape in the factories of this larger industry of the volatile oils. The original small distilling apparatus were replaced by larger and more rationally constructed ones which not only effected a better exhaustion of the vegetable matter and thus increased the yield, but also produced oils of a better and purer quality.

The apparatus commonly used in the factories about the middle of the present century, were the stills arranged for the so-called water-distillation, and others for the so-called dry steam-distillation.

The first type of still (fig. 44) is a simply constructed apparatus for the distillation of plant material in water, as well as for the rectification of crude oils by steam. The still is heated by means of steam admitted under pressure through the holes of a ring *d* at the bottom, or by allowing the steam to escape directly into the lower double walled jacket *B*. The aqueous distillate constantly flows back into the still through the tube *F*.

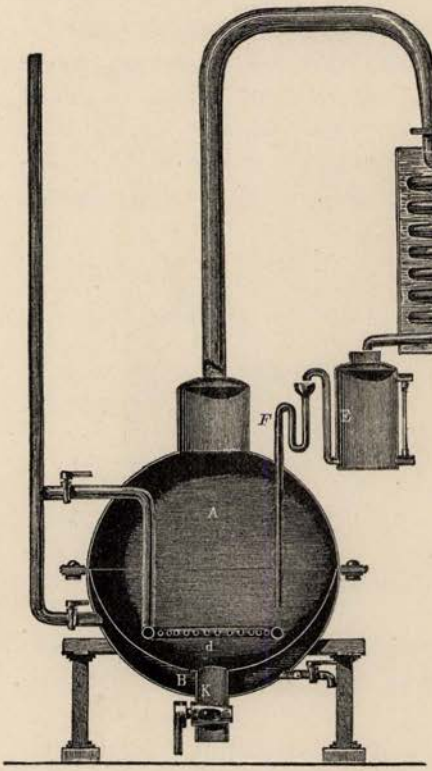

Fig. 44.

In the distillation with dry steam (fig. 45), the still is filled with the plant material without the addition of water and distilled with steam passing through the material from the bottom upwards. These or similarly constructed steam distilling apparatus are employed even at the present time for the distillation of some of the oils, only, in place of the spiral, a tube condenser is used.

With the introduction of these apparatus during the middle of the past century the volatile oil industry had taken its position as a branch of the rapidly developing chemical industry at large with southern France and central Germany as the principal centers of production.

Owing to the remarkable development of the entire perfume industry during the second half of the past century, the consumption and commerce of the volatile oils assumed entirely unanticipated proportions and importance. Scientific and technical attainment, commercial interests and business competition brought about numerous changes in rapid succession. More rational methods of distillation were devised, large apparatus

for the distillation of enormous quantities were constructed. Some of the largest have a capacity of from 30 000 to 60 000 liters.

The evolution of the modern distilling apparatus as applied to the distillation of volatile oils, like that of the theory and art of distillation in general, is replete with historical interest.

On the following pages will be found a number of illustrations of some of the modern stills used in the largest German factory. Looking backward it might seem as though there were no connection between the modern giant stills and their prototypes. Yet every one of them is but a link in the long chain of develop-

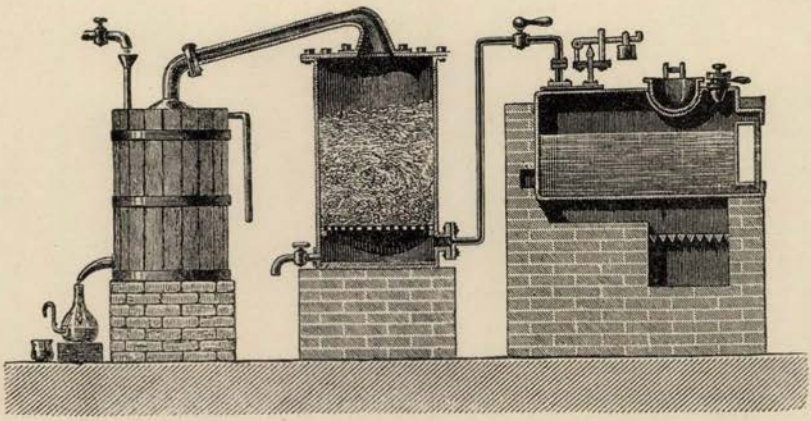

Fig. 45.

ment of the art of distillation. That the process of evolution has been exceedingly rapid during the past ten years does not affect the truth of this statement. Almost every one of these pieces of apparatus has been newly created out of the ruins of its immediate predecessor.

In modern chemical industry Germany unquestionably ranks first. Of the various branches of this industry that of the manufacture of volatile oils and synthetic aromatics has acquired an importance previously unexpected and with it a correspondingly influential position.

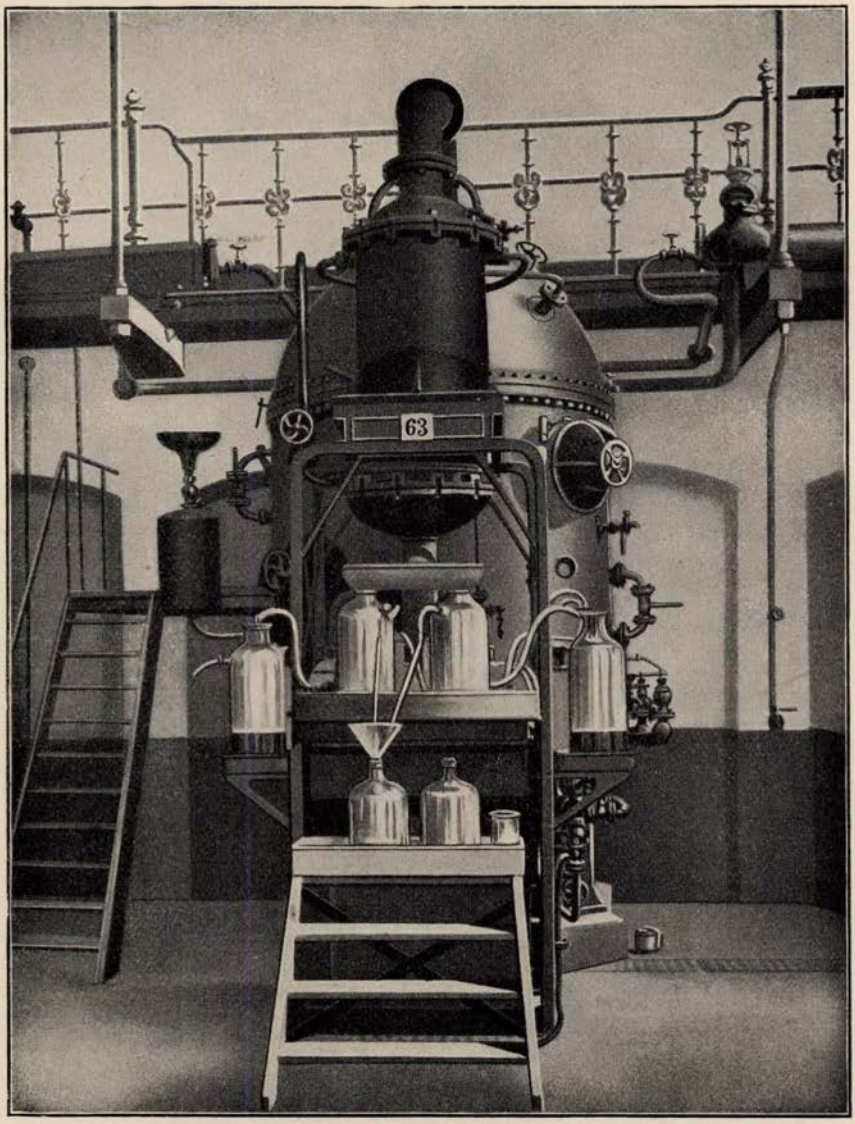

Fig. 46.

Modern distilling and rectifying apparatus.

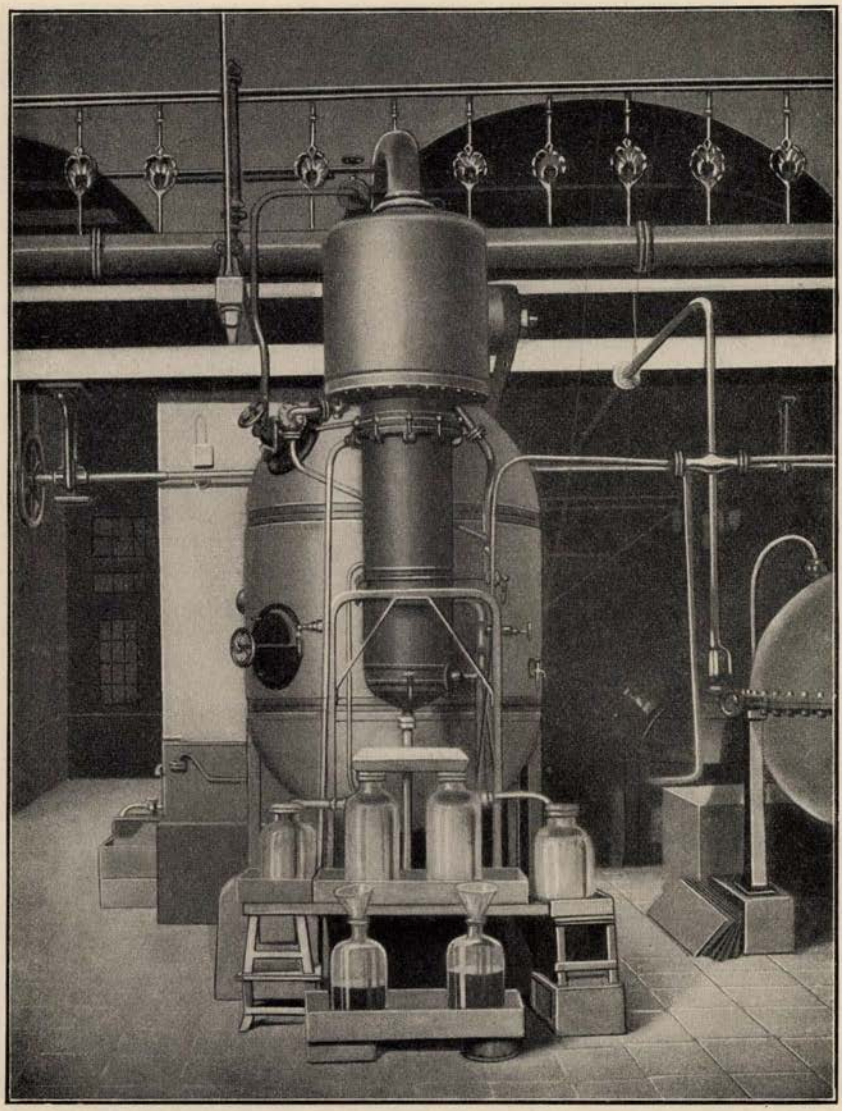

Fig. 47.

Distilling and rectifying apparatus.

Fig. 48.

Distilling apparatus for water distillation.

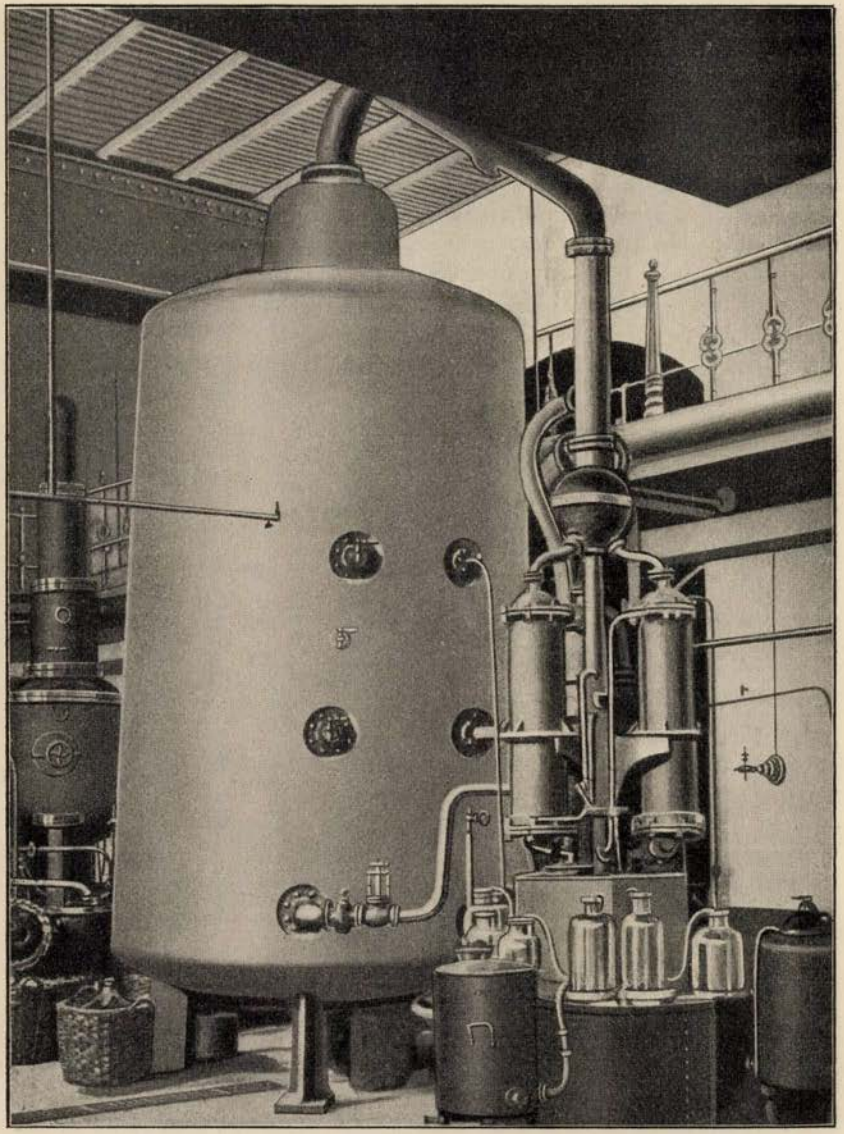

Fig. 49.

Distilling apparatus of 30000 liter capacity.

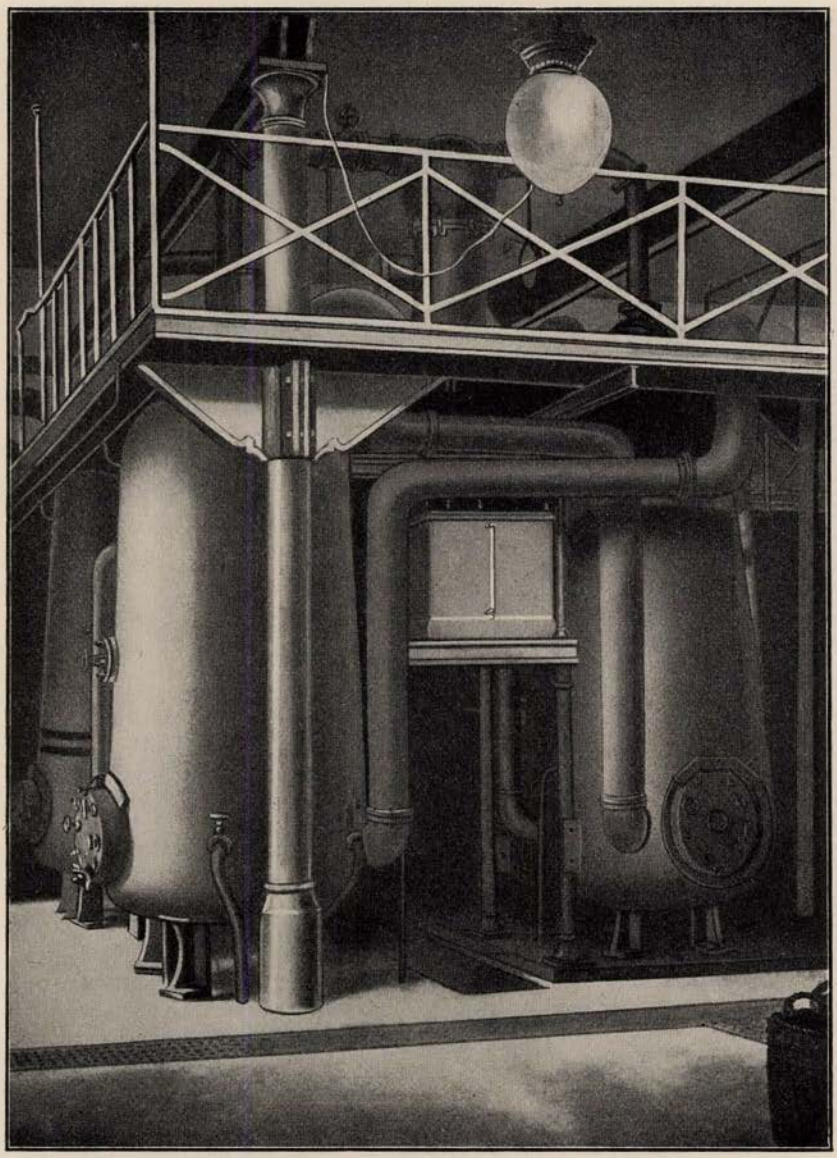

Fig. 50.

Distilling apparatus for spices.

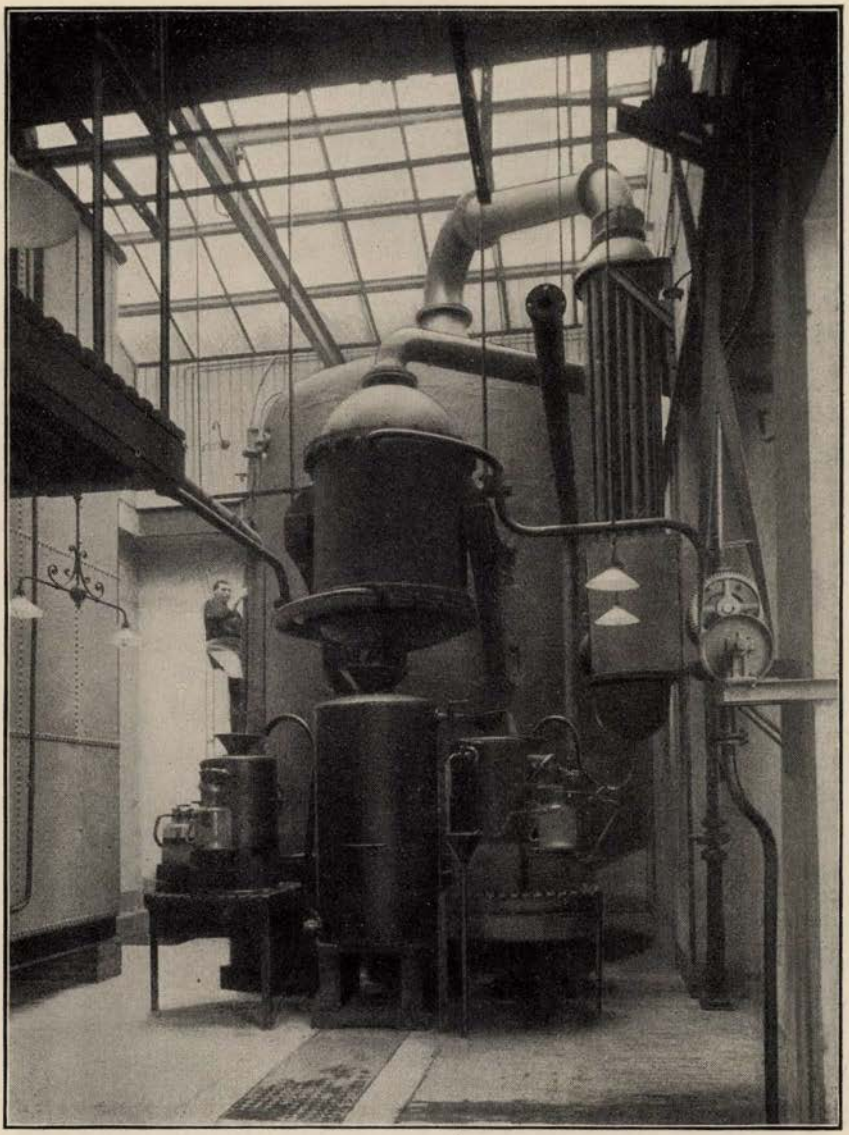

Fig. 51.

Giant distilling apparatus of 60 000 liter capacity.

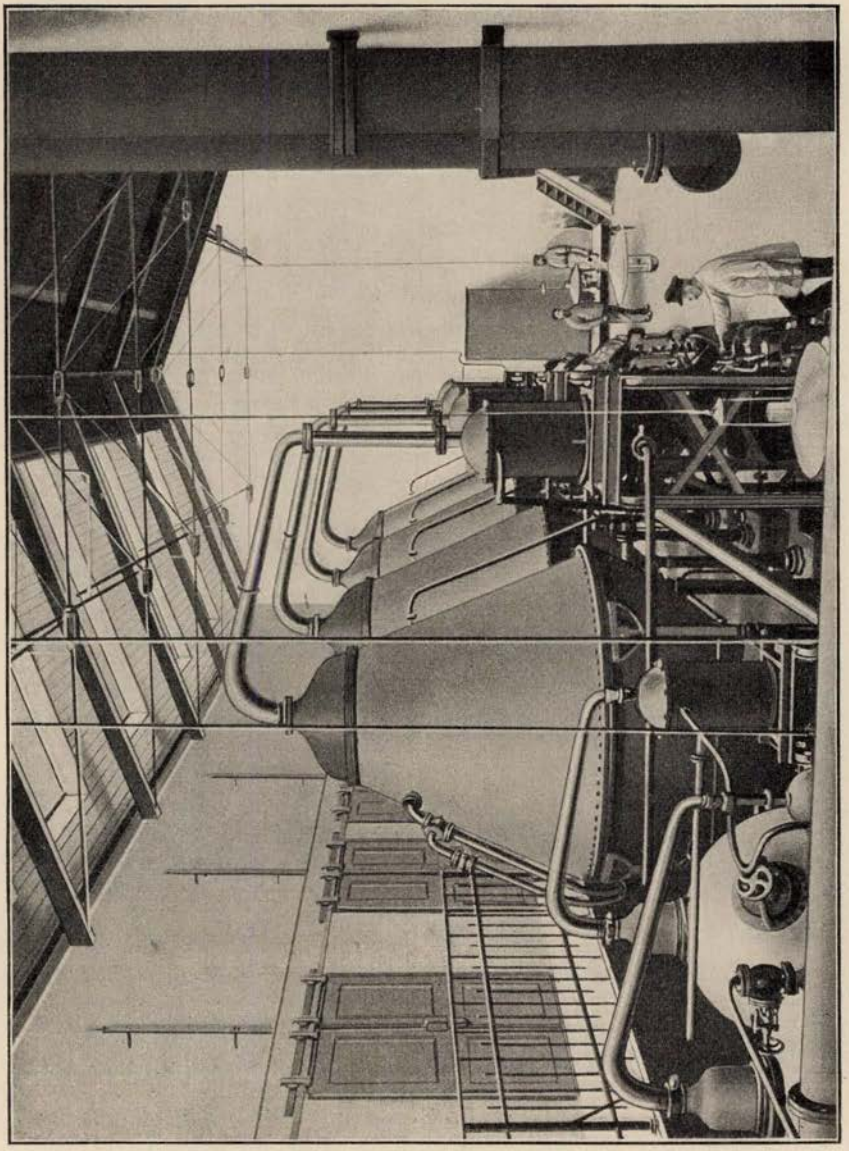

Fig. 52. Distillation of rose oil.

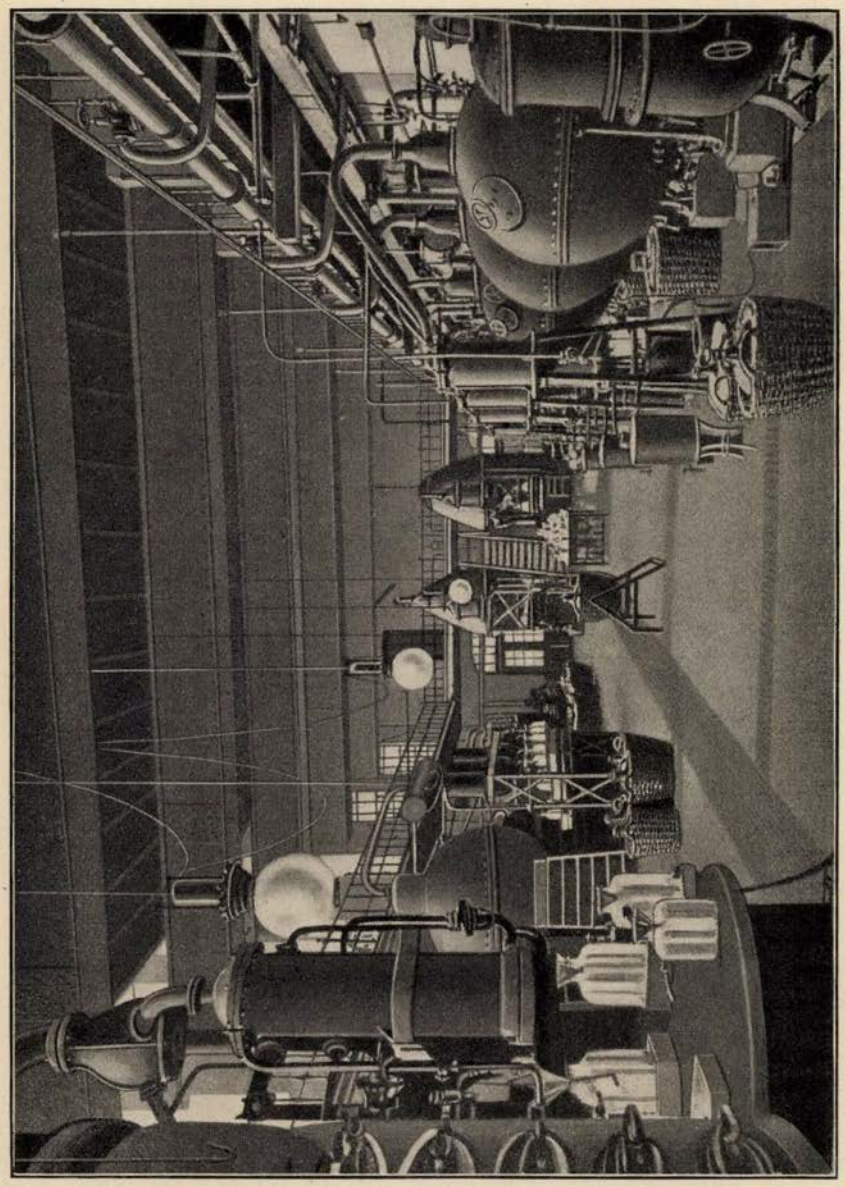

Fig. 53. Modern distilling apparatus.

THE PRODUCTION OF FLOWER PERFUMES

BY EXTRACTION, ENFLEURAGE, AND MACERATION.

The most common method for the production of volatile oils is that by steam distillation. This method not only produces the best yields and the purest oils, but also enables the operator to attain the end sought most cheaply and with the simplest apparatus. Furthermore, large quantities of oil can thus be produced without much human labor. In particular instances, however, distillation does not produce the desired result. This is particularly true when the high temperature of the steam destroys the unstable perfume substances, or when the amount of oil is relatively small, moreover if it is readily soluble in water. In such instances distillation may, under favorable circumstances, yield a fragrant water, which, even by cohobation, may not separate a volatile oil.

As a matter of fact, some of the most fragrant parts of plants, namely the flowers, are not suited to steam distillation. In order to prepare the odoriferous substances which impart to them their fragrant odor, other methods are employed. In such cases the volatile oils may be extracted either with volatile solvents or with fat, or they are allowed to be absorbed by fat.

Hence a distinction is made between:

A. Extraction with volatile solvents.
B. Extraction with nonvolatile solvents, *i. e.* fats.
    1. Without the aid of heat: enfleurage.
    2. With the aid of heat: maceration.

Which of these methods is best adapted to the extraction of the perfume of a particular flower has been determined in southern France by long years of experience.

Extraction with volatile solvents is applied to roses, Parma and Victoria violets, orange blossoms, jasmine, tuberose, jonquil,

cassie, and migonette, occasionally to carnations, lily of the valley, heliotrope, elder flowers, stock, narcissus, and mimosas. In like manner a concrete oil is prepared from the so called *Mousse de chêne,* the lichen *Evernia prunastri.*

Enfleurage yields the best results with jasmine, tuberose, jonquil, lily of the valley, and migonette.

Finally, the process of maceration is applied to rose, orange flower, violet, cassie, and lily of the valley.

As becomes apparent, some flowers *e. g.* rose, cassie and violet, can be treated equally well either with volatile solvents or with warm fats. It has been known for a long time that jasmin and tuberose when thus treated give an unsatisfactory yield, whereas the enfleurage process gives good returns.

Passy[1]) who first called attention to this fact, gives the following explanation for this difference in behavior of the several flowers.

"Flowers can be divided into two classes of which the one, to which rose and orange flower belong, contain their perfume ready made. The other, to which belong jasmin and tuberose, contain either no ready made volatile oil or but very little thereof. These, however, continually produce perfume as a part of the life process of the cells. If the flower be killed by petroleum, ether, or hot fat, the life process and with it the formation of volatile oil naturally ceases. If, however, the cut flower be placed over fat, it continues to live for a long time and to emanate odors which in the enfleurage process are absorbed by the fat."

When Hesse[2]) tested experimentally this hypothesis he arrived at the surprising result that in the case of jasmin the enfleurage process yields ten times the amount of oil yielded by the extraction with volatile solvents. In the case of tuberose the proportion is even greater. Hence the conclusion is justified that in the case of the jasmin and tuberose the production of odoriferous substances continues during the process of enfleurage, being absorbed as it is formed. This also proves the superiority of the enfleurage process over that of the extraction method for certain flowers. For other flowers this does not hold true.

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[1]) Compt. rend. **124** (1897), 783; Bull. Soc. chim. III. **17** (1897), 519.
[2]) Berl. Berichte **34** (1901), 293, 2928; **36** (1903), 1465.

Thus, according to Hesse and Zeitschel,[1]) 1000 ko. of orange blossoms yield only 100 grams of volatile oil when submitted to the enfleurage process, whereas maceration yields 400 grams and distillation with steam 1200 grams of oil, of which, however, about 400 grams are dissolved in the aqueous distillate.

A. EXTRACTION WITH VOLATILE SOLVENTS.

The first to suggest the use of volatile solvents for the extraction of flowers was Robiquet. In a paper[2]) contributed in 1835 he points out that some plants, such as jonquil, jasmine, heliotrope, and tuberose, in spite of their agreeable fragrance, yield no volatile oil when treated in the ordinary manner. He ascertained that the odoriferous principle of jonquil, could be obtained by extraction with ether and subsequent evaporation of this low-boiling solvent. A year later L. A. Buchner,[3]) stimulated by the report of Robiquet, ascertained that ether could also be used for the extraction of other flowers with a readily evanescent aroma, such as those of *Philadelphus coronarius, Tilia europæa,* and *Reseda odorata.* In 1838 Favrot[4]) proceeded in like manner with the extraction of the perfume of the *flores acaciæ* (presumably the flowers of *Robina pseudacacia?),* also of the flowers of *Syringa vulgaris.*

A more detailed study of the extraction of flowers with volatile solvents was made by Millon[5]) in Algiers. In addition to ether he recommended chloroform, carbon disulphide, wood alcohol and the low boiling fractions of benzin.

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[1]) Journ. f. prakt. Chem. II. **64** (1901), 245.

[2]) *Recherches sur l'arome de la jonquille.* Journ. de Pharm. **21** (1835), 335; Buchner's Repert. f. d. Pharm. **54** (1835), 249; Pharm. Zentralbl. **1835**, 553.

[3]) *Versuche zur Extraktion der Blüten mit Äther.* Buchner's Repert. f. d. Pharm. **56** (1836), 382.

[4]) Journ. de Chim. méd. **1838**, 221; Pharm. Zentralbl. **1838**, 442.

[5]) *Mémoire sur la nature des Parfums et sur quelques fleurs cultivables en Algérie.* Journ. de Pharm. et Chim. III. **30** (1856), 407; Compt. rend. **43** (1856), 197.

Millon placed the flowers into a percolator *(appareil à déplacement)* covered them with ether and renewed the menstruum after 10 to 20 minutes. The extract, obtained after evaporation of the ether, he kept in open containers because he thought that the air acted favorably on the odoriferous principle. This, however, was a deception. Unless the solvent is carefully removed with the aid of a vacuum, mere traces of it can be detected if the extract is kept in closed containers. Millon was not ignorant of the fact that the greater part of the extract consists of vegetable wax which is well nigh insoluble in alcohol. Hence he determined the amount of odoriferous substances by ascertaining the difference in weight of the extract before and after treatment with alcohol.

Millon also pointed out that the time of day in which the flowers are collected is an important factor. Thus carnations should be gathered after 2 to 3 hours of intensive sunshine, roses in the morning after they are fully blown, jasmine before sunrise. To a sensitive nose cassie flowers have a different odor according to the time of their collection, morning, noon or evening. Millon recommends that the following flowers be extracted: orange blossom, tuberose, heliotrope, stock and narcissus.

The substitution of petroleum ether for ether, a practice now in common use, was suggested by H. Hirzel[1]) of Leipzig. His apparatus constructed for this purpose, were patented as early as 1864 in France, England, Austria, and several of the German states. The problem of utilizing on a technical scale the extraction with ether, carbon disulphide, chloroform, and petroleum ether, was developed about the same time by A. Piver.[2]) The use of methyl chloride as a solvent was recommended by Camille Vincent.[3])

In the early seventies, Louis Roure[4]) devised a method for the preparation of the so called *essences concrètes,* concentrated alcoholic perfumes, obtained by extraction. These were exhibited at the Vienna Exposition in 1873. A very complicated apparatus was patented by Laurent Naudin[5]) in 1875. This permitted of the vacuum distillation of the solvent charged with the perfume.

However, it is only since the last 25 to 30 years that the method of floral extraction with volatile solvents has found industrial application. It was at that time that Massignon in Cannes erected a battery of extraction apparatus similar to the diffusion apparatus employed in sugar factories. The solvent saturated

[1]) Hirzel's *Toiletten-Chemie.* III. ed. Leipzig 1874, p. 77.
[2]) Ibidem p. 79.
[3]) Piesse, *Chimie des parfums.* 1903, p. 69.
[4]) Berichte von Roure-Bertrand Fils October **1900**, 27.
[5]) Bull. Soc. chim. II. **38** (1882), 586 to 600.

with the perfume was evaporated in a vacuum still. As menstruum Massignon first used ether, carbon disulphide, methyl chloride, and benzene. Finally he arrived at the conclusion that a petroleum ether of the specific gravity 0,650 was best suited. Later Massignon sold his factory and his patents to Léon Chiris. Gradually other factories were equipped with extraction batteries. At the present time there are about 15 larger establishments of this kind in Grasse. In Joffa, Garnier erected a factory for the extraction of cassie flowers, and in Kara-Sarlii near Karlova in Bulgaria, another for the treatment of roses according to the extraction method. Recently a factory has been established for the extraction of cassie flowers and of other flowers cultivated in the island for this purpose.

Practically the process of extraction with volatile solvents resolves itself into four steps:

1. Selection and purification of the solvent.
2. The systematic extraction of the flowers.
3. Evaporation of the solvent and production of the vegetable wax saturated with perfume *(cire parfumée)*.
4. Recovery of the solvent.

1. SELECTION AND PURIFICATION OF THE SOLVENT. The solvent most commonly used is petroleum ether of a specific gravity 0,650 (15°). It is purified by consecutive treatment with sulphuric acid and caustic soda, washing with water and rectification with the aid of a column in a still over solid paraffin for the purpose of removing the ligther as well as the heavier fractions. Less frequently benzene is used since it has the disadvantage of yielding a highly colored extract. Carbon disulphide is not serviceable since the extract always retains some of the disagreeable odor of the solvent. Neither has carbon tetrachloride maintained itself. The highprice of ether stands in the way of its general use.

2. THE SYSTEMATIC EXTRACTION OF THE FLOWERS. The extractors of the mounted extraction batteries are cylindrical vessels, varying in size, but usually of about 500 liter capacity. They contain 3 or 4 low cylinders made of wire gause or of perforated tin, one placed over the other. The extractors are

airtight and sealed with a removable cover. The batteries are mounted in one of several ways: either the extractors are all on a level in a circle or a row (fig. 56, p. 254), or in two tiers one over the other (fig. 54, p. 252). With the aid of a pump, the solvent can be passed from one extractor to another.

As a rule, 3 to 4 extractions are made within 24 hours. Hence the menstruum remains in contact with the flowers from 6 to 8 hours. Then the flowers are replaced by fresh ones. However, during the height of the harvest the flowers in the extractors are replaced every 8, or even every 4 to 5 hours. This hastening of the process, however, results in an imperfect extraction.

As a rule, each batch of flowers is extracted three times, more rarely twice or four times. For the third (or last) extraction fresh petroleum ether is used, for the second such which has served for a former third extraction, and for the first extraction (*i. e.* for fresh flowers) the menstruum which has once served for a second and once for a third extraction. The percolate of each extraction is collected in a separate receiver.

Whether the same batch of flowers is to be extracted two, three, or four times, or even oftener depends upon the nature of the flowers to be extracted and on the views of the manufacturer. There exists also a difference of opinion as to how often the same petroleum ether can be used before it is to be recovered by distillation.

In order to increase the yield, the extractors have been so constructed in several instances as to enable their being warmed. This has resulted in a larger yield of wax but not of odoriferous constituents.

3. EVAPORATION OF THE SOLVENT. The manufacturer operates one or several stills under ordinary pressure or in vacuum. As a rule the bulk of the solvent is recovered in a large still under atmospheric pressure until the temperature has reached a point that would prove detrimental to the fineness of the perfume. The distillation is then continued in a vacuum still and finally concluded in a glass flask.

The last traces of solvent are removed by passing small amounts of alcohol into the molten wax thus causing a violent ebullition.

The floral extracts thus obtained are designated "concrete oils" *(essences concrètes)*. The alcoholic extracts prepared from these, according to the method described below, are known as floral extracts (Ger. *Blüten extraits;* Fr. *extraits aux fleurs*); the pure oils remaining after the removal of the alcohol *quintessences.*[1])

4. RECOVERY OF THE SOLVENT. On account of the expense of the solvent, suitable devices are provided to prevent loss. Hence long and well cooled spirals are used to condense the vapors from the stills, the extractors and the reservoirs. The ejectors of the vacuum pump must also be provided with an efficient condenser. If the process is conducted without a vacuum, the petroleum ether losses are less, but evaporation under atmospheric pressure, as already pointed out, results in an impairment of the fragrance of some of the floral constituents.

The solvent adhering to the flowers after their extraction is recovered by passing steam through the extractors which, for this purpose, are connected with the condensers; or by transferring the flowers to a still from which the solvent is recovered by steam.

Yield. The yield varies greatly according to the solvent and temperature employed, also according to the duration of the extraction.

At ordinary temperature, petroleum ether yields for every kilo of flowers the following amounts of concrete oils.

Victoria violets	1,5	to	1,8	g
Roses	1,7	„	2,5	„
Orange flowers	2,0	„	4,0	„
Jasmine	1,6	„	2,25	„
Cassie	3,5	„	5,0	„
Mignonette	1,3	„	1,5	„

Removal of the plant wax from the concrete oils. For this purpose the *essences concrètes, i. e.* the extracts obtained by percolation and subsequent evaporation of the solvent, are shaken for several days with strong alcohol, preferably in shaking machines *(batteuses)*. The alcoholic solution, after being

[1]) Jeancard et Satie, *Abrégé de la Chimie des Parfums.* Paris 1904, p. 12.

separated from the insoluble wax, is cooled for some time to 0°. This causes the separation of the dissolved wax, which is removed by filtration. To the alcoholic filtrate a solution of common salt is added, and the perfume, which has risen to the surface, is separated. If necessary, the last traces of alcohol are removed with the aid of a vacuum.

In as much as the plant wax when shaken with alcohol agglutinates to a magma from which the perfume is extracted

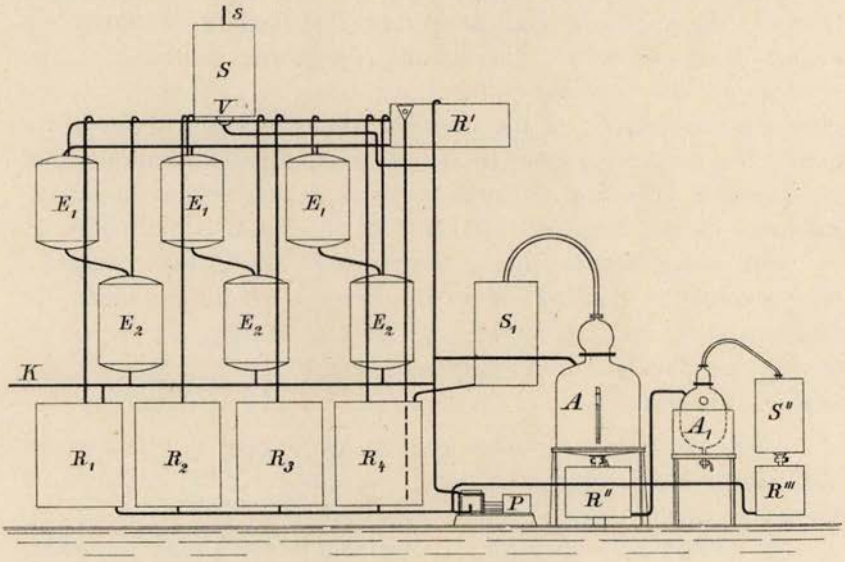

Fig. 54.
Elevation plan of an extraction battery.

with difficulty, Massignon[1]) has suggested to mix it with a very hard and odorless mineral wax, thus yielding a mass that can be broken up in a mortar. The particles then remain suspended in the alcohol and are more readily extracted by it.

DESCRIPTION AND OPERATION OF THE EXTRACTION BATTERY REPRESENTED BY FIG. 54, P. 252.

In the above plan the extractors are marked E_1 and E_2. They have a capacity of about 500 l. and are divided into compartments by means of 3 to 4 false bottoms of perforated tin or by means of wire baskets. The air tight

[1]) P. Jeancard, Volatile solvents applied to flowers. Americ. Perfumer 1 (1907), 10.

covers are provided with two pipes: one of these is used for introducing the solvent, the other for ventilation. The ends of the pipes are flexible and can be screwed to the cover. The bottom of the extractor is slightly conical thus admitting of a complete evacuation of the extract through the pipe fastened to its center.

S is a condenser in which the vapors that might otherwise escape are liquified. The condensate collects at V and flows into the reservoir R_4.

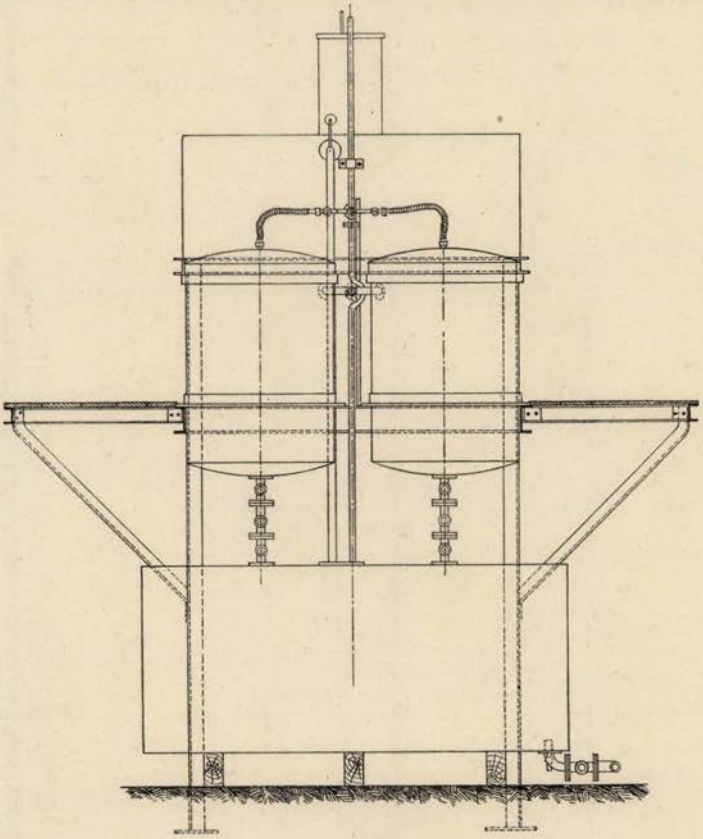

Fig. 55.
Side view of an extraction battery by Deroy Fils Aîné, Paris.

Vapors that have not been condensed as well as air escape through s. S_1 and S'' are the respective condensers for the stills A and A_1.

A is a larger still for distillation under atmospheric pressure. It is provided with a glass tube indicating the height of the liquid and with a thermometer. The distillate passes through the condenser S_1, into the reservoir R_4. The residue is allowed to flow into the container R'.

A_1 is a vacuum still which can be heated by means of a water bath. It is filled by suction from R''. The recovered solvent collects in R''' from which it is pumped to the larger reservoirs.

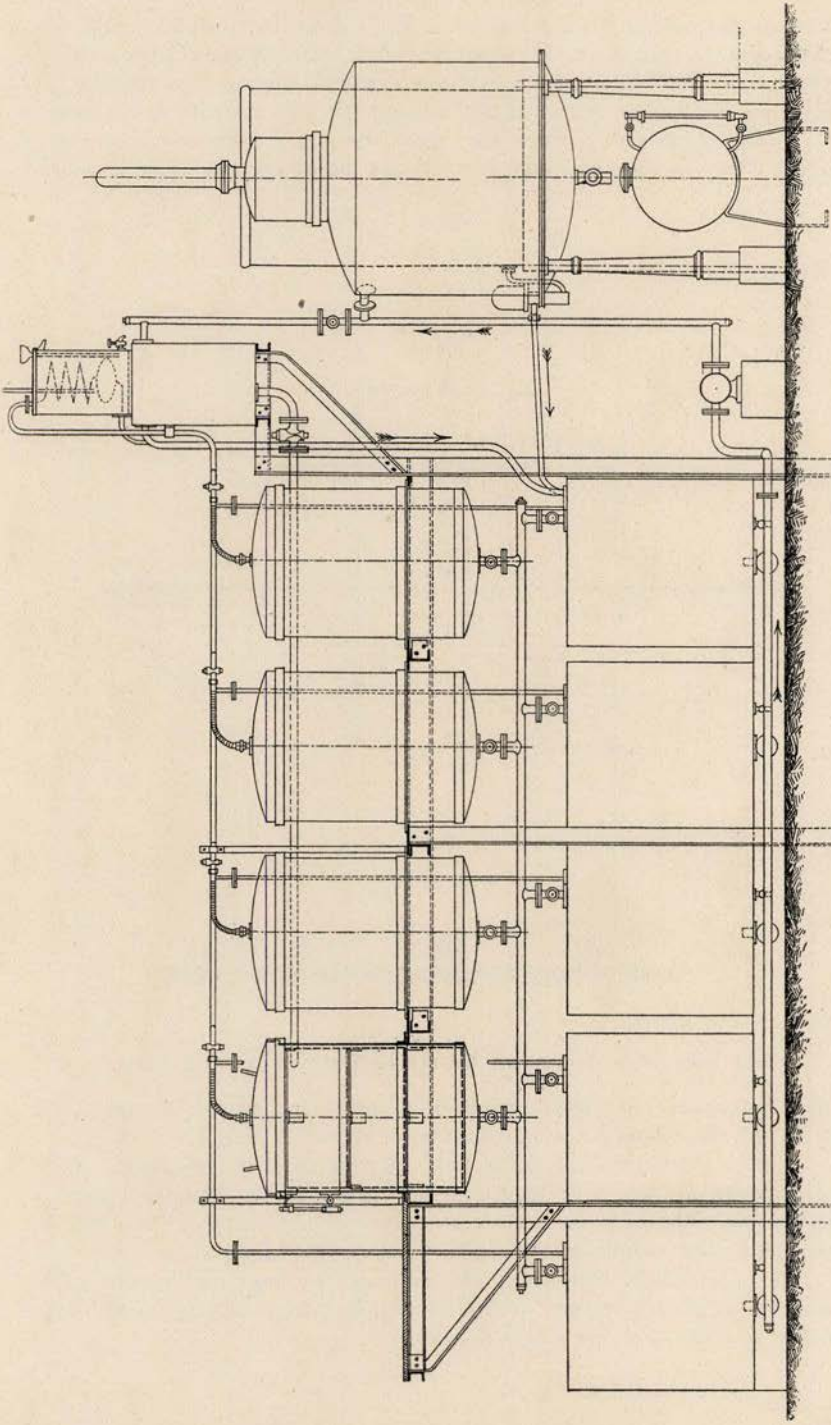

Fig. 56. Sectional front vien of an extraction battery by Deroy Fils Aîné, Paris.

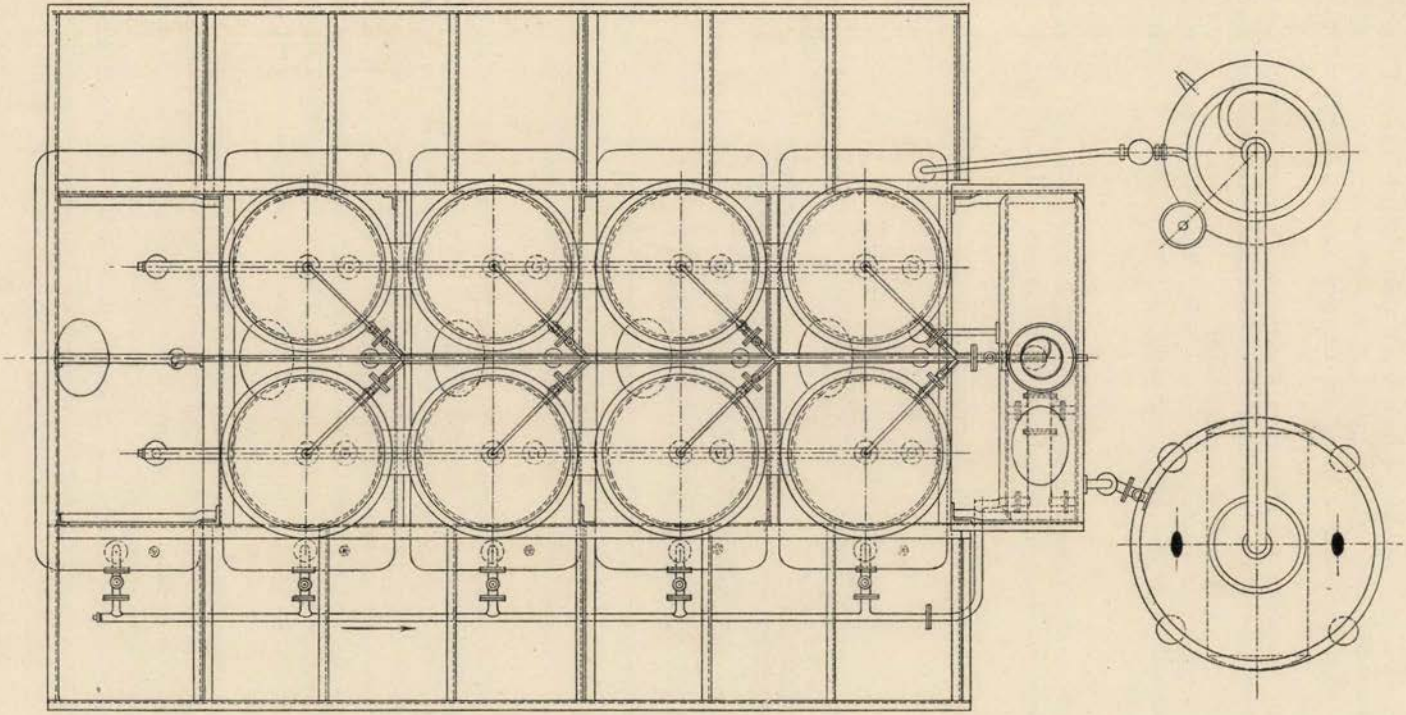

Fig. 57. Ground plan of an extraction battery by Deroy Fils Aîné, Paris.

R_1, R_2, R_3, R_4 are reservoirs of about 2000 l. capacity provided with glass tubes showing the height of the contents and with ventilation tubes. With the aid of a pump the contents can be transferred to the extractors.

The extractors are filled from R' which is provided with an overflow into which the solvent is pumped from the other reservoirs with the aid of pump P.

The pipes are indicated by heavy lines. All parts of the battery and the intersections of the pipes are provided with one-way or several-way stopcocks.

The purified solvent passes through pipe K into the reservoirs R_2, R_3, R_4, which are filled to about $^4/_5$ of their capacity. The flowers are then

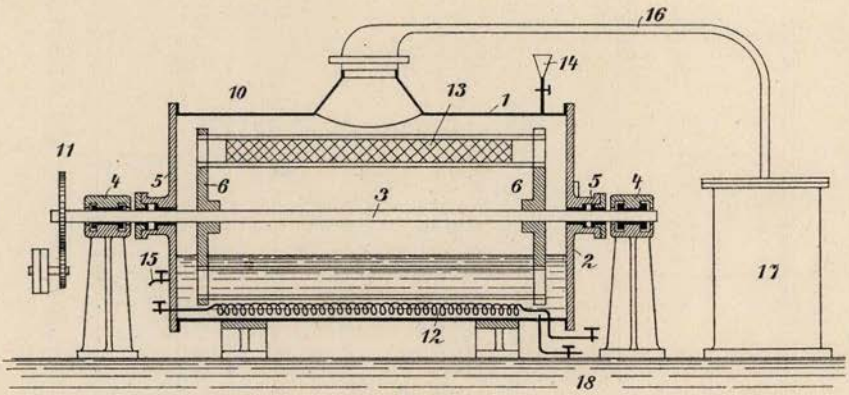

Fig. 58.

Longitudinal section of Garnier's extraction apparatus.

placed on the false bottoms in the extractors E, the covers are placed in position, the influx and ventilation pipes are adjusted, and the solvent is allowed to flow from R' into the extractors E_1 until the flowers are completely covered. The three extractors E_2 are next filled and the flowers are covered with the percolate of the upper tier of extractors, the flowers of which are covered with fresh solvent. In this manner the flowers are commonly extracted three times in succession. These three extractions are made within 24 hours, but in the rush of the floral harvest are sometimes made in 8 hours, or even in 4 to 5 hours.

The percolate of each extraction is stored away separately, reservoir R_1, containing the first percolate. After the petroleum ether has been sufficiently saturated with perfume it is recovered first by distillation in the still A, then under diminished pressure in A_1, and finally in a glass flask.

The exhausted flowers are allowed to drain well. The menstruum still adhering to them is recovered by steam distillation in the large still.

DESCRIPTION OF GARNIER'S APPARATUS FOR THE EXTRACTION OF FLOWERS.

Figures 58 to 60 illustrate an apparatus constructed by Garnier[1]) for the extraction of flowers. It consists of a stationary outer cylinder, (figs. 58 and 59) which at *2* is provided with a manhole that can be hermetically sealed. Within there is a drum that revolves about the shaft *3* (fig. 58), that passes through the outer cylinder at *5* and rests upon supports at *4*.

The end pieces of the inner drum has twelve circular openings *7* near the circumference (fig. 60). Each of these openings is connected with the corresponding one at the opposite end of the drum by means of a circle of rods which effect a hollow cylinder. Into these hollow cylinders, of

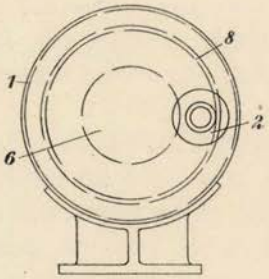

Fig. 59.
Transverse section of Garnier's extraction apparatus.

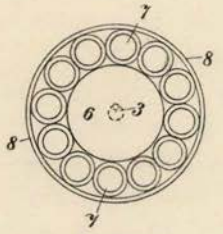

Fig. 60.
Transverse section of the inner drum of Garnier's extraction apparatus.

which each drum has twelve, cylindrical baskets *13* of perforated tin can be placed (fig. 58).

The power which is transmittet by cogwheels at *11* put the drum into rotary motion. By means of a spiral tube *12* the liquid in the outer cylinder can be gently heated. The tube *16* connects the apparatus with a condenser *17*, hence it can be used as a still.

Operation begins by introducing the cylindrical baskets *13* filled with flowers, through the man hole *2* (fig. 59) into the drum. Enough solvent, petroleum ether, is then introduced through the funnel *14* (fig. 58) so that the lowest flower basket is completely covered thereby. The drum being revolved causes the baskets one after the other to be dipped into the solvent. The flowers having been exhausted, the extract is withdrawn by means of a stopcock *18*. Steam is then passed through the apparatus in order to recover any solvent adhering to the flowers.

[1]) Comp. p. 249.

B. EXTRACTION WITH NON-VOLATILE SOLVENTS.

1. WITHOUT THE AID OF HEAT: ABSORPTION OR ENFLEURAGE À FROID.

The absorption method, known as *enfleurage,* applied to those flowers which continue to produce volatile oil even after they have been removed form the stem (p. 246), depends on the capacity of fats or fatty oils to absorb the oil volatilized by the flowers and to hold it. This process is carried out in a relatively primitive manner. As already stated on p. 246, it is applied to jasmine, tuberose, jonquil, lily of the valley, and mignonette.

For the purpose of enfleurage, so called *châssis* are used. These are wooden frames 5 cm high and 50 to 80 cm square. A glass plate is supported in the middle of the frame. On either side of this glass plate a layer of fat about 3 mm in thickness is spread in such a manner as to leave a margin 4 cm wide (fig. 61, p. 259). The flowers, deprived of their calices, are then spread over this layer of fat *(enfleurer)* (fig. 62, p. 261). In order to enlarge the surface of the fat exposed to the flowers criss cross furrows are drawn through it with the aid of a spatula. Thirty-five to forty of the châssis thus prepared are piled one on top of the other to the height of a man. As a result the flowers are enclosed in small chambers, as it were, between two layers of fat, which absorbs the aroma. The length of exposure depends on the kind of flower: jasmin 24 hours, jonquil 48 hours, tuberose 72 hours. Moreover, the last mentioned are placed on fat in the unopened stage and are allowed to expand while resting on the fat. If they are placed on the châssis fully developed they are spoiled by the next day *(pourri).* After the flowers have remained on the fat for the requisite length of time, they are removed by a rap on the frame or with the aid of the fingers *(défleurer)* (fig. 62, p. 261). The châssis are then charged anew but this time on the other side so that the flowers now rest on the layer of fat which in the previous exposure was the upper one, thus producing a more even

Fig. 61.
Spreading the layer of fat on châssis *(Pâtage des châssis)*. Parfumeries de Seillans, Dép. du Var, Southern France.

charging of the fat with perfume. This process can be repeated as often as desired until the fat has absorbed a sufficient amount of oil. The price of the pomade *(Pommade française)* depends on the number of exposures. As a rule the fat is exposed 30 times.

The production of a good pomade depends first of all on the character of the fat which must be purified with great care. In as much as lard is too soft and beef fat too hard, a mixture of both is commonly used for enfleurage, *e. g.* 40 parts of beef fat and 60 parts of lard. During the hottest months a mixture of equal parts of both is used. The fat of recently killed animals is cut into pieces and all impure or malodorus parts are removed. The good parts are then further reduced and rendered in a special apparatus, the tissues and other impurities being removed. In order to remove traces of blood, the mass thus resulting is ground between mill stones with the aid of water until the latter remains clear. The fat is next melted at the lowest possible temperature in a jacketed steam pan and alum is added. The alum facilitates the coagulation of impurities which rise to the surface and can be removed with the aid of a skimming spoon. The molten mass is allowed to stand for several days, the separated water is removed and the fat strained through linen. The fat thus obtained is preserved in one of several ways. The fat is digested for an hour with gum benzoes (about 1 to 3 g for each kilo of fat)[1]) and either orange flowers (according to Pillet 250 g for each kilo of fat)[2]) or, less frequently, with rose water (about 40 g for each kilo of fat). This mixture is then allowed to stand for several hours and the fat, freed from water drawn, into the containers. This is done in May at the time of the orange flower harvest. The fat thus prepared *(le corps préparé)* is said to be very stable. Occasionally a simpler method is employed. The purified fat is digested with gum benzoes *(axonge benzoinée)* or with tolu

[1]) Comp. S. Piesse, *Chimie des Parfums.* Paris 1897. pp. 59, 60; J.-P. Durvelle, *Fabrication des Essences et des Parfums.* Paris 1908. p. 77. See also Jeancard et Satie, *Recherches analytiques sur quelques essences de jasmin* [Bull. Soc. chim. III. **23** (1900), 555] and Hesse, *Über ätherisches Jasminblütenöl* [Berl. Berichte **34** (1901), 291].

[2]) Report of Schimmel & Co. Oktober **1900**, 37.

Fig. 62.
Enfleurage (to the left) and défleurage (to the right). Against the walls the piles of châssis.
Parfumeries de Seillans, Dép. du Var, Southern France.

balsam *(axonge toluinée)* or for a few moments only with poplar buds *(axonge populinée)*.

The process here described is used almost universally. In a few instances only other "fat bodies" have been used, *viz.*, olive oil or paraffin oil. These also must be of the very best quality, but do not have to be "prepared". Formerly behen oil (from *Moringa pterygosperma*, Gærtn.) was used extensively in southern France. It does not readily become rancid, but an excessive duty now prohibits its use.[1])

Paraffin enjoys the advantage over fats because of its indefinite keeping qualities, but is little used for the reason mentioned below. When liquid oils are used, the glass plates of the châssis are replaced by wire screens, which serve as supports for woolen cloths saturated with the oil in question. The flowers are strewn on these cloths. The process is otherwise as described above. The perfumed oil, *huile française, huile parfumée, huile antique,* is finally expressed from the cloths by means of hydraulic presses. The pure oil is obtained from the pomade or from the *huile française* as from the concrete oils. The pomade is extracted with strong alcohol, either in flasks by continuous shaking or in factories with the aid of special stirring apparatus illustrated in fig. 64. The cylindrical vessels are supplied with mechanical stirring apparatus which cause the fat and alcohol to be intimately mixed. Here also the last traces of fat are removed by freezing. From the *extraits aux fleurs* thus prepared, the *essences* are obtained by removal of the alcohol.[2])

The residual fat is no longer suited to enfleurage and, as *corps épuisé* finds its way into the soap industry. The waste flowers are used either as fertilizer, or occasionally for the production of *essences concrètes*.

According to Hesse[3]) the enfleurage with fat is preferable in every way to that with paraffin oil. Comparative experiments have revealed that paraffin has a much lower absorption capacity for odoriferous substances than fat, hence causing a much

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[1]) Heckel, Rev. cultures coloniales 5 (1901), 258.

[2]) Jeancard and Satie, *Abrégé de la Chimie des Parfums*. Paris 1904. p. 13.

[3]) Berl. Berichte 34 (1901), 293 ff.

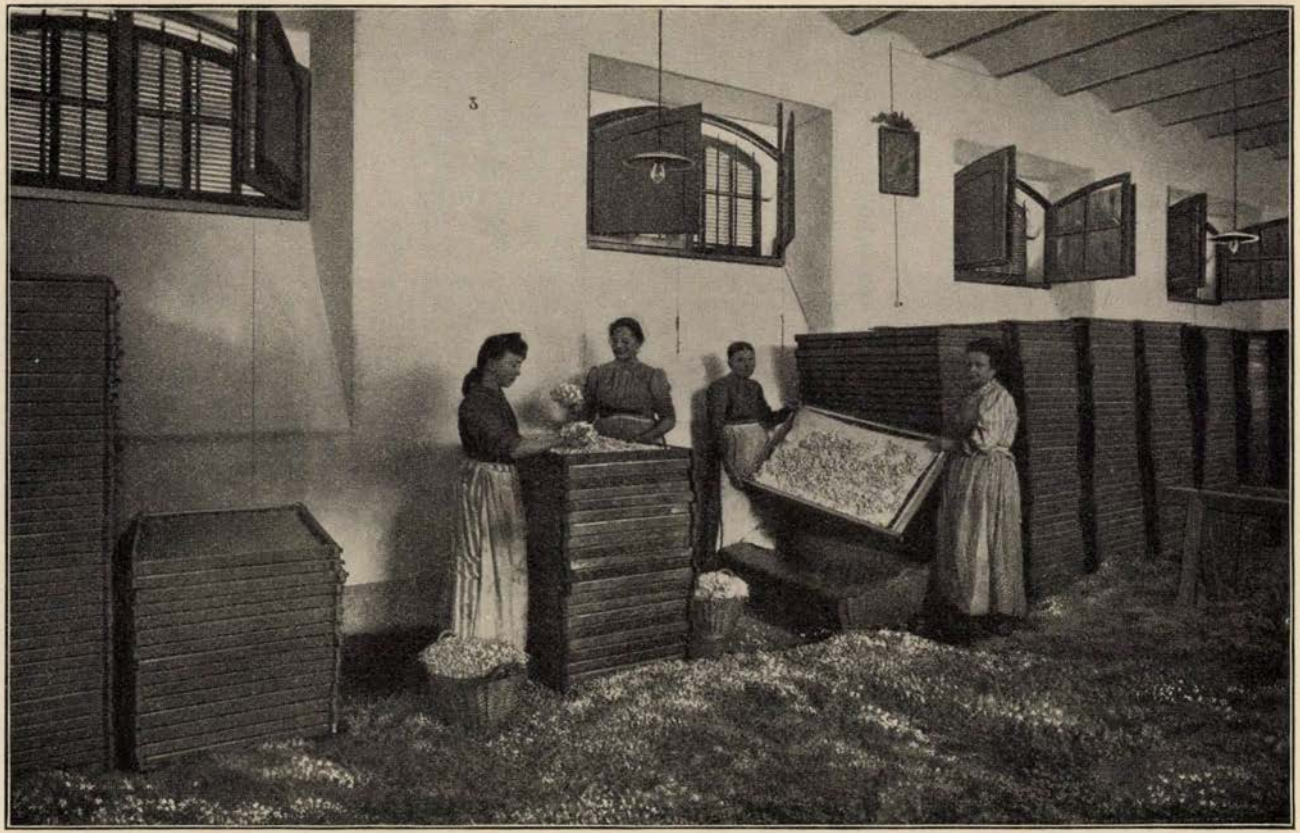


Fig. 63.

Enfleurage with the use of oil. On the châssis held in a diagonal position the cloath saturated with oil can be seen. Parfumeries de Seillans, Dép. du Var, Southern France.

lower yield. Thus the enfleurage of 1000 kilo of jasmine flowers with fat yielded 1684 g of ethereal oil, whereas enfleurage with paraffin yielded but 1053 g oil.[1])

PNEUMATIC METHOD. In the course of time a number of so called improvements of the enfleurage process have been tried, however, with but little or no success. Best known of these is the "pneumatic method" of A. Piver.[2]) It consists in passing a current of air, or better still of indifferent carbon dioxide (CO_2) over the flowers and then through the absorption liquid (liquid fat or alcohol). The current of air carries with it the volatile substances exhaled by the flowers and in turn gives them off to the liquid. The apparatus is so constructed that the gas passes through it, several times. The apparatus possesses the theoretical advantage that the fat does not come into contact with the flowers, thus avoiding loss of fat. Moreover, the use of fat can be circumvented since the *extraits aux fleurs* can be prepared directly. Practically, however, the process does not appear to have been used.

2. EXTRACTION WITH NON-VOLATILE SOLVENTS WITH THE AID OF HEAT: INFUSION, MACERATION OR ENFLEURAGE À CHAUD.

As a means of extraction purified animal and vegetable fats such as beef fat, lard, olive oil, sometimes also paraffin oil (comp. p. 260) are used in this process. Paraffin oil, as already mentioned under the enfleurage process, is less adapted since it has a lesser absorption capacity for perfumes than have the fats. However, even solid paraffin (m. p. 66°) is occasionally used. With its aid products are obtained which remain solid even in the tropics, hence do not require special containers for shipment.

The flowers to be extracted either, in bulk or tied into sacks made of fine linen, are immersed in the fat heated to about 50 to 70°. The time of extraction varies with the plant materials and lasts up to 48 hours. The fineness of the aroma of the pomade is inverse to the time of exposure of the flowers to the action of the fat. If prolonged unduly, other odoriferous substances that

[1]) According to Hesse, the extraction of 1000 g of jasmin flowers with petroleum ether yields only 178 g of volatile oil. Comp. Berl. Berichte **33** (1900), 1589.

[2]) Piver's absorption apparatus is illustrated in Wagner's Jahresbericht **1864**, p. 499.

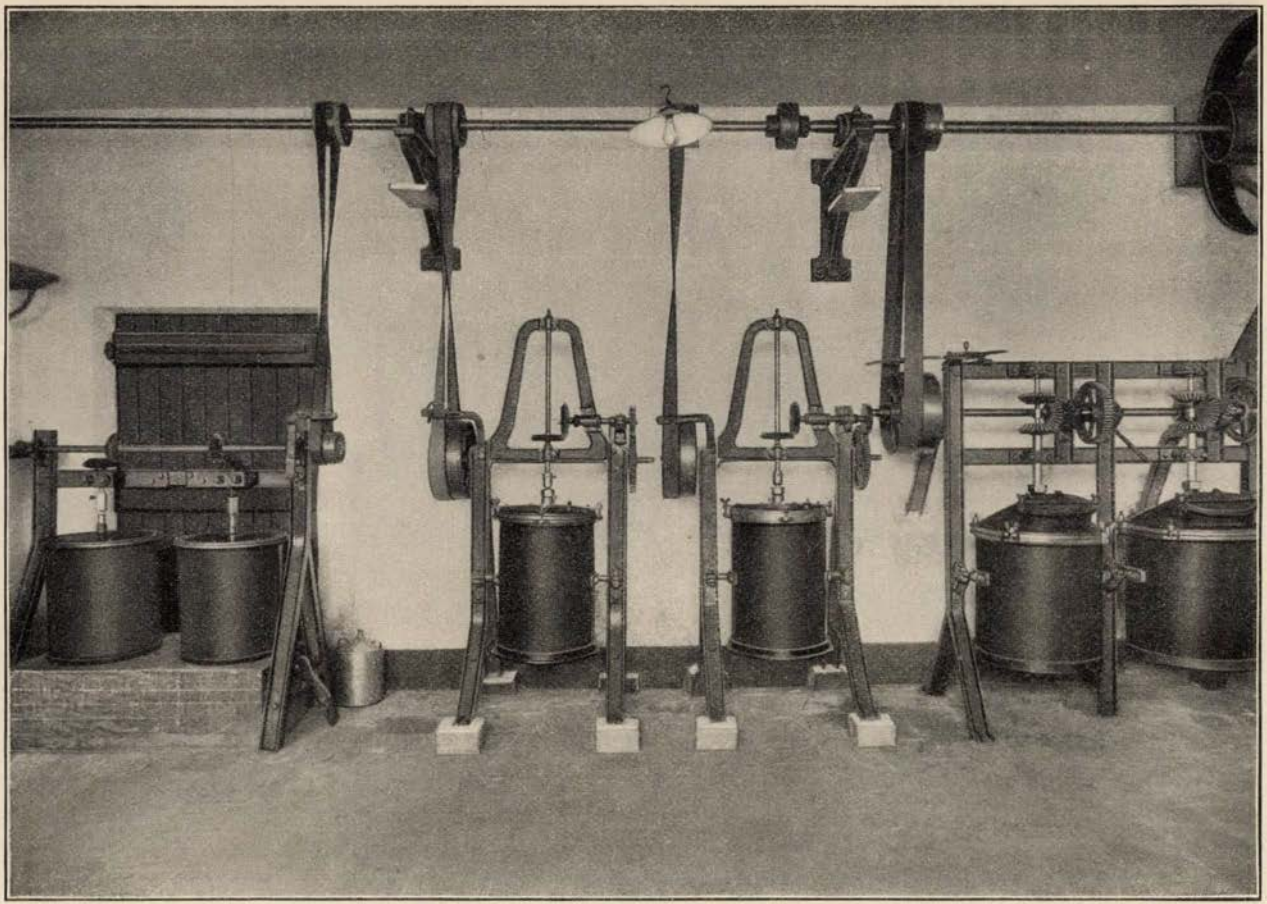


Fig. 64.
Apparatus for the extraction of pomades with alcohol *(Batteuses à extrait)*.
Parfumeries de Seillans, Dép. du Var, Southern France.

interfere with the quality of the perfume are also absorbed. The extraction being completed, the fat is expressed from the flowers with the aid either of hydraulic presses or of centrifuges (fig. 65, p. 267). The recovered, partly aromatized fat is treated with fresh flowers. This is repeated ten to fifteen times[1]) until the fat has acquired the desired strength as to odor. The floral extracts thus obtained are known by the same names as those obtained by the enfleurage process and are treated in like manner for the separation of the volatile oil. Here also the recovered fat, the *corps épuisé,* is not used again in the perfume factory but finds its way into the soap industry.

This process is applied to violets, roses, orange blossoms, lilies of the valley, &c., whereas jasmine, tuberose, and jonquil are not thus treated because of their small yield.

[1]) According to Labbé the average is 6 to 8 times. H. Labbé, *Essais des Huiles essentielles.* Paris. p. 11.

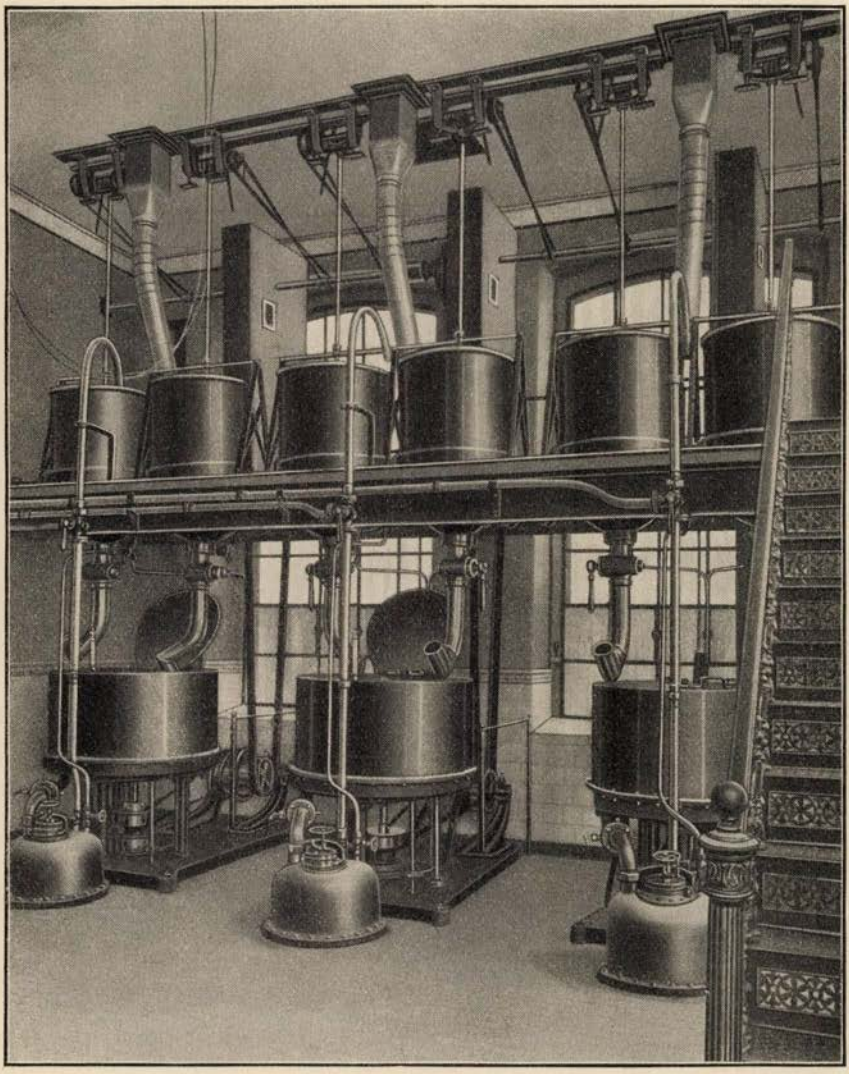


Fig. 65.

Apparatus for maceration and separation of the fat from the flowers by means of centrifuges. Schimmel & Co.

PRINCIPAL CONSTITUENTS OF VOLATILE OILS.

NATURAL AND ARTIFICIAL PERFUMES.

The volatile oils are widely distributed in the vegetable kingdom, more particularly among the phanerogams. However, volatile oils have also been isolated from several of the cryptogams.

In most cases the oils exist preformed in the various organs of the plant, the leaves, flowers, fruits, stems and roots. They occur secreted either in glands or in canal-like, intercellular receptacles. Only a few are formed by hydrolysis during the process of preparation from other substances in the plant, *e.g.* bitter almond oil from amygdalin, mustard oil from sinigrin. Nothing definite is known with regard to their function or their relation to the other constituents of the plant organism. It appears, however, to be well established that they are excretions formed during the life process of the plant, which are of no further importance in the processes of metabolism. It does not follow from this that they are therefore useless, for they act as a means of attracting insects that bring about fertilization, they also protect plants against enemies. These oils are not definite chemical units, but mixtures of substances belonging to many series and classes of compounds.

Not infrequently the oils obtained from different organs of the same plant differ in their chemical composition and in consequence reveal more or less striking differences in their properties. Thus the oil obtained from the root of the cinnamon shrub differs greatly in its composition from that of the bark, which in turn bears but little resemblance to that from the leaves. Moreover, the oils obtained from the same parts of the same species often reveal considerable differences, which are explained by differences in the stage of development of those parts, or by differences in the conditions of climate and soil. Even from identical material, different oils can be obtained by variation in the method of distillation.

Among the various constituents of an oil, one frequently attracts attention as the principal bearer of the odor. In many instances this constituent is the most valuable. The desire to obtain it in a concentrated and pure form may have given the first impetus to the scientific investigation of essential oils. So long as organic chemistry was in its infancy, these investigations could not be crowned with great success. Only after the methods of investigation had been improved hand in hand with the progress of science, was an insight into the nature of volatile oils obtainable. This insight revealed the fact that the oils are as a rule mixtures of a number of complex substances. How systematic research, more particularly in recent decades has afforded an insight into this field, has been revealed in the historical part. In the following pages the results of investigations are to be recorded so far as they concern the better characterized constituents found in volatile oils. Occasionally reference will also be made to substances that have been obtained only by synthesis. For reasons readily apparent a detailed account of their chemical behavior had to be omitted. Only those properties that pertain to their isolation, recognition and identification are enumerated. For further information the larger handbooks of organic chemistry will have to be consulted. To all who are concerned with the scientific investigation of volatile oils, the classic work of Otto Wallach[1]) *"Terpene und Campher"*, also the detailed handbook of Semmler[2]) will prove particularly useful. The latter affords a ready oversight over the enormous literature on the constituents of volatile oils, and discusses in detail all constituents found in volatile oils and not only particular classes of compounds.

The analysis of a volatile oil is difficult because most of the constituents are liquid, and can, therefore, be separated only by fractional distillation. This operation, imperfect at best, is often rendered more unsatisfactory by the fact that certain constituents are not volatile without decomposition. For this and

[1]) O. Wallach, *Terpene und Campher. Zusammenfassung eigener Untersuchungen a. d. Gebiete der alicyclischen Kohlenstoffverbindungen.* Leipzig 1909.

[2]) F. W. Semmler, *Die ätherischen Öle nach ihren chemischen Bestandteilen.* Leipzig 1906—1907.

other reasons it is best to subject an oil to a preliminary examination, the results of which often suggest modifications which simplify the examination considerably. The preliminary examination consists primarily in the determination of the physical properties of the oil and of its elementary composition; also in a study of the behavior of the oil toward certain group reagents, whereby the presence or absence of certain classes of chemical compounds can be ascertained.

Of the physical constants, the specific gravity, the optical properties and the behavior of an oil toward heat and cold allow conclusions to be drawn as to its composition. A specific gravity, *e. g.* of less than 0,90 indicates the presence of a large amount of terpenes or of compounds of the fatty series. The oil of *Pinus Sabiniana* with $d_{15^\circ} = 0{,}70$, heracleum oil with $d_{15^\circ} = 0{,}80$ to 0,88 and oil of rue with $d_{15^\circ} = 0{,}833$ to 0,840 belong to those with a very low specific gravity. These consist mainly of derivatives of the fatty series. Oil of orange, sp. gr. 0,848 to 0,857, consists largely of the terpene limonene; turpentine oil, with a specific gravity of 0,850 to 0,875, almost completely of hydrocarbons $C_{10}H_{16}$ of the terpene series. A specific gravity higher than 0,90, as is the case with most oils, indicates a mixture of several classes of compounds; whereas a specific gravity of more than 1,0 indicates the presence of compounds of the aromatic series, or if the compound contains sulphur or nitrogen, of sulphides, nitriles or *iso*sulphocyanides.

The optical properties, rotation and refraction, are of less importance unless pure chemical compounds are to be examined or adulterations to be looked for. The optical activity of an oil indicates the presence of a compound or compounds with one or more asymmetric carbon atoms; a high index of refraction the presence of a substance or substances with double bonds, thus enabling the investigator to draw conclusions as to the presence of aliphatic, cyclic or dicyclic compounds.

When exposed to low temperatures, a number of oils deposit one or more of their constituents in crystalline form. Some oils, like rose oil, contain crystals even at ordinary temperature, others, like orris oil and oil of ambrette seeds are butyraceous in consistency. These substances have been designated stearoptenes or camphors and are paraffins, higher members of the

series of fatty acids, such as lauric, myristic and palmitic acids, and derivatives of aromatic and hydroaromatic hydrocarbons. As an exception the methyl nonyl ketone of oil of rue should be mentioned.

Most oils, in case they can be distilled under ordinary pressure without decomposition, begin to boil above 150°. Exceptions to this rule are *e. g.* those containing sulphur, and such volatile oils which, like the distillation product of the turpentine from *Pinus Sabiniana* or the oil of *Pittosporum resiniferum*, contain low boiling hydrocarbons of the paraffin or olefin series. In the absence of oxygenated constituents, a boiling point below 200° indicates the presence of terpenes, between 250 and 280° that of sesquiterpenes, above 300° of polyterpenes.

In their elementary composition the volatile oils do not manifest great variety. All contain carbon and hydrogen; most of them also contain oxygen in larger or smaller quantity; few contain nitrogen or sulphur, or both. The presence or absence of oxygen can be determined by elementary analysis only. The presence of only a small amount of this element, up to 5 p. c., indicates a high hydrocarbon content. The presence of sulphur, which can be oxidized in sealed tubes to sulphuric acid by means of concentrated nitric acid indicates mustard oils, sulphides, or polysulphides. Nitrogenous compounds are converted into cyanides by heating with metallic sodium or potassium and are recognized by means of the Prussian blue reaction. The nitrogen content of an oil is mostly due to nitriles. If sulphur is also found, mustard oils are present which, as a rule, betray their presence by their characteristic odor.

After the elementary composition of an oil has been ascertained, a few group reagents can be applied to learn whether special attention should be given to one class or another of chemical compounds.

If an oil shows an acid reaction, it contains acids or phenols. Small amounts of fatty acids occur occassionally as decomposition products of esters present. Larger amounts reveal their presence by the diminution of volume when the oil is shaken with an aqueous solution of caustic or carbonated alkali. The presence of an ester or lactone can be ascertained when an oil is heated with alcoholic potassa of known strength and titrated

back with standard acid. This test presupposes the absence of free acids and aldehydes. Alcohols can be converted into acetic esters by heating the oil with acetic acid anhydride. Subsequent saponification will then reveal the presence or absence of an alcohol in the oil. Aldehydes and ketones can be recognized by their addition products with alkali bisulphites, or by their condensation products with hydroxylamine or semicarbazide in aqueous alcoholic solution. The latter contain nitrogen and as a rule are difficulty volatile with water vapor. Ethers, which are sometimes present as phenol ethers, can be recognized by means of Zeisel's method.

After these preliminary tests have revealed the presence of a substance belonging to one of the above mentioned classes, it is sometimes possible to separate it without fractional distillation; provided, however, that this method of separation does not change the other constituents of the oil. The analysis of the oil having been thus simplified, fractionation of the non-reacting portion can be resorted to. It should also be noted that these methods of separation never effect a perfect isolation because the other constituents of the oil prevent a part of the substance to be isolated from reacting. When, therefore, the non-reacting portion of the oil is fractionated small amounts of this substance should not be overlooked. Thus it is possible with these group reagents to separate aldehydes and many ketones with acid sulphite solution—a reaction that can at times be facilitated by the addition of alcohol. The crystalline addition product is washed with alcohol and ether and the aldehyde or ketone regenerated by the addition of alkali or dilute acid. Free acids and phenols can be shaken out with aqueous alkali; indifferent substances are then removed from the aqueous solution by shaking it with ether, and then the acid or phenol is set free with dilute mineral acid. If acids and phenols are both present, the former are separated with carbonate solution. Basic substances, such as indole and anthranilic esters can be separated by shaking out with dilute acids. Lactones yield salts of the corresponding hydroxyacids when heated with alcoholic potassa. They are precipitated from the alkaline solution as lactones or hydroxyacids by the addition of a mineral acid. Esters if present are saponified by this treatment with alkali. Aldehydes and ketones,

however, are modified thereby and at times destroyed. Sulphur derivatives can often be isolated in the form of their mercury compounds or as thioureas.

If none of these short cuts is possible, the oil is fractionated either under ordinary or diminished pressure. If esters are present, the oil is first saponified. It may be taken for granted that the apparatus to be used and the methods to be employed are known. A good guide for distillation under diminished pressure will be found in a small monograph on this subject by Anschütz.[1]) The various fractions obtained upon a careful fractionation are examined for compounds, in part according to the methods already mentioned. A trained sense of smell will prove an important additional factor. Suspected compounds are, if possible, converted into crystalline derivatives and thus purified and identified.

Ketones that will not combine with acid sulphites, such as menthone, camphor, fenchone, carvone, are converted into oximes or semicarbazones. Inasmuch as the oximes frequently suffer rearrangement with acids, the semicarbazones are at times to be preferred because the ketones can in most cases be regenerated. Certain ketones, such as carvone and pulegone, can be separated by means of their sodium sulphite compounds.

Alcohols are characterized by their capacity to form esters, also phenylurethanes with phenyl*iso*cyanate (carbanil). They can be purified by means of difficultly volatile esters of monobasic acids, such as benzoic acid; or by means of acid esters of dibasic acids, such as succinic acid, phthalic acid, etc. Some of the primary alcohols can also be purified by converting them into calcium chloride addition products from which they are easily regenerated by means of water.

From the hydrocarbons traces of oxygenated compounds can be removed by repeated treatment with metallic sodium. If low boiling hydrocarbons are to be distilled under diminished pressure, a liquid alloy of potassium and sodium is preferable.

As to the compounds themselves that are found in volatile oils, they belong in part to the aliphatic, in part to the aromatic and hydroaromatic series and are distributed over a large

[1]) *Die Destillation unter vermindertem Druck.* 2. ed. Bonn 1895.

number of classes. The hydrocarbons, especially those of the formula $C_{10}H_{16}$, are widely distributed. Of greater importance, however, are the oxygenated substances, because they are mostly the bearers of the characteristic odor of the oil in which they are contained. In addition to the hydrocarbons there have been found alcohols, aldehydes, acids, esters, ketones, phenols, phenol-ethers, lactones, quinones, and oxides; further, bases, sulphides, mercaptanes, nitriles, and *iso*thiocyanates.

HYDROCARBONS.

A. ALIPHATIC HYDROCARBONS.

The lowest member of the limit series of hydrocarbons C_nH_{2n+2} which has been found in volatile oils is the normal heptane, C_7H_{16} (b. p. 98,5 to 99°; $d_{15°}$ 0,6880). In addition to minimal amounts of other substances, it has been obtained by the distillation of the oleoresin of *Pinus Sabiniana* and *P. Jeffreyi,* both of which are found in California, also by the distillation of the fruits of *Pittosporum resiniferum.*

The higher members of the paraffin, and probably of the olefin series also, appear to be quite widely distributed in the vegetable kingdom. They constitute the wax-like coating and secretions on leaves, flowers, fruits etc. In volatile oils, however, they are not met with commonly because of their sparing volatility. Sometimes they separate in crystalline form when the oil is exposed to a low temperature, or they remain behind upon fractional distillation. In the oils of rose and chamomile, however, the amount of paraffin is so large, that the oil congeals even at middle temperature. Apparently these hydrocarbons seldom occur alone, but as mixtures of homologues as has been shown in the case of rose oil. Their melting points seldom if ever agree with those of known members of the series. With the exception of the heptane referred to, they are obtained principally as white, colorless, laminar-crystalline masses which are with difficulty soluble in cold alcohol, but readily soluble in hot alcohol

and other organic solvents. They are remarkable on account of their stability toward concentrated acids and oxidizing agents at ordinary temperatures.

The rose oil stearoptene melts at 35° and, when distilled in a vacuum, can be resolved into two fractions melting at 22° and 40—41° respectively. In addition to this solid mixture, paraffin (or olefin) hydrocarbons have been found more particularly in the oils distilled from flowers. The paraffins thus far isolated are recorded, with their melting points, in the following table:

Oil of *Kæmpferia Galanga*	m. p. 10°
Oil of poplar buds, a mixture of homologous paraffins with the melting points 53 to 54°, 57 to 58°, 62 to 63°, 67 to 68°	
Oil of birch buds	m. p. 50°
Oil of hemp	m. p. 63 to 64°
Oil of sassafras leaves	m. p. 58°
Oil of pelargonium	m. p. 63°
Oil of jaborandi leaves	m. p. 28 to 29°
Oil of neroli (aurade)	m. p. 55°
Oil of *Evodia simplex*	m. p. 80 to 81°
Oil of several *Cistus* species	m. p. 64°
Oil of caraway herb	m. p. 64°
Oil of dill	m. p. 64°
Oil of wintergreen (both *Betula* and *Gaultheria*)	m. p. 65,5°
Oil of verbena	m. p. 62,5°
Oil of *Helichrysum angustifolium*	m. p. 67°
Oil of Roman chamomile	m. p. 63 to 64°
Oil of German chamomile	m. p. 53 to 54°
Oil of *Chrysanthemum cinerariæfolium*	m. p. 64°
Oil of arnica flowers	m. p. 63°

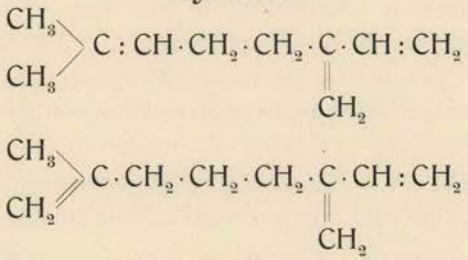
Additional occurrences of the paraffins have been established in the oils from species of *Spiræa* and *Turnera,* in oil of chervil, in the oil of elderblossoms, the oils of *Monarda didyma,* of *Inula viscosa* and others.

Of olefinic hydrocarbons, the octylene, C_8H_{16} (m. p. 123 to 124°; d 0,7275; n_D 1,4066) only has been found thus far, *viz.,* in the oils of bergamot and lemon. Possibly it also occurs in

lignaloe oil. Isoprene, C_5H_8, interesting because of its relation to the terpenes, has been observed only as decomposition product of caoutchouc and turpentine oil.

However, chain hydrocarbons of the formula of saturation C_nH_{2n-4} with three double bonds have been found. In composition they agree with the terpenes but differ in having a lower specific gravity and a lower index of refraction. These hydrocarbons, which have been termed "olefinic terpenes" by Semmler, show a great tendency to resinify, especially when distilled under ordinary pressure.

Myrcene.



or

The first representative of this class was found in oil of bay by Power and Kleber[1]) and named myrcene. Later its presence in the first fractions of the oil of *Lippia citriodora* was ascertained. Probably it also occurs in West Indian lemongrass oil and in oil of lignaloes. Barbier found myrcene among the dehydration products of linalool. Its constitution has not yet been definitely determined, but probably finds expression in one of the above formulas. The following constants have been recorded:

	b. p.	b. p. (20 mm)	$d_{15°}$	n_D
Power and Kleber[1])	167°	67 to 68°	0,8023	1,4673
Semmler[2])	171 to 172°	67 to 68°	—	1,4673
Enklaar[3])	166 to 168°	—	0,8013	1,4700 (at 19°)

According to Semmler, myrcene, upon reduction with sodium and alcohol, yields dihydromyrcene, $C_{10}H_{18}$, a liquid possessing

[1]) Pharm. Rundsch. (New York) **13** (1895), 61.

[2]) Berl. Berichte **34** (1901), 3126.

[3]) *Over Ocimeen en Myrceen, Eene Bijdrage tot de kennis van de aliphatische Terpenen.* Inaug.-Dissert., Utrecht 1905.

the following properties: b. p. 171,5 to 173,5°, d 0,7802, n_D 1,4501 (Semmler).[1]) B. p. 167 to 169° (corr. at 770 mm), $d_{15°}$ 0,7852, $n_{D17°}$ 1,4514 (Enklaar). From the dihydromyrcene Enklaar prepared a tetrabromide melting at 88°.

Upon hydration of myrcene with glacial acetic acid and sulphuric acid at 40° according to Bertram's method,[1]) Power and Kleber obtained an acetate with an odor reminding of lavender. Upon saponification it yielded, in their opinion, linalool. Barbier,[2]) however, supposed that the hydration yielded a new alcohol which he named myrcenol. From myrcenol Enklaar *(l. c.)* obtained a crystalline phenylurethane, m. p. 68°, which differs from that obtained from linalool. According to Enklaar, myrcenol has the following constants: b. p. 99° (10 mm), $d_{15°}$ 0,9032, $n_{D15°}$ 1,4806.

Potassium permanganate oxidizes myrcene to succinic acid. Myrcene can be identified by means of the dihydromyrcene mentioned above, also, according to Enklaar, by means of the dihydromyrcen tetrabromide, m. p. 88°. Myrcene polymerises readily to dimyrcene, which is characterized by a nitrosite that decomposes at 163°.

Ocimene.

This aliphatic terpene is isomeric with myrcene. It differs from the latter, presumably, in the position of the double bonds. It was discovered by van Romburgh in the oil of *Ocimum Basilicum*. Possibly it is also contained in esdragon oil. B. p. 73 to 74° (21 mm); $d_{22°}$ 0,794; $d_{15°}$ 0,801; n_D 1,4861.

The dihydro-ocimene, which results upon reduction with sodium and alcohol, is identical with dihydromyrcene.

Upon hydration, according to Bertram's method,[3]) Enklaar obtained ocimenol [b. p. 97° (10 mm); $d_{15°}$ 0,901; $n_{D15°}$ 1,4900], which yields a phenylurethane melting at 72°.

Upon heating, ocimene yields allo-ocimene, which possibly is stereoisomeric with ocimene. The physical constants are somewhat higher than those of ocimene: b. p. 81° (12 mm), $d_{15°}$ 0,8182, n_D 1,5296.

Additional aliphatic terpenes have been found in hop oil,[4])

[1]) Berl. Berichte **34** (1901), 3126.
[2]) Compt. rend. **132** (1901), 1048; Bull. Soc. chim. III. **25** (1901), 687.
[3]) D.R.P. 67255.
[4]) Chapman, Journ. chem. Soc. **67** (1895), 54.

in the oil of Indian hemp *(Cannabis indica)*[1]), in the oil of sassafras leaves,[2]) in rosemary oil[3]), and in the origanum oil of Smyrna.[4])

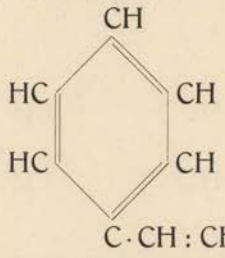
Mention should also be made of the occurrence of an olefinic sesquiterpene $C_{15}H_{24}$[5]) in oil of citronella. Its constants are: b. p. 270 to 280° (atmospheric pressure), 157° (15 mm); $d_{15°}$ 0,8643; $\alpha_{D15°} + 1°28'$; $n_{D15°}$ 1,51849.

B. AROMATIC HYDROCARBONS.

From the oil of the mammoth fir, *Sequoia gigantea,* Lunge and Steinkauler[6]) obtained a hydrocarbon $C_{13}H_{10}$ which they named sequoiene. It consists of laminar crystals, with a reddish fluorescence, that melt at 105° and boil between 290 to 300° (uncorr.). It has not been identified with any of the known hydrocarbons of like composition, such as fluorene etc. With picric acid an addition product of red crystalline needles results.

Noteworthy is also the occurrence of naphthalene which has been found in an oil of clove stems, in the oil of a storax bark, and in orris oil. It is readily characterized by its melting point (79 to 80°), its boiling point (218°), and by a picrate that melts at 149°.

Styrene.



The simplest aromatic hydrocarbon with an unsaturated side chain that is found in volatile oils is styrene (vinyl benzene). It occurs in storax oils and in xanthorrhœa resin oil. It is probably formed by the decomposition of cinnamic acid.

[1]) Journ. chem. Soc. **69** (1896), 539.
[2]) Report of Schimmel & Co. April **1896**, 66.
[3]) Arch. der Pharm. **235** (1897), 585.
[4]) Gildemeister, Arch. der Pharm. **233** (1895), 184.
[5]) Report of Schimmel & Co. October **1899**, 23.
[6]) Berl. Berichte **13** (1880), 1656; **14** (1881), 2202.

Styrene is a colorless, highly refractory liquid of a pleasant odor, which polymerizes to a transparent, glasslike and odorless mass, metastyrene $(C_8H_8)_n$, by being kept for some time, and more rapidly by heating, or by contact with acids.

As to its physical properties, the following statements have been recorded:

B. p. 144 to 144,5°.[1])

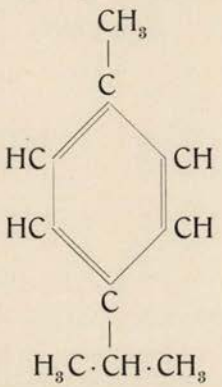
B. p. 140° (760 mm); $d_{20°}$ 0,9074; n_α 1,54030.[2])

B. p. 146,2°; $d_{0°}$ 0,9251,[3]) $d\frac{17°}{4°}$ 0,90595; n_D 1,54344.[4])

Pure styrene is optically inactive. Dilute nitric acid or chromic acid mixture oxidize it to benzoic acid. Upon reduction it yields ethyl benzene.

For identifying styrene the well crystallized styrene dibromide $C_6H_5 \cdot CHBr \cdot CH_2Br$ is used, and is obtained by allowing bromine (17 parts) to drop into a solution of the hydrocarbon (10 parts) in twice its volume of ether.[5]) On evaporation, the bromide separates in crystals, which after being recrystallized from 80 percent alcohol have the melting point 74—74,5°.

p-*Cymene.*



Of the hydrocarbons designated as cymenes $C_{10}H_{14}$, only the *meta* and *para* compounds are of importance to the chemistry

[1]) Observations made in the laboratory of Schimmel & Co.

[2]) Brühl, Liebig's Annalen **235** (1886), 13.

[3]) Weger, Liebig's Annalen **221** (1883), 69.

[4]) Nasini and Bernheimer, Gazz. chim. ital. **15** (1885), 59; Jahresber. d. Chem. **1885**, 314.

[5]) Zincke, Liebig's Annalen **216** (1883), 288.

of the volatile oils. While *m*-cymene has been observed only as a decomposition or "Abbau" product (Kelbe, dry distillation of colophony; Wallach, dehydration of fenchone; Baeyer, splitting off hydrogen from sylvestrene), *p*-cymene is a frequent constituent of volatile oils. Up to the present it has been found in Swedish and Russian turpentine oils, in the oil of *Cupressus sempervirens*, in staranise oil, oil of nutmeg, oil of boldo leaves, oil of Ceylon cinnamon, oil of Seychelle cinnamon bark, cascarilla oil, lemon oil, in the oil of *Canarium Cumingii*, in the oil of *Eucalyptus hæmastoma*, in oil of ajowan, in coriander oil, in cumin oil, in the oil of *Cicuta virosa*, in angelica root oil, in the oils of *Monarda punctata* and *M. fistulosa*, *Satureja hortensis*, *S. Thymbra*, in the origanum oils from Triest, Smyrna, and Cyprus, in sage oil, in the oils of *Thymus vulgaris*, *Th. Serpyllum*, *Th. capitatus*, and in American wormseed oil.

Like *m*-cymene, *p*-cymene has frequently been obtained as a transformation product, *e. g.* from pinene, terpinene, cumin alcohol, laurus camphor, sabinol, thujone, carvenone, dihydrocarvone, carvone, and citral.

The mixture of hydrocarbons known as "thymene", obtained from ajowan oil and used as a soap perfume, consists principally of cymene together with several terpenes (see ajowan oil).

Formerly it was thought that all terpenes were related to this hydrocarbon, that they were its hydroderivatives. According to recent investigations, however, this conception is not wholly correct. It is worthy of mention, that several compounds of the formula $C_{10}H_{16}O$ can be changed to *p*-cymene by the abstraction of water, for instance, camphor and citral.

Cymene is a colorless liquid with an agreeable odor.

B. p. 175 to 176°; $d_{15°}$ 0,8602.[1])

B. p. 175,2 to 175,9° (752 mm); $d\frac{20°}{4°}$ 0,8551; n_D 1,48456.[2])

B. p. 173,5 to 174,5° (763 mm); $d_{15°}$ 0,8595, $d_{20°}$ 0,8588; n_D 1,479.[3])

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[1]) Widmann, Berl. Berichte **24** (1891), 452.

[2]) Brühl, Berl. Berichte **25** (1892), 172.

[3]) Wolpian, Pharm. Zeitschr. f. Russl. **35** (1896), 115.

The following constants were observed in the laboratory of Schimmel & Co. in connection with a preparation obtained from camphor:

B. p. 174,5 to 176° (761 mm); $d_{15°}$ 0,863; $n_{D15°}$ 1,49015.

The pure hydrocarbon is optically inactive. Dilute nitric acid also chromic acid mixture oxidize it to *p*-toluic acid and finally to terephthalic acid. Potassium permanganate attacks it with difficulty. Hence terpenes having a like boiling point can be removed by treating it with dilute permanganate solution in the cold. Should cineol, which boils at the same temperature, be present, it can be removed as its hydrogen bromide addition product. For its identification, cymene is converted into *p*-hydroxy-*iso*propylbenzoic acid (m. p. 155 to 156°) with the aid of concentrated, hot potassium permanganate solution. This acid, when heated with dilute hydrochloric acid, splits off water yielding *p-iso*propenylbenzoic acid (m. p. 160 to 161°); when boiled with concentrated hydrochloric acid it yields an isomeric acid with a boiling point of 255 to 260°.[1]) For the preparation of hydroxy*iso*propylbenzoic acid Wallach[2]) has given the following directions: 2 g. at a time of the hydrocarbon, prepared as pure as possible, are heated with a solution of 12 g. of potassium permanganate in 330 g. of water on a water-bath with reflux condenser, the mixture being frequently agitated. When the oxidation is complete, the filtrate from the oxides of manganese is evaporated to dryness and the saline residue boiled with alcohol. The potassium salt which is soluble in the alcohol, is decomposed in aqueous solution with dilute sulphuric acid, and the precipitated acid recrystallized from alcohol.

The sulphonic acid, produced by treating the hydrocarbon with concentrated sulphuric acid, is also characteristic for cymene. Its barium salt $(C_{10}H_{13}\cdot SO_3)_2Ba$ crystallizes in shining, difficultly soluble laminæ and contains three molecules of water of crystallization which can be completely driven off at 100°. The sulphone amide which can be prepared from the

[1]) R. Meyer and Rosicki, Liebig's Annalen **219** (1883), 282.
[2]) Liebig's Annalen **264** (1891), 10.

chloride of this sulphonic acid melts at 115 to 116°. That cymene sulphonic acid may also result from the action of sulphuric acid on different terpenes must, however, be remembered, also that an isomeric acid is formed at the same time.

C. ALICYCLIC HYDROCARBONS.

The principal hydrocarbons occurring in volatile oils are alicyclic. The composition of by far the greater number is represented by the formula $C_{10}H_{16}$, hence they belong to that class of the terpenes in which the carbon atoms are arranged in a cycle. As to their formation in the plant organism nothing definite is known. Possibly they are genetically related to oxygenated chain compounds $C_{10}H_{18}O$, since these yield artificially hydrocarbons $C_{10}H_{16}$ upon dehydration. Possibly they are formed from carbohydrates or proteins. It is noteworthy, however, that the terpene content of an oil is greater, the less developed the plant at the time of distillation.

The majority of the known hydrocarbons of the terpene group are found ready formed in nature. Thus the presence of α- and β-pinene, camphene, limonene, dipentene, terpinolene, α- and γ-terpinene, α- and β-phellandrene, sylvestrene, and sabinene has been definitely established. With the exception of the inactive terpinene and terpinolene, these hydrocarbons exist, for the most part, in both optically active forms.

In as much as it is frequently necessary to work with small amounts, it is often impossible to isolate the terpenes in pure form by means of fractional distillation. As a rule it suffices to remove oxygenated compounds from the fraction 150 to 180° by repeated distillation over sodium. A further separation can be effected by distillation since the bicyclic hydrocarbons boil between the temperatures of 150 and 170°, the monocyclic between 170 and 180°. Both classes of terpenes also reveal appreciable differences in their molecular refraction. The physical constants having been determined, more or less definite conclusions can be drawn as to the nature of the terpenes under investigation, thus leading to the preparation of derivatives characteristic of the hydrocarbons in question. These derivatives are described in connection with the respective hydrocarbons.

Owing to the complicated structure of their molecules, also to the readiness with which these are inverted into isomeric forms, the synthesis of the terpenes and sesquiterpenes has been coupled with difficulties. A single compound is obtained but seldom, the principal product being associated with a mixture of several isomers. The following compilation of the synthesis, or more correctly artificial preparation, of the hydrocarbons makes no claim as to completeness. In each group the best known representatives only are enumerated.

I. DEHYDRATION OF TERPENE- AND SESQUITERPENE ALCOHOLS.

α-Terpineol	→ Dipentene[1])
γ-Terpineol	→ Terpinolene[2])
Terpinenol-4	→ Terpinene[3])
Dihydrocarveol	→ Limonene, *Iso*limonene,[4]) Terpinene[5])
Borneol | *Iso*borneol	→ Camphene[6])
Fenchylalcohol | *Iso*fenchylalcohol	→ Fenchene[7])
Pinocampheol	→ α-Pinene[8])
Cedrol	→ Cedrene[9])
Maalialcohol	→ Maalisesquiterpene[10])
Caryophyllene alcohol	→ Clovene.[11])

II. DEHYDRATION OF KETONES.

Camphor → *p*-Cymene[12]) Fenchone → *m*-Cymene.[13])

[1]) Wallach, Liebig's Annalen **230** (1885), 265; **275** (1893), 104; **291** (1896), 361.

[2]) Wallach, *Ibidem* **368** (1909), 10.

[3]) Report of Schimmel & Co. October **1909**, 72.

[4]) Tschugaeff, Berl. Berichte **33** (1900), 735.

[5]) Wallach, *Ibidem* **24** (1891), 3984; Liebig's Annalen **275** (1893), 113.

[6]) Wallach, Liebig's Annalen **230** (1885), 233; Bertram and Walbaum, Journ. f. prakt. Chem. II. **49** (1894), 8.

[7]) Wallach, Liebig's Annalen **284** (1895), 331; Bertram and Helle, Journ. f. prakt. Chem. II. **61** (1900), 298; Tschugaeff, Chem. Ztg. **24** (1900), 542.

[8]) Tschugaeff, Journ. russ. phys. chem. Ges. **30** (1908), 1324; Gildemeister and Köhler, *Wallach-Festschrift,* Göttingen 1909, p. 136.

[9]) Report of Schimmel & Co. October **1904**, 24.

[10]) *Ibidem* November **1908**, 137.

[11]) Wallach, Liebig's Annalen **271** (1892), 294.

[12]) Fittica, *Ibidem* **172** (1874), 307.

[13]) Wallach, *Ibidem* **275** (1893), 157; **284** (1895), 324.

III. DEAMMONIATION OF BASES.

Carvenylamine → Terpinene[1])
Thujylamine → Thujene[2])
Carylamine → Carvestrene[3])
Phellandrene diamine → *p*-Cymene.[4])

IV. BY SPLITTING OFF HYDROHALOGEN.

Dipentene dichlorhydrate → Dipentene[5])
Terpinene dichlorhydrate → Terpinene[6])
Sylvestrene dichlorhydrate → Sylvestrene[7])
Bornylchloride → Camphene[8])
Monochlorocarvenene → Terpinene[9])
Cadinene dichlorhydrate → Cadinene[10])
Limonene tetrabromide → Limonene[11]) / *p*-Cymene[12])
Pinene dibromide → Cymene.[13])

V. BY SPLITTING OFF CARBON DIOXIDE FROM ACIDS.

Nopinolacetic acid → *α*-Pinene[14]) / *β*-Pinene / Fenchene
Acid from sabinaketone and bromoacetic ester → *β*-Terpinene[15])
Bromocamphane carboxylic acid → Bornylene.[16])

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[1]) Harries and Majima, Berl. Berichte **41** (1908), 2516.
[2]) Wallach, Liebig's Annalen **272** (1893), 111; **286** (1895), 99.
[3]) Baeyer, Berl. Berichte **27** (1894), 3486; Baeyer and Villiger, *Ibidem* **31** (1898), 1402; comp. Semmler, *Ibidem* **34** (1901), 717.
[4]) Wallach, *Ibidem* **324** (1902), 276.
[5]) Wallach, *Terpene und Campher.* Leipzig 1909, p. 84.
[6]) Wallach, Liebig's Annalen **350** (1906), 148.
[7]) Wallach, *Ibidem* **230** (1885), 243, 270.
[8]) Wallach, *Ibidem* **230** (1885), 233.
[9]) Semmler, Berl. Berichte **41** (1908), 4474; **42** (1909) 522.
[10]) Wallach, Liebig's Annalen **238** (1887), 84; **271** (1892), 297.
[11]) Godlewsky and Roshanowitsch, Journ. russ. phys. chem. Ges. **31** (1899), 209.
[12]) Wallach, Liebig's Annalen **264** (1891), 21.
[13]) Wallach, *Ibidem* **264** (1891), 9.
[14]) Wallach, *Ibidem* **363** (1908), 1; **368** (1909), 1.
[15]) Wallach, *Ibidem* **357** (1907), 68; **362** (1908), 285.
[16]) Bredt, *Ibidem* **366** (1909), 46.

VI. SYNTHESIS WITH THE AID OF GRIGNARD'S REACTION.

Δ^2-*Iso*propylhexenone —> α-Phellandrene[1])
o-Cresol —> α-Terpinene.[2])

VII. RING-FORMATION ACCOMPANIED BY DEHYDRATION.

a) from aliphatic terpene alcohols:

Linalool —> Dipentene[3]) and Terpinene[3])
Geraniol —> Dipentene.[4])

b) from aliphatic terpene aldehydes:

Citral —> *p*-Cymene.[5])

VIII. POLYMERISATION OF HYDROCARBONS.

Isoprene —> Dipentene[6])
Valerylene —> Dipentene.[7])

IX. COMPLETE SYNTHESES.

In addition to the syntheses accomplished by Wallach[8]) with the aid of ketones and bromaceticester and its homologues, the following may here be mentioned: *viz.*, the synthesis of $\Delta^{2,4}$-menthadiene from succinyl succinic acid by v. Baeyer,[9]) that of dipentene[10]) and carvestrene[11]) by Perkin jun. and the more recent syntheses of Komppa in the camphor group.[12])

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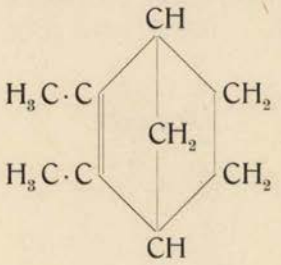
[1]) Wallach, Liebig's Annalen **359** (1908), 283.
[2]) Auwers and v. d. Heyden, Berl. Berichte **42** (1909), 2404.
[3]) Bertram and Walbaum, Journ. f. prakt. Chem. II. **45** (1892), 601.
[4]) Bertram and Gildemeister, *Ibidem* II. **49** (1894), 194; Tiemann and Schmidt, Berl. Berichte **28** (1895), 2134.
[5]) Tiemann and Semmler, Berl. Berichte **28** (1895), 2134.
[6]) Tilden, Journ. chem. Soc. **45** (1884), 410; Bouchardat, Compt. rend. **80** (1875), 1446; **87** (1878), 654; **89** (1879), 361, 1117.
[7]) Bouchardat, Bull. Soc. chim. II. **33** (1880), 24.
[8]) Wallach, *Terpene und Campher.* Leipzig 1909, p. 145.
[9]) Berl. Berichte **26** (1893), 232.
[10]) Journ. chem. Soc. **85** (1904), 654.
[11]) *Ibidem* **91** (1907), 480.
[12]) Liebig's Annalen **368** (1909), 110; **370** (1909), 209.

Santene = Norcamphene.



First of all there may be mentioned a lower homologue of the terpenes, the santene, C_9H_{14}, which has been observed repeatedly in recent years. Its occurrence has been observed in East-Indian sandalwood oil, in Siberian pine-needle oil, in the German *Fichtennadelöl,* in the needle oil of the German *Abies alba* and in the Swedish *Fichtennadelöl* from *Picea excelsa.* The following constants of this oil have been recorded:

B. p. 31 to 33° (9 mm); $d_{20°}$ 0,863; $\alpha_D \pm 0°$; n_D 1,46658.[1])
B. p. 140°; $d_{15°}$ 0,8698; $\alpha_D \pm 0°$; $n_{D19.2°}$ 1,46960.[2])

Upon hydration with the acetic acid-sulphuric acid mixture according to Bertram, santene is converted into a bicyclic saturated alcohol, the santenol (*π-nor*borneol), b. p. 195 to 196°; m. p. 97 to 98°. When treated with chlorinating agents this yields *nor*bornyl chloride, respectively *norisobornyl* chloride. By splitting off hydrogen chloride from these chlorides, Semmler[3]) obtained *nor*camphene, which is identical with santene.

Characteristic derivatives of santene are its nitrosochloride, m. p. 109 to 110°; its chlorhydrate, m. p. 80 to 81°; its tribromide, m. p. 62 to 63°; and its nitrosite, m. p. 124 to 125°. For its identification Semmler suggests its tribromide. However, according to Aschan's observations, the santenes of different sources yield tribromides with varying melting points. Hence Aschan considers the nitrosite as better adapted for the identification of santene. As a further derivative suitable for the identification of santene,

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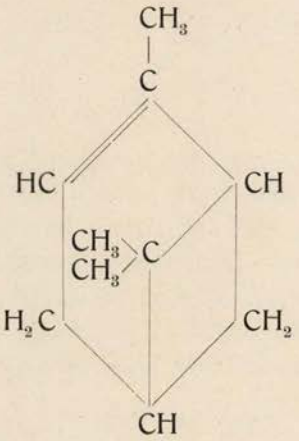
[1]) Semmler, Berl. Berichte **40** (1907), 4595.
[2]) Aschan, Berl. Berichte **40** (1907), 4920.
[3]) Berl. Berichte **41** (1908), 128.

Semmler and Bartelt[1]) mention the santene glycol (m. p. 197°; b. p. 135° at 10 mm), which is obtained by careful oxidation of the hydrocarbon in acetone solution with potassium permanganate.

α-Pinene.



α-Pinene is very widely distributed and occurs in the inactive as well as in both optically active forms. Whereas pinene does not often occur in flowers, it is found more frequently in the oils from leaves, barks, and woods. It is the principal constituent of the distillate from the oleoresins of the several species of *Pinus,* which distillates are known in commerce as turpentine oils. French and Spanish turpentine oils contain as principal constituent *l*-α-pinene, whereas in American and Greek oils the dextrogyrate modification predominates. However, there are also American oils which are lævogyrate or nearly inactive.

The hydrocarbon *d*-α-pinene (the australene of Berthelot), besides occurring in American and Greek turpentine oil, has been found in Burmese turpentine oil, in the turpentine oil from *Pinus sylvestris,* in German, Polish and Swedish pine tar oils, in larch needle oil, in German and Swedish *Kiefernadelöl,* in *Zirbelkiefernadelöl,* in the oil from the leaves of *Juniperus phœnicea* and *Callitris glauca,* sandarac oil, in oil from the leaves of *Sequoia gigantea,* in cypress oil, in oil from the leaves and

[1]) Berl. Berichte 41 (1908), 866.

twigs of *Thuja plicata,* in the oil of *Alpinia malaccensis,* in the oils of galangal, star anise, ylang-ylang, nutmeg, camphor, apopin, *Persea,* in the oil from the fruits of *Pittosporum undulatum,* in Chios turpentine oil, in the oils of myrtle and checken, in the oils of *Melaleuca uncinata* and *M. nodosa,* in niaouli oil, in the oils of *Leptospermum Liversidgei, Eucalyptus botryoides* and *E. dextropinea,* in ajowan oil, coriander oil, carrot oil, cumin oil, asafetida oil, galbanum oil, fennel oil, water fennel oil (?), rosemary oil and in the basilicum oil from Réunion.

l-α-Pinene (the terebenthene of Berthelot) is contained in French turpentine oil, in the turpentine oil from *Picea excelsa,* in the Canada balsam oil from *Abies balsamea, A. amabilis,* in Oregon balsam oil from *Pseudotsuga mucronata,* in the needle oil from *Pinus Strobus,* in *Fichtennadelöl,* in the *Seestrandkieferknospenöl,* in the needle oil from *Pinus montana,* in the English *Kiefernadelöl,* in hemlock needle oil, in the oils from the leaves and cones of *Abies alba,* in the needle oils from *Abies canadensis, Picea nigra, P. alba, Abies balsamea* and *A. sibirica,* in the oil of cubeb (?), the oils of *Asarum europæum* and *A. arifolium,* in the oils of Ceylon cinnamon and *Canella alba,* in the oil from *Umbellularia californica,* in the geranium oil from Réunion, in the oils of petitgrain, lemon, neroli, rue, frankincense, dacryodes resin and cajeput, in the oils from *Eucalyptus carnea, E. lævopinea* and *E. Wilkinsoniana,* in the oils from parsley, lavender, marjoran, American pennyroyal, spearmint (?), French peppermint, valerian, and kessoroot.

i-α-Pinene has been found in coriander oil, lemon oil, cumin oil, American peppermint oil, and oil of Levant wormseed.

α-Pinene has frequently been found in other oils, but its optical rotation has not been recorded. Thus in Venetian turpentine oil, in the pine tar oil from Finland, in the oil from the leaves and twigs of *Larix americana,* in Thuja oil, in juniper oil, in the oil from the resin of *Callitris verrucosa,* in matico oil, in pilea oil, in the oil from Canada snake-root, in boldo leaf oil, in cinnamon root oil, in the oil from Pichurim beans (?), in sassafras oil, the oil from sassafras leaves, in the oils from laurel leaves, massoy bark and Japanese pepper (?), in the oils of bergamot and lemon, in several elemi oils, in oil of myrrh, in the oil from the berries of *Schinus molle,* in the oils from the following species of *Eucalyptus, viz., acmenoides, affinis, aggre-*

gata, albens, amygdalina, angophoroides, apiculata, Bæuerleni, bicolor, Bosistoana, Bridgesiana, Cambagei, camphora, capitellata, cinerea, cneorifolia, conica, cordata, corymbosa, crebra, dealbata, dives, dumosa, eugenioides, eximia, fastigiata, Fletcheri, fraxinoides, Globulus, goniocalyx, gracilis, hemilampra, hemiphloia, intermedia, intertexta, lactea, longifolia, Luehmanniana, Macarthuri, macrorrhyncha, maculata, maculosa, Maideni, melanophloia, melliodora, microcorys, microtheca, Morrisii, nova-anglica, odorata, oleosa, ovalifolia, o. var. *lanceolata, paniculata, pendula, pilularis, polyanthema, polybractea, populifolia, propinqua, pulverulenta, punctata, p.* var. *didyma, quadrangulata, radiata, resinifera, Risdoni, robusta, Rossi, rostrata, r.* var. *borealis, rubida, saligna, siderophloia, sideroxylon, s.* var. *pallens, Smithii, squamosa, stricta, Stuartiana, tereticornis, tessellaris, trachyphloia, umbra, viminalis, viridis* and *Woollsiana,* in French parsley oil, rosemary oil, sage oil, in the oils of *Thymus capitatus* and *Satureja Thymbra,* in oil of spike, in golden rod oil, and in the oil of *Helichrysum Stœchas* (?).

In as much as a strongly active α-pinene yields little or no nitrosochloride, the formation of this substance is in reality indicative of *i*-pinene. Since in the above compilation of the occurrence of *d*- and *l*-pinene, the presence of pinene in more or less optically active fractions has been established by means of the nitrosochloride reaction, the presence of *i*-pinene should be assumed. The final determination of the presence of optically active pinene will, therefore, have to rest with the conversion of the optically active pinene into the corresponding optically active pinonic acid. Hence it becomes apparent how desirable it must be to revise the older investigations in the light of the new methods for the identification of pinene. (Comp. p. 297.)

α-Pinene is one of the few terpenes that can be obtained in a relatively pure state. It is obtained by heating the solid pinene nitrosochloride with aniline in alcoholic solution.[1]) The α-pinene thus obtained is always optically inactive and possesses the following physical constants:

B. p. 155 to 156°; $d_{20°}$ 0,858; $n_{D21°}$ 1,46553.[2])

[1]) Wallach, Liebig's Annalen **252** (1889), 132; **258** (1890), 343.
[2]) Wallach, Liebig's Annalen **258** (1890), 344.

An α-pinene regenerated from the nitrosochloride in the laboratory of Schimmel & Co. gave the following constants:

B. p. 154,5 to 155°; $d_{15°}$ 0,8634; $\alpha_D \pm 0$; $n_{D20°}$ 1,46644.

The inactive form was also obtained by the decomposition of pinocamphylxanthogenic acid ester.[1]) Gildemeister and Köhler[2]) obtained, upon decomposition of *d*-pinocamphylxanthogenic acid ester, active *d*-α-pinene, which, however, was rendered impure by the presence of another terpene.

The strict observation of certain conditions enabled Wallach[3]) to prepare *l*-α-pinene from nopinolacetic acid.

Most oils containing pinene presumably contain mixtures of *d*- and *l*-pinene. Hence the direction of the rotation in all probability depends on the predominance of the one or the other modification. In order to prepare optically active modifications of α-pinene, it is best to start with pinene fractions possessing a high angle of rotation. It should be borne in mind, however, that this high angle of rotation may be produced by camphene. The fractions boiling below 160° are purified by fractional distillation over sodium until the boiling point and other properties correspond with those of *i*-α-pinene. The highest angles of rotation thus far observed are the following:

for *d*-α-pinene from Greek turpentine oil:

$[\alpha]_D + 48{,}4°$ (b. p. 155 to 156°; $d_{25°}$ 0,8542; $n_{D25°}$ 1,4634),[4])
$[\alpha]_D + 46{,}73°$ (b. p. 156° at 760 mm; $d_{15°}$ 0,8642; $n_{D20°}$ 1,46565),[5])

for *l*-α-pinene from the oil of *Eucalyptus lævopinea:*

$[\alpha]_{D19°} - 48{,}63°$ (b. p. 157°; $d^{19°}_{16°}$ 0,8626).[6])

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[1]) Tschugaeff, Journ. russ. phys. chem. Ges. **39** (1908), 1324; Chem. Zentralbl. **1908**, I. 1179.

[2]) *Wallach-Festschrift.* Göttingen 1909. p. 436.

[3]) Liebig's Annalen **368** (1909), 1.

[4]) Vèzes, Bull. Soc. chim. IV. **5** (1909), 932.

[5]) Gildemeister and Köhler, *Wallach-Festschrift.* Göttingen 1909. p. 434; Report of Schimmel & Co. October **1909**, 69.

[6]) Smith, Journ. and Proceed. of the Royal Soc. of N. S. Wales **32** (1898), 195; Report of Schimmel & Co. April **1899**, 24.

α-Pinene is a colorless, mobile liquid, which, like most terpenes, undergoes autoxidation upon standing by taking oxygen from the air and partly resinifies. It is readily converted into other terpenes. Thus by a higher temperature (250 to 270°) it is changed into dipentene, by moist hydrogen chloride into dipentene or its dihydrochloride, by means of alcoholic sulphuric acid into terpinolene and terpinene, presumably through the dipentene as an intermediate stage. Through the action of dry hydrogen halides α-pinene is changed to derivatives of camphor, a reaction that has become of great importance in the artifical production of camphor.

In the presence of water and oxygen, pinene yields pinol hydrate (sobrerol) $C_{10}H_{18}O_2$, which is at times found in old turpentine oils as a crystalline deposit. The active modifications of pinol hydrate melt at 150°, the inactive modification at 130,5 to 131°. When boiled with acids, pinol hydrate yields the oxide pinol, $C_{10}H_{16}O$, with its characteristic odor. In contact with dilute mineral acids, pinene is converted into terpin hydrate, $C_{10}H_{18}(OH)_2$, H_2O (m. p. 116 to 117°). As an intermediate product terpineol is formed, which likewise results upon the hydration of pinene with sulphuric and acetic acids.

When shaken with a 3 to 5 percent. sulphuric acid, pinene is acted upon but slowly.[1]) A suitable method for the hydration of pinene, according to Barbier and Grignard,[2]) consists in acting on a solution of pinene in glacial acetic acid and acetic acid anhydride with a 50 percent. aqueous solution of benzene monosulphonic acid.

Oxidizing agents act on pinene in various ways. Whereas concentrated nitric acid produces so violent a reaction that ignition may take place, dilute nitric acid, like chromic acid mixture, produces — with pinol hydrate or pinol as intermediate products — in addition to lower fatty acids and other products, terephthalic acid, $C_8H_6O_4$, terebic acid, $C_7H_{10}O_4$, and terpenylic acid, $C_8H_{12}O_4$. Essentially different results are obtained with potassium permanganate. As shown by Wagner,[3]) dilute per-

[1]) Wallach, Nachr. K. Ges. Wiss. Göttingen **1908**. Meeting of February 8. p. 20.

[2]) Compt. rend. **145** (1907), 1425; Bull. Soc. chim. IV. **3** (1908), 139; **5** (1909), 512, 519.

[3]) Berl. Berichte **27** (1894), 2270; **29** (1896), 881.

manganate solution produces principally neutral oxidation products. When concentrated permanganate is used there results, in addition to other products, pinonic acid,[1]) $C_{10}H_{16}O_3$, a monobasic keto acid. Upon further oxidation this yields not only terebic acid, but also the "Abbau" products that are obtained upon oxidation of camphor derivatives.

According to the optical character of the initial material, a pinonic acid results that is optically active ($[\alpha]_D$ in chloroformic solution + or — 88 to 90°) respectively inactive. The inactive modification melts at 103 to 105°, its oxime at 150°; of the active modification the acids melt at 69,5 to 70,5°, the oximes at 129° and the semicarbazones at 203 to 204°. Upon inversion with sulphuric acid methoethylheptanonolid results, the active modification of which melts at 46 to 47°, the inactive modification at 63 to 64°.

These compounds are suitable for the characterization of the several modifications of α-pinene. When pinene is acted upon by ozone, ozonides result which, upon cleavage with water, yield pinonic acid.[2])

α-Pinene is an unsaturated hydrocarbon with one double bond. Upon addition it is readily converted into derivatives of camphor. When dry hydrogen chloride or hydrogen bromide are passed into well dried and cooled pinene, halogenides of borneol result. Of these the chloride (the socalled "pinene chlorhydrate"), $C_{10}H_{16}HCl$, was designated "artificial camphor" because of its camphor-like odor. It melts at 125 to 127°; the bromide, $C_{10}H_{16}HBr$, melts 90°. Both yield camphene when hydrohalogen is split off. True pinene monochlorhydrate was obtained by Wallach by the action of phosphorus pentachloride upon homonopinol. If bromine is allowed to act on pinene in dry solution, one molecule of bromine is readily decolorized and added. More bromine is added but slowly and is accompanied by the development of hydrogen bromide. When the addition product of one molecule of bromine to pinene is distilled with steam a dibromide melting at 169 to 170° is obtained.[3]) A better

[1]) Tiemann and Semmler, Berl. Berichte **28** (1895), 1345; **29** (1896); 529, 3027; Baeyer, Berl. Berichte **29** (1896), 22, 326, 1907, 1923, 2775; Gildemeister and Köhler, *Wallach-Festschrift.* Göttingen 1909. p. 426.

[2]) Harries and Neresheimer, Berl. Berichte **41** (1908), 38.

[3]) Wallach, Liebig's Annalen **264** (1891), 8.

yield, however, is obtained by allowing hypobromous acid to act on pinene. This dibromide also appears to be a camphor derivative.[1]) When this dibromide is acted upon with aniline, hydrogen bromide is split off and cymene results. However, when acted upon with zinc dust in alcoholic solution, a new terpene, the tricyclene, m. p. 65 to 66° results.[2])

The presence of α-pinene in a volatile oil can be ascertained by means of its nitrosochloride and its oxidation products. Provided the pinene reveals no high optical rotation, it is most readily identified by means of the nitrosochloride and by the conversion of the latter into its nitrolamine bases. For the preparation of the nitrosochloride, Wallach[3]) has given the following directions: A mixture of 50 g. each of turpentine oil (immaterial whether laevo- or dextrogyrate), glacial acetic acid and ethyl nitrite[4]) (preferably amyl nitrite)[5]) is well cooled in a freezing mixture and 15 cc. of crude (33 percent.) hydrochloric acid are gradually added. The nitrosochloride soon separates in a crystalline form, and is obtained in a fairly pure state when it is filtered off with a suction pump and well washed with alcohol. From the filtrate some more nitrosochloride separates on standing in the cold. It is profitable in regard to yield to work with small quantities, as only then can the low temperature be maintained which is necessary for the satisfactory conduct of the reaction; large quantities of pinol $C_{10}H_{16}O$ are formed as a by-product.

The nitrosochloride is a white crystalline powder, which is readily soluble in chloroform and may be again separated from this solution by methyl alcohol. The melting point of the recrystallized compound is 103°, though melting points as high as 115° have been observed. Like its derivatives it is optically inactive. According to observations by Baeyer[6]) pinene nitrosochloride is a bisnitroso compound $(C_{10}H_{16}Cl)_2N_2O_2$, which in

[1]) Wagner and Ginzberg, Berl. Berichte **29** (1896), 890.

[2]) Godlewsky and Wagner, Chem. Ztg. **21** (1897), 98.

[3]) Liebig's Annalen **245** (1888), 251; **253** (1889), 251.

[4]) This is easily obtained by allowing a mixture of 200 g. of concentrated sulphuric acid, 1,5 liters of water and 100 g. of alcohol to flow into a solution of 250 g. of sodium nitrite in 1 liter of water and 100 g. of alcohol. The ethyl nitrite which forms at once must be condensed in well cooled receivers.

[5]) Report of Schimmel & Co. November **1908**, 63.

[6]) Berl. Berichte **28** (1895), 648.

ethereal solution is changed by hydrochloric acid into hydrochlorocarvoxime.[1]) By splitting off hydrochloric acid with alcoholic potassa it is converted into nitrosopinene (m. p. 132°)[2]) which has been recognized as an oxime.[3]) Aromatic bases, such as aniline and toluidine split off nitrosylchloride, regenerating pinene with the formation of amidoazo-compounds. Quite different is the behavior of the nitrosochloride toward bases of the fatty series and those which possess their characteristics, as for instance, benzylamine and piperidine. With primary bases as well as with piperidine, nitrolamines result; the secondary bases, like diethylamine, however, produce a splitting-off of hydrochloric acid with the resulting formation of nitrosopinene.

As the nitrosochlorides of different terpenes show very similar melting points and besides decompose very readily, they are less suitable for characterization than the nitrolamines, which are very stable and crystallize readily; these have been prepared in large numbers, although the compounds produced by the reaction with benzylamine and piperidine are preferably used. For their preparation[4]) the nitrosochloride is treated in excess with the base dissolved in alcohol and heated on a water bath; the nitrolamine formed is separated by the addition of water. The melting point of pinene nitrolpiperidine is 118 to 119°, that of the nitrolbenzylamine 122 to 123°.

It has already been pointed out that the yield of nitrosochloride diminishes with the increased optical rotation of the hydrocarbon material.[5]) For the identification of pinene in highly active pinene fractions it is, therefore, more expedient to make use of the pinonic acid referred to above. 100 g. of pinene are shaken with 233 g. of potassium permanganate and 3 l. of water, the mixture being kept cool with ice. From the alkaline reaction mixture the excess of hydrocarbon is separated and

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[1]) Berl. Berichte **29** (1896), 12.

[2]) Wallach and Lorentz, Liebig's Annalen **268** (1891), 198.

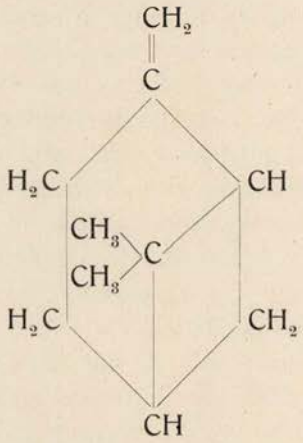
[3]) Urban and Kremers, Am. Chem. Journ. **16** (1894), 404; Baeyer, Berl. Berichte **28** (1895), 646; Mead and Kremers, Am. Chem. Journ. **17** (1895), 607.

[4]) Wallach, Liebig's Annalen **245** (1888), 253; **252** (1889), 130.

[5]) Tilden, Journ. Chem. Soc. N. S. **15** (1877), 554; **85** (1904), 759; Kremers, Pharm. Rundsch. (New York) **13** (1895), 135. Gildemeister and Köhler, *Wallach-Festschrift,* Göttingen 1909, p. 433.

the neutral products are removed by shaking with ether. The pinonic acid is then precipitated with dilute sulphuric acid. For the identification of the pinene it suffices to convert the acid into its semicarbazone (m. p. 204°). If it is desired to establish the presence of optically active as well as inactive pinene, it is necessary to isolate the acid in its pure form. In most instances this can be accomplished by fractionation under diminished pressure (b. p. 168° at 12 mm.). The identification is than completed by determining the angle of rotation and by preparing the derivatives of the acid already described.

β-Pinene.



Side by side with α-pinene, nopinene or β-pinene occurs in the turpentine oils, also in pine tar oil, in Siberian *Fichtennadelöl,* and in the oils of lemon,[1]) coriander,[2]) cumin,[3]) hyssop[4]) and nutmeg. Presumably it will be found in a large number of volatile oils. Synthetically it has been prepared by Wallach.[5]) Starting with nopinone, this was condensed with bromacetic ester to

[1]) Gildemeister and Müller, *Wallach-Festschrift,* Göttingen 1909, p. 442.

[2]) Walbaum and Müller, *Ibidem* 657; Report of Schimmel & Co. October 1909, 48.

[3]) Report of Schimmel & Co. October 1909, 50.

[4]) Gildemeister and Köhler, *Wallach-Festschrift,* Göttingen 1909, 417; Report of Schimmel & Co. April 1908, 58.

[5]) Liebig's Annalen 363 (1908), 1.

nopinolacetic ester, which, when treated with acetic acid anhydride yielded β-pinene.

The following properties have been determined:

B. p. 164 to 166°; $d_{15°}$ 0,8650; α_D — 19°29′ (from hyssop oil); $n_{D20°}$ 1,47548.[1])

In connection with two preparations obtained at different times, Wallach[2]) ascertained the following constants:

B. p. 163 to 164°; $d_{22°}$ 0,8675; α_D — 22°5′; $n_{D22°}$ 1,4749.

B. p. 162 to 163°; $d_{22°}$ 0,8660; α_D — 22°20′; $n_{D22°}$ 1,4724.[2])

When acted on with glacial acetic acid-sulphuric acid mixture, β-pinene is in the main converted into terpinene.[3])

β-Pinene yields no nitrosochloride. With hydrogen chloride it yields a mixture of dipentene dihydrochloride and bornylchloride. When acted upon by nitrous acid, nitroso-β-pinene results, which upon reduction is converted into amidoterebentene. This, in turn, when acted upon by nitrous acid, yields an alcohol, which when oxidized with chromic acid is converted into tetrahydrocuminic aldehyde (m. p. of the semicarbazone 201 to 203°) and cuminic acid (m. p. 115°).[4]) From α-pinene it is readily distinguished by means of its oxidation products. When oxidized with permanganate, there results nopinic acid (m. p. 126 to 127°) which is readily isolated by its difficultly soluble sodium salt. As a by product there also results a glycol melting at 76 to 78°. For the identification of β-pinene, fraction 160 to 170° is oxidized according to Wallach's[5]) directions for the preparation of nopinate of sodium. 300 g. of pinene are shaken, with the aid of a shaking machine, with a solution of 700 g. potassium permanganate in 9 l. water to which 150 g. of sodium hydroxide have been added. The reaction mixture becomes decidedly warm and the oxidation is completed in about 20 minutes. In the absence of alkali, about 12 hours are required before the per-

[1]) Report of Schimmel & Co. April 1908, 58.

[2]) Liebig's Annalen **363** (1908), 1.

[3]) Wallach, Liebig's Annalen **363** (1908), 1.

[4]) Pesci and Bettelli, Gazz. chim. ital. **16** (1886), 337; Wallach, Liebig's Annalen **346** (1906), 246.

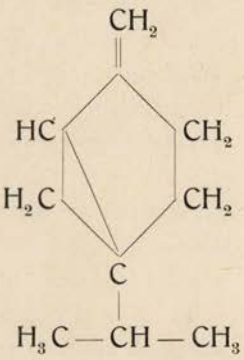
[5]) Wallach, Liebig's Annalen **356** (1907), 228.

manganate is consumed. The excess of hydrocarbon is distilled off with steam, the mixture filtered to remove the oxide of manganese and the filtrate evaporated to about 3 l. while a current of carbon dioxide is passed into the evaporating liquid. Upon cooling, nopinate of sodium crystallizes out, which is separated with the aid of a forcefilter and purified by recrystallization.

The free nopinic acid from *l*-β-pinene has the following properties: m. p. 126°; $d_{17°}$ 0,781; $[\alpha]_D$ — 15,64° (in ethereal solution).

For its further characterization nopinic acid can be oxidized to nopinone with either lead peroxide or permanganate in sulphuric acid solution. Nopinone is a ketone which has served as a steppingstone in the accomplishment of several interesting syntheses of terpenes and terpene derivatives. Of the derivatives of this ketone the following should be mentioned: the semicarbazone, m. p. 188°; the benzylidene compound, m. p. 106 to 107°; and the compound $C_{18}H_{29}OCl_3$ which results when HCl is passed into the alcoholic solution of the ketone and which melts at 148°.

Sabinene.



This hydrocarbon, which resembles β-pinene in some respects, has thus far been found in the oils of savin, Ceylon cardamom, marjoran and pilea. The following constants have been recorded:

B. p. 162 to 166°; $d_{20°}$ 0,840; α_D + 63°; n_D 1,466.[1])

B. p. 163 to 165°; $d_{20°}$ 0,842; α_D + 67,5°; n_D 1,4678.[2])

[1]) Semmler, Berl. Berichte **33** (1900), 1464.

[2]) Wallach, Liebig's Annalen **350** (1906), 163.

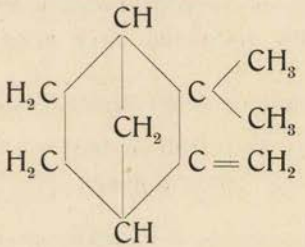
In connection with the fractionation of a larger amount of sabinene from savin oil, Schimmel & Co. determined the following constants:

20% boiling between 162 to 163°; $d_{15°}$ 0,8481; α_D + 59° 30′;
49% „ „ 163 „ 164°; „ 0,8480; „ + 63° 50′;
31% „ „ 164 „ 165°; „ 0,8482; „ + 68° 54′.

Significant is the low specific gravity which distinguishes sabinene from other hydrocarbons with a similar boiling point.

When boiled with dilute sulphuric acid, sabinene is converted into terpinene; with hydrohalogens the corresponding terpinene dihalogenhydrates result; when shaken with dilute sulphuric acid in the cold, sabinene yields active terpinenol-4 and terpinene terpin (see terpineol). The oxidation with permanganate is analogous to that of β-pinene. The resulting, sabinene glycol which melts at 54° and boils at 148 to 150° under 15 mm. pressure, has been used by Semmler for the identification of sabinene. Simpler, however, is the identification, according to Wallach, by means of the difficultly soluble sabinate of sodium which results upon oxidation in the presence of free sodium hydroxide.[1]) The free sabinic acid melts at 57°. Like nopinic acid it can be oxidized to a ketone $C_9H_{14}O$, the sabinaketone, which likewise has served as a starting point for synthesis in the terpene group. The semicarbazone melts at 141 to 142°. When hydrogen chloride is passed into a methylalcoholic solution of sabinaketone, a mono-hydrochloride $C_9H_{15}OCl$, m. p. 77 to 78°, results, whereas in glacial acetic acid solution a compound $C_{18}H_{29}OCl_3$, m. p. 124°, is obtained. Sodium hypobromite oxidizes sabinaketone to thuja-dicarboxylic acid melting at 142 to 143°.

Camphene.



Although camphene is the only solid hydrocarbon $C_{10}H_{16}$ which occurs in Nature, its isolation in a crystalline state from

[1]) Wallach, Liebig's Annalen **359** (1908), 266.

volatile oils has been accomplished but rarely. In this form *l*-camphene has been isolated from the Siberian *Fichtennadelöl;* from the first fractions of Ceylon citronella oil Schimmel & Co. likewise obtained solid camphene. In the vegetable kingdom this hydrocarbon is found in both active modifications.

As *d*-camphene (the austracamphene of Berthelot), it has been found in cypress oil, in Siberian *Fichtennadelöl,* in the oils of ginger, nutmeg, camphor, lemon, orange-petitgrain, sweet orange blossoms, of *Eucalyptus Globulus,* and spike.

As *l*-camphene (the terecamphene of Berthelot),[1]) it has been found in the oil from the twigs of *Juniperus phœnicea* and in the oils of lemon, neroli (?), valerian, kesso, *Artemisia Herba-alba,* and of *Chrysanthemum sinense* var. *japonicum.*

In addition, camphene has been found in the oils of juniper berries, of the Douglas fir, citronella, Japanese cinnamon oil, bergamot, rosemary, and fennel.

Artificially camphene can be obtained in various ways, principally by splitting off hydrohalogen from bornylchloride or bornyl bromide (from pinene or borneol). Most conveniently, however, it is obtained upon dehydration of isoborneol with zinc chloride, though in this manner frequently mixtures of different hydrocarbons are obtained.

Camphene occurs as a white crummy-crystalline mass, with a faint camphor-like odor, that tends toward sublimation. Otherwise it is much more stable toward air and light than the other terpenes. In as much as it can be obtained in solid form and since by careful precipitation from its alcoholic solution with water it can be purified from liquid impurities, it is one of the few terpenes that have been prepared with a fair degree of purity. As its constants the following have been recorded:

for camphene from borneol-bornylchloride:

M. p. 48 to 49°; b. p. 160 to 161°[2]); $d_{48°}$ 0,850; $n_{C48°}$ 1,4555[3]);

M. p. 53,5 to 54°; $d^{58.6°}_{4°}$ 0,83808; $n_{D58.6°}$ 1,45314[4]);

[1]) The term terecamphene is at times applied to any camphene prepared from pinenechlorhydrate.

[2]) Wallach, Liebig's Annalen **230** (1885), 234.

[3]) Wallach, *Ibidem* **245** (1888), 210.

[4]) Brühl, Berl. Berichte **25** (1892), 164.

for camphene from pinene-bornylchloride:

M. p. 51 to 52°; b. p. 158,5 to 159,5°; $d_{4°}^{54°}$ 0,84224; $n_{D54°}$ 1,45514[1]);

for camphene from *iso*borneol:

M. p. 50°; b. p. 159 to 160°;[2]) 56° at 15 mm.

The corresponding values at 20° should be approximately d 0,870 and n_D 1,470.

The angle of rotation of the camphene prepared artificially from pinene hydrochloride or bornyl chloride varies not only according to the angle of rotation of the initial material, but also according to the temperature — both height and duration — employed in the process. Thus Bouchardat and Lafont[3]) obtained hydrocarbons, the $[\alpha]_D$ of which lay between — 80° 37′ and — 30° 30′ when they allowed *l*-pinene-bornylchloride ($[\alpha]_D$ — 28° 30′) to be acted upon by an alcoholic solution of potassium acetate at a temperature of from 150 to 170°.

In connection with a *d*-camphene obtained from borneol-bornylchloride, Kachler[4]) observed $[\alpha]_{D85°}$ + 20° (100,3 mm.).

The camphene molecule does not rearrange itself to isomeric forms as do other terpenes. While it is true that prolonged heating at a higher temperature, or treatment with dehydrating agents such as zinc chloride, phosphoric acid anhydride, or concentrated sulphuric acid changes it, the resulting decomposition products do not correspond to the formula $C_{10}H_{16}$.

As a terpene with one double bond, camphene yields addition products with halogen (m. p. of the dibromide 91 to 91,5°) and with hydrohalogen, but not with nitrosylchloride. However, compounds of camphene with the oxides of nitrogen have been obtained both directly and indirectly. Extensive investigations have been made concerning the relation between pinene hydrochloride, camphene hydrochloride, and the corresponding derivatives of borneol and *iso*borneol.

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[1]) Brühl, Berl. Berichte **25** (1892), 162.

[2]) Bertram and Walbaum, Journ. f. prakt. Chem. II. **49** (1894), 8.

[3]) Compt. rend. **104** (1887), 694; Bull. Soc. chim. II. **47** (1887), 439.

[4]) Liebig's Annalen **197** (1879), 97.

Camphene chlorhydrate is obtained by passing gaseous hydrochloric acid into an alcoholic solution of camphene. It melts at about 155°. References[1]) do not agree, the melting points recorded varying from 142 to 160°.

Oxidizing agents, such as permanganate, nitric acid, chromic acid mixture, and ozone, do not act in like manner on the hydrocarbon. The oxidation with permanganate would seem to indicate that artificial camphene is not a unit, but consists of a mixture of at least three hydrocarbons. Thus the oxidation of a camphene, obtained from *iso*borneol, with permanganate yields three different products: camphene glycol, $C_{10}H_{16}(OH)_2$, m. p. 200°; camphene camphoric acid, $C_{10}H_{16}O_4$, m. p. 135,5 to 136°; and cyclene, $C_{10}H_{16}$, m. p. 68°, b. p. 152,8°.[2]) The further oxidation of camphene glycol yields camphenylic acid, $C_{10}H_{16}O_3$ (m. p. 171 to 172°) and camphenilone, $C_9H_{14}O$ (m. p. 36 to 38°). From natural camphene an isomeric camphene-camphoric acid (m. p. 142°) appears to result which is not identical with the one mentioned above.[3]) Nitric acid oxidizes camphene to the tribasic camphoylic acid (Marsh and Gardner), $C_{10}H_{14}O_6$ (Bredt's carboxylapocamphoric acid, m. p. 202°). In addition minor amounts of the above-mentioned ketone $C_9H_{14}O$ result. Chromic acid mixture yields principally camphor with little camphoric acid and other products. Oxidation with ozone produces camphenilone.

However, none of these derivatives can be used to advantage for the characterization of camphene. With fairly pure fractions rich in camphene, the latter can be separated in the form of its chlorhydrate. It is better, however, to identify camphene by converting it into *iso*borneol. Should larger amounts of pinene be present, the identification of camphene by this method is difficult since terpineol as well as *iso*borneol is formed, and since the separation of the two can be attained but imperfectly.

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[1]) Kachler and Spitzer, Liebig's Annalen **200** (1880), 343; Jünger and Klages, Berl. Berichte **29** (1896), 545; Reychler, *Ibidem* **32** (1899), 2302; Kondakow, Journ. f. prakt. Chem. II. **65** (1902), 201.

[2]) Moycho and Zienkowski, Liebig's Annalen **340** (1905), 17, 40.

[3]) Wallach, Liebig's Annalen **366** (1907), 84.

For the conversion of camphene into *iso*borneol the following method is used:[1])

100 parts of the camphene fraction are heated with 250 parts of glacial acetic acid and 10 parts of 50 percent. sulphuric acid for 2 to 3 hours to 50 to 60° with frequent shaking; the mixture which at first separates into two layers finally becomes homogeneous and has a slightly reddish color. When the reaction is ended, the acetate formed is separated by water, washed repeatedly, and then saponified by heating with a solution of 50 g. of potassium hydrate in 250 g. of alcohol. After removing the alcohol, the *iso*borneol is precipitated as a crumbly mass by the addition of water and is purified by recrystallization from petroleum ether. The melting point of *iso*borneol is about 212°; the determination must, however, be made in a sealed capillary tube on account of its great tendency to sublime. For the further characterization of the *iso*borneol, its bromal compound, m. p. 71 to 72° may be used.

It should be remembered, however, that this *iso*borneol always contains some borneol. The phenylurethanes of both alcohols melt at 138 to 139°.

Recent observations appear to render it probable that camphene occurs in several modifications which differ from each other not only by their physical constants, but also by their oxidation products. As to their constitution, however, no details are as yet known. Thus Wallach[2]) isolated from a Siberian pine needle oil a camphene with the following properties:

M. p. 39°; b. p. 160 to 161°; $d_{40°}$ 0,8555; $[\alpha]_D$ — 84,9°; $n_{D40°}$ 1,46207; mol. refr. 43,71; calculated for $C_{10}H_{16}$ 43,53.

Upon oxidation of this camphene with permanganate there resulted an acid, isomeric with camphene-camphoric acid, that melted at 142°. Its chlorhydrate melted at 51°. The same camphene has likewise been found in citronella oil.

By acting on bornylamine with sodium nitrite, Wallach[3]) obtained a camphene (m. p. 50°; b. p. 160 to 161°), which was characterized by a remarkably strong optical rotation ($[\alpha]_D$ + 103,89°).

[1]) Bertram and Walbaum, Journ. f. prakt. Chem. II. **49** (1894), 1. — In addition to *iso*borneol some borneol is formed. Aschan, Berl. Berichte **40** (1907), 4923.

[2]) Liebig's Annalen **357** (1907), 79.

[3]) *Ibidem* 84.

Fenchene.

A positive proof for the occurrence of fenchene in volatile oils has not yet been brought. The inference of its presence in terpene fractions boiling about 160° has been drawn from the formation of fenchyl alcohol. Thus Bouchardat and Tardy[1]) obtained from an oil of *Eucalyptus Globulus* a terpene which, when heated with benzoic acid, yielded fenchyl alcohol. Upon heating French turpentine oil with sulphuric acid ($^1/_{10}$ of its weight), and the reaction product with an excess of alcoholic potassa in an autoclave to 150°, these same authors obtained a readily soluble potassium salt which, upon addition of water, broke up into potassium acid sulphate and *d*-fenchylalcohol.[2]) When repeating this experiment, Schimmel & Co., however, could not find this alcohol.[3]) In as much as it is not impossible that this terpene may occur as such in nature, mention of these observations should here be made.

Artificially fenchene has been obtained by the dehydration of fenchyl alcohol, also by splitting off hydrogenchloride from fenchyl chloride.[4]) Synthetically it has also been obtained from nopinone, an "Abbau" product of β-pinene.[5]) Upon diazotation of fenchylamine with nitrous acid, Wallach[6]) obtained, in the main, a fenchene which boiled at 156 to 157°; $d_{19°}$ 0,869; α_D — 32° 12′; $n_{D19°}$ 1,4729.

The isomeric complexities are even greater in the case of the fenchenes than in that of the camphenes. Possibly not one of the fenchenes thus far obtained represents a chemical unit. Even when the method of preparation employed was the same, differences in the constants, more particularly in the angle of rotation, were observed. In addition to semicyclic fenchenes, there appear to be fenchenes with double linkage in the cycle, the boiling point of which is appreciably lower. Fenchene has thus far been obtained only in the liquid state. Its odor

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[1]) Compt. rend. **120** (1895), 1418.
[2]) Compt. rend. **125** (1897), 113.
[3]) Report of Schimmel & Co. April **1904**, 53.
[4]) Wallach, Liebig's Annalen **263** (1891), 149.
[5]) Wallach, *Ibidem* **357** (1907), 53; **363** (1908), 3.
[6]) *Ibidem* **362** (1908), 180.

reminds of that of camphene. The following constants have been determined:

B. p. 154 to 155°; $d_{18°}$ 0,8660; $n_{D18°}$ 1,4693.
B. p. 155 to 156°; $d_{18°}$ 0,8670; $n_{D18°}$ 1,47047;[1]) $\alpha_D + 21°$.[2])

Repeated determinations in the laboratory of Schimmel & Co. revealed the following constants:

B. p. 154 to 156° (765 mm.); $d_{15°}$ 0,8660 to 0,8665; $n_{D18°}$ 1,46733 to 1,46832.

From the *l*-fenchene ($[\alpha]_D$ — 32° 12′) mentioned above, Wallach[3]) prepared a dextrogyrate dibromide which melted at 87 to 88° and which revealed a specific rotation of + 42,83°. A dibromide prepared from *d*-fenchene (the fenchene being obtained from *l*-fenchone from thuja oil) likewise melted at 87 to 88°. A mixture of equal parts of both bromides, upon recrystallization, showed the melting point 62°.[4])

No other characteristic halogen or hydrohalogen or nitrosylchloride addition products are obtainable that might be used for the identification of fenchene. However, in like manner as camphene, fenchene can be hydrated to $C_{10}H_{18}O$ by means of the glacial acetic acid and sulphuric acid mixture. The alcohol thus obtained is *iso*fenchyl alcohol (m. p. 61,5 to 62°) which yields with phenyl*iso*cyanate a phenylurethane melting at 106 to 107°.[5])

From the semicyclic fenchenes there result, upon oxidation with potassium permanganate, hydroxyfenchene acids which are characterized by difficultly soluble sodium salts.

*ISO*FENCHENE. The *iso*fenchene obtained by Bertram and Helle[6]) from *iso*fenchyl alcohol was recognized by Wallach[7]) as *D-d*-fenchene.

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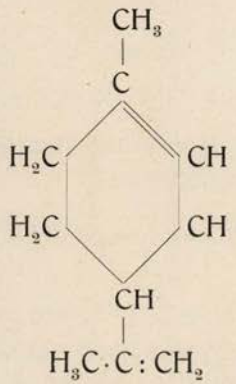
[1]) Wallach, Liebig's Annalen **300** (1898), 313.
[2]) Wallach, *Ibidem* **302** (1898), 376.
[3]) *Ibidem* **362** (1908), 182.
[4]) *Ibidem* 199.
[5]) Bertram and Helle, Journ. f. prakt. Chem. II. **61** (1900), 293; Report of Schimmel & Co. October **1898**, 48; April **1900**, 56.
[6]) Journ. f. prakt. Chem. II. **61** (1900), 303.
[7]) Liebig's Annalen **362** (1908), 193.

Limonene.



Limonene is a very widely distributed terpene. It is found in volatile oils, not only in the dextrogyrate and lævogyrate modifications, but also in the racemic modification, which is called dipentene and which is commonly treated as a separate hydrocarbon.

d-Limonene is contained in the oils of the *Aurantiaceæ,* most abundantly in the oils of orange, lemon, bergamot and mandarin, in Italian and West Indian limetta oil, in neroli oil and petitgrain oil, also in Virginian cedarleaf oil, in the needle oil from *Callitris glauca,* in gingergrass oil, in camphor oil, kuromoji oil, the oil from the fruits of *Pittosporum undulatum,* cedro oil, Manila elemi oil, oil of buchu leaves, caraway oil, dill oil, Macedonian fennel oil, celery oil, oil of *Monarda punctata* and erigeron oil.

l-Limonene has been found in the oils from the cones and leaves of *Abies alba,* in the turpentine oil of *Pinus serotina,* in Finland turpentine oil(?), in the oils of *Monodora Myristica* and *Eucalyptus Staigeriana,* in American peppermint oil, in Russian spearmint oil, in the oil of *Bystropogon origanifolius,* in American pennyroyal oil, in verbena oil, and in oil of goldenrod.

Limonene of unknown rotation has been found in the oils of rue and myrrh, in a fagara oil and in oil of *Monarda fistulosa.*

Synthetically, limonene has been prepared repeatedly.

By means of fractional distillation, *d*-limonene can be obtained with a fair degree of purity from oil of orange or oil of caraway; *l*-limonene can be obtained in like manner from the oil of the cones of *Abies alba.* When carefully purified, the

hydrocarbon has an agreeable lemon-like odor. The physical constants are approximately expressed by the following figures:

B. p. 175 to 176°; $d_{15°}$ 0,850; $n_{D20°}$ 1,475.

For *l*-limonene from the leaves of *Abies alba* Wallach found:

B. p. 175 to 176°; $d_{20°}$ 0,846; $n_{D20°}$ 1,47459.[1])

The angle of rotation is high, but varies with the method of preparation. The highest deviation recorded was observed in the laboratory of Schimmel & Co. in connection with a *d*-limonene obtained from caraway oil by fractionation in vacuum, *viz.*, $[\alpha]_D + 123° 40'$. A synthetic limonene prepared by Godlewski and Roshanowitsch[2]) gave $[\alpha]_D + 125° 36'$. For *l*-limonene from pine needle oil, Wallach[3]) records $[\alpha]_D - 105°$ (in alcoholic or chloroformic solution). In connection with *l*-limonene from pine cone oil, the following constants were observed in the laboratory of Schimmel & Co.

B. p. 176,5°; $d_{15°}$ 0,8472; $\alpha_D - 101° 10'$, $[\alpha]_D - 119,41°$; $n_{D20°}$ 1,47303.

Chemically both limonenes are alike, yielding the same derivatives which differ only in the direction in which they deviate polarized light. When *d*- and *l*-limonene are mixed, dipentene results. This also results when the active limonenes are heated to a higher temperature or when they are acted upon with acids. In the cold, acids frequently cause the hydration of limonene to terpineol and terpin hydrate. At elevated temperatures, however, acids dehydrate these same hydration-products with the reformation of hydrocarbons. Concentrated sulphuric acid changes limonene to cymene. When perfectly dry, limonene absorbs one molecule of hydrohalogen with the formation of limonene monochlorhydrate which, when treated with sodium acetate, yields active α-terpineol.[4]) A second molecule of hydrohalogen is added only in the presence of moisture when a derivative of dipentene (see p. 313) is formed.

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[1]) Liebig's Annalen **246** (1888), 222.

[2]) Journ. russ. phys. chem. Ges. **31** (1899), 209. According to Chem. Zentralbl. **1899**, I. 1241.

[3]) Liebig's Annalen **246** (1888), 222; Wallach and Conrady, *Ibidem* **252** (1889), 145.

[4]) Semmler, Berl. Berichte **28** (1895), 2190; Wallach, Liebig's Annalen **350** (1906), 154.

Limonene adds 4 atoms of bromine yielding an optically active limonene tetrabromide that melts at 104 to 105° (see below). Upon addition of nitrosyl chloride, each limonene yields two (α- and β-) nitrosochlorides[1]) which are physical isomers. These are prepared like pinene nitrosochloride and because of their different solubility in chloroform can be separated by means of this solvent. Chemically these nitrosochlorides behave alike. Upon withdrawal of hydrogen chloride with alcoholic potassa, they are converted into carvoxime melting at 72°. When treated with organic bases two series of nitrolamines[2]) result. Of these the α-nitrol piperidine base melts at 94°, the β-compound at 110°; the α-nitrol anilide base at 112°, the β-compound at 153°; the α-nitrol benzylamine base at 93°. The limonene monochlorhydrate mentioned above also yields a nitrosate.

With dilute permanganate solution limonene is oxidized to the saturated tetratomic alcohol limonetrite (m. p. 191,5 to 192°).[3]) The other oxidation products of limonene afford little that is characteristic.

Limonene is most readily identified by means of its tetrabromide, prepared according to Wallach's directions.[4]) The fraction is purified as much as possible and diluted with about four times its volume of glacial acetic acid. Bromine is added drop by drop to the well cooled solution as long as it is taken up with decoloration. The crystals separating after standing for some time are collected and recrystallized from acetic ether. As a rule they are distinguished from those of dipentene tetrabromide by having smooth surfaces, and by being soft and fleible.[5]) The melting point of the pure tetrabromide is about 104,5°, the specific rotation of the chloroform solution is + 73,27 and — 73,45° respectively.

In connection with the preparation of the tetrabromide, it should be noted that reagents absolutely free from water need not and should not be used. These are apt to give rise to the formation of a non-crystallizable tetrabromide. Nevertheless the crystalline product is to be regarded as the normal bromide.[6])

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[1]) Wallach, Liebig's Annalen **252** (1889), 109.
[2]) Wallach, *Ibidem* **270** (1892), 172.
[3]) Wagner, Berl. Berichte **23** (1890), 2315.
[4]) Liebig's Annalen **239** (1887), 3.
[5]) Wallach, Liebig's Annalen **227** (1885), 279.
[6]) Wallach, *Ibidem* **264** (1891), 14.

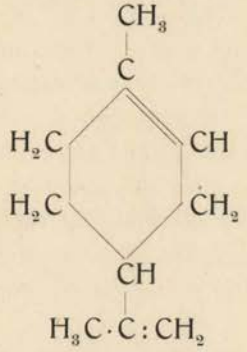
Wallach also advises not to use alcohol or ether as diluent since they give rise to the formation of liquid by-products. Like disturbing factors are encountered when the terpene fractions used are not sufficiently uniform in composition.

Minor modifications in the method of preparation have been recommended by various investigators. Baeyer and Villiger[1]) employ as diluent a mixture of 1 vol. of amylalcohol and 2 vol. ether, cool the mixture and add bromine drop by drop. In the proportion in which the ether evaporates, the tetrabromide is said to crystallize out.

Power and Kleber[2]) add the fraction to be tested for limonene drop by drop to a cooled mixture of glacial acetic acid and bromine until only a slight excess of bromine remains. The solution is then decolorized with an aqueous solution of sulphur dioxide and the bromide precipitated with water. Their object is to prevent the formation of hydrogen bromide and of non-crystalline bromides of isomeric terpenes.

Finally, a combination of both methods has been suggested by Godlewsky.[3]) He suggests that a solution of the terpene in a mixture of equal parts of amylalcohol and ether be added drop by drop to an ethereal solution of bromine which is kept cold by ice water during the course of the reaction.

Dipentene.



The optically inactive form of limonene, the dipentene, has been found frequently in nature, though not as commonly as

[1]) Berl. Berichte **27** (1894), 448.

[2]) Pharm. Rundschau (New York) **12** (1894), 160; Arch. der Pharm. **232** (1894), 646.

[3]) Chem. Ztg. **22** (1898), 827.

limonene. It must also be born in mind that the dipentene identified may have been formed from pinene or limonene during the process of fractionating the oil. Dipentene has been found in the following oils: In the oils from the turpentines of different species of *Pinus,* in pine tar oils, in the needle oil from *Picea excelsa,* in Swedish turpentine oil, in Siberian pine needle oil, in the needle oil from *Callitris glauca,* in the oils of palmarosa, lemongrass, citronella, gingergrass, cardamom, pepper, cubeb, nutmeg, boldo leaves, kuromoji, campher, cinnamon root, massoy-bark, apopin, bergamot, limette leaves, neroli, wartara, buchu, frankincense, myrrh, myrtle, ajowan, coriander, cumin, and fennel, also in the oils of *Satureja Thymbra, Thymus capitatus,* in American pennyroyal oil, in kessoroot oil and in goldenrod oil.

Aside from its formation from equal parts of *d*- and *l*-limonene, it is obtained synthetically by polymerization of the unsaturated aliphatic hydrocarbon isoprene, C_5H_8; also, together with terpinene, upon dehydration of the aliphatic alcohols linalool and geraniol. Furthermore, it results upon isomerization of other hydrocarbons $C_{10}H_{16}$, *e. g.* pinene, limonene, phellandrene; also by inducing the proper changes in related oxygenated compounds, such as cineol, terpineol, and terpinhydrate. Dipentene, together with cineol and limonene, was also obtained by the action of nitrous acid on fenchylamine.

A relatively pure dipentene can be obtained by the dry distillation of caoutchouc. After the removal of the isoprene, fraction 172 to 178° is carefully and repeatedly fractionated over sodium. The presence of any cineol, which has a like boiling point, can be ascertained by a corresponding increase in the specific gravity. A less pure preparation can be obtained from dipentene dihydrochloride by splitting off hydrogen chloride with aniline or sodium acetate in glacial acetic acid;[1]) also by the dehydration of crystalline terpineol by means of potassium acid sulphate.[2])

Physically, dipentene differs from limonene only by its optical inactivity. The boiling point of pure dipentene appears to be the

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[1]) Wallach, Liebig's Annalen **239** (1887), 3; **245** (1888), 196. Comp. also Tilden and Williamson, Journ. chem. Soc. **63** (1893), 294.

[2]) Wallach, Liebig's Annalen **275** (1893), 109.

same as that of limonene. However, when in research for dipentene, it is necessary to take into consideration fractions that boil somewhat higher than the corresponding limonene fractions.[1]) Specific gravity and index of refraction agree fully with those determined for limonene. For dipentene from caoutchouc the following data were ascertained in the laboratory of Schimmel & Co.:

B. p. 175 to 176°; $d_{20°}$ 0,844; $n_{D20°}$ 1,47194.

Dipentene is relatively stable. When heated it is not converted into isomeric hydrocarbons $C_{10}H_{16}$, but polymerizes. However, when heated with alcoholic sulphuric acid, it is changed to terpinene. Its derivatives are inactive and can be obtained from dipentene as well as by the union of equivalent amounts of the corresponding derivatives of limonene. The dipentene derivatives reveal minor differences from the corresponding limonene derivatives, notably in their melting points. Toward hydrohalogen, bromine and nitrosylchloride dipentene behaves like the active limonenes. The solid addition products that result upon the addition of two molecules of hydrohalogen, exist in two modifications, *viz.*, the *cis*- and *trans*-forms.[2]) Of these the one with the lower melting point and the greatest solubility is designated the *cis*-form. The higher melting *trans*-form is the more stable and always results when the reaction mixture is allowed to become warm. In the cold, both forms usually result simultaneously. In as much as the *trans*-form results in most cases, the following data pertain to this modification. The dichlor-, dibrom- and diiod-hydrates of dipentene result when hydrohalogen is passed to saturation into an ethereal or glacial acetic acid solution of either limonene or dipentene. Upon evaporation of the solvent, or upon the addition of water thereto the compounds separate in the form of an oil which soon crystallizes. Since terpinene yields analogous compounds, and since mixtures frequently cause very appreciable melting point depressions, these compounds may prevent each other from crystallizing. However, a separation of the dihydrohalogen addition products of dipentene

[1]) Wallach, Liebig's Annalen **286** (1895), 138; Berl. Berichte **40** (1907), 600.
[2]) Baeyer, Berl. Berichte **26** (1893), 2861.

and terpinene may be obtained by taking into consideration their difference in stability toward dilute alkali.[1])

Dipentene dichlorhydrate melts at 50° and can be crystallized from its alcoholic solution by the careful addition of water; the dibromhydrate forms rhombic, shiny plates that melt at 64°; the diiodhydrate crystallizes in various forms and melts between 77 to 81°. From all of these, dipentene can be regenerated upon the withdrawal of hydrohalogen. When shaken with dilute alkali, they yield α-terpineol and terpinhydrate.

As in the case of limonene, so the nitrosochloride of dipentene exists in two physically isomeric forms (α and β), which are more soluble than their active components. When treated with alcoholic potassa, they lose hydrogen chloride and yield inactive carvoxime m. p. 93°. When treated with organic bases, the nitrosochlorides yield two nitrolamines in each case; of these the nitrolamine bases melt at 154 and 152° respectively, the nitrol aniline bases at 125 and 149°, and the particularly characteristic α-nitrolbenzylamine base at 110°. A dipentene nitrosate, also a nitrosate of the dipentene monochlorhydrate are known.[2])

For the identification of dipentene the preparation of its tetrabromide[3]) is commonly resorted to. It is prepared, like the limonene tetrabromide, from dipentene, or when concentrated solutions of equal parts of *d*- and *l*-limonene tetrabromide are mixed.[4]) The crystals differ from those of limonene tetrabromide by their appearance, the dipentene tetrabromide revealing peculiar striations in the vertical zone. They are also very fragile. Dipentene tetrabromide also differs from the limonene tetrabromides by its lesser solubility and its higher melting point, *viz.*, 124 to 125°. For its identification the above-mentioned nitrosochloride and the corresponding nitrolbenzylamine base can be used, also the carvoxime obtained from the nitrosochloride and finally the dichlorhydrate described above.

In the case of mixtures of limonene and dipentene, which may not occur infrequently, it should be remembered that, as a rule, the dipentene compounds separate first.

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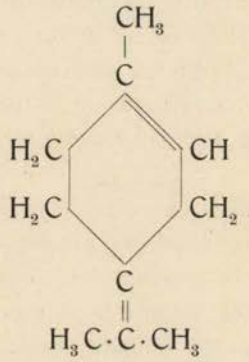
[1]) Wallach, Liebig's Annalen **350** (1906), 160.
[2]) Wallach, Liebig's Annalen **245** (1888), 258.
[3]) Wallach, Liebig's Annalen **227** (1885), 278.
[4]) Wallach, *ibidem* **246** (1888), 226.

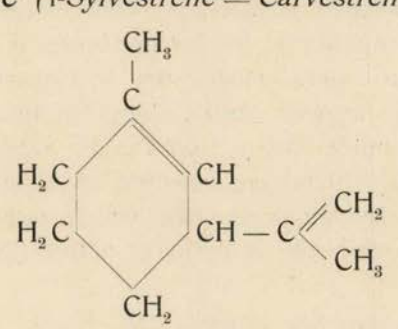
Terpinolene.



Thus far this terpene has been obtained by synthetical means only, although Clover[1]) claims to have found it in a Manila elemi oil, observing at the same time a gradual inversion into dipentene. Recently its presence in coriander oil has likewise been rendered probable.[2])

The boiling point of terpinolene is in the neighborhood of about 185 to 187°. As characteristic derivatives, the tetrabromide melting at 116° and the dibromide melting at 69 to 70° should be mentioned. The addition of hydrohalogen yields the corresponding dipentene derivatives. Upon oxidation with potassium permanganate, terpinolene erythritol, $C_{10}H_{16}(OH)_4 \cdot H_2O$, melting at 148 to 150°, results.

Sylvestrene (i-*Sylvestrene* = *Carvestrene*).



Sylvestrene is one of the less common natural terpenes. Thus far it has been found, always in the dextrogyrate modi-

[1]) Philippine Journ. of Sc. **2** (1907), A. 17.

[2]) Report of Schimmel & Co. October **1909**, 48.

fication, in the oils of the *Pinaceæ:* in the pine tar oils of Sweden and Finland, in the turpentine oils of Finland, Russia, and Sweden, in the needle oil of *Pinus sylvestris* of Germany, Sweden, and England, in the needle oil of *Pinus montana,* and in cypress oil. The statement by More[1]) that *l*-sylvestrene occurs in the oil from the resin of *Dacryodes hexandra,* still needs verification.

It can be obtained in a relatively pure state by preparing the dichlorhydrate from fractions rich in sylvestrene and by subsequent regeneration by boiling the hydrochloride either with aniline[2]) or with sodium acetate and glacial acetic acid.[3]) The hydrocarbon thus obtained closely resembles limonene in its physical and chemical properties. Like the limonene, it has a pleasant odor resembling that of limonene. Specific gravity and boiling point agree well with the corresponding constants of limonene.

Atterberg, the discoverer of sylvestrene, found the following constants:

B. p. 173 to 175°; $d_{16°}$ 0,8612; $[\alpha]_{D16°}$ + 19,5°.[4])

Wallach records the following:

B. p. 176 to 177°; $d_{16°}$ 0,851; n_D 1,47799.[5])

B. p. 175 to 176°; $d_{20°}$ 0,848; $[\alpha]_D$ + 66,32° (in chloroformic solution); n_D 1,47573.[6])

When heated to 250°, sylvestrene is polymerized, but not isomerized, neither is the latter change brought about by alcoholic sulphuric acid. Hence this hydrocarbon is one of the most stable of the terpene group. Like limonene, so sylvestrene contains two double bonds that can be satisfied either entirely or in part by hydrohalogen, bromine, or nitrosyl chloride. Peculiar, however, is the dichlorhydrate which, unlike the inactive dipentene dihydrochloride, is optically active (dextrogyrate) and from

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[1]) Journ. chem. Soc. **75** (1899), 718.
[2]) Wallach, Liebig's Annalen **230** (1885), 243.
[3]) Wallach, Liebig's Annalen **239** (1887), 25; **245** (1888), 197.
[4]) Berl. Berichte **10** (1877), 1206.
[5]) Liebig's Annalen **245** (1888), 198.
[6]) Liebig's Annalen **252** (1889), 149.

which active sylvestrene can be regenerated upon splitting off hydrohalogen. The tetrabromide, prepared like that of the limonene, melts at 135 to 136°; however, it is difficult to obtain it in solid state when, as is mostly the case, other terpenes are present in the fraction. With amyl nitrite and hydrochloric acid, pure sylvestrene yields a nitrosochloride melting at 106 to 107°, and this with benzylamine an nitrolamine base that melts at 71 to 72°.

For the separation of sylvestrene from mixtures, as well as for its identification, the chlorhydrate is best suited. This compound, which can be separated in crystalline form at considerably reduced temperatures only, is prepared in the following manner. The fraction in question is diluted with an equal volume of ether and saturated with hydrogen chloride gas. After standing for about two days, the ether is distilled off and the residue induced to crystallize by considerably reducing its temperature. With the aid of porous plates the crystalline magma is freed from oily admixture and recrystallized from an equal weight of alcohol. The hydrochloride thus partly purified, is freed from the corresponding dipentene compound by fractional crystallisation from ether, in which the latter is more difficultly soluble. The purified dihydrochloride melts at 72°.[1]) It should be remembered that, in the presence of dipentene or of such terpenes that yield dipentene dihydrochloride when acted upon by hydrogen chloride, mixtures of chlorhydrates result, the melting point of which is lowered with the increasing content of dipentene dihydrochloride. The dibromohydrate of sylvestrene melts at 72°, the diiodohydrate at 66 to 67°. By treating these dihalogen hydrates with dilute potassium hydroxide, sylveterpin, $C_{10}H_{18}(OH)_2$, m. p. 135 to 136°, also sylveterpineol, $C_{10}H_{17}OH$, b. p. 210 to 214°,[2]) result. These compounds correspond with those obtained in like manner from dipentene dihydrochloride.

If to a solution of a few drops of sylvestrene in acetic acid anhydride a drop of concentrated sulphuric acid be added, a beautiful blue color is produced. This reaction succeeds only then when the fraction to be tested is rich in sylvestrene.

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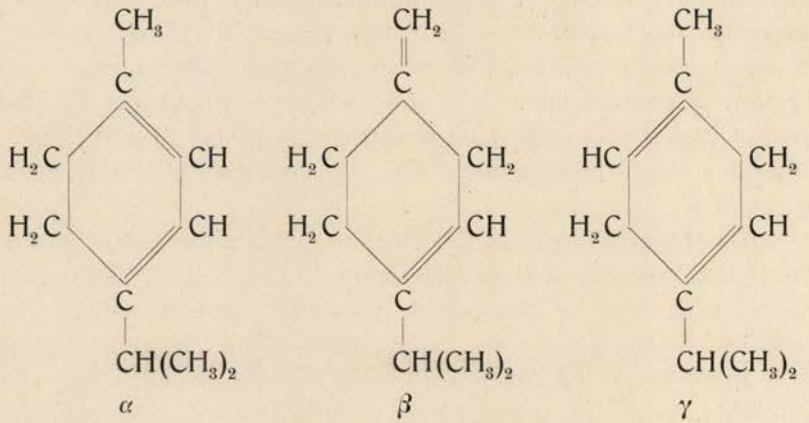
[1]) Wallach, Liebig's Annalen **230** (1885), 241; **239** (1887), 25.
[2]) Wallach, Liebig's Annalen **357** (1907), 72.

Terpinene.



Until very recently our knowledge of the occurrence of terpinene was very limited. Besides the dihalogen addition product, also yielded by other terpenes, the addition product of nitrous acid was the only characteristic derivative. The designation terpinene heretofore applied to a hydrocarbon which yielded, with nitrous acid, a nitrosite melting at 155°. The artificially prepared hydrocarbon is a mixture of two isomers, designated α- and γ-terpinene by Wallach, the composition of which varies with the method of preparation.

The hydrocarbon was first found by Weber[1]) in the oil of the long Ceylon cardamom. With the aid of the nitrosite m. p. 155°, its presence was likewise established in the oil of Levant wormseed, in Manila elemi oil, in the oil of dill herb, and in marjoran oil. The presence of both constituents, found by Wallach in what is designated artificial terpinene, in volatile oils was first revealed by the investigations in the laboratory of Schimmel & Co.[2]) Thus α-terpinene was found in coriander oil, γ-terpinene in ajowan oil, lemon oil, and coriander oil.

Artificially, terpinene is obtained by the action of acids upon such hydrocarbons as pinene, dipentene, and phellandrene; or upon such oxygenated compounds as linalool, geraniol, terpi-

[1]) Liebig's Annalen **238** (1887), 107.

[2]) Gildemeister and Müller, *Wallach-Festschrift,* Göttingen 1909, p. 443.

neol, terpinenol, terpinene terpin, terpinhydrate, dihydrocarveol, and cineol; further by splitting off hydrohalogen from the terpinene halogenides; and by special decomposition of carvylamine, carvenone, and methyl-dichlormethyl-ketodihydrobenzene. Especially adapted to the preparation of products rich in α-terpinene are the syntheses of Semmler[1]) and Auwers.[2]) Pure products, however, are not obtained; hence the constants are but approximations. For a terpinene obtained by the action of methylmagnesium iodide on sabinaketone and purified by repeated distillation over sodium, Wallach[3]) records the following constants:

B. p. 174 to 179°; $d_{22°}$ 0,842; n_D 1,4719;

and for a preparation regenerated from its hydrochloride by heating with aniline:[4])

B. p. 179 to 181°; $d_{20°}$ 0,846; n_D 1,4789.

In connection with a fraction from coriander oil consisting of α- and γ-terpinene, Schimmel & Co. observed the following constants:

B. p. 177 to 178°; $d_{15°}$ 0,8485; $\alpha_D + 0°32'$; $n_{D20°}$ 1,47650.

Terpinene bears a great resemblence to dipentene. When acted upon by the hydrohalogens, terpinene halogenhydrides result which might easily be confounded with those of dipentene. Both *cis*- and *trans*-modifications exist. However, the latter only are concerned so far as identification is meant, for the former are liquid.

Terpinene dihydrochloride melts at 51 to 52°, the dihydrobromide at 58 to 59°, the dihydroiodide at 76°. From the corresponding isomeric dipentene compounds they can be distinguished by the decided depression of the melting point of their respective mixtures. When the hydrochloride is boiled with bases, a mixture of several hydrocarbons results. When shaken with dilute potassium hydroxide solution, terpinene terpin (m. p. 137

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[1]) Berl. Berichte **41** (1908), 4474; **42** (1909), 522.
[2]) *Ibidem* **42** (1909), 2424.
[3]) Liebig's Annalen **362** (1908), 301.
[4]) Liebig's Annalen **350** (1906), 149.

to 138°), terpinenol-4, and γ-terpinenol result, also *cis*- and *trans*-terpin.

The addition of bromine to terpinene yields liquid compounds only. Neither could a nitrosochloride be obtained. Upon addition of nitrous acid, terpinene nitrosite melting at 155° results, which yields nitrolamines when acted upon with piperidine and nitrolamines. The nitrolpiperidine base melts at 153 to 154°, the nitrolbenzylamine base at 137°. Careful reduction of the terpinene nitrosite and its nitrolamines with zinc dust and glacial acetic acid yields carvenone. The use of more energetic reducing agents, such as sodium and alcohol, is apt to yield tetrahydrocarvone and tetrahydrocarvylamine. According to Wallach the nitrosite is a derivative of α-terpinene, which, upon oxidation with permanganate yields *i*-α, α′-dihydroxy-α-methyl-α′-*iso*propyladipic acid melting at 188 to 189°, and the lactone of which melts at 72 to 73°. Further oxidation of this acid yields dimethylacetonylacetone, the semicarbazide of which melts at 201 to 202°, and the dioxime at 137°.

When oxidized in like manner, γ-terpinene yields the erythritol $C_{10}H_{16}(OH)_4$ m. p. 237°. When acted upon by dilute sulphuric acid this is converted into carvacrol and thymol.

For the identification of terpinene in volatile oils, fraction 175 to 185° is examined. Some clue may be had from the formation of terpinene dihydrochloride, m. p. 52°, by passing hydrogen chloride gas into a glacial acetic acid solution of the hydrocarbon. Thujene and sabinene, also terpinenol and terpinene terpin, which also yield the same chloride, boil at either higher or lower temperatures. Particularly suited for identification is the terpinene nitrosite, which is prepared in the following manner: To 3 ccm. of the hydrocarbon fraction to be examined, in a narrow test tube, 1½ ccm. glacial acetic acid and 4½ ccm. of water are added. To the well cooled mixture a concentrated aqueous solution of 1,5 g. of sodium nitrite is added, a small portion at a time, causing the hydrocarbon to assume a green color. When the nitrous acid has been absorbed completely, a reddish-yellow color results. In order to avoid supersaturation, the reaction mixture is inoculated with a crystal of pure nitrosite. The crystals which separate in the course of time are washed

with water and petroleum ether and crystallized from alcohol (m. p. 155°).

The presence of one or the other modifications of terpinene can be established positively only by oxidation with permanganate. Wallach[1]) proceeds in the following manner: A mixture of 7 g. of the hydrocarbon, 33 g. of potassium permanganate, 14 g. potassium hydroxide, 400 g. ice and 400 ccm. water, contained in a copper flask, is shaken with a shaking machine for an hour. The excess of hydrocarbon is distilled off, the oxide of manganese separated by filtration, and the filtrate saturated with carbon dioxide while it is being evaporated to dryness. The residue is extracted with alcohol, the alcoholic filtrate evaporated to dryness, this residue dissolved with a small amount of hot water and the solution set aside for crystallization. The magma of cristals is separated, washed with a little cold water, dried on porous plate and recrystallized from 15 to 20 times its weight of 25 p. c. alcohol. The melting point of this oxidation product, the erythritol mentioned above, lies at 235 to 236°, or if heated rapidly at 237 to 238°. It is sparingly soluble in ether, ligroin, ethylacetate, or chloroform; not readily in cold alcohol or water, but more readily in these solvents when hot. The mother liquid from the erythritol is shaken out with ethylacetate and then supersaturated with sulphuric acid in the cold. This acid liquid is shaken out once with ether and then exhausted by shaking with ethyl acetate. The ethyl acetate takes up an acid which crystallizes out upon proper concentration of the solvent. Recrystallized from about six times its own weight of water, α,α'-dihydroxy-α-methyl-α'-*iso*propyladipic acid melts at 189° with the elimination of water.

Even in the cold, terpinene is readily attacked and destroyed by the chromic acid mixture prepared according to Beckmann's directions.[2]) This property can be made use of when terpinene is to be removed from mixtures containing pinene, camphene, limonene, terpinolene, cineol, and pinol since these substances are stable toward this oxidizing agent in the cold.

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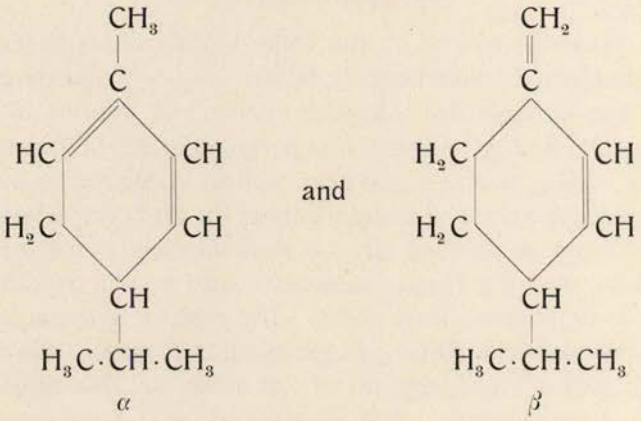
[1]) Liebig's Annalen **362** (1908), 297; comp. also Gildemeister and Müller, *Wallach-Festschrift*, Göttingen 1909, p. 443.

[2]) Berl. Berichte **27** (1894), 815.

Phellandrene.



Phellandrene belongs to those hydrocarbons $C_{10}H_{16}$ that are widely distributed. In nature it occurs in several modifications. According to Wallach[1]), phellandrene is defined as "a hydrocarbon $C_{10}H_{16}$, which when brought into contact with N_2O_3 in an indifferent, non aqueous solvent (ligroin) at a temperature below 0° — hence under conditions that exclude inversion as much as possible — yields *at once* a well characterized nitrite".

Of the natural phellandrenes the α- and the β-varieties should be kept quite distinct. Of the α-variety, the *d*-α-phellandrene has been found in gingergrass oil, schinus oil, bitter fennel oil, the Spanish dill herb oil, both Ceylon and Seychelle cinnamon oil, and elemi oil; the *l*-α-phellandrene in Australian eucalyptus oil and star anise oil.

β-Phellandrene has been found in water fennel oil *(d-)*, in lemon oil, schinus oil, star anise oil, in the oil of *Eucalyptus amygdalina* and probably in coriander oil and cumin oil.

In most other instances when the presence of phellandrene has been reported, it does not become apparent which phellandrene it is that has been identified. In most instances, however, it appears to be α-phellandrene which appears to be accompanied by traces of β-phellandrene. Hence the conditions appear to be similar to those observed in connection with α- and β-pinene. In addition to the occurences mentioned above, phellandrene has been found in the following volatile oils:

[1]) Liebig's Annalen **336** (1904), 10.

d-Phellandrene in Siberian pine-needle oil, in the oil from the wood of *Cæsalpinia Sappan* and in angelica root oil.

l-Phellandrene in the needle oil from *Picea excelsa*, the needle oil from *Pinus montana*, pimenta oil, bayberry oil from the Bermuda islands and in the oil from the seeds of *Monodora grandiflora*.

Without reference to the optical rotation, the presence of phellandrene has been recorded in the oils of *Juniperus phœnicea*, *Andropogon laniger*, curcuma, ginger, pepper, magnolia, *Monodora Myristica*, *Cinnamomum pedunculatum* (bark), cinnamon root, camphor, sassafras leaves, geranium, frankincense, *Eucalyptus acmenoides, angophoroides, capitellata, coriacea, crebra, Dawsoni, Delegatiensis, dives, fastigiata, Fletcheri, fraxinoides, hæmastoma, loxophleba, Luehmanniana, macrorrhyncha, melanophloia, meliodora, microtheca, nigra, obliqua, oreades, ovalifolia, o.* var. *lanceolata, pulverulenta, radiata, Risdoni, robusta, rostrata, siderophloia, sideroxylon* var. *pallens, Sieberiana, stellulata, viminalis, virgata, vitrea*, in German and English dill oil, in the oil of ajowan herb, and in the oils of peppermint, wormwood, goldenrod, and dog fennel.

The phellandrenes belong to the least stable of the terpenes. Hence, when it is desired to isolate phellandrene from a volatile oil or to identify it, the oil should not be distilled repeatedly under ordinary pressure, but should be fractionated under diminished pressure.

Synthetically, α-phellandrene was obtained by Harries and Johnson,[1]) also by Wallach.[2]) However, the products obtained were not of unquestioned purity. The only crystalline derivatives of the phellandrenes, the nitrosites, do not lend themselves to the regeneration of the hydrocarbon. They are decomposed with alkali,[3]) but no hydrocarbon $C_{10}H_{16}$ results. In the study of phellandrene, it is therefore necessary to be content with fractions rich in phellandrene. For this purpose the fraction 170 to 178° is usually taken. The properties of phellandrene, as recorded, pertain to such fractions.

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[1]) Berl. Berichte **38** (1905), 1832.

[2]) Liebig's Annalen **359** (1908), 283.

[3]) Wallach, Liebig's Annalen **287** (1895), 374; **336** (1904), 30.

Of the constants observed, the following may here be mentioned:

l-α-Phellandrene from the oil of *Eucalyptus amygdalina.*[1])

B. p. 173 to 175° (754 mm.), 50 to 52° (5 mm.); $d_{15°}$ 0,848; α_D — 84° 10′; $n_{D20°}$ 1,47694.

d-α-Phellandrene from gingergrass oil:[2]) b. p. 44 to 45° (4 mm.), 175 to 176° (754 mm.); $d_{15°}$ 0,8565; α_D + 40° 40′.

d-α-Phellandrene from elemi oil:[3]) b. p. 61° (11 mm.); $d_{19°}$ 0,844; $n_{D19°}$ 1,4732.

β-Phellandrene from water-fennel oil: b. p. 57° (11 mm.); $d_{20°}$ 0,8520; $n_{D20°}$ 1,4788[4]) and $d_{18°}$ 0,848; $[\alpha]_D$ + 14° 45′; $n_{D18°}$ 1,4759.[5])

The optical rotation is very variable. It is reduced by the action of sun light.[6])

As already pointed out, phellandrene is relatively unstable. When heated to its boiling point it is polymerized. By the action of acids it is even more readily changed to inactive isomers. Thus by the action of hydrohalogen it is converted into dipentene, by alcoholic sulphuric acid into terpinene. When acted upon by halogen or hydrohalogen, liquid compounds mostly result. When oxidized with potassium permanganate, α-phellandrene yields the oily α-hydroxy-β-*iso*propylglutaric acid, which, upon further oxidation with lead peroxide and sulphuric acid, is converted into *iso*propylsuccinic acid. The oxidation products obtained from β-phellandrene are α-hydroxy-β-*iso*propyladipic acid and α-*iso*propylglutaric acid respectively.[7]) Upon oxidation of β-phellandrene with a one percent. solution of potassium permanganate, Wallach[8]) obtained, in addition to Δ^2-*iso*propylcyclohexanone, α-*iso*propylglutaric acid, *iso*butyric acid, and an oily glycol. When acted upon with dilute sulphuric acid, this glycol yielded tetra-

[1]) Observations made in the laboratory of Schimmel & Co.
[2]) Report of Schimmel & Co. April **1904**, 56.
[3]) Wallach, Liebig's Annalen **336** (1904), 12.
[4]) *Ibidem* 43.
[5]) *Ibidem* **340** (1905), 2.
[6]) Bacon, Philippine Journ. of Sc. **4** (1909), A. 101.
[7]) Semmler, Berl. Berichte **36** (1903), 1749.
[8]) Liebig's Annalen **340** (1905), 12.

hydrocuminic aldehyde and some dihydrocuminic alcohol. When β-phellandrene is oxidized with oxygen from the air, Δ^2*iso*propylcyclohexanone results.[1])

The only solid derivative of phellandrene is its nitrite resulting upon the addition of nitrous acid, hence this is used for its identification. Both phellandrenes yield two nitrites, which, as first pointed out by Schreiner,[2]) are distinguished by their melting points. In order to ascertain whether an oil contains phellandrene, a solution of 5 g. of sodium nitrite in 8 g. water is placed beneath a layer of a solution of 5 cc. of the oil in 10 cc. of petroleum ether. 5 cc. of glacial acetic acid are then added while shaking the mixture for the purpose of generating the necessary nitrous acid. The voluminous crystalline magma is removed with the aid of a force filter, washed first with water and then with methyl alcohol, and finally purified by repeated solution in chloroform and subsequent precipitation with methyl alcohol.[3]) The crude phellandrene consists of two modifications and the more soluble nitrite is lost in the above process. If it is desired to ascertain which phellandrene is present in a given oil, it is necessary, therefore, to purify with the aid of acetone.[4]) When precipitated fractionally with water, the nitrite of α-phellandrene can be separated into its two modifications melting respectively at 112 to 113° (or 113 to 114°) and 105°; β-phellandrene into its two modifications melting at 102° and 97 to 98° respectively. All of these have different angles of rotation, partly dextrogyrate, partly lævogyrate.

Unlike terpinene nitrosites, the phellandrene nitrites cannot be converted into nitrolamines. When treated with sodium alcoholate, α-phellandrene nitrite yields nitro-α-phellandrene. Upon reduction with zinc and glacial acetic acid, this yields carvotanacetone and dihydrocarvylamine. The more energetic reduction with sodium in alcoholic solution yields tetrahydrocarvone and tetrahydrocarvylamine.[5]) β-Phellandrene, when treated with sodium alcoholate, yields nitro-β-phellandrene. When reduced, this is con-

[1]) Liebig's Annalen **343** (1905), 29.
[2]) Pharmaceutical Archives **4** (1901), 90.
[3]) Wallach and Gildemeister, Liebig's Annalen **246** (1888), 282.
[4]) Wallach, Liebig's Annalen **336** (1904), 13.
[5]) *Ibidem* 30, 44.

verted into dihydrocuminic aldehyde (m. p. of the semicarbazone 200 to 202°), tetrahydrocuminylamine and cuminylamine.

For the oxidation of β-phellandrene the oxidation with a one percent. solution with potassium permanganate may also be resorted to, yielding a syrupy glycol (b. p. 150° at 10 mm.).[1]) When heated with dilute sulphuric acid, this glycol is converted into dihydrocuminic alcohol and tetrahydrocuminic aldehyde (b. p. 220 to 230°; $d_{20°}$ 0,93; $n_{D20°}$ 1,4903; m. p. of the semicarbazone 204 to 205°. As byproducts *iso*propyl-1-*cyclo*hexene-2-one-4, and α-*iso*propylglutaric acid, and *iso*butyric acid result.

SESQUITERPENES.

In addition to the terpenes $C_{10}H_{16}$, the higher boiling fractions of many volatile oils, *viz.*, those between 250 and 280°, contain hydrocarbons corresponding to the formula $C_{15}H_{24}$ which have been named sesquiterpenes. Of these a considerable number have been isolated, but few have been investigated to any extent.

A few oils consist almost exclusively of sesquiterpenes. In most instances, however, they play but a secondary role. Their occurrence is so general that they must be regarded as belonging to the most common constituents of the volatile oils.

Artificially also sesquiterpenes have been prepared from the alcohols $C_{15}H_{26}O$ which accompany the former in many volatile oils. These alcohols seem to stand in the same relation to the sesquiterpenes as does terpineol, $C_{10}H_{18}O$ to the hydrocarbon $C_{10}H_{16}$. Nevertheless the addition of the elements of a molecule of water to a hydrocarbon $C_{15}H_{24}$ by means of the glacial acetic acid - sulphuric acid mixture has been carried out successfully in but one instance. Whether the hydrocarbons $C_{15}H_{24}$ obtained by the dehydration of the "sesquiterpene alcohols" are identical with the natural sesquiterpenes, has not yet been determined.

In general, the boiling points of the sesquiterpenes lie between 250 and 280°; their density 0,86 and 0,93, as a rule above 0,90. In most instances they are slightly colored. They are more viscid than the terpenes and have a faint odor. In part

[1]) Liebig's Annalen **340** (1905), 12.

they resinify as readily as do the terpenes and they are difficultly soluble in alcohol. As unsaturated hydrocarbons they add halogens, hydrohalogens, NOCl, N_2O_3 and N_2O_4. Some of them yield crystalline addition products which can be used for their identification. Their oxidation products, however, remain practically unexamined.

As to their constitution, nothing definite is known. Hence we are dependent on their physical properties for their classification. A better knowledge of the sesquiterpenes is rendered more difficult from the fact that the only method suitable for their isolation, namely that of fractional distillation, precludes the preparation of pure products. Based on their molecular refraction and relative density, they are classified as aliphatic, monocyclic, dicyclic and tricyclic sesquiterpenes.[1]) As with the terpenes, these groups are characterized by regularity with reference to boiling point and more particularly to density.

	Mol.-Refr. (calc.)	Density (15°)
aliphatic sesquiterpenes	69,5	about 0,86,
monocyclic „	67,76	„ 0,875 to 0,89,
bicyclic „	66,15	„ 0,90 „ 0,92,
tricyclic „	64,45	„ 0,93 „ 0,94.

In as much as only a few sesquiterpenes have been obtained in a pure state, it is frequently difficult to ascertain to which of the above groups they belong. The conditions of isomerism are even more complicated than among the terpenes. Nevertheless it is not at all probable that the 60 to 70 known sesquiterpenes are all different. No doubt, many of these will be found identical as soon as it becomes possible to obtain a clear view over this field as over that of the terpenes, since the terpenes have become one of the best known groups of organic compounds.

In the compilation which follows only those representatives of the sesquiterpenes will be discussed in detail the characterization of which has been made possible.

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[1]) Theoretically tetracyclic sesquiterpenes are also possible. In as much as none of these have yet been isolated, this mere reference to the group may suffice.

Aliphatic Sesquiterpenes.

To this group there possibly belongs the "light sesquiterpene" which was isolated by Schimmel & Co.[1]) from Ceylon citronella oil and which possesses the following properties:

B. p. under atmospheric pressure 270 to 280° with much decomposition, at 137° under 15 mm. pressure; $d_{15°}$ 0,8643; $\alpha_{D15°} + 1°28'$; $n_{D15°}$ 1,51849.

This sesquiterpene, of which no derivatives are known, is very unstable. When exposed to the air, it resinifies within a few days to a syrupy liquid.

Monocyclic Sesquiterpenes.

Bisabolene.

Bisabolene was first found by Tucholka[2]) in Bisabol myrrh oil. The same name was given later to sesquiterpenes which had originally been known by other designations, but which had been found to be identical with it.

In addition to its occurrence in Bisabol myrrh oil, it has been found in Siberian pine-needle oil, in the oil of *Piper Volkensii,* in camphor oil and in the oils of limette, lemon, bergamot and opopanax.

For the hydrocarbon fractionated from lemon oil, Gildemeister and Müller[3]) ascertained the following constants:

B. p. 110 to 112° (4 mm.); $d_{15°}$ 0,8813; $\alpha_D - 41°31'$; $n_{D20°}$ 1,49015. For the inactive sesquiterpene regenerated from the trichlorhydrate by means of sodium acetate and glacial acetic acid, they ascertained the following constants:

B. p. 261 to 262° (751 mm.); $\alpha_D \pm 0°$; $d_{15°}$ 0,8759; $n_{D20°}$ 1,4901.

With hydrogen chloride, bisabolene yields a trichlorhydrate, $C_{15}H_{24}3HCl$, which melts at 79 to 80° and which, according to Tucholka is optically active ($[\alpha]_D$ (+ or — ?) 35°17′ in chloroform

[1]) Report of Schimmel & Co. October **1899**, 23.

[2]) Arch. der Pharm. **235** (1897), 292.

[3]) *Wallach-Festschrift,* Göttingen 1909, p. 448; Report of Schimmel & Co. October **1909**, 64.

solution), but which, according to Gildemeister and Müller, is inactive. Neither a solid nitrosochloride, nor a nitrosite, nor a nitrosate could be obtained from bisabolene. It adds 6 atoms of bromine. Whether the hexabromide, obtained by Schmidt and Weilinger[1]) from the oil of *Piper Volkensii,* and melting at 154° is a derivative of bisabolene remains to be proven.

For the characterization of bisabolene, the trichlorhydrate, obtained by passing gaseous hydrogen chloride into an ethereal solution of the sesquiterpene, is especially suited. Upon evaporation of the ether, it separates in handsome crystals, which can be further purified by recrystallization from alcohol.

Zingiberene.

This sesquiterpene, first found by Tresh[2]) in ginger oil, was later examined by v. Soden and Rojahn,[3]) also by Schreiner and Kremers.[4]) The last mentioned investigators ascertained the following constants:

B. p. abt. 270° (with decomposition), 160 to 161° (32 mm.); $d_{20°}$ 0,8731; $[\alpha]_D$ — 73,38°; n_D 1,49399.

The nitrosochloride melts at 96 to 97°, the nitrosite at 97 to 98°, the nitrosate at 86 to 88° and the dihydrochloride at 168 to 169°. For the characterization of this hydrocarbon its dihydrochloride can be prepared by passing hydrogen chloride into its solution in glacial acetic acid. After standing for two days, it crystallizes out in fine needles. The nitrosate also can be used for its identification since, according to Schreiner and Kremers, the yield obtained almost equals the theoretical yield.

Bicyclic Sesquiterpenes.

Cadinene.

The best known representative of this subgroup as of the group of the sesquiterpenes in general is the cadinene, which is widely distributed and which occurs in both optical modifications.

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[1]) Berl. Berichte **39** (1906), 652.
[2]) Pharmaceutical Journ. III. **12** (1882), 243.
[3]) Pharm. Ztg. **45** (1900), 414.
[4]) Pharmaceutical Archives **4** (1901), 63; Chem. Zentralbl. **1901**, II. 1226.

d-Cadinene has thus far been found in the oil of the Atlas cedar, and probably also in West Indian sandalwood oil.

l-Cadinene has been found in cade oil, from which it derives its name, and in the oils of cypress, cubebs, paracoto bark, angostura bark and cedrella wood.

In most of the references on the occurrence of cadinene, the direction of the rotation is not mentioned, thus in German and Swedish oils from *Pinus sylvestris,* the oils from *Pinus montana,* of *Picea excelsa,* juniper berries, savin, cedar leaves, cedar wood, lemongrass, pepper, betel, ylang-ylang, camphor, *Amorpha fruticosa,* frankincense, African copaiba balsam (see below!), asafetida, galbanum, American peppermint, patchouli, wormwood and goldenrod.

Cadinene can be obtained in a relatively pure condition since it yields a well crystallized dihydrochloride from which it can be regenerated, like the terpenes, by heating with aniline or with sodium acetate in glacial acetic acid solution.[1]) For the hydrocarbon thus regenerated, Wallach found the following constants:

B. p. 272° (uncorr.)[2]), 274 to 275°; $d_{20°}$ 0,918; $[\alpha]_D$ —98,56°; n_D 1,50647.[3])

Schimmel & Co. found:

B. p. 271 to 273°; $d_{15°}$ 0, 9215; $[\alpha]_D$ — 105° 30′.

The optical rotation varies considerably. In a number of instances where the natural sesquiterpene has been pronounced an active modification of cadinene, it has not been definitely established whether the hydrocarbon is really identical with cadinene, or whether it has been converted into a cadinene derivative by the action of hydrogen chloride. This is true *e. g.* of the sesquiterpenes in West Indian sandalwood oil and African copaiba balsam. It is at least noteworthy that a derivative of *l*-cadinene should have been obtained from these dextrogyrate oils, whereas the dextrogyrate hydrocarbon from Atlas cedar oil yielded derivatives of *d*-cadinene.

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[1]) Wallach, Liebig's Annalen **238** (1887), 84.
[2]) Liebig's Annalen **271** (1892), 303.
[3]) *Ibidem* **252** (1889), 150; **271** (1892), 297.

When exposed to air, cadinene resinifies very readily with the formation of a polymerization product. When heated for a long time with dilute sulphuric acid, cadinene is altered, whereas the action of hydrohalogen appears to produce no essential change since the optical activity remains unaltered. Prolonged heating to 200° likewise changes cadinene. An isomeric hydrocarbon is thus produced with the following properties: b. p. 145 to 148° (20 mm); $d_{4^\circ}^{20^\circ}$ 0,9061; $[\alpha]_D$ — 2,80°; n_{D20° 1,5041.[1])

With nitrosyl chloride and nitrogen tetroxide, cadinene yields crystalline addition products. The nitrosochloride, of which only a small yield is obtained, melts at 93 to 94°; the nitrosate, which affords a better yield, melts at 105 to 110°.

Especially characteristic are the crystalline addition products obtained with two molecules of hydrohalogen, of which the dichlor- and the dibromhydrate are used for identification.

For the purpose of preparing the dichlorhydrate, fractions 260 to 280° are diluted with twice their volume of ether, well cooled and saturated with hydrogen chloride. After prolonged standing, the ether is in part distilled off, in part allowed to evaporate spontaneously. The crystals of dichlorhydrate thus obtained are dried on porous plate, washed with alcohol to remove oily impurities and recrystallized from acetic ether in which they can readily be dissolved with the aid of heat. The pure compound melts at 117 to 118°. It is optically active, $[\alpha]_D$ — 37° 27′ in a 5 p. c. chloroform solution.

The dichlorhydrate can also be prepared with the aid of glacial acetic acid that has been saturated with hydrogen chloride. This modification is especially adapted to the preparation of the dibromhydrate (m. p. 124 to 125°) and the diiodhydrate (m. p. 105 to 106°). The glacial acetic acid solution of the hydrohalogen is added to the glacial acetic acid solution of the hydrocarbon.

Caryophyllene.

A second well characterized hydrocarbon, which belongs to the bicyclic group of sesquiterpenes, is the caryophyllene. However, it is not as common as cadinene. Up to the present time it has

[1]) Lepeschkin, Journ. russ. phys. chem. Ges. **40** (1908), 698. According to Chem. Zentralbl. **1908**, II. 1354.

been found in appreciable amounts in the oil of cloves and the oil of clove stems, also in copaiba balsam oil. Furthermore, it has been found in the oils of pepper, betel, Ceylon cinnamon, Seychelles cinnamon (?), cinnamon root, canella alba, pimenta and lavender.

Up to the present time, caryophyllene has not been prepared in a pure state. The physical constants recorded refer to fractions of clove oil or of oil of clove stems that were not perfectly pure. Caryophyllene obtained by distillation only from oil of cloves mostly contains some aceteugenol[1]) from which it can be freed by saponification with alcoholic potassa. The sesquiterpene from oil of clove stems does not contain this impurity.

For the caryophyllene from oil of cloves

Wallach[2]) found: B. p. 258 to 260°; $d_{15°}$ 0,9085; n_D 1,50094.
Erdmann[3]) found: B. p. 119 to 120° (9 mm.), 123 to 124° (13 mm.), 258 to 259° (752 mm.); $d_{24°}$ 0,9038.
Kremers[4]) found: $d_{20°}$ 0,9032; $[\alpha]_{D20°}$ — 8,74°; $n_{D20°}$ 1,50019.

For the caryophyllene from Ceylon cinnamon oil, Walbaum and Hüthig[5]) found: B. p. 260 to 261°; $d_{15°}$ 0,9047; α_D — 7° 20′.

More recent investigations by Deussen and his colaborers[6]) would seem to indicate that the fractions of clove stem oil designated caryophyllene consist of at least two isomers, an optically inactive α-caryophyllene, and an active β-caryophyllene, both of which have been characterized by derivatives.

According to Schreiner and Kremers[7]) a dichlorhydrate, crystallizing in needles and melting at 69 to 70°, results from the action of hydrogen chloride upon the caryophyllene-containing fractions of oil of cloves. From the crude caryophyllene of clove stem oil, Schimmel & Co. obtained an active chloride of like melting point. Other investigators obtained from caryophyllene-containing fractions of various oils either liquid chlorides, or chlorides of a different melting point.

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[1]) E. Erdmann, Journ. f. prakt. Chem. II. **56** (1897), 146.
[2]) Liebig's Annalen **271** (1892), 298.
[3]) Journ. f. prakt. Chem. II. **56** (1897), 146.
[4]) Pharmaceutical Archives **1** (1898), 211.
[5]) Journ. f. prakt. Chem. II. **66** (1902), 54.
[6]) Liebig's Annalen **356** (1907), 1; **359** (1908), 245; **369** (1909), 41.
[7]) Pharmaceutical Archives **2** (1899), 296; Proceed. Americ. Pharm. Ass. **47** (1899), 158.

By the action of nitrosyl chloride on caryophyllene from clove stem oil, there results a nitrosochloride melting at about 160°. Upon fractional crystallization, however, it can be resolved into two compounds: an inactive α-caryophyllene nitrosochloride (m. p. 177°) and an active β-caryophyllene nitrosochloride (m. p. 159°). Corresponding with these nitrosochlorides there are an α-nitrolbenzylamine base melting at 126 to 128° and a β-nitrolamine base melting at 172 to 173°. Both of these can also be obtained from the mixture of nitrosochlorides. By splitting off hydrogen chloride the nitrosochlorides yields the corresponding nitrosocaryophyllenes, of which the α-form melts at 116°, the β-form at 120 to 121°.

With nitrous acid anhydride, caryophyllene forms an optically active nitrosite, which crystallizes in blue needles, melts at 115°, and is readily changed to other compounds by the action of solvents. There is also known an active caryophyllene nitrosate, which can be obtained by the action of amylnitrite and nitric acid on caryophyllene or by the oxidation of the blue nitrosite with chromic acid. It melts at 130,5°. Nitrosates of caryophyllene with different melting points are presumably derived from the α-form.

Upon oxidation with permanganate there results, according to Deussen[1]) and Haarmann[2]), in addition to a glycol $C_{14}H_{22}O_4$ (m. p. 120°), a ketoacid $C_{10}H_{16}O_3$ (semicarbazone melts at 186°), a monobasic acid $C_8H_8O_4$ (m. p. 179,5 to 180,5°), and a neutral substance $C_{10}H_{18}O_3$ (m. p. 145 to 146°). The liquid acids which result in this oxidation yield dimethyl succinic acid upon further oxidation.

When acted upon with glacial acetic acid-sulphuric acid mixture, caryophyllene yields a hydrate $C_{15}H_{26}O$, caryophyllene alcohol, melting at 94 to 96°. This alcohol, the phenyl urethane of which melts at 136 to 137°, is optically inactive.

It is noteworthy that upon the dehydration of caryophyllene alcohol caryophyllene is not regenerated, but that an isomeric tricyclic hydrocarbon $C_{15}H_{24}$, the clovene results. This differs materially in its properties from caryophyllene, but has not yet been found in volatile oils.

[1]) Liebig's Annalen **359** (1908), 258; **369** (1909), 52; Berl. Berichte **42** (1909), 376, 680.

[2]) Berl. Berichte **42** (1909), 1062.

When attempting to identify caryophyllene, it should be remembered that the nitrosochloride and the nitrosate are derived from a different hydrocarbon than the blue nitrosite.[1]) Hence the precaution should be taken to prepare the nitrosite as well as the nitrosochloride or nitrosate.

For the preparation of the nitrosochloride, 5 ccm. of alcoholic hydrogen chloride are added to a well cooled mixture of 5 ccm. caryophyllene, 5 ccm. acetic ether, 5 ccm. alcohol and 5 ccm. ethyl nitrite. Under the influence of sunlight the nitrosochloride soon separates.

For the preparation of the nitrosite, 5 ccm. of glacial acetic acid are cautiously added to a mixture of 5 ccm. caryophyllene, 12 ccm. petroleum ether and 5 ccm. of a saturated solution of sodium nitrite. In the cold the nitrosite crystallizes out.

For the preparation of the nitrosate, a solution of 5 ccm. of concentrated nitric acid in 5 ccm. glacial acetic acid are cautiously added to a well cooled mixture of 5 ccm. caryophyllene, 5 ccm. glacial acetic acid and 5 ccm. ethyl nitrite. Finally alcohol is added and after 2 hours the nitrosate separates out.

Quite convenient is the preparation of caryophyllene alcohol.[2]) 25 g. of the hydrocarbon are dissolved in a mixture of 1000 g. glacial acetic acid, 25 g. concentrated sulphuric acid and 40 g. water. After prolonged heating of the mixture, the more readily volatile products are removed by distillation with steam, after which the pure alcohol is obtained by continued distillation.

Selinene.

While investigating the highest boiling fractions of celery seed oil, Ciamician and Silber[3]) found a sesquiterpene which, however, they did not further characterize. When this sesquiterpene was later on examined in the laboratory of Schimmel & Co. it was ascertained that it was not identical with any of the known sesquiterpenes and was named selinene.

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[1]) Deussen, Liebig's Annalen **356** (1907), 1; **359** (1908), 245.
[2]) Wallach, Liebig's Annalen **271** (1892), 288.
[3]) Berl. Berichte **30** (1897), 492, 501.

Selinene constitutes about 20% of celery seed oil and can be obtained from fraction 265 to 273°. After repeated fractionation over sodium, it possessed the following properties:

B. p. 120 to 121° (6 mm.); $d_{17.5°}$ 0,9197; α_D + 35° 11'; $n_{D21°}$ 1,49863.

Regenerated from its dichlorhydrate, it possessed the following properties:

B. p. 268 to 272°; $d_{15°}$ 0,9232; $d_{20°}$ 0,9196; α_D + 49° 30'; $n_{D20°}$ 1,50483; mol. refr. 65,82, corresponding to $C_{15}H_{24}$ / 66,15.

The dichlorhydrate referred to is obtained by passing gaseous hydrogen chloride into an etheral solution of the sesquiterpene. It crystallizes in fine needles, which when pure melt at 72 to 74°; $[\alpha]_D$ + 18° (in 4,07% chloroform solution). Selinene dichlorhydrate differs from the caryophyllene dichlorhydrate though both have simular melting points. Upon splitting off hydrogen chloride, selinene is regenerated, whereas caryophyllene dichlorhydrate, when submitted to like treatment, yields a new hydrocarbon.

With nitrosylchloride or oxides of nitrogen, no solid derivatives could be obtained.

Judging from its molecular refraction, selinene belongs to the bicyclic group of sesquiterpenes.

Humulene.

This sesquiterpene, which was first discovered by Piccard, and which up to the present time has been found only in oil of hops and oil of poplar buds, closely resembles caryophyllene. Thus far the attempts to regenerate humulene from one of its derivatives have not been successful. Hence the constants had to be ascertained in connection with more or less pure fractions. Chapman,[1]) who has devoted much study to the characterization of this sesquiterpene, records the following:

B. p. 263 to 266° (760 mm.); $d_{15°}$ 0,9001; α_D — 0,5°; n_D 1,5021.

The hydrocarbon obtained from poplar bud oil was slightly dextrogyrate. It is probable, however, that humulene itself is optically inactive and that the slight rotation was due to impurities.

[1]) Journ. chem. Soc. 67 (1895), 54.

Hydrogen chloride, when added, yields a liquid dihydrochloride, bromine an oily tetrabromide. Upon hydration an alcohol results. Nitrosyl chloride is added with the formation of a nitrosochloride melting at 164 to 165°, respectively at 164 to 170°. The nitrolbenzylamine base melts at 136°, respectively at 132 to 133°; the nitrolpiperidine base at 153°. Nitrous acid is added with the formation of a nitrosite melting at 120 to 121°, and of an *iso*nitrosite melting at 166 to 168°. Both of these, when treated with sodium ethylate, yield nitroso- or *iso*nitrosohumulene, b. p. 185 to 195° (13 mm). The nitrosate, m. p. 162 to 163°, is also known. Humulene can be identified by means of its nitrosochloride in the usual manner.

Santalene.

In addition to the two santalols, East Indian sandalwood oil contains two sesquiterpenes, α- and β-santalene, so named by Guerbet.[1])

α-Santalene shows the following properties:

B. p. 252 to 252,5° (uncorr.), 253 to 254° (corr.); $d_{0°}$ 0,9134; α_D — 13,98° (Guerbet).

B. p. 118 to 120° (9 mm.); $d_{20°}$ 0,8984; α_D — 15°; n_D 1,491 Semmler.[2])

β-Santalene shows the following properties:

B. p. 261 to 262° (uncorr.), 263 to 264° (corr.); $d_{0°}$ 0,9139; α_D — 28,55° (Guerbet).

B. p. 125 to 127° (9 mm.); $d_{20°}$ 0,892; α_D — 35°; n_D 1,4932 (Semmler).

According to Semmler, α-santalene is to be regarded as a tricyclic sesquiterpene with one double bond, β-santalene as dicyclic with two double bonds.

α-Santalene combines with hydrochloric acid to a liquid hydrochloride. With nitrosylchloride a nitrosochloride, m. p. 122°, results, the nitrolpiperidine base of which melts at 108 to 109°. When oxidized with ozone, Semmler obtained the bicyclic eksantalal (b. p. 112 to 116° (9 mm.); $d_{20°}$ 1,00; α_D + abt. 4°; n_D 1,4872) which likewise results upon oxidation of α-santalol.

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[1]) Compt. rend. **130** (1900), 417, 1324; Bull. Soc. chim. III. **23** (1900), 217 and 540.

[2]) Berl. Berichte **40** (1907), 3321.

β-Santalene adds two molecules of hydrogenchloride with the formation of a liquid dihydrochloride.[1]) The nitrosochloride exists in two isomeric forms, which melt at 152° and 106° respectively, and to which two nitrolpiperidine bases (m. p. 101° and 104 to 105° respectively) correspond. When oxidized with ozone a dicyclic aldehyde results.

Hence the two santalenes appear to stand in genetic relationship to the two santalols. The two santalenes can be identified by means of their nitrosochlorides and by their oxidation products with ozone.

*Iso*santalenes. The hydrocarbons resulting upon dehydration of the santalols are, however, different from the santalenes. From the crude santalol Chapoteaut[2]) obtained two hydrocarbons, one $C_{15}H_{24}$, b. p. 260° and another $C_{15}H_{22}$, b. p. 245°. The hydrocarbons obtained from the two santalols, Guerbet[3]) named *iso*santalenes and recorded the following properties:

α-*Iso*santalene: b. p. 255 to 256°; $\alpha_D + 0{,}2°$.

β-*Iso*santalene: b. p. 259 to 260°; $\alpha_D + 6{,}1°$.

It is doubtful whether these two hydrocarbons are sesquiterpenes.

Of the lesser known sesquiterpenes the following may here be mentioned:

Atractylene.

This sesquiterpene, which has not yet been found in volatile oils, was obtained by Gadamer and Amenomiya[4]) by the action of dehydrating agents on atractylol, a sesquiterpene alcohol.

B. p. 125 to 126° (10 mm.); $d_{15°}$ 0,9154; $n_{D20°}$ 1,50893.

The liquid dihydrochloride, prepared from atractylol, when heated with aniline yields a hydrocarbon which differs from atractylene.

Caparrapene.

Caparrapene is a sesquiterpene which has been obtained by Tapia[5]) by the action of dehydrating agents on caparrapiol, a

[1]) von Soden and Müller, Pharm. Ztg. **44** (1899), 259.

[2]) Bull. Soc. chim. II. **37** (1882), 303.

[3]) *Ibidem* III. **23** (1900), 543.

[4]) Arch. der Pharm. **241** (1903), 33.

[5]) Bull. Soc. chim. III. **19** (1898), 638.

sesquiterpene alcohol occurring in the volatile oil from caparrapi-balsam. The hydrocarbon is a colorless liquid which is readily colored yellow when exposed to light. The following constants are recorded:

B. p. 240 to 250°; $d_{16°}$ 0,9019; $[\alpha]_D$ — 2,21°; n 1,4953.

When hydrogen chloride is passed into the glacial acetic acid solution of the sesquiterpene, an active dihydrochloride results melting at 83°.

Guajene.

Upon dehydrating guajol, a new sesquiterpene alcohol isolated by Schimmel & Co.[1]) from guajac wood oil, with zinc chloride, Wallach and Tuttle[2]) obtained a new sesquiterpene the properties of which did not correspond with those of any of the known ones.

B. p. 124 to 128° (13 mm.); $d_{20°}$ 0,910; n_D 1,50144.

For the sesquiterpene prepared from guajol according to Tchugaeff's xanthogenate method, A. Gandurin[3]) records the following properties:

B. p. 124° (11 mm.); $d^{0°}_{4°}$ 0,9133; $d^{25°}_{4°}$ 0,8954; $[\alpha]_{D25°}$ — 66,11°; $n_{D25°}$ 1,49468; mol. refr. 66,46.

Guajene obtained by heating guajol with potassium acid sulphate possesses, according to Gadamer and Amenomiya[4]) the following properties:

B. p. 123 to 124° (9 mm.); $d^{20°}_{4°}$ 0,9085; $[\alpha]_D$ — 40,35°; $n_{D20°}$ 1,50049; mol. refr. 66,2.

Hence, guajene appears to belong to the bicyclic sesquiterpenes. Crystalline derivatives are not known.

Sesquiterpene from Cade Oil.

According to Tröger and Feldmann,[5]) oil of cade contains, in addition to cadinene, a second, inactive sesquiterpene boiling between 250 to 260°. When treating oil of cade with hydrogen

[1]) Report of Schimmel & Co. April **1892**, 56; April **1893**, 42.
[2]) Liebig's Annalen **279** (1894), 396.
[3]) Berl. Berichte **41** (1908), 4363.
[4]) Arch. der Pharm. **241** (1903), 43.
[5]) Arch. der Pharm. **236** (1898), 692.

chloride, N. Lepeschkin[1]) obtained in addition to cadinenedihydrochloride, a liquid chloride. For the sesquiterpene regenerated from this liquid chloride, he records the following properties:

B. p. 262 to 266° (760 mm.); 135 to 140° (20 mm.); $d_{4°}^{20°}$ 0,9204; $n_{D20°}$ 1,5159.

Crystalline derivatives could not be obtained. Upon heating with hydrogen iodide to 200°, Lepeschkin obtained a hydrocarbon (b. p. 250 to 258°; $d_{4°}^{20°}$ 0,8946; $n_{D20°}$ 1,4972) which he supposes may be identical with humulene. However, according to Schindelmeiser,[2]) it is a mixture of tetrahydrocadinene, cadinene and a new, optically inactive sesquiterpene. Schindelmeiser is further of the opinion that the sesquiterpene of Lepeschkin still contains cadinene. For the pure sesquiterpene he records the following constants:

B. p. 263 to 265°; $d_{20°}$ 0,908; $\alpha_D \pm 0°$; n_D 1,5006.

None of these investigators, however, succeeded in characterizing this new sesquiterpene.

Sesquiterpene from Minjak-Lagam-Balsam Oil.

According to Haussner[3]) the oil of Lagam balsam, which is closely related to gurjun balsam, consists almost exclusively of sesquiterpenes:

B. p. 249 to 251°; $d_{15°}$ 0,923; α_D —9,9°.

The sesquiterpene is a light colored oil which resinifies quickly when exposed to the air. With hydrogen chloride it yields a chloride $C_{15}H_{24} \cdot 3HCl$, which crystallizes in long needles and which melts at 114°.

The formation of a trichlorhydride from a sesquiterpene with a density of 0,923 is somewhat strange. Aside from this, the properties of the sesquiterpene as well as those of its chloride would seem to indicate cadinene.

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[1]) Journ. russ. phys. chem. Ges. **40** (1908), 126. According to Chem. Zentralbl. **1908**, I. 2040.

[2]) Journ. russ. phys. chem. Ges. **40** (1908), 181. According to Chem. Zentralbl. **1908**, II. 598.

[3]) Arch. der Pharm. **221** (1883), 245.

Sesquiterpene from the Oil of the Bark of Ocotea usambarensis.

According to Schmidt and Weilinger,[1]) the sesquiterpene from this oil has the following properties:

B. p. 136 to 142° (12 mm.); $d_{20°}$ 0,915; $\alpha_D + 7° 46'$; n_D 1,505.

When acted upon with hydrogen chloride, a dihydrochloride (m. p. 116 to 117°) results which is not identical with cadinene dihydrochloride.

Tricyclic Sesquiterpenes.

Cedrene.

The term cedrene was originally applied to a sesquiterpene obtained by the dehydration of cedrol.[2]) Upon finding a similar sesquiterpene in oil of cedar, this likewise was designated cedrene. In as much as the identity of these two hydrocarbons has not been proven conclusively, it is best to treat them separately.

The constants of the natural cedrene are recorded as follows:[3])

B. p. 124 to 126° (12 mm.); $d_{15°}$ 0,9354; $\alpha_D - 55°$; n_D 1,50233.

Natural cedrene has been examined by a number of investigators, more recently particularly by Semmler and Hoffmann.[4]) Upon oxidation with chromic acid in glacial acetic acid solution, cedrone, $C_{15}H_{24}O$, results, which boils at 148 to 151° (11 mm.) and upon reduction is converted into *iso*cedrol (b. p. 148 to 151° at 9 mm.). Upon oxidation with permanganate in acetone solution, cedrene yields a glycol, $C_{15}H_{26}O_2$, m. p. 160°; a diketone or a ketoaldehyde $C_{15}H_{24}O_2$, the semicarbazone of which melts at 234°; and a cedrene keto acid, $C_{15}H_{24}O_3$, the semicarbazone of which melts at 245°, the oxime between 180 to 190°.

When oxidized with ozone, cedrene yielded essentially the same products. For its identification, the oxidation with permanganate is resorted to.

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[1]) Berl. Berichte **39** (1906), 752.

[2]) Walter, Liebig's Annalen **39** (1841), 247.

[3]) The constants of the artificial cedrene are recorded in the table of the artificially prepared sesquiterpenes on p. 346.

[4]) Berl. Berichte **40** (1907), 3521.

Clovene.

Upon dehydration with zinc chloride or phosphorus pentoxide of the caryophyllene alcohol, obtained by hydration of the the hydrocarbon, Wallach[1]) secured the clovene, a sesquiterpene thus far not found in volatile oils.

B. p. 261 to 263°; $d_{18°}$ 0,930; $n_{D18°}$ 1,50066; mol. refr. 64,77.

Upon hydration, clovene is not again converted into caryophyllene hydrate. For its identification a comparison of the physical constants has to be resorted to. By the action of para formaldehyde on clovene, Genvresse[2]) obtained an alcohol $C_{15}H_{23}CH_2OH$, m. p. 170° (12 mm.); $d_{0°}$ 1,001; α_D — 7° 40′ (in a 6,03 p. c. chloroform solution); n_D 1,508. This ought to be suited to the identification of the hydrocarbon.

Heerabolene.

A sesquiterpene, probably tricyclic, has been found in Heerabol myrrh oil by O. v. Friedrichs[3]) and designated heerabolene by him.

B. p. 130 to 136° (16 mm.); $d_{20°}$ 0,943; α_D 14° 12′; $n_{D20°}$ 1,5125; mol. refr. 64,98.

Neither a characteristic bromide, nor a solid nitrosochloride or nitrosate could be obtained. With hydrogen chloride, however, a dihydrochloride melting at 98 to 99° resulted. As is the case with the sesquiterpene of galangal oil, the hydrogen chloride appears to have caused the cleavage of a cycle.

Heveene.

This sesquiterpene is obtained, together with isoprene and dipentene, upon the destructive distillation of caoutchouc or gutta percha.[4]) Thus, 5 ko. of para caoutchouc[5]) yield about

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[1]) Liebig's Annalen **271** (1892), 292.

[2]) Compt. rend. **138** (1904), 1228.

[3]) Arch. der Pharm. **245** (1907), 208.

[4]) Williams, Jahresber. d. Chem. **1860**, 495; comp. also Beilstein, *Handbuch d. org. Chem.* 3rd ed., vol. 3, p. 538.

[5]) G. Bouchardat, Bull. Soc. chim. II. **24** (1875), 108. Comp. also A. Bouchardat, Liebig's Annalen **27** (1838), 30; Himly, *ibidem* **27** (1838), 40.

250 g. isoprene, 2000 g. dipentene and 600 g. heveene.[1]) To a smaller extent polyterpenes also are formed. Bouchardat records 255 to 265° as boiling temperature. With hydrogen chloride a readily decomposible monhydrochloride $C_{15}H_{24}HCl$ is stated to be formed.

In the tables which follow, those sesquiterpenes are mentioned which have been found in volatile oils and of which some of the physical constants are known and which do not appear to be identical with known, well characterized sesquiterpenes.

Sesquiterpene from	B. p.	d	α_D	n_D	Remarks
Ageratum oil[2])	260°	—	—	—	—
Angelica root oil[3])	240 to 270°	—	—	—	—
Angostura bark oil[4]) (Galipene)	255 to 260°	0,912 (19°)	±0°	1,50513	With hydrogen chloride, readily decomposible liquid products are formed.
Oil from the leaves of *Amorpha fruticosa*[5])	250 to 260°	0,916 (15°)	—	1,50652	The presence of cadinene has also been proven.
Oil from the rhizome of *Aralia nudicaulis* (Araliene)[6])	260 to 270°	0,9086 (20°)	−7 to −8° (benzene solution)	1,49936	—
Boldo leaf oil[7])	265 to 275°	—	−7°	—	—
Calamus root oil[8])	255 to 258°	0,942 (0°) 0,9323 (20°)	—	—	—

[1]) The name heveene was suggested by Bouchardat from the name of the plant *Hevea guianensis* which yields the caoutchouc.

[2]) van Romburgh, Report of Schimmel & Co. April **1898**, 53.

[3]) Ciamician and Silber, Berl. Berichte **29** (1896), 1811.

[4]) Beckurts and Trœger, Arch. der Pharm. **236** (1898), 397.

[5]) Pavesi, *Estratto dall' Annuario della Soc. Chimica di Milano* **11** (1904), 3; *Estratto dai "Rendiconti" del R. Ist. Lomb. di sc. e lett.* (II.) **37** (1904), 487; Report of Schimmel & Co. October **1904**, 9.

[6]) Alpers, Americ. Journ. Pharm. **71** (1899), 370.

[7]) Tardy, Journ. de Pharm. et Chim. VI. **19** (1904), 132.

[8]) Kurbatow, Liebig's Annalen **173** (1874), 4; comp. Schimmel's Bericht April **1889**, 7 and Apotheker Ztg. **21** (1906), 987.

Sesquiterpene from	B. p.	d	α_D	n_D	Remarks
Oil of *Carlina acaulis*[1] (Carlinene)	139 to 141° (20 mm.)	0,8733 (22,8°)	—	1,492	—
Cascarilla oil[2] I	178 to 181° (100 mm.) 255 to 257° (760 mm.)	0,911 (20°)	$[\alpha]_D + 23,49°$	—	Neither of these sesquiterpenes yielded a solid hydrochloride, bromide or nitrosite.
Cascarilla oil II	185 to 190° (100 mm.) 260 to 265° (760 mm.)	0,924 (20°)	$[\alpha]_D + 7,36°$	—	
Ceylon Citronella oil[3] (heavy sesquiterpene)	170 to 172° (16 mm.) 272 to 275° (760 mm.)	0,912 (15°)	+ 5° 50′	—	Crystalline derivatives were not obtained.
Conima resin oil[4] (Conimene)	264°	—	—	—	—
Cryptomeria oil[5] (Suginene)	—	0,918	$[\alpha]_D - 10° 34′$	—	Cadinene also is found in the oil. Suginene produces liquid addition products with 2 mol. of hydrohalogen.
Cubeb oil[6]	262 to 263°	—	lævogyrate	—	The sesquiterpene fraction consists chiefly of cadinene.
Oil from *Eucalyptus hæmastoma*, also from several other eucalyptus oils[7] (Aromadendrene)	260 to 265°	0,9249 (19°)	—	—	—
Fire weed oil[8]	240 to 310°	—	—	—	Adds 1 mol. of hydrogen chloride.

[1]) Semmler, Chem. Ztg. **13** (1889), 1158.

[2]) Thoms, Apotheker Ztg. **14** (1899), 562; Fendler, Arch. der Pharm. **238** (1900), 688.

[3]) Schimmel's Bericht October **1899**, 19.

[4]) Stenhouse and Groves, Liebig's Annalen **180** (1876), 253; Journ. chem. Soc. **29** (1876), 175.

[5]) Kimura, Berichte d. deutsch. pharm. Ges. **19** (1909), 369.

[6]) Wallach, Liebig's Annalen **238** (1887), 18.

[7]) H. G. Smith, Journ. and Proceed. Royal Soc. of N. S. W. **35** (1901); Report of Schimmel & Co. April **1902**, 41.

[8]) Beilstein and Wiegand, Berl. Berichte **15** (1882), 2854.

Sesquiterpene from	B. p.	d	α_D	n_D	Remarks
Galangal oil[1])	230 to 240°	0,932 (20°)	— 27° 12′	1,4922	With hydrogen chloride it yields a dihydrochloride melting at 51°.
Gurjun balsam oil[2]) (Gurjunene)	115 to 118° (7 mm.)	0,9207 to 0,9247 (15°)	— 35° up to — 130°	1,50252 (20°)	Crystalline derivatives were not obtained.
Hemp oil[3]) (Cannabene)	256 to 258°	0,9289 (0°)	$[\alpha]_D$ — 10,81°	—	With hydrogen chloride a solid hydrochloride results.
Hemp resin oil[4])	258 to 260°	0,898 (18°)	$[\alpha]_D$ — 8,6°	—	—
Kesso root oil[5])	260 to 280°	—	—	—	A solid hydrochloride could not be obtained.
Laurel berry oil[6])	abt. 250°	0,925 (15°)	— 7,227°	—	—
Lavender oil[7])	130° (15mm.)	—	—	—	—
Oil from *Leptospermum Liversidgei*[8])	—	0,9024 (15°)	—	1,5052 (16°)	—
Lignaloe oil[9]), Mexican	130 to 140° (10 mm.)	—	—	—	Adds four atoms of bromine.
Oil from *Nardostachys Jatamansi*[10])	250 to 254°	0,932 (15°)	—	—	—

[1]) Schindelmeiser, Chem. Ztg. **26** (1902), 308.

[2]) Unpublished observation made in the laboratory of Schimmel & Co.

[3]) Valenta, Gazz. chim. ital. **10** (1880), 479 and **11** (1881), 191; Berl. Berichte **13** (1880), 2431 and **14** (1881), 1717.

[4]) Wood, Spivey and Easterfield, Journ. chem. Soc. **69** (1896), 539.

[5]) Bertram and Gildemeister, Arch. der Pharm. **228** (1890), 486.

[6]) Blas, Liebig's Annalen **134** (1865), 1.

[7]) Semmler and Tiemann, Berl. Berichte **25** (1892), 1187.

[8]) Baker and Smith, Journ. and Proceed. Royal Soc. of N. S. W. **1906**; Report of Schimmel & Co. October **1906**, 46.

[9]) Barbier and Bouveault, Compt. rend. **121** (1895), 168.

[10]) Y. Asahina, Journ. pharm. Soc. of Japan **1907**, 355; Report of Schimmel & Co. October **1907**, 65.

Sesquiterpene from	B. p.	d	α_D	n_D	Remarks
Patchouli oil[1])					
I. Sesquiterpene	264 to 265° (760 mm.) 59 to 96° (3 to 4 mm.)	0,9335 (15°)	−58° 45′	—	—
II. Sesquiterpene	273 to 274°	0,930 (15°)	+0° 45′	—	—
Oil from *Pittosporum undulatum*[2])	263 to 274°	0,910 (15°)	±0°	1,5030 (20°)	—
Sage oil[3])	264 to 270°	0,9072 (24°)	+3° 14′	—	—
Sandarach resin oil[4])	260 to 280°	0,9386 (15°)	—	1,5215	No crystalline derivatives could be obtained with hydrogen chloride, nitrosyl chloride and nitrogen oxide.
Valerian oil[5])	160 to 165° (50 mm.)	—	−9,2°	—	—
Vetiver oil[6]) (Vetivene)	262 to 263° (740 mm.) 135° (12 mm.)	0,932 (20°)	+18° 19′	—	Adds 4 atoms of bromine.
Winters bark oil[7]) (Winterene)	260 to 270° (265°)	0,9344 (13°)	+11,2°	—	The hydrochloride is liquid.
Oil of European Wormseed[8])	255°	0,9170	—	—	—

[1]) von Soden and Rojahn, Berl. Berichte **37** (1904), 3353.

[2]) Power and Tutin, Journ. chem. Soc. **89** (1906), 1083.

[3]) Sugiura and Muir, Pharmaceutical Journ. III. 8 (1877), 191, 994; Journ. chem. Soc. **1877**, II. 548; Journ. chem. Soc. **37** (1880), 678.

[4]) Henry, Journ. chem. Soc. **79** (1901), 1149.

[5]) Oliviéro, Compt. rend. **117** (1893), 1096; Bull. Soc. chim. III. **11** (1894), 150; **13** (1895), 917.

[6]) Genvresse and Langlois, Compt. rend. **135** (1902), 1059.

[7]) Arata and Canzonari, *Anales de la Sociedad Cientifica Argentina.* According to Arch. der Pharm. **227** (1889), 813.

[8]) Report of Schimmel & Co. October **1908**, 69.

Of the artificially prepared sesquiterpenes that have not been identified with any of the well characterized ones, the following may be mentioned:

Sesquiterpene	B. p.	d	α_D	n_D	Remarks
Caryophyllene dichlorhydrate of the m. p. 69 to 70° [1]	—	0,9191 (20°)	— 35,39°	1,49801	—
Cedrol [2] (Cedar camphor resp. cypress camphor)	263,5 to 264°	0,9367 (15°)	— 85° 57′	1,49798 (20°)	A small yield of nitrosochloride, m. p. 100 to 102°, was obtained.
Cubeb camphor [3]	—	—	—	—	This sesquiterpene is said to possess constants similar to those of the hydrocarbon found with cadinene in oil of cubeb.
Sesquiterpene alcohol from *Eucalyptus Globulus* [4]					
I. Sesquiterpene	102 to 103° (6 mm.) 247 to 248° (748 mm.)	0,8956 (15°)	— 55° 48′	1,49287 (20°)	—
II. Sesquiterpene	265,5 to 266° (750 mm.)	0,9236 (15°)	+ 58° 40′	1,50602 (20°)	—
Gonystylol [5]	137 to 139° (17 mm.)	0,9183 (17°)	+ 40°	—	Mol. refr. found 66,7.
Ledum camphor [6] (Ledol)	264° (752 mm.)	0,9349 (0°) 0,9237 (19°)	—	—	—
Maali alcohol [7]	270,8 to 271° (754 mm.)	0,9190 (15°)	$[\alpha]_D$ +131,99°	1,52252 (20°)	Mol. refr. found 67,98.
Patchouli alcohol [8]	255 to 256°	0,9334 (15°)	— 36° 52′	—	—

[1]) Schreiner and Kremers, The Sesquiterpenes, Milwaukee 1904, p. 108.

[2]) Report of Schimmel & Co. October **1904**, 24 and April **1910**, 46.

[3]) E. Schmidt, Berl. Berichte **10** (1877), 188.

[4]) Report of Schimmel & Co. April **1904**, 52.

[5]) Eyken, Recueil des trav. chim. des P.-B. **25** (1906), 44. According to Chem. Zentralbl. **1906**, I. 842.

[6]) Rizza, Journ. russ. phys. chem. Ges. **1887**, 319; Berl. Berichte **20** (1887), Ref. 562.

[7]) Report of Schimmel & Co. November **1908**, 139.

[8]) Report of Schimmel & Co. April **1904**, 69.

Sesquiterpenes that have not yet been further characterized have been found in the volatile oil of *Blumea balsamifera,* in the oils of basilicum, cajeput, *Abies alba,* fennel, hemlock needles, laurel leaves, wild thyme, and milfoil.

ALCOHOLS.

ALIPHATIC ALCOHOLS.

Of the monatomic alcohols of the saturated or methane series but few representatives have thus far been found in volatile oils. In the free state they are found but rarely and then only the lower homologues; more commonly, however, combined with fatty acids. The occurrence of both free alcohol and free acid may in most instances be attributed to the saponification of esters during the process of distillation. If the material to be distilled contains carbohydrates, it may occur that the presence of free alcohols is due to fermentation previous to the distillation. Thus, *e. g.* ethyl alcohol has been observed in the distillate of rose petals that had been bulked for a short time only.

The methods of preparation of these alcohols are those commonly in vogue. In factory practice, volatile oils containing esters, particularly of the higher members, are used as first materials. Very serviceable is also the method of Bouveault and Blanc,[1]) according to which primary alcohols are obtained upon reduction of the esters of the respective acids by means of sodium and alcohol.

With the increase in the number of carbon atoms, the properties of the aliphatic alcohols undergo material change. Hence, so far as seemed necessary, attention is directed thereto.

The individual alcohols can be identified by means of their constants, also by their oxidation products. As specially charac-

[1]) G. I. P. 164294. Comp. also Compt. rend. **136** (1903), 1676; **137** (1903), 60.

teristic derivatives, the phenylurethanes should be mentioned. These are obtained by mixing equimolecular parts of phenyl*iso*-cyanate and the alcohol in question. Upon standing of the mixture, the urethane separates in crystalline form.

Methyl alcohol, CH_3OH, occurs frequently among the products of distillation of plant material with water vapors. On account of its ready solubility in water it is frequently found in the aqueous distillate only, together with furfurol and diacetyl. It is assumed that these three substances result as decomposition products of the cellulose of the crude material during the process of distillation. Up to the present time, methyl alcohol has been found in the aqueous distillate of the oils of cypress, savin, vetiver, and orris, of the oils from the leaves of *Indigofera galegoides,* the leaves from the Guatamala indigo plant, coca leaves, sappan leaves, also in the aqueous distillates from the West-Indian sandalwood oil, tea oil, oil of cloves, oil of *Eucalyptus amygdalina,* bay oil, pastinaca oil, garden chervil oil, the oils of *Heracleum Sphondylium,* and *H. giganteum,* also of ageratum oil. In addition it has been found as myristic ester in orris oil, as benzoic ester in the oils of tuberose (?) and ylang-ylang, as cinnamic ester in the oil from the root of *Alpinia malaccensis* and watara oil, as salicylic ester in the oil from tuberose pomade, birch bark oil, cananga oil, oil of rue, oil of cassie flowers, tea oil and wintergreen oil, as ester of methyl anthranilic acid in mandarin oil and as anthranilic ester in the oils of neroli and jasmin.

Methyl alcohol can be identified by its boiling point 64°, its density 0,810 at 15° and chemically by its conversion into methyl iodide and neutral oxalate which melts at 54°.

Ethyl alcohol, C_2H_5OH. As normal constituent of volatile oils, ethyl alcohol has been observed only in a few instances: thus in the first fraction of the oils of *Indigofera* and of the fruit of *Morinda citrifolia,* also in the aqueous distillate of *Eucalyptus amygdalina,* of chevril oil, pastinaca, and *Heracleum giganteum.* Its occurrence in the distillate of rose petals that have undergone fermentation has already been mentioned. As ester it occurs as butyrate in the oils of *Heracleum Sphondylium*

and *H. giganteum,* as caprinate in cognac oil, and as cinnamate in storax oil and kæmpferia oil.

As one of the most common adulterants of volatile oils, alcohol plays an important role.

It is identified by means of its constants (b. p. 78°; $d_{15°}$ 0,794) also by its conversion into either ethyl iodide or iodoform.

n-*Butyl alcohol,* $CH_3(CH_2)_2CH_2OH$, occurs as ester in Roman chamomile oil. At 20° its density is 0,810 and it boils at 117°. Its phenyl urethane melts between 55 and 56°.[2])

Iso*butyl alcohol,* $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CHCH_2OH$, is contained, according to H. G. Smith, in the aqueous distillate of *Eucalyptus amygdalina.* It boils at 108,4°; sp. gr. 0,8003 at 18°. Its phenyl urethane melts at 80°.[1])

Iso*amyl alcohol,* $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CHCH_2CH_2OH$, occurs as such in the oils of *Eucalyptus Globulus, E. amygdalina,* in geranium oil from Réunion,[2]) lavender oil and French peppermint oil. As ester it occurs in the oils of *Eucalyptus Globulus, E. aggregata,* in Roman chamomile oil and in cognac oil.

It is readily recognized by its irritating odor, boiling point 131°, its phenyl urethane melting at 52 to 53° and by its oxidation to *iso*valeric aldehyde and *iso*valerianic acid.

n-*Hexyl alcohol,* $CH_3(CH_2)_4CH_2OH$, occurs as ester in the oil of male fern and in the oils of *Heracleum Sphondylium* and *H. giganteum.* It boils at 157° and has a specific gravity of 0,8204 at 20°. Upon oxydation it yields capronic acid b. p. 205°.

Active hexyl alcohol (β,β-methyl ethyl propyl alcohol)

$$\begin{matrix}C_2H_5\\CH_3\end{matrix}\!\!>\!CHCH_2CH_2OH,$$

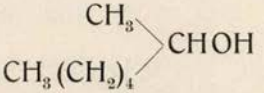
occurs as ester of angelic acid in Roman chamomile oil. It is

[1]) Blaise, Bull. Soc. chim. III. **29** (1903), 327.

[2]) It has not been definitely established whether this is the common *iso*amyl alcohol or not.

dextrogyrate, $[\alpha]_D + 8{,}2°$; $d_{15°}$ 0,829°; b. p. 154°. Chromic acid mixture oxidizes it to active capronic acid boiling between 196 to 198°.

Heptyl alcohol. Of the heptyl alcohols, the *methyl*-n-*amyl carbinol,*



has been found in oil of cloves by Masson.[1]) He enumerates the following constants: b. p. 157 to 158°; $d_{0°}$ 0,8344. Upon oxidation with chromic acid mixture it is converted into methyl-*n*-amyl ketone, the semicarbazone of which melts at 122 to 123° and can be used for identification purposes. For this the pyruvic acid ester is likewise suited, the semicarbazone of which melts at 118 to 119°.

n-*Octyl alcohol,* $CH_3(CH_2)_6CH_2OH$, probably occurs in the free state in the oils of *Heracleum Sphondylium* and *H. giganteum,* in which it also occurs as acetate. As propionate (?) it has been found in pastinaca oil, as butyrate in male fern and pastinaca oils, as *iso*valerate in male fern oil, as capronate, caprinate and laurinate in the oil of *H. Sphondylium.*

It is identified by means of its constants (b. p. 196 to 197°; $d_{16°}$ 0,8278), also by its oxidation to octylic aldehyde (the β-naphthocinchoninic acid of which melts at 234°), or to caprylic acid (m. p. 16,5° and b. p. 232 to 234°).

n-*Nonyl alcohol,* $CH_3(CH_2)_7CH_2OH$, has been found as ester of caprylic acid in sweet orange oil. Under ordinary pressure it boils at 213,5° and has a rose-like odor somewhat resembling that of citronellol. For the alcohol, purified through the phthalic ester, Stephan[2]) records the following properties:

B. p. 98 to 101° (12 mm.); $d_{15°}$ 0,840; $\alpha_D \pm 0°$; $n_{D15°}$ 1,43582.

Nonyl alcohol can be identified by means of its oxidation products (nonyl aldehyde and pelargonic acid, m. p. 12,5°), also by means of its phenylurethane which melts at 62 to 64°.

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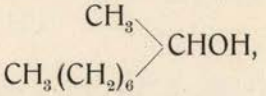
[1]) Compt. rend. **149** (1909), 630.

[2]) Journ. f. prakt. Chem. II. **62** (1900), 532.

As secondary nonyl alcohol, *methyl*-n-*heptylcarbinol,*

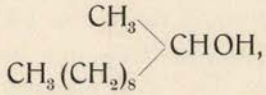


has been found by Power and Lees[1]) in an Algerian oil of rue, and by Masson[2]) in clove oil. Its properties are recorded as follows:

B. p. 198 to 200° (765 mm.); $d_{16°}^{19°}$ 0,8273; α_D (50 mm.) — 3° 44′ (Power and Lees); b. p. 195 to 196°; $d_{0°}$ 0,8399 (Masson).

It can be identified by its oxidation product, methyl-*n*-heptylketone and the semicarbazone of the latter (m. p. 118 to 119°). With pyrouvic acid it forms an ester which boils at 126 to 127° (16 mm.), and the semicarbazone of which melts at 117°.

Undecyl alcohol. A secondary undecyl alcohol, methyl-*n*-nonyl-carbinol



has also been found in the Algerian oil of rue mentioned above. For the purified alcohol, Power and Lees record the following constants:

B. p. 231 to 233°; α_D (25 mm.) — 1° 18′.

It is identified by means of its oxidation product, the methyl-*n*-nonyl ketone, the oxime of which melts at 46°, the semicarbazone at 123 to 124°.

Of unsaturated aliphatic alcohols the hexylene alcohol $C_6H_{12}O$ which occurs in the tea leaf oil, and the alcohol $C_8H_{16}O$, probably an octylene alcohol, which occurs in Gaultheria oil, may be mentioned as representatives of the lower members of the series. Of much greater interest, however, are the terpene alcohols $C_{10}H_{18}O$, linalool, geraniol, and nerol; furthermore, the unsaturated chain alcohol $C_{10}H_{20}O$, citronellol. These occur as such and as esters in volatile oils of which they are important constituents because of their fragrance.

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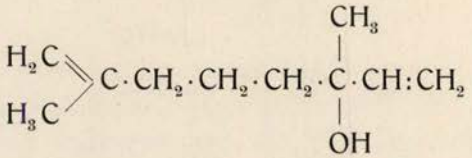
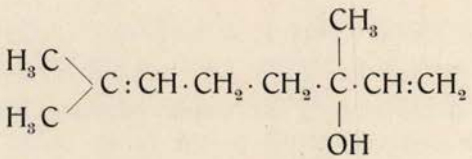
[1]) Journ. chem. Soc. **81** (1902), 1592.

[2]) Compt. rend. **149** (1909), 630.

Linalool.



or



Linalool, the "licareol" of Barbier, which is more or less widely distributed and which occurs in both optical modifications, constitutes the bulk of lignaloe oil. The Mexican lignaloe oils contain both *d*- and *l*-linalool: the dextrogyrate alcohol in the oil of the seeds, the lævogyrate in the oil of the wood. In the Cayenne lignaloe oil *l*-linalool only has been found. *d*-Linalool has also been found in the oil of Canada snake root, and the oils of nutmeg, wartara, sweet orange, and coriander; *l*-linalool in ylang-ylang oil, the oils of champaca flowers, Ceylon cinnamon, of the leaves of *Cinnamomum Loureirii,* laurel leaves, sassafras leaves, rose, Réunion geranium, bergamot, neroli, petitgrain, lemon, Italian limetta, spike, thyme, Spanish hops, Muscatelle sage, German and French basilicum, and Russian spearmint. In the following oils linalool has been found, but no record has been made of the direction of optical rotation, *viz.,* in the oils of citronella, hops, kuromoji, limetta leaves, the bark of *Cinnamomum pedunculatum,* the root of *C. Loureirii,* mandarin, and gardenia. As acetate, linalool has been found in the oil of sassafras leaves, the oil of the root of *Cinnamomum pedunculatum,* the oils of bergamot, petitgrain, lemon, neroli, Italian limette, in jasmin flower oil, in lavender oil, in Muscatelle sage oil, in the leaf oil of *Mentha citrata* and in gardenia oil. As butyrate, linalool has been found in lavender oil, as *iso*butyrate in Ceylon cinnamon oil and as *iso*valerate in sassafras leaf oil. An ester of linalool also occurs in oil of hops.

The isolation of pure linalool from a crystalline derivative has not yet succeeded. Hence it is necessary to obtain it by

fractionation of the oil which has previously been saponified. As a result, the constants recorded for linalool apply to products thus obtained. If it is desired to free the alcohol from indifferent substances, such as the terpenes, it can be converted into the sodium salt of the acid phthalic ester according to Tiemann's method[1]) by allowing phthalic acid anhydride to act on sodium linalool. The sodium salt of this acid phthalic ester of linalool is soluble in water and can be saponified with alcoholic potassa. In as much as linalool is subject to changes when distilled from an alkaline solution with water vapor[2]) — changes that are indicated by a reduction in the optical rotation — the regenerated alcohol must be shaken out of the alcoholic-alkaline solution by means of ether.

According to the nature of the crude material, also according to the method of preparation, products have been obtained that varied slightly in their properties. In judging the purity of a product the following data may be used for comparison.

B. p. 197 to 199°, 85 to 87° (10 mm.); $d_{15°}$ 0,870 to 0,875; $n_{D20°}$ 1,4630 to 1,4690.[3])

B. p. 86 to 87° (14 mm.); $d_{20°}$ 0,8622 (?); n_D 1,46108.[4])

B. p. 198 to 199° (760 mm.), 88,3 to 89,5° (13 mm.); $d_{15°}$ 0,870; $n_{D20°}$ 1,4668.[5])

In connection with technical products obtained in the laboratory of Schimmel & Co., the following constants have been observed:

B. p. 197 to 199°, 69 to 71° (4 mm.); $d_{15°}$ 0,869 to 0,873; α_D — 3° to — 17°, resp. + 9° to + 13°; $n_{D20°}$ 1,462 to 1,464; soluble in 10 to 15 vols. of 50 p. c. alcohol, in 4 to 5 vols. of 60 p. c. and 1 to 2 vols. of 70 p. c. alcohol.

The angle of rotation is not fixed, the highest thus far observed is that for *l*-linalool from limette oil $[\alpha]_D$ — 20° 7',[3]) for

[1]) Berl. Berichte **31** (1898), 837.

[2]) These changes appear to be of a chemical nature and not due merely to inversion. The angle of rotation of *l*-linalool is not altered by boiling with potassium hydroxide. Charabot, Bull. Soc. chim. III. **21** (1899), 549.

[3]) Stephan, Journ. f. prakt. Chem. II. **58** (1898), 110.

[4]) Tiemann, Berl. Berichte **31** (1898), 834.

[5]) Gildemeister, Arch. der Pharm. **233** (1895), 179.

d-linalool from sweet orange oil $[\alpha]_D + 19°18'$.[1]) In most instances, and more particularly in specimens with a low angle of rotation, the products are, no doubt, mixtures of both optical modifications, in which one or the other predominates.

Artificially linalool can be obtained, though in the inactive modification only, when geraniol is heated with water to 200° in an autoclave;[2]) or by the action of hydrogen chloride on geraniol and subsequent treatment of the linalyl chloride thus obtained with alcoholic potassa or silver nitrate.[3]) As to its formation from geranylphthalate of sodium see p. 361.

As an unsaturated alcohol with two double bonds, linalool reveals additive capacity. It combines with bromine, also with hydrohalogen to compounds which, with the exception of linalyl chloride,[4]) $C_{10}H_{17}Cl$ (b. p. 95 to 96° at 6 mm.), have been investigated but little.

The unsaturated tertiary character of the alcohol is revealed by its behaviour towards reagents. Whereas alkalies act on it but little in the cold, organic acids convert it either into geraniol, nerol, or — in the presence of a little sulphuric acid — into terpineol. Mineral acids change it to cyclic compounds, the change being accompanied either by the abstraction of water or the addition of water. Thus, when shaken with a 5 p. c. sulphuric acid, terpin hydrate is formed;[5]) when heated with glacial acetic acid and acetic anhydride, there are formed geranyl acetate, the acetate of the solid terpineol[6]) with an optical rotation opposite to that of the linalool used as starting point, also neryl-acetate.[7]) Formic acid at room temperature (20°) converts it into its own formate, also into the formate of the solid terpineol with opposite rotation. However, when gently heated (60 to 70°) formic acid dehydrates it, yielding the hydrocarbons dipentene and terpinene.[8])

[1]) Stephan, Journ. f. prakt. Chem. II. **62** (1900), 529.

[2]) Report of Schimmel & Co. April **1898**, 27.

[3]) Tiemann, Berl. Berichte **31** (1898), 832; Berichte von Roure-Bertrand Fils October **1909**, 27.

[4]) Dupont and Labaune, Berichte von Roure-Bertrand Fils October **1909**, 21.

[5]) Tiemann and Schmidt, Berl. Berichte **28** (1895), 2137.

[6]) Stephan, Journ. f. prakt. Chem. II. **58** (1898), 109.

[7]) Zeitschel, Berl. Berichte **39** (1906), 1780.

[8]) Bertram and Walbaum, Journ. f. prakt. Chem. II. **45** (1892), 601.

Oxidizing agents produce varying results when allowed to act on linalool. With very dilute permanganate solution polyatomic alcohols appear to be formed at first which cannot be isolated in a pure form. Upon further oxidation with permanganate or chromic acid mixture, they yield acetone and lævulinic acid.[1]) In accordance with these results, and taking into consideration that linalool is optically active and hence must contain an assymmetric carbon atom, the following formula has been derived,[2]) namely dimethyl-2,6-octadiene-2,7-ol-6

$$CH_3 \cdot C(CH_3) : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3)(OH) \cdot CH : CH_2.$$

Possibly, however, the formula given on p. 352 should be assigned to it. If linalool is oxidized with chromic acid mixture only, it first suffers a rearrangement due to the acid character of the oxydizing agent, and is then oxidized to citral, the aldehyde of geraniol.[3]) As a rule the oxidation is carried farther yielding "Abbau" products of citral, *viz.*, methyl heptenone, lævulinic acid, &c. The crystallyzed oxidation product with hydrogen peroxide, observed by Bertram and Walbaum,[3]) has revealed itself as terpin hydrate, the formation of which is, in all probability, largely due to mineral acid present in the hydrogen peroxide used.

When heated with sulphur to 160°, linalool and linalyl acetate yield sulphur-containing compounds which Erdmann[4]) has named "thiozonides". The monothiozonide of linalylacetate, which appears to possess the composition expressed by the formula $C_{12}H_{20}O_2S_3$, is a blackish-brown syrup of a peculiar odor. In suitable solvents it produces precipitates with the salts and sulphides of the heavy metals. Of these the gold compound is especially characteristic. Linalool appears to react with both double bonds forming a dithiozonide, which, however, could not be isolated, since hydrogen sulphide was given off and the compound $C_{10}H_{16}OS_5$ was formed.[5])

When acted upon with reducing agents, linalool does not add hydrogen, but readily loses its oxygen with the formation of a doubly unsaturated hydrocarbon linaloolene $C_{10}H_{18}$. This hydrocarbon results when linalool is converted into its sodium

[1]) Tiemann and Semmler, Berl. Berichte **28** (1895), 2130.

[2]) *Ibidem* 2131.

[3]) Journ. f. prakt. Chem. II. **45** (1892), 599.

[4]) Liebig's Annalen **362** (1908), 137.

[5]) H. Erdmann, *loc. cit.*

derivative, or is treated with metallic sodium in alcoholic solution, or when it is heated to 220 to 230° with zinc dust.[1]) The sodium derivative of linalool is readily soluble in an excess of linalool and can be utilized for preparing this alcohol in a pure state.

When reducing linalool with nickel and hydrogen, Enklaar[2]) obtained, in addition to 2,6-dimethyloctane, 2,6-dimethyloctanol-6,

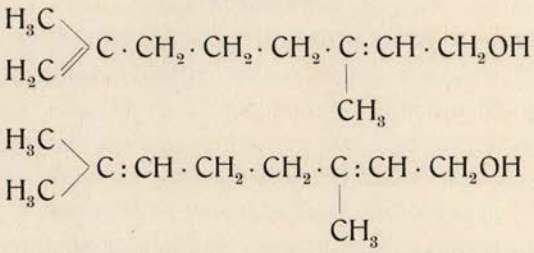
$$CH_3 \cdot CH(CH_3) \cdot (CH_2)_3 \cdot C(OH)(CH_3) \cdot CH_2 \cdot CH_3,$$

thus supporting the correctness of the formula of Tiemann and Semmler given above.

The esters of linalool, so far as those occurring in volatile oils are concerned, are liquids with a more or less strong and agreable odor, which cannot be distilled without decomposition under ordinary pressure. The synthetic preparation of these esters, however, is coupled with difficulties since linalool is rather susceptible toward acids. Hence, when linalool is boiled with acid anhydrides or when treated in accordance with the G. I. P. 80711, the products which result consist in the main of esters of linalool, but also contain those of geraniol and terpineol.

Compounds suited to the identification of linalool are the phenylurethane, melting at 65 to 66°, and the α-naphthylurethane melting at 53°. For its further identification it can be oxidized to citral and this characterized by the citral-β-naphthocinchoninic acid discovered by Doebner. If citronellal be present with citral, both are first separated by means of their acid sulphite addition products.

Geraniol.



or

Isomeric with linalool is geraniol $C_{10}H_{18}O$ which is distinguished from the former by its optical inactivity, higher boiling

[1]) Semmler, Berl. Berichte **27** (1894), 2520.

[2]) Berl. Berichte **41** (1908), 2083; Recueil des trav. chim. des P.-B. **27** (1908), 411; Chem. Zentralbl. **1908**, II. 1926.

point and higher specific gravity. It is the "lemonol" of Barbier and Bouveault, the "rhodinol" of Erdmann and Huth and of Poleck. Both as such and as ester it is found rather frequently in volatile oils. It constitutes the bulk of palmarosa oil, of German and Turkish rose oils, and is found in appreciable quantities in the oils of geranium, citronella and lemongrass. It has further been found in the oils of gingergrass, Canada snakeroot, ylang-ylang, champaca flowers, nutmeg, sassafras leaves, laurel leaves, kuromoji, tetranthera (?), cassie flowers (from *Acacia Cavenia* and *A. Farnesiana*), neroli, petitgrain, coriander, Mexican and Cayenne lignaloe, of *Darwinia fascicularis* (?), *Eucalyptus Macarthuri, E. Staigeriana, Leptospermum Liversidgei,* verbena, spike (?) and lavender. As acetate it occurs in the needle oil of *Callitris glauca,* the oils of palmarosa, lemongrass, sassafras leaves, kuromoji, lemon, petitgrain, *Eucalyptus Macarthuri, E. Staigeriana, Leptospermum Liversidgei,* Darwinia fascicularis and lavender; as *iso*valerianate in sassafras leaf oil; as *n*-capronate in palmarosa and lavender oils; and as tiglinate in geranium oil.

As a primary alcohol, geraniol forms a crystalline addition product with calcium chloride,[1]) which is insoluble in ether, ligroin, benzene and chloroform, and which is resolved into its components by water. By this extremely simple method, geraniol can be obtained chemically pure (see below). With magnesium chloride, calcium nitrate and magnesium nitrate, crystalline derivatives are likewise formed.[2])

For the isolation of geraniol from mixtures with hydrocarbons and other substances a number of other methods have been suggested. All of them have this in common that they aim at the preparation of an acid phthalate of geraniol. This ester can be prepared either by the action of phthalic acid anhydride on the sodium compound of crude geraniol,[3]) or by heating geraniol with phthalic acid anhydride without solvent in the water bath[4]) or in benzene solution.[5]) The ester can be purified through the

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[1]) Jacobsen, Liebig's Annalen **157** (1871), 234.

[2]) Report of Schimmel & Co. April **1895**, 44.

[3]) Tiemann and Krüger, Berl. Berichte **29** (1896), 901.

[4]) H. and E. Erdmann, Journ. f. prakt. Chem. II. **56** (1897), 15.

[5]) Flatau and Labbé, Compt. rend. **126** (1898), 1725; Bull. Soc. chim. III. **19** (1898), 633; Stephan, Journ. f. prakt. Chem. II. **60** (1899), 248.

crystalline silver salt. The geraniol is regenerated by saponifying either the acid ester, or its sodium salt, the latter being prepared from the silver salt. These methods, however, do not possess any advantages over the calcium chloride method. Indeed, they are more complicated and yield no purer product.

Purified geraniol, prepared by one or the other of the above mentioned methods, is a colorless, oily liquid with a rose-like odor which is optically inactive. When exposed to the air it is modified, taking up oxygen and suffering in its fragrance. Its properties are recorded as follows:

B. p. 110 to 111° (10 mm.), 121° (18 mm.), 230° (under atmospheric pressure).[1])

B. p. 120,5 to 122,5° (17 mm.); $d_{20°}$ 0,8894 (!); $n_{D20°}$ 1,4766.[2])

B. p. 110,5 to 111° (corr., at 10 mm.); $d_{4°}^{16°}$ 0,8812.[3])

$d_{15°}$ 0,880 to 0,883; $n_{D17°}$ 1,4766 to 1,4786.[4])

In connection with products prepared by themselves on a large scale Schimmel & Co. observed the following properties:

B. p. 229 to 230° (757 mm.), 114 to 115° (12 mm.); $d_{15°}$ 0,883 to 0,886; $n_{D20°}$ 1,476 to 1,478; soluble in 8 to 15 vols. of 50 p. c. alcohol and in 2,5 to 3,5 vols. of 60 p. c. alcohol.

Upon oxidation geraniol, as primary alcohol, yields citral, from which it can again be obtained by reduction.[5]) In as much as citral has been obtained synthetically, geraniol also belongs to those substances that can thus be obtained.

Upon application of Sabatier and Senderens'[6]) method, Bouveault[7]) succeeded in converting geraniol well nigh quantitatively into citral. This method consists in the catalytic action of copper on primary alcohols at high temperature.

Geraniol, or rather its acetate, results together with terpineol and nerol, when linalool is heated for a long time with acetic

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[1]) Bertram and Gildemeister, Journ. f. prakt. Chem. II. **56** (1897), 508.

[2]) Tiemann and Semmler, Berl. Berichte **26** (1893), 2711.

[3]) H. and E. Erdmann, Journ. f. prakt. Chem. II. **56** (1897), 3; Berl. Berichte **31** (1898), 359, Anm. 1.

[4]) Stephan, Journ. f. prakt. Chem. II. **58** (1898), 110; **60** (1899), 244.

[5]) Tiemann, Berl. Berichte **31** (1898), 828.

[6]) Compt. rend. **136** (1903), 738, 921, 983.

[7]) Bull. Soc. chim. IV. **3** (1908), 119.

acid anhydride.[1]) The reverse reaction takes place when geraniol is heated with water to 200° in an autoclave. At higher temperatures hydrocarbons and their polymerization products are formed.[2]) When hydrogen chloride is allowed to act on a mixture of geraniol and toluene, linalyl chloride results which, with silver nitrate, yields linalool.[3]) Hence it can be explained how Tiemann[3]) could obtain linalool when treating geraniol with hydrogen chloride and saponifying the reaction product with alcoholic potassa.

In general, geraniol is not as readily acted upon by acids as is linalool. However, the action of acid reagents may cause ring formation, *cyclo*geraniol being produced. When boiled with acetic acid anhydride it is quantitatively converted into the acetate, but not isomerized. When shaken with dilute sulphuric acid it is converted into terpinhydrate, as is linalool, but not as readily.[4]) Concentrated formic acid, like potassium acid sulphate or phosphoric acid, acts as dehydrating agent. Whereas the action of potassium acid sulphate is said to produce an open chain hydrocarbon,[5]) the other reagents produce terpenes. Thus formic acid produces α-terpineol, dipentene and terpinene.[6]). Upon reduction of geraniol with platinum sponge and hydrogen, Willstätter and Mayer[7]) obtained a mixture of 2,6-dimethyl octane and 2,6-dimethyloctanol-8. The same products were obtained by Enklaar[8]) with Sabatier's method. In addition, however, there resulted a cyclic alcohol $C_{10}H_{20}O$ not further characterized.

In the cold geraniol is scarcely acted upon by alkalies. When heated with concentrated alcoholic potassa to 150°, there is formed, according to Barbier,[9]) a tertiary alcohol $C_9H_{18}O$

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[1]) Bouchardat, Compt. rend. **116** (1893), 1253; Tiemann and Semmler, Berl. Berichte **26** (1893), 2714; Stephan, Journ. f. prakt. Chem. II. **58** (1898), 111.

[2]) Report of Schimmel & Co. April **1898**, 27.

[3]) Tiemann, Berl. Berichte **31** (1898), 832; Dupont and Labaune, Berichte von Roure-Bertrand Fils October **1909**, 27.

[4]) Tiemann and Schmidt, Berl. Berichte **28** (1895), 2138.

[5]) Semmler, Berl. Berichte **24** (1891), 683.

[6]) Bertram and Gildemeister, Journ. f. prakt. Chem. II. **49** (1894), 195; **53** (1896), 236; Stephan, Journ. f. prakt. Chem. II. **60** (1899), 244.

[7]) Berl. Berichte **41** (1908), 1475.

[8]) *Ibidem* 2083.

[9]) Compt. rend. **126** (1898), 1423.

while carbon dioxide is being split off. However, this statement is based on an error since the resulting alcohol is methyl heptenol $C_8H_{16}O$.[1])

The addition products of bromine and hydrohalogen are mostly liquid and readily decomposible. However, a crystalline tetrabromide of geraniol, melting at 70 to 71°, can be prepared.[2])

As already pointed out on p. 358 geraniol yields upon oxidation with chromic acid mixture first an aldehyde, citral, $C_{10}H_{16}O$.[3]) Under special conditions, however, methylheptenone can also be obtained.[4]) Other "Abbau" products are likewise obtained, so that the reaction is by no means a quantitative one. When shaken with very dilute permanganate solution polyatomic alcohols are presumably first formed. With chromic acid mixture these are oxidized to acetone, lævulinic acid and oxalic acid.[5]) In as much as geraniol is optically inactive and a primary alcohol, the above oxidation products have lead to the adoption of the following formula, *viz.,* that of dimethyl-2,6-octadiene-2,6-ol-8.

$$CH_3 \cdot C(CH_3):CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3):CH \cdot CH_2OH.$$[6])

The isomeric formula given above, however, appears to have some points in its favor. Like citronellol, geraniol can add sodium acid sulphite, namely two molecules since it has two double bonds.[7])

The occurrence of esters of geraniol in volatile oils has already been mentioned. In as much as geraniol is relatively stable toward acids, its esters can be obtained either by the action of acid anhydrides on geraniol, or by the action of acid chlorides on geraniol in the presence of pyridine.[8]) The esters of the fatty acids are all liquid and their odor becomes fainter with the increase of the radicle of the acid introduced. The formate and the acetate are described among the esters.

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[1]) Report of Schimmel & Co. October **1898**, 27; Tiemann, Berl. Berichte **31** (1898), 2991.

[2]) v. Soden and Treff, Berl. Berichte **39** (1906), 913.

[3]) Semmler, Berl. Berichte **23** (1890), 2965; **24** (1891), 203.

[4]) Semmler, Berl. Berichte **26** (1893), 2720.

[5]) Tiemann and Semmler, Berl. Berichte **28** (1895), 2130.

[6]) *Ibidem* 2132.

[7]) Labbé, Bull. Soc. chim. III. **21** (1898), 1079.

[8]) H. and E. Erdmann, Journ. f. prakt. Chem. II. **56** (1897), 14; Berl. Berichte **31** (1898), 356.

Of the other esters of geraniol the diphenylcarbaminic acid ester and the acid phthalic acid ester should be mentioned. Both are crystalline. The former may well be used for the identification of geraniol (see p. 362) whereas the latter (m. p. 47°)[1] may be employed in the preparation of pure geraniol. It should be noted, however, that geranylphthalate of sodium is partly converted into linalool when subjected to distillation with steam.[2] A tetrabromide of the geranylphthalic acid is also known which melts at 114 to 115°. The silver salt melts at 133°. When preparing this acid it is best to work in benzene solution for the purpose of avoiding higher temperatures, for otherwise the geraniol is completely destroyed. The following derivatives remain to be mentioned, *viz.*, geranyl-α-naphthylurethane (m. p. 47 to 48°), geranyl-di-β-naphthylurethane (m. p. 105 to 107°), and the geranylurethane (m. p. 124°).

For the purpose of separating geraniol from a geraniol-containing oil one can proceed, according to Bertram and Gildemeister,[3] in the following manner: Equal parts of the oil and finely powdered calcium chloride are carefully mixed in a mortar. The mixture, which as a result of the reaction has heated itself to 30 to 40°, is set acide for several hours in a desiccator in a cool place. The solid mass is pulverized and triturated with anhydrous ether, benzene or low boiling petroleum ether, transferred to a force filter and washed with ether, respectively benzene or petroleum ether. To the mixture of geraniol-calcium chloride with the excess of calcium chloride, water is added thus causing the geraniol to be regenerated. The separated oil is washed repeatedly with warm water and finally distilled with steam.

The separation of geraniol from its mixtures according to this method is not quantitative. Moreover, the oil to be thus treated should contain at least 25 percent. of geraniol. If only small amounts of material are available, it is best to use for characterization the diphenylurethane of geraniol

$$(C_6H_5)_2NCOOC_{10}H_{17},$$

first recommended by Erdmann and Huth.[4] For its preparation

[1] Flatau and Labbé, Compt. rend. **126** (1898), 1725.
[2] Stephan, Journ. f. prakt. Chem. II. **60** (1899), 252.
[3] Journ. f. prakt. Chem. II. **53** (1896), 233; **56** (1897), 507.
[4] Journ. f. prakt. Chem. II. **53** (1896), 45.

the following directions are given:[1]) 1 g. of oil, 1,5 g. diphenylcarbamine chloride and 1,35 g. pyridine are heated for two hours on a water bath. The reaction product is subjected to steam distillation and the residue, which solidifies upon cooling, crystallized from alcohol. If much citronellol is present with the geraniol, it is difficult to obtain a pure product, since citronellol yields also a diphenylurethane which, however, remains liquid. In such a case, urethanes with a low melting point (40 to 50°) are first obtained which after repeated recrystallization from alcohol may show the melting point of the diphenylurethane of geraniol, *viz.*, 82,2°.

If geraniol is to be further characterized, it can be oxidized to citral and this converted into the citryl-β-naphthocinchoninic acid (see Citral). For this purpose, however, the alcohol must be fairly pure and not contain linalool, since this likewise yields citral with chromic acid mixture. If citral is present with geraniol the former must first be removed which removal may be accomplished by treatment with sulphurous acid.

A conversion of geraniol to citronellol is possible through the geranic acid. This is reduced to citronellic acid and the latter to citronellol.[2]) Thus the proof is established that citronellol is dihydrogeraniol.

Nerol.

This alcohol which is stereoisomeric with geraniol was found in 1902 in neroli oil[3]) in which it occurs principally as acetate. Furthermore, nerol has been found in the oils of petitgrain, rose, Mexican lignaloes and *Helichrysum angustifolium*. Synthetically it is obtained, together with geraniol and terpineol, by the action of acetic acid anhydride on linalool.[4]) It is likewise obtained in small amount (about 5 p. c.) upon the reduction of citral.

Nerol of unquestioned purity has not yet been obtained. The following constants were observed on a specially purified product: B. p. 226 to 227° (755 mm.); 125° (25 mm.); $d_{15°}$ 0,8813; $\alpha_D \pm 0°$.[5])

[1]) Journ. f. prakt. Chem. II. **56** (1897), 28.

[2]) Tiemann, Berl. Berichte **31** (1898), 2899; Bouveault and Gourmand, Compt. rend. **138** (1904), 1699.

[3]) Hesse and Zeitschel, Journ. f. prakt. Chem. II. **66** (1902), 502.

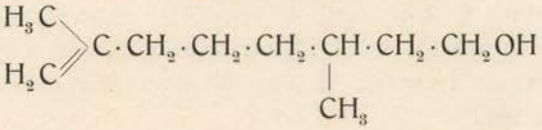
[4]) Zeitschel, Berl. Berichte **39** (1906), 1780.

[5]) v. Soden and Treff, Chem. Ztg. **27** (1903), 897.

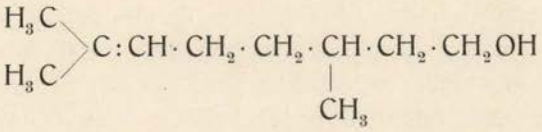
Nerol possesses an agreable, rose-like odor and in its chemical behavior reveals close similarity with geraniol. When shaken with dilute sulphuric acid, it readily yields terpin hydrate. Upon oxidation it yields either citral or an aldehyde that possesses the odor of citral. Like geraniol it is unstable toward formic acid at higher temperature. With calcium chloride it does not form a crystalline addition product, hence it can be separated, at least in part, from geraniol. A like separation may be affected by the diphenylurethanes because of their different solubilities in certain solvents such as petroleum ether and methyl alcohol.

Of its derivatives the tetrabromide[1]) melting at 118 to 119° and the diphenylurethane[2]) melting at 52 to 53° should be mentioned.

Citronellol.

I. 

or

II. 

(The rhodinol of Barbier?)

Citronellol, $C_{10}H_{20}O$, was first obtained by Dodge[3]) by the reduction of citronellal from citronella oil. The citronellol thus prepared like the aldehyde from which it is obtained, is dextrogyrate. In volatile oils citronellol has been found repeatedly. Both optical modifications occur in the geranium oils, *l*-citronellol in oil of rose, and *d*-citronellol in citronella oil from Java and in the oil of *Barosma pulchellum*. Citronellol has also been found in savin oil. Probably its esters as well as the free alcohol occur in volatile oils.

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[1]) v. Soden and Treff, Berl. Berichte **39** (1906), 907.

[2]) v. Soden and Treff, Chem. Ztg. **27** (1903), 897; comp. Report of Schimmel & Co. April **1904**, 109.

[3]) Americ. chem. Journ. **11** (1889), 456.

As has been demonstrated, the alcohols described as "rhodinol"[1]) and "reuniol"[2]) revealed themselves as mixtures of citronellol and geraniol. The "roseol" of Markownikoff and Reformatsky,[3]) that constitutes the bulk of oil of rose, has likewise been found to consist of a mixture of citronellol and geraniol. However, as a result of more recent investigations, Barbier and his colaborers, more particularly Bouveault, insist that the lævogyrate alcohol $C_{10}H_{20}O$ which occurs in pelargonium oil and oil of rose differs from the ordinary *d*-citronellol more than by being merely its lævogyrate modification. Bouveault,[4]) therefore, insists on the retention of the name "rhodinol". Whether this is justified remains to be seen. The work thus far done on this subject by Hesse,[5]) Wallach and Naschold,[6]) Erdmann and Huth,[7]) Bertram and Gildemeister,[8]) Tiemann and Schmidt[9]) has not yet settled the question. This much, however, is demonstrated that rhodinol consists at least in part of citronellol.

According to Bouveault[10]) formula I should be assigned to citronellol, formula II to rhodinol. He is lead to this assumption by the different behavior of the corresponding aldehydes (comp. under citronellal).

Of the citronellol, obtained by the reduction of citronellal, Schimmel & Co.[11]) prepared the pyrouvic ester and the semicarbazone and thus established the identity of the latter derivative with that obtained by Bouveault from "rhodinol". The respective melting points are 110 to 111° and 112°.

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[1]) Eckart, Arch. der Pharm. **229** (1891), 355; Berl. Berichte **24** (1891), 4205; Barbier and Bouveault, Compt. rend. **117** (1893), 177, 1092; **118** (1894), 1154; **119** (1894), 281, 334; **122** (1896), 530, 673.

[2]) Hesse, Journ. f. prakt. Chem. II. **50** (1894), 472.

[3]) *Ibidem* II. **48** (1893), 293; Berl. Berichte **23** (1890), 3191; **27** (1894), Ref. 625.

[4]) Bull. Soc. chim. III. **23** (1900), 458.

[5]) Journ. f. prakt. Chem. II. **50** (1894), 472.

[6]) Nachr. K. Ges. Wiss. Göttingen **1896**, Session of February 8.; Chem. Zentralbl. **1896**, I. 809.

[7]) Journ. f. prakt. Chem. II. **53** (1896), 42.

[8]) *Ibidem* II. **49** (1894), 185; comp. also Report of Schimmel & Co. October **1894**, 29; April **1895**, 44.

[9]) Berl. Berichte **29** (1896), 903; **30** (1897), 33.

[10]) *Loc. cit.* and Compt. rend. **138** (1904), 1699; comp. also Barbier and Bouveault, Compt. rend. **122** (1896), 737.

[11]) Report of Schimmel & Co. October **1904**, 119.

Recent publications by Harries and Himmelmann[1]) would seem to indicate that citronellol also consists of a mixture of two isomers, to which two separate formulas should be assigned. This conception may lead to an explanation of the differences in the investigations of citronellol found by Bouveault on the one hand and by Tiemann and Schmidt and Schimmel & Co. on the other hand.

Geraniol and citronellol occur frequently together. In as much as they cannot be separated by fractional distillation either as such or in the form of their esters, and since the calcium chloride method does not admit of a quantitative separation, it was difficult to obtain pure citronellol. In this Wallach[2]) first succeeded, who observed that when geraniol is heated with water in an autoclave to 250° it is completely decomposed with the formation of hydrocarbons, whereas citronellol remains unchanged. A method of separation suggested by Tiemann and Schmidt[3]) depends on the action of phosphorus trichloride on the alcohols in ethereal solution. Geraniol is thereby converted partly into hydrocarbons, partly into geranyl chloride; citronellol, however, into a chlorinated acid ester of phosphorous acid which is soluble in alkalies and can thus be separated from the other compounds. The crude citronellol regenerated by the saponification of the ester is purified by distillation with water vapor. A separation of the two can also be affected by heating the mixture of alcohols with phthalic acid anhydride to 200°. Whereas the geraniol is thus destroyed, the citronellol is converted into the acid phthalic acid ester, the sodium salt of which is soluble in water and which can be saponified by means of alcoholic potassa. According to Walbaum and Stephan[4]) the mixture can be heated with strong formic acid, whereby the geraniol is decomposed and the citronellol converted into the formate. According to Barbier and Bouveault[5]) the geraniol can also be destroyed by heating with benzoyl chloride to from 140 to 160°.

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[1]) Berl. Berichte **41** (1908), 2187.
[2]) Nachr. K. Ges. Wiss. Göttingen **1896**, Session of February, 8.
[3]) Berl. Berichte **29** (1896), 921.
[4]) Berl. Berichte **33** (1900), 2307.
[5]) Compt. rend. **122** (1896), 530.

Artificially citronellol can be obtained from citronellal, its corresponding aldehyde, by means of reduction with sodium amalgam and glacial acetic acid.[1]) Other methods of formation, starting with geranic acid, have been suggested by Tiemann[2]) and by Bouveault and Gourmand.[3]) The products thus obtained are optically inactive. Furthermore, by the cleavage of menthonoxime and change in the resulting aliphatic compound, Wallach[4]) obtained an alcohol $C_{10}H_{20}O$ which very much resembles citronellol, but is not identical with it.

Pure citronellol is a colorless oil with an agreable, rose-like odor, but finer than that of geraniol. According to its method of formation it reveals slight variations in its physical properties. Wallach[5]) determined the following constants in connection with a citronellol (reuniol) obtained according to his method (see above):

B. p. 114 to 115° (12 to 13 mm.); $d_{22°}$ 0,856; α_D — 1° 40′; $n_{D22°}$ 1,45609.

According to Tiemann and Schmidt,[6]) *d*-citronellol obtained by reduction of citronellal, possesses the following properties:

B. p. 117 to 118° (17 mm.); $d_{17,5°}$ 0,8565; $[\alpha]_{D17,5°}$ + 4°; n_D 1,45659.

l-Citronellol, prepared from rose oil by means of the phosphorus trichloride method, boils at 113 to 114° at 15 mm. pressure; $d_{20°}$ 0,8612; n_D 1,45789; and deviates polarized light 4° 20′ to the left.[7])

For the alcohol, obtained from Réunion geranium oil according to a method similar to that of Wallach, the following constants are recorded:

B. p. 225 to 226° (764,5 mm.); $d_{15°}$ 0,862; α_D — 1° 40′; $n_{D22°}$ 1,45611.[8]).

[1]) Dodge, Americ. chem. Journ. **11** (1889), 463; Tiemann and Schmidt, Berl. Berichte **29** (1896), 906; Erdmann, Journ. f. prakt. Chem. II. **56** (1897), 38.

[2]) Berl. Berichte **31** (1898), 2899.

[3]) Compt. rend. **138** (1904), 1699.

[4]) Liebig's Annalen **278** (1894), 316; **296** (1897), 129.

[5]) Nachr. K. Ges. Wiss. Göttingen **1896**, Session of February 8.; Naschold, *Beiträge zur Kenntnis aliphatischer Terpenverbindungen. Inaug.-Dissert.* Göttingen 1896. p. 56.

[6]) Berl. Berichte **29** (1896), 906.

[7]) Tiemann and Schmidt, Berl. Berichte **29** (1896), 923.

[8]) Report of Schimmel & Co. April **1898**, 58.

In the laboratory of Schimmel & Co. the following constants were observed in connection with their own preparations:

Citronellol from Java citronella oil: B. p. 109° (7 mm.); 103° (5 mm.); $d_{15°}$ 0,8604 to 0,8629; α_D + 2°7′ to + 2°32′; $n_{D22°}$ 1,45651 to 1,45791; m. p. of the silver salt of the acid phthalic acid ester 125 to 126°.[1])

Citronellol from geranium oil: B. p. 225 to 226° (764,5 mm.); $d_{15°}$ 0,862 to 0,869; α_D slightly lævogyrate to — 1°52′; $n_{D20°}$ 1,459 to 1,463; soluble in about 14 vols. 50 p. c. alcohol and in 3 to 4 vols. of 60 p. c. alcohol.

Citronellol is much more stable than geraniol and is not acted upon when heated with alkali. When shaken with a 10 p. c. sulphuric acid it adds water and is converted into a diatomic alcohol from which dehydrating agents regenerate citronellol.[2]) Attempts to prepare a cyclic hydrocarbon $C_{10}H_{18}$ by dehydration have not been successful thus far. Its stability toward phosphorus trichloride in the cold, phthalic acid anhydride and formic acid at higher temperatures, and toward the united action of heat and pressure in the presence of water, has already been referred to in the discussion of the methods by which citronellol can be separated from the other alcohols. It is also worth mentioning that sulphurous acid and sodium acid sulphite can be added to the doubly linked carbon atoms of citronellol.

As a primary alcohol, citronellol first yields the aldehyde citronellal, $C_{10}H_{18}O$, which, upon reduction with sodium amalgam, can be reconverted into the alcohol. As is the case with geraniol, the oxidation to the aldehyde is by no means quantitative, other oxidation products, such as citronellic acid, &c., resulting.[3]) If citronellol is first hydroxylized with dilute permanganate solution and the resulting glycol oxidized further with chromic acid mixture, acetone and β-methyladipinic acid result. According to the optical character of the citronellol, the latter oxidation product is obtained more or less active, or optically inactive. The melting point also varies accordingly from 82 to 96°. In as much as

[1]) Report of Schimmel & Co. April 1902, 14.

[2]) Tiemann and Schmidt, Berl. Berichte 29 (1896), 907.

[3]) Tiemann and Schmidt, Berl. Berichte 30 (1897), 34.

citronellol can also be converted into the cyclic alcohol *iso*-pulegol and this into pulegone, it has been assigned the formula dimethyl-2,6-octene-2-ol-8.

$$CH_3 \cdot C(CH_3) : CH \cdot CH_2 \cdot CH_2 \cdot CH(CH_3)CH_2 \cdot CH_2OH.$$ [1])

Opposed to this view are the observations of Harries and Himmelmann,[2]) referred to above, also those of Bouveault, *viz.*, that citronellol is a mixture of two isomeric alcohols; to one of which may be assigned the above formula and to the other the formula

$$CH_3 \cdot C(: CH_2) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(CH_3)CH_2CH_2OH.$$

The esters of citronellol, of which the acetate occurs in volatile oils, are readily obtained by the action of the corresponding acid anhydrides on the alcohol. For further statements see under esters.

The acid phthalic acid ester, which results when citronellol and phthalic acid anhydride are heated together, differs from that of geraniol in being liquid. However, it yields a well crystallizable silver salt from which pure citronellol can be regenerated.[3])

Citronellol can be characterized by its oxidation to citronellal (which see) and this in turn by means of its citronellyl-β-naphthocinchoninic acid, or by means of its semicarbazone[4]) which melts at 84°. In the absence of geraniol, citronellol can be identified by means of the silver salt of citronellyl phthalic acid which melts at 125 to 126°. Its identification by means of the citronellyl-pyrouvic acid ester, the semicarbazone of which melts at 110 to 111°, can be carried out in the presence of geraniol. For the quantitative determination of citronellol in the presence of other alcohols, its stability toward concentrated formic acid is resorted to. Whereas the other alcohols are destroyed, citronellol, under certain conditions, is converted into the formate. For further details see the chapter "The examination of volatile oils".

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[1]) Tiemann and Schmidt, Berl. Berichte **29** (1896), 908.

[2]) Berl. Berichte **41** (1908), 2187.

[3]) Erdmann and Huth, Journ. f. prakt. Chem. II. **56** (1897), 41.

[4]) Tiemann and Schmidt, Berl. Berichte **30** (1897), 34; **31** (1898), 3307. However, other semicarbazones with different melting points are known. See under citronellal.

Of other alcohols, found in volatile oils, that are regarded as aliphatic compounds, the following should be mentioned:

Androl[1]) is the name assigned to an alcohol of like composition with citronellol, which appears to impart to water fennel *(Phellandrium aquaticum)* its characteristic odor. It may be recognized by its physical constants (b. p. 197 to 198°; $d_{15°}$ 0,858; α_D — 7° 10′; $n_{D20°}$ 1,44991) and by its phenylurethane which melts at 42 to 43°. Nothing further is known about its constitution.

Uncineol, $C_{10}H_{18}O$, is the name given by Baker and Smith[2]) to an alcohol which they found in that portion of cajeput oil *(Malaleuca uncinata)* which boils above 197°. When pure, this alcohol consists of snowwhite crystalline needles which melt at 72,5°; $[\alpha]_D$ + 36,99° in alcoholic solution.

An *alcohol with a rose-like odor* has also been found in fraction 230° of waterfennel oil.[3]) Its phenylurethane melts between 87 to 90°. In patchouli oil[4]) there likewise has been found an alcohol with a rose-like odor. However, nothing further has as yet been recorded.

CYCLIC (AROMATIC) ALCOHOLS.

Benzyl alcohol.

$C_6H_5 \cdot CH_2OH$.

This alcohol, which is of importance because of its application in perfumery, has been found as such in the oils of tuberose, ylang-ylang, jasmin, cloves and of cassie flowers *(Acacia Farnesiana* and *A. Cavenia).* Possibly it is also found in small amounts in cherry laurel oil. As acetate it occurs in the oils of ylang-ylang, hyacinth, jasmin and gardenia; as benzoate in the oils of tuberose, ylang-ylang, Peru balsam and tolu balsam; as cinnamate in storax oil and in the two balsams just mentioned; as salicylate in ylang-ylang oil; and as phenyl acetic acid ester in neroli oil.

[1]) Report of Schimmel & Co. October **1904**, 92.
[2]) Journ. and Proceed. Royal Soc. of N. S. W. **41** (1907), 196.
[3]) Report of Schimmel & Co. October **1904**, 92.
[4]) Report of Schimmel & Co. April **1904**, 69.

It is prepared by heating benzyl chloride with water and freshly precipitated lead oxide to 100° or by prolonged heating of the chloride with water or potassium carbonate solution. Or it can be obtained, as suggested by Cannizzaro,[1]) by double decomposition between benzyl chloride and potassium acetate and subsequent saponification of the benzyl acetate. Still another method consists in shaking benzaldehyde with alkali, whereby one half of the aldehyde is oxidized, the other half reduced. In order to remove the last traces of aldehyde the alcohol is shaken with an acid sulphite solution before it is distilled. In this case the sulphurous acid should be washed out with alkali. Otherwise the sulphuric acid resulting will convert a large part of the benzyl alcohol into the benzyl ether.[2])

Benzyl alcohol is a colorless liquid which, when freshly prepared, has a faintly aromatic odor. Upon exposure to air it oxidizes and assumes an odor of bitter almond oil. B. p. 205°; $d_{15°}$ 1,05; $n_{D20°}$ about 1,540. It is soluble in about 35 vols. of water, in 8 to 9 vols. of 30 p. c. alcohol and in 1,5 vol. of 50 p. c. alcohol. With other solvents it is miscible in all proportions. In as much as it can be prepared from benzyl chloride, special care should be devoted in its examination to the test for chlorides. (For details see the chapter "The examination of volatile oils".)

Upon oxidation benzaldehyde and benzoic acid result. Characteristic derivatives are the phenylurethane[3]) melting at 78° and acid phthalic acid ester melting at 106 to 107°.[4]) The semicarbazone of the pyrouvic acid ester (m. p. 176°)[5]) may also be used for this purpose.

Phenylethyl alcohol.

$C_6H_5 \cdot CH_2 \cdot CH_2OH$.

Phenylethyl alcohol, which is used in the preparation of artificial volatile oils, has been observed as constituent of the

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[1]) Liebig's Annalen **96** (1855), 246.
[2]) Meisenheimer, Berl. Berichte **41** (1908), 1420.
[3]) Report of Schimmel & Co. April **1899**, 28, footnote.
[4]) *Ibidem* October **1903**, 19.
[5]) Masson, Compt. rend. **149** (1909), 630.

leaf oil of *Pinus halepensis*, of oil of rose (especially that distilled from dried rose leaves) and of neroli oil. In the oils of rose and neroli, the alcohol appears also to be combined as ester with benzoic acid and phenylacetic acid.

Artificially it can be prepared from phenyl acetaldehyde by reduction with sodium amalgam;[1]) likewise from phenylacetic acid esters by reduction with sodium and absolute alcohol, a method patented by Bouveault and Blanc.[2]) In connection with a preparation, made in the laboratory of Schimmel & Co. according to the latter method and purified by means of the calcium chloride compound, the following constants were observed:

B. p. 220 to 222° (740 mm.), abt. 104° (12 mm.), 93° (6 mm.); $d_{15°}$ 1,0242; $n_{D20°}$ 1,53212.

According to observations thus far made the latter two constants for technical products fall within the following limits:

$d_{15°}$ 1,023 to 1,024; $n_{D20°}$ 1,532 to 1,533.

Phenylethyl alcohol is a colorless liquid that is optically inactive and possesses a very mild and faint odor. As a result of its partial oxidation to phenyl acetaldehyde it becomes honey-like in consistency in the course of time. It is readily soluble in all of the common organic solvents. It is soluble in 2 vols. of 50 p. c. alcohol and in 18 vols. of 30 p. c. alcohol. Even in water it is soluble in the ratio of 1:60. Because of this appreciable solubility in water, rose oil contains only a small fraction of the phenylethyl alcohol found in the leaves. The larger part of the alcohol remains in the aqueous distillate from which it cannot be separated by cohobation because of its great dilution.

With anhydrous calcium chloride phenylethyl alcohol forms a solid compound which can be used for its purification. Oxidation with chromic acid mixture yields phenyl acetaldehyde and phenylacetic acid, at times also its phenylacetic acid ester which

[1]) Radziszewski, Berl. Berichte **9** (1876), 372.

[2]) G. I. P. 164294. Comp. also Compt. rend. **136** (1903), 1676 and **137** (1903), 60.

melts at 28°. For the identification of phenylethyl alcohol its phenylurethane (m. p. 80°), its diphenylurethane (m. p. 99 to 100°) and acid phthalic acid ester (m. p. 188 to 189°) are used.

Phenylpropyl alcohol.

$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2OH$.

As cinnamic acid ester, normal phenylpropyl alcohol has been found in several resins and balsams, *e. g.* in Sumatra benzoes, in Oriental and American styrax and in the Honduras balsam which is frequently misnamed white Peru balsam. Probable is likewise its occurrence as cinnamate in xanthorrhœa resin and as acetate in cassia oil.

The phenylpropyl alcohol isolated from the above named resins is always accompanied by cinnamic alcohol from which it cannot be separated completely by fractionation. According to the method patented by Schimmel & Co.[1]) it can be obtained in a pure state by heating the mixture of alcohols with an equal part of concentrated formic acid. The cinnamic alcohol is thus resinified whereas the phenylpropyl alcohol is converted into the formate. The ester can be distilled with steam and then saponified.

Synthetically phenylpropyl alcohol can be obtained by the reduction of cinnamic alcohol with sodium amalgam in the presence of much water;[2]) or, according to the method of Bouveault and Blanc,[3]) by the reduction of cinnamic acid ester or the benzylacetic acid ester with sodium and absolute alcohol.

Phenylpropyl alcohol is a colorless, thick liquid possessing a faint peculiar odor resembling somewhat that of cinnamic alcohol and reminding of certain species of hyacinth. In ordinary solvents it is readily soluble. It is soluble in all proportions in 70 p. c. alcohol, in 1,5 vols of 60 p. c. alcohol and in about 3 vols. of 50 p. c. alcohol. In water it is not soluble in the ratio of 1:300.

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[1]) G. I. P. 116091. Comp. Chem. Zentralbl. **1901**, I. 69.

[2]) Rügheimer, Liebig's Annalen **172** (1874), 123. Comp. also Hatton and Hodgkinson, Chem. News **43** (1881), 1930; Chem. Zentralbl. **1881**, 407.

[3]) G. I. P. No. 164294.

In the above mentioned patent, Schimmel & Co. record the following constants:

B. p. 235°, resp. 119° (12 mm.); $d_{15°}$ 1,007.

When oxidized with chromic acid in glacial acetic acid, it yields hydrocinnamic acid (m. p. 49°). It can be more readily identified by its phenylurethane[1]) melting at 47 to 48°.

Cinnamic alcohol.

$C_6H_5 \cdot CH : CH \cdot CH_2OH$.

Cinnamic alcohol, formerly also designated styrone, is found in volatile oils, not as such, but as ester. As acetate it occurs in cassia oil; as cinnamate (styracin) in storax, also in the oils of hyacinth (?), xanthorrhœa resin, Peru balsam and Honduras balsam.

It is commonly obtained by saponification of the styracin in storax. Synthetically it can be obtained by reduction of cinnamic aldehyde diacetate and subsequent saponification of the resulting cinnamyl acetate.[2])

Cinnamic alcohol occurs in long, fine white needles which possess a hyacinth-like odor. At 33° they melt to a colorless, strongly refractive liquid, which boils at 257,5° (758 mm.), respectively at 117° (5 mm.) At $\frac{35°}{15°}$ its specific gravity lies between 1,01 and 1,03. In water it is sparingly soluble (about 1 : 250), also in petroleum ether. In the other solvents it is readily soluble. Of 30 p. c. alcohol about 50 to 60 vols., of 50 p. c. alcohol 4 to 5 vols. and of 60 p. c. alcohol about 2 vols. are needed to effect solution.

With platinum black, cinnamic alcohol is oxidized to cinnamic aldehyde, upon more violent oxidation to cinnamic acid (m. p. 133°) and finally to benzaldehyde and benzoic acid. Upon reduction with sodium amalgam in the presence of much water it can be converted into phenylpropyl alcohol.

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[1]) Walbaum, Berl. Berichte **33** (1900), 2300, footnote.
[2]) Barbier and Léser, Bull. Soc. chim. III. **33** (1905), 858.

Characteristic derivatives are the phenylurethane melting at 90 to 91,5° and the diphenylurethane melting at 97 to 98°.[1]) The latter is to be preferred to the phenylurethane since it has the more sharply marked melting point.

ALICYCLIC (HYDROAROMATIC) ALCOHOLS.

Dihydrocuminic alcohol.

This alcohol, the constitution of which has not yet been definitely determined, was recently found in the laboratory of Schimmel & Co.,[2]) to occur free and as ester, also in both optical modifications in gingergrass oil.

This alcohol is a colorless, rather viscid oil of a peculiar odor reminding of linalool and terpineol. From geraniol, its companion in gingergrass oil, it can be separated only with difficulty. Its isolation can best be effected by heating the mixture of alcohols with 2 parts of 90 p. c. formic acid on a waterbath to a temperature of 80°,[3]) whereby only the geraniol is destroyed. For two preparations thus purified, Walbaum and Hüthig[4]) record the following constants:

B. p. 226 to 227° (767 mm.), 92 to 93,5° (5 mm.); $d_{15°}$ 0,9510; α_D — 13° 18′; $n_{D20°}$ 1,49629.

B. p. 228 to 229° (755 mm.), 94 to 96° (4 to 5 mm.); $d_{15°}$ 0,9536; α_D + 12° 5′; $n_{D20°}$ 1,49761.

When oxidized with Beckmann's chromic acid mixture, dihydrocuminic aldehyde, $C_{10}H_{14}O$, results, thus proving that the alcohol in question, $C_{10}H_{16}O$, is a dihydrocuminic alcohol. Since no crystalline derivative of the alcohol has yet been obtained, it is identified by its oxidation to the aldehyde, the semicarbazone of which melts at 198 to 198,5°.

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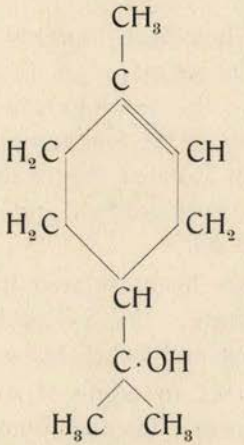
[1]) Report of Schimmel & Co. April **1910**, 173.

[2]) Report of Schimmel & Co. April **1904**, 57; October **1904**, 44; Walbaum and Hüthig, Journ. f. prakt. Chem. II. **71** (1905), 464.

[3]) Stronger formic acid and higher temperatures are to be avoided since the alcohol is thereby dehydrated to cymene. Even when the precautions stated are taken this change will take place to a slight extent.

[4]) *Loc. cit.* 466.

α-Terpineol.



By the action of dilute sulphuric acid on terpin hydrate (see p. 384) the liquid terpineol of commerce results. This, however, is not a chemical unit, but a mixture of isomeric compounds $C_{10}H_{18}O$, among which the α-terpineol, m. p. 35°, predominates. The presence of β-terpineol, m. p. 32°[1]) and the liquid terpineol-1[2]) has likewise been established.

In nature there apparently occurs only the α-terpineol, either optically active or inactive, the constitution of which has been established by the researches of Wallach,[3]) Wagner,[4]) Semmler and Tiemann.[5]) Although liquid terpineols have been isolated, it seems highly probable that they can be otained in the solid condition.

Solid *d*-α-terpineol has been observed in the oils of Malabar cardamom, sweet oranges, petit-grain, neroli, in Cayenne- and the lævogyrate Mexican lignaloe oils, also in oil from lovage-root. In Malabar cardamom oil it occurs probably for the most part as acetate. As ester only, namely as acetate and valerianate (?),

[1]) Stephan and Helle, Berl. Berichte **35** (1902), 2147.

[2]) Wallach, Liebig's Annalen **356** (1907), 218; **362** (1908), 269.

[3]) Liebig's Annalen **275** (1893), 103, 150; **277** (1893), 110; **291** (1896), 342; Berl. Berichte **28** (1895), 1773.

[4]) Berl. Berichte **27** (1894), 1652, 2273.

[5]) Semmler, Berl. Berichte **28** (1895), 2189; Tiemann and Semmler, *ibidem* **28** (1895), 1778; Tiemann and Schmidt, *ibidem* 1781; Tiemann, *ibidem* **29** (1896), 2616.

it occurs in cypress oil. In liquid form it has been isolated from marjoran oil.

Solid *l*-α-terpineol has been found in the wood turpentine oil from *Pinus palustris,* in camphor oil, in the oil from the leaves of *Laurus Camphora,* in the dextrogyrate Mexican lignaloe oil, in limette oil and niaouli oil, in the last mentioned also as valerianate. As a liquid it has been isolated from Canada snakeroot oil, the bark oil from *Ocotea usambarensis* and both free and as ester in European wormseed oil.

Solid *i*-terpineol has been isolated from cajeput oil in which it also occurs as acetate. As a liquid it has been obtained from the oils of nutmeg and boldo leaves.

Without reference as to angle of rotation, the presence of terpineol has been recorded for the following oils: kuromoji oil, lemon oil, oil of *Melaleuca uncinata* (?), gardenia oil, valerian oil (?). kesso root oil and erigeron oil. Probably the acetate also occurs in the German oil of *Pinus sylvestris.*

According to the statement of Bouchardat and Voiry,[1]) solid inactive terpineol m. p. 30 to 32° is formed by the action of very dilute sulphuric acid on terpin. However, it has not yet been definitely settled whether this is α- or β-terpineol. The solid, optically active modifications of α-terpineol can be obtained either, according to the method of Semmler,[2]) by boiling the *d*- or *l*-limonene monobromhydrate with the oxides of silver or lead; or, according to Wallach[3]) by shaking limonene monochlorhydrate with dilute potassium hydroxide solution, or by shaking homonopinol with dilute sulphuric acid.[4]) The simplest method is to prepare them as acetates by the simultaneous action of glacial acetic acid (comp. under camphene, p. 305) and sulphuric acid on limonene, or by the action of glacial acetic acid and zinc chloride on pinene.[5]) Note-worthy is also the formation of optically active solid terpineols from linalool by the action of acetic acid

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[1]) Compt. rend. **104** (1887), 996.

[2]) Berl. Berichte **28** (1895), 2189.

[3]) Liebig's Annalen **350** (1906), 154.

[4]) Liebig's Annalen **360** (1908), 98.

[5]) Ertschikowsky, Journ. russ. phys chem. Ges. **28** (1896), 132. According to Bull. Soc. chim. III. **16** (1896), 1584.

anhydride or formic acid,[1]) also of solid inactive terpineol from geraniol and formic acid.[2])

The solid inactive α-terpineol possesses the elder-blossom-like odor of the liquid to a slight degree only. It is very readily soluble in organic solvents and possesses the following properties:

M. p. 35°[3]); b. p. 217 to 218° (760 mm.), 104 to 105° (10 mm.); $d_{15°}$ 0,935 to 0,940; $n_{D20°}$ 1,48084.[4])

The following constants were observed in the laboratory of Schimmel & Co.:

M. p. 35°; b. p. 85° (3 mm.); $d_{15°}$ (supercooled) 0,9386; $n_{D20°}$ 1,48268.

In connection with a strongly active α-terpineol, obtained by shaking homonopinol with dilute sulphuric acid, Wallach[5]) observed the following constants:

M. p. 37 to 38°; b. p. 218 to 219°; $[\alpha]_D$ — 106° in 16,34 p. c. ethereal solution.

The optical activity is variable. The highest deviation observed in connection with a natural terpineol is $[\alpha]_D$ + 95° 9′ for the *d*-terpineol from oil of orange,[6]) and $[\alpha]_D$ — 27° 20′ for the *l*-terpineol from lignaloe oil.[7]) The highest deviation has been revealed by an artificially prepared *l*-terpineol, namely $[\alpha]_D$ — 117,5°.[8])

In connection with the commercial liquid products of their own manufacture, which consist only in part of α-terpineol and contain some β-terpineol and terpinenol-1, Schimmel & Co. observed the following constants:

B. p. 217 to 219°; $d_{15°}$ 0,935 to 0,940; $\alpha_D \pm 0°$; $n_{D20°}$ 1,481 to 1,484; soluble in about 9 vols. 50 p. c. alcohol, in 3 to 5 vols. of

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[1]) Stephan, Journ. f. prakt. Chem. II. **58** (1898), 109.

[2]) Stephan, *ibidem* **60** (1899), 244.

[3]) Wallach, Liebig's Annalen **275** (1893), 104.

[4]) Stephan, Journ. f. prakt. Chem. II. **58** (1898), 110; **60** (1899), 244.

[5]) Liebig's Annalen **360** (1908), 89.

[6]) Stephan, Journ. f. prakt. Chem. II. **62** (1900), 530.

[7]) Report of Schimmel & Co. October **1905**, 48.

[8]) Ertschikowsky, Journ. russ. phys. chem. Ges. **28** (1896), 132. According to Bull. Soc. chim. III. **16** (1896), 1584.

60 p. c. alcohol, and in abt. 2 vols. of 70 p. c. alcohol. With petroleum ether it should be miscible in all proportions, *i. e.* it should be free from water.

As to their chemical properties the inactive and both active modifications of α-terpineol behave alike. The derivatives, however, differ in part:

	Inactive modifications	Active modifications
Melting point	35°	37 to 38°
Nitrosochloride	112 to 113°	107 „ 108°
Nitrolpiperidide	159 „ 160°	151 „ 152°
Methoethyl heptanonolid	64°	46 „ 47°

α-Terpineol is a tertiary, unsaturated alcohol which yields addition products with bromine, nitrous acid anhydride, nitrogentetroxyde and nitrosylchloride. The nitrosochloride and the nitrolamine bases derived therefrom are especially adapted for the characterization of the α-terpineol (see p. 380).

The liquid dibromide yields a tribromide when treated with hydrogen bromide in glacial acetic acid solution. Further treatment with bromine converts it into dipentene tetrabromide melting at 124°.

With hydrohalogen acids the corresponding dipentene dihalogen hydrides result. The dihydriodide $C_{10}H_{18}I_2$ (m. p. 77 to 78°), obtained by shaking the alcohol with concentrated hydriodic acid, can be utilized for the identification of terpineol.[1]) Toward mineral acids and also toward some organic acids, terpineol is rather unstable. Whereas shaking with dilute sulphuric acid hydrates it to terpinhydrate,[2]) boiling therewith causes it to be dehydrated with the formation of terpinene together with a little dipentene and cineol. Potassium acid sulphate has a similar effect producing principally dipentene; also phosphoric acid producing principally terpinolene with small amounts of terpinene and cineol; also oxalic acid which likewise produces terpinolene.[3]) Acetic acid anhydride also dehydrates terpineol, especially when heated, producing dipentene. Hence it is not possible to esterify

[1]) Wallach, Liebig's Annalen **230** (1885), 265.

[2]) Tiemann and Schmidt, Berl. Berichte **28** (1895), 1781.

[3]) Wallach, Liebig's Annalen **275** (1893), 104; Baeyer, Berl. Berichte **27** (1894), 447.

terpineol quantitatively with this agent without exercising special precautions.[1]) For further details concerning terpinylacetate see the chapter on esters.

When oxidized with dilute permanganate solution, terpineol is first converted into the polyatomic alcohol $C_{10}H_{20}O_3$, 1,2,8-trihydroxymenthane (m. p. of the inactive modification 122°). Chromic acid mixture oxidizes this to a ketolactone $C_{10}H_{16}O_3$ (m. p. of the active modification 46 to 47°, of the inactive 64°). The study of this compound has contributed much toward the establishment of the constitution of terpineol as expressed by the formula Δ^1-terpene-8-ol. More violent oxidation of the terpineol and of the ketolactone with chromic acid mixture or nitric acid yields terpenyl and terebinic acids.[2])

Of special interest is the conversion of terpineol, through the tribromide and the nitrosochloride, into derivatives of carvone.[3])

The hydroxy group of terpineol reacts with phenyl*iso*cyanate when both compounds are mixed and set aside at room temperature for a time. Sometimes crystals of diphenylurea separate at first, from which the liquid mixture is separated with the aid of cold anhydrous ether or, better still, with low boiling petroleum ether. After careful evaporation of the solvent, the urethane separates in fine needles. Recrystallized from alcohol, the inactive compound melts at 113°.[4]) The urethane obtained from optically active terpineol is likewise inactive. The α-naphthylurethane,[5]) melting at 147 to 148° can also be utilized for the identification of α-terpineol. Especially suited to this purpose is the nitrosochloride.

According to Wallach[6]) the preparation of the nitrosochloride is accomplished in the following manner: To a solution of 15 g. terpineol in 15 ccm. glacial acetic acid and 11 ccm. ethylnitrite,

[1]) Ginsberg, Journ. russ. phys. chem. Ges. **29** (1897), 249. According to Chem. Zentralbl. **1897**, II. 417; Report of Schimmel & Co. October **1897**, 63. Compare also the chapter "Examination of volatile oils" under acetylation.

[2]) Wallach, Liebig's Annalen **227** (1893), 117, 120; **291** (1896), 345; Berl. Berichte **28** (1895), 1775; Tiemann and Mahla, Berl. Berichte **29** (1896), 928; Tiemann, *ibidem* 2616.

[3]) Wallach, Liebig's Annalen **281** (1894), 140; **291** (1896), 346.

[4]) Wallach, Liebig's Annalen **275** (1893), 104.

[5]) Report of Schimmel & Co. October **1906**, 41.

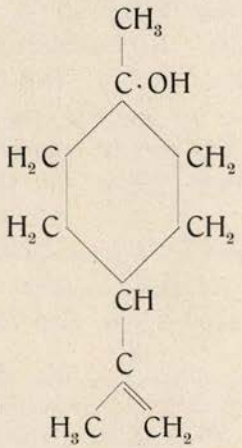
[6]) Liebig's Annalen **277** (1893), 120; **360** (1908), 90.

well cooled in a freezing mixture and while well shaken, 6 ccm. of hydrochloric acid dissolved in an equal volume of glacial acetic acid, are added drop by drop. At the close of the reaction the nitrosochloride is precipitated with ice water in the form of an oil which, however, soon crystallizes. The solid compound is purified by recrystallization from hot acetic ether or methyl alcohol and melts at 112 to 113°. The active modification melts at 107 to 108°.

With piperidine in alcoholic solution, the nitrosochloride yields the nitrolpiperidine base $C_{10}H_{17}(OH)NONC_5H_{10}$, which is difficultly soluble in ether, crystallizes from methyl alcohol in needles that melt at 159 to 160°. These data by Wallach refer to the derivative obtained from an optically inactive terpineol. The nitrol piperidide obtained from an optically active material melts several degrees lower, namely at 151 to 152°.[1])

With aniline a terpineol nitrolanilide, m. p. 155 to 156°, is obtained.

β-Terpineol.



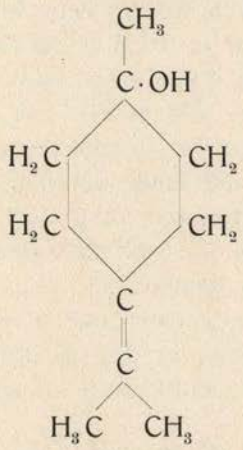
As already mentioned under α-terpineol, β-terpineol results together with α-terpineol when terpin hydrate is acted upon by dilute acids. Thus far β-terpineol has not been found in volatile

[1]) Report of Schimmel & Co. October 1897, 11; Wallach, Liebig's Annalen 360 (1908), 90.

oils. Schimmel & Co.[1]) have isolated the inactive modification from fraction 212 to 215° of commercial terpineol by freezing. It crystallizes in needles that melt at 32 to 33°; b. p. 209 to 210° (752 mm.); $d_{15°}$ 0,923 (in the supercooled condition); $n_{D20°}$ 1,47470.

Of its derivatives the following may here be mentioned: the nitrosochloride (m. p. 103°),[2]) the nitrolpiperidine base (m. p. 108°), the nitrolaniline base (m. p. 110°) and the phenylurethane (m. p. 85°). When oxidized with permanganate, β-terpineol yields trihydroxyterpane melting at 118°.

γ-Terpineol.



γ-Terpineol has not yet been found in nature. v. Baeyer[3]) obtained it by reducing tribrom-1,4,8-terpane, which in time he had obtained by brominating dipentene dihydrobromide.

It also results when terpin is heated with oxalic acid or phosphoric acid.[4])

Recrystallized from ether, γ-terpineol forms thick prisms melting at 69 to 70°, which possess the agreable odor of elderblossoms. In order to identify γ-terpineol, it can be converted into the acetate, the blue nitrosochloride of which melts at 82°.

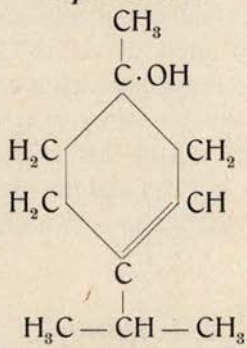
[1]) Report of Schimmel & Co. April **1901**, 79; Stephan and Helle, Berl. Berichte **35** (1902), 2147.

[2]) Wallach, Liebig's Annalen **345** (1903), 128; Comp. also Wallach, *Terpene u. Campher*, p. 333.

[3]) Berl. Berichte **27** (1894), 443.

[4]) *Ibidem* 715.

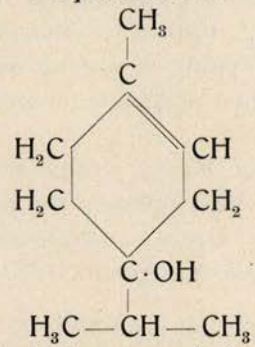
Terpinenol-1.



This alcohol also has not yet been found in volatile oils. Of interest is its occurrence in the first fraction of commercial liquid terpineol.[1]) Synthetically it was prepared by Wallach[2]) from Δ^3-*iso*-propylhexenone. — B. p. 208 to 210°; $d_{18°}$ 0,9265; $n_{D18°}$ 1,4781.[1])

With hydrohalogens the alcohol is converted into terpinene derivatives. Oxidation with dilute permanganate solution converts it into 1,3,4-trihydroxyterpane, m. p. 120 to 121°. Further oxidation converts it into α,α'-dihydroxymethyl *iso*propyladipinic acid, m. p. 189°. When heated with acids the trihydroxyterpane yields a mixture of *p*-cymene and Δ^1-menthenone, the semicarbazone of which melts at 224 to 225°. These compounds can be utilized for the identification of terpinenol-1.

Terpinenol-4.



This alcohol which in its general characteristics closely resembles α-terpineol, is derived from terpinene. It has been dis-

[1]) Wallach, Liebig's Annalen **356** (1907), 218.

[2]) *Ibidem* **362** (1908), 280.

covered only recently. In nature it has been found in the oils of juniper, Ceylon cardamoms, nutmeg, marjoram and European wormseed. Synthetically, the active modification has been obtained by shaking sabinene, sabinene hydrate and thujene with dilute sulphuric acid,[1]) the inactive modification by shaking terpinene dihydrochloride with dilute potassium hydroxide solution. (Comp. also p. 320.)

The properties of the active modification have been recorded as follows:

B. p. 209 to 212°; $d_{19°}$ 0,9265; $\alpha_D + 25° 4'$; $n_{D19°}$ 1,4785.[2])

Those of the inactive modification are:

B. p. 212 to 214°; d 0,9290; n_D 1,4803.[3])

This alcohol is known only in the liquid condition. Its odor is less pleasant than that of terpineol. When acted upon in glacial acetic acid solution with hydrohalogen the corresponding terpinene dihydrohalides result. When shaken with dilute sulphuric acid terpinene terpin, m. p. 137°, results. In as much as this hydration is much slower than that of terpineol to terpin hydrate, this serves as a means for the separation of the two alcohols.

Upon oxidation with dilute permanganate solution, Δ^1-terpinenol-4 yields in the main 1,2,4-trihydroxyterpane, $C_{10}H_{17}(OH)_3$. With its water of crystallization it melts at 116 to 117°, freed therefrom at 128 to 129°; $[\alpha]_D$ abt. 21,5°. When distilled with hydrochloric acid, this compound yields carvenone (m. p. of the semicarbazone 200 to 201°), with little cymene. Upon further oxidation with alkaline permanganate solution a mixture of active and inactive α,α'-dihydroxy-α-methyl-α'-*iso*propyl-adipinic acid, $C_{10}H_{18}O_6$, results. It melts at 205 to 206°, respectively at 188 to 189°. Distilled with steam they readily pass over in the form of the volatile dilactones which melt at 63 to 64° and 72 to 73° respectively. By more energetic oxidation the dihydroxy acid yields ω-dimethyl acetonyl acetone as "Ab-

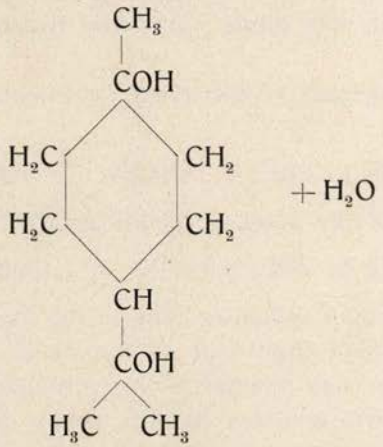
[1]) Wallach, Liebig's Annalen **356** (1907), 215; **360** (1908), 94, 97; **362** (1908), 279; Berl. Berichte **40** (1907), 594.

[2]) Wallach, Liebig's Annalen **356** (1907), 215.

[3]) *Ibidem* **350** (1906), 155.

bau" product. The melting point of its dioxime is 137°, that of its semicarbazone 201 to 202°.

Terpinhydrate.



From the theoretical and historical points of view, terpinhydrate is an important compound. But technically also it is of importance as the material from which terpineol is made. (Comp. p. 375.) It is readily formed from turpentine oil by letting this stand with water containing an acid. It is characterized by a remarkable capacity for crystallization, hence it was observed relatively early. According to older statements, terpinhydrate is said to occur in the oils of cardamom and basilicum. However, these statements have not been substantiated by recent observations. This much appears certain that the terpinhydrate was not present in the original oil but must have been formed upon prolonged standing.

Terpinhydrate melts at 116 to 117°. When heated, it looses a molecule of water with the formation of anhydrous terpin which melts at 104 to 105° and boils at 258° (corr.).[1])

Terpin exists in two stereoisomeric modifications, namely a *cis*- and a *trans*-form. The *cis*-terpin only, however, is capable of yielding a hydrate.[2])

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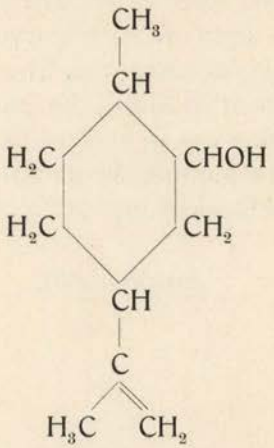
[1]) Wallach, Liebig's Annalen **230** (1885), 248.

[2]) Baeyer, Berl. Berichte **26** (1893), 2865.

Dihydrocarveol.



Dihydrocarveol, $C_{10}H_{18}O$, has only recently been found in caraway oil.[1]) Artificially prepared it has been known for a longer period. Thus it has been prepared from carvone by reduction with sodium and alcohol; also by the reduction of carvoxime to carvylamine which, upon treatment with nitrous acid, yields dihydrocarveol.

Dihydrocarveol is a liquid which possesses the following properties:

B. p. 224°; $d_{22°}$ 0,935; n_D 1,48506 (for dihydrocarveol from dihydrocarvylamine).[2])

B. p. 112° (14 mm.), 224 to 225° (under ord. pressure); $d_{20°}$ 0,927; n_D 1,48168 (for dihydrocarveol from carvone).[3])

In the laboratory of Schimmel & Co. the following constants were observed in connection with a dihydrocarveol isolated from caraway oil:

B. p. 100 to 102° (7 to 8 mm.); $d_{15°}$ 0,9368; α_D — 6° 14′; $n_{D20°}$ 1,48364.[4])

Dihydrocarveol deviates the ray of polarized light in the same direction as does the carvone used for its preparation.

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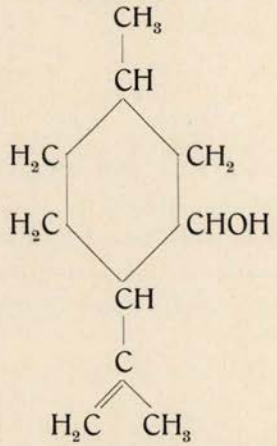
[1]) Report of Schimmel & Co. April **1905**, 20.
[2]) Wallach, Berl. Berichte **24** (1891), 3990.
[3]) Wallach, Liebig's Annalen **275** (1893), 111.
[4]) Report of Schimmel & Co. April **1905**, 20.

When oxidized with chromic acid in glacial acetic acid,[1]) dihydrocarvone results (b. p. 221 to 222°; $d_{19°}$ 0,928; n_D 1,47174). The dihydrocarvone from *d*-dihydrocarveol is lævogyrate, that from *l*-dihydrocarveol is dextrogyrate. The corresponding active dihydrocarvoxime melts at 88 to 89°, the inactive modification at 115 to 116°. This oxidation can be utilized for the identification of dihydrocarveol. For this purpose the phenylurethane is also serviceable. The active modifications melt at 87°, the inactive one at 93°.[2])

Iso*pulegol.*



*Iso*pulegol, $C_{10}H_{18}O$, has not yet been found in volatile oils. It results from citronellal when this is treated with acids. The observation made by Schimmel & Co.[3]) *viz.,* when the oil of *Barosma pulchellum* is distilled the odor of *iso*pulegol is noticeable, is possibly referrable to this circumstance.

*Iso*pulegol boils at 91° (13 mm.); $d_{17.5°}$ 0,9154; α_D — 2° 40′; n_D 1,47292.[4])

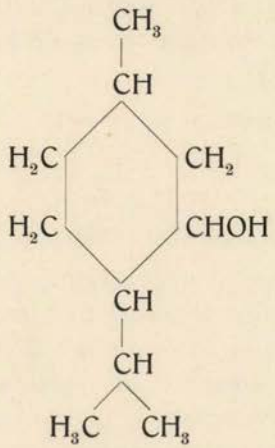
The acetate boils at 104 to 105° (10 mm.).[5])

For purposes of identification, the alcohol is oxidized to pulegone[6]) and this characterized by means of its oxime (m. p.

[1]) Wallach, Liebig's Annalen **275** (1893), 115.
[2]) Wallach, *ibidem* 112.
[3]) Report of Schimmel & Co. April **1909**, 96.
[4]) Tiemann and Schmidt, Berl. Berichte **29** (1896), 914.
[5]) Barbier and Léser, Compt. rend. **124** (1897), 1309.
[6]) Wallach, Liebig's Annalen **365** (1909), 251.

of the active modification abt. 121°, of the inactive abt. 140°), or its semicarbazone (m. p. of the active modifications 172 to 173°, of the inactive 182 to 183°).

Menthol.



Menthol (peppermint camphor), $C_{10}H_{20}O$, is found in the peppermint oils of which the lævogyrate menthol constitutes the principal constituent. The oil of *Hyptis suaveolens* also consists in large part of menthol, but the direction of its optical rotation has not yet been ascertained. Menthol separates from peppermint oil upon cooling. If the menthol content be large the separation takes place even at ordinary temperature. In peppermint oil, menthol is likewise contained as acetate and *iso*valerate, also as ester of an acid $C_8H_{12}O_2$. Artificially menthol is obtained from menthone and pulegone.[1]) In the presence of an excess of hydrogen, menthone yields menthol only; if, however, solvents are used which themselves do not generate hydrogen with the sodium, menthopinacone is also formed. Both *l*- and *d*-menthone yield according to both methods, also with change of temperature, a strongly lævogyrate mixture from which *l*-menthol (m. p. 43,5°) also a slightly dextrogyrate *iso*menthol (m. p. 78 to 81°; $[\alpha]_D + 2°$) can be isolated.[2])

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[1]) Beckmann and Pleissner, Liebig's Annalen **262** (1891), 30, 32.

[2]) Beckmann, Journ. f. prakt. Chem. II. **55** (1897), 19, 30.

Menthol crystallizes in colorless needles or prisms which belong to the hexagonal system. It is characterized by its strong, peppermint-like odor and cooling taste.

Of physical constants the following are recorded:

M. p. 42°; b. p. 211,5° (736 mm.).[1])

M. p. 42,3°; b. p. 212,5° (corr. 742 mm.); $d_{4°}^{20°}$ 0,890 for solid and $d_{4°}^{44.6°}$ 0,8810 for liquified menthol; $[\alpha]_{D46°}$ — 49,86° likewise for molten menthol.[2])

B. p. 215,5° (758 mm.); $\alpha_{D31°}$ — 43°45′ for menthol in supercooled condition.[3])

M. p. 43°; $[\alpha]_{D20°}$ — 49,35° (in 20 p. c. alcoholic solution), — 50,59° (in 10 p. c. alcoholic solution):[4]) $n_{C43°}$ 1,4479.[5])

According to recent observations, the melting point of perfectly pure menthol lies between 43,5 and 44,5°.

Menthol is a saturated secondary alcohol. When dehydrated with potassium acid sulphate, zinc chloride, &c., it is converted mainly into the hydrocarbon $C_{10}H_{18}$, Δ^3-*p*-menthene. The compounds obtained by replacing the hydroxy group by halogen are liquid and little characteristic. With hydrogen iodide and phosphorus it is reduced to hexahydrocymene, $C_{10}H_{20}$.[6]) With chromic acid mixture it is oxidized to the corresponding ketone $C_{10}H_{18}O$, menthone.[7]) With potassium permanganate the same oxidation products result that are obtained from the oxidation of menthone, *viz.*, ketomenthylic acid and β-methyladipic acid melting at 88 to 89°. As a result of these oxidation experiments the above-mentioned formula has been assigned to menthol. This formula has been strengthened by the conversion of menthone into 3-chlorcymene effected by Jünger and Klages.[8]) That menthol

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[1]) Arth, Annal. de Chim. et Phys. VI. 7 (1886), 438.

[2]) Long, Chem. Zentralbl. 1892, II. 525.

[3]) Power and Kleber, Pharm. Rundschau (New York) 12 (1894), 162; Arch. der Pharm. 232 (1894), 647, 653.

[4]) Beckmann, Liebig's Annalen 250 (1889), 327; Journ. f. prakt. Chem. II. 55 (1897), 15.

[5]) Brühl, Berl. Berichte 21 (1888), 457, table.

[6]) Berkenheim, Berl. Berichte 25 (1892), 688.

[7]) Beckmann, Liebig's Annalen 250 (1889), 325.

[8]) Berl. Berichte 29 (1896), 314.

could be converted into cymene by heating it with anhydrous copper sulphate to 250 to 280° had previously been demonstrated by Brühl.[1])

Of menthol esters a considerable number has been prepared. The above mentioned acetate, also the *iso*valerate are described in the chapter on "Esters". For other esters special reference should be had to the paper by Tschugaeff[2]) who has given special attention to their optical rotation.

According to Monteil,[3]) chloral yields two liquid compounds with menthol, *viz.*, chloralmonomenthol and chloraldimenthol. They result upon melting together the calculated amounts of the components.

Owing to the peculiar physical properties of menthol, its identificaton ought to afford but few difficulties. If necessary its phenylurethane obtained by the action of phenyl*iso*cyanate on menthol may be utilized. This derivative, which was first prepared by Leuckart, melts at 111 to 112° and turns the plane of polarized light in the same direction as does menthol. It can be decomposed by sodium ethylate, but the menthol is thereby inactivated.[4])

Other derivatives by means of which menthol can readily be characterized, are menthylbenzoate, resulting upon heating menthol with benzoic acid anhydride, which is difficultly volatile with water vapor and which melts at 54,5°;[5]) the dimenthyl ester of oxalic acid, melting at 67 to 68°; the dimethyl ester of succinic acid, melting at 62°; the monomenthyl ester of phthalic acid, melting at 110° and the dimenthyl ester of the same acid melting at 133°.

A mixture of menthol and menthone can be separated by converting the latter into its oxime and shaking out the oxime from the ethereal solution by means of dilute sulphuric acid.[6])

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[1]) Berl. Berichte **24** (1891), 3374.

[2]) Berl. Berichte **31** (1898), 364.

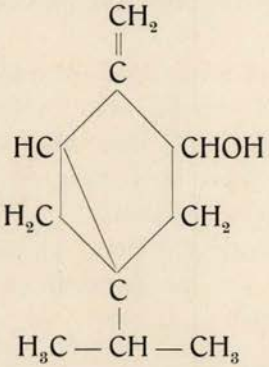
[3]) l'Union Pharm. Acc. to Zeitschr. d. allg. österr. Apoth. Ver. **46** (1908), 272.

[4]) Beckmann, Journ. f. prakt. Chem. II. **55** (1897), 29.

[5]) Beckmann, Liebig's Annalen **262** (1891), 31; Journ. f. prakt. Chem. II. **55** (1897), 16.

[6]) Beckmann, Journ. f. prakt. Chem. II. **55** (1897), 17.

Sabinol.



Sabinol, $C_{10}H_{16}O$, is contained in oil of savin partly free, partly as acetate. Presumably it also occurs in oil of cypress.

The constants of sabinol from oil of savin are as follows:

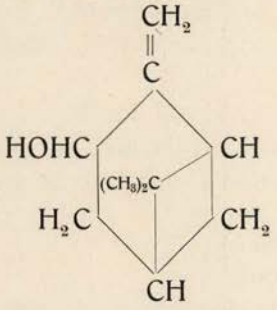
B. p. 210 to 213°, 105 to 107° (20 mm.).[1])

Semmler[2]) records $d_{20°}$ 0,9432; n_D 1,488.

When oxidized with dilute permanganate solution, sabinol glycerol (m. p. 152 to 153°) is formed, which upon further oxidation yields α-tanacetogendicarboxylic acid (m. p. 140°). This reaction may be used for the identification of sabinol.

In general, the derivatives of this alcohol have been but little investigated.

Pinocarveol.



This dicyclic alcohol, the constitution of which is probably correctly expressed by the above formula, occurs in all probability

[1]) Report of Schimmel & Co. October 1895, 44.

[2]) Berl. Berichte 33 (1900), 1459.

in the last fractions of the oil of *Eucalyptus Globulus.*[1]) Artificially it can be obtained by the action of nitrous acid upon pinylamine acetate or nitrate.[2])

For the alcohol isolated from eucalyptus oil Wallach records the following constants:

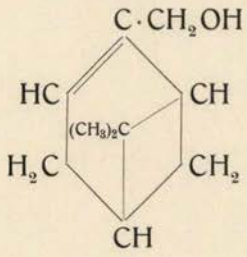
B. p. 92° (12 mm.); $d_{20°}$ 0,9745; $n_{D20°}$ 1,49630;

for artificial pinocarveol:

B. p. 215 to 218°; $d_{22°}$ 0,978; $n_{D20°}$ 1,49787.

For its identification the phenylurethane is suited. It melts at 82 to 84° (a small part thereof melts at 95°).

Myrtenol.



Myrtenol, $C_{10}H_{16}O$, is the name applied by v. Soden and Elze[3]) to an alcohol which they found, mostly as acetic ester, in oil of myrtle.

Its acid phthalic ester melts at 116° from which the alcohol can be regenerated as a colorless oil possessing the odor of myrtle. Its constants are:

B. p. 220 to 221° (751 mm.), 79,5 to 80° (3,5 mm.); $d_{15°}$ 0,985; $\alpha_D + 49° 25'$.

Myrtenol has been examined closer by Semmler and Bartelt[4]) who have found the following constants:

B. p. 222 to 224°, 102,5° (9 mm.); $d_{20°}$ 0,9763; $\alpha_D + 45° 45'$; n_D 1,49668.

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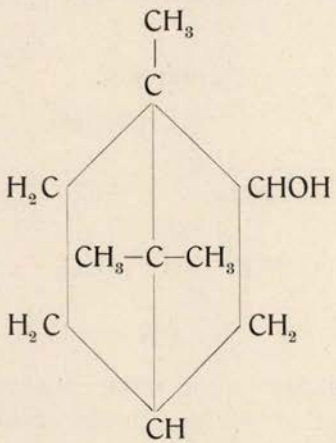
[1]) Wallach, Liebig's Annalen **346** (1906), 227.
[2]) Wallach, Liebig's Annalen **277** (1893), 149.
[3]) Chem. Ztg. **29** (1905), 1031.
[4]) Berl. Berichte **40** (1907), 1363.

With phosphorus pentachloride, a chloride $C_{10}H_{15}Cl$ was obtained which upon reduction with alcohol and sodium yielded pinene. The above formula by Semmler and Bartelt is based on these facts. Upon oxidation with chromic acid, the aldehyde myrtenal $C_{10}H_{14}O$ results (b. p. 87 to 90° under 10 mm.; $d_{20°}$ 0,9876; n_D 1,50420). It is further characterized by its semicarbazone, m. p. 230°, and its oxime melting at 71 to 72°. For identification, myrtenol can be either converted into the acid phthalic ester (m. p. 114 to 115°) or oxidized to myrtenal.

Borneol.



As such borneol, $C_{10}H_{18}O$, is found in both optically active modifications, as ester mostly in the lævogyrate modification. Borneo camphor from *Dryobanalops Camphora* is *d*-borneol, Ngai camphor (or *Ngai-fên*)[1]) from *Blumea balsamifera* consists entirely or in part of lævogyrate borneol.

In addition, *d*-borneol has been found in the oils of Siam cardamoms, nutmeg, lavender, rosemary, and spike; *l*-borneol in the oil from the buds of *Pinus maritima,* also in the oils of thuja, citronella, Canada snake root, coriander, yellow pine, valerian, kesso root and feverfew. Furthermore the occurence of borneol is reported in a number of oils without mention of the direction of rotation, *viz.,* in larch needle oil, in the oil from the needles and cones of *Picea rubens,* in cedar leaf oil, in the

[1]) Report of Schimmel & Co. April 1895, 76; April 1909, 147.

oils of ginger, *Piper camphoriferum,* camphor, cinnamon root, sage, thyme, golden rod, and *Achillea nobilis.*

As ester borneol occurs in the oils from the leaves and cones (?) of *Abies alba,* in that of the needles of *Picea excelsa,* the oil of *Pinus montana,* in the German and Swedish oils of *Pinus sylvestris* (?), in the oil of hemlock leaves, in the oils of the needles and cones of *Picea canadensis* and *P. rubens,* in the oils of the needles and twigs of *Larix americana,* in the oil of the twigs of *Abies canadensis,* furthermore in the needle oils of *Picea nigra, Abies balsamea, Abies sibirica, Larix europea* (?) and *Callitris glauca;* also in the oils of coriander, *Satureja Thymbra, Thymus capitatus,* valerian, kesso root and golden rod. As butyrate borneol has been found in valerian oil, and as *iso*valerate in valerian oil and kesso root oil.

Artificially borneol can be obtained by the reduction of *d*- or *l*-camphor by means of sodium in alcoholic solution[1]) or in indifferent solvents.[2]) However, the borneol thus obtained is never pure since it consists of a mixture of borneol and *iso*borneol, the latter being probably stereoisomeric with the former. When alcohol is used, less *iso*borneol is obtained than when indifferent solvents are employed. In the latter case as much as 5 p. c. camphor pinacone is also formed.[3]) From the mixture of the two borneols, pure borneol can be obtained by converting it into the acetate or benzoate. Upon cooling, the borneol acetate, respectively benzoate crystallizes out and can be saponified. From pinene (turpentine oil) also borneol can be obtained, either as ester by heating with acids, *e. g.*, benzoic acid, oxalic acid, or by converting the pinene into bornylchloride and subsequent change of this compound into borneol or into camphor and *iso*borneol (see under camphane).

Crystallized from ligroin, pure borneol forms shiny leaflets or plates belonging to the hexagonal system.[4]) It possesses an odor similar to camphor but also reminding of ambra. It melts at 203 to 204° (preparations containing *iso*borneol melt at 206 to 208°) and boils at 212°. Like camphor, borneol is volatile at

[1]) Wallach, Liebig's Annalen **230** (1885), 225.
[2]) Beckmann, Berl. Berichte **21** (1888), rep. 321.
[3]) Beckmann, Journ. f. prakt. Chem. II. **55** (1897), 36.
[4]) Traube, Journ. f. prakt. Chem. II. **49** (1894), 3.

ordinary temperature but not to the same degree as the former. According to Plowman,[1]) the specific gravity of *d*-borneol is 1,011, that of *l*-borneol 1,02.

The angle of rotation, as found by Beckmann,[2]) is $+37{,}44°$ for *d*-borneol. In agreement therewith is the statement by Haller[3]) who found $[\alpha]_D$ $+37{,}63°$ for an alcohol regenerated from the crystallized acetate. For natural *l*-borneol, Beckmann found $[\alpha]_D$ $-37{,}74°$,[2]) Haller $[\alpha]_D$ $-37{,}77°$.[3]) A somewhat higher angle of rotation, *viz.*, $-39°25'$, was observed for the *l*-borneol known as *Ngai-fên.*[4]) The borneol found in most volatile oils is more or less of a racemic mixture.

The dextrogyrate and lævogyrate modifications of borneol behave alike chemically. Although borneol is a saturated alcohol, it forms unstable addition products with bromine and hydrohalogen[5]) which, however, are not suited for purpose of identification. Hydrohalogens, or better phosphorus halides, also convert borneol into the bornyl halides, which, however, are more satisfactorily prepared from pinene. As a secondary alcohol, borneol upon oxidation is first converted into the corresponding ketone $C_{10}H_{16}O$, camphor. A change in the direction of rotation is not effected thereby. When stronger or acid oxidizing agents are employed, oxidation products of camphor, *viz.*, camphoric acid, or those of camphene may also be produced. Toward dehydrating agents, such as zinc chloride and dilute sulphuric acid, borneol is very stable.[6]) In this respect it behaves very differently from the isomeric *iso*borneol. When treated with phosphorus pentachloride it yields bornylchloride which upon boiling with aniline is converted into camphene.

Numerous ethers and esters of borneol have been prepared. Some of the latter are crystalline and can be utilized for the identification of the borneol. The formate, acetate, valerate and benzoate are described in the chapter on "Esters".

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[1]) Pharmaceutical Journ. **33** (1874), 711.

[2]) Liebig's Annalen **250** (1889), 353; Journ. f. prakt. Chem. II. **55** (1897), 33.

[3]) Compt. rend. **109** (1889), 30; see also Haller, Compt. rend. **112** (1891), 143, On the influence of solvents on the angle of rotation.

[4]) Report of Schimmel & Co. April **1895**, 76.

[5]) Wallach, Liebig's Annalen **230** (1885), 226.

[6]) Bertram and Walbaum, Journ. f. prakt. Chem. II. **49** (1894), 8.

By heating borneol with potassium hydroxide to 250 to 280°, Guerbet[1]) accomplished an almost quantitative direct change to campholic and *iso*campholic acids.

In order to determine the presence of borneol in volatile oils, fraction 205 to 215° is used. Upon cooling borneol not infrequently crystallizes out.

For its identification the bornylphenylurethane is prepared with the aid of carbanil. It melts at 138 to 139[2]) and is optically active in the same direction as the underlying borneol. The acetate melting at 29° can also be used, as well as the addition products of borneol with chloral and bromal. That with chloral melts at 55 to 56°,[3]) that with bromal at 105 to 106°.[4]) Finally, borneol can be oxidized with Beckmann's chromic acid mixture to camphor and the latter identified by means of its oxime which melts at 118 to 119°.

Occasionally it is necessary to separate a mixture of borneol and camphor. In such a case one can proceed according Haller's[5]) method whereby the mixture is heated with succinic acid anhydride, thus converting the borneol into its acid succinic acid ester, the sodium salt of which is soluble in water and hence can readily be separated from the camphor. In place of succinic acid anhydride, phthalic acid anhydride can be employed. The benzoic and stearic esters of borneol, which can be obtained by heating with the corresponding acid anhydrides, are difficultly volatile. Hence any camphor can be separated from these by steam distillation. On the other hand, camphor can be converted into its oxime and this be separated from the mixture by shaking with 25 p. c. sulphuric acid.

For the quantitative determination of borneol in such a mixture, a very concentrated solution thereof in a suitable solvent (xylene) can be acetylized and the alcohol content ascertained by means of the ester number.

If *iso*borneol be present, this can be converted into camphene by heating with benzoic acid, benzoic acid anhydride or stearic

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[1]) Compt. rend. **147** (1908), 70; **148** (1909), 98.

[2]) Bertram and Walbaum, Journ. f. prakt. Chem. II. **49** (1894), 5.

[3]) Haller, Compt. rend. **112** (1891), 145.

[4]) Minguin, Compt. rend. **116** (1893), 889; Bertram and Walbaum record, *loc. cit.*, 98 to 99°.

[5]) Compt. rend. **108** (1889), 1308.

acid and the borneol regenerated from its ester. By heating for 1/4 to 1/2 hour with a mixture of 20 p. c. sulphuric acid and 80 p. c. methyl alcohol, the *iso*borneol only[1]) is converted into the methyl ether. In order to differentiate borneol from *iso*borneol Tschugaeff's method, based on the behavior of nitric acid toward the two alcohols, is well suited.[2]) With pure concentrated nitric acid, borneol develops red vapors, but pure *iso*borneol never. Oxidizing agents attack borneol more readily. It is also noteworthy that the derivatives of borneol are more difficultly soluble than those of *iso*borneol.

By treating camphene hydrochloride with milk of lime, Aschan[3]) prepared a new borneol designated *camphene hydrate*. It consists of a hard, white crystaline mass that melts at 142° and boils at 205°. The melting point of the sublimed substance is 150 to 151°. The odor is moldy and menthone-like. Characteristic of the new alcohol is the readiness with which it looses water thus regenerating camphene. The loss of water results even when the alcohol is shaken with warm, dilute mineral acids, or when it is boiled with glacial acetic acid, or sometimes even upon distillation.

Iso*borneol.*

This alcohol which results together with borneol upon reduction of camphor, and which, according to the latest views, is regarded as stereoisomeric with borneol, can also be obtained upon hydration of camphene.[4]) According to Bertram and Walbaum it melts at 212° in the sealed tube. Its boiling point cannot be ascertained since the alcohol begins to sublime before the boiling temperature has been reached. Its phenylurethane melts at 138 to 139° and regenerates *iso*borneol when treated with alcoholic potassa. When heated with dehydrating agents camphene results. The reactions by means of which *iso*borneol can be distinguished from borneol have already been discussed under the latter.

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[1]) Bertram and Walbaum, Journ. f. prakt. Chem. II. **49** (1894), 8; Hesse, Berl. Berichte **39** (1906), 1144.

[2]) Chem. Ztg. **26** (1902), 1224.

[3]) Berl. Berichte **41** (1908), 1092.

[4]) Bertram and Walbaum, Journ. f. prakt. Chem. II. **49** (1894), 1.

Thujyl alcohol.

Thujyl alcohol (tanacetyl alcohol), $C_{10}H_{18}O$, occurs in oil of wormwood, in part as such, in part as esters of acetic, valeric and possibly also of palmitic acids.

Artificially it was obtained by Semmler[1]) and by Wallach[2]) by the reduction of thujone. The constitution of thujone has not yet been definitely ascertained. (Comp. thujone).

Semmler[1]) found:

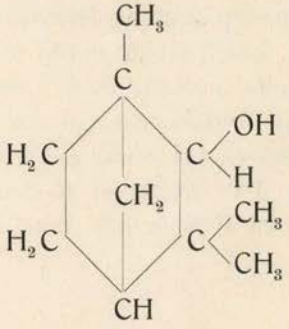
B. p. 92,5° (13 mm.); $d_{20°}$ 0,9249; n_D 1,4635.

Wallach[2]) has recorded the following constants:

B. p. 210 to 212°; $d_{20°}$ 0,9265.

Thujyl alcohol reveals the properties of a secondary alcohol; it is readily oxidized to the ketone thujone. It is this property that is used for its identification. Thujone oxime melts at 54°.

Fenchyl alcohol.



Fenchyl alcohol, to which Semmler has assigned the above formula, has thus far been found but once in a volatile oil,[3]) namely in the oil obtained by steam distillation from the stumps of the yellow pine or *Pinus palustris* several years after the timber had been cut. Artificially it is obtained by the reduction of fenchone. According to Barbier and Grignard[4]) fenchyl

[1]) Berl. Berichte **25** (1892), 3344.
[2]) Liebig's Annalen **272** (1893), 109.
[3]) Report of Schimmel & Co. April **1910**, 107.
[4]) Bull. Soc. chim. IV. **5** (1909), 512, 519.

alcohol results together with other alcohols when French turpentine oil is hydrated. These investigators assume that it is formed from the β-pinene present, an assumption that has not yet been proven.

Fenchyl alcohol obtained by reduction of fenchone is optically active in an opposite direction from that of the ketone.

Wallach records the following properties:

B. p. 201°; $d_{50°}$ 0,933; $[\alpha]_D$ — 10,35°;[1]) m. p. 45°.[2])

Bertram and Helle[3]) found:

M. p. 45°; b. p. 201 to 202°; $[\alpha]_D$ — 10,9°.

The *i*-fenchyl alcohol isolated from yellow pine oil possessed the following constants:

M. p. 33 to 35°; b. p. 202 to 203°; $[\alpha]_D \pm 0°$.

An inactive product obtained by Wallach by mixing *d*- and *l*-fenchyl alcohol had the same melting point.

When oxidized, fenchyl alcohol yields fenchone, when dehydrated, fenchene.

For the identification of active fenchyl alcohol, the acid fenchylphthalic acid ester, which melts at 145 to 145,5°, and the phenylurethane, which melts at 82 to 82,5°, are used. Of the inactive derivatives the acid phthalic ester melts lower (at 143°) and the phenyl urethane higher (at about 88°) than the corresponding active derivatives. The oxidation to fenchone and the characteristic derivatives of this ketone may be used for identifying fenchyl alcohol.

Corresponding to the aliphatic sesquiterpenes there are oxygenated derivatives found in volatile oils which, judging from their properties, must be regarded as derivatives of this class of sesquiterpenes. While they have been observed but rarely and though but little is known as to their constitution, it is to be expected that a more thorough investigation will reveal their more frequent occurrence.

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[1]) Liebig's Annalen **263** (1891), 145.

[2]) *Ibidem* **284** (1895), 331.

[3]) Journ. f. prakt. Chem. II. **61** (1900), 295.

ALIPHATIC SESQUITERPENE ALCOHOLS.

Nerolidol, $C_{15}H_{26}O$, has been found in the high-boiling fractions of orange blossom oil.

B. p. 276 to 277°, 128 to 129° (6 mm.); d 0,880; $\alpha_D + 13° 32'$.[1])

While it itself possesses but a faint odor, it has the capacity to fix other perfumes.

Farnesol, $C_{15}H_{26}O$, occurs as ester in the oil of ambrette seeds, the oil of linden blossoms and in the flower oils of several species of acacia, possibly also in oil of rose.

B. p. 160° (10 mm.); $d_{18°}$ 0,885; n_D 1,488.[2])
B. p. 149° (4 mm.); $d_{15°}$ 0,894; $\alpha_D \pm 0°$.[3])

Its odor is faint, reminding of that of cedarwood. Upon oxidation it yields the aldehyde farnesal, $C_{15}H_{24}O$, the semicarbazone of which melts at 133 to 135°.[3])

More important than the aliphatic are the cyclic sesquiterpene alcohols. As a rule the amount in which they occur in the oils is smaller than that of the sesquiterpenes; though there are oils, like the East Indian sandalwood oil, that consist almost entirely of sesquiterpene alcohols. Many of them are characterized by a marked capacity to crystallize. This is particularly true of the tertiary compounds. Hence they occasionally separate from the oils in crystalline form upon standing. Formerly such separations were designated as "camphor", hence some of the conventional names are still in use.

For the crystalline sesquiterpene alcohols, the melting point serves as a characteristic constant. Their isolation from the volatile oils seldom affords difficulties since they can be separated by crystallization. In order to isolate the liquid sesquiterpene alcohols, fractional distillation has to be resorted to. Under ordinary pressure they distill at about 300°.

Chemically, a distinction is made between primary, secondary, and tertiary sesquiterpene alcohols. From another point of view they can be classified into dicyclic and tricyclic compounds. In

[1]) Hesse and Zeitschel, Journ. f. prakt. Chem. II. **66** (1902), 504.
[2]) Haarmann & Reimer, G. I. P. 149603; Chem. Zentralbl. **1904**, I. 975.
[3]) v. Soden and Treff, Berl. Berichte **37** (1904), 1095.

addition, there are compounds of the formulas $C_{15}H_{24}O$ and $C_{15}H_{22}O$ which stand in very close relation to the sesquiterpene alcohols. But very little is known concerning the constitution of these as of the sesquiterpene alcohols. Herewith there follows a compilation of the representatives of this group that have thus far been found in volatile oils.

DICYCLIC SESQUITERPENE ALCOHOLS.

Santalols, $C_{15}H_{24}O$. The principal component of East Indian sandalwood oil (from *Santalum album*) is a mixture of two primary unsaturated alcohols, which have been designated α- and β-santalol. The former, in all probability, is tricyclic, the latter dicyclic. Quantitatively the α-compound predominates. For two crude santalols Semmler[1]) records the following constants:

B. p. 161 to 168° (10 mm.); $d_{20°}$ 0,973; α_D — 21°; n_D 1,50974; $d_{16°}$ 0,9762; α_D — 18° 30′; n_D 1,50974.

v. Soden[2]) records the following maxima and minima:

$d_{15°}$ 0,976 to 0,978; α_D — 16° 30′ to — 20°.

In the laboratory of Schimmel & Co. the following constants were observed in connection with crude santalol of their own manufacture:

$d_{15°}$ 0,973 to 0,982; α_D — 14° to — 24°; $n_{D20°}$ 1,504 to 1,509, soluble at 20° in 3 to 4 vols. of 70 p. c. alcohol.

For the two varieties of santalol the following constants have been recorded:

α-Santalol: b. p. 300 to 301° (760 mm.); 162 to 163° (13 mm.); $d_{0°}$ 0,9854; α_D — 1,2°.[3])

B. p. 301 to 302° (752 mm.), 155° (8 mm.); $d_{15°}$ 0,977;[4])

β-Santalol: b. p. 309 to 310° (760 mm.), 170 to 171° (14 mm.); $d_{0°}$ 0,9868; α_D — 56°.[5])

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[1]) Berl. Berichte **40** (1907), 1132.
[2]) Pharm. Ztg. **54** (1909), 251.
[3]) Guerbet, Compt. rend. **130** (1900), 1326.
[4]) v. Soden, Arch. der Pharm. **238** (1900), 362.
[5]) Guerbet, *loc. cit.*

Concerning its chemical properties, santalol has been examined thoroughly by a number of investigators. Hence a large number of derivatives is known. Upon oxidation with chromic acid, the aldehyde santalal, $C_{15}H_{22}O$, results, the semicarbazone of which melts at 230°.[1]) Oxidation with permanganate in acetone solution converts it mainly into tri*cyclo*eksantalic acid, $C_{11}H_{16}O_2$, m. p. 71 to 72°.[2])

The other derivatives are scarcely suited for identification purposes, hence are not mentioned in this connection.

It should be mentioned, however, that santalal also is possibly a constituent of East Indian sandalwood oil.

A so-called santal camphor, a compound $C_{15}H_{24}O_2$ has been separated from the oil of a South Australian sandalwood *(Santalum Preissianum)*. It melts at 104 to 105°.[3]).

Amyrols, $C_{15}H_{24}O$ and $C_{15}H_{26}O$, were obtained from the West Indian sandalwood oil distilled from *Amyris* species. They apparently constitute mixtures of compounds possessing the above formulas. Upon esterification, dehydration is apt to take place.

Betulol, $C_{15}H_{24}O$, occurs free and as acetate in the oil of birch buds. B. p. 284 to 288° (743 mm.); 138 to 140° (4 mm.); $d_{15°}$ 0,975; α_D — 35°; n_D abt. 1,50179. It can be esterified quantitatively.

TRICYCLIC SESQUITERPENE ALCOHOLS.

Cedrol (cedar camphor, cypress camphor), $C_{15}H_{26}O$, has been found in oils of cedarwood *(Juniperus virginiana), Juniperus chinensis* (?), cypress and *Origanum smyrnæum* (?) as the dextrogyrate modification. M. p. 86 to 87°; b. p. 291 to 294° (ord. pressure), 157 to 160° (8 mm.); $[\alpha]_D + 9°31'$ (in chloroform solution). Treated with phosphorus pentoxide or formic acid, it readily splits off water, yielding cedrene. The phenylurethane melts at 106 to 107°.[4])

[1]) Semmler and Bode, Berl. Berichte **40** (1907), 1126.

[2]) *Ibidem* 1133.

[3]) Report of Schimmel & Co. April **1891**, 65; October **1891**, 45.

[4]) Report of Schimmel & Co. October **1906**, 49; April **1910**, 46.

Cubeb camphor, $C_{15}H_{26}O$, is reported to separate from oil of cubeb when the latter is exposed to the air for a long period. It is lævogyrate, melts at 68 to 70° and boils at 248° with loss of water. This loss of water can also be brought about readily by other means.

Ledum camphor, $C_{15}H_{26}O$, has been obtained from the oil of Labrador tea in long, colorless needle-like prisms, melting at 104° and boiling at 281°. Its alcoholic solution is slightly dextrogyrate. It produces a toxic effect on the human organism. It is readily converted into the sesquiterpene ledene.

Patchouli alcohol or *-camphor,* $C_{15}H_{26}O$, is an odorless constituent of patchouli oil from which it separates in crystals that melt at 56°. It is strongly lævogyrate, $[\alpha]_D - 97°42'$ (in chloroformic solution). Like a liquid compound from the same oil, which however deviates the angle of polarized light to a lesser degree, it readily looses water, forming patchoulene.

Atractylol, $C_{15}H_{26}O$, separates from the oil distilled from the roots of *Atractylis ovata.* M. p. 59°; b. p. 290 to 292° (760 mm.); 162° (15 mm.); n_D 1,51029 to 1,51101. It is distinguished from patchouli alcohol by being optically inactive. The odor is said to remind of that of lillies of the valley. If a few drops of sulphuric acid be added to a chloroform solution, a red-brown color is produced changing to violet. This alcohol also readily looses water yielding atractylene.

Guajol, $C_{15}H_{26}O$. This sesquiterpene alcohol is contained in the oil of the wood of *Bulnesia Sarmienti* and in that obtained from the wood known as *"Kajoe garoe".*[1]) Its properties are:

M. p. 91°; b. p. 288°; $\alpha_{D20°} - 29,8°$.

The properties of the compound obtained from *Kajoe garoe* deviate somewhat. Guajol does not loose water as readily as do some of the other sesquiterpene alcohols. When water is split off it yields the blue-colored guajene.

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[1]) Eyken, Recueil des trav. chim. des P.-B. **25** (1906), 40, 44; Chem. Zentralbl. **1906**, I. 841.

For guajyl methyl ether, obtained by the action of methyl iodide on guajol potassium, Gandurin[1]) found the following constants:

B. p. 141 to 143° (9 mm.); $d_{4°}^{0°}$ 0,9513; $d_{4°}^{25°}$ 0,9332; $[\alpha]_{D20°}$ —31,81°; $n_{D18,5°}$ 1,48963.

Matico camphor, $C_{15}H_{26}O$, formerly obtained from the oil of matico leaves, is no longer found in this material. It crystallizes in thick, hexagonal columns melting at 94°; $[\alpha]_D$ — 28,73° in chloroform solution. It looses water when heated for several hours with 50 p. c. sulphuric acid.

Sesquiterpene alcohol from eucalyptus oil. From the oil of *Eucalyptus Globulus* a sesquiterpene alcohol $C_{15}H_{26}O$ of the following properties has been isolated:

M. p. 88,5°; b. p. 283° (755 mm.); $[\alpha]_D$ — 35°29′ (in chloroform solution).

When water is split off, two distinct sesquiterpenes are formed.

There can be no doubt that sesquiterpene alcohols are widely distributed in volatile oils. A number of compounds have been isolated which evidently belong to this group. Thus from oil of juniper berries a substance melting at 165 to 166°, from ylang-ylang oil one melting at 138°, and from the oil of *Piper Lowong* one melting at 164°. So far as the present stage of investigation seems to indicate, the presence of sesquiterpene alcohols may be suspected in the oils of Atlas cedar, *Cryptomeria japonica,* vetiver, paradise grains, paracoto bark, *Nectandra Caparrapi,* Maali resin, laurel leaves, camphor, copaiba balsam, pelargonium, neroli, angostura bark, opopanax resin, cascarilla, *Aralia nudicaulis,* asafetida, valerian, Spanish hops, and *Blumea balsamifera.*

In this connection several alcoholic constituents of volatile oils with more than 15 carbon atoms in the molecule should be mentioned:

Turmerol, $C_{19}H_{28}O$, contained in oil of turmeric (b. p. 285 to 290°; $d_{17°}$ 0,9016; $[\alpha]_D$ + 33,52°); and an

[1]) Berl. Berichte 41 (1908), 4362.

Alcohol, $C_{20}H_{32}O$, isolated from the oil of *Erythroxylon monogynum* (m. p. 117 to 118°; $[\alpha]_D + 32°28'$ in chloroform solution). This alcohol can be esterified quantitatively, the acetate melting at 72 to 73°.

The fact that the sesquiterpene fractions of certain oils are colored blue should not fail to receive mention. This blue color is most intense in the fractions boiling between 275 to 300°, though also observable in the lower fractions. The color varies from the most intense indigo-blue to greenish shades. As is the case with chamomile oil, the oil itself may be colored strongly blue. Certain oils obtained by the dry distillation of resins reveal a similar color, as do also some of the sesquiterpenes obtained artificially (guajene, atractylene). As to the cause of the color not the least is known. There would appear to be some indication, however, that it is due to the formation of oxydation products. The following list contains the names of those oils in which the blue color has been observed, *viz.,* the oil of *Piper Lowong,* the oil from the berries of *Piper Cubeba,* the oil of Canada snake root, camphor oil, the oil of pichurim beans, Réunion geranium oil, the oils of guaiac resin, cedrella wood, damiana leaves, *Aralia nudicaulis, Meum athamanticum,* the root of *Pimpinella nigra,* Japanese angelica root, asafetida, galbanum resin, sumbul root, opopanax resin, patchouli, dilem leaves, valerian, kesso root, chamomile, wormwood, milfoil, European pennyroyal, Roman chamomile, *Achillea coronopifolia, A. moschata,* and elecampane.

ALDEHYDES.

ALIPHATIC ALDEHYDES.

Aside from the aldehydes citral and citronellal, which are to be mentioned later in this chapter and which occur rather frequently, the aliphatic aldehydes constitute only minor constituents of the volatile oils. In as much, however, as the charac-

teristic odor of some oils is dependent on the presence of small amounts of these aldehydes, they are, nevertheless, of great importance. Because of this property, such aldehydes as nonylic aldehyde and decylic aldehyde, play an important role in the production of synthetic oils.

Like the corresponding alcohols, the lower members of this series, which are probably formed during the process of steam distillation, are found principally in the aqueous distillate or in the first distillate obtained during the fractionation of the oil. Their presence is frequently revealed by their pungent odor. They are most readily isolated by means of bisulphite. Lower aldehydes are contained in the oils of ginger, kesso root, sabadilla, *Allium ursinum,* milfoil, *Eucalyptus Globulus.* In the following account brief mention is made of the aldehydes thus far found in volatile oils.

Formaldehyde, $H \cdot CHO$, has thus far been identified with certainty in apopin oil. For its identification, the liquid, in which its presence is suspected, is evaporated with ammonia on a water bath. If present, the characteristic crystals of hexamethylene tetramine are formed.

Acetaldehyde, $CH_3 \cdot CHO$, has been observed rather frequently, more particularly in seed oils. It has been found in the oils of orris, camphor, anise, caraway, rosemary (?) and peppermint, especially when working with larger amounts of these oils. It is identified by means of the color reaction[1]) with trimethylamine and sodium nitroprusside.

Butyric aldehyde, $C_3H_7 \cdot CHO$, boils at 75° and presumably occurs in the oils of *Eucalyptus Globulus* and cajeput. It can be identified by means of its *p*-nitrophenylhydrazone[2]) which melts at 91 to 92°.

Iso*valeric aldehyde,* $C_4H_9 \cdot CHO$, can frequently be recognized by its disagreeable, irritating odor which causes

[1]) Rimini, Annali Farmacoterapia e Ch. **1898**, 249; Chem. Zentralbl. **1898**, II. 277.

[2]) Dakin, Journ. of Biol. Chem. 4 (1908), 235; Chem. Zentralbl. **1908**, I. 1259.

coughing. It possibly occurs in the oils of cajeput, niaouli, *Eucalyptus rostrata, E. Globulus,* and cloves. In addition *iso*-valeric aldehyde has been found in American and French peppermint oil, in kesso oil (?), and in lavender oil (?). It can be characterized by its oxidation to *iso*valeric acid. *Iso*valeric aldehyde boils at 92°. Its thiosemicarbazone melts at 52 to 53°.[1])

Capronic aldehyde, $C_5H_{11}\cdot CHO$, boils at 128° and is very likely contained in the oil of *Eucalyptus Globulus.* The unpleasant, irritating odor of several eucalyptus oils is probably due to the presence of this aldehyde as well as that of butyric and valeric aldehydes.[2])

n-*Octylic aldehyde,* $C_7H_{15}\cdot CHO$, is possibly contained in lemon oil. It possesses a strong odor reminding of œnanthol. The following properties were ascertained by Schimmel & Co.[3]) in connection with a preparation obtained by the oxidation of octylic alcohol and purified through the bisulphite compound:

B. p. 60 to 63° (10 mm.); $d_{15°}$ 0,827.

Semmler[4]) records the following constants:

B. p. 60 to 61° (9 mm.); $d_{20°}$ 0,8211; n_D 1,41955; b. p. of the oxime 60°; m. p. of the semicarbazone 101°.

Octyl-β-naphthocinchoninic acid forms small, white crystals which melt at 234°. With phosphonium iodide, octylic aldehyde combines to a compound that melts at 115,5°.

n-*Nonylic aldehyde,* $C_8H_{17}\cdot CHO$, is a constituent of the oil of orris root, of Ceylon cinnamon oil, of German rose oil, of mandarin oil, and probably also of lemon oil. The following constants have been observed in connection with an aldehyde isolated from oil of rose:

B. p. 80 to 82° (13 mm.), $d_{15°}$ 0,8277; $n_{D16°}$ 1,42452.[5])

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[1]) Neuberg and Neimann, Berl. Berichte **35** (1902), 2052.
[2]) Schimmel's Bericht April **1888**, 18.
[3]) Report of Schimmel & Co. April **1899**, 26.
[4]) Berl. Berichte **42** (1909), 1161.
[5]) Report of Schimmel & Co. October **1900**, 54.

Upon oxidation it yields pelargonic acid which boils at 252 to 253°. The aldehyde is characterized by its oxime which melts at 69° and by its semicarbazone which melts at 100°.

n-Decylic aldehyde, $C_9H_{19}\cdot CHO$, occurs in the oils of lemongrass, orris root, sweet orange, mandarin, neroli, cassie blossoms, and coriander. Furthermore, its presence in the leaf oil of *Abies alba* seems probable. Stephan[1]) records the following constants for a decylic aldehyde isolated from oil of sweet orange:

B. p. 207 to 209° (755 mm.) with slight decomposition, 93 to 94° (12 mm.); $d_{15°}$ 0,828; $n_{D15°}$ 1,42977.

For decylic aldehyde from lemongrass oil the following constants were observed:

B. p. 80 to 81° (6,5 mm.); $d_{15°}$ 0,8361.[2])

Characteristic are the naphthocinchoninic derivative, obtained by condensation of the aldehyde with β-naphthylamine and pyrotartaric acid, and which melts at 237°; the oxime, which melts at 69°; the semicarbazone, which melts at 102°; and the *n*-caprinic acid, which results upon oxidation and which melts at 30 to 31° and boils at 267 to 269° (753 mm).

Laurinic aldehyde, $C_{11}H_{23}\cdot CHO$, occurs in the leaf oil of *Abies alba* and possibly also in oil of rue. At ordinary temperature it is solid. Exposed to air it oxidizes to laurinic acid which melts at 43°. The semicarbazone melts at 101,5 to 102,5°.

Of much greater importance than the aldehydes thus far enumerated are the aliphatic terpene aldehydes citral, $C_{10}H_{16}O$, and citronellal, $C_{10}H_{18}O$; also a number of aromatic aldehydes. The former are especially noteworthy because of their relation to other volatile oil constituents, more particularly the alcohols. Of the latter, benzaldehyde and cinnamic aldehyde occur in considerable amounts in some oils.

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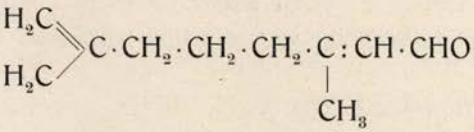
[1]) Journ. f. prakt. Chem. II. **62** (1900), 525.

[2]) Report of Schimmel & Co. October **1905**, 45.

Citral.



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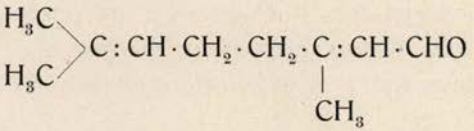

Citral[1]) is the only aliphatic aldehyde of the formula $C_{10}H_{16}O$ that has thus far been isolated from volatile oils. It is also known as geranial, because of its close relation to geraniol, being the first oxidation product of the latter. Its occurrence in nature is rather common. It was first found by J. Bertram[2]) in the oil of *Backhousia citriodora.* In as much as it was shown to be identical with the lemon-scented constituent of oil of lemon, it was named citral. Larger amounts are contained in the lemongrass oil as well as in the Backhousia oil just referred to. It occurs also in Java citronella oil, ginger oil, kobushi oil, sassafras leaf oil, Japanese cinnamon oil, the oils from the fruit, bark and leaves respectively of *Tetranthera citrata,* German rose oil, the oils from the leaves and twigs of the sweet orange tree and the lemon tree, cedro oil, West-Indian limette oil, mandarin oil, oil of sweet orange (?), Japanese pepper oil, may oil, oil of bay, oil of pimenta, the oils of *Eucalyptus patentinervis, E. Staigeriana, E. vitrea* (?), *Leptospermum Liversidgei,* verbena, *Monarda citriodora,* and melissa. In these oils citral occurs in two modifications, designated citral "a" and citral "b", which appear to be stereoisomeric.[3]) In practically all cases citral "a" predominates.

From all of the oils enumerated above, citral can be isolated by means of its crystalline addition product with bisulphite (see below). From this compound, after previous purification by washing with alcohol and ether, citral can be obtained in a pure state by decomposition with alkali carbonate.

[1]) Concerning the history of citral see Tiemann, Berl. Berichte **31** (1898), 3278.

[2]) Schimmel's Bericht October 1888, 17.

[3]) Tiemann, Berl. Berichte **33** (1900), 877.

To the extent of 30 to 40 p. c. yield citral can be obtained artificially by the oxidation of geraniol with chromic acid mixture.[1]) In like manner the tertiary alcohol linalool (likewise nerol) yields the same oxidation product, since the acid oxidizing agent first causes the rearrangement of linalool to geraniol. Synthetically, citral has been obtained by the distillation of the calcium salt of geranic acid with calcium formate.[2])

Citral is a thin, light yellow liquid, which is optically inactive and which possesses a penetrating odor of lemon. Under atmospheric pressure it distils at 228 to 229° with slight decomposition. Its constants, as recorded by Tiemann and Semmler,[3]) are as follows:

B. p. 110 to 112° (12 mm.); 117 to 119° (20 mm.); 120 to 122° (23 mm.); $d_{15°}$ 0,8972; n_D 1,4931; $d_{22°}$ 0,8844; n_D 1,48611.

In addition Tiemann[4]) records the following constants:

For citral "a": B. p. 118 to 119° (20 mm.); $d_{20°}$ 0,8898; n_D 1,4891.

For citral "b": B. p. 117 to 118° (20 mm.); $d_{20°}$ 0,8888; n_D 1,49001.

In the laboratory of Schimmel & Co. the following observations have been made in connection with citral carefully purified through the bisulphite or the hydrosulphonic acid addition products:

For citral from lemongrass oil:

B. p. 110 to 111° (12 mm.); $d_{15°}$ 0,893; $n_{D17°}$ 1,49015.[5])

For citral from lemon oil:

B. p. 92 to 93° (5 mm.); $d_{15°}$ 0,8926; $n_{D20°}$ 1,48853.

For citral from the oil of the fruits of *Tetranthera citrata:*

$d_{15°}$ 0,8941; $n_{D20°}$ 1,8767.

Commercial products prepared by Schimmel & Co. had the following properties:

$d_{15°}$ 0,892 to 0,895; $n_{D20°}$ 1,488 to 1,489; soluble in about 7 vols. of 60 p. c. alcohol.

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[1]) Tiemann, Berl. Berichte **31** (1898), 3311.
[2]) Tiemann, Berl. Berichte **31** (1898), 827.
[3]) Berl. Berichte **26** (1893), 2709.
[4]) Berl. Berichte **32** (1899), 117, 120; **33** (1900), 880.
[5]) Report of Schimmel & Co. April **1899**, 64.

As diolefinic aldehyde citral adds two molecules of bromine, but does not yield a solid bromide. Toward acids and acid reagents it is very susceptible, being altered materially by them. Like many of its derivatives, it can readily be converted into cyclic compounds. Dilute sulphuric acid and potassium acid sulphate act very energetically with the formation of cymene.[1]) Alkalies likewise attack citral. When boiled with potassium carbonate solution it is broken up into acetaldehyde and methylheptenone, $C_8H_{14}O$.[2]) The same ketone results upon the oxidation of citral and is found accompanying the citral in lemongrass oil (see also under "Ketones").

Citral reveals all of the properties of an aldehyde. It reacts with the well-known reagents for aldehydes and when reduced with sodium amalgam in acetic acid solution it is converted into geraniol.[3]) Toward sodium acid sulphite solution it behaves in a peculiar manner.[4]) If the solution does not contain too large amounts of free sulphurous acid, the difficultly soluble, normal crystalline addition product, $C_9H_{15} \cdot CH(OH)SO_3Na$, is formed when the aldehyde is shaken with such a solution. From this compound sodium carbonate and sodium hydroxide regenerate the citral, but not quantitatively. If, however, this crystalline addition product is gently heated with an excess of bisulphite solution, it is dissolved with the formation of a "labile" dihydrodisulphonic acid derivative of citral, $C_9H_{17} \cdot (SO_3Na)_2 \cdot CHO$. From this the citral can be regenerated no longer by means of alkali carbonate, but by means of caustic alkali. If, however, the temperature is allowed to rise too high, the "labile" compound has been changed to a "stabile" dihydrodisulphonic acid derivative, which is no longer yields citral even when acted upon with caustic alkali. This same compound results likewise when the normal compound is suspended in water and subjected to the action of steam until it has gone into solution. If the solution of the "labile" citral dihydrosulphonate of sodium is shaken with citral,

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[1]) Semmler, Berl. Berichte **24** (1891), 204.

[2]) Verley, Bull. Soc. chim. III. **17** (1897), 175; Tiemann, Berl. Berichte **32** (1899), 107.

[3]) Tiemann, Berl. Berichte **31** (1898), 828.

[4]) Tiemann and Semmler, Berl. Berichte **26** (1893), 2708; Tiemann, Berl. Berichte **31** (1898), 3310.

it is changed back to the citral hydromonosulphonate of sodium, $C_9H_{16}(SO_3Na)\cdot CHO$.

The "labile" citral dihydrodisulphonate of sodium results likewise when an aqueous solution of sodium sulphite is shaken with citral:

$$C_9H_{15}CHO + 2Na_2SO_3 + 2H_2O = C_9H_{17}(SO_3Na)_2CHO + 2NaOH.$$

In as much as the sodium hydroxide set free would regenerate the citral from the compound just formed, it must be combined with dilute acetic acid, sulphuric acid, or an acid salt such as sodium bisulphite or sodium bicarbonate. According to Tiemann,[1]) the following method may be followed: A solution of 350 g. of sodium sulphite, $Na_2SO_3 + 7H_2O$, in 1 liter of water, colored red with a little phenolphthalein solution, is shaken with 100 g. of pure citral. The strongly alkaline reaction produced is reduced from time to time by the gradual addition of a standardized sulphuric acid of about 20 p. c. strength. The solution should always be slightly alkaline as revealed by the red color of the indicator. Otherwise the normal sodium acid sulphite addition product of citral, which is difficultly soluble, is exclusively formed and separated.

Inasmuch as the derivatives of citral with hydroxylamine, phenylhydrazine, and ammonia are liquid, they cannot be utilized for the characterization of citral. When dehydrated with the aid of acetic acid anhydride, the oxime is converted into the nitrile of geranic acid. When acted upon by semicarbazide, citral yields several well crystallizable semicarbazones.[2]) Under certain conditions[3]) this mixture of semicarbazones can be resolved into two compounds melting at 164° and 171° respectively. Hence these can be utilized for the identification of citral. (See below.)

Moderate oxidation, *e. g.* with silver oxide in ammoniacal solution yields the liquid geranic acid $C_{10}H_{16}O_2$,[4]) the odor of which resembles that of the higher fatty acids. More energetic oxidation with chromic acid mixture yields methylheptenone which, upon

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[1]) Berl. Berichte **31** (1898), 3317.

[2]) Wallach, Berl. Berichte **28** (1895), 1957; Tiemann and Semmler, ibidem 2133; Tiemann, Berl. Berichte **31** (1898), 821, 2315.

[3]) Tiemann, Berl. Berichte **31** (1898), 3331.

[4]) Semmler, Berl. Berichte **23** (1890), 3555; **24** (1891), 203.

further oxidation with potassium permanganate and chromic acid mixture, breaks up into acetone and lævulinic acid.[1]) Because of these results the above-mentioned formula, corresponding to that for geraniol, has been assigned to citral. This formula agrees well with the properties of citral.

When condensed with acetone, citral yields a ketone $C_{13}H_{20}O$, pseudoionone. When heated with dilute sulphuric acid, this ketone yields ionone which is isomeric with the irone of orris oil. (See under Ionone.)

Inasmuch as citral possesses a penetrating odor, this will as a rule indicate its presence in volatile oils. For its positive identification, the aldehyde is separated by means of its solid acid sulphite derivative. Regenerated, it is then converted into the α-citryl-β-naphthocinchoninic acid, discovered by Doebner,[2]) by condensation with pyrotartaric acid and β-naphthylamine. For the preparation of this compound, Doebner has given the following directions: 20 g. of pyrotartaric acid and 20 g. of citral (or of the corresponding oil) are dissolved in absolute alcohol. To this solution, 20 g. of β-naphthylamine, likewise dissolved in absolute alcohol, are added and the mixture heated for three hours on a waterbath, the flask being connected with a reflux condenser. Upon cooling, the citrylnaphthocinchoninic acid, which has separated in a crystalline form, is separated by filtration and purified by washing with ether. If the acid is very impure, it is dissolved in ammonia and precipitated from the filtered ammoniacal solution by means of acetic acid. The substance thus purified crystallizes from alcohol in yellow laminæ. Doebner[3]) gives the melting point at 197°. However, it lies somewhat higher being found at 200° or even slightly above that temperature.

It should be remembered, however, that, in the presence of but small amounts of citral or other aldehydes, α-methyl-β-naphthocinchonic acid is formed by the interaction of pyrotartaric acid and β-naphthylamine. This acid melts at 310° and is less soluble in alcohol than is citrylnaphthocinchoninic acid. Hence it remains in the residue when the crude naphthocinchoninic acid is extracted with hot alcohol.

[1]) Tiemann and Semmler, Berl. Berichte **26** (1893), 2718.

[2]) Berl. Berichte **87** (1894), 354, 2026.

[3]) *Loc. cit.*; Berl. Berichte **31** (1898), 1891; Comp. *ibidem* 3197, 3327.

It should further be remembered that when other aldehydes are present the corresponding naphthocinchoninic acids are formed. Thus Doebner found not only citryl- but also citronellyl-β-naphthocinchoninic acid (m. p. 225°) in fractions of lemon oil.

As already pointed out, natural citral apparently consists of two stereoisomeric forms, which have been designated citral "a" and citral "b" by Tiemann. The semicarbazone melting at 164° corresponds to the former and can be prepared in accordance with the following directions:

To a solution of 5 parts of citral (or of the fraction to be tested) in 30 parts of glacial acetic acid, a solution of 4 parts of semicarbazide hydrochloride in a little water is added. After standing for a short time, a considerable quantity of semicarbazone separates in needle-like crystals. After having been recrystallised two or three times from methyl alcohol, they melt at 164°. From the mother liquid of this semicarbazone, the semicarbazone corresponding to citral "b" and melting at 171° can be separated.[1]) Mixtures of both semicarbazones reveal melting points varying from 130 to 171°. As related compounds, the thiosemicarbazone, melting at 107 to 108°, and the semioxamazone, melting at 190 to 191°, should be mentioned.

Citrylidene cyanacetic acid, $C_9H_{15}\cdot CH{:}C(CN)\cdot COOH$, obtained by condensation of citral with cyanacetic acid, is another derivative melting at 122° that crystallizes well and hence can be used for the identification of citral. It can be prepared according to the following directions: To a solution of one molecule of cyanacetic acid in three times its weight of water, two molecules of sodium hydroxide (as 30 p. c. sodium hydroxide solution) and one molecule of citral are added. If the citral be pure, it will dissolve without turbidity upon shaking. If the solution be turbid it is shaken out with ether. From the clear solution the citrylidene cyanacetic acid is precipitated by means of acids. It separates either in crystalline form or as an oil that readily congeals. Recrystallized from the benzene solution to which ligroin has been added, it is obtained in short, yellow crystals.[2])

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[1]) Tiemann, Berl. Berichte **31** (1898), 3331; **32** (1899), 115; **33** (1900), 877.

[2]) Tiemann, Berl. Berichte **31** (1898), 3329.

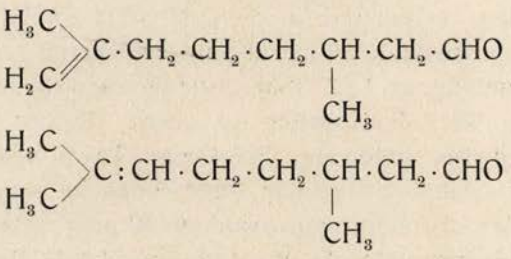
In as much as citral "b" condenses more slowly than does citral "a", this method can be utilized for the separation of both modifications. Citrylidene cyanacetic acid "a" melts at 122°, the "b"-variety at 94 to 95°.[1])

Still another solid condensation product of citral is obtained with acetyl acetone. It is obtained by condensing 15,2 g. citral and 20 g. of acetyl acetone at room temperature with the aid of piperidine. After standing for three days the entire reaction mass congeals to a crystalline magma. Recrystallized from a mixture of alcohol, ether and ligroin, citrylidene bisacetylacetone is obtained in light yellow wart-like crystals that melt at 46 to 48°.[2])

Tiemann[3]) recommended that the presence of citral be established by condensing it with acetone to pseudo ionone and by identifying this by means of its semicarbazone. This method, however, is more complicated than the preparation of citryl naphthocinchoninic acid which is, therefore, given the preference.

A method for effecting the separation of citral, citronellal, and methylheptenone is given under the two last-mentioned compounds.

Citronellal.



or

The second aliphatic terpene aldehyde with ten carbon atoms that is found in volatile oils is the citronellal, $C_{10}H_{18}O$. It occurs occasionally as companion to citral, of which it is the dihydroderivative. Differing from citral, citronellal is optically active. However, with but one exception, it has been found in the dextro-

[1]) Tiemann, Berl. Berichte **33** (1900), 880.

[2]) K. Wedemeyer, *Über Kondensationen mittelst aromatischer Basen usw. Inaug. Dissert.* Heidelberg 1897. p. 24.

[3]) Berl. Berichte **31** (1898), 822.

gyrate modification only. It is probable that whenever citronellal is found with a low angle of rotation it is a mixture of both active modifications.

d-Citronellal has been found in citronella oil, in the oils of *Barosma pulchellum*, *Eucalyptus maculata* var. *citriodora*, *E. dealbata*, and of balm; *l*-citronellal in "Java lemon olie". With certainty the presence of citronellal has been ascertained in the oil from the bark of *Tetranthera polyantha* var. *citrata*, but its angle of rotation has not been recorded. Its presence in oil of lemon and in mandarin oil is still doubtful.

In as much as citronellal can be separated by means of its crystalline bisulphite compound, its isolation from oils containing a large percentage of aldehyde, such as citronella oil and oil of *Eucalyptus maculata*, offers no difficulties. Since citronellal is very susceptible towards acids as well as toward alkalies, alkali carbonate is used to decompose the bisulphite compound. Artificially citronellal has been obtained upon oxidation of the primary alcohol citronellol $C_{19}H_{20}O$; however, the yield is even smaller than when geraniol is oxidized to citral. In this manner the *l*-citronellol from rose oil is converted into *l*-citronellal, which has been designated rhodinal by Bouveault.

Upon the ring cleavage of menthoxime to aliphatic compounds Wallach obtained an aldehyde $C_{10}H_{18}O$ which he designated "Menthocitronellal", and which closely resembles the natural citronellal, but is not identical with the latter.[1])

According to Tiemann and Schmidt[2]) citronellal boils at 205 to 208° under atmospheric pressure and at 103 to 105° under a pressure of 25 mm.; $d_{17,5°}$ 0,8538; n_D 1,4481; mol. refr. 48,29, computed for $C_{10}H_{18}O$ 47,92.

For a citronellal regenerated from a recrystallized sodium acid sulphite double compound, Tiemann[3]) records the following constants:

B. p. 203 to 204°; 89 to 91° (14 mm.); $d_{17,5}$ 0,8554; n_D 1,4461; mol. refr. 48,00.

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[1]) Liebig's Annalen **278** (1894), 317; **296** (1897), 131.
[2]) Berl. Berichte **29** (1896), 905.
[3]) Berl. Berichte **32** (1899), 818.

As angle of rotation, Kremers[1]) recorded $[\alpha]_D + 8{,}18°$. Later $[\alpha]_D + 12°30'$ was observed for a preparation purified by means of its acid sulphite derivative.[2])

In the laboratory of Schimmel & Co. the following constants were observed in connection with products obtained on a commercial scale:

B. p. 205 to 208° (ord. pressure); 72 to 73° (4,5 mm.); $d_{15°}$ 0,855 to 0,860; $\alpha_D + 10$ to $+ 11°$; $n_{D20°}$ 1,444 to 1,449; soluble in 5 to 6 vols. of 70 p. c. alcohol.

Citronellal isolated from "Java lemon olie" revealed the following properties:

B. p. 205 to 208°; $d_{15°}$ 0,8567; $\alpha_D - 3°$; $n_{D20°}$ 1,44791.[3])

Citronellal is an unsaturated aldehyde with one double bond. When reduced in alcoholic solution, that is kept slightly acid by the addition of acetic acid, with sodium amalgam it is converted into the primary alcohol citronellol, $C_{10}H_{20}O$.[4]) Like citral, citronellal is very susceptible toward alkalies and acids. Whereas citral is broken up into acetaldehyde and methylheptenone when treated with alkali, citronellal resinifies. In contact with acids citral loses the elements of a molecule of water and yields cymene; whereas citronellal is converted into an isomeric compound, the *iso*pulegol[5]) $C_{10}H_{18}O$ (comp. p. 386). This alcohol, which is likewise isomeric with pulegol, is obtained upon reduction of pulegone, and can be oxidized to the ketone *iso*pulegone, $C_{10}H_{16}O$, which can be inverted to natural pulegone. According to Harries and Roeder,[6]) the semicarbazones of *iso*pulegone melt at 173° (α-modification) and 183° (β-modification). This ring-formation of citronellal to *iso*pulegone takes place very readily, so that commercial citronellal, at least when purified through the bisulphite compound, always contains *iso*pulegol.[7])

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[1]) Americ. chem. Journ. **14** (1892), 203.

[2]) Tiemann and Schmidt, *loc. cit.*

[3]) Report of Schimmel & Co. April **1903**, 22.

[4]) Tiemann and Schmidt, Berl. Berichte **29** (1896), 906.

[5]) Tiemann and Schmidt, Berl. Berichte **29** (1896), 913; **30** (1897), 22.

[6]) Berl. Berichte **32** (1899), 3367.

[7]) Tiemann, Berl. Berichte **32** (1899), 825; Labbé, Bull. Soc. chim. III. **21** (1899), 1023.

The change to *iso*pulegol can also be utilized for the quantitative determination of citronellal. For this purpose compare the chapter "The examination of volatile oils".

Toward sodium acid sulphite, citronellal behaves similar to citral. In addition to the crystalline normal double compound with one molecule of $NaHSO_3$, in which the bisulphite has been added to the aldehyde group, it also yields hydrosulphonic acid derivatives with one or two molecules of $NaHSO_3$. In these latter compounds the sodium acid sulphite molecule is added to the double linkage between carbon and carbon. However, if two molecules are added, one must necessarily add to the aldehyde group, there being but one double linkage between carbon and carbon.[1]) It is from the first-mentioned compound only that citronellal can be regenerated, whereas it cannot be regenerated from the hydrosulphonic acid derivatives by either sodium carbonate or alkali hydrate. With neutral sulphite, citronellal likewise reacts with the formation of a non-decomposable hydrosulphonic acid derivative. However, the reaction then only takes place when a strong current of carbon dioxide is passed into the mixture or if a sufficient amount of some other acid is added. This behavior of citronellal can be utilized for its separation from citral, which combines with neutral sulphite without addition of acid. Care must be taken, however, to neutralize the sodium hydroxide as it is liberated.

Another method of separation is based on the property of the citronellal to combine only with a concentrated solution of sodium sulphite and sodium bicarbonate, whereas citral also combines with dilute solutions.[2])

Since methylheptenone does not combine with even a concentrated solution of sodium sulphite and sodium bicarbonate, this reagent also serves as a means to separate citronellal from any admixture of methylheptenone.[3])

As with citronellol, so with citronellal, there is a difference of opinion concerning the identity of the products from different sources. Whereas *e. g.* Tiemann and Schmidt, also Schimmel & Co.,

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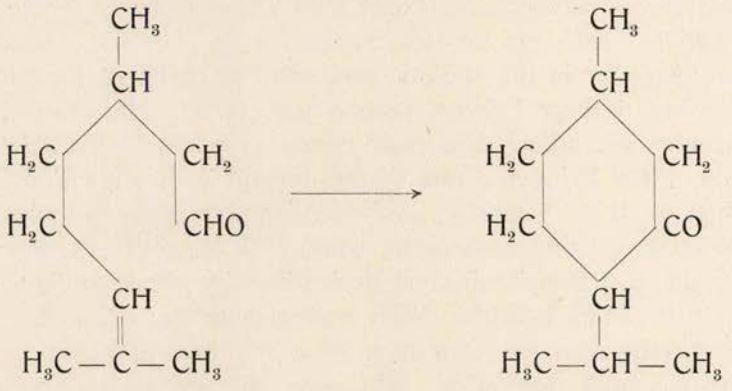
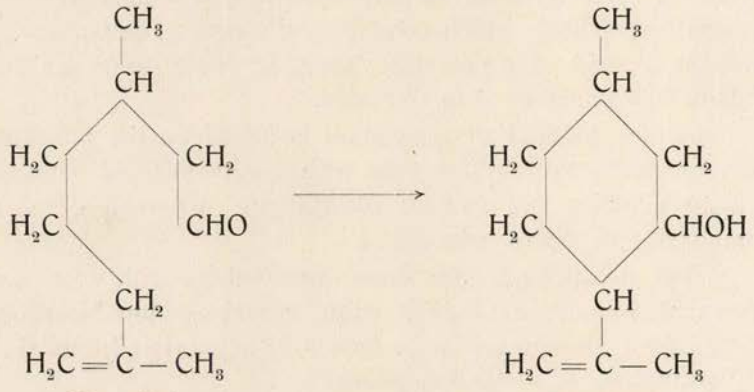
[1]) Tiemann, Berl. Berichte **31** (1898), 3305.
[2]) Tiemann, Berl. Berichte **32** (1899), 815.
[3]) *Ibidem* 834.

regarded them as identical, Barbier and Bouveault[1]) claimed them to be isomeric. They state that citronellal from citronella oil has a different constitution (the first formula, p. 414) from that obtained upon the oxidation of citronellol from rose oil (the second formula, p. 414). To the latter they apply the name "rhodinal". They base their claims on the rearrangement of rhodinal to menthone,



Rhodinal. Menthone.

whereas citronellal rearranges itself to *iso*pulegol.



Citronellal. *Iso*pulegol.

The change of rhodinal to menthone is regarded as non-proven by Tiemann and Schmidt.[2]) According to the examinations of

[1]) Compt. rend. **122** (1896), 737; Bouveault and Gourmand, *ibidem* **138** (1904), 1699; Bouveault, Bull. Soc. chim. III. **23** (1900), 458.

[2]) Berl. Berichte **30** (1897), 38.

these investigators, the rhodinal semicarbazone described by Barbier and Bouveault is a mixture of racemic citronellal semicarbazone and little *iso*pulegone semicarbazone, whereas their supposed menthone semicarbazone is racemic *iso*pulegone semicarbazone. When hydrolyzed with hydrochloric acid, *iso*pulegone is regenerated which has an odor resembling that of menthone. It is on this that the erroneous assumption of the French scientists is said to be based.

The observations made by Harries and Himmelmann,[1]) while studying the action of ozone on citronellal, seem to indicate that the latter is not a chemical unit but a mixture of two isomeric aldehydes to which the two formulas, given at the beginning of this chapter, may be assigned. In the commercial products from different sources, the ratio of these two isomers varies. This assumption would seem to throw light on much that was previously little understood.

When carefully oxidized with silver oxide, citronellal yields the corresponding oily citronellic acid,[2]) $C_{10}H_{18}O_2$. Energetic oxidation yields the same products obtained from citronellol, *viz.*, acetone and β-methyladipic acid.[3]) With hydroxylamine, citronellal yields a liquid oxime which when dehydrated, yields the nitrile of citronellic acid.[4]) The phenylhydrazone is likewise oily. So far as present observations go, the semicarbazone obtained with semicarbazide is a chemical unit and hence is well suited for the identification of citronellal. It is obtained quantitatively when an alcoholic solution of the aldehyde is shaken with a solution of semicarbazide hydrochloride and sodium acetate. When recrystallized from chloroform or ligroin it is obtained in white laminæ which melt at 82,5°.[5]) The racemic modification melts at 96°, the thiosemicarbazone at 54 to 55°.

Like citral, so citronellal yields with pyrotartaric acid and β-naphthylamine a naphthocinchoninic acid,[6]) which can be utilized

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[1]) Berl. Berichte **41** (1908), 2187.

[2]) Semmler, Berl. Berichte **24** (1891), 208; **26** (1893), 2256.

[3]) Tiemann and Schmidt, Berl. Berichte **29** (1896), 908.

[4]) Semmler, Berl. Berichte **26** (1893), 2255.

[5]) Tiemann and Schmidt, Berl. Berichte **30** (1897), 34; Tiemann, *ibidem* **31** (1898), 3307.

[6]) Doebner, Berl. Berichte **27** (1894), 2025.

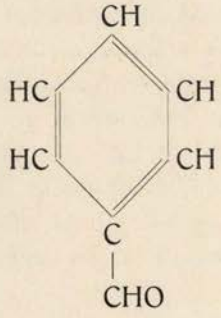
for purposes of identification. It is prepared like the corresponding citral derivative. The crude α-citronellyl-β-naphthocinchoninic acid is recrystallized from alcohol containing hydrogen chloride. The hydrochloride is dissolved in ammonia and the ammonium salt decomposed by acetic acid. The compound thus purified crystallizes from dilute alcohol in colorless needles that melt at 225°. When heated beyond its melting point, the acid splits off carbon dioxide and is converted into citronellyl-β-naphthoquinoline, a base that crystallizes from dilute alcohol or ligroin in the form of needles with a silky lustre and melts at 53°.

More rapid, however, than the identification by means of the naphthocinchoninic acid, is that by means of the semicarbazone (see above).

Upon condensation with acetone, citronellal yields citronellylidene acetone which yields a semicarbazide-semicarbazone that melts at 167°.[1]) Citronellylidene cyanacetic acid,[2]) prepared like the corresponding citral compound, melts at 137 to 138° and yields a characteristic, difficultly soluble sodium salt that can be utilized for the separation of citral.

CYCLIC (AROMATIC) ALDEHYDES.

Benzaldehyde.



Benzaldehyde occurs rather frequently in volatile oils. Its existence in these oils is due to the presence, in parts of plants,

[1]) Rupe and Lotz, Berl. Berichte **36** (1903), 2796; Rupe and Schlochoff, *ibidem* 4377.

[2]) Tiemann, Berl. Berichte **32** (1899), 824.

of certain glucosides which, upon hydrolysis, yield benzaldehyde, hydrocyanic acid, and glucose. Such glucosides are amygdalin, laurocerasin, prulaurasin and sambunigrin.

Bitter almond oil consists almost entirely, wild cherry bark oil and cherry laurel oil in large part of benzaldehyde. Its presence has also been established in the oils of Ceylon cinnamon and cinnamon leaf, in indigofera oil, in the oils of Roman and French cassie blossoms, in neroli oil, niaouli oil, patchouli oil, &c. Almost invariably hydrocyanic acid is present with the benzaldehyde. (Compare under hydrocyanic acid where the names of all plants yielding benzaldehyde and hydrocyanic acid upon distillation are recorded.)

As first material for the artificial preparation of benzaldehyde, toluene, $C_6H_5CH_3$, from coal tar is used. This hydrocarbon is chlorinated to either benzylchloride, $C_6H_5CH_2Cl$, or benzalchloride, $C_6H_5CHCl_2$, and the chlorides are converted into benzaldehyde.

Benzaldehyde is a colorless liquid and has the characteristic odor of moistened comminuted almonds. Contrasted with bitter almond oil containing hydrocyanic acid, it is comparatively harmless.[1]) It is readily soluble in the ordinary solvents and is dissolved even by water in the ratio of about 1 : 200. It is reported to boil at 179°. The following constants have been observed in the laboratory of Schimmel & Co.:

B. p. 177,3° (733 mm.), 45° (5 mm.); $d_{15°}$ 1,050 to 1,055; $\alpha_D \pm 0°$; $n_{D20°}$ 1,544 to 1,546; soluble in 8 vols. of 50 p. c., 2,5 to 3 vols. of 60 p. c., and 1 to 1,5 vols. of 70 p. c. alcohol.

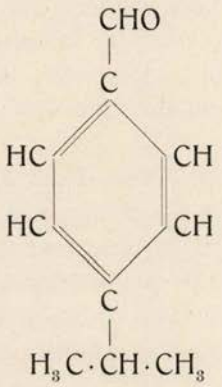
Of the numerous derivatives that have been prepared, particularly in condensation reactions, the following may serve for the identification of benzaldehyde: the acid sulphite addition product, the semicarbazone melting at 214° and the phenylhydrazone melting at 156°. Atmospheric oxygen readily oxidizes benzaldehyde to benzoic acid which frequently crystallizes out when bottles are not completely filled with the aldehyde. The addition of 10 p. c. alcohol retards this oxidation, the addition of a smaller amount accelerates it.[2])

[1]) Report of Schimmel & Co. October **1893**, 6.

[2]) Report of Schimmel & Co. April **1895**, 12.

Because of its method of preparation, artificial benzaldehyde almost invariably contains more or less chlorinated products, which impair its odor. Hence these render it unsuited for perfumery purposes and for the production of liqueurs. However, by means of careful purification, artificial benzaldehyde can be made absolutely free from chlorine. A good product should, therefore, be free from chlorine and the absence of halogen should be ascertained by proper tests. (Compare the chapter: "The examination of volatile oils".)

Cuminic aldehyde.



Cuminic aldehyde (*p-iso*propyl benzaldehyde, cuminol) has been observed repeatedly in volatile oils. It is the principal constituent of oil of cumin and has also been found in the oils of boldo leaves, Ceylon cinnamon, myrrh, cassie blossoms, *Eucalyptus hæmastoma, E. hemiphloia, E. odorata, E. oleosa, E. populifera,* and water hemlock.

Cuminic aldehyde purified through the acid sulphite addition product has the following properties:

Sp. gr. 235,5°; $d_{15°}$ 0,9818; $\alpha_D \pm 0°$;[1]) b. p. 232° (760 mm.), 109,5° (13,5 mm.);[2]) $d_{13°}$ 0,972.[3])

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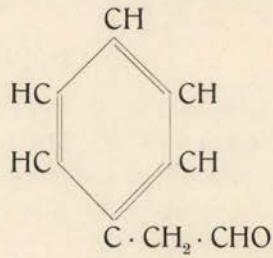
[1]) Journ. chem. Soc. **69** (1896), 1199.

[2]) Anschütz and Reitter, *Die Destillation unter vermindertem Druck.* p. 73.

[3]) Kopp, Liebig's Annalen **94** (1855), 319.

The semicarbazone of cuminic aldehyde melts at 210 to 211°, the phenyl hydrazone at 126 to 127°, the oxime at 58 to 59°. Upon oxidation it yields cuminic acid which melts at 115°.

Phenylacetic aldehyde.



Although this aldehyde has not yet been found in a volatile oil, it may be mentioned here since it finds application in perfumery on account of its hyacinth-like odor. It can be prepared in one of several ways. Phenyl-α-chloro lactic acid, phenyl-α-bromo lactic acid or α-bromo styrene are commonly used as starting point.

Pure phenylacetic aldehyde is a colorless liquid of an exceedingly intensive hyacinth-like odor. In contact with the skin it colors the latter yellow. Radziszewski[1]) enumerates the following constants:

B. p. 205 to 207°; d 1,085.

Schimmel & Co. have determined the following constants:

B. p. abt. 75° (5 mm.); $d_{15°}$ 1,0315 to 1,0521; $\alpha_D \pm 0°$; $n_{D20°}$ 1,52536 to 1,53370; soluble in about 3 vols. of 70 p. c. alcohol.

Phenylacetic aldehyde oxidizes readily to phenylacetic acid. Oxidized with nitric acid it yields benzoic acid. It manifests a decided tendency to polymerize, hence it is difficult to preserve it unchanged. It should be tested for halogen, the presence of which would indicate insufficient purification. (Compare the chapter "The examination of volatile oils", under benzaldehyde.)

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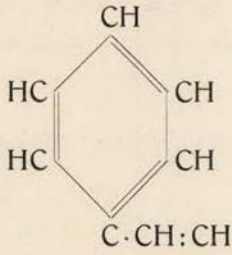
[1]) Berl. Berichte 9 (1876), 372.

Cinnamic aldehyde.



Cinnamic aldehyde occurs in Ceylon cinnamon oil, in cinnamon leaf oil, cinnamon root oil, Japanese cinnamon oil, oil of myrrh, oil of cassia and oil of patchouli.

Artificially it is obtained by the condensation of benzaldehyde with acetic aldehyde.

It is a yellow liquid possessing a characteristic cinnamon-like odor. Products made by Schimmel & Co. revealed the following properties.

B. p. under atmospheric pressure abt. 252° with partial decomposition, 128 to 130° (20 mm.), 118 to 120° (10 mm.); $d_{15°}$ 1,054 to 1,058; $\alpha_D \pm 0°$; its index of refraction, $n_{D20°}$ 1,61949,[1]) is the highest observed in connection with volatile oils. When cooled, it congeals to a solid, light yellow mass that melts at — 7,5°. It is soluble in about 25 vols. or more of 50 p. c. alcohol, also in about 7 vols. of 60 p. c. alcohol and in 2 to 3 vols. of 70 p. c. alcohol. In petroleum ether it is practically insoluble.

Cinnamic aldehyde reacts with both acid and neutral sulphite. When it is to be separated by means of the bisulphite addition product, an excess of the bisulphite solution should be avoided since a second molecule will combine with the formation of the water-soluble $C_6H_5 \cdot C_2H_3(SO_3Na) \cdot CH(OH) \cdot SO_3Na$. Other derivatives that are suited to the identification of cinnamic aldehyde are the semicarbazone, m. p. 208°, the phenylhydrazone, m. p. 168°. Furthermore cinnamic acid, which is formed even by the action of atmospheric oxygen, and its oxidation products benzaldehyde and benzoic acid.

In connection with artificial cinnamic aldehyde care should be taken that it be free from chlorine, since the presence of

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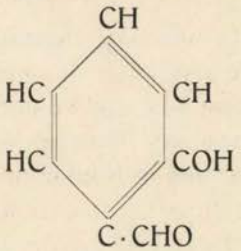
[1]) Brühl, Liebig's Annalen **235** (1886), 18, 31.

chlorine is an indication of insufficient purity. For the detection of chlorine, also for the quantitative determination of cinnamic aldehyde compare the chapter "The examination of volatile oils".

In addition to the aromatic aldehydes already mentioned, a number of others should be enumerated in which benzene hydrogen has been replaced by hydroxy or alkyloxy groups. Although widely distributed in the vegetable kingdom, they occur in small amounts only. In as much as they possess valuable properties as perfumes, most of them are also prepared synthetically, hence there exists an extensive patent literature.

Salicylic aldehyde.



Salicylic aldehyde (*o*-hydroxybenzaldehyde) has been found in the oils of *Spiræa (S. Ulmaria, S. Filipendula, S. digitata, S. lobata),* in the leaves of *Homalium tomentosum,* in *Cordia asperrima* (?), and in the oil of *Crepis fœtida.*

Formerly it was obtained by the oxidation of saligenin prepared from willow bark. At present it is produced according to the well-known synthesis of Reimer and Tiemann[1]) by the action of chloroform and aqueous alkali on phenol.

According to Perkin,[2]) salicylic aldehyde boils at 197°. Its sp. gr. is $d_{15°}$ 1,1698. In the ordinary solvents it is readily soluble, and but slightly in water. The latter solution is colored a deep violet by ferric chloride.

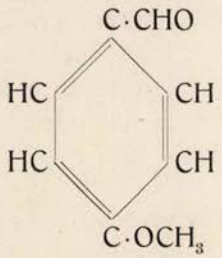
For the purpose of isolating salicylic aldehyde, its phenol nature (solubility in alkali) as well as its aldehyde character

[1]) Berl. Berichte **9** (1876), 824.
[2]) Journ. chem. Soc. **69** (1896), 1200.

(acid sulphite addition product) can be utilized. When reduced it yields saligenin, m. p. 86°, when oxidized salicylic acid, m. p. 155 to 156°. The oxime melts at 57°, the phenyl hydrazone at 96°.

Salicylic aldehyde is of special importance as the starting point in the manufacture of coumarin.

Anisic aldehyde.



Anisic aldehyde (*p*-methoxy benzaldehyde), also known as aubépine, results upon oxidation of anethol. Hence it is found in old, anethol-containing oils, such as anise oil, staranise oil and fennel oil. Its presence has likewise been demonstrated in the extract of Tahiti vanilla, and in Roman and French cassie blossom oils. The odor of the flowers of *Cratægus Oxyacantha, Pyrus communis, Sorbus Aucuparia, Viburnum Tinus,* and *Erica arborea,* would seem to indicate[1]) that anisic aldehyde is contained in them, but as yet no chemical proof has been brought forward.

Artificially, anisic aldehyde is prepared by the oxidation of anethol by means of nitric acid or chromic acid mixture, or by methylation of *p*-hydroxy benzaldehyde. When purified by means of the acid sulphite addition product, anisic aldehyde is a colorless liquid which boils at 248° (corr.).[2]) Its odor resembles that of the flowers of *Cratægus Oxyacantha.* The properties of anisic aldehyde, as prepared on a large scale, have been determined by Schimmel & Co.:

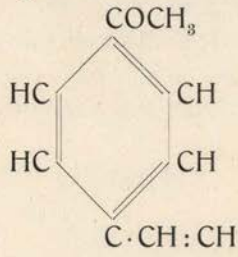
B. p. 91° (4 mm.); $d_{15°}$ 1,126 to 1,129; $\alpha_D \pm 0°$; $n_{D20°}$ 1,572 to 1,574; soluble in 7 to 8 vols. of 50 p. c. alcohol. The aldehyde can be characterized by means of its oxidation to anisic acid

[1]) Report of Schimmel & Co. October **1903**, 20; Verschaffelt, Chem. Weekblad **1908**, No. 25, 1; Report of Schimmel & Co. October **1908**, 161.

[2]) Perkin, Journ. chem. Soc. **69** (1896), 1200.

(m. p. 184°) into which it passes over when improperly kept. Furthermore, by means of its semicarbazone (m. p. 203 to 204°), or of its oximes, of which one modification melts at 63°, the other at 132°.

p-*Methoxycinnamic aldehyde.*

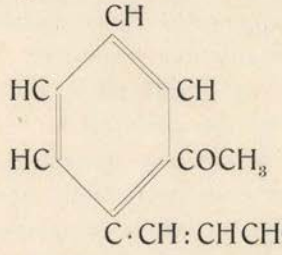


p-Methoxycinnamic aldehyde (*p*-cumaric aldehyde methyl ether) has been found in esdragon oil by Daufresne.[1]) Its constants are: B. p. 170° (14 mm.); $d_{0°}$ 1,137. The semicarbazone melts at 222°, the oxime at 154°.

The bisulphite addition product is not readily decomposed. When oxidized with potassium permanganate in acid solution, anisic acid results. Silver oxide oxidizes it to *p*-methoxy cinnamic acid (m. p. 170°).

The aldehyde is identical with the artificial product prepared by Scholtz and Wiedemann.[2])

o-*Methoxycinnamic aldehyde.*



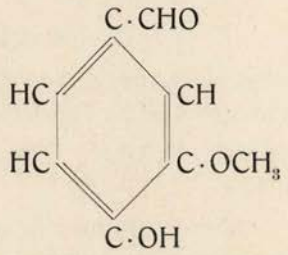
o-Methoxycinnamic aldehyde (*o*-cumaric aldehyde methyl ether) occurs occasionally as stearoptene in the oil of the Chinese

[1]) *Etude de l'essence d'estragon et de quelques dérivés de l'estragol.* Thèse, Paris 1909; Compt. rend. **145** (1907), 875; Bull. des Sciences pharmacologiques, January **1908**, 11; Report of Schimmel & Co. April **1908**, 49.

[2]) Berl. Berichte **36** (1903), 853.

cinnamon cassia[1]) and separates in solid form from the last fractions of cassia oil. M. p. 45 to 46°; b. p. abt. 295° with partial decomposition, 160 to 161° under 12 mm. pressure. It dyes the skin intensively yellow and is readily decomposible even away from air and light. Oxidation with permanganate converts it into methyl salicylic acid, m. p. 99°, which when boiled with hydriodic acid is converted into salicylic acid. With silver oxide it yields β-methylcumaric acid which melts at 182 to 183°. The oxime melts at 125 to 126°, the phenylhydrazone at 116 to 117°.

Vanillin.



Vanillin, the methyl ether of protocatechuic aldehyde, occurs widely distributed in the Vegetable Kingdom but mostly in very small amounts. Moreover, in the living plant it does not appear to occur as such, but is presumably the product of fermentation of a glucoside. It is the characteristic constituent of vanilla beans. It has also been found in the flowers of *Nigritella suaveolens,* in the oil of *Spiræa Ulmaria,* in Peru balsam, and in oil of cloves. It appears to be contained in the wood substance of numerous plants and can frequently be recognized by means of its characteristic agreeable odor, especially after proper preliminary treatment of the material to be tested. Of plants and plant materials in which its presence may be assumed, the following may be mentioned: Siam benzoes, Asa fetida, umbelliferous opopanax, the rosin of species of larch, maté, potato skins, fresh linden bark, cork, bulbs of dahlia, asparagus shoots, crude beet sugar, and the aqueous extract of the seed of *Lupinus albus.* Traces of vanillin can also be obtained from the sulphite wastes of the manufacture of cellulose, also from saw-dust by heating it under pressure with water to 180°.

[1]) Bertram and Kürsten, Journ. f. prakt. Chem. II. 51 (1895), 316.

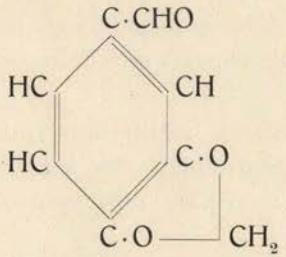
Artificially vanillin was first obtained from coniferin, a glucoside found in the cambial juice of conifers.[1]) Other methods have been devised since then. At present it is obtained principally by the oxidation of *iso*eugenol.

Vanillin constitutes colorless, prismatic needles which are readily soluble in the common organic solvents. It is also readily soluble in boiling water, but difficultly soluble in cold water. Both the aqueous and alcoholic solutions are colored blue by ferric chloride. Its melting point is usually recorded as 80 to 81°. Schimmel & Co., however, observed 82 to 84° in connection with pure preparations. When carefully heated it sublimes without decomposition. It boils at 285° (in a current of carbon dioxide), or at 170° under 15 mm. pressure.

Of crystalline derivatives the following may be mentioned: the methyl ether, m. p. 42 to 43°; the ethyl ether, m. p. 64 to 65°; the acetyl derivative, m. p. 77°; the benzoate, m. p. 75°; and the oxime, m. p. 121 to 122°. Upon oxidation its yields vanillic acid, m. p. 207°. Its isolation can be accomplished by means of alkali bisulphite, *p*-bromphenylhydrazine or *m*-nitrobenzylhydrazine. For the quantitative determination of vanillin compare the chapter "The examination of volatile oils".

In commerce vanillin is frequently found adulterated. The following list of substances has thus far been found as adulterants, *viz.*, acet*iso*eugenol, antifebrine, benzoic acid, coumarin, terpin hydrate, and sugar. The melting point, its solubility in water, alcohol and ether, and its behavior toward acid sulphite are the principal criteria in testing vanillin for its purity.

Heliotropin.



Heliotropin, also known as piperonal, is the methylene ether of protocatechuic aldehyde. It has been observed but once in a

[1]) Tiemann and Haarmann, Berl. Berichte 7 (1874), 613.

volatile oil and then only in minimal amount, namely in the oil from the flowers of *Spiræa Ulmaria*. The supposed occurrence in some varieties of vanilla bean assumed by Busse[1]) is still doubtful.[2]) Furthermore, it is not known whether the heliotropin-like odor of certain flowers, such as the heliotrope, is due to the presence of this aldehyde or not.

As source for the artificial preparation of piperonal, piperin was formerly used. At present it is obtained much more cheaply by the oxidation of *iso*safrol.

Heliotropin constitutes colorless, lustrous crystals that have a heliotrope-like odor, that melt at 35 to 36° and that boil at 236°. It is readily soluble in alcohol, ether and similar solvents; difficultly soluble in cold water, more readily in boiling water. From hot water it can be obtained in crystals an inch long and more. In glycerin it is very sparingly soluble, somewhat more in paraffin oil, comparatively readily soluble in olive oil (about 6 p. c.). At a temperature of 10° it is soluble to the extent of about 5 p. c. in 70 percent. alcohol.

As aldehyde, heliotropin combines with acid sulphite. Upon reduction piperonyl alcohol, m. p. 51°, results; upon oxidation piperonylic acid, m. p. 227,5 to 228°. Other derivatives are its monobromide, m. p. 129°, its mononitro compound, m. p. 94,5°, the anilide, m. p. 65°, the thiosemicarbazone, m. p. 185°, and the semicarbazone, m. p. 224 to 225°.

It may be mentioned that heliotropin possesses antipyretic and antiseptic properties, and that it may be used as antidote in strychnine poisoning.

Heliotropin should be stored in a cool, dark place since it turns yellow or even brown and is decomposed when exposed to light.[3])

When examined for adulterants, the melting point and solubility should be determined. Its behavior toward acid sulphite with which it reacts readily may also be ascertained.

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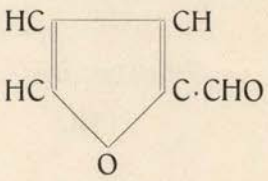
[1]) Arbeiten a. d. Kaiserl. Ges.-Amt **15** (1898 to 1899), 108.

[2]) Walbaum, *Wallach-Festschrift.* Göttingen 1909. p. 649; Report of Schimmel & Co. October **1909**, 142.

[3]) Report of Schimmel & Co. April **1904**, 128.

In this connection a heterocyclic aldehyde may be mentioned, namely,

Furfurol.



Its presence in volatile oils is possibly due to the united action of heat and acid on the cell-membrane and other carbohydrates of the crude materials subjected to distillation in the presence of water.[1])

In as much as this aldehyde is relatively soluble in water (in 11 parts at 13°) it is contained mostly in the aqueous distillate or in the first fraction of the oil.

Furfurol has been found in the following oils, *viz.,* pine tar oil, oil of cade, the first fraction of orris oil, clove oil,[2]) oil of Ceylon cinnamon, petitgrain oil, in the oil of *Apocynum androsæmifolium,* in the aqueous distillates from oils of cypress, savin, vetiver, orris, West Indian sandalwood, ambrette seeds, cloves, clove stems, caraway, and in the first distillate of bay and lavender oils. As a matter of interest, it may here be mentioned that E. Erdmann[3]) observed furfurol and furfuric alcohol in the volatile oil of the roasted coffee beans.

The boiling point of the pure compound is 160,5° (742 mm.); its density $d_{4°}^{20°}$ 1,1594. When oxidized it yields pyromucic acid, m. p. 132 to 133°. Of its derivatives the following may here be mentioned, *viz.,* the phenyl hydrazone, m. p. 97 to 98°, the semicarbazone, m. p. 197°, and the semioxamazone, m. p. 264°. It can be identified most conveniently by means of the well-known color reaction with *p*-toluidine or aniline hydrochloride.

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[1]) Report of Schimmel & Co. October 1899, 36.

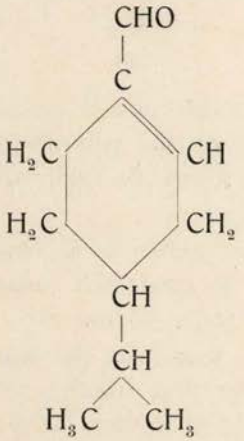
[2]) Oil of cloves also contains α-methyl- and a dimethyl furfurol.

[3]) Berl. Berichte 35 (1902), 1851.

ALICYCLIC (HYDROAROMATIC) ALDEHYDES.

So far as occurrence in volatile oils is concerned, this group of aldehydes is much less important than the others already considered.

Phellandral.



Phellandral, to which in all probability the above formula may be assigned, is found in small amounts in the oil of water-fennel. B. p. 89° (5 mm.); $d_{15°}$ 0,9445; α_D — 36° 30′; $n_{D20°}$ 1,4911.[1]) When exposed to air, or when treated with silver oxide, phellandral is readily oxidized to the corresponding acid which melts at 144 to 145°. Of its derivatives the oxime, m. p. 87 to 88°, the semicarbazone, m. p. 202 to 204°, and the phenylhydrazone, m. p. 122 to 123°, may be mentioned.

Aldehyde $C_{10}H_{16}O$ *from lemongrass oil.* B. p. 68° (6 mm.); $d_{15°}$ 0,9081; α_D + 0° 50′; $n_{D20°}$ 1,45641. M. p. of the semicarbazone 188 to 189°.

Aldehyde $C_{10}H_{16}O$ *from gingergrass oil.* B. p. 221 to 224° (754 mm.), 76 to 78° (5 mm.); $d_{15°}$ 0,9351; $\alpha_D \pm 0°$; $n_{D20°}$ 1,47348. Upon reduction an alcohol $C_{10}H_{18}O$ results, the phenylurethane of which melts at 100 to 101°. When exposed

[1]) Report of Schimmel & Co. October 1904, 88.

to the air this aldehyde is oxidized to an acid $C_{10}H_{16}O_2$, m. p. 106 to 107°, which can also be obtained from the saponification liquid of gingergrass oil. Derivatives: oxime, m. p. 115 to 116°, semicarbazone, m. p. 169 to 170°, semioxamazone, m. p. 244 to 245°, phenylhydrazone, m. p. 63°, β-naphthocinchoninic acid, m. p. 261°.

KETONES.

ALIPHATIC KETONES.

Of the aliphatic ketones only a few are found in volatile oils. They are mostly methyl ketones which can be isolated by means of their acid sulphite addition products. The lower members are water-soluble and hence are found either in the aqueous distillate or in the first portion of the oil which distils over.

Acetone, $CH_3 \cdot CO \cdot CH_3$. This ketone has been observed not infrequently during the distillation of volatile oils, more particularly of leaf oils. Presumably it is formed during the process of distillation, but the reaction by which it is produced is not known. It has been found in the Atlas cedar oil, coca leaf oil, clove oil and in the distillate of patchouli leaves. Together with hydrocyanic acid, it has been found in the distillate of numerous plants, thus in that of *Triglochin maritima*[1]), *Thalictrum aquilegifolium, Nandina domestica, Phaseolus lunatus, P. Mungo, Linum usitatissimum, L. perenne, Hevea brasiliensis, H. Spruceana, Jatropha angustidens, Manihot bankensis, M. Glaziovii, M. palmata, M. utilissima, Passiflora alata, P. cœrulea, P. edulis, P. fœtida, P. hybrida, P. laurifolia, P. maculata, P. princeps, P. quadrangularis, P. suberosa, Tacsonia spec.* and *T. van Volxemii.*[2])

Acetone boils at 56,5° and has the density $d_{14°}$ 0,79945. As characteristic derivatives the *p*-bromphenylhydrazone, m. p. 94°, and the oxime, m. p. 59 to 60°, may be mentioned. With iodine-potassium iodide solution a precipitate of iodoform results.

[1]) Greshoff, Pharm. Weekblad **45** (1908), 1165; Chem. Zentralbl. **1908**, II. 1446.
[2]) Greshoff, Arch. der Pharm. **244** (1906), 665.

Methyl-n-amyl ketone, $CH_3 \cdot CO \cdot (CH_2)_4 \cdot CH_3$, is contained in the low boiling portions of clove oil and is of importance so far as the characteristic odor of this oil is concerned. Its presence in Ceylon cinnamon oil has also been demonstrated. B. p. 151 to 152°; $d_{0°}$ 0,8366. The semicarbazone melts at 122 to 123°.

Ethyl-n-amyl ketone, $CH_3 \cdot CH_2 \cdot CO \cdot [CH_2]_4 \cdot CH_3$, occurs in the first fraction of French lavender oil. B. p. 169,5 to 170°; $d_{15°}$ 0,8254; $n_{D20°}$ 1,41536; m. p. of semicarbazone 117 to 117,5°. It does not react with acid sulphite. Its oxidation with chromic acid yields *n*-capronic acid.[1])

Methyl-n-heptyl ketone, $CH_3 \cdot CO \cdot [CH_2]_6 \cdot CH_3$, frequently constitutes the bulk of Algerian oil of rue. In small amounts it is also found in French and Spanish oils of rue and in oil of cloves. It is a colorless oil with an agreeable odor resembling that of rue.

For methyl heptyl ketone isolated from oil of rue, the following constants have been ascertained:

M. p. —17°; cong. p. —19°; b. p. 85 to 90° (7 mm.), 95,8 to 102° (24 mm.); $d_{20°}$ 0,83178.[2])

Cong. p. —15°; b. p. 193 to 194° (740 mm.); $d_{20°}$ 0,821.[3])

B. p. 194,5 to 195,5° (763 mm.); $d^{14°}_{16°}$ 0,8296.[4])

B. p. 194 to 196°; 80 to 82° (15 mm.).[5])

It reacts but slowly with acid sulphite solution. M. p. of the semicarbazone 118 to 119° or 119 to 120°. Oxidized with hypobromite it yields *n*-caprylic acid.

Methyl-n-nonyl ketone, $CH_3 \cdot CO \cdot [CH_2]_8 CH_3$, has long been known as the principal constituent of the common oil of rue from France and Spain. In Algerian oil of rue it usually plays but a subordinate role as compared with methyl heptyl ketone. For its preparation the French oil is commonly used, the ketone being isolated either by freezing it out, or by means of the acid sulphite addition product.

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[1]) Report of Schimmel & Co. April **1903**, 47; October **1903**, 44.

[2]) Thoms, Berichte d. deutsch. pharm. Ges. **11** (1901), 16.

[3]) v. Soden and Henle, Pharm. Ztg. **46** (1901), 277.

[4]) Power and Lees, Journ. chem. Soc. **81** (1902), 1588.

[5]) Houben, Berl. Berichte **35** (1902), 3588.

Methylnonyl ketone is a colorless liquid at room temperature and possesses an odor similar to that of methylheptyl ketone. Its constants, as determined by different investigators, are as follows:

B. p. 226° (766 mm.), 230,65° (corr.), 122 to 123° (24 mm., corr.).[1])

M. p. + 13,5°; cong. p. + 12°; b. p. 223 to 224° (774 mm.), 99° (7 mm.); $d_{20°}$ 0,82623.[2])

B. p. 230 to 231° (740 mm.).[3])

B. p. 229 to 233° (759 mm.), after regeneration from the semicarbazone 231,5 to 232,5° (761 mm.); $d^{20.5°}_{16°}$ 0,8263.[4])

Cong. p. + 13°; b. p. 228 to 230°, 120° (20 mm.), 118° (18 mm.); $d_{15°}$ 0,8295; $d_{20°}$ 0,8263.[5])

In connection with a synthetically prepared product Gorup-Besanez and Grimm[6]) observed the following constants:

M. p. + 15 to 16°; b. p. 224°; $d_{17,5°}$ 0,8295.

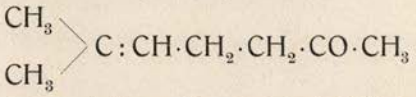
The oxime melts at 46 to 47°, the semicarbazone at 123 to 124°. Hypobromite oxidizes it to caprinic acid.

Diacetyl, $CH_3 \cdot CO \cdot CO \cdot CH_3$. Like furfurol, this aliphatic diketone, which has been observed rather frequently in volatile oils, presumably owes its origin to the decomposition of certain plant constituents during the process of distillation. Inasmuch as it is rather water-soluble, it also is apt to concentrate in the cohobated aqueous distillate or in the first fractions. At times it even reveals its presence by means of its yellowish-green color and its quinone-like odor. In most instances, diacetyl is found together with methyl alcohol and furfurol. It has been observed in the first distillate of a pine tar oil from Finland, in the cohobated aqueous distillate from the oils of cypress, savin, vetiver, orris, West Indian sandalwood, bay, and caraway.

B. p. 87,5 to 88°; density 0,9734 at 22°. Characteristic are its monophenylhydrazone, m. p. 133 to 134°; the oxime of the latter, *viz.* the diacetylhydrazoxime, m. p. 158°, and the osazone, m. p. 243°.

[1]) Carette, Journ. de Pharm. et Chim. II. **10** (1899), 256.
[2]) Thoms, *loc. cit.* 8.
[3]) v. Soden and Henle, *loc. cit.*
[4]) Power and Lees, *loc. cit.*
[5]) Houben, *loc. cit.* 3590.
[6]) Liebig's Annalen **157** (1871), 279.

Methyl heptenone.



Of greater interest than the saturated ketones already enumerated, is the unsaturated methyl heptenone, $C_8H_{14}O$. It occurs as constituent of several volatile oils and has been obtained as decomposition product of related compounds. As companion to the closely related linalol, geraniol and citral, it occurs in Mexican lignaloe oil, citronella oil and lemongrass oil. It also occurs in lemon oil, palmarosa oil and in the oil of *Barosma pulchella*. Apparently it owes its existance to the decomposition of the above-mentioned compounds. This decomposition can likewise be brought about artificially by oxidation. From the fractions boiling between 160 and 180° it can readily be isolated by means of its acid sulphite addition product.

As "Abbau" product it was first obtained in the dry distillation of cineolic acid anhydride.[1]) It was then observed during the saponification of geranic acid nitrile,[2]) and as oxidation product of citral.[3]) It also results from the latter when treated with alkalies.[4]) Synthetically it has been obtained from amylene bromide and acetyl acetone,[5]) also by the interaction of the iodide of acetopropylalcohol, acetone and zinc dust.[6])

It is a colorless, mobile liquid, with a penetrating odor reminding of amyl acetate, and is optically active. The physical constants as recorded do not agree any too well. For the ketone obtained from cineolic anhydride, Wallach records the following:

B. p. 173 to 174°; $d_{20°}$ 0,8530; $n_{D20°}$ 1,44003.[7])

For natural methyl heptenone Tiemann and Krüger determined:

B. p. 170 to 171° (760 mm.); $d_{20°}$ 0,8499; n_D 1,4380.[8])

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[1]) Wallach, Liebig's Annalen **258** (1890), 323.
[2]) Tiemann and Semmler, Berl. Berichte **26** (1893), 2721.
[3]) *Ibidem* 2719.
[4]) Verley, Bull. Soc. chim. III. **17** (1897), 175.
[5]) Barbier and Bouveault, Compt. rend. **122** (1896), 1422.
[6]) Verley, Bull. Soc. chim. III. **17** (1897), 191.
[7]) Liebig's Annalen **258** (1890), 325.
[8]) Berl. Berichte **28** (1895), 2123.

For the "Abbau" product of citral Verley records:

B. p. 168°, 84° (56 mm.); $d_{14°}$ 0,910 (!); $n_{D31°}$ 1,437.[1])

For the methyl heptenone isolated from lemongrass oil and regenerated from the acid sulphite addition product, Schimmel & Co. observed:

B. p. 173° (758 mm.); $d_{15°}$ 0,855; $n_{D20°}$ 1,43805;[2])

and for a product obtained by boiling citral with potassium carbonate solution:

B. p. 173 to 174°; $d_{15°}$ 0,8656.

When reduced in alcoholic solution with sodium, methyl heptenone is reduced to the secondary alcohol methyl heptenol, $C_8H_{16}O$.[3]) This alcohol is likewise found among the decomposition products of geraniol and the saponification products of geranic acid nitrile. Methyl heptenone combines with acid sulphites to crystalline addition products, with hydroxylamine and phenylhydrazine to liquid condensation products, and with semicarbazide to a crystalline semicarbazone which can be utilized for the identification of the ketone. When oxidized, methyl heptenone breaks down into acetone and lævulinic acid, $C_5H_8O_3$[4]) in accordance with the above formula. Dehydrating agents, such as zinc chloride, convert it into dihydro-*m*-xylene, C_8H_{12}.[5])

Methyl heptenone is readily recognized by its characteristic odor reminding of amylacetate. For its identification it is converted into the semicarbazone. As in the case of citral, this appears to be a mixture of isomers. However, a product with a constant melting point is obtained when prepared according to the directions of Tiemann and Krüger.[6]) According to these investigators, a solution of 12 g. of semicarbazide hydrochloride and 15 g. sodium acetate in 20 cc. of water is added to a mixture of 12 g. methyl heptenone and 20 cc. of glacial acetic acid, and the mixed solutions set aside for half an hour. Upon the addition of water the semicarbazone separates as oil which soon

[1]) Verley, *loc. cit.* 176.
[2]) Report of Schimmel & Co. April 1899, 65.
[3]) Wallach, Liebig's Annalen 275 (1893), 171.
[4]) Tiemann and Semmler, Berl. Berichte 28 (1895), 2128.
[5]) Wallach, Liebig's Annalen 258 (1890), 326.
[6]) Berl. Berichte 28 (1895), 2124.

congeals to a crystals which, when recrystallized from dilute alcohol, melt at 136 to 138°.

A compound well suited for identification is obtained when methyl heptenone is treated with bromine in the presence of soda lye.[1]) Hypobromous acid is added and bromine simultaneously substituted with the formation of the well crystallized derivative $C_8H_{12}Br_3O \cdot OH$. For its preparation 3 g of ketone are shaken with a solution of 3 g of sodium hydroxide and 12 g of bromine in 100 to 120 cc. of water. The reaction product separates as a heavy oil which soon congeals. It is taken up with ether, the ethereal solution shaken out with dilute soda solution. The residue left upon the evaporation of the ether is recrystallized from ligroin to which some animal charcoal has been added. The melting point of the pure, white crystals lies between 98 and 99°. Upon keeping they gradually decompose.

A method for the identification of methyl heptenone in the presence of citronellal and citral has been worked out by Tiemann.[2]) It is based on the fact that methyl heptenone does not react with either a dilute or a concentrated solution of sodium sulphite and sodium acid carbonate, whereas the two aldehydes can be successively removed by shaking the oily mixture with the respective solutions of these salts.

AROMATIC KETONES.

As constituents of volatile oils, these ketones play but a minor role. The following may here be mentioned.

o-*Hydroxyacetophenone*, $CH_3 \cdot CO \cdot C_6H_4 \cdot OH$, and possibly its methyl ether, are contained in the oil of *Chione glabra*. B. p. 160 to 165° (34 mm.). With ferric chloride it produces a deep red color, with bromine water a yellow crystalline precipitate. The oxime melts at 112°, the phenylhydrazone at 108°. When fused with potassa, salicylic acid (m. p. 155°) results.

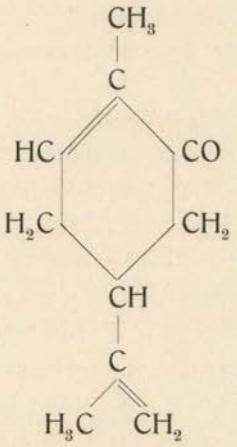
Anise ketone (*p*-methoxyphenylacetone), $CH_3 \cdot CO \cdot CH_2 \cdot C_6H_4 \cdot OCH_3$ possibly occurs in Russian anise oil and in bitter fennel oil. B. p. 263°; $d_{0°}$ 1,095. The oxime melts at 72°.

[1]) Tiemann and Semmler, Berl. Berichte **26** (1893), 2723.

[2]) Berl. Berichte **32** (1899), 823.

ALICYCLIC (HYDROAROMATIC) KETONES.

Carvone.



The dextrogyrate modification of carvone, $C_{10}H_{14}O$, occurs to the extent of from 50 to 60 p. c. in caraway oil, also in dill oil in much the same amount. *l*-Carvone is not as common and has been found in kuromoji oil and in spearmint oil. Inactive carvone has been found only in gingergrass oil. In the oil from the Spanish dill herb, carvone has likewise been observed.

In order to obtain the ketone in the pure state from the oil, it can be converted into its crystalline hydrogen sulphide addition product, $(C_{10}H_{14}O)_2 \cdot H_2S$. When a solution of 20 parts of the carvone fraction, 5 parts of alcohol and 1 part ammonia ($d_{15°}$ 0,96) is saturated with hydrogen sulphide, the addition product crystallizes out. Drained, and recrystallized from methyl alcohol it is decomposed by boiling with alcoholic potassa, and the regenerated carvone purified by distillation with steam. A slightly modified method of preparation is given by Wallach.[1])

The same object is accomplished much more readily by isolating the carvone by means of normal sodium sulphite with which carvone combines to form a water-soluble compound. The oil is shaken with a sufficient amount of a concentrated aqueous sodium sulphite solution, the sodium hydroxide which is set free being neutralized from time to time. The reaction being com-

[1]) Liebig's Annalen **305** (1899), 224.

pleted, those oily compounds that have not united with the sulphite are shaken out repeatedly with ether and removed. The carvone is then set free with soda lye and distilled with steam. This method may also be utilized for the quantitative determination of carvone. (See the chapter in "The examination of volatile oils".)

Artificially, carvone and its derivatives have been obtained in a variety of ways. However, a detailed account of the relationship between carvone, pinene, limonene, pinol, and terpineol would lead too far.

Carvone is a colorless liquid possessing a decided odor of caraway. At a low temperature it congeals.[1]) In the laboratory of Schimmel & Co. the following properties have been determined:

For *d*-carvone prepared from caraway oil by means of the sulphite addition product:

B. p. 230° (755 mm.), 91° (5 to 6 mm.); $d_{15°}$ 0,9645; $\alpha_D + 59° 57'$; $n_{D20°}$ 1,49952.

For *l*-carvone prepared from spearmint oil by means of the sulphite addition product:

B. p. 230 to 231° (763 mm.); $d_{15°}$ 0,9652; $\alpha_D - 59° 40'$; $n_{D20°}$ 1,4988; soluble in 17 vols. of 50 p. c. alcohol and in 4 vols. of 60 p. c. alcohol.

Commercial preparations, own manufacture, varied as follows:

$d_{15°}$ 0,963 to 0,966; $\alpha_D + 57° 30'$ to $+ 60°$; $n_{D20°}$ 1,497 to 1,500; soluble in 16 to 20 vols. of 50 p. c. alcohol, in 4 vols. of 60 p. c. alcohol, and in 1,5 to 2 vols. of 70 p. c. alcohol.

Carvone is an unsaturated ketone which combines with hydrogen chloride to form a liquid compound,[2]) and with hydrogen bromide to one melting at 32°.[3]) If hydrogen bromide be split off from the latter, an isomeric ketone $C_{10}H_{14}O$, eucarvone results.[4]) The bromine substitution products obtained by the action of bromine on hydrobromcarvone, *viz.*, the tribromide,

[1]) Wallach, Liebig's Annalen **252** (1889), 129, footnote.

[2]) Goldschmidt and Kisser, Berl. Berichte **20** (1887), 487, 2071.

[3]) *Ibidem* 2071; Baeyer, Berl. Berichte **27** (1894), 811.

[4]) Baeyer, Berl. Berichte **27** (1894), 811; Wallach, Liebig's Annalen **305** (1899), 234; **339** (1905), 94.

$C_{10}H_{14}O \cdot HBr \cdot Br_2$, the tetrabromide, $C_{10}H_{14}OBr_4$, and the pentabromide, $C_{10}H_{13}OBr_5$, have been examined by Wallach.[1])

With acid sulphites, carvone yields salts of the carvone dihydrosulphonic acid. It also adds sulphurous acid. With hydroxylamine it yields a well crystallizable oxime,[2]) of which the optically active modifications melt at 72°.[3]) Union of equal parts of *d*- and *l*-carvoxime yields the inactive carvoxime which melts at 93°.[4])

In the preparation of carvoxime, care should be exercised not to use too large an excess of hydroxylamine, otherwise an addition product of hydroxylamine to carvoxime, $C_{10}H_{14}NOH \cdot NH_2OH$ (m. p. 174 to 175°) may be formed.[5]) If the freshly prepared oxime does not congeal readily, it can at times be made to crystallize by driving it over with steam. Artificially the oximes of carvone are obtained by splitting off hydrogen chloride from the nitrosochlorides of limonene and dipentene.[6]) With phenylhydrazine, carvone yields a phenylhydrazone that melts at 109 to 110°,[7]) with semicarbazide *d*- and *l*-carvone yield the semicarbazones. Whereas the *d*- and *l*-carvone semicarbazone melt at 162 to 163°,[8]) *i*-carvone semicarbazone melts at a lower temperature, *viz.*, at 154 to 156°.[9])

By allowing an excess of free hydroxylamine to act on hydrobromcarvone and subsequently splitting off hydrogen bromide, *iso*carvoxime melting at 142 to 143° results.[10]) Under the dehydrating influence of dilute acids, the latter yields carvoline.[11])

[1]) Liebig's Annalen **286** (1895), 119.

[2]) Goldschmidt, Berl. Berichte **17** (1884), 1578; Harries, in Meyer-Jacobson, *Lehrbuch der organischen Chemie,* Leipzig (1902), Vol. II. part 1, p. 939.

[3]) Wallach, Liebig's Annalen **246** (1888), 226.

[4]) Wallach, *ibidem* **245** (1888), 268.

[5]) Wallach and Schrader, Liebig's Annalen **279** (1894), 368; Harries and Jablonski, Berl. Berichte **31** (1898), 1384; Harries, *ibidem* 1810.

[6]) Goldschmidt and Zürrer, Berl. Berichte **18** (1885), 2220; Wallach, Liebig's Annalen **245** (1888), 256, 268; **246** (1888), 226.

[7]) Baeyer, Berl. Berichte **27** (1894), 811; see also Goldschmidt, *ibidem* **17** (1884), 1578.

[8]) Baeyer, *ibidem* **27** (1894), 1923.

[9]) Baeyer, *ibidem* **28** (1895), 640.

[10]) Goldschmidt and Kisser, Berl. Berichte **20** (1887), 2073.

[11]) Goldschmidt, *ibidem* **26** (1893), 2086; Wallach, Liebig's Annalen **346** (1906), 266.

When reduced in alcoholic solution with sodium, carvone is not reduced to carveol, $C_{10}H_{16}O$, but takes up four hydrogen atoms at once with the formation of dihydrocarveol. (See p. 385). If in alcoholic-alkaline solution, carvone be reduced with zinc dust, two atoms of hydrogen are added, but the resulting compound is no alcohol but a ketone $C_{10}H_{16}O$, dihydrocarvone.[1]) As a by-product a bimolecular ketone, α-dicarvelone, m. p. 148 to 149°, results.[2])

When carvone is shaken with 40 p. c. sulphuric acid a hydroxy dihydrocarvone[3]) results which melts at 41 to 42°. Potassium permanganate oxidizes carvone to hydroxyterpenylic acid, $C_8H_{12}O_5$[4]) which melts at 190 to 192°. It is because of these oxidation products as well as because of those obtained by Tiemann and Semmler[5]) from dihydrocarveol and dihydrocarvone that these investigators adopted as the most probable expression for the constitution of carvone the formula given above, a formula previously suggested by Wagner.

When heated with sulphuric acid, phosphoric acid, phosphorus oxychloride, zinc chloride, or alkalies, carvone is converted into the isomeric benzene derivative, carvacrol, $C_6H_3 \cdot CH_3^{[1]} \cdot OH^{[2]} \cdot C_3H_7^{[4]}$. A similar intermolecular rearrangement takes place when carvoxime is heated with alcoholic sulphuric acid or with a strong solution of alkali to 230 to 240°, whereby the oxime is changed to carvacrylamine.[6]) When carvoxime is added to concentrated sulphuric acid, it rearranges itself to *p*-amido thymol,[7]) m. p. 173 to 174°.

When carvone is heated with ammonium formate, dihydrocarvylamine is formed.[8]) The same base results when carvoxime is reduced in alcoholic solution with sodium.[9])

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[1]) Wallach and Schrader, Liebig's Annalen **279** (1894), 377.

[2]) Wallach and Schrader, *ibidem* 380; Wallach, *ibidem* **305** (1899), 223.

[3]) Rupe and Schlochoff, Berl. Berichte **38** (1905), 1719.

[4]) Best, Berl. Berichte **27** (1894), 1218; Wallach, *ibidem* 1495.

[5]) Berl. Berichte **28** (1895), 2148.

[6]) Wallach, Liebig's Annalen **275** (1793), 118; **279** (1894), 374.

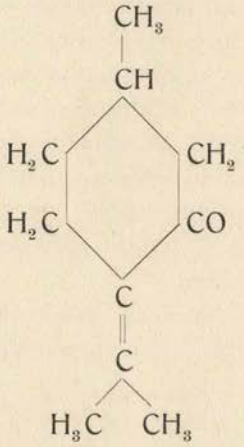
[7]) Wallach, Liebig's Annalen **279** (1894), 369.

[8]) Leuckart and Bach, Berl. Berichte **20** (1887), 113; Wallach, Berl. Berichte **24** (1891), 3984.

[9]) Wallach, Liebig's Annalen **275** (1893), 119.

Carvone is characterized by its peculiar odor by means of which it can readily be recognized. If it is to be isolated from a volatile oil, its hydrogen sulphide addition product or the sodium acid sulphite addition product may be utilized for this purpose. (See above.) It should be noted, however, that the hydrogen sulphide addition product does not melt at 187°, as stated by Baeyer,[1]) but at 210 to 211°.[2])

Pulegone.



Pulegone, a ketone $C_{10}H_{16}O$, has thus far been found in labiate oils only. In these it frequently occurs in large amounts, occasionally together with menthol and menthone. European pennyroyal oil contains about 80 p. c. of this ketone. Diptam origanum oil likewise consists largely of pulegone. Its presence in the following oils has also been determined, *viz.,* in the oils of *Hedeoma pulegioides, Pycnanthemum lanceolatum, Bystropogon origanifolius* and *Calamintha Nepeta.* In all of these oils it occurs in the dextrogyrate form. Its presence has further been ascertained in Canadian mint oil, in Japanese peppermint oil, and in marjoran oil. In these cases, however, references to the rotation are wanting.

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[1]) Arch. der Pharm. **221** (1883), 285.

[2]) Claus and Fahrion, Journ. f. prakt. Chem. II. **39** (1889), 365; Report of Schimmel & Co. April **1898**, 47, footnote.

In as much as European pennyroyal oil consists chiefly of this ketone, pulegone can be obtained relatively pure by fractional distillation of this oil. In a purer state it can be separated from its compound with sodium acid sulphite or with neutral sodium sulphite. To cause the pulegone to combine with acid sulphite, the oil diluted with 1/4 its volume of alcohol is subjected to prolonged shaking with the aqueous sulphite solution.[1]) Its capacity to react with normal sulphite, also makes possible the quantitative estimation of pulegone. (See the chapter "The examination of volatile oils" under determination of ketones.) Furthermore, the semicarbazone, which can be hydrolyzed with acids, can be used for the purification of pulegone.

In a round-about way, pulegone has been obtained synthetically from citronellal.[2]) Another ketone, which is not identical with natural pulegone, Wallach[3]) obtained by condensation of 1,3-methyl*cyclo*hexanone with acetone.

Pulegone is a colorless liquid which turns slightly yellow upon prolonged standing. It possesses a peppermint-like, sweetish odor reminding of menthone.

For pulegone purified only by means of distillation, Beckmann and Pleissner[4]) found the following constants:

B. p. 130 to 131° (60 mm.); $d_{20°}$ 0,9323; $[\alpha]_D + 22{,}89°$; n_D 1,47018.

Barbier[5]) records the following:

B. p. 222 to 223°; $d_{23°}$ 0,9293; $[\alpha]_D + 25° 15'$.

For pulegone regenerated from the bisulphite addition product, Baeyer and Henrich[6]) observed the following constants:

B. p. 100 to 101° (15 mm.); $[\alpha]_D + 22{,}94°$;

and Wallach:[7])

B. p. 221 to 222°; d 0,936; n_D 1,4846.

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[1]) Baeyer, Berl. Berichte **28** (1895), 652.
[2]) Tiemann and Schmidt, Berl. Berichte **29** (1896), 913; **30** (1897), 22.
[3]) Berl. Berichte **29** (1896), 1597, 2955; Liebig's Annalen **300** (1898), 267.
[4]) Liebig's Annalen **262** (1891), 3, 4, 20.
[5]) Compt. rend. **114** (1892), 126.
[6]) Berl. Berichte **28** (1895), 653.
[7]) *Ibidem* 1965.

In connection with technical products prepared in the laboratory of Schimmel & Co., the following constants were observed:

$d_{15°}$ 0,939 to 0,941; α_D + 20 to + 23°; $n_{D20°}$ 1,484 to 1,488; soluble in 4,5 vol. of 60 p. c. alcohol and in 1,5 vol. of 70 p. c. alcohol.

For a pure pulegone regenerated from its sulphite compound the following constants were observed:

B. p. 224° (750 mm.); 93 to 94° (8 to 9 mm.); 85° (5 mm.); $d_{15°}$ 0,9405; α_D + 20° 48′; $n_{D20°}$ 1,48796.

As an unsaturated compound pulegone combines with bromine but yields a liquid dibromide. When heated with sodium ethylate, this yields pulegenic acid, $C_{10}H_{16}O_2$, from which a long series of derivatives has been obtained and which has served as the starting-point for extensive investigations. With hydrogen chloride and hydrogen bromide, pulegone yields crystalline addition products.[1])

Pulegone reveals the character of a ketone. When carefully reduced in alcoholic solution with metallic sodium, pulegol,[2]) $C_{10}H_{18}O$, the corresponding alcohol is presumably first formed. Further addition of hydrogen reduces it to the saturated *l*-menthol, $C_{10}H_{20}O$.[3])

When pulegone is heated with anhydrous formic acid or with alkali or with water in an autoclave to 250° it is hydrolyzed yielding acetone and 1,3-methyl*cyclo*hexanone, $C_7H_{12}O$.[4])

Pulegone reacts with hydroxylamine, but the oxime of the normal ketone is not yet known. What was formerly regarded as such, is *iso*pulegone oxime, since Wallach[5]) has shown that in the presence of alkali and hydroxylamine pulegone undergoes isomerization to (active) *iso*pulegone. At the same time the pulegone undergoes partial hydrolysis as indicated above, so that the yield of oxime leaves much to be desired.

[1]) Beckmann and Pleissner, Liebig's Annalen **262** (1891), 21; Baeyer and Henrich, Berl. Berichte **28** (1895), 653.

[2]) Tiemann and Schmidt, Berl. Berichte **29** (1896), 914.

[3]) Beckmann and Pleissner, loc. cit. 30.

[4]) Wallach, Liebig's **289** (1896), 338; **365** (1909), 243.

[5]) Liebig's Annalen **365** (1909), 240.

Wallach[1]) obtained the best results by observing the following directions:

To a solution of 10 g. of pulegone in 30 ccm. of absolute alcohol a solution of 30 g. solid potassa in 20 ccm. of water are added and then as rapidly as possible a solution of 1 g. of hydroxylamine hydrochloride in 1 ccm. of water. Care should be taken that the temperature of the reaction mixture does not exceed 75°. Finally, the mixture is heated for 10 minutes to 85° on a water bath. When cooled, the mass is poured on ice and allowed to stand. The oxime, which usually separates in large flakes, is shaken out with ether, the ether recovered by distillation and the residue subjected to steam distillation. The oxime passes over with the steam and separates in the form of fine needles which can be collected on an asbestos filter and recrystallized from ether or ligroin, when they melt at 120 to 121°. By repeated recrystallization from methyl alcohol, Wallach succeeded in raising the melting point to 123 to 124°. The oxime is lævogyrate, $[\alpha]_{D22°} - 25{,}833°$. When hydrolyzed by heating with oxalic acid, the oxime yields *iso*pulegone. With sulphuric acid, however, pulegone is regenerated, since the sulphuric acid isomerizes the *iso*pulegone back to pulegone.

In addition to this oxime two addition reaction products of pulegone with hydroxylamine are known: first, a compound $C_{10}H_{16}O \cdot NH_2OH$[2]) which results from the addition of hydroxylamine to the pulegone and which melts at 155 to 157°; and secondly, a dioxime or rather hydroxamino oxime, $C_{10}H_{16}NOH \cdot NH_2OH$, which melts at 118°.[3])

The semicarbazone which results from the action of semicarbazide on pulegone melts at 167,5 to 168°.[4]) It is difficultly soluble in ether.

According to Baeyer and Henrich,[5]) the identification, however, can be brought about more readily by means of the

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[1]) Liebig's Annalen **365** (1909), 244.

[2]) Beckmann and Pleissner, Liebig's Annalen **262** (1891), 6; Wallach, *ibidem* **365** (1909), 246.

[3]) Semmler, Berl. Berichte **38** (1905), 146.

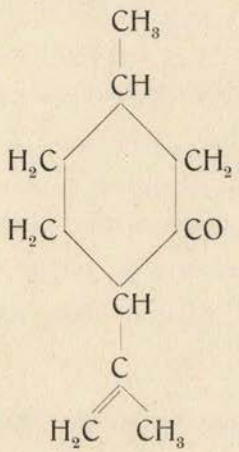
[4]) Wallach, Liebig's Annalen **365** (1909), 246.

[5]) Berl. Berichte **28** (1895), 654; comp. Baeyer and Prentice, Berl. Berichte, **29** (1896), 1078; Gage, Pharm. Review **16** (1898), 413.

characteristic bisnitrosopulegone. For its preparation a very small amount of hydrochloric acid is added to a solution of 2 ccm. of pulegone or pulegone-containing oil in 2 ccm. of ligroin and 1 ccm. of amyl nitrite which has been cooled down in a good freezing mixture. After a short time the bisnitroso compound separates in the form of fine needles which can be purified by drying them on porous plates and washing them with petroleum ether, when they melt at 81,5°. When recrystallized they decompose. *Iso*pulegone does not give this reaction.

When oxidized with potassium permanganate, pulegone yields acetone and active methyladipic acid, $C_7H_{10}O_4$ melting at 84 to 85°. Because of these results, Semmler[1]) has assigned to pulegone the above formula which also seems to explain the hydrolysis of this ketone into acetone and methyl hexanone.

Iso*pulegone*.



This ketone, which has thus far not been found in volatile oils, may receive brief mention at least. As described on p. 446, it can be prepared by way of the oxime from pulegone. It can also be obtained by treating pulegone hydrobromide with basic lead nitrate.[2]) Furthermore from citronellal, by converting this

[1]) Berl. Berichte **25** (1892), 3515.

[2]) Harries and Roeder, Berl. Berichte **32** (1899), 3368.

into *iso*pulegol (see p. 416) and the subsequent oxidation of this alcohol to *iso*pulegone.[1])

Whereas the first two methods mentioned yield a single, active product, the change from citronellal to *iso*pulegone results in a mixture of active and inactive ketone, the ratio of which varies according to the conditions of the experiment.[2]) The active *iso*pulegone yields a likewise active oxime which melts at 120 to 121° (respectively at 123 to 124°. See p. 446). The inactive ketone yields an inactive oxime which melts, according to Wallach, at 138 to 139°.[3]) According to Wallach, the separation of the two oximes is best accomplished by repeated recrystallization from methyl alcohol, in which the lower-melting oxime is more readily soluble. However, it is difficult to free the latter entirely from the higher-melting oxime, hence the poorly marked melting points.

The active *iso*pulegone yields a semicarbazone which melts at 172 to 174° and which is readily soluble in ether, the inactive ketone a semicarbazone which melts at 182 to 183° and which is difficultly soluble in ether.

For an *iso*pulegone obtained from *d*-citronellal, Tiemann and Schmidt[4]) record the following constants:

B. p. 90° (12 mm.); $d_{17.5°}$ 0,9213; α_D + 10° 15′; n_D 1,4690.

For an *iso*pulegone obtained from pulegone hydrobromide, Harries and Roeder[5]) observed the following constants:

B. p. 98 to 100° (13 mm.); $d_{19.5°}$ 0,9192; α_D — 7° 8′.

For its characterization the above-mentioned derivatives can be used.

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[1]) Tiemann and Schmidt, Berl. Berichte **30** (1897), 22; Tiemann, *ibidem* **32** (1899), 825.

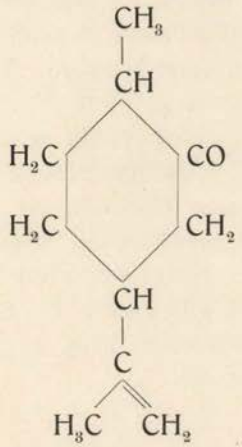
[2]) Wallach, Liebig's Annalen **365** (1909), 253. Harries and Roeder assumed the existence of two stereoisomeric ketones, *viz.*, α- and β-*iso*pulegone. Berl. Berichte **32** (1899), 3362. The former is identical with the active, the latter with the inactive *iso*pulegone.

[3]) Harries and Roeder as well as Semmler found 143°. Wallach *(loc. cit.)* explains this discrepancy by assuming that these investigators had an inactive oxime totally free from the active modification.

[4]) Berl. Berichte **30** (1897), 28.

[5]) *loc. cit.* 3371.

Dihydrocarvone.



It is only recently that this ketone has been found in caraway oil by the chemists of Schimmel & Co.[1])

Artificially it is obtained by the oxidation of dihydrocarveol with chromic acid in glacial acetic acid solution,[2]) also by the reduction of carvone with zinc dust and alkali or glacial acetic acid.[3]) In the latter case some dihydrocarveol always results.

Dihydrocarvone combines readily with sodium acid sulphite[2]) and can be obtained in a pure state by means of this addition product.

It is a liquid, the odor of which resembles that of menthone as well as that of carvone. Wallach *(loc. cit.)* records the following properties:

B. p. 221 to 222°; $d_{19°}$ 0,928; $n_{D19°}$ 1,47174. The optical rotation varies according to the material from which it is prepared: *d*-carvone yields lævogyrate dihydrocarvone, *l*-carvone yields dextrogyrate dihydrocarvone.

Schimmel & Co. *(loc. cit.)* record the following constants for a dihydrocarvone isolated from caraway oil:

B. p. 221° (735,5 mm.); $d_{15°}$ 0,9297; α_D — 16° 18′; $n_{D20°}$ 1,47107.

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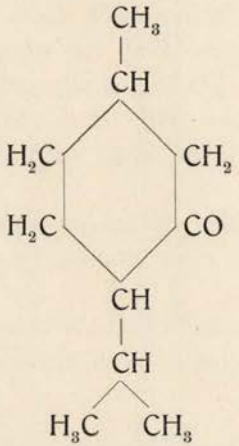
[1]) Report of Schimmel & Co. April **1905**, 20.

[2]) Wallach, Liebig's Annalen **275** (1893), 115.

[3]) Wallach and Schrader, *ibidem* **279** (1894), 377.

The following characteristic derivatives may here be mentioned. According to Wallach[1]) the dibromide is readily obtained by the addition of bromine to a solution of dihydrocarvone in glacial acetic acid-hydrogen bromide. The active modifications of the dihydrobromide melt at 69 to 70°, the racemic mixture at 96 to 97°. The active oxime melts at 88 to 89°, the racemic mixture at 115 to 116°. The oximes deviate the plane of polarized light in the same direction as do the corresponding ketones.[2]) The melting point of the semicarbazone is given by Wallach[3]) as 189 to 191°. Harries and Roeder[4]) record 201 to 202° for a preparation washed with ether. In addition to the constants, the above-mentioned derivatives may be utilized for the characterization of dihydrocarvone.

Menthone.



Both optical modifications of menthone, $C_{10}H_{18}O$, are found in nature. *d*-Menthone has been found in the oil of *Barosma pulchellum* and in American pennyroyal oil from *Hedeoma pulegioides; l*-menthone in Réunion geranium oil, buchu-leaf oil, peppermint oil and American pennyroyal oil. Menthone has also been found in European pennyroyal oil from *Mentha pulegium,*

[1]) Wallach and Schrader, Liebig's Annalen **279** (1894), 389; **286** (1895), 127.
[2]) Wallach, Liebig's Annalen **275** (1893), 117; **279** (1894), 381.
[3]) Berl. Berichte **28** (1895), 1960.
[4]) *Ibidem* **32** (1899), 3372, footnote.

in the oil of *Bystropogon origanifolius* and in the oil from cassie blossoms (?), but the direction of rotation has not been recorded in these instances.

Inasmuch as menthone does not combine with acid sulphites, and since it cannot be obtained pure by fractional distillation, it must be isolated either by means of its oxime or by means of its semicarbazone which are prepared from the menthone fractions. It should be noted, however, that when these compounds are hydrolyzed, mostly with the aid of dilute sulphuric acid, the angle of rotation is altered.

Pure *l*-menthone with normal optical activity is readily obtained from menthol by oxidation with the chromic acid mixture recommended by Beckmann.[1])

Synthetically, menthone has been obtained by several methods.

Pure menthone is a mobile, colorless liquid with a peppermint-like odor and a slightly cooling, bitter taste. For the ketone obtained by the oxidation of menthol, Beckmann[2]) found the following constants:

B. p. 207°; $d_{20°}$ 0,8960; $[\alpha]_{D20°}$ — 28,18°; $n_{D12°}$ 1,4525;

and Binz[3]) the following ones:

$d_{24°}$ 0,8934; $[\alpha]_{D24°}$ — 27,67°.

According to Wallach,[4]) menthone regenerated from its semicarbazone (m. p. 184°) possesses the following properties:

B. p. 208°; d 0,894; n_D 1,4496.

In the laboratory of Schimmel & Co. the following were observed:

$d_{15°}$ 0,894 to 0,899; α_D — 20° 27′ to — 26°10′; $n_{D20°}$ 1,450 to 1,451; soluble in 3 vols. of 70 p. c. alcohol.

$d_{15°}$ 0,8971; α_D — 26°10′; $[\alpha]_D$ — 29,17°.

If *l*-menthone is treated at a low temperature with concentrated sulphuric acid it is changed to its dextrogyrate isomer.[5]) In this

[1]) Beckmann, Liebig's Annalen **250** (1889), 325.
[2]) *Ibidem* 327.
[3]) Zeitschr. f. physik. Chem. **12** (1893), 727.
[4]) Berl. Berichte **28** (1895), 1963.
[5]) Beckmann, *loc. cit.* 334.

manner Beckmann obtained what he regarded as *d*-menthone of the same angle of rotation ($[\alpha]_D + 28{,}1°$) as the *l*-menthone ($[\alpha]_D - 28{,}5°$) from which he started. It was shown, however, that the former was not the optical antipode of the latter, but a mixture of *l*-menthone with the much more strongly active *d-iso*menthone. A highly dextrogyrate *d-iso*menthone he obtained in the following manoer: Menthoxime was reduced, the resulting menthylamine treated with nitrous acid and the menthol thus obtained oxidized. This *iso*menthone had a specific angle of rotation of $+ 93{,}2°$.[1])

Beckmann is of the opinion that the change in the angle of rotation brought about by acids is due to intermediary enolising. This interpretation is favored by the observation made by Mannich and Hâncu,[2]) namely that *l*-menthone ($[\alpha]_D - 22{,}4°$) when subjected to prolonged heating with acetic acid anhydride to 240° yields the ester of 1-methyl-4-methoethyl cyclohexene-(2 or 3)-ol-3 (b. p. 98° at 11 mm.; $\alpha_D + 6{,}65°$) which upon saponification yields a dextrogyrate menthone ($\alpha_D + 1{,}54°$ in a 20 mm. tube).

In general, the change in the angle of rotation brought about by acids and alkalies is noteworthy.

When reduced in alcoholic solution with sodium, it is converted into the corresponding secondary alcohol, the *l*-menthol, $C_{10}H_{20}O$. As a by-product small amounts of the slightly dextrogyrate *iso*menthol result. When indifferent solvents are used some menthopinacone,[3]) m. p. 94°, also is formed.

In dilute alcoholic solution, *l*-menthone condenses readily with hydroxylamine to *l*-menthoxime, m. p. 60 to 61°.[4]) The other modifications of menthone yield oximes that are either liquid or possess a higher melting point.

If the oxime is treated with dehydrating agents, it is converted into an aliphatic nitrile, $C_9H_{17}CN$. When further modified this yields compounds that very much resemble the corresponding members of the citronellal group.[5]) Upon molecular rearrange-

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[1]) Berl. Berichte **42** (1909), 847.

[2]) Berl. Berichte **41** (1908), 570.

[3]) Beckmann, Journ. f. prakt. Chem. II. **55** (1897), 18, 30.

[4]) Beckmann, Liebig's Annalen **250** (1889), 330; Wallach, Liebig's Annalen **277** (1893), 157; **278** (1894), 304.

[5]) Wallach, Liebig's Annalen **278** (1894), 308; **296** (1897), 120; **312** (1900), 171.

ment, induced by sulphuric acid, *l*-menthoneoxime yields a lactam, the menthone isoxime, m. p. 119°.[1])

Semicarbazide reacts on menthone with the formation of a semicarbazone that crystallizes in needles which melt at 184°.[2]) Noteworthy is also the thiosemicarbazone, m. p. 155 to 157° and the semioxamazone, m. p. 177°.

If menthone is oxidized with a solution of chromic acid in glacial acetic acid, there results as first oxidation-product a keto acid $C_{10}H_{18}O_3$ (keto- or hydroxymenthylic acid).[3]) Upon further oxidation with either potassium permanganate or chromic acid mixture, this is converted into the dibasic β-methyl adipic acid (β-pimelic acid of Arth),[4]) hence into the same "Abbau" product obtained from pulegone and citronellal.

If *iso*amyl nitrite and hydrochloric acid are allowed to react on menthone in the cold, bisnitrosomenthone, $(C_{10}H_{17}O \cdot NO)_2$, m. p. 112,5° and the oxime of ketomenthylic acid, m. p. 103°, *i. e.* of the first oxidation product of menthone, are formed.[5])

If bromine (2 mol.) is allowed to act on menthone (1 mol.) in chloroformic solution, there results a crystalline dibromementhone, $C_{10}H_{16}Br_2O$ (m. p. 79 to 80°). When acted upon by quinoline, this looses hydrogen bromide and is converted into thymol.[6])

These changes, as also the conversion of menthone into 3-chlorcymene brought about by Jünger and Klages,[7]) are in harmony with the structural formula given above, which also expresses the relation of menthone to pulegone.

For the identification of menthone, the preparation of the semicarbazone or oxime is resorted to. For further characteri-

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[1]) Beckmann and Mehrländer, Berl. Berichte **20** (1887), 1508; Wallach, Liebig's Annalen **278** (1894), 304.

[2]) Wallach, Berl. Berichte **28** (1895), 1963; Beckmann, Liebig's Annalen **289** (1896), 366.

[3]) Beckmann and Mehrländer, Liebig's Annalen **289** (1896), 368.

[4]) Arth, Annal. de Chim. et Phys. VI. **7** (1886), 433; Beckmann and Mehrländer, loc. cit. 378; Manasse and Rupe, Berl. Berichte **27** (1894), 1818.

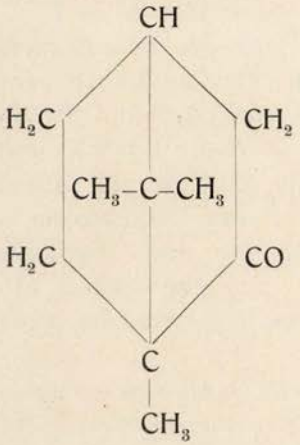
[5]) Baeyer and Manasse, Berl. Berichte **27** (1894), 1913, 1914; see also Baeyer and Oehler, Berl. Berichte **29** (1896), 27.

[6]) Beckmann and Eickelberg, Berl. Berichte **29** (1896), 418.

[7]) Berl. Berichte **29** (1896), 315.

zation the ketone can be reduced to menthol and this converted into the benzoic ester (see menthol). For the quantitative determination of menthone consult the chapter on "The examination of volatile oils", ketone determinations.

Camphor.



d-Camphor, known also as Japanese or Laurus camphor in order to distinguish it from borneo camphor (*d*-borneol), is obtained on a large scale together with camphor oil by the distillation of the wood of *Cinnamomum Camphora* with water vapor. *d*-Camphor has also been found in Siam cardamom oil, American wormseed oil, camphor leaf oil, sassafras oil, apopin oil (?), rosemary oil, spike oil, in the oil of *Lavandula Stœchas,* Réunion basilicum oil, in the oil of *Basilicum canum,* and in Dalmatian sage oil; *l*-camphor in an oil of sage (*Salvia grandiflora* [?]), *Artemisia Herba-alba, A. cana* (?), feverfew, tansy, and *Blumea balsamifera; i*-camphor in the oil of *Chrysanthemum sinense* var. *japonicum.* Camphor has also been reported as being present in a number of other oils, however, without record as to the angle or direction of rotation: in the oils of *Piper camphoriferum, P. angustifolium* var. *ossanum,* cinnamon root, and of Seychelles cinnamon bark. It may be added that an animal, the *Polyzonium rosalbum,* probably secretes camphor.[1])

[1]) Cook, Chem. Zentralb. **1901**, I. 191.

Synthetically, camphor has been obtained by the dry distillation of the lead[1]) or calcium[2]) salts of homocamphoric acid (Haller's hydroxycamphocarboxylic acid). However, this synthesis was only a partial one, since the homocamphoric acid was obtained from a derivative of camphor. The complete synthesis of camphor was later successfully accomplished by Komppa[3]) who likewise succeeded in effecting the synthesis of camphoric acid.

Camphor can be isolated from the volatile oils containing it by freezing, if necessary after fractionation. It consists of a granular-crystalline, colorless, translucent mass with a decided tendency toward sublimation. It has a characteristic odor and is readily soluble in organic solvents. When cast on water, small pieces rotate in a very lively manner. By various observers its properties have been recorded as follows:

$d_{18°}$ 0,9853 (determined for *l*-camphor);[4])

m. p. 176,3 to 176,5°; b. p. 209,1° (759 mm., mercury completely within the vapor);[5])

m. p. 178,4°; $[\alpha]_D + 41{,}44°$ and $-42{,}76°$;[6])

m. p. 175°; b. p. 204°;[7])

m. p. 175°; b. p. 204°; $[\alpha]_D \pm 44{,}22°$ in 20 p. c. alcoholic solution.[8])

The world's consumption of camphor is very large, for the manufacture of celluloid ware alone enormous quantities are used. It is also used extensively in the manufacture of smokeless powder, for disinfection and for medicinal purposes. This great demand has given rise to its synthetic production from turpentine spirits on a commercial scale. In general, one of two methods is followed: Either pinene is converted into bornyl

[1]) Haller, *Contrib. à l'étude du camphre. Thèse.* Nancy 1879, p. 34; Bull. Soc. chim. III. **15** (1896), 324.

[2]) Bredt and v. Rosenberg, Liebig's Annalen **289** (1896), 5.

[3]) Berl. Berichte **36** (1903), 4332; **41** (1908), 4470; Liebig's Annalen **368** (1909), 110; **370** (1909), 209.

[4]) Chautard, Jahresber. d. Chem. **1863**, 555.

[5]) Foerster, Berl. Berichte **23** (1890), 2983.

[6]) Haller, Compt. rend. **105** (1887), 229.

[7]) Landolt, Liebig's Annalen **189** (1877), 333.

[8]) Beckmann, Liebig's Annalen **250** (1889), 353. — As to the influence exerted by the solvent and by the degree of concentration of the solution, compare Landolt, *loc. cit.*, also Rimbach, Zeitschr. f. physik. Chem. **9** (1892), 701.

chloride by means of hydrogen chloride, which by way of camphene and *iso*borneol is changed to camphor; or pinene is directly converted into esters of borneol or *iso*borneol.

At all times camphor has aroused the interest of chemists, hence the literature on this subject has grown to large dimensions. In conformity with the object of this book, only those derivatives will be considered that are suited to its identification.

Camphor is a ketone, $C_{10}H_{16}O$, but does not combine with acid sulphite. With hydroxylamine it yields an oxime (see below) from which, however, the ketone cannot be regenerated in a pure state for the reason that the oxime, when treated with acids, looses water and yields the amide and nitrile, $C_9H_{15}CN$, of campholenic acid.

If in ethylalcoholic solution, or better still in amylalcoholic solution, camphoroxime is reduced with sodium, two isomeric bornylamines result (m. p. 163° and 180° respectively).[1]) A similar base melting at 159 to 160° results when camphor is heated with ammonium formate to 220 to 230°.[2])

Upon reduction with hydrogen camphor is converted into the alcohol borneol, $C_{10}H_{18}O$. If the addition of hydrogen takes place in indifferent solvents, some *iso*borneol results, also camphor pinakone, m. p. 157 to 158°.[3]) In alcoholic solution it is reduced essentially to a mixture of borneol and *iso*borneol.[4])

Oxidation with nitric acid yields dibasic camphoric acid, $C_{10}H_{16}O_4$ (m. p. of the active compound 187°, of the inactive modification 204 to 205°), and, if oxidized farther, tribasic camphoronic acid, $C_9H_{14}O_6$ (m. p. 139°). From the constitution of the decomposition products of these acids, numerous conclusions as to the constitution of camphor itself have been drawn. Of the many formulas proposed for this ketone, that of Bredt[5]) given above is alone generally recognized at present.

Dehydrating agents act energetically on camphor. Thus the action of phosphoric acid anhydride yields *p*-cymene, of sulphuric

[1]) Forster, Journ. chem. Soc. **73** (1898), 386.

[2]) Leuckart and Bach, Berl. Berichte **20** (1887), 104; Wallach and Griepenkerl, Liebig's Annalen **269** (1892), 347.

[3]) Beckmann, Berl. Berichte **27** (1894), 2348; Liebig's Annalen **292** (1896), 1.

[4]) Beckmann, Journ. f. prakt. Chem. II. **55** (1897), 35.

[5]) Berl. Berichte **26** (1893), 3049.

acid and zinc chloride yields other products as well. The action of iodine results in the formation of carvacrol.

For the identification of camphor it is converted into the oxime. This compound discovered by Naegeli[1]) is best prepared according to the method of Auwers.[2]) To a solution of 10 p. camphor in 10 to 20 times its weight of 90 p. c. alcohol, a solution of 7 to 10 p. of hydroxylamine hydrochloride and 12 to 17 p. of soda lye are added. The mixture is digested on a boiling water bath until the substance precipitated by water dissolves to a clear solution in soda lye. The oxime precipitated by water is recrystallized from alcohol or ligroin. It melts at 118 to 119°.[3]) The oxime from *d*-camphor is lævogyrate, that from *l*-camphor, dextrogyrate.[4]) $[\alpha]_D$ in alcoholic solution $\pm 41{,}3°$.

For the identification of camphor the following compounds may also be utilized, *viz.* the semicarbazone, m. p. 236 to 238°, the *p*-bromphenylhydrazone, m. p. 101°,[5]) the oxymethylene derivative, m. p. 80 to 81°, and the benzylidene derivative, the active modification of which melts at 95 to 96° and the inactive modification at 78°.

Frequently it is necessary to identify camphor mixed with borneol. According to Haller's method,[6]) the mixture is heated with succinic or phthalic acid anhydride and rendered alkaline causing the acid ester of borneol to go into solution. From this alkaline solution the camphor can be extracted with ether. According to another method, the borneol can be converted into esters with high boiling point, such as the succinate or stearate, and the camphor distilled over with water vapor. According to a third method, the camphor can be converted into its oxime and dissolved in dilute sulphuric acid. Shaking with ether then removes the borneol. However, the ethereal solution should in turn be shaken repeatedly with dilute sulphuric acid, since the ether also dissolves some of the camphor oxime.

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[1]) Berl. Berichte **16** (1883), 497.

[2]) *Ibidem* **22** (1889), 605.

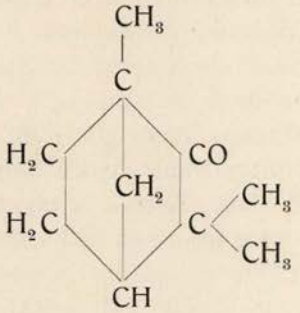
[3]) Bertram and Walbaum, Journ. f. prakt. Chem. II. **49** (1894), 10; Bredt and v. Rosenberg, Liebig's Annalen **289** (1896), 6.

[4]) Beckmann, Liebig's Annalen **250** (1889), 354.

[5]) Tiemann, Berl. Berichte **28** (1895), 2191.

[6]) Compt. rend. **108** (1889), 1308.

Fenchone.



Fenchone is a ketone $C_{10}H_{16}O$ which closely resembles camphor but is liquid at ordinary temperature. In volatile oils both optically active modifications occur. *d*-Fenchone has been found in fennel oil and in the oil of *Lavandula Stœchas,* whereas *l*-fenchone has been found in the oil of *Arbor vitæ*. For the fenchone found in the oil of *Thuja plicata* the direction of rotation has not been recorded.

For its purification,[1]) the accompanying substances found in fraction 190 to 195° are removed by oxidation with either concentrated nitric acid or permanganate solution. Fenchone, being very stable toward oxidizing agents, is effected but little. Having thus been purified in a fair measure, it congeals in the cold and can be further purified by crystallization. However, small amounts of camphor, resulting from the oxidation of borneol esters, cannot be removed in this manner. Methods for the separation of these two ketones are given below. Artificially fenchone is obtained by the oxidation of fenchyl alcohol.

Pure fenchone is a water-white, somewhat oily liquid, with an intense, camphor-like odor and a bitter taste. As to its physical properties, Wallach[2]) records the following data:

M. p. + 5 to 6°; $d_{19°}$ 0,9465, $d_{23°}$ 0,943; $[\alpha]_{D18°}$ +71,97° and — 66,94° resp. (in alcoholic solution);[3]) $n_{D19°}$ 1,46306.

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[1]) Wallach, Liebig's Annalen **263** (1891), 130.

[2]) Liebig's Annalen **263** (1891), 131; **272** (1893), 102.

[3]) The lower angle of rotation is explained by a small camphor content of the oxime examined. Wallach, Liebig's Annalen **353** (1907), 215.

For a *d*-fenchone regenerated from semicarbazone, Wallach[1]) ascertained the following constants:

B. p. 192 to 193°; $d_{18°}$ 0,948; $[\alpha]_D$ + 62,76°, resp. + 68,43° (in 13,76 percent. alcoholic solution); $n_{D18°}$ 1,46355.

The constitution of fenchone appears to find its expression in the formula given above. This formula was first suggested by Semmler[2]) and has gained in probability by the more recent work of other investigators.[3])

In its chemical properties, fenchone closely resembles camphor. It has been examined into in detail by Wallach. The following account takes into consideration those derivatives only that are useful for its identification.

Like camphor, fenchone does not combine with acid sulphite; neither does it react with phenylhydrazine. However, with hydroxylamine[4]) it yields an oxime which is best prepared according to the directions of Wallach.[5]) To a solution of 5 g. of fenchone in 80 ccm. of absolute alcohol a solution of 11 g. hydroxylamine hydrochloride and 6 g. of powdered potash in 11 g. of hot water is added. After standing for some time, more particularly after some alcohol has evaporated, the oxime crystallizes out. It can be purified by recrystallization from alcohol, acetic ether, or ether. The active modifications melt at 164 to 165°, the inactive modification melts at 158 to 160°. Fenchone oxime resembles camphor oxime in so far as upon dehydration it yields the nitrile of fencholenic acid, $C_{10}H_{15}N$, which acid is isomeric with campholenic acid.

Upon reduction, active fenchone yields fenchyl alcohol, $C_{10}H_{18}O$,[6]) which melts at 45° and which deviates the ray of polarized light in the direction opposite to that of the fenchone from which it is obtained. Upon oxidation with permanganate, fenchone yields dimethylmalonic acid $(CH_3)_2 \cdot C \cdot (COOH)_2$, m. p. 188

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[1]) Liebig's Annalen **362** (1908), 195, footnote.

[2]) Chem. Ztg. **29** (1905), 1313; Berl. Berichte **39** (1906), 2581; **40** (1907), 439.

[3]) Bouveault and Levallois, Compt. rend. **146** (1908), 180; Wallach, Liebig's Annalen **369** (1909), 63.

[4]) Wallach, Liebig's Annalen **263** (1891), 136.

[5]) Liebig's Annalen **272** (1893), 104.

[6]) Liebig's Annalen **263** (1891), 143.

to 189°,[1]) also acetic and oxalic acids. Upon oxidation with concentrated nitric acid it also yields *iso*camphoronic acid and dimethyltricarballylic acid.[2])

In like manner as camphor yields *p*-cymene when treated with phosphoric acid anhydride, so fenchone yields *m*-cymene. When acted on by concentrated sulphuric acid, fenchone yields 4-acetyl-1, 2-xylene.[3])

By the action of sodium amide on fenchone, Semmler[4]) obtained a dihydrofencholenic acid amide melting at 94°.

The semicarbazone of fenchone is formed exceedingly slowly. Only recently Wallach[5]) has pointed out a convenient method for its preparation. 10 g. semicarbazide hydrochloride and 10 g. sodium acetate are dissolved in 20 ccm. of water. To this reagent a solution of 10 g. fenchone in 50 ccm. alcohol is added. The clear solution is set aside at room temperature for at least two weeks when the reaction product is distilled with steam. Alcohol and uncombined fenchone distil over, whereas the semicarbazone congeals in part to a compact mass, in part crystallizes from the hot water in which it is not completely insoluble. From dilute alcoholic solutions it crystallizes in thick, well-defined, shiny rhombic prisms, one centimeter long, which melt at 182 to 183°. The inactive form melts at 172 to 173° and does not possess the same crystallising capacity.

Inasmuch as the semicarbazone of camphor is formed much more readily, this difference in behavior can be utilized for the separation of camphor from fenchone.[6]) Another method of separation, proposed by Semmler,[7]) is based on the different behavior of the two ketones when boiled with sodium. Camphor reacts with the formation of sodium camphor, whereas fenchone is said to remain unchanged. Wallach's[8]) investigations, however, have revealed that fenchone also does not remain unchanged

[1]) Wallach, *ibidem* **263** (1891), 134.

[2]) Gardner and Cockburn, Journ. chem. Soc. **73** (1898), 708.

[3]) Marsh, Journ. chem. Soc. **75** (1899), 1058; Wallach, Liebig's Annalen **315** (1901), 295.

[4]) Berl. Berichte **39** (1906), 2578.

[5]) Liebig's Annalen **353** (1907), 211.

[6]) Wallach, Liebig's Annalen **353** (1907), 213ff.

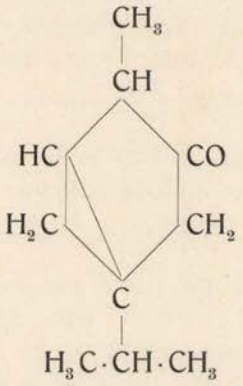
[7]) Berl. Berichte **40** (1907), 4591.

[8]) Liebig's Annalen **369** (1909), 65.

when boiled with sodium, but that ultimately the change is as complete as with camphor, the reaction only progresses more slowly. Hence the separation of fenchone from camphor by means of distillation over sodium is accompanied by considerable loss.

Finally, the method of separation by means of aluminium chloride recently suggested by Leroide[1]) should be mentioned.

Thujone.



Thujone, $C_{10}H_{16}O$, occurs in two physically isomeric forms, namely as lævogyrate α-thujone and as dextrogyrate β-thujone (the tanacetone of Semmler). These two modifications are not optical antipodes. They can be clearly distinguished by means of their semicarbazones, and by treatment with alkali can be converted partly into each other.[2]) Thujone was discovered simultaneously by Wallach[3]) and Semmler:[4]) the lævogyrate thujone by Wallach in thuja oil, the dextrogyrate thujone by Semmler in tansy oil. To the latter ketone Semmler applied the name tanacetone, whereas Wallach named this dextrogyrate modification β-thujone.

In addition to the oils already mentioned, α-thujone occurs in the leaf oil of *Thuja plicata,* in oil of sage, and in the oil of

[1]) Scientific and Industrial Bulletin of Roure-Bertrand Fils October **1909**, 39; Report of Schimmel & Co. April **1910**, 184.

[2]) Wallach, Liebig's Annalen **336** (1904), 249.

[3]) Liebig's Annalen **272** (1893), 99.

[4]) Berl. Berichte **25** (1892), 3343.

Artemisia Barrelieri; β-thujone in oil of sage, in the oil of *Artemisia Barrelieri,* and particularly in oil of wormwood. From oils rich in thujone, such as tansy oil and the oil of *Artemisia Barrelieri,* the ketone can readily be separated in the form of its bisulphite addition product, which, upon decomposition with soda, yields pure thujone. For the preparation of the acid sulphite addition product, ammonium bisulphite is used, some alcohol is added to the mixture, which is set aside for some time and is frequently shaken.

Thujone is a colorless liquid with a pleasant, refreshing odor. For the ketone regenerated from the bisulphite addition product or from the semicarbazone, Wallach found the following constants:[1])

$d_{19°}$ 0,9175; n_D 1,45109; $d_{20°}$ 0,916; n_D 1,4507.

For α-thujone regenerated from the semicarbazone by means of dilute sulphuric acid, Wallach[2]) found:

B. p. 200 to 201°; d 0,912; α_D — 5° 13′; $n_{D22°}$ 1,4503.

When phthalic acid anhydride was used for the regeneration an optical rotation $[\alpha]_D$ — 10,23° was observed. For β-thujone, obtained from the semicarbazone, $[\alpha]_D$ + 76,16° was observed. When acted upon with alkali, α-thujone is very readily changed to β-thujone, a change that must not be overlooked in the attempt to identify a natural thujone.

Thujone is a saturated ketone, nevertheless it is readily acted upon by permanganate. Bromine produces substitution products.

As already pointed out thujone differs in its behavior from camphor and fenchone in the formation of an acid sulphite addition product. With hydroxylamine it yields an oxime[3]) which melts at 54 to 55° and which corresponds to β-thujone, whereas the oxime of α-thujone is liquid. When acted upon by phosphorus pentachloride, the crystalline oxime is changed to an isoxime[4]) melting at 90°, and, when heated with dilute alcoholic sulphuric acid,

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[1]) Berl. Berichte **28** (1895), 1965.

[2]) Liebig's Annalen **336** (1904), 263.

[3]) Wallach, Liebig's Annalen **277** (1893), 159; Semmler, Berl. Berichte **25** (1892), 3344.

[4]) Wallach, Liebig's Annalen **286** (1895), 94; **336** (1904), 270.

into carvacrylamine.[1]) With semicarbazide solution,[2]) α-thujone yields a semicarbazone that melts at 186 to 188°.[3]) There exists also an amorphous modification which melts at about 110°. From β-thujone a hexagonal semicarbazone, melting at 174 to 175°, can be derived which changes spontaneously into a stable rhombic form that melts at 170 to 172°.

Upon reduction thujone is changed to thujyl alcohol, $C_{10}H_{18}O$, the corresponding secondary alcohol,[4]) which has already been described on p. 397.

When oxidized with permanganate in the cold, thujone yields a saturated ketonic acid $C_{10}H_{16}O_3$,[5]) the α-thujaketonic acid, which melts at 75 to 76°. When heated or distilled *in vacuo,* it is readily changed into the isomeric, unsaturated β-thujaketonic acid, which melts at 78 to 79°. When acted upon by hypobromite, the corresponding dicarboxylic acids $C_9H_{14}O_4$ result,[6]) of which the α-acid melts at 141,5°, the β-acid at 116 to 118°. Upon destructive distillation, both ketonic acids yield thujaketone,[7]) $C_9H_{16}O$, the odor of which resembles that of methylheptenone. As "Abbau" product, both ketones also yield δ-(ω-)dimethyllævulinic acid, which melts at 32°.[8])

If thujone is heated for a long time to 280° in sealed tubes, it is changed into an isomeric, unsaturated ketone $C_{10}H_{16}O$, the odor of which resembles that of carvone, and which has been named carvotanacetone.[9]) Judging from the reduction in the angle of rotation, this change appears to take place even upon prolonged boiling. Another isomeric, unsaturated ketone, *iso*thujone, results when thujone is moderately heated with dilute sulphuric acid.[10])

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[1]) Semmler, Berl. Berichte **25** (1892), 3352.

[2]) Wallach, Liebig's Annalen **286** (1895), 94; **336** (1904), 270.

[3]) This melting point applies to the perfectly pure compound only. Commonly 184,5 to 186° is found.

[4]) Semmler, Berl. Berichte **25** (1892), 3344.

[5]) Semmler, *Ibidem* 3347; Wallach, Liebig's Annalen **272** (1893), 111; Berl. Berichte **30** (1897), 423.

[6]) Semmler, *Ibidem* 3346.

[7]) Wallach, Liebig's Annalen **272** (1893), 116; **275** (1893), 164.

[8]) Tiemann and Semmler, Berl. Berichte **30** (1897), 429; **31** (1898), 2311.

[9]) Semmler, Berl. Berichte **27** (1889), 895.

[10]) Wallach, Liebig's Annalen **286** (1895), 101; **323** (1902), 334; Berl. Berichte **28** (1895), 1959; **30** (1897), 26.

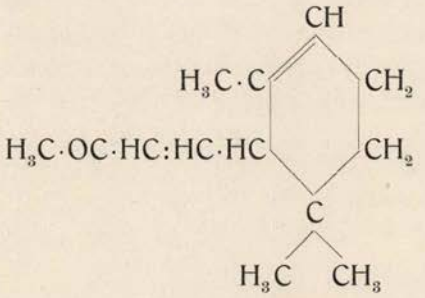
Upon reduction, *iso*thujone is converted into the saturated thujamenthol. When boiled with a solution of ferric chloride, thujone is converted into carvacrol.

The structural formula given above was based by Semmler[1]) on the physical and chemical properties of thujone. Somewhat later it was accepted by Wallach.[2])

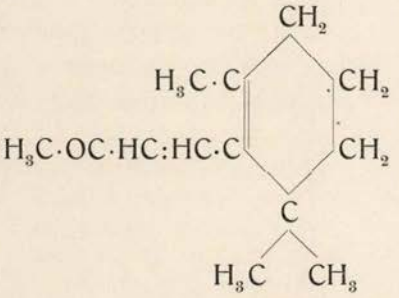
The tribromide is best suited for the characterization of thujone. According to Wallach[3]) it is prepared by adding at once 5 ccm. of bromine to a solution of 5 g. of thujone in 30 ccm. petroleum ether contained in large beaker. After a few seconds a rather violent reaction sets in accompanied by the evolution of hydrogen bromide. Upon evaporation of the solvent, the tribromide separates gradually as a crystalline mass which is freed from adhering oil by washing it with cold alcohol, and which can be recrystallized from hot acetic ether. The melting point of the pure compound lies at 121 to 122°. When acted on with methylalcoholic or ethylalcoholic potassium hydroxide solution, the phenols $C_{10}H_{11}Br(OH)(OCH_3)$ and $C_{10}H_{11}Br(OH)(OC_2H_5)$ respectively result. The former melts at 156 to 157°, the latter at 144 to 145°.

For the identification of the α- and β-modifications of thujone the semicarbazones described above are made use of.

Ionone.



α-Ionone.



β-Ionone.

This violet perfume of the formula $C_{13}H_{20}O$, the presence of which in nature has not yet been definitely established, was

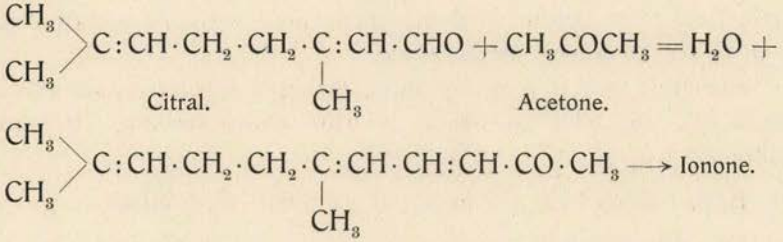
[1]) Berl. Berichte **33** (1900), 275, 2454.

[2]) Liebig's Annalen **323** (1902), 371.

[3]) *Ibidem* **275** (1893), 179; **286** (1895), 109.

first obtained synthetically in 1893 by Tiemann and Krüger.[1]) Since then a considerable number of patents have been issued for the preparation of "violet ketones" *i. e.*, for that of ionone and its homologues.

The preparation of ionone is based on the condensation of the olefinic aldehyde citral with acetone. In the presence of alkalies the olefinic ketone, the pseudoionone of the formula $C_{13}H_{20}O$, results. In the presence of acid reagents, whether weak or strong, either at low or higher temperatures, this pseudoionone rearranges itself to the cyclic, isomeric ketone, the ionone.



Pseudoionone.

The inversion of pseudoionone to ionone may be brought about more particularly by concentrated sulphuric acid, phosphoric acid, formic acid, and oxalic acid, also by dilute mineral acids and solutions of acid alkali sulphates, even by neutral salts such as sodium acetate and magnesium sulphate in an autoclave. In the case of the concentrated acids, the action should be restricted to a lower temperature, also to a shorter time. In the case of dilute acids and other substances, prolonged heating is required. In all of these reactions a mixture of two isomers, the α- and β-ionone, is formed.

If in place of acetone its homologues be employed, the corresponding homologues of pseudoionone are formed, which can be inverted into the isomeric ionone derivatives as stated above.

Reduced pseudoionones and homologues thereof are obtained by the condensation of citronellal with acetone and its homologues. These in turn can be isomerised to the corresponding ionones

[1]) Berl. Berichte **26** (1893), 2691.

and homologues by means of acids. Acetyl pseudoionones and acetyl ionones have also been prepared. As the most important representative of the cyclocitral series, ionone is of considerable scientific interest.

PSEUDOIONONE. Although this ketone does not react immediately with sodium acid sulphite solution at ordinary temperature, it does combine with it upon prolonged heating to a hydrosulphonic acid derivative which is soluble.[1]) This compound can be utilized for the preparation of pure pseudoionone. The solution is first shaken repeatedly with ether or other immiscible solvent for the purpose of removing aldehyde resins or other impurities. The ketone is then regenerated with the aid of alkali at ordinary or lower temperature.

Pseudoionone is a light yellow, strongly refractive, somewhat viscid oil, the odor of which is little characteristic. Its constants are:

B. p. 143 to 145° (12 mm.); $d_{20°}$ 0,8980; n_D 1,53346.

Of characteristic derivatives the *p*-bromphenylhydrazone, melting at 102 to 104°, may be mentioned.

IONONE. As already pointed out, the production of ionone results invariably in the formation of a mixture of two isomers. If concentrated sulphuric acid be used, or if dilute sulphuric acid be allowed to react for a longer period[2]), the resulting mixture consists largely of β-ionone. If, however, the inversion be brought about by concentrated phosphoric or formic acids, α-ionone results almost exclusively. Toward acid sulphite solution ionone behaves like pseudoionone. The resulting hydrosulphonic acid can be well utilized for the purification of ionone.

Freshly distilled ionone is a colorless oil with a decided odor of cedarwood. It is only in dilute solution, *e. g.* in alcohol, that its odor of violets, reminding at the same time somewhat of grape blossoms, becomes apparent. Noteworthy is also the property of ionone to benumb the sense of smell.

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[1]) Tiemann, Berl. Berichte **31** (1898), 842.
[2]) Tiemann, Berl. Berichte **31** (1898), 868, 870.

Even the ionones purified through the hydrosulphonic addition products vary more or less in their α- and β-ionone content according to the reagents employed in their isomerization. Hence their physical constants vary appreciably. For a pure ionone, consisting however of a mixture of the two isomers, Tiemann[1]) records the following constants:

B. p. 126 to 128° (10 mm.); $d_{20°}$ 0,9351; n_D 1,507;

whereas Schimmel & Co. observed the following on their own products:

B. p. 104 to 109° (4 to 5 mm.); $d_{15°}$ 0,9350 to 0,9403; $d_{20°}$ 0,9335; $n_{D20°}$ 1,50335 to 1,50510; soluble in 2,5 to 3,0 vols. of 70 percent. alcohol.

As to odor, the differences between α- and β-ionone are but slight, yet nevertheless recognizable by the expert. That of α-ionone is fresher and more fragrant than that of its isomer, which is rather strong and reminds more of the odor of the leaves of the violet. Hence the former is preferred.

To α-IONONE Tiemann[2]) assigns the following properties:

B. p. 123 to 124° (11 mm.); $d_{20°}$ 0,932; n_D 1,4980.

Chuit[3]) found:

B. p. 127,6° (12 mm.); $d_{15°}$ 0,9338; $n_{D17.2°}$ 1,50001.

The *p*-bromphenylhydrazone, which is best suited for the characterization of α-ionone, melts at 142 to 143°. It is prepared in glacial acetic acid solution and recrystallized from dilute methyl alcohol or ligroin. The semicarbazone melts at 107 to 108°, respectively at 137 to 138°, the thiosemicarbazone at 121°, the oxime at 89 to 90°.

For pure β-IONONE Tiemann[4]) determined the following constants:

B. p. 127 to 128,5° (10 mm.); $d_{17°}$ 0,946; $n_{D17°}$ 1,521;

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[1]) Berl. Berichte **31** (1898), 851.
[2]) Berl. Berichte **31** (1898), 876.
[3]) Rev. gén. de Chim. **6** (1903), 432; Chem. Zentralbl. **1904**, I. 280.
[4]) Berl. Berichte **31** (1898), 871, 879.

Chuit[1]) the following: B. p. 134,6° (12 mm.); $d_{15°}$ 0,9488; $n_{D17,5°}$ 1,52008.

β-Ionone can best be identified by means of its semicarbazone[2]) which melts at 148 to 149°. Its *p*-bromphenylhydrazone melts at 116 to 118°, its thiosemicarbazone at 158°, its hydrazone at 104 to 105°. The oxime is liquid.

Concentrated sulphuric acid inverts α-ionone to β-ionone. Inversely, β-ionone can be changed, though more difficultly, to α-ionone by means of alcoholic potassa.

The physical constants of commercial ionone do not afford a definite clue as to its purity. In order to test such a preparation as to its purity, the by-products that result during its manufacture should be removed.

For this purpose the oil to be examined is boiled for 10 to 15 hours with thrice its weight of sodium acid sulphite solution in which the free sulphurous acid has been neutralized with dilute soda solution. The duration is dependent on the reaction of the ionone with the bisulphite. According to Schimmel & Co., the addition of alcohol suggested by Schmidt,[3]) is not necessary. In order to remove those substances that have not combined with the acid sulphite, the solution after having been diluted with water is extracted four times with ether. If the ionone is comparatively pure, the addition of water will cause but a slight turbidity, if impure the separation of an oil. Should the separated portion smell of ionone, a second treatment with acid sulphite is necessary. The difference between the amount originally used and the amount extracted is computed as ionone. Some idea as to the relative proportions of α- and β-ionone present can be obtained from the physical constants of the mixed ionones separated from the acid sulphite addition product by means of lye, also by means of the semicarbazone and *p*-bromphenylhydrazone.

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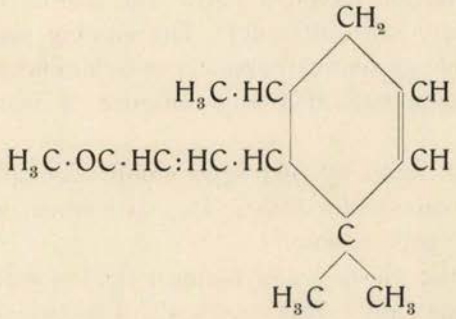
[1]) *Loc. cit.*

[2]) For the purification and separation of the ionone semicarbazones compare Tiemann, Berl. Berichte **31** (1898), 875, 1736.

[3]) Zeitschr. f. angew. Chem. **13** (1900), 189.

Irone.



Irone, $C_{13}H_{20}O$, has thus far been found only in orris oil, the German "Veilchenwurzelöl" (from *Iris florentina, I. pallida, I. germanica*). Tiemann and Krüger[1]) were the first tho isolate it from orris root and to recognize it as a cyclic ketone isomeric with ionone. They obtained it by extracting orris root with organic solvents and distilling the evaporated extract with steam. Since liquid orris oil is to be had in the market, irone can be obtained from it by fractional distillation. It collects in fraction 105 to 120° obtained under a pressure of 4 mm. It is purified through the oxime or phenylhydrazone from either of which it can be conveniently regenerated.

Irone is a colorless oil. Its peculiar odor,[2]) which reminds of certain species of violets, is brought out only in extreme dilution. For the carefully purified ketone, Tiemann and Krüger *(loc. cit.)* report the following constants:

B. p. 144° (16 mm.); $d_{20°}$ 0,939; α_D abt. + 40°; $n_{D20°}$ 1,50113.

For a preparation isolated from the sodium salt of the phenylhydrazine sulphonic acid derivative,[3]) Schimmel & Co. observed the following constants:

B. p. 111 to 112° (2 mm.); $d_{15°}$ 0,9391; α_D + 33° 31′; $n_{D20°}$ 1,50173.

For the characterization of irone its *p*-bromphenylhydrazone is well suited. According to Schimmel & Co. it melts at 174

[1]) Berl. Berichte **26** (1893), 2675.

[2]) Tiemann's observation that irone possesses a pungent odor is not correct.

[3]) For the technique to be observed in the preparation of this compound compare the expert testimony given by v. Baeyer, Berlin 1899, p. 22.

to 175°.[1]) It is crystallized from methyl alcohol. According to Chuit[2]) the thiosemicarbazone melts at 181°. The oxime, which melts at 121,5°, crystallizes with difficulty. The melting point of 70 to 80°, found for amorphous semicarbazone[3]) by Schimmel & Co., gives rise to the suspicion that this is a mixture of isomeric derivatives.

When irone is acted upon by hydrogen iodide, dehydration and ring-formation take place and irene, $C_{13}H_{18}$, is formed, which hydrocarbon is isomeric with ionene.

It is only recently that Merling and Welde[4]) have succeeded in preparing irone synthetically. This synthesis is based on the formation of Δ^4-*cyclo*citral which, upon condensation with acetone, yields irone. *Iso*propylideneacetoacetic ester is condensed with sodium acetoacetic ester to *iso*phorone carboxylic acid ester. From this *d*-chlor*cyclo*geranioldiene carbonic acid and Δ^4-*cyclo*-geranic acid are obtained. According to a special method[5]) the latter is converted into Δ^4-*cyclo*citral.

PHENOLS AND PHENOL ETHERS.

The phenols and their ethers occur frequently in volatile oils. On account of the practical importance which many have acquired, they are prepared on a large scale. Thus thymol finds application on account of its antiseptic properties, anethol is used in pharmacy and in the production of liqueurs, eugenol and safrol are basal substances from which vanillin and heliotropin are manufactured.

The lower homologues of the series in question occur but rarely in volatile oils.

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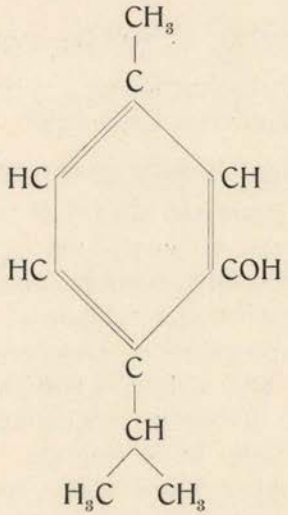
[1]) Tiemann and Krüger mention 168 to 170° as the melting point.
[2]) Rev. gén. de Chim. **6** (1903), 433; Chem. Zentralbl. **1904**, I. 281.
[3]) Compare Berl. Berichte **28** (1895), 1755.
[4]) Liebig's Annalen **366** (1909), 119.
[5]) Merling, Berl. Berichte **41** (1908), 2064.

Thymol.



Thymol (*iso*propyl-*m*-cresol), $C_{10}H_{14}O$, is frequently accompanied by carvacrol. In addition to *p*-cymene and terpenes, it constitutes the larger part of ajowan oil. It occurs also in the oils of *Ocimum viride, Monarda punctata, Satureja Thymbra, Origanum floribundum,* thyme, *Thymus capitatus,* wild thyme, *Mosla japonica* and probably also in Canadian mint oil and in culina oil. Occasionally it separates from the oils at ordinary temperature.

As a source for thymol on a large scale, ajowan oil is mostly used.

Artificially it can be prepared in a variety of ways. Of interest is its production from dibrommenthone by splitting off hydrogen bromide by means of quinoline.[1])

Thymol consists of colorless, transparent, monoclinic or hexagonal crystals, the odor of which reminds of thyme. They melt at 50,5 to 51,5° and boil at 232° (752 mm., the entire mercury thread in the vapor). Thymol crystals sink in water, hence have a density greater than 1. Liquid thymol, however, floats on the surface of water. It can be cooled considerably below its congealing point without solidifying. In

[1]) Beckmann and Eickelberg, Berl. Berichte **29** (1896), 420.

connection with liquid thymol, Perkin[1]) has observed the following densities:

$d_{4°}$ 0,9872; $d_{15°}$ 0,9790; $d_{20°}$ 0,9757; $d_{25°}$ 0,9723; $d_{50°}$ 0,9624.

As for the index of refraction ($n_{D24.4°}$) Nasini and Bernheimer[2]) record 1,51893. Schimmel & Co. found:

$d_{15°}$ 0,9760 and $n_{D20°}$ 1,52269 (supercooled).

Thymol is but sparingly soluble in water (1 : 1200) and in glycerin (1 : 1000), more so in paraffin oil (about 1 : 20), readily in alcohol, ether, chloroform, benzene, glacial acetic acid, volatile and fatty oils. In distinction to carvacrol, the alcoholic solution is not colored by ferric chloride. However, the aqueous solution of thymol sulphonic acid, $C_6H_2(SO_3H)(CH_3)(C_3H_7)(OH)$ resulting upon the solution of thymol in concentrated sulphuric acid produces a violet color with ferric chloride.

As a phenol, thymol forms water soluble "salts" with the alkalies. Hence it can be shaken out from its ethereal solution by means of 5 to 10 p. c., aqueous solutions of alkali. This property is utilized for the quantitative estimation of thymol. (Comp. the chapter on "The estimation of volatile oils" under Phenol determinations.)

Of thymol derivatives the following may here be mentioned: the phenylurethane, m. p. 107°, and the nitroso compound, m. p. 160 to 162°[3]) which results from the action of nitrous acid upon thymol. Upon oxidation it can be converted into thymoquinone.

Like its derivatives, thymol possesses decided disinfecting properties. These are, however, destroyed in the presence of oxidizing ferments in the presence of air.[4])

Ethers from neither thymol nor carvacrol have been found in volatile oils. Guillaumin[5]) has prepared and described isomerides of thymol, but as yet it is not known whether or not these occur in volatile oils.

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[1]) Journ. chem. Soc. **69** (1896), 1183.

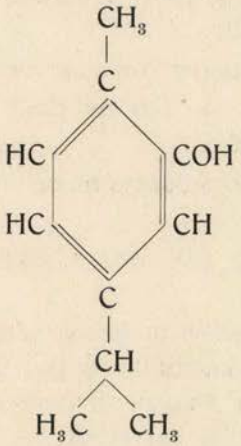
[2]) Gazz. chim. ital. **15** (1885), 59; Jahresber. d. Chem. **1885**, 314.

[3]) For the method of preparation comp. Klages, Berl. Berichte **32** (1899), 1518.

[4]) Cousin and Hérissey, Journ. de Pharm. et Chim. VI. **26** (1907), 487.

[5]) *Étude chimique et pharmacologique des thymols synthétiques dérivés des acides crésotiniques. Inaug. Dissert.*, Paris 1909; Report of Schimmel & Co. April **1909**, 136.

Carvacrol.



Carvacrol (*iso*propyl-*o*-cresol), $C_{10}H_{14}O$, occurs principally in labiate oils. Thus far its presence has been demonstrated in camphor oil, schinus oil, the oils of *Monarda punctata* (?), *M. fistulosa, M. citriodora, Satureja hortensis, S. montana, Origanum vulgare,* in the origanum oils from Trieste, Smyrna, Cyprus, and Syria, in the oils of thyme and wild thyme, and in the oil of *Thymus capitatus* (?).

Artificially carvacrol can be obtained from its isomeride carvone by treating this ketone with potassa, sulphuric acid, or phosphoric acid; from camphor by heating it with iodine; from cymene sulphonic acid by fusion with potassa; also from a number of terpene derivatives, thus from thujone, carvenone, carvotanacetone, dihydrocarvone, nitrosopinene, ketoterpin, and terpinene erythrite.

Freshly distilled, carvacrol is a colorless, viscid oil which becomes yellowish in the course of time, and which congeals in the cold. Its alcoholic solution is colored green by ferric chloride. The following constants are recorded:

M. p. + 0,5 to + 1°; b. p. 236 to 237° (corr.); $d_{15°}$ 0,981; n_D 1,525.[1])

B. p. 119° (16 mm.); $d_{20°}$ 0,9782; n_D 1,5228.[2])

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[1]) Jahns, Berl. Berichte **15** (1882), 817.

[2]) Semmler, Berl. Berichte **25** (1892), 3353.

For carvacrol from origanum oil Gildemeister found:[1])

M. p. + 0,5°; b. p. 235,5 to 236,2° (742 mm.); $d_{15°}$ 0,980; $d_{20°}$ 0,976; $n_{D20°}$ 1,52338;

and for carvacrol prepared from carvone:

M. p. + 0,5°; b. p. 236 to 236,5° (742 mm.); d_{15} 0,983; $d_{20°}$ 0,979; $n_{D20°}$ 1,52295.

In connection with products made on a large scale, Schimmel and Co. observed:

$d_{15°}$ about 0,98; $\alpha_D \pm 0°$; $n_{D20°}$ 1,523 to 1,524; soluble in 3 vols. of 70 p. c. alcohol.

Like thymol, carvacrol can be extracted from oils with aqueous alkali and determined quantitatively (see the chapter "Examination of volatile oils" under Phenol determination): It should be remembered, however, that carvacrol can be completely extracted from its alkaline solution by shaking with ether.[2]) It can likewise be distilled from strongly alkaline solutions with steam, a property which, so far as phenols are concerned, is shared only by thymol.[3])

Prolonged moderate heating with caustic potassa converts carvacrol into *iso*hydroxycuminic acid, $(CH_3)_2CHC_6H_3(OH)CO_2H$ (4-metho ethyl-phenol-2-methyl acid-1),[4]) which is readily volatile with water vapors and which melts at 93°. Chromic acid mixture oxidizes it to thymoquinone, which crystallizes in yellow plates that melt at 45,5°.[5]) When reduced according to Sabatier and Senderens a mixture of two isomeric alcohols, α- and β-carvacromenthol, is obtained. The latter yields *i*-tetrahydrocarvone upon oxidation.[6])

For the identification of carvacrol, the phenylurethane,[7]) m. p. 140°, and nitroso carvacrol are well suited. The latter is best prepared according to the directions of Klages.[8]) To a solution of carvacrol in four times its volume of alcoholic hydro-

[1]) Arch. der Pharm. **233** (1895), 188.

[2]) Jahns, Berl. Berichte **15** (1882), 817.

[3]) Klages, *ibidem* **32** (1899), 1517.

[4]) Jacobsen, Berl. Berichte **11** (1878), 573, 1061.

[5]) Reychler, Bull. Soc. chim. III. **7** (1892), 34; Chem. Zentralbl. **1892**, I. 380.

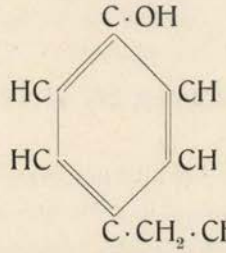
[6]) Brunel, Compt. rend. **141** (1905), 1245; **145** (1907), 1427.

[7]) Goldschmidt, Berl. Berichte **26** (1893), 2086, footnote; comp. also Gildemeister, Arch. der Pharm. **233** (1895), 188.

[8]) Berl. Berichte **32** (1899), 1518.

chloric acid, saturated at 0°, and kept cool with ice, a concentrated solution of sodium nitrite is added drop by drop. Within a few minutes, the entire liquid congeals to a thick mass of nitroso compound. This is first washed with water and then recrystallized from dilute alcohol. It crystallizes in yellow needles that melt at 153°. The benzoyl compound of nitroso carvacrol melts at 110°.

Chavicol.

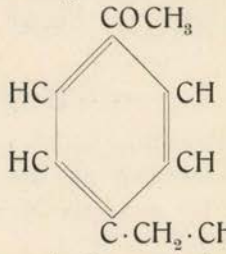


Chavicol (*p*-allylphenol), $C_9H_{10}O$, occurs in some of the betel leaf oils, also in oil of bay, and possesses strongly antiseptic properties.

It is a colorless liquid that boils at about 237°. According to Eykman[1]) $d_{18°}$ 1,033 and n_D 1,5441.

For its identification the crude phenols from betel leaf oil, separated by means of aqueous alkali, are fractionated. Fraction 235 to 240° is methylated and thus converted into methylchavicol which can easily be identified. The aqueous solution of chavicol is colored an intensive blue by ferric chloride, the alcoholic solution scarcely blue.

Methylchavicol.



Methylchavicol (estragol, *iso*anethol, *p*-allylanisol), $C_{10}H_{12}O$, was first found in anise bark oil, later also in staranise oil,

[1]) Berl. Berichte **23** (1890), 862.

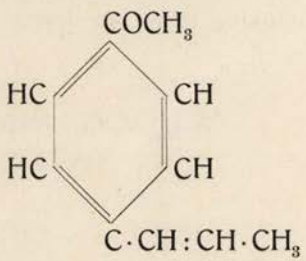
Japanese staranise oil, kobuschi oil (?), in the oils of *Persea gratissima,* bay, anise, chervil, fennel, *Pseudocymopterus anisatus,* in German, French and Japanese basilicum oils, in esdragon oil, and in American wood turpentine oil. It has also been obtained synthetically.

Methylchavicol is a colorless liquid with a slight anise-like odor, but which does not possess the intensively sweet taste of anethol. It is optically inactive; boils at 215 to 216° (corr.);[1] $d_{11,5°}$ 0,979; n_D 1,5244.[2] According to Schimmel & Co. the ether isolated from esdragon oil possesses the following properties:

B. p. 97 to 97,5° (12 mm.); 86° (7 mm.); $d_{15°}$ 0,9714 to 0,972; $n_{D16°}$ 1,52355 to 1,52380.

Methylchavicol can be characterized by its conversion into the solid anethol by boiling it with alcoholic potassa, or by its conversion into homoanisic acid (*p*-methoxy phenyl acetic acid)[3] which melts at 86°. In addition, however, anisic acid, m. p. 184°, which likewise results from anethol, is also formed. A confounding of the two phenol ethers, however, can be avoided by attention to the differences in the physical constants. Monobrommethylchavicol dibromide,[4] which melts at 62,4°, can also be used for the identification of the ether.

Anethol.



Anethol (*p*-propenylanisol), $C_{10}H_{12}O$, is the principal constituent of anise and staranise oils and is an important constituent of fennel oil. Its presence in the oil of *Osmorrhiza*

[1] Grimaux, Compt. rend. **117** (1893), 1091.
[2] Eykman, Berl. Berichte **23** (1890), 862.
[3] Bertram and Walbaum, Arch. der Pharm. **235** (1897), 179, 182.
[4] Hell and Gaab, Berl. Berichte **29** (1896), 344.

longistylis and in kobuschi oil has likewise been demonstrated. It is usually obtained from anise oil, staranise oil or fennel oil, ether by freezing the oils themselves or the corresponding fractions. Synthetically it has also been obtained in several ways.

Anethol constitutes a white, crystalline mass with an odor of anise and with an intensely sweet taste. It melts to a colorless, optically inactive, strongly refractive liquid. The following properties have been recorded:

M. p. 21°; $d_{25°}$ 0,986; $n_{D18°}$ 1,56149;[1]) $d_{11.5°}$ 0,999; n_D 1,5624.[2])

In connection with anethol produced on a large scale, Schimmel & Co. observed the following values:

M. p. 22,5 to 23°; congealing point 21 to 22°; b. p. 233 to 234° (751 mm.); $d_{25°}$ 0,984 to 0,986; $n_{D25°}$ 1,559 to 1,561; soluble in 2 to 3 vols. of 90 p. c. alcohol.

Of characteristic bromine derivatives of anethol, the anethol dibromide, $C_6H_4 \cdot OCH_3 \cdot C_3H_5Br_2$, m. p. 67°,[3]) and the monobrom anethol dibromide, $C_6H_3BrOCH_3C_3H_5Br_2$, m. p. 107 to 108°,[4]) may be mentioned. These are formed by the action of bromide on anethol under varying conditions. By the action of alcoholic potassa on anethol dibromide in the cold, anethol glycol, $C_6H_4 \cdot OCH_3 \cdot C_3H_5(OH)_2$,[5]) results. When acted upon with 20 p. c. sulphuric acid, this is converted to anise ketone. The same glycol is likewise formed by the action of mercuric acetate upon anethol.[6]) Anethol nitrite, $C_{10}H_{12}O \cdot N_2O_3$, m. p. 121°, and anethol nitrosochloride, $C_{10}H_{12}O \cdot NOCl$, m. p. 127 to 128°, should also be mentioned.

Dilute nitric acid oxidizes anethol to anisic aldehyde, chromic acid oxidizes it to anisic aldehyde and anisic acid, potassium permanganate to *p*-methoxyphenylglyoxylic acid $C_6H_4 \cdot (OCH_3)^{[1]} \cdot CO \cdot COOH^{[4]}$, m. p. 89°, the oxime of which melts at 145 to 146°.

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[1]) Stohmann, Sitzungsber. d. Akad. d. Wiss. Leipzig **1892**, 318.

[2]) Eykman, Berl. Berichte **23** (1890), 862.

[3]) Hell and v. Günthert, Journ. f. prakt. Chem. II. **52** (1895), 198.

[4]) Hell and Gärttner, Journ. f. prakt. Chem. II. **51** (1895), 424; Hell and v. Günthert, loc. cit. 194.

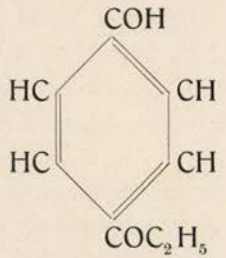
[5]) Varenne and Godefroy, Compt. rend. **140** (1905). 591.

[6]) Balbiano and Paolini, Berl. Berichte **35** (1902), 2997.

When acted upon by light and air,[1]) anethol gradually loses its capacity to crystallize and finally no longer even congeals. At the same time it becomes viscid, acquires a yellow color and an unpleasant, bitter taste, both of which no larger remind of anise. This change is accompanied by an increase in the solubility and an increase in specific gravity which may rise above 1. These phenomena are attributed to the formation of oxidation[2]) (anisic aldehyde, anisic acid) and other products. Of the latter de Varda[3]) has isolated a compound named photoanethol which he regards as a polymer of anethol. According to Hoering and and Grälert,[4]) de Varda's interpretation is not correct, but photoanethol is regarded as identical with di-*p*-methoxystilbene. This substance is characterized by its insolubility and is possibly the cause of the turbidity produced in freshly prepared anethol upon standing.

Recrystallized from glacial acetic acid and benzene, di-*p*-methoxystilbene is obtained in shiny leaflets that melt at 214 to 215°, which show a blue fluorescence both in the solid condition and in solution. Probably di-*p*-methoxystilbene is not formed directly from anethol but from the intermediate anisic aldehyde.

p-*Hydroquinone ethyl ether.*



p-Hydroquinone ethyl ether (*p*-hydroxyphenetol), $C_8H_{10}O_2$, occurs in small amount in staranise oil. It can be obtained synthetically by boiling *p*-diazophenetolsulphate with dilute sul-

[1]) According to Grimaux anethol also looses its capacity to crystallize upon prolonged heating. Bull. Soc. chim. III. **15** (1896), 778.

[2]) Report of Schimmel & Co. October **1904**, 11.

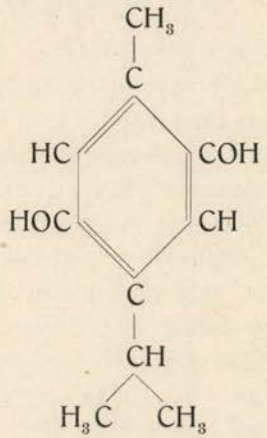
[3]) Gazz. chim. ital. **21** (1891), 183; Chem. Zentralbl. **1891**, I. 788.

[4]) Berl. Berichte **42** (1909), 1204.

phuric acid,[1]) or from hydroquinone by heating it with ethyl iodide and potassium hydroxide using a reflux condenser.[2])

The synthetic product consists of thin leaflets with satiny lustre, which are readily soluble in hot water, melt at 66° and boil at 246 to 247°.

Thymohydroquinone.



Thymohydroquinone, $C_{10}H_{14}O_2$, has been found in the oil of *Callitris quadrivalvis,* Algerian fennel oil (?) and in the oil of *Monarda fistulosa.* Artificially it is obtained by the reduction of thymoquinone with sulphurous acid.[3])

Thymohydroquinone occurs in four-sided, shiny prisms. According to Carstanjen[3]) they melt at 139,5°, according to Ciamician and Silber[4]) at 143°. According to the latter authorities thymohydroquinone boils at 290°. It is somewhat readily soluble in hot water, but difficultly in cold water. When oxidized it is changed to thymoquinone.

The dimethyl ether of thymohydroquinone is the principal constituent of arnica root oil, also of ayapana oil. It boils at 248 to 250°; $d_{22°}$ 0,998.[5])

[1]) Hantzsch, Journ. f. prakt. Chem. II. **22** (1880), 462.

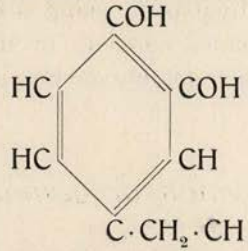
[2]) Wichelhaus, Berl. Berichte **12** (1879), 1501, footnote; comp. Hesse, Liebig's Annalen **200** (1880), 254.

[3]) Carstanjen, Journ. f. prakt. Chem. II. **3** (1871), 54.

[4]) Atti della Reale Accademia dei Lincei Rendiconti (5) **10**, I. (1901), 96.

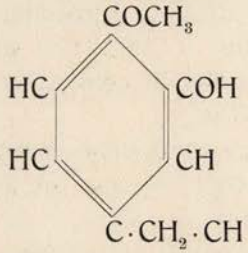
[5]) Reychler, Bull. Soc. chim. III. **7** (1892), 33.

Allylpyrocatechin.



The presence of allylpyrocatechin, $C_9H_{10}O_2$, in Javanese betel leaf oil was demonstrated by Schimmel & Co.[1]) Previously this phenol had not been known to exist in the vegetable kingdom, neither had it been prepared synthetically. It is one of the phenols extracted by means of dilute caustic soda solution from fraction 137 to 139° (4 mm.). Crystallized from benzene and petroleum ether, it is obtained in long colorless, filt-like needles which melt at 48 to 49° and boil at 139° (4 mm.). The odor is but faint, reminding somewhat of creosote. In water and alcohol it is readily soluble. The alcoholic solution is colored a deep green by ferric chloride. The alkaline solution of the phenol quickly assumes a dark red color. The dibenzoyl compound, prepared according to Schotten-Baumann, melts at 71 to 72°. The diacetyl compound is a colorless oil which boils at 229° (157° at 7 mm.). When methylated with dimethyl sulphate, the phenol is converted into methyleugenol.

Betelphenol.



Betelphenol[2]) (allylguaiacol), $C_{10}H_{12}O_2$, has thus far been found only in betel oil, from which it can be isolated in the usual manner

[1]) Report of Schimmel & Co. October 1907, 16.

[2]) The name betelphenol, given to this compound by its discoverers, was later changed to chavibetol by others.

by shaking it out with caustic soda solution. It is a strongly refractive solution characterized by the following properties:

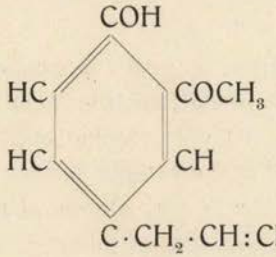
B. p. 254 to 255°, 131 to 133° (12 to 13 mm.); $d_{15°}$ 1,067.[1])
B. p. 107 to 109° (4 mm.); $d_{15°}$ 1,0690; $n_{D20°}$ 1,54134.[2])

In a freezing mixture it congeals to a crystalline mass which melts at + 8,5°.

For its identification the benzoyl compound, m. p. 49 to 50° is utilized. The acetyl compound melts at — 5°; b. p. 275 to 277°.

In alcoholic solution, betelphenol gives an intensively blue-green color with ferric chloride.

Eugenol.



Eugenol, $C_{10}H_{12}O_2$, an isomer of position to betelphenol is found widely distributed, especially among the *Myrtaceæ* and *Lauraceæ.* In largest amount it is found in oil of cloves and oil of clove stems. It also occurs in the oils of calamus, galangal, *Asarum arifolium, A. Blumei,* Japanese staranise, kobuschi, ylang-ylang, cananga (from yellow blossoms), nutmeg, boldo leaves, cinnamon leaves, cinnamon root, the bark of *Cinnamomum pedatinervium, C. pedunculatum,* in the oil from Seychelles cinnamon bark, in the oils from the leaves and stem of *Cinnamomum Loureirii,* in the oils of camphor, culilawan, clove bark (?), sassafras, massoy bark, laurel leaves, apopin, Californian laurel, rose, *Geum urbanum,* cassie buds, myrrh, cascarilla, canella alba, pimenta, bay, Bermuda bay berries, Japanese basilicum, in the oil of a species of *Basilicum* from Mayotta, and in patchouli.

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[1]) Bertram and Gildemeister, Journ. f. prakt. Chem. II. **39** (1889), 350.
[2]) Report of Schimmel & Co. October **1907**, 17.

In plants, eugenol is occasionally found in the form of a glucoside from which it can be obtained by means of hydrolysis produced by ferment action.

It is a liquid of a slightly yellowish color, with an intensive odor of cloves, and a burning taste, which, besides being optically inactive, is further characterized by the following properties:

B. p. 252° (749,5 mm.); 123° (12 to 13 mm.);[1]) $d_{14,5°}$ 1,072; n_D 1,5439.[2])

In connection with eugenol prepared on a large scale, Schimmel & Co. observed:

$d_{15°}$ 1,0713 to 1,074; $n_{D20°}$ 1,541 to 1,542; soluble in 5 to 6 vols. of 50 p. c. alcohol, in 2 to 3 vols. of 60 p. c. and in 1 to 2 vols. of 70 p. c. alcohol.

In alcoholic solution, eugenol produces a blue color with ferric chloride. Upon oxidation (the best results are obtained with the acetic ester), it yields vanillin and vanillic acid, together with small amounts of homovanillic acid.

It is readily characterized by means of the benzoate, m. p. 69 to 70°, obtained with the aid of benzoyl chloride; also by the phenylurethane, m. p. 95,5°,[3]) and its diphenylurethane, m. p. 107 to 108°.[4]) Of its bromides, the dibromide, $C_{10}H_{12}Br_2O_2$, m. p. 80°, and the tetrabromide, m. p. 118 to 119°, should be mentioned. For the quantitative determination of eugenol see the chapter on the "Estimation of volatile oils".

Eugenol is used in perfumery as well as in pharmacy. By far the largest amounts, however, are used in the manufacture of vanillin.

Aceteugenol.

In addition to eugenol, oil of cloves, but not oil of clove stems, contains some aceteugenol, $CH_3COOC_6H_3 \cdot C_3H_5 \cdot OCH_3$. This compound can be freed from eugenol by treating it with

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[1]) Erdmann, Journ. f. prakt. Chem. II. **56** (1897), 146.
[2]) Eykman, Berl. Berichte **23** (1890), 262.
[3]) Snape, Berl. Berichte **18** (1885), 2432.
[4]) Herzog, Berl. Berichte **40** (1907), 1834.

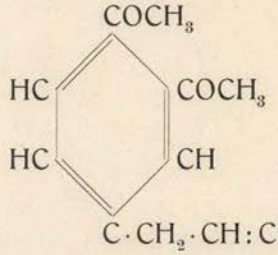
dilute alkali in the cold and can be prepared readily by boiling eugenol with acetic acid anhydride. The following constants have been found:

Erdmann:[1]) m. p. 29°; b. p. 281 to 282° (752 mm.); 145 to 146° (8,5 mm.); $d_{15°}$ 1,0842 (supercooled).

Schimmel & Co.:[2]) M. p. 29°; b. p. 142 to 143° (6 mm.); $d_{15°}$ 1,087; $n_{D20°}$ 1,52069.

Acethomovanillic acid, acetvanillic acid and acetvanillin result upon oxidation with potassium permanganate.

Methyleugenol.



Eugenol is frequently accompanied by its methyl ether, the methyleugenol (allylveratrol), $C_{11}H_{14}O_2$. It occurs in citronella oil, Japanese calamus oil, matico oil (?), betel oil, Canada snakeroot oil, in the oils of *Asarum europæum* (?), champaca flowers (?), paracoto bark, in the oil from the bark of *Cinnamomum pedatinervium,* in culilawan oil, laurel oil, in California laurel oil, in the oil of cassie buds, and in the oils of *Evodia simplex,* bay, and pimenta.

Its odor reminds of that of eugenol, but is fainter. It boils at 248 to 249° (128 to 129° at 11 mm.);[3]) $d_{11°}$ 1,041; and n_D 1,5373.[4])

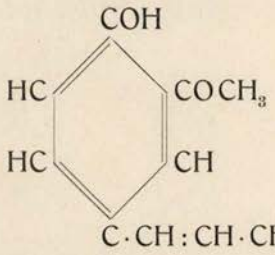
In the laboratory of Schimmel & Co., the following constants were observed in connection with technical products:

$d_{15°}$ 1,04 to 1,043; $n_{20°}$ 1,534 to 1,540; soluble in 4 vols. of 60 p. c. and in 1 to 2 vols. of 70 p. c. alcohol.

[1]) Journ. f. prakt. Chem. II. **56** (1897), 147.
[2]) Report of Schimmel & Co. Oct. **1903**, 30, footnote.
[3]) Bertram and Gildemeister, Journ. f. prakt. Chem. II. **39** (1889), 354.
[4]) Eykman, Berl. Berichte **23** (1890), 862.

When boiled with alcoholic potassa, methyl*iso*eugenol results. Bromine is added with the formation of the handsome crystalline tribrommethyleugenol, $C_6H_2Br \cdot (OCH_3)_2 \cdot C_3H_5Br_2$, which melts at 78°.[1]) Upon oxidation with potassium permanganate it is converted into dimethoxybenzoic acid (veratric acid) which melts at 179 to 180°.[2]) This same acid is likewise obtained upon the oxidation of methyl*iso*eugenol. Both compounds, as also the methyleugenol nitrite,[3]) m. p. 125°, can be utilized for the identification of methyleugenol.

Iso*eugenol.*



When eugenol in heated with an excess of solid potassa,[4]) or in amyl alcoholic solution,[5]) or when eugenol potassium is heated to about 200°[6]) with exclusion of air, it is converted into the isomeric *iso*eugenol. This is also found in ylang-ylang oil and in oil of nutmeg. The following constants have been recorded:

B. p. 261° (not corr.);[7]) $d_{18°}$ 1,09; n_D 1,5680;[8])

B. p. 111 to 112° (3,5 mm.); $d_{15°}$ 1,087 to 1,091; $n_{D20°}$ 1,570 to 1,576; soluble in 5 to 6 vols. of 50 p. c. alcohol.[9])

In a freezing mixture eugenol congeals to a mass of radiating needles which liquify at room temperature.[10])

[1]) Wassermann, Jahresber. d. Chem. **1879**, 520; Bertram and Gildemeister, Journ. f. prakt. Chem. II. **39** (1889), 354.

[2]) Comp. also Wallach and Rheindorff, Liebig's Annalen **271** (1892), 306.

[3]) Wallach, Liebig's Annalen **271** (1892), 307.

[4]) Einhorn and Frey, Berl. Berichte **27** (1894), 2455.

[5]) Tiemann, Berl. Berichte **24** (1891), 2870.

[6]) D. R. P. 179948.

[7]) Tiemann, Berl. Berichte **24** (1891), 2872.

[8]) Eykman, Berl. Berichte **23** (1890), 862.

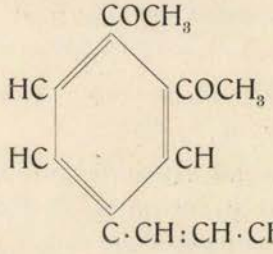
[9]) Observations made in the Laboratory of Schimmel & Co.

[10]) Tiemann, Berl. Berichte **24** (1891), 2872.

Upon oxidation it yields vanillin, in the manufacture of which it is largely used.

For its identification the following compounds may be employed: monobrom*iso*eugenol dibromide, m. p. 138 to 139°; the acetyl derivative, m. p. 79 to 80°; the benzoyl derivative, m. p. 103 to 104°; and the diphenylurethane, m. p. 112 to 113°. In alcoholic solution *iso*eugenol produces an olive-green color with ferric chloride, whereas eugenol produces a blue color.

*Methyl*isoeugenol.

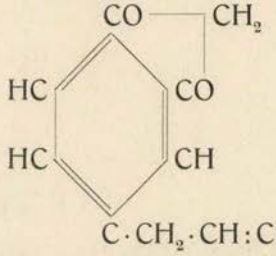


Thus far methyl*iso*eugenol has been found only in the oil from *Asarum arifolium*. Artificially it is obtained by the methylation of *iso*eugenol and by the inversion of methyleugenol. The following properties have been recorded:

B. p. 263°;[1]) $d_{11,5°}$ 1,064; n_D 1,5720.[2])

It yields a characteristic dibromide, m. p. 101 to 102°, and can be oxidized to veratric acid.

Safrol.



Safrol, $C_{10}H_{10}O_2$, is the principal constituent of oil of sassafras. It is also contained in appreciable amount in camphor oil from

[1]) Ciamician and Silber, Berl. Berichte **23** (1890), 1165.

[2]) Eykman, Berl. Berichte **23** (1890), 862.

which it is obtained technologically. In addition it has been found in the oils of *Asarum arifolium, A. Blumei,* American wormseed oil, Japanese staranise oil, in the common staranise oil (traces), in the oils of apopin, ylang-ylang (?), nutmeg, cinnamon leaves, cinnamon root, in the oil from the bark of *Cinnamomum Mercadoi,* in pichurimbean oil (?), in California laurel oil, and in massoy bark oil. Safrol is the methylene ether of *m*-allylpyrocatechin.

It is a colorless or slightly yellowish, optically inactive liquid, which upon cooling congeals to a crystalline mass, and possesses the following additional properties:

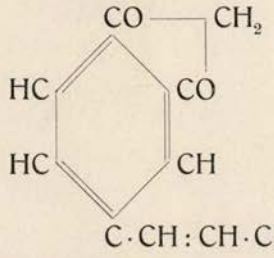
Congealing point about + 11°; b. p. 91° (4 mm.), 233° (759 mm.); $d_{15°}$ 1,105 to 1,107; $n_{D20°}$ 1,536 to 1,540.[1])

Eykman[2]) found: M. p. + 8°; b. p. 229 to 231° (uncorr.); $d_{15°}$ 1,0960; $d_{12°}$ 1,110; n_D 1,5420.

Subjected to careful oxidation with potassium permanganate, it yields first of all a glycol (m. p. 82 to 83°), which upon further oxidation yields α-homopiperonylic acid. $C_6H_3 \cdot (OOCH_2) \cdot CH_2COOH$ (m. p. 127 to 128°). When oxidized with chromic acid mixture, piperonal (heliotropin), m. p. 37°, and piperonylic acid, $C_6H_3 \cdot (OOCH_2) \cdot COOH$ (m. p. 228°) result.

When reduced in alcoholic solution with sodium, or with nickel in a current of hydrogen, safrol as well as *iso*safrol yield the dihydroderivative $C_{10}H_{12}O_2$ (b. p. 228°) and *m*-propylphenol (b. p. 228°).[3])

Iso*safrol.*



When boiled with alcoholic potassa, safrol is changed to *iso*safrol.

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[1]) Observations made in the laboratory of Schimmel & Co.

[2]) Recueil des trav. chim. des P.-B. **4** (1885), 32; Berl. Berichte **23** (1890), 862.

[3]) Henrard, Chem. Weekblad 4 (1907), 630; Chem. Zentralbl. **1907**, II. 1512.

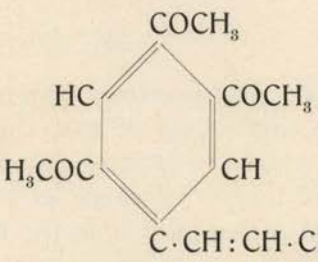
For this compound, which possibly occurs in ylang-ylang oil, the following constants have been determined:

$d_{15°}$ 1,124 to 1,129; $n_{D20°}$ 1,580.[1])
B. p. 253 to 254°; $d_{11.5°}$ 1,126.[2])

With an excess of bromine, *iso*safrol yields a pentabromide, m. p. 196,5 to 197°.[3]) Oxidized with chromic acid, it yields piperonal (heliotropin).

In commercial *iso*safrol, Hoering and Baum[4]) have demonstrated the presence of two geometric isomers, which they designated α- and β-*iso*safrol and of which the latter predominates by far. They are distinguishable only by their odor and their physical constants. Those of α-*iso*safrol lie between those of safrol and β-*iso*safrol. Chemically no difference could be observed between the two *iso*compounds.

Asarone.



Asarone (4-propenyl-1, 2, 5-trimethoxybenzene), $C_{12}H_{16}O_3$, is a constituent of Asarum oil. It has been found in the oils of calamus, matico and *Asarum arifolium*. If present in larger amounts, it separates upon prolonged standing. Asarone has likewise been obtained synthetically.

In the pure state asarone is devoid of odor and taste and is further characterized by the following properties:

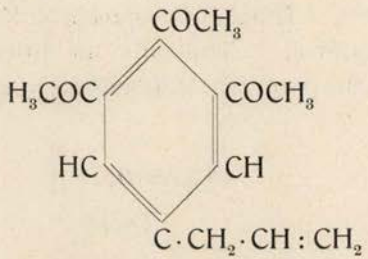
M. p. 61°;[5]) $d_{11°}$ 1,091; n_D 1,5719.[6])

[1]) Observation made in the laboratory of Schimmel & Co.
[2]) Eykman, Berl. Berichte **23** (1890), 859.
[3]) Hoering, Berl. Berichte **38** (1905), 3466; **40** (1907), 1101.
[4]) Berl. Berichte **42** (1909), 3076.
[5]) Gattermann and Eggers, Berl. Berichte **32** (1899), 290.
[6]) Eykman, *ibidem* **23** (1890), 862.

Upon bromination it yields the well crystallizable dibromide, $C_{12}H_{16}Br_2O_3$, m. p. 86°. When treated with sodium methylate in the cold, this in turn yields the crystalline $C_6H_2(OCH_3)_3 \cdot CH \cdot (OCH_3) \cdot CHBrCH_3$, which melts at 77,5°.

Oxidized with chromic acid, asarone yields asaryl aldehyde $C_{10}H_{12}O_4$, m. p. 114°. Together with asaronic acid [trimethoxybenzoic acid, $C_6H_2(OCH_3)_3 \cdot COOH$, m. p. 144°], this is also formed when asarone is oxidized with permanganate.

Elemicin.



Elemicin (4-allyl-1,2,6-trimethoxy benzene), $C_{12}H_{16}O_3$, constitutes the principal constituent of Manila elemi oil, in which it was discovered by Semmler[1]) who also gave it its name. It is found in fraction 277 to 280° of elemi oil.[2]) In order to isolate elemicin, the fraction in question is boiled for half an hour with formic acid. As Semmler has demonstrated by experiments made on anethol and safrol, allyl compounds remain unchanged, whereas propenyl compounds are destroyed. Elemicin purified in this manner possessed the following properties:

B. p. 144 to 147°; $d_{20°}$ 1,063; n_D 1,52848.

When oxidized in acetone solution with potassium permanganate trimethylgallic acid, $C_{10}H_{12}O_5$, m. p. 169°; b. p. 225 to 227°, results.

When heated with sodium or with alcoholic potassa, *iso*-elemicin, an isomer of position to asarone, results. *Iso*elemicin

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[1]) Berl. Berichte 41 (1908), 1768, 1918, 2183, 2556.

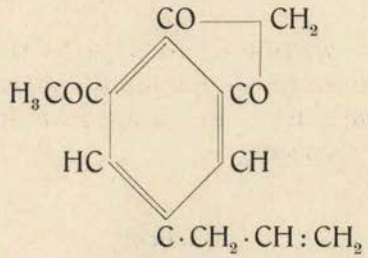
[2]) Report of Schimmel & Co. October 1896, 29; April 1907, 41; October 1908, 51.

is 4-propenyl-1,2,6-trimethoxy benzene and is characterized by the following constants:

B. p. 153 to 156° (10 mm.); $d_{20°}$ 1,073; n_D 1,54679.

*Iso*elemicin is characterized chemically by its dibromide, m. p. 88 to 89°. Like elemicin, it yields trimethylgallic acid upon oxidation with permanganate.

Myristicin.



Thus far myristicin (4-allyl-6-methoxy-1,2-methylenedihydroxy benzene),[1]) $C_{11}H_{12}O_3$, has been found only in the oils of nutmeg and mace, also in French parsley oil. It is characterized by the following constants:

B. p. 171 to 173° (40 mm.); $d_{20°}^{20°}$ 1,1437; $n_{D20°}$ 1,54032; $n_{D45,5°}$ 1,52927;[2])

B. p. 149,5° (15 mm.); $d_{19°}$ 1,1425.[3])

Even in a freezing mixture myristicin does not congeal. With bromine it yields dibrommyristicindibromide,

$$C_6Br_2(C_3H_5Br_2)(OCH_3)(O_2CH_2),\ \text{m. p. } 130°,$$

upon oxidation myristicinic aldehyde and myristicinic acid (see below).

When boiled with alcoholic potassa, or when treated with sodium, the allyl group is rearranged to the propenyl group

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[1]) This is not to be confounded with the "myristicin" of John and Mulder, a stearoptene that occasionally crystallizes out of old oils and which consists of myristinic acid as shown by Flückiger [Pharmaceutical Journ. III 5 (1874), 136].

[2]) Power and Salway, Journ. chem. Soc. **91** (1907), 2054.

[3]) Thoms, Berl. Berichte **36** (1903), 3447.

and the myristicin thereby changed to solid *iso*myristicin for which Power and Salway[1]) record the following constants:

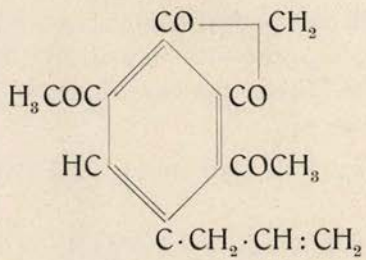
M. p. 44°; b. p. 166° (18 mm.); $n_{D45,5°}$ 1,56551.[1])

Characteristic derivatives are the dibromide, m. p. 109°, and the dibrom*iso*myristicin dibromide, m. p. 156°. Like myristicin, *iso*myristicin yields myristicinic aldehyde, m. p. 130° and myristicinic acid, m. p. 210°, upon oxidation with permanganate.

With nitrous acid both phenol ethers yield addition products from which a series of derivatives can be obtained.

The isomeric *apiols* $C_6H \cdot C_3H_5 \cdot (O_2CH_2) \cdot (OCH_3)_2$ are derivatives of an unsaturated, tetratomic phenol. With reference to their occurrence they are designated apiol, dillapiol, also allyltetramethoxy benzene.

Apiol.



Apiol (4-allyl-3,6-dimethoxy-1,2-methylenedihydroxy benzene), $C_{12}H_{14}O_4$, is a constituent of parsley seed oil and of Venezuelan camphorwood oil and matico oil from which it congeals upon cooling. Apiol has been examined more particularly by v. Gerichten,[2]) Ginsberg,[3]) Ciamician and Silber,[4]) and Thoms.[5]) The complicated constitution of this substance was almost completely revealed by Ciamician and Silber, but the final questions involved in establishing the above structural formula were settled by Thoms.

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[1]) Power and Salway, Journ. chem. Soc. **91** (1907), 2055.
[2]) Berl. Berichte **9** (1876), 258, 1477.
[3]) *Ibidem* **21** (1888), 1192, 2514; **23** (1890), 323.
[4]) *Ibidem* **21** (1888), 913, 1621; **22** (1889), 2481; **23** (1890), 2283.
[5]) *Ibidem* **36** (1903), 1714.

Apiol crystallizes in long colorless needles which possess a faint parsley odor and is characterized by the following constants:

M. p. 30°; b. p. 294° (ord. pressure), 179° (33 to 34 mm.);[1] $d_{14°}$ 1,176; n_D 1,5380.[2]

B. p. 296 to 299° (755 mm., mercury entirely in the vapor); $d_{15°}$ 1,1788 (supercooled).[3]

Apiol is almost insoluble in water, soluble in alcohol, ether and the fatty oils. With bromine it combines to form tribromapiol,

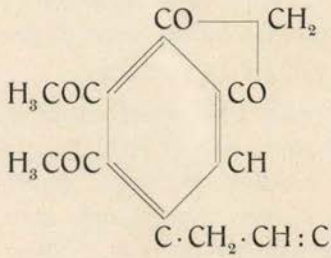
$$C_6Br(O_2CH_2)(OCH_3)_2C_3H_5Br_2,$$ m. p. 88 to 89°.

Oxidation converts it into apiol aldehyde and apiolic acid (see below).

*Iso*apiol, which results from the action of alcoholic potassa on apiol, crystallizes in monoclinic crystals which melt at 55 to 56°. Three bromine derivatives are known, a monobromide, m. p. 51°, a dibromide, m. p. 75°, and a tribromide, m. p. 120°.

Like apiol, *iso*apiol yields, upon oxidation with potassium permanganate, apiol aldehyde, $C_{10}H_{10}O_5$, m. p. 102°, and apiolic acid, $C_{10}H_{10}O_6$, m. p. 175°. Both phenol ethers also react with nitrous acid.

Dillapiol.



Dillapiol occurs in matico oil, in East Indian, Japanese, and Spanish dill oils, also in the oil of *Crithmum maritimum*. It is a viscid, oily liquid, which boils at 285° under ordinary pressure

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[1]) Ciamician and Silber, Berl. Berichte **21** (1888), 1622.

[2]) Eykman, *ibidem* **23** (1890), 862.

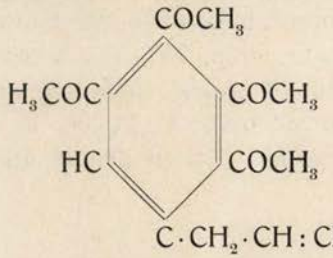
[3]) Observations made in the laboratory of Schimmel & Co.

and at 162° under a pressure of 11 mm.[1]) Its constitution finds expression in the formula given above, the correctness of which has been established by Thoms.[2])

When acted upon with an excess of bromine, dillapiol yields a substance $C_{12}H_{13}Br_3O_4$, which crystallizes in colorless prisms, melts at 110°, and which is the dibromide of monobromapiol.[3])

Dill*iso*apiol, which is obtained by inversion, is solid, and can be obtained in monoclinic crystals that melt at 44°. Its boiling point is 296°. The melting point of the tribromide is 115°. When oxidized with alkaline permanganate solution, it yields dillapiol aldehyde, $C_{10}H_{10}O_5$, m. p. 75°, and dillapiolic acid, $C_{10}H_{10}O_6$, m. p. 151 to 152°. Whether dill*iso*apiol occurs in nature or not has not yet been ascertained.

Allyltetramethoxybenzene.



From a French oil of parsley Thoms[4]) isolated a substance $C_{13}H_{18}O_4$, which he recognized as a phenol ether characterized by the above formula, and for which he records the following constants:

M. p. 25°; $d_{25°}$ 1,087; $n_{D25°}$ 1,51462.

When oxidized with potassium permanganate, a good yield of tetramethoxy benzoic acid, $C_6H(OCH_3)_4COOH$ results, which crystallizes in long needles and melts at 87°.[5])

In conclusion, several compounds may here be mentioned that are ketones as well as phenols. They are diosphenol and phloracetophenone dimethyl ether.

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[1]) Ciamician and Silber, Berl. Berichte **29** (1896), 1800.

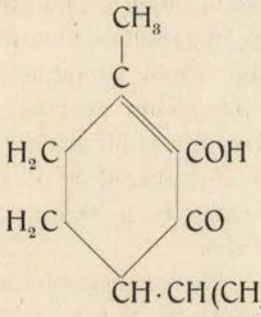
[2]) Arch. der Pharm. **242** (1904), 344.

[3]) Ciamician and Silber, *loc. cit.*

[4]) Berl. Berichte **41** (1908), 2761.

[5]) Bignami and Testoni, Gazz. chim. ital. **30** (1900), I. 240; Report of Schimmel & Co. October **1900**, 48.

Diosphenol.



Diosphenol (buchu camphor), $C_{10}H_{16}O_2$, is a constituent of the oil of buchu leaves, in which it was first found by Flückiger.[1]) Since then it has been subjected to investigation repeatedly. Its chemical constitution was revealed by Semmler and Mc Kenzie,[2]) who regard it as a cyclic reduced ketophenol of the above formula.

The diosphenol content of buchu oils varies with their botanical source. From some oils it separates as a crystalline mass upon standing at ordinary temperature, whereas other oils contain but little of this phenol. It is obtained from the oils either by freezing out, or by shaking out with dilute caustic alkali. If the latter method be followed, it should be remembered that a part of the diosphenol is removed when the alkaline solution is shaken out with ether.

Synthetically diosphenol is obtained by the oxidation of oxymethylene-menthone, $C_{11}H_{18}O_2$. A diketone $C_{10}H_{16}O_2$ results which is inverted to diosphenol by means of acids or alkalies.[3])

Diosphenol has a peculiar minty odor, is optically inactive, and crystallizes in monoclinic crystals that melt at 83°. It boils at 109 to 110° under 10 mm. pressure and with partial decomposition at 232° under atmospheric pressure. With ferric chloride it produces a dark green color.

With acetic acid anhydride and benzoylchloride, diosphenol yields the respective esters, with carbanil a phenylurethane melting at 41°. On account of the neighboring hydroxy group, the ketone group possess but little capacity for reaction. However, an oxime is known, which melts at 156° according to Kondakow and Bjalobrzeski,[4])

[1]) Pharmaceutical Journ. III. **11** (1880), 174, 219.
[2]) Berl. Berichte **39** (1906), 1158.
[3]) Semmler and Mc Kenzie, *ibidem* 1169.
[4]) Journ. f. prakt. Chem. II. **54** (1896), 437.

but Semmler and Mc Kenzie *(loc. cit.)* record the melting point as 125°. When reduced in alkaline solution with sodium amalgam a diol alcohol, $C_{10}H_{18}O_2$,[1]) results which melts at 159°. Reduction with sodium and alcohol yields *i*-menthol and a glycol $C_{10}H_{20}O_2$. Upon oxidation with potassium permanganate, the latter yields α-*iso*propyl-α'-methyladipinic acid, which melts at 104°.[2])

Characteristic for diosphenol is its ready oxidation which property explains its capacity to reduce Fehling's solution, also ammoniacal silver solution.

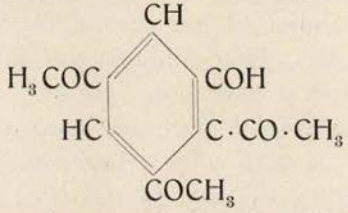
Upon oxidation with ozone Semmler and Mc Kenzie *(loc. cit.)* obtained α-*iso*propyl-γ-acetyl-*n*-butyric acid, m. p. 41°, whereas with potassium permanganate they obtained a ketoacid, $C_{10}H_{14}O_3$ which melts at 104 to 105° and yields an oxime melting at 182°. As an intermediate product an acid $C_{10}H_{16}O_4$ is formed from which the keto acid results by splitting off a molecule of water.

When diosphenol is heated with concentrated hydrochloric acid in a sealed tube to 150 to 180°, thymol, together with little carvacrol, results quantitatively.

When heated with alcoholic potassa in a sealed tube to 150 to 160°, it yields an alcohol acid $C_{10}H_{18}O_3$, which can readily be recrystallized from water in needles that melt at 94°.

Diosphenol is readily recognized by its properties. For its identification its behavior toward Fehling's solution and ammoniacal silver solution can be utilized. Of its derivatives the phenylurethane and the alcohol acid mentioned may also be used.

Phloracetophenone dimethyl ether.



Brief mention may be accorded to the phloracetophenone dimethyl ether, which was recently found by Jonas[3]) in the oil of

[1]) Shimoyama, Arch. der Pharm. **226** (1888), 413.

[2]) Kondakow and Bachtschiew, Journ. f. prakt. Chem. II. **63** (1901), 61; Semmler and Mc Kenzie, Berl. Berichte **39** (1906), 1162.

[3]) Report of Schimmel & Co. April **1909**, 150.

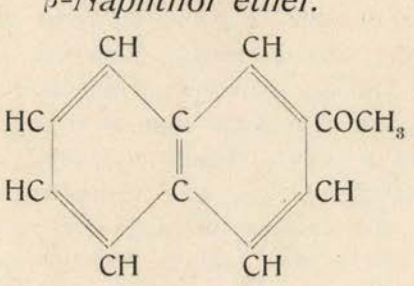
Blumea balsamifera. This compound can be shaken out of the oil with the aid of caustic soda solution. From this alkaline solution, acids precipitate it as a solid, yellowish substance which after repeated recrystallization from benzene or light petroleum ether is obtained colorless and melts at 82 to 83°.

Phloracetophenone dimethyl ether had previously been obtained synthetically by Friedländer and Schnell[1]) and was later made the subject of careful study by v. Kostanecki and Tambor.[2])

Of its derivatives the oxime melts at 108 to 110°, the acetyl compound at 106 to 107°, the methyl ether at 103°, and a yellow crystalline monobromide at 187°.

Condensed with benzaldehyde it yields 2-hydroxy-4, 6-dimethoxychalcone (m. p. 91 to 92°).

β-Naphthol ether.



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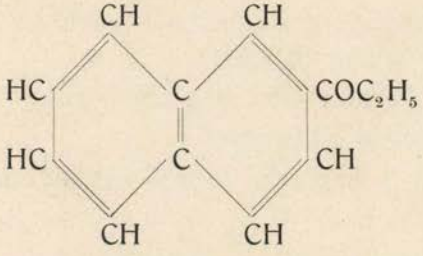

The methyl and ethyl ethers of β-naphthol are both used extensively for perfuming cheaper grades of soap. In commerce these ethers are known as nerolin. The methyl ether is sometimes differentiated as nerolin "old" or "jara-jara", the ethyl ether as nerolin "new" or "bromelia". Neither of these ethers have

[1]) Berl. Berichte **30** (1897), 2152.
[2]) *Ibidem* **32** (1899), 2262.

been found in nature thus for. They are prepared artificially by digesting for several hours β-naphtholpotassium with the molecular amounts of the respective alkyl halides in methyl or ethyl alcoholic solution.[1]) According to another method,[2]) one part of β-naphthol, three parts of methyl or ethyl alcohol and one part of hydrochloric acid are heated in an autoclave to 150°. Simpler, however, is the method of Henriques, originally used for the preparation of α-naphthol ethers, but which, according to Gattermann,[3]) is likewise well suited to the preparation of β-naphthol ethers. It consists in heating β-naphthol with the respective alcohol and sulphuric acid to 125 to 140° using a reflux condenser. The methyl ether results better when a slight pressure is employed.

Both ethers consist of colorless crystalline laminæ, which are rather difficultly soluble in methyl and ethyl alcohol, but readily soluble in other organic solvents. The odor of both ethers is strong and persistent, however, that of the ethyl ether is more delicate than that of the methyl ether. In great dilution their odor resembles that of orange blossom oil, for which they are a cheap, though not perfect, substitute. The odor of the ethyl ether is also compared with that of pine apple, though the comparison does not seem fully justified. It is possibly due to this analogy that the name Bromelia may be traced.

The following constants for β-naphthol methyl ether are recorded in chemical literature:

M. p. 72°;[4]) m. p. 70°, b. p. 274°;[5])

and for β-naphthol ethyl ether:

M. p. 37°;[6]) b. p. 274 to 275°;[7]) 282° (corr.); $d_{40°}$ 1,0547, $d_{50°}$ 1,501.[8])

[1]) Schaeffer, Liebig's Annalen **152** (1869), 286.
[2]) Liebermann and Hagen, Berl. Berichte **15** (1882), 1428.
[3]) Liebig's Annalen **244** (1888), 72.
[4]) Städel, Liebig's Annalen **217** (1883), 43.
[5]) Marchetti, Gazz. chim. ital. **9** (1879), 544; Jahresber. d. Chem. **1879**, 543.
[6]) Orndorff and Kortright, Americ. chem. Journ. **13** (1891), 162.
[7]) Liebermann and Hagen, Berl. Berichte **15** (1882), 1428.
[8]) Perkin, Journ. chem. Soc. **69** (1896), 1190.

ACIDS.

The aqueous distillate obtained as a byproduct in the preparation of volatile oils occasionally contains free fatty acids such as acetic, propionic, butyric or valeric acids. Like the methyl and ethyl alcohol obtained in like manner, these acids are in all probability decomposition products of esters contained in the parts of plants subjected to distillation. In as much as the lower fatty acids remain dissolved in the aqueous distillates they are readily overlooked. In certain cases the amounts are not inappreciable. Thus *e. g.* in a distillation of 40 kg. of seeds of *Heracleum giganteum* 120 g. of oil were obtained and 30 g. of acetic acid were separated from the aqueous distillate.[1])

Although as a rule the percentage of acid in an oil is relatively low, there are a few oils consisting principally of acids. By way of example, orris oil contains 85 p. c. of myristic acid, the oil from *Polygonum Persicaria* consists largely of a mixture of volatile fatty acids,[2]) in Mexican valerian oil 89 p. c. of valeric acid have been found,[3]) and the oil of *Morinda citrifolia* contains as much as 90 p. c. of acid.[4]).

In the compilation of acids which follows, no differentiation is made between free acids and combined acids. This failure is due to two reasons. First, accurate statements are mostly wanting on this point. And, secondly, it may well be assumed that in most instances the presence of free acid is due to decomposition during the process of distillation. Upon saponification of the oils, the acids are obtained in the form of their salts.

Formic acid, H·COOH, has been found in turpentine oil (?), in thuja oil, the oils of Ceylon cardamoms, ylang-ylang, nutmeg, California laurel, in the oil from the fruits of *Pittosporum undulatum,* in the oils of myrrh and carrot, in the oil from the

[1]) Zincke, Liebig's Annalen **152** (1869), 21.

[2]) Horst, Chem. Ztg. **25** (1901), 1055.

[3]) Report of Schimmel & Co. April **1897**, 44.

[4]) van Romburgh, Koninklijke Akademie van Wetenschappen te Amsterdam **1909**, 17; Report of Schimmel & Co. October **1909**, 78.

wood of *Goupia tomentosa,* in the oils of American pennyroyal, valerian, *Achillea nobilis,* and in the aqueous distillates of *Pinus Sabiniana, Eucalyptus Globulus, Æthusa Cynapium, Micromeria Chamissonis, Lippia scaberrima* and *Arnica montana.*

Formic acid is characterized by its great capacity for reduction. For purposes of identification, its solution, neutralized with alkali, is heated with mercuric chloride, where upon a precipitate of mercurous chloride and mercury results. The silver salt results upon the addition of silver nitrate to a solution of the formate. Upon heating it is decomposed and thus distinguished from acetic acid.

Acetic acid, $CH_3 \cdot COOH$, is the most common of the acids found in volatile oils. An enumeration of its occurrences would include almost all of the volatile oils. Its esters are mostly characterized by an especially agreable odor. Hence they find manifold application in perfumery. This is especially true of linalyl and geranyl acetates. A few oils consist largely of acetic esters, *e. g.* the oils of lavender, bergamot, petitgrain, Siberian pine needle oil, &c.

For the purpose of identifying acetic acid, silver nitrate is added to the neutralized aqueous solution. The silver salt thus obtained is analysed. As a rule this method is generally applicable for the identification of most fatty acids.

Of the remaining fatty acids, the following have been found in volatile oils:

Propionic acid, $C_2H_5 \cdot COOH$, in the oils of chamomile, male fern (?), pastinaca and lavender.

n-*Butyric acid,* $C_3H_7 \cdot COOH$, in the oils of male fern, *Polygonum Persicaria,* nutmeg, *Eucalyptus Globulus,* niaouli, *Æthusa Cynapium, Heracleum Sphondylium, H. giganteum,* lavender, valerian, American pennyroyal, and in the aqueous distillate of *Lippia scaberrima* and *Micromeria Chamissonis.*

Iso*butyric acid* has been found in laurel leaf oil, in the oil of Ceylon cinnamon (?), carrot oil (?), Cretan origanum oil (?), arnica root oil and Roman chamomile oil.

Iso*valeric acid* (*iso*propyl acetic acid), $C_4H_9 \cdot COOH$, has been found, in the oils of male fern (?), cypress, citronella, laurel leaves, in the oil from the fruits of *Pittosporum undulatum,* in the oils of geranium (?), niaouli, *Eucalyptus goniocalyx, E. paludosa, E. saligna,* and senega root, in the oil from the wood of *Goupia tomentosa,* and in the oils of lavender (?), American peppermint, valerian, Mexican valerian, kesso root and wormwood.

Methyl ethyl acetic acid in the oils of champaca, angelica root and coffee.

Caproic acid, $C_5H_{11} \cdot COOH$, in the oils of male fern (?), *Juniperus phœnicea,* lemongrass, palmarosa, laurel leaves (?), *Heracleum Sphondylium,* pastinaca, in the oil from the wood of *Goupia tomentosa,* and in the oils of lavender and of the fruits of *Morinda citrifolia.*

Iso*heptoic acid,* $C_6H_{13} \cdot COOH$, in American pennyroyal oil.

Caprylic acid, $C_7H_{15} \cdot COOH$, in the oils of wormseed (?), nutmeg, camphor, sweet orange, American pennyroyal, in the oil from the fruits of *Morinda citrifolia* and the oil of *Artemisia Herba-alba.*

Caprinic acid, $C_9H_{19} \cdot COOH$, crystallizes in needles melting at 31° and has been found in lemongrass oil, kobuschi oil, heracleum oil, American pennyroyal oil, chamomile oil, and in the oil of *Artemisia Herba-alba.*

Lauric acid, $C_{11}H_{23} \cdot COOH$, crystallizes as needles which melt at 43,6°. It occurs in the oils from the laurel berry, the pichurim bean, *Psoralea bituminosa* (?), the wood of *Goupia tomentosa* and Heracleum.

Myristic acid, $C_{13}H_{27} \cdot COOH$, crystallizes in laminæ that melt at 53,8°. It occurs in the oils of nutmeg, *Blumea balsamifera* and orris root.

Palmitic acid, $C_{15}H_{31} \cdot COOH$, crystallizes as scales that melt at 62°. It occurs in the oils of Canada snakeroot, Japanese star anise, myrrh, cascarilla, ambrette seeds (?), the fruit of

Pittosporum undulatum, pimenta, the seeds of *Monodora grandiflora,* celery seed, parsley seed, carrot, *Micromeria Chamissonis,* the stems and leaves of *Tagetes patula,* carline thistle, arnica flowers, wormwood, and *Blumea balsamifera* (?).

Stearic acid, $C_{17}H_{35}\cdot COOH$, crystallizes in laminæ that melt at 69,2° and occurs in cascarilla oil.

Unsaturated acids have been found in only a few instances.

Methacrylic acid, $CH_2:C(CH_3)COOH$, crystallizes in long prisms and melts at 15 to 16°, b. p. 160,5°. It probably occurs in Roman chamomile oil.

Angelic acid, $CH_3\cdot CH:C(CH_3)COOH$, melts at 45 to 45,5° and boils at 185°. It has been found in the aqueous distillate of the oils of angelica root and Roman chamomile.

Tiglic acid, $CH_3\cdot CH:C(CH_3)COOH$, melts at 64,5°, boils at 198,5° and occurs in geranium oil.

Oleic acid, $C_8H_{17}\cdot CH:CH(CH_2)_7COOH$, crystallizes in needles that melt at 14° and boil at 223° (10 mm.). It occurs in orris oil and kobuschi oil.

Of *hydroxy acids* the following have been identified:

Hydroxymyristic acid, $C_{14}H_{28}O_3$, crystallizes in pearly laminæ that melt at 51°. It occurs in sabadilla seed oil and in angelica seed oil.

Hydroxypentadecylic acid, $C_{15}H_{30}O_3$, crystallizes in needles that melt at 84°. It occurs in angelica root oil and possibly in Japanese angelica oil.

A *dibasic acid* has been observed but once as a natural constituent of a volatile oil, *viz.*

Succinic acid, $COOH\cdot CH_2\cdot CH_2\cdot COOH$, in the oil from the wood of *Goupia tomentosa.*

Of *aliphatic acids* there remain to be mentioned

Citronellic acid, $C_9H_{17}\cdot COOH$, which boils at 257° or 143,5° (5 mm.). It occurs in the oil of *Barosma pulchellum.*

Teresantalic acid, a reduced cyclic acid, $C_{10}H_{14}O_2$, which melts at 157°, $[\alpha]_D$ —70°24′ (in 25 p. c. solution) occurs in sandal wood.

Of *aromatic acids* the following should be mentioned:

Benzoic acid, $C_6H_5 \cdot COOH$, crystallizes in shiny laminæ that melt at 121,4°, and boil at 249° (760 mm.). It occurs in the oils of vetiver, tuberose, hyacinth, champaca, ylang-ylang, cinnamon leaves, wild cherry bark, neroli, tolubalsam and cloves.

Phenylacetic acid, $C_6H_5 \cdot CH_2 \cdot COOH$, crystallizes in thin laminæ that melt at 76,5° and boil at 265,5°. It occurs in neroli oil.

Cinnamic acid, $C_6H_5CH:CH \cdot COOH$, melts at 133° and boils at 300°. It occurs in the oils of Alpinia, Kæmpferia, xanthorrhœa resin, storax, American storax, cassia and wartara.

Salicylic acid, $C_6H_4 \cdot OH \cdot COOH$, m. p. 155 to 157°, occurs widely distributed as methyl ester (see p. 504). In addition it has been found in the oils of spicewood, ylang-ylang, *Pittosporum undulatum,* and American pennyroyal.

Anisic acid, *p*-methoxybenzoic acid, $C_6H_4 \cdot OCH_3 \cdot COOH$, melts at 184°, occurs in the Tahiti vanilla. It is also found in all oils which, like anise oil, contain much anethol, from which it results upon oxidation.

Veratric acid, $(CH_3O)_2 \cdot C_6H_3 \cdot COOH + H_2O$, melts between 179,5 and 181°, and has been found in the oil of sabadilla seed.

*Methyl-*p*-cumaric acid,* *p*-methoxycinnamic acid, $CH_3O \cdot C_6H_4 \cdot CH:CH \cdot COOH$, melts at 171° and occurs in Kæmpferia oil.

ESTERS.

Esters occur in most volatile oils and are frequently of essential import so far as the fragrance of these oils is concerned. On account of their mostly pleasant odor they play an important role in perfumery. As illustrations of oils rich in esters, the oils of bergamot, lavender, geranium, Siberian pine needle and Roman chamomille may be mentioned. It rarely happens that an oil consists almost exclusively of esters. Such is the case with the distillates of *Gaultheria procumbens* and *Betula lenta,* which consist to the extent of about 99 p. c. of methyl salicylate, and which are commonly known as wintergreen oil. With the exception of those esters which are solid at ordinary temperature and hencc can be readily isolated, the identification of esters is not an easy matter. Characteristic derivatives, such as can be prepared of alcohols, ketones and hydrocarbons, are known only in exceptional cases. Hence one is dependant on fractional distillation and the characterization of the saponification products. To this difficulty is added the circumstance that the boiling points of esters of different composition are close to each other. As a result separation by fractionation is rendered impossible. A further difficulty arises from the decomposition of many esters when distilled under ordinary pressure. Some decompose even when distilled under diminished pressure.

As a rule, esters can be readily obtained synthetically. A common method consists in passing hydrogen chloride into a mixture of the components, which mixture is some times diluted with a suitable solvent. In many instances, however, this method cannot be applied because of the susceptibility of some of the acids and alcohols toward hydrogen chloride. In such cases the ester can be obtained by the action of the alkyl iodide on the silver salt of the acid, or by the action of acid anhydrides or acid chlorides on alcoholates. Not infrequently mere boiling of the alcohol with the acid anhydride suffices. Thus many alcohols can be converted quantitatively into their acetates by boiling them with acetic acid anhydride and some anhydrous sodium acetate.

Methyl benzoate.

$C_6H_5 \cdot COOCH_3$.

The methyl ester of benzoic acid, also known as oil of Niobe, occurs in ylang-ylang oil and probably also in the oils of cloves and of tuberose. It is a colorless, optically inactive liquid, of a strong but pleasant odor.

B. p. 199,2° (746,4 mm.); $d_{0°}$ 1,1026,[1]) $d^{15°}_{15°}$ 1,0942.[2])

In the laboratory of Schimmel & Co. the following constants have been observed:

$d_{15°}$ 1,0935 to 1,0955; $n_{D20°}$ 1,517 to 1,418; sol. in 4 vol. of 60 p. c. and in 1,5 vol. of 70 p. c. alcohol.

Characteristic for methyl benzoate is its crystalline derivative with phosphoric acid.[3]) The benzoates of the homologous alcohols do not possess this property.

Methyl cinnamate.

$C_6H_5 \cdot CH{:}CH \cdot COOCH_3$.

The only oils in which this ester has been found are those from the rootstock and leaves of *Alpinia malaccensis* and from the seeds of wartara.

At ordinary temperature methyl benzoate is a solid possessing a peculiar, intensive odor, and characterized by the following properties:

M. p. 33,4°; b. p. 263°.[4])

M. p. 36°; b. p. 259,6°; $d^{36°}_{0°}$ 1,0415.[5])

For the methyl cinnamate from wartara oil, Schimmel & Co.[6]) observed:

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[1]) Kopp, Liebig's Annalen **94** (1855), 307, 309.
[2]) Perkin, Journ. chem. Soc. **69** (1896), 1174.
[3]) Raikow, Chem. Ztg. **24** (1900), 368.
[4]) Anschütz and Kinnicutt, Berl. Berichte **11** (1878), 1220.
[5]) Weger, Liebig's Annalen **221** (1883), 74.
[6]) Report of Schimmel & Co. April **1901**, 59.

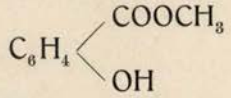
M. p. 36°; b. p. 256° (745 mm.);

and for technical preparations of their own manufacture:

M. p. 34 to 35°; $d_{15°}^{40°}$ 1,0663; $n_{D32°}$ 1,56816; $n_{D34°}$ 1,56729; $d_{15°}^{35°}$ 1,0712; $n_{D35°}$ 1,56816.

Methyl cinnamate is readily soluble in the ordinary organic solvents, likewise in olive oil and paraffin oil. Of 70 p. c. alcohol 2 vol. are requisite to effect solution.

Methyl salicylate.



Methyl salicylate (salicylic acid methyl ester, artificial oil of wintergreen) is one of the most important perfumes and is also highly esteemed on account of its antiseptic properties. It has been known for a long time, and, as has been demonstrated in the course of years, is very widely distributed in the vegetable kingdom. Neither is its occurrence restricted to a certain part of the plant, but is found in all organs from the root to the flower. It constitutes the bulk of the oils of gaultheria and sweet birch. It has also been found in the oils of tuberose (from pomade), ylang-ylang, beech seedlings, in Roman and French cassie flowers, rue, tea, cloves, *Viola tricolor,* likewise in the following plants:[1]) *Podocarpus chinensis, P. Nageia, Gnetum Gnemon β ovalifolium, Castanopsis javanica, C. j.* var., *C. Tungurrut, C.* spec., *Quercus* spec. div., *Q. bancana, Q. glandulifera, Q. Junghuhnii, Q. pseudomoluccana, Q. spicata, Q. Teysmannii, Cecropia Schiedeana, Cinocephalus ovatus, C. suaveolens, C.* spec., *Urostygma acamptophyllum, Ficus elastica, F. Benjamina, F. B.* var. *crassinerve, F. annulata, F. geniculata, F. pilosa, F. p.* var. *chrysocannia, F. retusa* var. *nitida, F. xylophylla, Slœtia Sideroxylon, Streblus mauritianus, Gironniera subæqualis, Myristica intermedia, Lindera Benzoin, Parinarium*

[1]) Compare: van Romburgh, *Verslag van 's lands plantentuin te Buitenzorg* **1897**, 37; **1898**, 29; **1901**, 58; Kremers and James, Pharm. Review **16** (1898), 100; Report of Schimmel & Co. Oct. **1899**, 56; Tailleur, Compt. rend. **132** (1901), 1235.

spec., *Photinia serrata, Rubus sundaicus, Spiræa Ulmaria, Acacia Intsia, A. pluricapitata, A. sarmentosa, A. tenerrima, Bauhinia pyrrhaneura, Cæsalpinia Bonducella, Guilandina* spec., *Mucuna gigantea, Erythroxylon Coca, E. bolivianum, Canarium* spec., *Garuga* spec., *Polygala Senega, P. S.* var. *latifolia, P. Baldwini, P. variabilis, P. javana, P. oleifera, P. serpyllacea, P. calcarea, P. vulgaris, Epirixanthes elongata, E. cylindrica, Adenocrepis javanica, Antidesma diandrum, Agyneia multiflora, A.* spec., *Baccaurea* spec., *Cyclostemon macrophyllus, Bridelia tomentosa, Elateriospermum Tokbrai, Cluytia oblongifolia, Leiocarpus arboreus, L.* spec., *Pierardia dulcis, P.* spec. div., *Phyllanthus zeylanicus, Rottlera dispar, Sphenodesme Wallichiana, Trewia* spec., *Mangifera* spec., *Semecarpus* spec., *Turpinia sphærocarpa, T.* spec., *Capura alata, Harpullia imbricata, H.* spec., *Meliosma pendula, Mischocarpus fuscescens, Elæocarpus resinosus, Wormia triquetra, Thea chinensis, T. cochinchinensis, Calpandria lanceolata, Hydnocarpus Wightiana, H. alpina, H. venenata, Scolopia Roxburghii, Taraktogenos Blumei, Alsodeia cymulosa, Viola tricolor, Homalium tomentosum, H. javanicum, Carallia symmetria, Memecylon* spec., *Nania vera, Barringtonia rubra, B. spicata, B.* spec. div., *Monotropa Hypopithys, Gaultheria fragrantissima, G. leucocarpa, Ardisia humilis, A. lurida, A. fuliginosa, A. macrophylla, A. purpurea, A. reclinata, A. sanguinolenta, A. speciosa, A.* spec., *Sideroxylon obovatum, Diospyros aurea, D. cauliflora, D. acuminata, D. Gardneri, Maba* spec., *Symplocos* spec. div., *S. fasciculata, Chionanthus elliptica, C. latifolia, C. montana, C. ramiflora, C.* spec., *Allamanda Hendersoni, Chilocarpus densiflorus, C. denudatus, C.* spec., *Melodinus lævigatus, M. orientalis, Landolphia Watsonii, Alstonia angustifolia, A. Hœdti, A. macrophylla, A. villosa, A.* spec., *Hunteria corymbosa, Rauwolfia spectabilis, Cryptolepis laxiflora, Marsdenia tenacissima, Cordia asperrima, Bignonia Chamberlaynii, B. exoleta, Tecoma mexicana, Hexacentris coccinea, Nyctocalos brunfelsiæflorus, Thunbergia grandiflora, Canthium palembanicum, C.* spec., *Gardenia Fitzalani, G. Schœmannii, Nauclea fagifolia, N. polycephala, N.* spec., *Pavetta angustifolia, P. arborea, P. barbata, P. grandiflora, P. g.* var. *lutea, P. g.* var. *aurantiaca, P. littorea, P. longiflora, P. rosea, P. paludosa, P. longipes, P.* spec.,

Petunga variabilis, *P.* spec., *Psychotria celastroides*, *P. robusta*, *P. undata*, *Wendlandia* spec., *Anthocephalus Cadamba*, *Coffea densiflora*, *C. lepidophloia*, *C. liberica*, *C. stenophylla*, *Griffithia acuminata*, *G. eucantha*, *Mussænda frondosa*, *M. officinalis*, *M. rufinervia*, *Polyphragmon* spec., *Randia densiflora*, *R. dumetorum*, *R. uliginosa*, *Sarcocephalus subditus*, *Scyphostachys coffeoides*, *Viburnum sundaicum*, *Stifftia chrysantha* and *Vernonia arborea*.

As a rule, methyl salicylate does not occur as such in the vegetable kingdom, but in the form of a glucoside. Thus in the leaves of *Gaultheria procumbens* and in sweet birch bark it occurs as gaultherin from which it is set free by ferment action. Hence the yield of methyl salicylate from these sources is greatly increased if the material is moistened and set aside for several hours. In the case of many of the above mentioned plants the distillate from fresh material contains no methyl salicylate whatever.

As to the nature of the methyl salicylate-yielding glucosides little is as yet known. In addition to the gaultherin already mentioned primverin and primulaverin yield methyl salicylate. Both glucosides occur in the *Primulaceæ* and are hydrolysed by primverase, the accompanying ferment.[1])

Artificially methyl salicylate is obtained by heating methyl alcohol and salicylic acid in the presence of sulphuric acid. On a large scale this ester has been manufactured by Schimmel & Co. since 1886 and is placed upon the market as artificial oil of wintergreen.

Methyl salicylate is a colorless liquid, which is optically inactive and possesses an intense, peculiar odor. As to its other properties, the following data have been recorded:

B. p. 217° (730 mm.);[2])
B. p. 223,7° (corr.), $d_{0°}$ 1,1969, $d_{16°}$ 1,1819;[3])
M. p. — 8,3°;[4])
B. p. 222,2° (corr.), $d_{4°}$ 1,1992, $d_{15°}$ 1,1890.[5])

[1]) Goris and Mascré, Compt. rend. **149** (1909), 947.
[2]) Schreiner, Liebig's Annalen **197** (1879), 17.
[3]) Kopp, *Ibidem* **94** (1855), 301, 302.
[4]) v. Schneider, Zeitschr. f. physik. Chem. **22** (1897), 233.
[5]) Perkin, Journ. chem. Soc. **69** (1896), 1187.

In connection with technical products, Schimmel observed the following constants:

$d_{15°}$ 1,185 to 1,190; $n_{D20°}$ 1,536 to 1,538; soluble in 6 to 8 vol. of 70 p. c. alcohol.

Methyl salicylate dissolves in potassium hydroxide solution of medium concentration forming the readily soluble ester salt potassium methyl salicylate. From such a solution it can be recovered unchanged by means of dilute acids. Sodium hydroxide solution precipitates the difficultly soluble sodium methyl salicylate. When heated with an excess of alkali, both ester salts are saponified. From these saponified solutions, acid precipitates salicylic acid.

Characteristic for salicylates is the violet color produced by ferric chloride.

Ethyl acetate.

$CH_3COOC_2H_5$.

The presence of ethyl acetate (acetic ether) in volatile oils has not yet been demonstrated. However, an observation by Göppert[1]) is on record, according to which the flowers of *Magnolia fuscata,* more particularly the fallen petals, develope an odor closely resembling that of ethyl acetate. Hence this ester, though of technical and particularly of pharmaceutical importance, is of little interest to the perfume chemist. Ethyl acetate is a colorless, neutral liquid possessing a refreshing odor. It boils at approximately 76° and at 15° has a specific gravity of 0,90 to 0,91. With the ordinary organic solvents it is miscible in all proportions. For many substances it acts as a good solvent. 18 p. of water dissolve 1 p. of acetic ether. On the other hand 28 p. of acetic ether dissolve 1 p. of water.

Ethyl benzoate.

$C_6H_5COOC_2H_5$.

Thus far ethyl benzoate has not been found in nature. Its odor resembles that of the methyl ester, but is somewhat milder. Its constants are:

[1]) Liebig's Annalen 111 (1859), 127.

B. p. 211,2° (729 mm.); $d_{16°}$ 1,0502;[1]) b. p. 212,9° (745,5 mm.).[2])

In connection with technical preparations of their own manufacture, Schimmel & Co observed:

$d_{15°}$ 1,0515 to 1,0523; $n_{D20°}$ 1,50501 to 1,50630; soluble in 7,5 vol. of 60 p. c. and in 2 vol. of 70 p. c. alcohol.

Ethyl salicylate.

$$C_6H_4\begin{cases}COOC_2H_5\\OH\end{cases}.$$

Salicylic acid ethyl ester is of interest only in so far as it finds application in perfumery. In volatile oils it has not yet been found. It is a colorless liquid, the odor of which is more faint than that of wintergreen. Perkin[3]) records the following properties:

B. p. 233,5 to 234,0° (corr.); $d_{15°}$ 1,1372.

Schimmel & Co. found:

B. p. 234 to 235° (743 mm.), 91° (5 mm.); $d_{15°}$ 1,1352; $\alpha_D \pm 0°$; $n_{D20°}$ 1,52338; soluble in 4 vol. of 80 p. c. alcohol.

When strongly cooled it can be made to congeal and then melts at + 1,3°.[4])

Ethyl cinnamate.

$$C_6H_5 \cdot CH : CH \cdot COOC_2H_5.$$

Cinnamic acid ethyl ester is one of the more rarely occurring constituents of volatile oils. Its occurrence is restricted to the oils of kæmpferia and storax. Artificially it is obtained by passing hydrogen chloride gas into the alcoholic solution of cinnamic acid. The ester is a liquid which has a pleasant odor, congeals at lower temperature, is optically inactive and possesses the following additional properties:

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[1]) Linnemann, Liebig's Annalen **160** (1871), 208.
[2]) Kopp, *Ibidem* **94** (1855), 309.
[3]) Journ. chem. Soc. **69** (1896), 1176.
[4]) v. Schneider, Zeitschr. f. physik. Chem. **19** (1896), 158.

M. p. 12°;[1]) b. p. 271°;[2]) $d_{0°}$ 1,0656, $d_{20.2°}$ 1,0498;[3])
B. p. 195,5° (103 mm.); $d_{15°}$ 1,0546.[4])

In connection with technical products Schimmel & Co. observed:

$d_{15°}$ 1,053 to 1,055; $n_{D20°}$ 1,559 to 1,561; soluble in 5 to 7 vol. of 70 p. c. alcohol.

Amyl salicylate.

$$C_6H_4\begin{cases}COOC_5H_{11}\\OH\end{cases}.$$

While not a constituent of volatile oils, salicylic acid amyl ester, also known as orchidée, trèfle or trefol, finds extensive application in perfumery and may, therefore, be mentioned. It is a colorless or yellowish liquid, the strongly aromatic odor of which reminds of some of the orchids. In connection with products of their own make Schimmel & Co. observed the following properties:

B. p. 276 to 277° (743 mm.), 151 to 152° (15 mm.); $d_{15°}$ 1,049 to 1,055; α_D slightly dextrogyrate, up to + 2°; $n_{D20°}$ 1,505 to 1,507; soluble in about 3 vol. of 90 p. c. alcohol.

In as much as the ester is not readily saponifiable, it is necessary for a quantitative saponification to heat it with an excess of alkali for two hours on a wather bath. Indeed, it is well to apply this precaution to other esters of salicylic acid.

In addition to its use as a perfume, amyl salicylate is also employed to fix the odor of finer perfumes. Therapeutically it has also been successfully employed as a remedy against rheumatism.[5])

Linalyl acetate.

$CH_3COOC_{10}H_{17}$.

Linalyl acetate, the most valuable and characteristic constituent of the oils of bergamot and lavender, is rather widely

[1]) Wegener, Private communication by Friedländer, Liebig's Annalen **221** (1883), 75.
[2]) Anschütz and Kinnicutt, Berl. Berichte **11** (1878), 1220.
[3]) Kopp, Liebig's Annalen **95** (1855), 320.
[4]) Perkin, Journ. chem. Soc. **69** (1896), 1228.
[5]) According to Pharm. Zentralh. **43** (1902), 637.

distributed. In addition to the above mentioned two oils, it has been found in the oils of Canada snakeroot (?), ylang-ylang (?), sassafras leaves, the bark of *Cinnamomum pedatinervium,* petitgrain, lemon, neroli, the Italian limette, jasmine, muscatelle sage (?), the oil of the leaves of *Mentha citrata* and gardenia.

Since both linalool and linalyl acetate readily undergo change and decomposition, the artificial preparation of the ester is not readily accomplished. Thus the common method of acetylation yields but poor results since the linalool is partly decomposed, partly rearranged to terpineol, geraniol and nerol. According to Tiemann[1]) a pure linalyl acetate can be obtained by the interaction between sodium linalool and acetic acid anhydride.

Linalyl acetate is a colorless liquid with a pleasant odor reminding of bergamot. In accordance with the linalool employed, it deviates the ray of polarized light ether to the right or left. In connection with a linalyl acetate prepared according to Tiemann's method, Hesse and Zeitschel[2]) observed the following constants:

B. p. 96,5 to 97° (10 mm.), 115 to 116° (25 mm.), about 220° with decomposition (762 mm.); $d_{15°}$ 0,913; $[\alpha]_D$ — 6° 35′; ester content 97,6 p. c.

Under the name of bergamiol, Schimmel & Co. introduce into the market a product that possesses approximately the following properties:

$d_{15°}$ 0,90 to 0,91; $n_{D20°}$ 1,451 to 1,454; soluble in 10 to 15 vol. of 60 p. c. and in 3 to 5 vol. of 70 p. c. alcohol.

Geranyl formate.

$HCOOC_{10}H_{17}$.

This ester, which has not yet been observed in nature, is formed even upon standing of a solution of geraniol in crystallized formic acid,[3]) better still upon the addition of a small amount of a mineral acid.[4]) According to Tiemann *(loc. cit.)* the ester

[1]) Berl. Berichte **31** (1898), 839.
[2]) Journ. f. prakt. Chem. II. **64** (1901), 256.
[3]) Tiemann and Schmidt, Berl. Berichte **29** (1896), 907, footnote.
[4]) Bertram, G. I. P. 80711.

boils at 113 to 114° (15 mm.), according to Bertram at 104 to 105° (10 to 11 mm.).

In connection with a technical product of about 91 p. c. ester content, Schimmel & Co. observed the following constants:

$d_{15°}$ 0,9248; $\alpha_D \pm 0°$; $n_{D20°}$ 1,46456; soluble in 10 parts and more of 70 p. c. alcohol.

Like all formates, the ester is prone to decomposition.

Geranyl acetate.

$CH_3COOC_{10}H_{17}$.

Like linalyl acetate, geranyl acetate occurs rather commonly in volatile oils. It is the principal constituent of the oil of *Darwinia fascicularis,* and has also been found in the oils of the needles of *Callitris glauca,* palmarosa, lemongrass, sassafras leaves, kuromoji, geranium (?), petitgrain, neroli, coriander, *Eucalyptus Staigeriana, E. Macarthuri, Leptospermum Liversidgei* and lavender. Artificially geranyl acetate is obtained by heating geraniol with acetic acid anhydride and some anhydrous sodium acetate. In connection with a product obtained by this method, Bertram and Gildemeister[1]) observed:

B. p. 242 to 245° with decomposition (764 mm.); 127,8 to 129,2° (16 mm.); $d_{15°}$ 0,9174; $n_{D15°}$ 1,4628.

In connection with technical products of their own make Schimmel & Co. observed:

$d_{15°}$ 0,910 to 0,917; $\alpha_D \pm 0°$; $n_{D20°}$ 1,462 to 1,466; soluble in 7 to 10 vol. of 70 p. c. alcohol.

The odor of geranyl acetate is pleasant and flower-like, reminding of that of linalyl acetate.

Citronellyl formate.

$HCOOC_{10}H_{19}$.

The formic ester of citronellol has thus far not been found in volatile oils. It is readily formed by boiling citronellol with

[1]) Journ. f. prakt. Chem. II. 49 (1894), 189.

twice its volume of strong formic acid,[1]) also by setting aside for several days a solution of citronellol in anhydrous formic acid.[2])

The ester decomposes readily, and according to Tiemann and Schmidt *(loc. cit.)* boils between 97 and 100° (10 mm.).

In connection with a technical product containing 93,2 p. c. of ester Schimmel & Co. observed the following properties:

$d_{15°}$ 0,9105; α_D — 1° 9′; $n_{D20°}$ 1,45111; soluble in 12,5 vol. of 70 p. c. and in 2,5 vol. of 80 p. c. alcohol.

Citronellyl acetate.

$CH_3COOC_{10}H_{19}$.

Citronellyl acetate is probably a constituent of citronella oil and oil of geranium, but its presence in either oil has not yet been definitely established. Artificially it can readily be obtained by the action of acetic acid anhydride on citronellol. It is a colorless liquid with a pleasant odor faintly resembling that of bergamot oil. According to Naschold[3]) it boils at 121,5° under 15 mm. pressure. Tiemann and Schmidt[4]) record the following properties:

B. p. 119 to 121° (15 mm.); $d_{17.5°}$ 0,8928; $[\alpha]_{D17.5°}$ + 2,37°; $n_{D17.5°}$ 1,4456.

In the laboratory of Schimmel & Co. the following constants were observed:

$d_{15°}$ 0,9013; α_D — 1° 15′; $n_{D20°}$ 1,44891; soluble in 6 vol. of 70 p. c. alcohol.

Benzyl acetate.

$CH_3COOCH_2C_6H_5$.

Benzyl acetate is the principal constituent of the oil of jasmine flowers and of gardenia oil. It is also contained in ylang-ylang oil and in hyacinth oil. Artificially this ester can be obtained in a variety of ways. The simplest method is to acetylize

[1]) Walbaum and Stephan, Berl. Berichte **33** (1900), 2307.

[2]) Tiemann and Schmidt, Berl. Berichte **29** (1896), 907.

[3]) *Beiträge zur Kenntnis aliphatischer Terpenverbindungen. Inaug.-Dissert.* Göttingen 1896, p. 49.

[4]) *Loc. cit.*

benzyl alcohol with acetic acid anhydride, or to act on benzyl alcohol with acetic acid in the presence of sulphuric acid.[1]) According to Seelig[2]) a mixture of benzyl chloride, fused potassium or sodium acetate and glacial acetic acid are boiled for 20 to 30 hours in a flask connected with a reflux condenser. The latter is provided with a calcium chloride tube to keep out moisture. Tiemann[3]) uses benzaldehyde as starting point which he gently boils with zinc dust and glacial acetic acid for about 12 hours in a flask connected with a reflux condenser.

Benzyl acetate is a colorless liquid of a refreshing odor reminding of jasmine. According to Hesse and Müller[4]) it boils between 215 and 216° and has a specific gravity of 1,060 at 15°.

In connection with their own products prepared on a technical scale, Schimmel & Co. have observed the following constants: b. p. 215° (760 mm.), 95° (10 mm.), 69° (4 mm.); $d_{15°}$ 1,060 to 1,062; $n_{D20°}$ 1,502 to 1,504; ester content 98 to 100 p. c.; soluble in 2 vol. of 70 p. c., 6 vol. of 60 p. c., 20 vol. of 50 p. c., 70 vol. of 40 p. c., 120 vol. of 35 p. c., and 200 vol. of 30 p. c. alcohol.

The benzyl acetate content is the principal criterion as to the purity of the product. In as much as benzyl chloride may be used in its production, the absence of chlorinated products should be ascertained.

On account of its ready solubility in dilute alcohol, benzyl acetate is particularly adapted to the preparation of perfumes with low alcohol content.

Benzyl benzoate.

$C_6H_5COOCH_2C_6H_5$.

This ester is an essential constituent of cinnamein or Peru balsam oil. It likewise occurs in the oils of tuberose, ylang-ylang and tolu balsam.

According to Claisen,[5]) benzyl benzoate can be prepared by dissolving $1^1/_2$ g. of sodium in the requisite amount of benzyl

[1]) S. Cannizaro, Liebig's Annalen 88 (1853), 130.
[2]) Journ. f. prakt. Chem. **39** (1889), 162.
[3]) Berl. Berichte **19** (1886), 355.
[4]) Berl. Berichte **32** (1899), 744.
[5]) Berl. Berichte **20** (1887), 649.

alcohol to effect solution. 200 g. of benzaldehyde are then added and the mixture heated for several days on a water bath. The reaction product is acidulated with glacial acetic acid, the oil thrown out of solution with water and destilled.

Benzyl benzoate is a somewhat viscid colorless liquid which is difficultly volatile with water vapor and possesses a faint odor. A ta low temperature it congeals to white crystals which melt again at about 20°. Claisen[1]) records the following properties:

M. p. 21°; b. p. 323 to 324°; $d_{19°}$ 1,1224 (liquid).

In the laboratory of Schimmel & Co. the following constants have been observed:

M. p. 19 to 20°; b. p. 156° (4,5 mm.); $d_{15°}$ 1,121 to 1,125; $n_{D20°}$ 1,569 to 1,570; soluble in 10 vol. of 80 p. c. and in 1,5 to 2 vol. of 90 p. c. alcohol.

In perfumery benzyl benzoate finds extensive application as solvent and fixing agent for other more volatile perfumes. Thus, *e. g.* it is used in making concentrated solutions of artificial musk.

Benzyl cinnamate.

$C_6H_5CH:CH\cdot COOCH_2C_6H_5$.

Cinnamic acid benzyl ester, $C_{16}H_{14}O_2$, has been found in the oils of storax, tolu balsam and Peru balsam. According to Grimaux,[2]) it can be obtained artificially by boiling sodium cinnamate, alcohol and benzyl chloride in a flask connected with a reflux condenser. It forms white, shiny crystals which possess an aromatic odor, boil at 39° and decompose at about 350°.[3]) Occasionally it remains liquid for hours even at a temperature of 0°. When it congeals, the ester forms a wax-like looking mass of radiating crystals.

A product containing 98 p. c. of ester, when examined in the laboratory of Schimmel & Co., was found to possess the following properties:

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[1]) Berl. Berichte **20** (1887), 647.
[2]) Compt. rend. **67** (1868), 1049.
[3]) Grimaux, *Ibidem*, 1051.

M. p. 31,5 to 32,5°; b. p. 195 to 200° (5 mm.), 335 to 340° with decomposition (ordinary pressure); soluble with slight turbidity in 7,5 vol. of 90 p. c. and in 1 vol. of 95 p. c. alcohol.

Cinnamyl cinnamate.

$C_6H_5CH:CH\cdot COOCH_2CH:CH\cdot C_6H_5$.

The cinnamyl ester of cinnamic acid, also known as styracin, $C_{18}H_{16}O_2$, is found in storax, also in the oils of hyacinth (?), xanthorrhœa resin, Peru balsam and Honduras balsam.

When pure it constitutes shiny white crystalline masses which melt at 44°,[1]) are insoluble in water, and rather difficultly soluble in alcohol. With water vapor the ester is difficultly volatile.

Of its derivatives the dibromide, $C_6H_5CH:CH\cdot CO_2CH_2\cdot CHBr\cdot CHBr\cdot C_6H_5$, which melts at 151° should be mentioned. According to Miller[2]), it is obtained by adding bromine to an ethereal solution of styracin until it is no longer decolorized. After 24 hours the white powder that has been deposited is removed by filtration, washed with ether and recrystallized from hot alcohol.

Terpinyl formate.

$HCOOC_{10}H_{17}$.

Terpinyl formate possibly occurs in Ceylon cardamom oil, but its presence therein has not yet been definitely established. Artificially, the ester has been obtained by Lafont[3]) who allowed two parts of lævogyrate turpentine oil to stand for several weeks with one part of crystallized formic acid. The product thus obtained revealed the following constants:

B. p. 135 to 138° (40 mm.); $d_{0°}$ 0,9986; $[\alpha]_D$ — 69,25°.

Dextrogyrate turpentine yields the dextrogyrate ester with otherwise the same constants.

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[1]) Miller, Liebig's Annalen **188** (1877), 202.

[2]) Liebig's Annalen **189** (1877), 344.

[3]) Compt. rend. **106** (1888), 140; Bull. Soc. chim. II. **49** (1888), 325.

Terpinyl acetate.

$CH_3COOC_{10}H_{17}$.

The acetate of terpineol has been found only occasionally in volatile oils: the dextrogyrate ester in cypress oil and the oil of Malabar cardamom, the inactive in oil of cajeput. It possibly, occurs also in Siberian pine needle oil and in the German oil from the needles of *Pinus silvestris,* and in niaouli oil. However, reliable data are still wanting.

Artificially, terpinyl acetate has been obtained by Bouchardat and Lafont[1]) by heating a mixture of pinene and acetic acid for 64 hours. According to Bertram[2]) this reaction is accelerated greatly by the addition of small amounts of an inorganic acid. Likewise from terpineol and acetic acid anhydride a good yield of ester can be obtained by observing the proper conditions.

Terpinyl acetate is a colorless liquid of a relatively faint odor. According to the character of its source it is dextrogyrate, lævogyrate, or optically inactive. According to Bouchardat and Lafont *(loc. cit.)* it boils at 110 to 115° under 10 mm. pressure; and at 220° under ordinary pressure, but with partial decomposition. For a terpinyl acetate obtained by heating 1 vol. of oil of lemon with $1^1/_2$ vol. of glacial acetic acid, Lafont[3]) determined the following properties:

B. p. 140° (40 mm.); $d_{0°}$ 0,9828; $[\alpha]_D + 52° 30'$.

In the laboratory of Schimmel & Co. technical products with a 90 p. c. ester content have been found to possess the following properties:

B. p. 90 to 94° (5 mm.); $d_{15°}$ 0,9544 to 0,961; $\alpha_D \pm 0°$, $n_{D20°}$ 1,46526 to 1,46585; soluble in about 5 vol. of 70 p. c. alcohol. Terpinyl acetate is rather difficultly saponifiable. Hence a large excess of alkali should be used in quantitative determinations and the mixture should be heated for two hours, for otherwise values will be obtained that are too low.

[1]) Annal. de Chim. et Phys. VI. 16 (1889), 244.
[2]) G. I. P. 67255.
[3]) Annal. de Chim. et Phys. VI. 15 (1888), 153.

Bornyl formate.

$HCOOC_{10}H_{17}$.

Bornyl formate occurs in valerian oil and possibly in the oil of *Achillea nobilis*. It results upon the interaction of borneol on formic acid in the presence of some mineral acid.[1]) It is a colorless liquid with a strong but pleasant odor. According to the borneol employed, the ester is either dextrogyrate or lævogyrate. The following constants have been recorded in chemical literature:

d-Bornyl formate:

B. p. 225 to 230°;[2]) 98 to 99° (15 mm.); $d_{15°}$ 1,017[3]).

B. p. 90° (10 mm.); $d_{15°}$ 1,013; $\alpha_D + 31°$; $n_{D15°}$ 1,47078[4]).

B. p. 106 to 108° (21 mm.), 90° (10 to 11 mm.); $d_{0°}$ 1,027, $d_{22°}$ 1,009; $[\alpha]_D + 48° 45'$.[5])

l-Bornyl formate:

B. p. 106 to 108° (21 mm.); $d_{0°}$ 1,026, $d_{22°}$ 1,009; $[\alpha]_D - 48° 56'$ (Béhal, *loc. cit.*).

B. p. 97° (15 mm.); $d\frac{20°}{4°}$ 1,0058; $[\alpha]_D - 40,46°$,[6])

B. p. 215°; $[\alpha]_D - 49°$ (4,55 p. c. solution in alcohol).[7])

A technical product examined in the laboratory of Schimmel & Co. and containing 98,8° p. c. ester had the following properties:

B. p. 85 to 86° (7 mm.); $d_{15°}$ 1,0126; $\alpha_D - 47° 32'$.

Bornyl acetate.

$CH_3COOC_{10}H_{17}$.

This ester, which is a characteristic constituent of many coniferous oils, also occurs in several other oils. The dextrogyrate acetate occurs in the needle oil of *Callitris glauca,* the lævogyrate acetate in the needle oil of *Abies alba,* in the oil from the twigs

[1]) Bertram, G. I. P. 80711.

[2]) Bruylants, Berl. Berichte **11** (1878), 455.

[3]) Bertram and Walbaum, Journ. f. prakt. Chem. II. **49** (1894), 7.

[4]) Bertram and Walbaum, Arch. der Pharm. **231** (1893), 305.

[5]) Béhal, Annal. de Chim. et Phys. VII. **20** (1900), 421.

[6]) Tschugaeff, Berl. Berichte **31** (1898) 1775.

[7]) Minguin and de Bollemont, Compt. rend. **134** (1902), 609.

of *A. canadensis, A. balsamea* and Siberian pine needle oil, also in the oils of coriander, valerian and kesso root. The acetate has likewise been found in the following oils but observations as to its direction of rotation are wanting, *viz.*, in the oil from the cones of *Abies alba* (?), the oil of *Pinus montana,* the oils from the cones and needles of *Picea canadensis* and *P. rubens,* the oil from the twigs and needles of *Larix americana,* in German and Swedish oils of *Pinus silvestris* (?), in the needle oil of *Picea nigra,* and in the oils from *Satureja Thymbra, Thymus capitatus* and golden rod.

The artificial preparation of bornyl acetate affords no difficulty. It can be obtained when borneol is acetylized in the ordinary manner, also by heating borneol with anhydrous acetic acid in the presence of some sulphuric acid.[1])

It is the only bornyl ester of a fatty acid which has thus far been obtained in a crystalline state. From petroleum ether it is obtained in handsome hemiedric crystals, which melt to a colorless liquid at 29°.[2]) Molten bornyl acetate may remain in a liquid condition for a long time. Its aroma is typical of that of pine needles imparting to it its freshness and strength. The direction of rotation of the ester corresponds with that of the borneol. The following properties have been recorded:

M. p. 29°; b. p. 98° (10 mm.); $d_{15°}$ 0,991; α_D — 38° 21′; $n_{D15°}$ 1,46635;[3]) b. p. 106 to 107° (15 mm.);[4])

B. p. 107° (15 mm.); $d^{20°}_{4°}$ 0,9855; $[\alpha]_D$ — 44,40°;[5])

$d_{15°}$ 0,9908; α_D — 43° 40′; $n_{D20°}$ 1,46387; $d_{15°}$ 0,9912; α_D — 43° 40′; $n_{D20°}$ 1,46446; soluble in 2,7 vol. of 70 p. c. alcohol; m. p. 28,5°; $d_{15°}$ 0,9912; $\alpha_{D19°}$ + 40° 28′; $n_{D20°}$ 1,46397; soluble in 3 vol of 70 p. c. alcohol.[6])

In connection with two liquid commercial products Schimmel & Co. observed the following properties:

$d_{15°}$ 0,9905; α_D — 2° 22′; and $d_{15°}$ 0,9901; α_D + 29° 4′.

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[1]) G. I. P. 80711.

[2]) Bertram and Walbaum, Arch. der Pharm. **231** (1893), 304.

[3]) Bertram and Walbaum, *Ibidem* 305.

[4]) Bertram and Walbaum, Journ. f. prakt. Chem. II. **49** (1894), 7.

[5]) Tschugaeff, Berl. Berichte **31** (1898), 1775.

[6]) Observations made by Schimmel & Co.

For the identification of bornyl acetate, fraction 220 to 230° is employed. It is strongly chilled and inoculated with a little solid bornyl acetate. If the desired results are not thus obtained, the sample in question is saponified and the components identified.

Bornyl iso*valerate.*

$C_4H_9COOC_{10}H_{17}$.

Bornyl *iso*valerate occurs in oil of valerian and in kesso root oil. In the latter it is found in the lævogyrate modification. Artificially it is obtained by the esterification of borneol with *iso*valeric acid. It is a colorless, aromatic liquid, the odor and taste of which remind both of valerian and borneol. According to Bruylants[1]) it boils between 255 and 260°.

In connection with technical products showing an ester content of 86 to 89%, Schimmel & Co. observed the following constants:

$d_{15°}$ 0,954 to 0,955; α_D — 34° 25′ to — 35° 31′; $n_{D20°}$ about 1,462; soluble in about 4 vol. of 80 p. c. alcohol.

For its quantitative saponification, heating for two hours with a large excess of potassa is required.

Bornyl *iso*valerate is reputed to produce good results in all sorts of nervous troubles, especially in nervous heart affections. It is also said to stimulate the appetite.

Menthyl acetate.

$CH_3COOC_{10}H_{19}$.

Menthyl acetate, a liquid having a peppermint-like odor, has thus far been observed only in oil of peppermint. It can readily be obtained by boiling menthol with acetic acid anhydride and some sodium acetate. Its properties are:

B. p. 227 to 228°; $d_{0°}^{20°}$ 0,925; $[\alpha]_D$ — 79,26°.[2])

$d_{15°}$ 0,9296 to 0,9298; α_D — 72° 47′ to — 73° 18′; $n_{D20°}$ 1,44669 to 1,44680; soluble in about 15 vol. of 65 p. c. and in about 6 vol. of 70 p. c. alcohol.[3])

[1]) Berl. Berichte 11 (1878), 456.

[2]) Kishner, Journ. russ. phys. chem. Ges. 27 (1895), 480.

[3]) Observation in the laboratory of Schimmel & Co.

Menthyl iso*valerate.*

$C_4H_9COOC_{10}H_{19}$.

Up to the present time this ester has been found only in American peppermint oil. It is a colorless liquid the odor of which reminds of both components. Artificially it is obtained by the esterification of menthol with *iso*valeric acid. In connection with technical products thus obtained and containing about 80 p. c. ester, Schimmel & Co. observed the following properties:

$d_{15°}$ 0,9067 to 0,908; α_D — 56° 28′ to — 56° 51′; $n_{D20°}$ 1,44851 to 1,44861; soluble in 5 to 7 vol. of 80 p. c. alcohol.

This ester also is saponifiable with difficulty. For quantitative determinations the process of heating on the water bath with the excess of alkali should be extended over two hours.

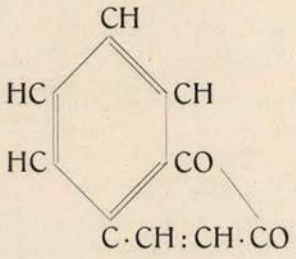
Menthyl *iso*valerate has been recommended as analeptic and antineuralgic. It is also reported to have been effective in the treatment of sea sickness.

LACTONES.

Lactones also have been found in volatile oils. Some of them, like sedanolid, coumarin, and hydrocoumarin are characterized by a strong odor. Alantolactone and the lactone $C_{10}H_{16}O_2$ from peppermint oil have but a faint odor.

In this connection only two of the most important, *viz.*, coumarin and alantolactone, are to be considered.

Coumarin.



Coumarin (o-hydroxycinnamic acid anhydride), $C_9H_6O_2$, the odoriferous principle of the "Waldmeister" *(Asperula odorata)*, is widely distributed in the vegetable kingdom. It was first observed in the tonka beans, the fruit of *Dipteryx odorata* in which it occurs in largest amount. Later is was found in the "Waldmeister", also in dates, in Peru balsam, in the salikounda beans of *Copeifera Salikounda*, in lavender oil, in the bulbs of *Vitis sessilifolia*, in the resin and bark of *Ceratopetalum apetalum* also in the following plants: *Adiantum pedatum, A. peruvianum, A. trapeziforme, Anthoxanthum odoratum, Cinna arundinacea, Hierochloa alpina, H. australis, H. borealis, Milium effusum, Aceras anthropophora, Angræcum fragrans, Nigritella angustifolia, Orchis fusca, Orchis militaris* (?), *Herniaria glabra, Achlys triphylla, Prunus Mahaleb, Ruta graveolens, Dipteryx odorata, D. oppositifolia, D. pteropus, Melilotus alba, M. altissima, M. hamata, M. leucantha, M. officinalis, Chrysophyllum imperialis, Peristrophe angustifolia, Alyxia stellata, Galium triflorum, Spermacoce semierecta, Liatris odoratissima, L. spicata, Ageratum mexicanum, A. conyzoides, Eupatorium Ayapana* and *E. africanum* (?).[1]) As melilotate, coumarin also occurs in *Lindsaya cultrata* and in *Melilotus officinalis*. Apparently coumarin does not always exist as such in the plant, but is frequently formed by ferment action since its odor often becomes noticeable only after drying. Synthetically it was obtained by Perkin[2]) by the action of acetic acid anhydride and sodium acetate on salicylic aldehyde. However, it is also obtained by other methods and in recent years has constituted an important article of chemical industry.

Coumarin forms colorless, shiny laminæ or rhombic prisms and possesses a pleasant, spicy odor and a bitter taste. In

[1]) Literature: Bley, Arch. der Pharm. **142** (1857), 32; Poulsen, Bot. Zentralbl. **15** (1883), 415; Lojander, Just Jahresbericht **1887**, Bd. I. 181; Molisch and Zeisel, Berichte d. deutsch. botan. Gesellschaft **6** (1888), 353; Greshoff, Berichte d. deutsch. pharm. Ges. **9** (1899), 214; Peckolt, Zeitschr. d. allg. österr. Apoth. Ver. **31** (1893), 829; Molisch, Apotheker Ztg. **17** (1902), 45, 137; Busse, Berichte d. deutsch. pharm. Ges. **14** (1904), 205; Peckolt, *Ibidem* 45; Senft, Pharm. Zentralh. **45** (1904), 599; Tschirch, *Ibidem* **46** (1905), 803; Schimmel's Bericht April **1889**, 46; October **1889**, 58; Report of Schimmel & Co. April **1890**, 66; October **1900**, 79; April **1902**, 93.

[2]) Berl. Berichte **8** (1875), 1599.

extreme dilution its odor resembles that of new mown hay. According to Zwenger and Dronke it melts at 67°.[1]) Schimmel & Co. observed the melting point of 69 to 70° in connection with the best commercial products. It sublimes without decomposition and boils at 290,5 to 291°.[2])

Coumarin dissolves difficultly in cold, somewhat more readily in hot water, easily in alcohol, and ether and in volatile and fatty oils. As to its solubility in alcohol of different strengths, Schimmel & Co. have made the observations recorded in the following table.[3])

100 parts *alcohol*	at 0° C.	at 16 to 17° C.	at 29 to 30° C.
of 90 vol.-percent.	7,1 parts	13,7 parts	42,5 parts
of 80 vol.-percent.	6,0 parts	12,3 parts	38,3 parts
of 70 vol.-percent.	4,4 parts	9,1 parts	26,0 parts
of 60 vol.-percent.	3,2 parts	6,0 parts	16,0 parts
of 50 vol.-percent.	1,7 parts	3,4 parts	8,9 parts
of 40 vol.-percent.	0,7 parts	1,5 parts	3,9 parts
of 30 vol.-percent.	0,3 parts	0,6 parts	1,7 parts
of 20 vol.-percent.	0,2 parts	0,4 parts	0,8 parts
of 10 vol.-percent.	0,15 parts	0,25 parts	0,5 parts
100 parts *water*	0,12 parts	0,18 parts	0,27 parts

When boiled with concentrated potassa solution, coumarin is hydrolized to *o*-coumaric acid, $HO \cdot C_6H_4 \cdot CH : CH \cdot COOH$, which melts at 207 to 208°. When fused with potassium hydroxide it yields salicylic acid (m. p. 156 to 157°). When reduced with sodium amalgam, melilotic acid, $HO \cdot C_6H_4CH_2 \cdot CH_2 \cdot COOH$ (m. p. 81°) is obtained, whereas reduction with sodium and alcohol yields a phenol alcohol, *o*-hydroxydihydrocinnamic alcohol, the

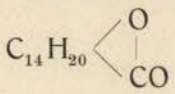
[1]) Liebig's Annalen **123** (1862), 148.
[2]) Perkin, Liebig's Annalen **147** (1868), 232.
[3]) Report of Schimmel & Co. April **1899**, 66.

benzoyl compound of which melts at 99 to 100°.[1]) Bromine adds to form dibromcoumarin melting at 100°.[2])

Coumarin and its solutions should be kept in a cool, dark place. In the course of even a few weeks light colors it yellow with polymerization to hydrocoumarin melting at 262°,[3]) which is an odorless compound difficultly soluble in alcohol.

When ascertaining its purity, the determination of its melting point is of first importance, then that of its solubility in various solvents. Adulteration with acetanilid has been observed repeatedly. A method for the quantitative determination of coumarin in the presence of vanillin and acetanilid has been worked out by Winton and Bailey.[4])

Alantolactone.



The commercial helenin,[5]) also known as alant camphor, is chemically alantolactone and is the principal constituent of the oil of elecampane root (from *Inula Helenium*).

Kallen[6]) originally regarded it as alantic acid anhydride, whereas Bredt and Posth[7]) recognized its lactone character and changed the name accordingly to alantolactone.

Recrystallized from dilute alcohol, alantolactone is obtained in colorless, prismatic needles which melt at 76°[8]) and which

[1]) Semmler, Berl. Berichte **39** (1906), 2856.

[2]) Perkin, Liebig's Annalen **157** (1871), 116.

[3]) Ciamician and Silber, Berl. Berichte **35** (1902), 4130; **36** (1903), 4266.

[4]) Pharmaceutical Journ. **75** (1905), 476.

[5]) The name helenin is applied to no less than three different substances. Gerhardt [Annal. de Chim. et Phys. II. **72** (1839), 163 and III. **12** (1844), 188; Liebig's Annalen **34** (1840), 192 and **52** (1844), 389] applied the name to his impure alantolactone. Kallen [Berl. Berichte **6** (1873), 1506; compare also Kallen, *Über Alantolacton und die Anlagerung von Blausäure an ungesättigte Lactone, Inaug.-Dissert.* Rostock 1895] applied it to an impure alantolactone contaminated with traces of oil of elecampane. Finally, the name is also applied to the inulin of the elecampane root. The helenin of commerce is well nigh pure alantolactone.

[6]) Berl. Berichte **9** (1876), 154.

[7]) Liebig's Annalen **285** (1895), 349.

[8]) Most of the commercial products reveal a somewhat lower melting point.

possess a slight odor and taste. It sublimes when only moderately heated and boils at 275° with partial decomposition. Under 10 mm. pressure it boils at 192°.[1]) Even in hot water it is but sparingly soluble, but readily in alcohol, ether, chloroform, glacial acetic acid, benzene and petroleum ether. Cold sodium carbonate solution does not dissolve it. When gently heated with dilute alkalies it dissolves forming solutions of the salts of the corresponding hydroxy acid, the alantic acid, $C_{14}H_{20} \cdot OH \cdot COOH$. From these solutions the lactone is precipitated upon the addition of mineral acids. Characteristic derivatives of alantolactone are its monochlorhydrate, m. p. 117°, the monobromhydrate, m. p. 106°, the dichlorhydrate, m. p. 127 to 134°, and the dibromhydrate, m. p. 117°.

Alantolactone is accompanied by a small amount of a substance which Kallen designated helenin and which was later isolated by Sprinz[2]) and studied more carefully by him. Because of the same elementary composition with alantolactone, $C_{15}H_{20}O_2$, and because of its chemical behavoir, Sprinz has named this compound *iso*alantolactone. When pure it forms white prisms which melt at 115°, and which dissolve in benzene, ether, chloroform and absolute alcohol. In contrast to the behavior of alantolactone, it crystallizes unchanged from hot soda solution. It is only after boiling for about 5 to 6 hours that it is changed to the sodium salt of *iso*alantolic acid which is precipitated from the solution when acidulated with hydrochloric acid. When melted this loses water and is reconverted to *iso*alantolactone.

Medicinally, alantolactone is used as internal antiseptic. Added to urine it prevents putrifaction even in dilutions of 1:10000.

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[1]) Bredt and Posth, Liebig's Annalen **285** (1895), 349.

[2]) Arch. der Pharm. **239** (1901), 201.

OXIDES.

Oxides have been found in volatile oils in isolated cases only, those of the aliphatic series having not yet been observed. Of synthetic products, however, several are known. Of special importance is the *pinol,* $C_{10}H_{16}O$, which is closely related to to pinene.

It is obtained as a by-product in the preparation of pinene nitrosochloride. It is also formed when pinolhydrate (sobrerol) is heated with dilute sulphuric acid[1]) or terpineol dibromide with sodium alcoholate.[2])

According to Wagner and Slawinsky,[3]) an optically active pinol can be obtained when hypochlorous acid is allowed to act on pinene and subsequent reduction of the *cis*-pinolglycol-2-chlorhydrin, in alcoholic solution, with zinc dust.

Pinol is a liquid which boils at 183 to 184° and possesses an odor resembling that of cineol and camphor. $d_{20°}$ 0,9455; $n_{D20°}$ 1,47096. It is very stable toward reducing agents and can be distilled over sodium without decomposition. When oxidized with permanganate or dilute nitric acid it is converted into terebic acid (m. p. 175 to 176°). Inorganic acids react with pinol forming cineol. Bromine is added forming a dibromide which melts at 94° and which is suited to its identification.

Another artificially prepared oxide is the

1,4-Cineol which, together with terpineol, is formed when 1, 4-terpin is heated with oxalic acid. It is a liquid which boils at 172 to 173° and which, unlike cineol, does not congeal when cooled. d 0,987; n 1,4485.[4])

Prileschajew[5]) has succeeded in preparing the oxides of a number of so-called terpene alcohols, and other terpene compounds the properties of which are indicated in the following table:

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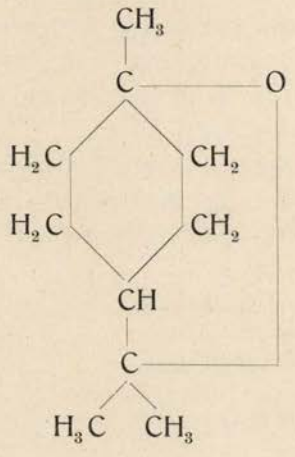
[1]) Wallach, Liebig's Annalen **259** (1890), 315.
[2]) Wallach, *Ibidem* **277** (1893), 115.
[3]) Berl. Berichte **32** (1899), 2070.
[4]) Wallach, Liebig's Annalen **356** (1907), 205.
[5]) Berl. Berichte **42** (1909), 4811.

	boil. point	$d\frac{0°}{0°}$	$d\frac{16°}{16°}$	$n_{D16°}$	
Geraniol monoxyde	157 to 168° (25 mm.)	0,9716	0,9610	1,4681	When hydrated, a glycerol, b. p. 205 to 207° (20 mm.) results
Geraniol dioxyde	180 to 183° (25 mm.)	1,0587	1,0472	1,4653	When hydrated, a glycerol oxyde, b. p. 220° (15 mm.), m. p. 137 to 138° results
Linalool monoxyde	95° (25 mm.)	0,9660	0,9507	1,4554	$[\alpha]_D$ — 4,98°. Hydration yields a two-fold unsaturated aldehyde, b. p. 120 to 122° (25 mm.), m. p. of the semicarbazone 138,5°.
Linalool dioxyde	131 to 133° (25 mm.)	1,0552	1,0423	1,4616	When hydrated, there results a glycerol oxyde, b. p. 210 to 212° (25 mm.)
Citral oxyde	146 to 148° (20 mm.)	1,0091	0,9740	1,4604	When hydrated, there results a glycol aldehyde, b. p. 141 to 142° (24 mm.)
Citronellal oxyde	130 to 131° (25 mm.)	0,9437	0,9344	1,4421	Upon hydration there results a glycol aldehyde, b. p. 180 to 182° (18 mm.)
Limonene monoxyde	113 to 114° (50 mm.)	0,9435	0,9303	1,4693	$[\alpha]_D$ — 6,76°. Upon hydration there results a glycol, m. p. 66,5 to 67,5°.
Limonene dioxyde	146,5 to 147° (50 mm.)	1,0471	1,0338	1,4702	$[\alpha]_D$ + 52,23°. Upon hydration there results an amorphous erythrol, b. p. 220° (23 mm.)
Pinene oxyde	102 to 103° (50 mm.)	0,9812	0,9689	1,4708	$[\alpha]_D$ — 92°. Upon hydration pinol hydrate results.

Wellnigh the only oxide which occurs in volatile oils is cineol.

Cineol.



Cineol (eucalyptol), $C_{10}H_{18}O$, is very widely distributed. It is the principal constituent of the oil of *Eucalyptus Globulus,* of cajeput oil, niaouli oil and of the oil of wormseed. In varying amounts it has also been found in American wood turpentine oil, Java "lemon olie", safran oil, oil of zedoary oil of galangal, ginger oil, oil of paradise grains (?), Ceylon, Bengal, Malabar and Kamarun cardamom oil, in the oil from the fruit of *Amomum Mala,* in matico oil, betel oil, star anise oil, in Japanese star anise oil, magnolia oil, kobuschi oil, boldo leaf oil, camphor oil, in the oil from the leaves of *Laurus Camphora,* in cinnamon root oil, in the bark oil from *Cinnamomum Oliveri,* in nikkei oil, in apopin oil, in laurel leaf oil, in the oil of laurel berries, in the leaf oil from *Tetranthera polyantha* var. *citrata,* in the oil of *Umbellularia californica,* in the bark oil of *Ocotea usambarensis,* in kuromoji oil, in carqueja oil, in the oils of rue, canella alba, myrtle, cheken leaf, and pimenta, in the oils of *Melaleuca acuminata, M. linariifolia, M. nodosa, M. thymifolia* and *M. uncinata,* in the oils of *Eucalyptus acmenioides, E. affinis, E. albens, E. amygdalina, E. angophoroides, E. apiculata, E. Bæuerleni, E. Behriana, E. bicolor, E. Bosistoana, E. botryoides, E. bridgesiana, E. Cambagei, E. camphora, E. capitellata, E. carnea, E. cinerea, E. cneorifolia, E. conica, E. cordata, E. coriacea, E. corymbosa. E. crebra, E. Dawsoni, E. dealbata, E. dumosa, E. eugenioides, E. fastigata, E. fraxinoides, E. goniocalyx, E. gracilis, E. hæmastoma, E. hemilampra, E. hemiphloia, E. intermedia, E. lactea, E. longifolia, E. Luehmanniana, E. macrorhyncha, E. maculata, E. maculosa, E. Maideni, E. melanophloia, E. melliodora, E. microcorys, E. microtheca, E. Morrisii, E. nigra, E. obliqua, E. odorata, E. oleosa, E. oreades, E. ovalifolia, E. o.* var. *lanceolata, E. paludosa, E. paniculata, E. pendula, E. piperita, E. polyanthema, E. polybractea, E. populifolia, E. propinqua, E. pulverulenta, E. punctata, E. p.* var. *didyma, E. quadrangulata, E. radiata, E. resinifera, E. Risdoni, E. robusta, E. Rossei, E. rostrata, E. r.* var. *borealis, E. rubida, E. saligna, E. siderophloia, E. sideroxylon, E. s.* var. *pallens, E. Smithii, E. squamosa, E. stricta, E. Stuartiana, E. tessellaris, E. teretricornis, E. t.* var. *linearis, E. trachyphloia, E. umbra, E. viminalis, E. v.* var. *α virgata, E. viridis, E. vitrea, E. Wilkinsoniana* and *E. Woolsiana,* in the oils from the leaves of *Vitex Agnus Castus,*

and *V. trifolia,* in the oils of rosemary, lavender and spike, also in the oils of *Lavandula dentata, L. pedunculata, L. Stœchas,* in sage oil, in Spanish majoran oil, in American, French and Russian peppermint oils, in spearmint oil, in Java- and Réunion basilicum oil, in the oils of *Blumea balsamifera, Osmitopsis asteriscoides* (?), *Achillea millefolium, A. moschata, Artemisia vulgaris, A. frigida, A. Herba-alba, A. Leudoviciana* and in yomugi oil.

The preparation of this substance from oils, such as the oil of *Eucalyptus Globulus* rich in cineol is not difficult, since the cineol, purified as carefully as possible by fractional distillation, crystallizes in the cold. For the identification or isolation of small amounts of cineol, the hydrogen chloride addition product, or better still that with hydrogen bromide, is resorted to. Upon decomposition with water both yield cineol.

As a product of molecular rearrangement, cineol results when terpineol, or terpin hydrate, is boiled with dilute acids.

Pure cineol is a colorless, optically inactive liquid, the odor of which resembles that of camphor and which crystallizes in the cold. For the cineol regenerated from its chlorhydrate, Wallach[1]) observed the following constants:

B. p. 176; $d_{20°}$ 0,9267; n_D 1,45839.

In connection with products obtained on a technical scale, Schimmel & Co. observed:

Congealing point about + 1°; m. p. between + 1 and 1,5°; b. p. 176 to 177° (764 mm.); $d_{15°}$ 0,928 to 0,930; $n_{D20°}$ 1,456 to 1,459; soluble in about 12 vol. of 50 p. c., in 4 vol. of 60 p. c. and in 1,5 to 2 vol. of 70 p. c. alcohol.

Cineol yields characteristic, loose addition products with bromine, iodine, chlorine and hydrogen bromide,[2]) phosphoric acid, arsenic acid, α- and β-naphthol, iodol and resorcinol. Some of them can be utilized for isolating and characterizing cineol. The resorcinol compound is also adapted to the quantitative determination of cineol. (Compare the chapter "The examination of volatile oils".) Dehydrating agents convert cineol into dipentene,[3])

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[1]) Liebig's Annalen **245** (1888), 195.

[2]) Liebig's Annalen **225** (1884), 300, 303; **230** (1885), 227; **246** (1888), 280.

[3]) Wallach and Brass, Liebig's Annalen **225** (1884), 310.

other suitable reagents convert it directly into derivatives of dipentene. Thus *e. g.* dipentene dihydriodide results when dry hydrogen iodide is passed into cineol. The oxygen of the cineol is of the oxide type, hence it does not react with hydroxylamine or phenylhydrazine, neither does metallic sodium act on it. Hence cineol can be distilled without decomposition over metallic sodium.

When oxidized with potassium permanganate and the aid of heat, cineol yields the dibasic cineolic acid,[1]) $C_{10}H_{16}O_5$, m. p. 196 to 197°. Acetic acid anhydride dehydrates this dibasic acid to its anhydride, which, in turn, upon destructive distillation yields methyl heptenone, $C_8H_{14}O$, which likewise occurs in nature.

Toward reducing agents cineol is very stable. Molle[2]) found that hydrogen iodide only will reduce it. When heated with this reagent for an hour in a sealed tube to 220 to 225° with the addition of metallic mercury as iodine binding agent, cineol yielded a hydrocarbon $C_{10}H_{18}$ (b. p. 165 to 170°; $d_{18°}$ 0,8240; $\alpha_D \pm 0°$; n_D 1,45993) which Molle named cineolene, and a polymeric hydrocarbon $(C_{10}H_{16})_n$.

Cineol has a characteristic odor which usually directs attention to its presence in mixtures. For its ready detection Hirschsohn's[3]) iodol reaction can be employed. A small amount of iodol is dissolved with the aid of gentle heat in a few drops of the oil to be tested. If cineol be present the equimolecular addition product of the components crystallizes out. Recrystallized from alcohol or benzene this melts at about 112°.[4])

If cineol is to be isolated as such, dry hydrogen bromide is passed into the well cooled petroleum ether solution (equal volumes) of the cineol fraction. The white crystalline precipitate resulting is removed by suction and washed with petroleum ether. The hydrobromide thus obtained is fairly stable, melts at 56 to 57°. Water readily breaks it up into cineol and hydrogen bromide.

In the presence of a sufficient cineol content, resorcin can be used to adventage for its isolation. For this purpose the

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[1]) Wallach and Gildemeister, Liebig's Annalen **246** (1888), 268.

[2]) *Über die Zusammensetzung des ätherischen Lorbeeröles und zur Kenntnis seines Hauptbestandteils, des Cineols, Inaug.-Dissert.* Basel 1904, p. 62. Comp. also Thoms and Molle, Arch. der Pharm. **242** (1904), 181.

[3]) Pharm. Zeitschr. f. Russland **32** (1893), 49, 67.

[4]) Bertram and Walbaum, Arch. der Pharm. **235** (1897), 178.

cineol fraction is stirred with two volumes of a 50 p. c. resorcinol solution. If necessary a small amount of cineol resorcinol is added. The resulting addition product, consisting of 1 mol. resorcinol and 2 mol. cineol,[1]) is removed by suction, pressed between filter paper and decomposed with alkali. Cineol resorcinol crystallizes in needles that melt at about 80°. They are readily soluble in alcohol, ether and benzene, but very difficultly in petroleum ether and water. It is relatively much more stable than the addition product of phosphoric acid to cineol, which is also used for the isolation of the latter. However, it also decomposes gradually with the liberation of cineol when exposed to the air — more readily in vacuum — so that finally resorcinol alone remains. The same change can be observed when cineol resorcinol is heated with water or petroleum ether,[2]) or even when the compound is washed with these solvents. Dry and well crystallized, cineolresorcinol can be obtained by crystallizing 1 part of resorcinol from 10 parts of cineol (Baeyer and Villiger, *loc. cit.*).

For further characterization cineol can be oxidized with potassium permanganate to cineolic acid.

Cineol possesses antiseptic properties. In medicine it finds external as well as internal application, the latter *e. g.* as vermifuge. Toxic results have been observed in connection with cineol or eucalyptus oils only then when larger amounts were administered.

The only other oxide found in volatile oils is the *Carlina oxide,* $C_{13}H_{10}O$, which constitutes the principal constituent of the carline thistle. It is probably phenyl-1-α-furyl-3-allene.[3])

B. p. 167 to 168° (20 mm); $d_{17°}^{17°}$ 1,066; $\alpha_D \pm 0°$; n_D 1,586.

When oxidized with potassiumpermanganate, it yields quantitatively benzoic acid; when reduced with sodium and alcohol, tetrahydrocarlina oxide, $C_{13}H_{14}O$, which is oxidized by potassium permanganate to γ-phenylbutyric acid, m. p. 52°.

[1]) Baeyer and Villiger, Berl. Berichte **35** (1902), 1209.

[2]) Report of Schimmel & Co. October **1907**, 47.

[3]) Semmler, Berl. Berichte **39** (1906), 726; Semmler and Ascher, *Ibidem* **42** (1909), 2355.

NITROGEN- AND SULPHUR-CONTAINING COMPOUNDS.

Compounds containing nitrogen or sulphur are frequently obtained during the distillation of such parts of plants which are rich in albuminous substances (protoplasm) or similar bodies, *e. g.* during the distillation of fresh herbs and seeds. The readily volatile compounds, ammonia, trimethylamine, sulphureted hydrogen and hydrocyanic acid largely escape during the process of distillation. Smaller amounts are dissolved in the aqueous distillate. Rarely do they enter into combination with constituents of the volatile oil in the preparation of which they are produced.

Ammonia is produced during the distillation of many drugs, *e. g.* that of cubebs, pepper, pimento, ginger, &c. Möslinger[1]) found ammonia in the aqueous distillate of heracleum oil.

Narcotic smelling bases were observed by Schimmel & Co. in connection with caraway oil and the oils of other umbelliferous fruits[2]), also in connection with patchouli oil[3]) and the oil of *Barosma pulchellum.*[4])

NITRILES.

Hydrocyanic acid.

The principal representative of the nitriles is that of formic acid, *viz.,* hydrogen cyanide, HCN. It is formed during the production of the oils of bitter almond and cherry laurel, but also occurs in the distillates of a large number of plants.[5])

[1]) Liebig's Annalen **185** (1877), 37.

[2]) Report of Schimmel & Co. April **1905**, 20.

[3]) *Ibidem* April **1904**, 70; April **1905**, 60.

[4]) *Ibidem* April **1909**, 95.

[5]) *Verslag omtrent den staat van 's lands Plantentuin te Buitenzorg over het jaar* **1889**, 29; **1897**, 37; Greshoff, Distribution of prussic acid in the vegetable kingdom, British Association, York 1906; Arch. der Pharm. **244** (1906), 397, 665; Weehuizen, Pharm. Weekblad **43** (1906), 907; Guignard, Compt

According to data found in phytochemical literature the following plants yield hydrogen cyanide only: *Hygrophorus agathomus, H. cerasinus* (?), *Marasmius oreades, Pholiota radicosa, Russula fœtens, Gymnogramme aurea,* species of *Lastrea* and *Athyrium, Triglochin palustris, T. maritima, Scheuchzeria palustris, Glyceria aquatica, Sorghum halepense, S. nigrum, S. vulgare, Stipa hastricina, St. leptostachya, St. tortilis, Gynerium argenteum, Melica altissima, M. ciliata, M. nutans, M. uniflora, Zea Mays, Briza minor, Lamarkia aurea, Holcus lanatus, Poa pratensis, Festuca Poa, Arum maculatum, Alocasia Veitchii, Colocasia gigantea, Cyrtosperma lasioides, C. Merkusii, Lasia aculeata, L. Zollingeri, Salix triandra (amygdalina), Sponia virgata, Aquilegia chrysantha, A. vulgaris, Thalictrum aquilegifolium, Ranunculus arvensis, R. repens, Nandina domestica, Lepidium sativum* (?), *Ribes aureum, R. rubrum, Grossularia nigrum, Lotus arabicus, L. australis, Phaseolus lunatus, P. Mungo, Cicer arietinum, Dolichos Lablab, Linum perenne, L. usitatissimum, Citrus medica* (?), *Chailletia cymosa, Bridelia ovata, Elateriospermum Tapos, Hevea brasiliensis, H. Spruceana, Jatropha angustidens, Manihot Bankensis, M. Glaziovii, M. palmata, M. utilissima, Ricinus communis, Kurrimia ceylanica, Cupania* spec., *Rhamnus frangula, Sterculia* spec., *Gynocardia odorata, Hydnocarpus alpina, H. anthelminthica, H. inebrians, Kiggelaria africana, Pangium ceramense, P. edule, Ryparosa cæsia, R. longipedunculata, Taraktogenos Blumei, T. Kurzii, Trichadenia ceylanica, Psidium montanum* (?), *Combretum constrictum* (?), *Homalium (Blackwellia) tomentosum, Tacsonia* spec., *T. Van-Volxemii, Modecca Wightiana, Ophiocaulon gummifer, Passiflora alata, P. cœrulea, P. edulis, P. fœtida, P. hybrida, P. laurifolia, P. maculata, P. Princeps, P. quadrangularis, P. suberosa, Ipomœa obscura, Isonandra (Bassia) Mottleyana* (?), *Payena latifolia, Merremia vitifolia, Osmohydrophora nocturna* (?), *Aplotaxis candicans, Centaurea montana, C. solstitialis, Pyrethrum caucasicum, Dimorphoteca pluvialis, Cirsium arvense.*

rend. **143** (1906), 451; Hérissey, Journ. de Pharm. et Chim. VI. **24** (1906), 350, 537; Jitschy, *Ibidem* 355; Hébert, Bull. Soc. chim. III. **35** (1906), 919; Bertrand, Compt. rend. **143** (1906), 832; Guignard, Bull. Sciences pharmacol. **13** (1906), 603; Dunstan and Henry, Annal. de Chim. et Phys. **10** (1907), 118; Greshoff, Pharm. Weekblad **45** (1908), 770.

Hydrocyanic acid and benzaldehyde are yielded by the following plants: *Pteris aquilina, Panicum maximum, P. muticum, Ximenia americana, Amelanchier alnifolia, A. canadensis, A. vulgaris, Chamæmeles coriacea, Cratægus orientalis, C. oxyacantha, Eriobotrya japonica, Nuttallia cerasiformis, Osteomeles* spec., *Photinia arbutifolia, P. Benthamiana, P. serrulata, P. variabilis, Pyrus americana, P. Aria, P. Aucuparia, P. Cydonia, P. germanica, P. japonica, P. Malus, P. mespilus, P. pinnatifida, P. Ringo, P. spectabilis, P. torminalis, Prunus adenopoda, P. americana, P. Amygdalus, P. alleghaniensis, P. Armeniaca, P. avium, P. Besseyi, P. Capollin, P. caroliniana, P. Cerasus, P. Chamæcerasus, P. divaricata, P. domestica, P. javanica, P. Laurocerasus, P. lusitanica, P. nana, P. occidentalis, P. Padus, P. paniculata, P. pendula, P. pennsylvanica, P. Puddum, P. serotina, P. sphærocarpa, P. spinosa, P. subhirtella, P. undulata, P. virginiana, P. Persica, Cotoneaster affinis, C. bacillaris, C. buxifolia, C. Francheti, C. frigida, C. horizontalis, C. integerrima, C. microphylla, C. multiflora, C. panosa, C. thymæfolia, Exochorda Alberti, Kerria japonica, Neviusia alabamensis, Pygeum africanum, P. latifolium, P. parviflorum, Spiræa Aruncus, S. japonica, S. Kneiffii, S. Lindleyana, S. prunifolia, S. sorbifolia, Rhodotypos kerrioides, Stranvæsia glaucescens, Indigofera galegoides, Vicia angustifolia, V. canadensis, V. hirsuta, V. macrocarpa, V. sativa, Corynocarpus lævigata, Schleicheria trijuga, Echinocarpus Sigun, Lucuma Bonplandia, L. mammosa, L. pomifera, Memecylon* spec., *Ipomœa dissecta, I. sinuata, I. vitifolia, Gymnema latifolium, Sambucus nigra, Plectronia dicocca, Chardinia xeranthemoides, Xeranthemum annuum, X. cylindricum.*

The presence of hydrocyanic acid is ascertained in the ordinary manner by means of the Prussian blue test. To a small amount of the distillate are added first a few drops of caustic soda solution and then a few drops of ferrous sulphate solution containing ferric salt. The mixture is once more thoroughly shaken and acidified with dilute hydrochloric acid. The precipitate of ferrous and ferric hydroxides is thus dissolved and in the presence of hydrocyanic acid, the characteristic blue precipitate of Prussian blue reveals itself. The reaction is so delicate that even the smallest traces of hydrocyanic acid can thus be detected.

For the rapid detection of hydrocyanic acid in a plant the observation of Mirande[1]) can be utilized. Under the influence of anæsthetics, such plants as contain hydrocyanic acid in complex combination, set free hydrogen cyanide, the presence of which can be detected by means of sodium picrate paper,[2]) which is colored red by hydrogen cyanide.

For the quantitative determination of hydrogen cyanide see the chapter on "The examination of volatile oils".

Hydrogen cyanide does not occur as such in most plants but is contained in them in the form of a glucoside, of which amygdalin is the most common.

In plants amygdalin is accompanied by the ferment emulsin, which, in the presence of water, hydrolyses the glucoside to benzaldehyde, glucose and hydrogen cyanide:

$$C_{20}H_{27}NO_{11} + 2H_2O = C_6H_5 \cdot CHO + HCN + 2C_6H_{12}O_6.$$

In recent years much attention has been directed to amygdalin and its hydrolysis by means of emulsin. The rather complicated relationship cannot here be discussed. Suffice it to refer to the original literature on this subject.[3])

In addition to amygdalin a number of other glucosides are known which upon hydrolysis yield hydrogen cyanide, *viz.*: corynocarpin, dhurrin, gynocardin, laurocerasin, linamarin (= phaseolunatin(?), lotusin, manihotoxin, prulaurasin, sambunigrin and vicianin.

Other nitriles occurring in volatile oils are those of phenylacetic acid, of phenylpropionic acid and of vinylacetic acid.

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[1]) Compt. rend. **149** (1909), 140.

[2]) Guignard, *Ibidem* **142** (1906), 552.

[3]) Van Rijn, *Die Glycoside*. Berlin 1900; Walker, Journ. chem. Soc. **83** (1903), 472; Dakin, Journ. chem. Soc. **85** (1904), 1512; Bourquelot and Hérissey, Journ. de Pharm. et Chim. VI. **26** (1907), 5; Caldwell and Courtauld, Journ. chem. Soc. **91** (1907), 666, 671; Hérissey, Journ. de Pharm. et Chim. VI. **26** (1907), 194, 198; Arch. der Pharm. **245** (1907), 638, 641; Feist, *Ibidem* **246** (1908), 206, 509; Rosenthaler, *Ibidem* 365; Auld, Journ. chem. Soc. **93** (1908), 1251, 1276; Rosenthaler, Arch. der Pharm. **246** (1908), 710; Biochem. Zeitschr. **14** (1908), 238; **17** (1909), 257; Auld, Journ. chem. Soc. **95** (1909), 927; Feist, Arch. der Pharm. **247** (1909), 226, 542; Bourquelot, Journ. de Pharm. et Chim. VI. **29** (1909), 576; Tutin, Journ. chem. Soc. **95** (1909), 663; Walker and Krieble, *Ibidem* 1369, 1437.

Phenylacetic acid nitrile, Benzyl cyanide, $C_6H_5CH_2CN$, according to A. W. Hofmann, is the principal constituent of the oil of *Tropæolum majus,*[1]) also of that of *Lepidium sativum.*[2]) It is probably also contained in neroli oil.

Gadamer[3]) has since shown that the observations of Hofmann with regard to *Tropæolum majus* are only conditionally true. When properly distilled, this plant yields benzyl mustard oil. The formation of benzyl cyanide is due to improper mothods. (For further details see the oil of *Tropæolum majus.*)

Benzyl cyanide boils at 231 to 232° and at 18° has a specific gravity of 1,0146. When hydrolysed it yields phenylacetic acid, m. p. 77°.

Phenylpropionic acid nitrile, $C_6H_5CH_2CH_2CN$, is the principal constituent of water cress oil *(Nasturtium officinale).*[4]) It boils at 261° and when acted upon by alkali is converted into phenylpropionic acid which melts at 47°.

Vinylacetic acid(Crotonic acid)nitrile, Allyl cyanide, $CH_2:CH\cdot CH_2CN$, traces of which are always found in mustard oil, can be obtained in larger amounts by careless distillation as decomposition product from allyl *iso*thiocyanide. In as much as allyl cyanide is light ($d_{17.5°}$ 0,835), the presence of larger amounts of this substance would be revealed by a depression of the specific gravity of the mustard oil.

NITRO COMPOUNDS.

Nitrobenzene.

$C_6H_5NO_2$.

This compound, also known as oil of mirbane, which is prepared in large quantities, principally for the dye stuff industry, is also used in perfumery as a cheap substitute for oil of bitter

[1]) Berl. Berichte 7 (1874), 518.
[2]) *Ibidem* 1293.
[3]) Arch. der Pharm. 237 (1899), 111.
[4]) A. W. Hofmann, *loc. cit.* 520.

almonds. The quality of the product depends on the purity of the benzene employed. In perfumery, only the socalled light nitrobenzene (sp. gr. 1,2) is used, which, if necessary, is freed from the last traces of impurities by distillation over sodium hydroxide.

Nitrobenzene is a strongly refractive, faintly yellow liquid which upon standing becomes darker. Its odor resembles that of bitter almond oil. It is but sparingly soluble in water, readily soluble in alcohol, ether, benzene, &c. It is readily volatile with water vapors. In the cold it congeals and, according to Linebarger,[1]) melts again at $+3{,}6°$. Friswell[2]) records the following properties:

Cong. p. $+5°$; b. p. 209° (corr., 760 mm.); $d^{15°}_{4°}$ (solid) 1,3440, $d^{3.8°}_{4°}$ (liquid) 1,2220, $d^{13°}_{4°}$ 1,2116.

In connection with commercial preparations Schimmel & Co. observed the following constants:

Cong. p. $+5{,}5°$; m. p. $+5{,}6°$; b. p. 208 to 209° (741 mm.); $d_{15°}$ 1,20 to 1,21; $\alpha_D \pm 0°$; $n_{D20°}$ 1,552 to 1,553; soluble in 1 vol. of 90 p. c. alcohol.

Nitrobenzene which is to be used for perfuming soaps should stand the soap test, *i. e.,* when boiled with 15 p. c. potassa solution, it should not color the latter. If colored yellow or brown, the presence of other nitrocompounds (nitrotoluene) is indicated. The test can be carried out in a wide test tube by heating 2 to 3 ccm. of nitrobenzene with an equal or twice its volume of potassa solution for 1 to 2 minutes. While boiling the test tube should be shaken otherwise the mixture is apt to be thrown out with explosive violence.

For its detection, nitrobenzene is reduced to aniline with tin and hydrochloric acid or with zinc and dilute sulphuric acid. The aqueous solution of aniline is identified by the violet color produced upon the careful addition of chlorinated lime solution; also by the dark green or black precipitate produced when potassium bichromate is added to the solution of aniline prepared with an excess of sulphuric acid. This precipitate is soluble in

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[1]) Americ. chem. Journ. **18** (1896), 437.

[2]) Journ. chem. Soc. **71** (1897), 1011.

hot water or alcohol with a dark green color. The first of these two tests is the more delicate one.

Nitrobenzene is a strong poison. Cases are known when 20, or even 7 to 8 drops have proven fatal.[1]) Contact of nitrobenzene with the skin can also prove dangerous.

Artificial musk.

Natural musk owes its odor to a ketone, muscone, which is contained in the natural product to the extent of from 0,5 to 2%. As to its chemical composition only this much is known that either the formula $C_{15}H_{28}O$ or $C_{16}H_{30}O$ applies to it.[2]) Muscone is a dark, colorless oil, which is but sparingly soluble in water, soluble in alcohol in all proportions. It has a strong, very agreable, pure musk odor, which, in a concentrated condition, reminds of the fragrance of dried pine needles. In great dilution it is particularly agreable. Like ionone it possesses the property to fatigue the nerves very readily. Hence it is possible to recognize the musk odor of the muscone for a short time only. It boils at 142 to 143° (2 mm.) and at 327 to 330° (752 mm.). Under the latter conditions partial decomposition appears to take place. Of muscone derivatives there are known the oxime, which crystallizes in needles that melt at 46°, and the semicarbazone, which crystallizes from alcohol in fine, white prisms that melt at 133 to 134°. Both compounds are odorless. From the semicarbazone the muscone can be liberated by means of dilute sulphuric acid.

The socalled artificial musk, however, is something very different. The only similarity between natural and socalled artificial musk is that of odor, such as is observed not infrequently, *e. g.* between nitrobenzene and bitter almond oil. In both instances the substitute is very different chemically from the original product and reproduces the odor only to a certain degree. At the present time there are found in the market a considerable number of "artificial musks". Most of these are highly nitrated tertiary butyl toluenes and tertiary butylxylenes or stand in close relation

[1]) Kobert, *Lehrbuch der Intoxikationen,* vol. II, p. 799. Stuttgart 1906.

[2]) Walbaum, Journ. f. prakt. Chem. II. **73** (1906), 488; comp. also Report of Schimmel & Co. April **1906**, 93.

to these nitrocompounds. Characteristic for these compounds is the tertiary butyl group. If other alkyl radicles take its place, the compounds resulting have either only a faint musk-like odor, or none at all.[1]) Those compounds containing three nitro groups are characterized by a strong musk-like odor. However, the strength of the musk odor is not interfered with if one of these nitro groups is replaced by a cyanogen or aldehyde group or by halogen or an acid radicle. With reference to these groups the artificial musks are distinguished as cyanide musk, aldehyde musk, halogen musk and ketone musk. The most important of these compounds are here described briefly.

Trinitro-tert.-butyltoluene, $C_6H \cdot CH_3 \cdot C(CH_3)_3 \cdot (NO_2)_3$, is of special interest since it is the first musk-like smelling-substance which was placed upon the market as "Tonquinol" and "Musc Baur". It is obtained by condensation of *iso*butyl chloride and toluene with the aid of aluminium chloride and subsequent nitration of the butyl toluene. During the condensation a rearrangement of the *iso*butyl to the tertiary butyl group takes place. It is adventageous to purify the hydrocarbon carefully before nitrating it. Trinitrobutyl benzene crystallizes from alcohol in yellowish-white needles, which melt at 96 to 97°.

Trinitro-tert.-butylxylene, $C_6(CH_3)_2 \cdot C(CH_3)_3 \cdot (NO_2)_3$, is prepared in like manner. It crystallizes in white needles that melt at at 110°.

Trinitro-tert.-butylethylbenzene, $C_6H \cdot C_2H_5 \cdot C(CH_3)_3 \cdot (NO_2)_3$, is readily soluble in alcohol and hence cannot readily be obtained in a crystalline condition.

Dinitro-tert.-butylxylene iodide, $C_6I(CH_3)_2 \cdot C(CH_3)_3 \cdot (NO_2)_2$, results when tert.-butylxylene iodide is nitrated. It forms yellow crystals that melt at 105°.

Dinitro-tert.-butylxylene cyanide, $C_6(CH_3)_2CN \cdot C(CH_3)_3 \cdot (NO_2)_2$, cyanide musk. Prismatic crystals that melt at 110°.[2])

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[1]) Comp. Baur, Berl. Berichte **24** (1891), 2832; **31** (1898), 1344; Baur and Bischler, *Ibidem* **32** (1899), 3647.

[2]) Baur-Thurgau, Berl. Berichte **33** (1900), 2567.

Dinitro-tert.-butylxylene aldehyde, $C_6(CH_3)_2 \cdot C(CH_3)_3 \cdot (NO_2)_2 \cdot CHO$, aldehyde musk, is soluble in alcohol and benzene and crystallizes from ligroin in plate-like, faintly yellowish crystals that melt at 112°.

Ketone musk is obtained by condensation of the corresponding acid chloride with tert.-butyltoluene or xylene in the presence of aluminium chloride and subsequent nitration of the condensation product. Baur[1]) has prepared the following representatives of this class.

Dinitroaceto-tert.-butyltoluene, $C_6H \cdot CH_3 \cdot C(CH_3)_3 \cdot (NO_2)_2CO \cdot CH_3$, or methyldinitrobutyltolyl ketone, broad needles that melts at 131°.

Dinitroaceto-tert.-butylxylene, $C_6(CH_3)_2 \cdot C(CH_3)_3 \cdot (NO_2)_2 \cdot CO \cdot CH_3$, m. p. 136°; soluble in alcohol, ether, benzene, &c., more difficultly in ligroin and 60 p. c. acetic acid.

Dinitrobutyryl-tert.-butylxylene, $C_6(CH_3)_2 \cdot C(CH_3)_3 \cdot (NO_2)_2 \cdot CO \cdot C_3H_7$, is the butyryl ketone of dinitro-tert.-butylxylene, and melts at 128°.

Dinitrovaleryl-tert.-butylxylene, $C_6(CH_3)_2 \cdot C(CH_3)_3 \cdot (NO_2)_2 \cdot CO \cdot C_4H_9$, when crystallized from alcohol, is obtained as long, faintly yellowish needles that melt at 151°.

In addition to those enumerated above, other substances with a musk-like odor are to be found in the market. Moreover, mixtures of these are likewise found, for upon careful fractional crystallization compounds with different melting points are obtained.

Artificial musk is insoluble in water and, as a rule, is but difficultly soluble in alcohol. For the preparation of relatively concentrated solutions that are durable, cinnameine and benzyl benzoate have been recommended. According to Koehler,[2]) the latter solvent when gently heated dissolves as much as 20 p. c. of musk "Baur" and retains it in solution at + 10°. Neither does the addition of absolute alcohol cause precipitation. With

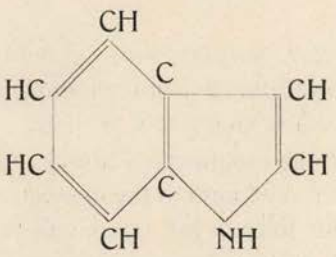
[1]) Baur-Thurgau, Berl. Berichte **31** (1898), 1344.
[2]) Pharm. Ztg. **49** (1904), 1083.

cinnamein, Mann[1]) claims even to have obtained a 50 p. c. solution. According to Schimmel & Co.,[2]) both solvents possess much the same solvent capacity, but benzyl benzoate appears to be a somewhat better solvent than cinnamein. Much, naturally, depends on the musk product dissolved.

Artificial musk is frequently adulterated with acetanilide. Formerly products of "Musk Baur" were placed upon the market which according to statements of the manufacturer contained up to 90 p. c. of antifebrine. Adulterations with cinnamic acid have also been observed. These added substances can be separated from the musk by means of hot water. Others are recognized by means of their solubility in alcohol in which solvent most artificial musk preparations are rather difficultly soluble. Antifebrine can be identified by means of the *iso*nitrile and acetic acid reactions.

AMIDO AND IMINO DERIVATIVES.

Indol.



Indol has long been known to occur in the animal organism as a product of intestinal digestion. It has also been produced artificially for some time, but it is only recently that its occurrence in the vegetable kingdom has been established: first by Hesse[3]) who found it in the oil obtained from jasmine flowers. Since then it has been found in neroli oil, also in the wood of

[1]) Seifensieder Ztg. **32** (1905), 112; Report of Schimmel & Co. April **1905**, 117.

[2]) Report of Schimmel & Co. April **1905**, 118.

[3]) Berl. Berichte **32** (1899), 2612.

the trunk of *Celtis reticulosa.*[1]) By means of color reactions its presence has likewise been established in the flowers of *Caladium* species, *Murraya exotica* and *Visnea Mocanera.*

Indol consists of shiny white laminæ, which, however, soon assume a dark color under the influence of light and air. They melt at 52°, b. p. 253 to 254° (corr.). It is readily soluble in hot water and is volatile with water vapor. The common commercial article has an exceedingly disagreable, fecal odor. It is only when carefully purified that a product is obtained the odor of which is not decidedly disagreable and which when properly diluted reveals a floral odor.

Solutions of oxalic acid[2]) and of *p*-dimethylaminobenzaldehyde[3]) are colored red by indol.

When an ethereal solution of indol is shaken with an aqueous alcoholic solution of sodium acid sulphite a hydrosulphonate results which crystallizes from methyl alcohol in white laminæ with a silky lustre.[4])

For the isolation of indol, the picrate, crystallizing in long, red, shiny needles, is best suited. For the identification and quantitative determination of indol, Hesse[5]) gives the following directions:

To the crude floral oil about 10 p. c. of picric acid are added. The mixture is heated to from 50 to 60° until the precipitate, first formed on the addition of the picric acid, is dissolved. To the cooled solution, from which an abundant precipitate of indol picrate has separated, a large excess of petroleum ether is added. The crystalline precipitate, consisting of indol picrate and the larger amount of uncombined picric acid, and which is colored more or less red in accordance with its indol picrate content, is

[1]) Herter, Journ. biol. Chem. 5 (1909), 489. According to Apotheker Ztg. 24 (1909), 885.

[2]) Borzi, Rendiconti della R. Accad. dei Lincei 13 (1904), 372; Verschaffelt, Rec. trav. bot. Néerland. 1 (1904). Comp. also Report of Schimmel & Co. October 1905, 123.

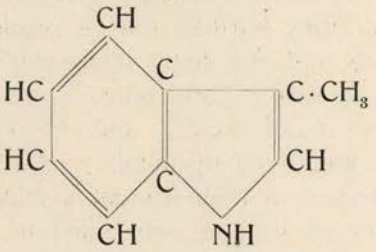
[3]) Weehuizen, Pharm. Weekblad 45 (1908), 1325; Steensma, Zeitschr. f. physiol. Chem. 47 (1906), 15; Gautier and Noyer, Compt. rend. Soc. biol. December 19th 1908; abstract in Bull. Soc. chim. IV. 5 (1909), 256. Comp. also Report of Schimmel & Co. April 1909, 140 and October 1909, 213.

[4]) Hesse, *loc. cit.* 2615.

[5]) *Loc. cit.* 2612.

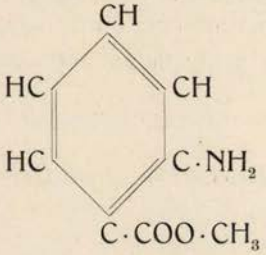
removed by filtration and repeatedly washed with petroleum ether. The crystals thus purified are dissolved in ammonia or soda solution with the aid of gentle heat. Upon cooling the solution is shaken out with ether, and the ethereal residue distilled with water vapor. Thus the total indol of the floral oil is obtained in an almost pure state.

Skatol.



Skatol, β-methylindol, has thus far been found in civet and in the wood of *Celtis reticulosa,* also in a wood[1]) obtained from German East Africa. It crystallizes in white laminæ which melt at 95° and boil at 265 to 266° and which possess a strong fecal odor. The hydrochloride, $2\,C_9H_9N\cdot HCl$, melts at 167 to 168°. The picrate crystallizes from benzene in dark red, shiny needles, m. p. 172 to 173°.[2]) The solution of *p*-dimethylaminobenzaldehyde is colored blue by skatol.[3]) Like indol, skatol is used in the preparation of artificial floral perfumes.

Anthranilic acid methyl ester.



[1]) Report of Schimmel & Co. April **1903**, 79.

[2]) Observations made in the laboratory of Schimmel & Co.

[3]) Weehuizen, Pharm. Weekblad **45** (1908), 1325; Steensma, Zeitschr. f. physiol. Chem. **47** (1906), 25; Gautier and Noyer, Compt. rend. Soc. biol. December 19th 1908; abstr. in Bull. Soc. chim. IV. **5** (1909), 256. Comp. also Report of Schimmel & Co. April **1909**, 140; October **1909**, 213.

Among the basic constituents of volatile oils the methyl ester of anthranilic acid should be mentioned. It was discovered in 1895 by Walbaum in neroli oil and has since been found in the oils of tuberose, champaca flowers (?), ylang-ylang, Spanish orange blossoms, sweet orange rind, West Indian limette (?), bergamot leaves, jasmin flowers, and gardenia. Judging from the odor, this ester is likewise contained in the flowers of *Lathyrus odorata, Robinia Pseudo-Acacia, Philadelphus Coronarius* and of several species of apples. Artificially it is readily obtained by passing hydrogen chloride into the methylalcoholic solution of anthranilic acid.

The methyl ester of anthranilic acid forms large crystals with numerous faces. Both crystals and solution, especially the alcoholic solution, reveal a beautiful fluorescence. Molten, it remains liquid for a long time, even at low temperature. The odor of the ester as such is not especially agreable, but characteristic. Diluted, it reminds of the odor of orange blossoms. The constants of the compound isolated from neroli oil are:

Congealing point 24°; m. p. 24 to 25°; b. p. 132° (14 mm.); $d_{15°}$ 1,168 (in the supercooled condition).[1]).

The ester is readily soluble in alcohol, ether and dilute inorganic acids, fairly readily in water and is volatile with water vapor.

Of its derivatives the following should be mentioned. The picrate crystallizes in yellow needles that melt at 103,5 to 104°.[2]) The thiophenyl ketotetrahydroquinazoline results quantitatively when anthranilic acid methylester is heated with phenyl mustard oil to from 100 to 120°. This compound is readily soluble in caustic soda solution, very difficultly in alcohol. It melts above 300° but sublimes at 160 to 170°.

From volatile oils the ester can readily be separated by shaking with dilute sulphuric acid. The sulphate crystallizes out in the cold, can be purified by recrystallization from alcohol, and is decomposed by means of soda.[3])

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[1]) Walbaum, Journ. f. prakt. Chem. II. **59** (1899), 352.

[2]) Freundler, Bull. Soc. chim. III. **31** (1904), 882. In the laboratory of Schimmel & Co. 105 to 106° were observed.

[3]) Walbaum, *Loc. cit.*

Hesse and Zeitschel[1]) utilized the sulphate for the quantitative determination of the ester. They proceeded according to the following method:

About 25 g. of the oil to be examined are dissolved in twice or thrice the amount of dry ether. In a freezing mixture the temperature is reduced to at least 0°. Amidst constant stirring a solution of 1 vol. of concentrated sulphuric acid in 5 vols. of ether is added drop by drop until no further precipitate is produced. The precipitate is collected on a filter and washed with dry ether until it is odorless. It is then dissolved in water, if necessary with the aid of alcohol, and, without previous filtration,[2]) is tritated with half normal caustic alkali. If for s grams of oil a ccm. of alkali are used, the percentage of ester in the oil equals

$$\frac{a \cdot 3{,}775}{s}.$$

To the solution an excess of half normal alkali is now added and the mixture heated on a water bath for half an hour. The amount of alkali not used for saponification is titrated back with half normal sulphuric acid. The percentage of ester is computed according to the following formula:

$$\frac{b \cdot 7{,}55}{s},$$

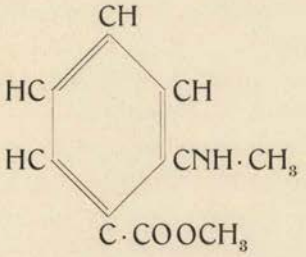
in which b represents the amount of half normal alkali used for saponification. a should be again as large as b.

This method not only determines anthranilic acid methyl ester, but other basic substances as well (methylanthranilic acid methyl ester). In order to avoid this, E. Erdmann[3]) has suggested another method in which he utilizes the property of the ester as primary base to form azodyes. The ester is shaken out of the oil with either dilute sulphuric or dilute hydrochloric acid; the acid solution is diazotized with a 5 p. c. solution of sodium nitrite, and titrated with an alkaline solution of β-naphthol (0,5 g. β-naphthol in a solution of 0,5 g. of caustic soda and 15 g. sodium carbonate in 150 ccm. of water). The insoluble dyestuff

[1]) Berl. Berichte **34** (1901), 296.
[2]) Hesse and Zeitschel, Journ. f. prakt. Chem. II. **64** (1901), 246, footnote.
[3]) Berl. Berichte **35** (1902), 24.

is precipitated and the end of the reaction ascertained by testing a drop removed from time to time. According to Hesse and Zeitschel,[1]) the method of Erdmann suffers from the fact that the isolation of the ester is not a quantitative one. In order to obtain satisfactory results the ester should be isolated as sulphate as described above. For the rest either the one or the other method can be followed. If anthranilic acid methyl ester and methylanthranilic acid methyl ester are to be determined side by side it is advisable to combine both methods.

Methylanthranilic acid methyl ester.



Methylanthranilic acid methyl ester occurs in mandarin oil, also in mandarin leaf oil and possibly also in oil of rue. Like the anthranilic acid methyl ester, it shows a blue fluorescence, as such as well as in solution. The constants of the ester isolated from mandarin oil are as follows:

M. p. 18,5 to 19,5°; b. p. 130 to 131° (13 mm.); $d_{15°}$ 1,120.[2])

In connection with a synthetic product containing 98 p. c. of ester, Schimmel & Co. observed the following constants:

Congealing point 17,8°; m. p. 18°; $d_{20°}$ 1,1238; $\alpha_D \pm 0°$; $n_{D20°}$ 1,57963; soluble in 10 vol. of 70 p. c. and in 3 vol. of 80 p. c. alcohol.

For further characterization the saponification products can be utilized. Methylanthranilic acid crystallizes from alcohol in white prisms which melt at 179° and which reveal a blue fluorescence in solution.

[1]) Berl. Berichte **35** (1902), 2355.

[2]) Walbaum, Journ. f. prakt. Chem. II. **62** (1900), 136.

SULPHIDES.

Sulphuretted hydrogen, H_2S, is frequently observed during the distillation of seeds, *e. g.* anise and particularly of caraway. Small amounts of *carbon disulphide,* CS_2, are contained in the oil of black mustard. Both products presumably result as products of decomposition.

Dimethyl sulphide, $(CH_3)_2S$, b. p. 37°, has been found in American peppermint oil, also in Réunion and African oils of geranium.[1]) Traces of a *mercaptan* have been found in the oil of *Allium ursinum,* whereas the bulk of this oil consists of *vinyl sulphide,* $(C_2H_3)_2S$, (b. p. 101°; d 0,9125) and its higher sulphides. Other unsaturated sulphides and polysulphides, among them presumably *allyl disulphide,* $(C_3H_5)_2S_2$, and *allylpropyl disulphide,* $C_3H_5 \cdot C_3H_7 \cdot S_2$, occur together with other sulphur compounds in the oils of garlic, onion and asafetida.

All of these compounds are characterized by a most disagreeable, penetrating odor. In the plants they are said to be contained in part, in combination as glucosides.

In this connection attention should be directed to Hartwich's[2]) list of plants in which the presence of sulphur-containing volatile oils has been demonstrated or inferred because of their odor.

MUSTARD OILS.

The esters of *iso*thiocyanic acid, characterized by their penetrating odor, and commonly known as mustard oils, constitute a special group of sulphur compounds. Their typical representative is the common allyl mustard oil.

Iso*thiocyanallyl.*

$CSN \cdot CH_2 \cdot CH : CH_2$.

*Iso*thiocyanallyl, allyl mustard oil or commonly mustard oil, constitutes the bulk of the volatile oil of mustard. It has also been obtained from the following plants: *Alliaria officinalis, Capsella Bursa pastoris,* species of *Cardamine* and *Sisymbrium, Cochlearia Armoracia* and *Thlaspi arvense.*

[1]) Report of Schimmel & Co. April 1909, 55.

[2]) Apotheker Ztg. 17 (1902), 339.

Neither in the mustard seed nor in the other plants mentioned does the mustard oil occur as such but in the form of a glucoside known as sinigrin (myronate of potassium), which in the presence of the ferment myrosin and water, is hydrolized to mustard oil, *d*-glucose and potassium acid sulphate:

$$C_{10}H_{16}NS_2KO_9 + H_2O = CSNC_3H_5 + C_6H_{12}O_6 + KHSO_4.$$

However, side reactions also take place which account for the presence of cyanallyl and carbon disulphide, two substances that are never completely wanting in natural mustard oil.

Above 70° myrosin is decomposed and becomes inactive as ferment. At a temperature of 0° traces of rhodan allyl, $CNSC_3H_5$,[1]) isomeric with allyl mustard oil, are also formed. Of interest is also the observation made by Guignard[2]) that mustard oil is set free when the plants are subjected to the vapors of mercury, carbon disulphide or anæsthetics.

Chemically, mustard oil is obtained by the distillation of allyliodide or allylbromide with an alcoholic solution of potassium rhodanate, or by the dry distillation of this salt with the equivalent amount of a salt of allylsulphuric acid. Under the influence of the heat an inversion of this cyanate or rhodanate group to the *iso*thiocynate group takes place.

*Iso*thiocyan allyl is a colorless oil which gradually turns yellow. It is optically inactive and possesses a very penetrating odor causing the flow of tears. Applied to the skin, it produces a burning sensation and causes blistering. The vapors are particularly harmful to the lungs. It is soluble in 8 vol. of 70 p. c. alcohol and is miscible in all proportions with 90 p. c. alcohol, likewise with ether, amyl alcohol, chloroform, benzene and petroleum ether. In water it is but sparingly soluble.

B. p. 150,7° (728,9 mm.); $d_{10.1°}$ 1,0173.[3])

According to observations made on technical products in the laboratory of Schimmel & Co., synthetic mustard oil possesses the following properties:

B. p. (the bulk of the oil) 151 to 153° (760 mm.), 30,2° (5 mm.); $d_{15°}$ 1,020 to 1,025; $n_{D20°}$ 1,527 to 1,530.

[1]) E. Schmidt, Berl. Berichte **10** (1877), 187.
[2]) Compt. rend. **149** (1909), 91.
[3]) Kopp, Liebig's Annalen **98** (1856), 375.

When small amounts of mustard oil are mixed with twice their volume of concentrated sulphuric acid a violent evolution of carbon oxysulphide[1]) and sulphur dioxide[2]) takes place and allylamine sulphate, $C_3H_5NH_2 \cdot H_2SO_4$, is formed. This remains in the test tube as a clear, slightly colored liquid, or occasionally congeals. As an unsaturated compound, mustard oil adds bromine with the formation of an oily dibromide, $CSN \cdot C_3H_5Br_2$, which is volatile with water vapors.

For the identification of mustard oil, allylthiourea (thiosinamine), $CS\langle^{NHC_3H_5}_{NH_2}$, is particularly suited. It crystallizes in rhombic prisms that melt at 74°, has a faint leek-like odor and taste, and is readily soluble in water, alcohol and ether. The compound results when an excess of ammonia and some alcohol are added to mustard oil. The reaction is accelerated by gentle heat. For the quantitative determination of mustard oil, see the chapter on "The examination of volatile oils".

Exposed to light, mustard oil gradually acquires a reddish-brown color and the bottle is coated with a dirty orange-yellow film containing carbon, nitrogen, hydrogen and sulphur.

Prolonged contact with water or with heavy metals, such as copper, silver, tin, mercury, causes decomposition of the mustard oil with formation of cyanallyl. The metals combine with the sulphur to sulphides. Ethyl alcohol also gradually causes a change forming a partially sulphuretted allylurethane:

$$CSN \cdot C_3H_5 + C_2H_5OH = CS\langle^{NHC_3H_5}_{OC_2H_5} .$$

It is because of this reaction that spirit of mustard gradually looses its therapeutic action.

The source of the carbon disulphide always found in mustard oil, even in the artificial product, has not yet been definitely ascertained. Experiments have shown[3]) that, whereas boiling of mustard oil with water in a flask connected with a reflux condenser for an hour does not yield carbon disulphide, appreciable amounts

[1]) A. W. Hofmann, Berl. Berichte 1 (1868), 182.
[2]) Flückiger, Arch. der Pharm. 196 (1871), 214.
[3]) Gadamer, Arch. der Pharm. 235 (1897), 53.

of this substance, together with carbon dioxide, are produced when mustard oil and water are heated in a sealed tube under pressure for several hours to a temperature of 100 to 105°. It may be assumed that in the nascent state mustard oil possesses a greater capacity for reaction and that under such conditions it reacts with water according to the following equation.

$$2CSNC_3H_5 + 2H_2O = 2C_3H_5NH_2 + CO_2 + CS_2.$$

Carbon disulphide is also formed when mustard oil is allowed to remain in prolonged contact with water at ordinary temperature.

Of other mustard oils the following may be briefly described in this connection.

Iso*thiocyanpropenyl*, $CSN \cdot CH : CH \cdot CH_3$. According to Pomeranz,[1]) traces of this occur in mustard oils. He assumes to have established its presence in artificial mustard oil by having identified acetic acid as well as formic acid among the oxidation products.

Secondary butyl mustard oil, $CSN \cdot CH(CH_3) \cdot CH_2 \cdot CH_3$, the *iso*thiocyanate of secondary butyl alcohol, is the principal constituent of the oil of *Cochlearia officinalis*, and has been isolated from the oil of the herb of *Cardamine amara*. This mustard oil likewise does not occur as such, but in the form of a glucoside known as glucocochlearin.[2])

Secondary butyl mustard oil is an optically active, colorless liquid possessing the characteristic odor of cochlearia oil.

B. p. 159,5°; $d_{12°}$ 0,944.[3])

Heated with ammonia to 100° it yields a thiourea which melts at 135 to 136° and which is optically active. In alcoholic solution, the oil gradually looses its original pungency. Presumably a partially sulphuretted urea is formed as in the case of allyl mustard oil.

The commercial "artificial oil of spoon wort" is *iso*butyl mustard oil, $CSN \cdot CH_2 \cdot CH \cdot (CH_3)_2$, hence not identical with the natural product. It boils at 162° and yields a thiourea melting at 93,5°.

[1]) Liebig's Annalen **351** (1907), 354.

[2]) Ter Meulen, Recueil des trav. chim. des P.-B. **24** (1905), 444. According to Chem. Zentralbl. **1905**, II. 1255.

[3]) A. W. Hofmann, Berl. Berichte **7** (1874), 513.

Crotonyl mustard oil, $CSN \cdot CH_2 \cdot CH_2 \cdot CH : CH_2$, is contained in a rape seed *(Brassica Napus),* likewise in the form of a glucoside.[1]). It is obtained when the seeds are mashed with white mustard which is rich in myrosin and subjecting the mixture to steam distillation. Ter Meulen[2]) succeeded in isolating the glucoside gluconapin though not in absolutely pure condition.

Crotonyl mustard oil is a colorless, strongly refractive liquid, the odor of which reminds of horse-raddish and allyl mustard oil. B. p. 174° with slight decomposition; $d_{4^\circ}^{10^\circ}$ 0,933. With alcoholic ammonia the thiourea is obtained in fine needles that melt at 64°.

Attention was first directed to the presence of crotonyl mustard oil in rape seed because of the observation of poisoning in cattle fed on rape seed presscake. The natural mustard oil, however, is not identical with the artificial crotonyl mustard oils prepared by Hofmann[3]) and Charon,[4]) but only isomeric.

Benzyl mustard oil, $CSN \cdot CH_2C_6H_5$, results upon the hydrolysis, produced by ferments, of the glucoside glucotropæolin, $C_{14}H_{18}KNS_2O_9 + xH_2O$, contained in *Tropæolum majus,* and which probably also occurs in the ordinary cress, *Lepidium sativum.*[5]) It has the pungant odor of cress, and with ammonia orms a thiourea melting at 162°.

Phenylethyl mustard oil, $CSN \cdot C_2H_4 \cdot C_6H_5$, constitutes the principal constituent of the oil from mignonette root. It is a liquid the odor of which reminds of horse-reddish. The thiourea melts at 137°.

p-*Hydroxybenzyl mustard oil,* $C_6H_4 \cdot OH^{(1)} \cdot CH_2NCS^{(4)}$. The glucoside sinalbin, $C_{30}H_{42}N_2S_2O_{15}$, which occurs in white mustard seed, yields upon the action of myrosin, the above mustard oil together with *d*-glucose and sinapine bisulphate. Only traces of this sinalbin mustard oil are volatile with water vapor. Hence the water with which white mustard has been triturated, has a pungent taste but is wellnigh odorless.

[1]) Sjollema, Recueil des trav. chim. des P.-B. **20** (1901), 237. According to Chem. Zentralbl. **1901**, II. 299.

[2]) Recueil des trav. chim. des P.-B **24** (1905), 444. According to Chem. Zentralbl. **1905**, II. 1255.

[3]) Berl. Berichte **7** (1874), 514.

[4]) Annal. Chim. Physiol. VII. **17**, 262. According to Chem. Zentralbl. **1901**, II. 300.

[5]) Gadamer, Arch. der Pharm. **237** (1899), 510; Berl. Berichte **32** (1899), 2338.

THE EXAMINATION OF VOLATILE OILS.

As the various oils are fully described in the second vol. of this treatise, it will be expedient, in order to avoid repetition, to discuss briefly in a special chapter the general methods used in their investigation and the most common adulterants met with.

The practice of adulteration of the volatile oils, which is probably as old as the manufacture itself, had in the beginning a certain justification, as with the incomplete technical equipment of the early times the addition of fatty oils, turpentine oil, or alcohol was often necessary in order to extract from the plants their odorous principle. Later, when the preparation of the pure oils was already known, the practice of making these additions was still retained.

Even forty years ago, it was customary to distill coriander with the addition of orange oil and to put the distillate on the market as coriander oil. Since pure coriander oil can now be prepared without difficulty, the product obtained by using orange oil, as it is found now and then even at the present time, must be considered as adulterated and if the foreign ingredient is not made known, its sale is a fraud.

The adulteration need not always be by the addition of a less valuable body, it sometimes consists in that the more valuable constituent of the oil has been partially removed. The effect is the same, whether from a caraway oil of the specific gravity 0,910 so much carvone be removed that an oil of the specific gravity 0,890 remains behind, or whether the same result is attained by the addition of limonene to the same oil.

Although the adulterations themselves mostly find a sufficient explanation in the profitableness and the pecuniary advantage to the adulterator, it cannot, however, be denied, that often the ignorance of the consumer, and above all the desire to buy as

cheaply as possible, is the cause of the spurious composition of many an oil. More than once the producer may have been induced to adulterate, because he found no buyers for his pure products at a reasonable price, while his adulterating competitor was able to do a lucrative business at lower prices.

The main reason for the extensive adulteration to which volatile oils have been subjected at times, is to be sought in the fact that the detection of adulterants was very difficult and often entirely impossible.

Owing to the development of the chemistry of the terpenes and their derivatives, great progress has been made during the last twenty five years in the detection of adulterations. Knowing the composition of not a small number of volatile oils, it has become possible not only to distinguish between a pure and an adulterated oil, but also to judge the quality of these oils. This is effected by estimating the amount of the principal, or the most important constituent. In lavender oil, bergamot oil, petitgrain oil and others, the amount of esters present are therefore determined; in thyme oil, clove oil, pimenta oil, bay oil, and Cretian origanum oil the amount of phenols are estimated; in cassia oil and lemongrass oil the amount of aldehyde; in caraway oil the amount of carvone. The assay of santalwood oil shows how much santalol, that of palmarosa oil, how much geraniol is contained in the oil. The quality of the oils named finds numerical expression in the percentage strength of the active constituents such as esters, phenols, aldehydes, ketones and alcohols.

In a second class of oils, whose composition is likewise sufficiently known, an assay is not yet possible. The reason for this is twofold: first the value of the oil depends not upon a single constituent but upon the blending of the properties of several; and secondly the chemical methods of investigation are not sufficiently developed.

With these oils, the examination is restricted as a rule to the determination of the normal composition of the oil and the absence of commonly used adulterants. Such oils are lemon oil, orange oil, rosemary oil and spike oil, which should be tested particularly for turpentine oil.

The incomplete knowledge of the composition and the defectiveness of the methods of testing most of the oils, do not at

present allow of an investigation resting on a rational chemical basis. With this class of oils the entire examination consists in determining the physical constants. As the average and limit values of specific gravity, optical rotation, solubility, &c., of the more common oils are well known through observations extending over many years, variations from these values call the attention of the investigator to adulterants.

Indeed, the physical behavior of an oil is in general very well suited to indicate rapidly the addition of foreign substances; the investigation of volatile oils should therefore begin with the determination of the physical properties, no matter whether the investigation be for practical or for scientific purposes. After this, the special methods are to be used, such as saponification, acetylation, aldehyde and phenol determinations, and finally, if it appears necessary, the tests for turpentine oil, fatty oil, alcohol or petroleum should be applied.

It is of course evident that when the practical value of an oil is to be considered, the examination as to its odor[1]) and

[1]) Attention may here be called to the interesting publications by H. Zwaardemaker: *Die Physiologie des Geruchs* (Leipzig 1895); *Die Riechkraft von Lösungen differenter Konzentration* (Arch. f. Anatomie u. Physiologie, Physiol. Abtlg. **1900**, 415); *Die Kompensation von Geruchsempfindungen* (*Ibidem* **1900**, 423); *Geruch* (Ergebnisse der Physiologie **1** (1902), 896); *Riechen und schmecken* (Arch. f. Anatomie u. Physiologie, Physiol. Abtlg. **1903**, 120; Report of Schimmel & Co. October **1904**, 107); *Präzisions-Olfaktometrie* (Arch. f. Laryngologie Bd. **15**, Heft 2; Report of Schimmel & Co. October **1904**, 105); *Geschmack* (Ergebnisse der Psysiologie **2**, 2 (1903), 699); *Eine bis jetzt unbekannt gebliebene Eigenschaft des Geruchssinnes* (Arch. f. Anatomie u. Physiologie, Physiol. Abtlg. **1904**, 43; Report of Schimmel & Co. October **1904**, 109); *Die Empfindung der Geruchlosigkeit* (Untersuchungen aus dem physiologischen Laboratorium 5. Reihe IV, II, 376; Report of Schimmel & Co. October **1904**, 107); *Odorimetrie von prozentischen Lösungen und von Systemen im heterogenen Gleichgewicht* (Untersuchungen aus dem physiologischen Laboratorium 5. Reihe IV, II, 387; Report of Schimmel & Co. October **1904**, 105); *Über die Proportionen der Geruchskompensation* (Arch. f. Anatomie u. Physiologie, Physiol. Abtlg. **1907**, 59; Report of Schimmel & Co. April **1908**, 173); *Die vektorielle Darstellung eines Systems von Geruchskompensationen* (Arch. f. Anatomie u. Physiologie **1908**, 51; Report of Schimmel & Co. October **1908**, 160). Comp. also E. Erdmann, *Über den Geruchssinn und die wichtigsten Riechstoffe* (Zeitschr. f. angew. Chem. **1900**, 103) and J. van der Hoeven Leonhard, *Riechschärfen und Farbsinnabweichungen* (Die Umschau **12** (1908), 367; Report of Schimmel & Co. October **1908**, 160).

taste must accompany the chemical and physical investigation, for these are the properties on account of which the volatile oils are used in the perfume and soap industries, in the manufacture of candies and liquors, and partly at least in medicine.

It is necessary, or at least greatly to be desired, to have for comparison a sample of a genuine, faultlessly distilled oil. A few drops each, of the genuine oil and of the oil to be tested, are put on a strip of filter paper, and compared by smelling alternately of both. This odor test is repeated after the larger part of the oil has volatilized, and in this manner readily volatile as well as more difficultly volatile foreign substances may be recognized.

It is possible, however, to give only a very imperfect expression in language of odor and taste perceptions; moreover, odor and taste are purely subjective and are also quite differently developed faculties in each individual. The perceptions made with the sense of odor and of taste do not admit of expression and comparison by means of figures like other observations. An adulteration may, therefore, be subjectively recognized, but cannot be objectively proven. A good sense of smell is in spite of this limitation of great value in the examination, as it often directs the investigation into the proper channel in the shortest time.

Poorly distilled oils, possessing an empyreumatic odor or "Blasengeruch", or oils carelessly kept but otherwise unadulterated are almost altogether recognized by the sense of smell, rarely by any other means of investigation.

DETERMINATION OF THE PHYSICAL PROPERTIES.

SPECIFIC GRAVITY.

On account of its ready determination the specific gravity is the most frequently taken and, therefore, the best known property of the volatile oils. Even concerning the rare and little investigated oils statements of their density are to be found.

Further, as the maximum and minimum values of the more commonly used oils are fixed, the determination of the specific gravity belongs to the most important and also most convenient means of investigation. The specific gravity of an oil is changeable within certain limits, and dependent, outside of age, on the manner of the distillation and also upon the source and the state of ripeness of the plant material used. The extent of this variation is so different in the individual oils that no general rules can be formulated. With normal bergamot oil, for instance, the specific gravity lies between 0,881 and 0,886. The difference between the highest and the lowest density, therefore, amounts in this case to only five places in the third decimal. As a rule, however, the limit values lie much further apart.

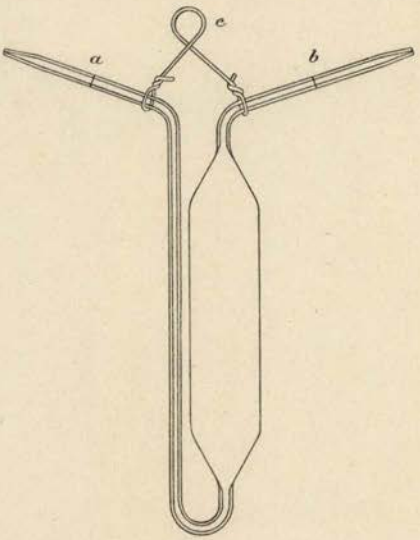


Fig. 66.

Most oils are lighter, some, however, heavier than water, especially those which contain larger amounts of oxygenated constituents of the aromatic series (*e. g.* wintergreen oil, clove oil, sassafras oil). The lowest specific gravity of all volatile oils is that of *Pinus Sabiniana* with 0,6962; the highest is that of wintergreen oil with 1,188.

The determination is conveniently performed with an hydrostatic balance according to Mohr or Westphal[1]), as the accuracy attained with this instrument, if rightly handled, is sufficient. The values obtained thereby are reliable to the third decimal. For the more accurate determination, or when only small quantities of an oil are at disposal, a pycnometer is used. The modifications of Sprengel (Fig. 66) and of Ostwald (Fig. 67) are especially to be recommended. For practical reasons it is expedient to mark

[1]) The hydrostatic balance with steel axes by F. Sartorius, Göttingen, may be especially recommended.

the capillaries at *a* and *b* and to bend these slightly upward as shown in the accompanying illustrations. The instrument is suspended from the balance by means of the platinum wire *c*. The capillaries can be sealed by means of the glass caps *d* and *e*. The pycnometer likewise yields more accurate results with viscid oils in which the thermometer body of the Mohr-Westphal balance does not move up and down with sufficient ease. For viscid oils

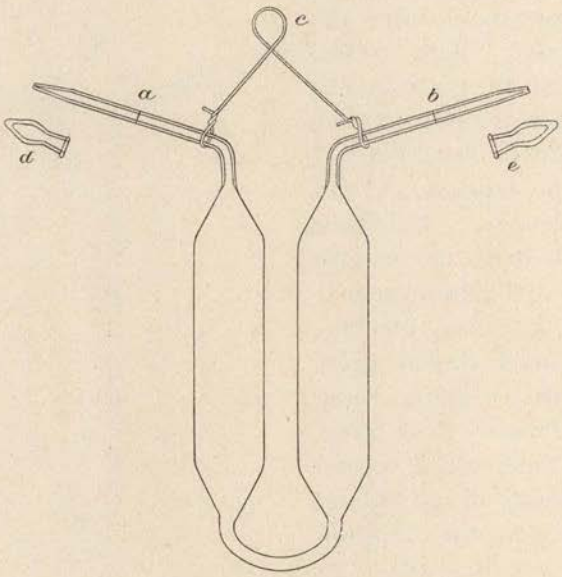


Fig. 67.

the capillaries should be relatively large otherwise the filling and emptying of the instrument is accompanied with difficulties. For the determination of the specific gravity, the weight of the completely dry instrument should be known, also its water value. For the determination of the latter, the pycnometer, previously filled with distilled water, is placed into a water bath of constant temperature (usually $+15^{\circ}$ C.) for about a quarter of an hour or until it has assumed the temperature of the water bath. In the mean time distilled water is either added or withdrawn so as to bring the contents to the marks on the capillaries, when th weight is determined accurately. These two values, *viz.*, P_1 (weight of the pycnometer) and P_2 (weight of the pycnometer plus water) are determined once and for all for a given instrument.

$P_2 - P_1$ is the water value W of the pycnometer. If the specific gravity of an oil is to be ascertained, the pycnometer is filled with the oil in question, the same conditions as to temperature being observed as before, and weighed. If the pycnometer filled with oil weighs P_3, then the specific gravity of the oil is

$$s = \frac{P_3 - P_1}{W}.$$

In order to enable the convenient filling and evacuation of the instrument, a tube with glass ground connection with the capillary, as illustrated in fig. 68, is employed. In the case of viscid oils these operations are facilitated with the aid of gentle heat.

Fig. 68.

The specific gravity is naturally dependent on the temperature. For its determination + 15° C. has been chosen as a matter of expediency. The water value is likewise determined at this temperature.[1]) The instruments used in Germany are calibrated in accordance with this rule, including the Mohr-Westphal balance. Only the specific gravity of such oils as are too viscid at 15° C. or congeal either entirely or in part, is taken at higher temperatures, however, with reference to water at 15°, so that the same instruments can be used for these determinations at higher temperatures.

Experiments have shown[2]) that for the temperature of water at 15° C. the specific gravity of the volatile oils varies from 0,0007 to 0,0008 for each degree centigrade, *i. e.* on an average 0,00075. With the aid of this factor, the specific gravity of an oil can be recomputed for any temperature. If the temperature at which the specific gravity was determined was higher, 0,00075 should be added for each degree difference, if lower, the corresponding value should be deducted.

If, however, the specific gravities have been determined, not with reference to water at 15° but with reference to water at the same temperature at which the density of the oil was as-

[1]) Unless otherwise specified, the specific gravities recorded in this book are for the temperature of + 15° C. with reference to water at 15°.

[2]) Report of Schimmel & Co. October **1905**, 87.

certained, corrections can be made in like manner. According to Schreiner and Downer[1]) the correction factor for observations between 15 and 25° is 0,00064 for each degree.

As a matter of course such computed values can be regarded as approximations only. For accurate data the specific gravity should be actually determined at the temperature in question.

OPTICAL ROTATION.

The optical rotation is such a characteristic property of most of the volatile oils that its determination should never be omitted in an examination. Especially adapted for this purpose is the half-shadow polariscope according to Lippich[2]) with polarisor in two parts. The best division of the circle for the purpose in question is that into degrees and minutes in such a way that the numbers on each side of the zero point run up to 180°. If the dark color of the oil does not allow of making the observation in a 100 mm. tube, which is the one usually employed, one of 50 or even 20 mm. may be used and the values obtained are multiplied by 2 and 5 respectively. If the color permits, inactive substances are observed in 200 mm. tubes in order that slight deviations may be detected. When no special mention is made of the temperature, room temperature is to be understood. In general it is not necessary, although desirable, to make the observation at a fixed temperature, as the natural variations in the rotation of an oil are usually greater than the differences due to a variation in temperature of several degrees. Exceptions to this are the oils of lemon and orange, the rotation of which is relatively strongly influenced by even small changes in temperature. It is necessary, in order to get comparable figures, to determine the rotation of these two oils at + 20° or else to reduce the result to this temperature by calculation. The details of this will be found in the description of these oils in the special part.

[1]) Pharmaceutical Archives 4 (1901), 165. Comp. also Report of Schimmel & Co. April **1906**, 71.

[2]) With regard to the manipulation of the polariscope the reader is referred to the wellknown work by H. Landolt, *Das optische Drehungsvermögen organischer Substanzen,* II. ed., Braunschweig, 1898.

In the following, α_D is the observed angle of rotation in a 100 mm. tube with sodium light, and $[\alpha]_D$ is the specific rotation as calculated by the formula

$$[\alpha]_D = \frac{\alpha}{l \cdot d}$$

where α is the observed angle of rotation, l the length of the tube in decimeters and d the specific gravity of the liquid.

Solid substances are dissolved in an optically inactive liquid. The computation is effected acording to one of two formulas, depending as to how the concentration is expressed: either by *c, i. e.* the number of grams of substance in 100 cc. of solution, or by percentage, *i. e.* the number of grams of active substance in 100 g. of solution. In the latter instance the specific gravity *(d)* of the solution must be known. If the solution deviates the ray of polarized light α degrees the specific angle of rotation follows from the following equation:

$$[\alpha]_D = \frac{100 \cdot \alpha}{l \cdot c} = \frac{100 \cdot \alpha}{l \cdot p \cdot d}.$$

The angle of rotation thus ascertained is not strictly constant for most substances, but varies with the nature of the solvent, the concentration, and the temperature.[1]) Consequently it is necessary to record the conditions observed with the specific angle of rotation, *e. g.* $[\alpha]_{D20°} + 10°$ in a 43,5 p. c. alcoholic solution.

REFRACTION.

The determination of the index of refraction n_D has been recommended repeatedly for the examination of the volatile oils. As is well known, certain relations exist between chemical constitution and refraction and in many cases conclusions as to the position and number of double bonds may be drawn from the molecular refraction. Chemical individuals carefully purified are, however, necessary in order to obtain useful results. As the refractive coefficients of the constituents of the volatile oils are on the whole only slightly different from each other, they are not so well suited for the detection of adulterations as are

[1]) As to the influence of the solvent on the angle of rotation compare Landolt, Liebig's Annalen **189** (1877), 311; Rimbach, Zeitschr. f. physik. Chem. **9** (1892), 701.

other methods of examination. The addition of turpentine oil, for instance, influences the refraction of lemon oil only slightly, but changes the rotation to a marked degree.[1])

In isolated cases, the index of refraction may nevertheless serve as a valuable supplement to the other constants and should, therefore, not be omitted on principle. Hence, in the discussion of the individual oils, reference will frequently be made to these constants and limit values will be given.

For this purpose the Pulfrich refractometer can be especially recommended. The observations are made with sodium light.

The variations in the index of refraction due to differences in temperature vary somewhat for different oils and average about 0,00035[2]) for each degree of temperature. These variations are noteworthy in as much as the indices of refraction of the different volatile oils vary but little among themselves, *viz.*, from 1,43 (oil of rue and cognac oil) and 1,61 (cassia oil). Great care with reference to temperature should, therefore, be exercised in the determination. As a rule, the observations are made at 20°. Only in such cases, as that of oil of rose, in which the consistence of the oil does not admit of the determination, a higher temperature is chosen. Hence $n_{D20°}$ signifies the index of refraction for sodium light at 20° C. A recomputation with the aid of the above mentioned factor yields approximate values only and is not admissible for accurate values.

As a result of the formation of oxidation and polymerization products, the index of refraction increases with age. An exception is found in the behavior of anethol.[3])

Mention should yet be made of the specific and molecular index of refraction although they apply to chemical individuals only.

The specific index of refraction finds expression in the formula

$$\frac{n_2 - 1}{n_2 + 2} \cdot \frac{1}{d}$$ [4])

in which d is the specific gravity determined at the same temperature at which the index of refraction is determined. The

[1]) Report of Schimmel & Co. October 1893, 55.

[2]) According to observations by Schimmel & Co.

[3]) Comp. Report of Schimmel & Co. October 1904, 42.

[4]) The above formula has been proposed by Lorenz and Lorentz. The older formula by Gladstone, *viz.* $\frac{n-1}{d}$ does not always yield constant values.

molecular index of refraction or the molecular refraction is obtained by multiplying the specific index of refraction with the molecular weight.

CONGEALING POINT.

With certain oils, especially anise, star anise, fennel and rue oils, the congealing point affords a good means for judging the quality. With the first three oils a high congealing point shows a large content of anethol, with rue oil one of methyl nonyl ketone.

In isolated cases the melting point has been recommended for the determination of volatile oils. However, it is little suited to this end, since the volatile oils are not individual compounds but mixtures which reveal no sharp melting point throughout the entire mixture, but soften at first and then gradually change to a clear liquid. As a result no fixed melting point can be observed, but a temperature interval between which the oil melts. Contrasted with the melting point, the congealing point can be clearly and sharply observed.

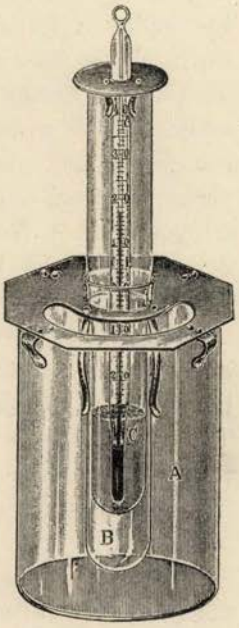


Fig. 69.

1/4 der wirklichen Größe.

The determination of the congealing point can be very well performed with Beckmann's well-known apparatus for the determination of the molecular weight by the lowering of the freezing point. A few slight changes make it especially suited for this purpose. They consist principally in doing away with the cork connections which hinder the free inspection of the mercury thread of the thermometer. The laboratory of Schimmel & Co.[1]) has the form shown in fig. 69. The battery jar *A* serves as the receptacle for the cooling liquid or freezing mixture. The glass tube *B* hanging in the metal cover serves as an air jacket for the freezing tube *C* and prevents the premature congealing of the oil to be tested. The freezing

[1]) Report of Schimmel & Co. October 1898, 43.

tube *C* is wider at the top and becomes narrower at the place where it rests on the edge of the tube *B*. In order to retain *C* in fixed position, three glass projections are fastened on the inside of the tube *B*, about 5 cm. below its upper edge. The thermometer, which is graduated into half degrees is held in position in a metal plate by three springs which allow of sliding the thermometer up or down.

To carry out the test, the battery jar is filled with either water and pieces of ice or with chopped ice, according to the reduction of temperature desired. Only occasionally it is necessary to employ a freezing mixture of ice and salt. Then pour into the freezing tube so much of the oil to be tested that it stands at a height of about 5 ccm. in the tube and bring the thermometer, which must not touch the sides of the tube at any place, into the liquid. During the cooling the undercooled oil is to be protected from disturbances, which would produce a premature congealation.[1]) When the oil has been sufficiently undercooled, crystallization is to be induced by rubbing and scratching the thermometer against the sides of the tube. If this proceeding should not prove successful a small crystal of congealed oil or some solid anethol or methyl nonyl ketone is brought into the liquid, when congealation will take place with liberation of heat. The solidification is hastened by continued stirring with the thermometer, the mercury thread of which rises rapidly and finally reaches a maximum which is called the congealing point of the oil.

The oil should be sufficiently undercooled, otherwise the congelation will proceed too slowly thus rendering the observation more difficult. Again, the oils should not be undercooled too much, otherwise the results observed will be too low. Practically useful results are obtained when the oils are undercooled about 5°. It is desirable always to work under like conditions in order that the various qualities of the respective oils may be judged from a common view point. Schimmel & Co. subcool as follows:

Anethol	to + 16°,	Anise oil	to + 12°.
Staranise oil	to + 10°,	Fennel oil	to + 3°.

[1]) A premature congealation often takes place when the oil has not been filtered clear, as suspended dust particles may give rise to congealation.

In certain cases it is desirable to record the temperature to which an oil was subcooled.

It should be mentioned that reference is had to the congealing temperature of oil of rose. This refers to the temperature at which the paraffin crystals are formed when the oil is slowly cooled.

BEHAVIOR ON BOILING AND FRACTIONAL DISTILLATION.

Inasmuch as the volatile oils are mixtures of substances with different boiling points, it is improper to speak, as is so often done, of the boiling point of a volatile oil. It is more correct to speak of a boiling temperature, by which is meant the temperature interval within the limits of which the oil distills over in a single distillation from an ordinary distilling flask (fig. 70) without the application of a fractionating arrangement. It is of the greatest importance that the entire column of the mercury be surrounded by the vapors of the distilling oil, a circumstance that is often ignored and leads to erroneous results. The thermometer should be adjusted in such a manner that the respective boiling point is placed slightly above the exit tube of the distilling flask. Care, however, should be exercised that the mercury bulb of the thermometer does not project into the body of the flask, much less into the liquid. In order to avoid this, thermometers with shortened scales are preferably used.

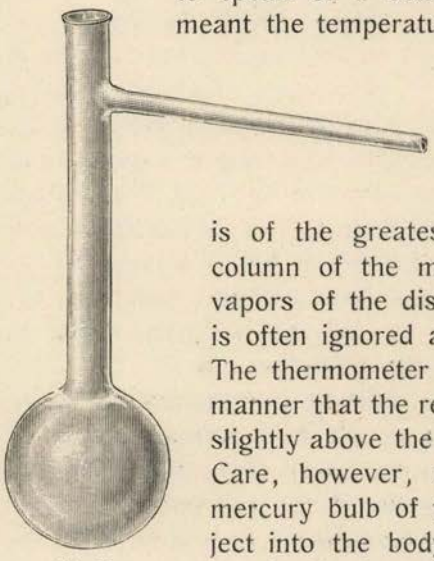


Fig. 70.

Of great importance is also the rate of distillation which is best regulated so that 40 or at most 60 drops are collected per minute. If the distillation is conducted too rapidly and if the exit tube is not large enough the vapors are choked causing an increase in pressure and a corresponding rise in temperature. The consequence is this that the observed boiling point is too high.

In order to avoid bumping, small pieces of pumice, tiling or or talcum are added to the liquid.

Whereas the determination of the boiling point is of importance in the examination of chemical individuals, fractional distillation yields better results in the examination of volatile oils. The several fractions are collected separately, their amounts ascertained, and each fraction examined separately if necessary.

The observations recorded by different observers of the amounts of the same oil which distill over between certain limits of temperature, seldom agree, because the results are not only greatly influenced by the form of the distilling flask, but also by the rapidity of the distillation and the height of the barometer. In the examination of certain fractions of individual oils it is therefore necessary, to use flasks of fixed dimensions and to observe a certain rapidity of distillation. For testing lemon oil, rosemary oil and spike oil, Schimmel & Co. use distilling flasks according to Ladenburg of the dimensions given in fig. 71.[1]) From 50 cc. of the oils mentioned, 5 cc. are distilled over in such a manner that about 1 drop falls in a second, and the distillate tested in the polariscope, as will be described more in detail under the individual oils.

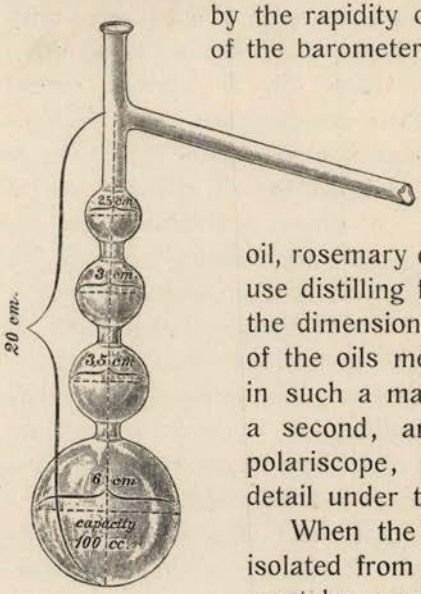


Fig. 71.

When the different constituents are to be isolated from an oil, the fractional distillation must be repeated many times and preferably by employing one of the well known distilling columns. In order to avoid decomposition, it is best to distill the fractions boiling above 200° in vacuum. Oils containing esters must first be saponified, as the acids, which are easily split off by the boiling, disturb the fractionation and may act upon the other constituents of the oils.

SOLUBILITY.

The volatile oils are readily soluble in the ordinary solvents, such as alcohol, ether, chloroform, benzene, acetic ether, carbon

[1]) Report of Schimmel & Co. October 1898, 41.

disulphide, &c. Mention of this general property is not made in the description of the individual oils. A phenomenon which is sometimes considered as an incomplete solubility may be mentioned here. The turbidity noticed when certain oils are mixed with petroleum ether, paraffin oil[1]) or carbon disulphide may be caused by the small amount of water which the oils have retained from their preparation. The richer an oil is in oxygen, the more water it is capable of dissolving and the more cloudy does it become with petroleum ether.[2]) The turbidity does not take place when the oil has been thoroughly dried with anhydrous sodium sulphate.

Fig. 72.

Although all oils are readily soluble in strong alcohol, only some of them are entirely soluble in dilute alcohol. For the last class this property becomes a practical and rapid means of examination. The presence of the difficultly soluble turpentine oil can, for instance, be readily shown in this manner in the oils soluble in 70 p. c.[3]) alcohol. The solubility determination is very simple. Bring into a small graduated cylinder (fig. 72) $^1/_2$ to 1 cc. of the oil to be tested and add small portions of the alcohol at a time until with vigorous shaking solution is effected. If an oil which is soluble under normal conditions does not dissolve, it is sometimes possible to draw conclusions as to the adulterant from the character of the turbidity and the separation of the insoluble part. Petroleum floats on the 70 p. c. alcohol, whereas a fatty oil settles in drops at the bottom.

For the examination of volatile oils, alcohol of different percentage strength is used. In the following table the strengths thus far employed are enumerated together with their specific gravities for $\frac{15°}{15°}$.[4])

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[1]) Cinnamic aldehyde is an exception to this rule. It is practically insoluble in petroleum ether and paraffin oil. Hence cassia oil and Ceylon cinnamon oil dissolve but incompletely in these solvents.

[2]) When an oil rich in oxygen, such as bergamot oil, is mixed with one rich in terpenes, as turpentine oil or orange oil, the mixture becomes turbid due to the separation of water.

[3]) The statements in this book always refer to volume percent.

[4]) According to K. Windisch, *Tafeln zur Ermittelung des Alkoholgehaltes von Alkohol-Wassermischungen aus dem spezifischen Gewicht.* Berlin, 1893.

30 percent by volume	$d_{15°}^{15°}$ 0,9656	69 percent by volume	$d_{15°}^{15°}$ 0,8928
40	0,9521	70	0,8904
50	0,9347	80	0,8642
56	0,9226	82	0,8586
60	0,9139	85	0,8499
62	0,9094	90	0,8343
65	0,9025	95	0,8165
68	0,8953	98	0,8040

In order to avoid the necessity of keeping on hand alcohol of different percentage strenght, Dowzard[1]) has recommended a method which is worth mentioning though it has not established itself. 5 cc. of an oil are dissolved in 10 cc. of absolute alcohol ($d_{15,5°}$ 0,799) and the solution diluted with water from a burette until the solution becomes permanently turbid. By multiplying the number of cc. of water by 100 the "solubility value" is obtained. In connection with bergamot oil, Dowzard determined values between 220 and 290.

The same author suggests the determination of the *viscosity*[2]) as a means for examining volatile oils. For the volatile oils, however, this method has never attained practical significance.

CHEMICAL METHODS OF TESTING.

The rational examination of a volatile oil in a chemical manner is possible only if its composition or at least its main constituents are known. The chemical investigation must be directed as much as possible toward the isolation and quantitative estimation of the constituents recognized as being the most valuable. The methods of testing must, therefore, conform to the analysis of the oil. If this really self-evident supposition had been generally recognized earlier, those methods of investigation, which are designated as quantitative reactions, as for instance the iodine absorption, or Maumené's sulphuric acid test, which had given good results with the fatty oils, would not have been applied offhand to the volatile oils.

[1]) Chemist and Druggist **53** (1898), 749.

[2]) Chemist and Druggist **57** (1900), 169. Report of Schimmel & Co. April **1901**, 31.

The fatty oils are a group of chemically closely related bodies; they are glycerides of the fatty and oleic acid series. The constituents of the volatile oils, however, recruit themselves from the greatest variety of classes of bodies. Among them may be found terpenes, sesquiterpenes, paraffins, alcohols, aldehydes, ketones, phenols, ethers, oxides and esters. It should be no matter for surprise, therefore, that the methods of testing which are useful with the fatty oils, fail utterly with the volatile oils. Nor is there any sense in subjecting the fatty and the volatile oils to the same reactions, just because they both bear the same designation "oils".

The application of Hübl's iodine addition method to volatile oils has been recommended by Barenthin,[1]) Kremel,[2]) Williams,[3]) Davies[4]) and Snow.[5]) By a direct comparison of the results of these separate observers it could not have been difficult for Cripps[6]) to show the utter uselessness of this method. This result is not altered by the fact that individual analysts again and again recommend this method.[7])

The use of bromine in place of iodine was first suggested by Levallois[8]) and later by Klimont.[9]) More recently it has again been recommended by Vaubel[10]) and Mosler.[11]) In as much, however, as the variety in the composition of volatile oils renders it impossible to pass judgement as to which of the constituents

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[1]) Arch. der Pharm. **224** (1886), 848.

[2]) Pharm. Post **21** (1888), 789, 821.

[3]) Chem. News **60** (1889), 175.

[4]) Pharmaceutical Journ. III. **19** (1889), 821.

[5]) Pharmaceutical Journ. III. **20** (1889), 4.

[6]) Chem. News **60** (1889), 236.

[7]) Sanglé-Ferrière and Cuniasse, Journ. de Pharm. et Chim. II. **17** (1903), 169; Report of Schimmel & Co. April **1903**, 82; F. Hudson-Cox and W. H. Simmons, Analyst **29** (1904), 175; Pharmaceutical Journ. **72** (1904), 861; Report of Schimmel & Co. October **1904**, 80; Worstall, Journ. Soc. chem. Industry **23** (1904), 302; Report of Schimmel & Co. October **1904**, 85; Harvey, Journ. Soc. chem. Industry **23** (1904), 413; Report of Schimmel & Co. October **1904**, 86.

[8]) Compt. rend. **99** (1884), 977.

[9]) Chem. Ztg. **18** (1894), 641.

[10]) Zeitschr. f. öff. Chem. **11** (1905), 429; Chem. Zentralbl. **1906**, I. 199; Report of Schimmel & Co. April **1906**, 66.

[11]) Zeitschr. d. allg. österr. Apoth. Ver. **45** (1907), 223, 235, 251, 267, 283, 299; Report of Schimmel & Co. October **1907**, 116.

it is with which the bromine combines, the value of the results obtained will remain problematical. The method will, therefore, find application in emergency cases only.

According to Maumené's test the fatty oil to be investigated is mixed in a certain proportion with concentrated sulphuric acid and the rise in temperature which takes place is observed. Its application to volatile oils was recommended by Williams[1]) as well as by Duyk[2]) but it has found just as little favor in practice as the other methods named above.

With these methods are also to be classed the much recommended color reactions. They mostly consist in bringing together a volatile oil and *e. g.* sulphuric acid or nitric acid, whereby some coloration is produced, which only in rare cases can be ascribed to a definite chemical change. As the shades of color produced are difficult to describe, and often change from one to the other, these tests may therefore easily give rise to mistakes. Hence the color reactions in general are to be designated as useless. This does not exclude, however, the occasional use of a color reaction in the detection of adulterants. This is especially true if these color tests are used for the characterization of chemical individuals isolated from the volatile oils (*e. g.* cadinene, sylvestrene). It is, however, never to be considered as conclusive in itself.

Besides the methods of testing already enumerated, many others have been suggested in the course of time, which however have acquired as little practical importance as these. Only such methods are to be discussed here as have really proven satisfactory in the investigation of volatile oils.

SAPONIFICATION.

Through scientific investigation it has been established that many volatile oils contain ester-like compounds, the components of which, on the one hand are alcohols, usually of the composition $C_{10}H_{18}O$ or $C_{10}H_{20}O$ and acid radicals of the fatty series, on the other.

[1]) Chem. News **61** (1890), 64.

[2]) *Bull. de l'Académie roy. de médec. de Belgique.* 1897.

The esters, which are nearly without exception of a pleasant odor, are often to be considered as the most important constituents of the oils. Thus, linalyl acetate is the carrier of the odor in bergamot oil; the same ester is found in lavender oil and also occurs along with other compounds in petitgrain oil.

The esters of borneol, found in the different pine-needle oils, play an important part in the formation of the pine aroma. Menthyl acetate is found in the peppermint oils and the geranyl ester of tiglic acid in the different geranium oils.

The quantitative estimation of the ester is always valuable for judging the oils, even when the esters are of little consequence to the odor. But it is much more important, and really the only rational test of quality in such cases where the esters are the carriers of the characteristic odor, as with bergamot oil and with lavender oil. The determination is made according to the method of quantitative saponification, as it has long been used in the analysis of the fats. Its application to the volatile oils was first urged by A. Kremel.[1]) However, it did not acquire practical importance until the nature of the saponifiable compounds was ascertained through scientific investigation.

Kremel distinguishes acid value (acid v.), ester value (ester v.), and saponification value (sap. v.). The acid value expresses how many mg. of KOH are necessary to neutralize the amount of free acid contained in 1 g. of oil. The ester value gives the amount of potassa in milligrams used in the saponification of the ester contained in 1 g. of oil. The saponification value is the sum of acid value and ester value. As the volatile oils with exception of *e. g.* geranium oil and vetiver oil usually contain only a small amount of free acid, this may in general be neglected. Only old, partly spoilt oils, tend to show somewhat higher acid values. It is urged that in all cases the acid and ester values be determined separately, for the reason that acids are occasionally added to increase the apparent ester content.

It should be mentioned that in all oils which contain aldehydes, the ester determination by saponification cannot be made, as a consumption of alkali takes place due to the decomposition of the aldehyde which increases with the length of the reaction,

[1]) Pharm. Post **21** (1888), 789, 821.

but which gives no information as to the amount of aldehyde decomposed.

Errors in the determination likewise result from the presence of phenols. Hence these should first be removed with the aid of a dilute (3 to 5 percent) aqueous alkali, unless the ester determination is abandoned in such cases.

Fig. 73.

The saponification is conducted in a wide necked flask of potash glass of 100 cc. capacity (fig. 73). A glass tube about 1 m. in length and passing through a stopper serves as a reflux condenser. Into such a flask about 1,5 to 2 g. of oil are weighed accurately to 1 cg. and about twice its volume of acid-free alcohol is added. After the addition of a few drops of alcoholic phenol-phthalein solution, half-normal potassa is carefully added. The reaction is completed when the red color produced no longer disappears upon shaking. A later decoloration is due to the saponification of the ester by the alkali. After the neutralization of the free acid, which usually requires but 2 to 3 drops of halfnormal alkali, 10 cc. or more[1]) of the solution are added, and the mixture is heated on a water bath for an hour[2]) after the usual precaution to prevent bumping

[1]) In most cases 10 cc. suffice. Only in the case of oils with high ester content (Roman chamomile oil, wintergreen oil) 20 to 30 cc. should be taken. Care should always be taken to have a sufficient excess of alkali. For the same reason 20 cc. of alkali should be taken when oils of unknown ester content are to be saponified. If esters as such are to be saponified even larger amounts should be used depending upon the size of the molecule and the number of carboxyl groups present. Thus, *e. g.* the saponification of 2 g. of methyl formate requires 67 cc. of halfnormal potassium hydroxide solution.

[2]) The saponification of most esters can be accomplished in a much shorter time, that of the ester of bergamot oil being accomplished in 10 minutes. However, in order to be certain of the results and to work under the same conditions, the time of heating is extended whereby no harm is done. Comp. Report of Schimmel & Co. October 1895, 25. The method of Helbing (Helbing's Pharmacological Record No. 30, p. 4), according to which the saponification of bergamot oil is conducted in a closed vessel, hence under pressure, yields, as the investigations of Schimmel & Co. revealed, results that are 1 to 2 percent

has been taken and the reflux condenser has been adjusted. After cooling, the contents of the flask are diluted with 50 cc. of water and the excess of alkali is titrated with half-normal sulphuric acid.

The computation is carried out with the aid of the following formula:

$$\left.\begin{array}{l}\text{Acid. V. (Acid value)}\\ \text{Ester. V. (Ester value)}\\ \text{Sap. V. (Saponification value)}\end{array}\right| = \frac{28 \cdot a}{s}.$$

in which a stands for the number of cc. of half-normal alcoholic potassa solution and s for the number of grams of oil of used.

If for 1,5 g. of bergamot oil employed 0,1 cc. of half-normal potassa has been used to neutralize the free acid, 6,0 cc. for saponification, then

$$\text{the acid value (acid v.)} = \frac{28 \cdot 0{,}1}{1{,}5} = 1{,}87;$$

$$\text{the ester value (ester v.)} = \frac{28 \cdot 6{,}0}{1{,}5} = 112{,}0; \text{ and}$$

$$\text{the saponification value (sap. v.)} = \frac{28 \cdot (0{,}1 + 6{,}0)}{1{,}5} = 113{,}87 = 1{,}87 + 112{,}0.$$

From the ester value the percentage of ester or of alcohol respectively can be computed with the aid of the following formulas:

$$\%\text{ ester} = \frac{\text{Ester V.} \cdot m}{560 \cdot b}; \quad \%\text{ alcohol} = \frac{\text{Ester V.} \cdot m_1}{560},$$

in which m stands for the molecular weight of the respective ester, m_1 for that of the corresponding alcohol, and b for the basicity of the corresponding acid.

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higher than those conducted in an open flask. The explanation lies in the fact that the linalool itself is affected by the caustic potash when heated with it under pressure whereas it suffers no change in the open flask. Later Helbing and Passmore [Chemist and Druggist 47 (1895), 585], substantiated the conclusion that the saponification in an open flask is to be preferred to that in an autoclave. Neither does the process of cold saponification appear to be applicable, which has the additional disadvantage of loss of time. According to Henriques (Zeitschr. f. angew. Chem. 1897, 399), linalool reveals a saponification value of 4,2, geraniol one of 2,8 when acted upon by alkali for 12 hours. In isolated cases only boiling for one hour does not suffice for the quantitative saponification of esters, thus *e. g.* with terpinyl acetate, bornyl and menthyl *iso*valerate, which must be boiled for from 2 to 3 hours with a sufficient excess of alkali.

For the more common alcohols found in volatile oils, *viz.*, $C_{10}H_{18}O$ (geraniol, linalool, borneol, *iso*pulegol), $C_{10}H_{20}O$ (menthol, citronellol), $C_{15}H_{24}O$ (santalol), $C_{15}H_{26}O$ (cedrol), and their esters the formulas read as follows:

1. $C_{10}H_{18}O$: % acetic ester $= \frac{\text{Ester V.} \cdot 196}{560}$; % alcohol $= \frac{\text{Ester V.} \cdot 154}{560}$,
2. $C_{10}H_{20}O$: % acetic ester $= \frac{\text{Ester V.} \cdot 198}{560}$; % alcohol $= \frac{\text{Ester V.} \cdot 156}{560}$,
3. $C_{15}H_{24}O$: % acetic ester $= \frac{\text{Ester V.} \cdot 262}{560}$; % alcohol $= \frac{\text{Ester V.} \cdot 220}{560}$,
4. $C_{15}H_{26}O$: % acetic ester $= \frac{\text{Ester V.} \cdot 264}{560}$; % alcohol $= \frac{\text{Ester V.} \cdot 222}{560}$.

In the above formulas the factor *b* drops out since acetic acid is monobasic.

For the bergamot oil illustration given on the previous page, the ester of which is linalyl acetate ($CH_3COOC_{10}H_{17}$) and the alcohol of which is linalool ($C_{10}H_{18}O$), the following values result:

$$\% \text{ linalyl acetate} = \frac{112{,}0 \cdot 196}{560} = 39{,}20,$$

$$\% \text{ linalool} = \frac{112{,}0 \cdot 154}{560} = 30{,}80.$$

Avoiding the ester value, the percentage of ester and of alcohol can be computed directly with the aid of the following formulas:

$$\% \text{ ester} = \frac{a \cdot m}{20 \cdot s \cdot b}; \quad \% \text{ alcohol} = \frac{a \cdot m_1}{20 \cdot s}.$$

In these formulas the symbols have the same significance as in the previous formulas.

For the alcohols mentioned above, *viz.*, $C_{10}H_{18}O$, $C_{10}H_{20}O$, $C_{15}H_{24}O$ and $C_{15}H_{26}O$ tables will be found at the end of this chapter (table I, p. 618), in which the percentage of acetic ester and of alcohol can be found for each ester value.[1]) The use of the table is quite apparent without further explanation. If in a given case 112 has been found as the ester value for bergamot oil, all that is necessary is to trace the corresponding figure in the column headed $C_{10}H_{18}O$ and in the one headed "acetate", *viz.*, 39,20. This figure reveals the percentage of linalyl acetate in bergamot oil, whereas the corresponding number 30,80 in the column headed "alcohol" reveals the percentage of linalool.

[1]) For geraniol the percentage of tiglate is also given. Table I, p. 618.

In order to save time in the computation of these alcohols, a second table (table II, p. 632) has been added in which the ester value (acid value, saponification value) as well as the corresponding percentage content of acetate or alcohol can be traced from the number of cc of half-normal potassium hydroxide solution used, provided exactly 1,50 g. of oil have been employed.

ACETYLATION.

Many volatile oils contain as important constituents alcohols varying in composition, for instance, borneol, geraniol, terpineol, linalool, thujylalcohol, menthol, citronellol and santalol. For the quantitative estimation, their behavior toward acetic acid anhydride, with which they form acetic esters when heated, may be used. Taking geranyl acetate as an illustration, their formation takes place according to the equation:

$$C_{10}H_{17}OH + (CH_3CO)_2O = CH_3CO_2C_{10}H_{17} + CH_3CO_2H.$$

Fig. 74.

For the quantitative acetylation[1]) 10 cc. of the oil, mixed with an equal volume of acetic acid anhydride and about 2 g. of dry sodium acetate, are boiled uniformly for 1 hour in a small flask provided with a condensing tube which is ground into the neck of the flask and some small fragments of tiling to prevent bumping (fig. 74). After cooling, some water is added to the contents of the flask and then heated for $^1/_4$ hour on a water bath, to decompose the excess of the acetic acid anhydride. The oil is then separated in a separating funnel, and washed with water, or better still with sodium chloride solution, until the reaction is neutral.[2])

Of the acetylized oil, dried with anhydrous sodium sulphate, 1,5 to 2,0 g. are saponified with 20 cc. of half-normal potassium

[1]) Report of Schimmel & Co. October 1894, 62.

[2]) One can also proceed to neutralize the free acid with sodium carbonate solution and then to wash with water until the reaction is neutral. In this case, however, one occasionally encounters the difficulty of removing the soda solution from the oil, a difficulty that is obviated when proceeding as indicated above.

hydroxide solution according to the method described on p. 572, any free acid present having previously been carefully neutralized. The percentage of alcohol corresponding to the ester value found, and referring to the original non acetylized oil, can be looked up in the table appended to this chapter, *viz.*, table I[1]), p. 618. These values are derived with the aid of the following formula:

$$\% \text{ alcohol in the original oil} = \frac{a \cdot m}{20 \cdot (s - a \cdot 0{,}021)}, \text{ in which}$$

m = the molecular weight of the respective alcohol,
a = the number of cc. of half-normal potassium hydroxide solution
s = the number of grams of acetylized oil used. [used,

Attention should, however, be directed to the circumstance that this formula does not take into consideration that a part of the alcohol may be contained as ester in the original oil. A small percentage of ester in the original oil may be disregarded since the error caused thereby is small. If, however, the ester content is large, or if more accurate results are desired, this error should be eliminated. For this purpose the amount of free alcohol is computed from the difference between the ester number of the original oil and the ester number of the acetylized oil (table I, p. 618, alcohol in original oil). To this is added the amount of esterified alcohol computed from the ester number. The sum is that of the percentage of total alcohol.

By way of illustration. A peppermint oil has yielded 26,43 as ester value before and 173,57 as ester value after acetylation. In order to ascertain the amount of total menthol present one proceeds as follows:

173,57 — 26,43 = 147,14 = 46,07 p. c. of free menthol;
26,43 = 7,36 p. c. of ester menthol;
hence total menthol = 46,07 + 7,36 = 53,43 p. c.

Without this recalculation the amount of total menthol, as computed from the ester value after acetylation, would be 55,59 p. c.

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[1]) When 1,50 g. of acetylized oil are used the alcohol content can be ascertained directly with the aid of table II on p. 632 from the number of cc. of half-normal potassium hydroxide solution employed.

The values obtainable from the ester content can also be expressed by means of the following formulas:

$$\%\text{ of free alcohol in the orig. oil} = \frac{m \cdot (a_2 - a_1)}{20 \cdot [s - (a_2 - a_1) \cdot 0{,}021]},$$

$$\%\text{ of total alcohol in the orig. oil} = \frac{m \cdot [a_2 \cdot s - (a_2 - a_1) \cdot a_1 \cdot 0{,}021]}{20 \cdot s \cdot [s - (a_2 - a_1) \cdot 0{,}021]}.$$

In the above formulas

m stands for the molecular weight of the respective alcohol,

a_1 for the number of cc. of half-normal potassium hydroxide solution consumed by s grams of the original oil,

a_2 for the number of cc. of half-normal potassium hydroxide solution consumed by s grams of acetylized oil.

Hence in both instances the amounts of potassium hydroxide solution pertain to equal amounts of oil.

For purely practical reasons the statements found in the second volume as to the total alcohol are made throughout without reference to the ester content of the original oils. In other words, they are the values derived directly from the ester values of the acetylized oil. For practical purposes this will suffice in general, as the differences are not appreciable. In the case of geranium oil, however, appreciable differences occur. This is due not only to the presence of a higher ester content, but also to the fact that the esterified alcohol of the original oil is combined with tiglic acid, whereas the formula considers only acetic acid. In this instance, therefore, the amount of originally esterified alcohol and the amount of free alcohol receive separate consideration; also the total amount of alcohol derived from the two is recorded. But here also the apparent alcohol content derived from the acetylation value (ester value after acetylation) is also recorded.

The reaction between alcohol and acetic acid anhydride is quantitative in the case of borneol, *iso*borneol, geraniol,[1]) menthol[2]) and santalol, hence enables an accurate determination of these substances. Less fortunate are the conditions with the tertiary alcohols linalool and terpineol, as these, on boiling with acetic acid anhydride, are partly decomposed by splitting off water

[1]) Bertram and Gildemeister, Journ. f. prakt. Chem. II. **49** (1894), 189.

[2]) Power and Kleber, Pharm. Rundsch. (New York) **12** (1894), 162; Arch. der Pharm. **232** (1894), 653.

with the formation of terpenes. Comparative figures, however, can also be obtained with these alcohols if the same amount of acetic acid anhydride is always used and the boiling continued for the same length of time. With linalool there was found as a favorable result after 2 hours of boiling, a deficiency of 15 percent of alcohol.[1]) Terpineol behaves toward acetic acid anhydride as follows:

Time of boiling:	Terpinyl acetate formed:
10 minutes	51,2 percent
30 „	75,5 „
45 „	84,4 „
2 hours	77,9 „ .

With terpineol, therefore, heating longer than 45 minutes has a detrimental effect.

Better results are obtained if the suggestion of Boulez[2]) is followed and a diluent in the ratio of 1:5 is employed. For this purpose either turpentine oil or xylene may be used. Turpentine oil, however, yields a small acetylation number for which a correction should be made, whereas xylene remains totally unchanged. At the same time the period of acetylation must be prolonged. Schimmel & Co.[3]) report that the maximum of ester determination is reached after boiling 5 to 7 hours. Longer boiling again reduces the amount of ester formed as shown by the following table.

Even with this modification, satisfactory results are obtained only with terpineol, whereas the accuracy of the results obtained with linalool leaves much to be desired. The quantitative acetylation reported to have been observed by Boulez depended on wrong computation as pointed out by Schimmel & Co.[3])

I. 20 parts linalool + 80 parts xylene.

Duration of acetylation	3 hrs.	5 hrs.	7 hrs.	12 hrs.	20 hrs.
Ester v.	53,3	60,4	63,0	63,3	51,6
% $C_{10}H_{18}O$	15,3	17,4	18,2	18,3	14,8
Found with reference to 100 parts of the alcohol	76,5	87,0	91,0	91,5	73,8

[1]) Report of Schimmel & Co. April **1893**, 45.

[2]) Corps gras industriels **33** (1907), 178; Bull. Soc. chim. IV. **1** (1907), 117.

[3]) Report of Schimmel & Co. April **1907**, 121.

II. 20 parts terpineol + 80 parts xylene.

Duration of acetylation	3 hrs.	4 hrs.	5 hrs.	7 hrs.	12 hrs.
Ester v.	55,2	67,7	68,8	68,1	65,1
% $C_{10}H_{18}O$	15,8	19,6	20,0	19,8	18,8
Found with reference to 100 parts of the alcohol	94,6	98,0	99,8	98,8	94,0

As in the case of the saponification, the presence of phenols and aldehydes exerts an unfavorable influence on the acetylation. If larger amounts of these substances are present they must be removed before the alcohol content can be determined. Citronellal, however, constitutes an exception. During the process of acetylation this is converted quantitatively into *iso*pulegyl acetate. Hence it can be assayed like an alcohol.[1]) In this case, however, two hours are necessary for the acetylation as well as for the saponification. It is also necessary to add the right amount of sodium acetate, namely about 2 gr. for every 10 cc. of oil and acetic acid anhydride. Unless these conditions are observed, incorrect values are obtained as becomes apparent from the experiments made in the laboratory of Schimmel & Co.[2])

	Grams of sodium acetate for every 10 cc. of oil and acetic acid anhydride		1 g.		2 g.		2,5 g.	
	Duration of acetylation		1 hr.	2 hrs.	1 hr.	2 hrs.	1 hr.	2 hrs.
Citronellal pure	Duration of saponification	1 hr.	79,7%	94,2%	82,1%	96,9%	91,0%	103,8%
		2 hrs.	77,3%	94,8%	82,4%	99,8%	95,9%	104,4%
Mixture of Citronellal . . 40,0 Geraniol . . . 40,0 Pinene 20,0	Duration of saponification	1 hr.	70,6%	76,2%	73,7%	78,8%	74,0%	79,0%
		2 hrs.	70,8%	76,9%	75,0%	80,3%	74,6%	79,9%

[1]) Report of Schimmel & Co. October **1896**, 43. According to more recent investigations by Semmler it would seem probable that all aldehydes, the CHO group of which is next to a CH or CH_2 group, react with acetic acid anhydride with the formation of mono esters. The aldehydes apparently change to the corresponding *enol* forms. For several aldehydes of this class Semmler has supplied the experimental proof. In the case of the change from citronellal to *iso*pulegyl acetate, the closing of the cycle is preceeded, according to Semmler, by the formation of an enol acetate. Berl. Berichte **42** (1909), 584, 963, 1161, 2014.

[2]) Comp. also Report of Schimmel & Co. April **1910**, 156.

Verley and Bölsing[1]) have tried to simplify the acetylation process. They esterify the oil with a definite amount of acetic acid anhydride in the presence of pyridine, titrate the acetic acid not combined with the alcohol, and compute the alcohol content. The method has not proven satisfactory with the terpene alcohols, but yields better results with the phenols. Hence it is applied, if at all, in connection with the latter (comp. p. 593).

In like manner, the attempts to apply Schryver's method for the determination of phenols (p. 592) to alcohols has proven a failure.[2])

FORMYLATION.

As has already been pointed out under citronellol (p. 365), this alcohol is converted into the formate when boiled with formic acid, whereas other terpene alcohols, such as geraniol and linalool, are either dehydrated to terpenes or are completely decomposed. The course of the reaction is so quantitative that it can be utilized for the assay of citronellol-containing oils.[3]) In the presence of larger amounts of other alcohols the results are apt to be too high, due to the disturbance in the ratio of constituents produced by the formation of water. For practical purposes, however, the results may suffice.

The formylation is effected by heating for an hour 10 cc. of oil with twice its volume of strong formic acid ($d_{15°}$ 1,226) in an acetylation flask either on a water bath or better still on a sand bath so as to maintain gentle boiling. If a water bath is used the mixture should be shaken repeatedly. When cooled the contents of the flask are diluted with water and washed until neutral. The remaining part of the process is conducted as described under acetylation.

The citronellol content can be computed with the aid of the following formula:

$$\% \; C_{10}H_{20}O = \frac{a \cdot 7{,}8}{s - a \cdot 0{,}014}$$

in which a represents the number of cc. of half-normal alcoholic

[1]) Berl. Berichte **34** (1901), 3354.

[2]) Report of Schimmel & Co. October **1904**, 129.

[3]) Report of Schimmel & Co. April **1901**, 47.

potassium hydroxide solution consumed in the saponification, and *s* the amount in grams of formylated oil saponified.

The above formula takes no account of the precence of citronellol ester in the original oil (comp. under acetylation, p. 576). Applied to mixtures of known citronellol content, Schimmel & Co. obtained the following results:

	Formylation for one hour	
	on the water bath	on the sand bath
25% Citronellol . . . 50% Geraniol . . . . 25% Limonene	27,9% Citronellol	27,1% Citronellol
40% Citronellol . . . 35% Geraniol . . . . 25% Pinene	42,5% Citronellol	41,3% Citronellol

In like manner, citronellal, which is converted into *iso*pulegylformate during the process of formylation, can be determined separately, whereas in the process of acetylation, the alcohols are determined as well. In this case, however, the value of 7,7 should be substituted for that of 7,8 in the above formula.

DETERMINATION OF ALDEHYDES AND KETONES.

Although attempts have been made repeatedly to work out a general method for the determination of aldehydes and ketones, this problem has not yet been solved in a satisfactory manner. Failure has been due to the fact that not all aldehydes and ketones react equally well with a given reagent, but that in each case only a few yield quantitative results. The first attempt in this direction was made by Benedikt and Strache.[1]) According to their method the aldehyde or ketone content of a volatile oil is determined by means of the carbonyl oxygen it contains. The oil to be investigated is heated with a weighed amount of phenyl

[1]) Monatsh. f. Chem. 14 (1893), 270. Watson Smith has tried to improve on the method by driving over the nitrogen with a current of carbon dioxide and not with steam as suggested by Benedikt and Strache. Chem. News **93** (1906), 83. According to Chem. Zentralbl. **1906**, I. 1289. Comp. also Report of Schimmel & Co. October **1906**, 103.

hydrazine, after some time the hydrazone which has formed is separated by filtration, and the unchanged phenyl hydrazine in the filtrate oxidized with boiling Fehling's solution. By this treatment all the nitrogen of the phenyl hydrazine which has not taken part in the reaction is liberated as gas. From the volume of the collected nitrogen the amount of the unused phenyl hydrazine can be calculated. From this the amount which has gone into combination is known and consequently the amount of the ketone or aldehyde present. The amount of carbonyl oxygen, expressed in $^1/_{10}$ percents is designated as carbonyl number.

With bitter almond oil (benzaldehyde), cumin oil (cuminic aldehyde), and rue oil (methyl nonyl ketone) this method yields fairly good results. With cassia oil, caraway oil, fennel oil and lemon oil, however, the determinations fall far too low,[1]) possibly because the time allowed does not suffice for the quantitative completion of the reaction.

The modification of the above method proposed by Rother[2]) has met with a similar fate. It likewise yields satisfactory results in a few instances only. The aldehydes and ketones are converted into phenylhydrazones by means of a definite amount of phenylhydrazine. It differs, however, from the original method in this that the excess of phenylhydrazine is allowed to react with iodine and the excess of iodine is titrated with thiosulphate solution.

For the assay of aldehydes and ketones we are, therefore, dependant on several methods, of which the most important in actual practice are here described. The determination is mostly volumetric or titrimetric, seldom gravimetric. The best known and most commonly used method is the

Bisulphite method. It was first introduced in 1890[3]) by Schimmel & Co. for the cinnamic aldehyde assay of cassia oil. At present it plays an important role in the assay of oils containing cinnamic aldehyde or citral. The method depends on the property of both cinnamic aldehyde and citral to dissolve in hot concentrated sodium bisulphite solution with the formation of sulphonates, hence can be abstracted quantitatively from the oils, whereas the

[1]) Report of Schimmel & Co. October **1893**, 52.

[2]) *Die Bestimmung der Aldehyde und Ketone zur Beurteilung ätherischer Öle. Inaug. Dissert.* Dresden 1907.

[3]) Report of Schimmel & Co. October **1890**, 15.

non-aldehyde constituents remain undissolved. The amount of dissolved oil reveals its aldehyde content.

For this determination a special glass flask (cassia flask, aldehyde flask, fig. 75) is used. It has a capacity of about 100 cc., is provided with a neck 13 cc. long, the inner diameter of which is 8 mm., and which is calibrated into $^1/_{10}$ cc. The entire neck of the flask has a capacity of about 6 cc. The zero point of the scale is placed slightly above the transition point of the flask into the neck.

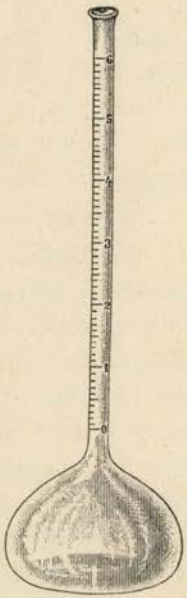

Fig. 75.

By means of a pipette, 10 cc.[1]) of oil are transferred to the flask and an equal volume of 30 p. c. sodium acid sulphite[2]) solution is added. The mixture is shaken and the flask placed in a boiling water bath. After the solid mass has become liquid more acid sulphite solution is added until the flask is at least three-quarters full, the mixture being constantly heated and occasionally shaken. The solution is heated until no more solid particles are visible and the odor of aldehyde has disappeared. When the clear oil floats upon the salt solution, flask and contents are allowed to cool and sufficient acid sulphite solution is added until the oily layer is well within the neck of the flask. Should drops of oil adhere to the flask these are induced to rise into the neck by gentle tapping and rotation of the flask. The number of cc. of oil is read off, and by deducting this number from ten, the aldehyde content in percentage by volume is ascertained by multiplying the resultant with ten. In order to obtain the percentage by weight the number obtained is multiplied with the specific gravity of the aldehyde in question and the product divided by the specific gravity of the oil.

[1]) In the case of oils that contain less than 40 p. c. of aldehyde only 5 cc. are taken or a flask is used the neck of which has a capacity of 10 cc. and is calibrated from 1 to 10.

[2]) Care should be taken that the solution does not contain too much free sulphurous acid since this retards the reaction. If necessary, the solution should be neutralized somewhat by the addition of sodium carbonate.

As already pointed out, this method is used for the quantitative determination of cinnamic aldehyde and citral, which go into solution as sulphonates. It can, however, be used also in connection with those aldehydes the bisulphite addition products of which are soluble in water as such, *e. g.* benzaldehyde, anisic aldehyde, phenyl acetaldehyde. 10 cc. of the aldehyde in question are shaken with 40 to 50 cc. of a 30 p. c. sodiumbisulphite solution in an aldehyde flask, and the reaction product dissolved, with the aid of gentle heat, in additional water (not sodium bisulphite solution). The oil that has not taken part in the reaction is driven into the calibrated neck by adding more water. Its volume is read off as soon as the contents of the flask have assumed room temperature. Prolonged standing frequently causes the bisulphite compound to crystallize out again.

Closely related to the bisulphite method is the

Sulphite method, which is based on the observation that certain aldehydes and ketones react with neutral sodium sulphite to form water soluble compounds with the simultaneous formation of sodium hydroxide. In as much as the latter tends to reverse the reaction, it should be neutralized with dilute acid from time to time as it is formed. It was Tiemann[1]) who, in connection with his studies on citral, first pointed to the application of this reaction for quantitative determinations. Somewhat later Sadtler[2]) claimed that the method was generally applicable for the quantitative determination of saturated and unsaturated aldehydes both of the aliphatic and aromatic series, and was also applicable in the case of several ketones. According to his method the free alkali is titrated with half-normal hydrochloric acid. It suffers from the disadvantage that the sodium sulphite solution cannot be titrated sharply, hence the end of the reaction can be determined only approximately. Accurate results are, therefore, not obtainable.

Practical significance the sulphite method has acquired only through the modification suggested by Burgess.[3]) The process is as follows:

[1]) Berl. Berichte **31** (1898), 3317.

[2]) Americ. Journ. Pharm. **76** (1904), 84; Journ. Soc. chem. Industry **23** (1904), 303; Journ. Americ. chem. Soc. **27** (1905), 1321.

[3]) Analyst **29** (1904), 78.

To 5 cc. of the oil to be examined and contained in a cassia flask[1]) a freshly prepared saturated (40 p. c.) solution of neutral, crystalline sodium sulphite and a few drops of phenolphthalein are added. The mixture is heated in a water bath while frequently shaken. The sodium hydroxide set free is almost neutralized from time to time with dilute acetic acid (1 : 5) until even the addition of more sodium sulphite solution causes no further reddening while the mixture is being heated. Water is then added to drive the non-dissolved oil into the neck of the flask where, upon cooling, its volume is read off on the scale. Multiplication of the number of cc. of oil with 20 yields the volume percentage of aldehyde or ketone in the oil.

Although this method is by no means as applicable[2]) as claimed by Sadtler and Burgess, it is applicable in several cases where the bisulphite method fails. Its principal value lies in the possibility to assay carvone and pulegone, of which the former reacts smoothly and rapidly with neutral sodium sulphite. In the case of pulegone the reaction is much slower, several hours being required at times to bring the process to completion.

Satisfactory results are also obtained with citral and cinnamic aldehyde. It should be remembered, however, that the results may deviate somewhat from those obtained with the bisulphite method in the case other aldehydes are present. This is true *e. g.* in the case of lemongrass oil which gives higher results with the bisulphite method than with the sulphite method. This is due to the fact that neutral sodium sulphite reacts with citral only whereas the other aldehydes present in lemongrass oil, likewise a part of the methylheptenone react with the bisulphite. It is urged, therefore, that in connection with statements as to the aldehyde content of oils, the method be mentioned according to which the aldehyde assay was made.

Which of the two methods is to be preferred in individual cases depends alltogether on the nature of the oil in question.

[1]) Burgess makes use of a flask of 200 cc. capacity which differs from the ordinary cassia flask in being furnished with a tube, attached to the side of the neck, that leads to the bottom of the flask and serves for the addition of the liquids. The common cassia flasks, however, are much more convenient and serviceable, but it is best to use one with 200 cc. capacity and to take 10 cc. of oil for the sake of greater accuracy.

[2]) Report of Schimmel & Co. April **1905**, 103.

According to Burgess, one of the advantages of the sulphite method consists in the absence of crystalline deposits which are occasionally formed at the zone of contact between oil and water in the case of the bisulphite method and which disturbing factor at times prevents an accurate reading of the volume of the oily layer. Schimmel & Co., however, observed that such depositions are also produced in the case of the sulphite method.

For the assay of cinnamic aldehyde the gravimetric method of Hanuš[1]) can be utilized. It yields very accurate results and is especially applicable when only small amounts of oil are available. In the case of the Ceylon cinnamon oil, the results deviate from those obtained with the bisulphite method by as much as 4 to 5 p. c., even if the latter are computed in percentage by weight. Presumably this difference is due to the presence of other aldehydes which are determined with the cinnamic aldehyde by the bisulphite method.[2])

Hanuš separates the cinnamic aldehyde as semioxamazone

$$\begin{array}{l} CONH \cdot N : CH \cdot CH : CH \cdot C_6H_5 \\ | \\ CONH_2 \end{array}$$

and proceeds according to the following method:

To 0,15 to 0,2 g. of oil, contained in a 250 cc. Erlenmeyer flask, 85 cc. of water are added and the oil finely divided by shaking. In order to make possible a fine division of the oil and thus to prevent a part of the aldehyde to be coated by semioxamazone thereby preventing it from taking part in the reaction, it is expedient to dissolve the oil in 10 cc. of alcohol (95 to 96 percent by volume) before adding the water. One and one-half times the amount of semioxamazide,[3]) dissolved in 15 cc. of hot water, are then added and the mixture shaken thoroughly for 5 minutes. It is then set aside for 24 hours with occasional shaking. Care should be taken to shake the mixture repeatedly during the first three hours. The flocculent precipitate of semi-

[1]) Zeitschr. Untersuch. der Nahrungs- u. Genußmittel **6** (1903), 817. Comp. also Report of Schimmel & Co. April **1904**, 19.

[2]) Report of Schimmel & Co. April **1904**, 21.

[3]) As to the method of preparation comp. Kerp and Unger, Berl. Berichte **30** (1897), 585; also Weddige, Journ. f. prakt. Chem. **10** (1874), 196.

oxamazone is filtered by means of a Gooch crucible (prepared with asbestos, dried and weighed), washed with cold water and dried at 105° until of constant weight. If *a* is the amount of cinnamic aldehyde semioxamazone, *s* the amount of oil used, the percentage of cinnamic aldehyde can be computed with the aid of the formula

$$\frac{a \cdot 60{,}83}{s}$$

This method can also be used for determining the amount of cinnamic aldehyde in cinnamon bark. For this purpose Hanuš gives special directions.

For the determination of small amounts of aldehyde neither the bisulphite nor the sulphite method is adapted since both yield results that may vary from 1 to 2 p. c. Hence the error is too great for small amounts of aldehyde. For cinnamic aldehyde the method of Hanuš affords a reliable assay in such cases.

Small amounts of benzaldehyde can be determined, according to Hérissey,[1]) as phenylhydrazone according to the following method:

50 cc. of the solution to be examined, which should contain only so much aldehyde as to yield 0,1 to 0,25 g. of phenylhydrazone, are mixed with a solution of 0,5 cc. freshly distilled phenylhydrazine and 0,25 cc. glacial acetic acid in 50 cc. of water and the mixture heated for 20 to 30 minutes on a water bath. After 12 hours the phenylhydrazone formed is filtered through a weighed Gooch crucible, washed with 20 cc. water and dried in a vacuum desiccator.

Very similar is the method of Denis and Dunbar.[2]) Woodman and Lyford[3]) have suggested a colorimetric method for this purpose which need not be considered here.

The problem of the citral assay of lemon oil, which contains about 4 to 7 p. c. of this aldehyde, has received much attention from chemists, particularly in recent years. Of the many methods proposed not one has thus far been found practi-

[1]) Journ. de Pharm. et Chim. VI. **23** (1906), 60.

[2]) Journ. Ind. and Eng. Chem. **1909**, 256. According to Chem. Ztg. Repert. **33** (1909), 281.

[3]) Journ. Americ. chem. Soc. **30** (1908), 1607.

cable since all fall short in the desired degree of accuracy. (For details see under oil of lemon.) If approximate results are sufficient the method proposed by Walther[1]) and as improved by A. H. Bennet[2]) can be recommended: To a mixture of 20 cc. lemon oil with 20 cc. alcoholic (80 p. c. alcohol) half-normal hydroxylamine hydrochloride solution, 8 cc. of alcoholic normal potassium hydroxide solution and 20 cc. of strong, aldehyde-free alcohol are added and the whole boiled for $^1/_2$ hour, the flask being connected with a reflux condenser. After cooling the contents are diluted with 250 cc. of water, part of which is used to rinse the condenser. The hydrochloric acid still combined with hydroxylamine is then neutralized, phenolphthalein being used as indicator. The hydroxylamine not combined with citral can now be titrated with half-normal sulphuric acid, the end of the reaction being ascertained by testing a drop at a time with dilute methylorange solution. A blank test is made in like manner without lemon oil for the purpose of determining the hydroxylamine factor. The difference between the number of cc. of half-normal sulphuric acid used in both tests reveals the amount of hydroxylamine that has entered into reaction. By multiplying this with 0,076 the amount of citral can be computed.

As has been ascertained by Schimmel & Co.[3]) the results obtained by this method average about 10 p. c. too low as compared with the amount of citral present. For lemon oils, with their low citral content, the error may not be too great, but for oils, such as lemongrass, with a high percentage of aldehyde the method cannot be used.

Vanillin. For the assay of vanillin, its compounds with β-naphthylhydrazine und *p*-bromphenylhydrazine may, according to Hanuš,[4]) be utilized. For every part of vanillin 2 to 3 parts of hydrazine are taken. After 5 hours the reaction products are collected in a Gooch crucible, washed, and dried at 90 to 100° until of constant weight.

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[1]) Pharm. Zentralh. **40** (1899), 621; **41** (1900), 614.

[2]) Analyst **34** (1909), 14. According to Zentralbl. **1909**, I. 593.

[3]) Report of Schimmel & Co. October **1909**, 153.

[4]) Zeitschr. Untersuch. der Nahrungs- u. Genußmittel **3** (1900), 531. According to Chem. Zentralbl. **1900**, II. 693.

For the determination of vanillin in the presence of piperonal Hanuš[1]) has, likewise, worked out a method. It is based on the condensation of vanillin with platinum hydrogen chloride, whereby presumably dehydrovanillin results. If the conditions of the reaction, as determined by Hanuš are carefully observed, vanillin reacts quantitatively whereas piperonal remains unchanged.

A quantitative method for the separation of vanillin, cumarin and acetanilid has been published by Winton and Bailey.[2])

The assay of citronellal is acomplished by means of acetylation (comp. p. 579). The bisulphite method is not applicable in this case because the citronellal sulphonate is very difficultly soluble in the bisulphite solution. Hence it remains suspended in both the aqueous and oily layers and renders even an approximate reading impossible. Neither is the sulphite method serviceable although it is possible to bring the citronellal into solution gradually if the mixture is heated for a longer period and if acetic acid is added from time to time without reference to any alkalinity of the solution.

Ketones. As already pointed out, carvone and pulegone can be assayed by means of the sulphite method. This is particularly important in the case of carvone, since the absence of a practicable method was formerly keenly felt.

The method proposed some years ago by Kremers and Schreiner[3]) yields very inaccurate results. According to this method, the carvone is converted into the oxime, this is separated from the other constituents by steam distillation and weighed. The difficulty lies in determining the point when the distillation should be interrupted, hence a sharp separation of the slightly volatile carvoxime from the other constituents of the oil is impossible. A titrimetric method proposed by Walther,[4]) which also makes use of hydroxylamine, has likewise not attained practical significance.

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[1]) Zeitschr. Untersuch. der Nahrungs- u. Genußmittel **3** (1900), 657. According to Chem. Zentralbl. **1900**, II. 1165.

[2]) Pharmaceutical Journ. **75** (1905), 476.

[3]) Pharm. Review **14** (1896), 76. Comp. also Alden and Nolte, Pharmaceutical Archives **2** (1899), 81 and Kremers, Journ. Soc. chem. Industry **20** (1901), 16.

[4]) Chem. Ztg. Repert. **23** (1899), 264.

Menthone. Thus far the direct assay of menthone has not been a success. Hence one is still dependent on the indirect method first proposed by Power and Kleber,[1]) whereby the ketone is reduced to menthol by means of sodium and alcohol, and the menthol determined quantitatively. As has been shown in connection with mixtures of known menthone content, approximate results only are obtained. For practical purposes they may, however, suffice in most instances. The assay is carried out as follows: 15 cc. of oil, contained in a round bottomed flask, are diluted with about four times their volume of absolute alcohol,[2]) the flask connected with a reflux condenser and the solution heated to boiling. To the boiling solution 5 to 6 g. metallic sodium are added very gradually. After all of the sodium has been consumed, the mixture is allowed to cool, diluted with water and acidulated with acetic acid. By means of a separating funnel the oil is separated from the aqueous liquid, washed repeatedly with sodium chloride solution for the purpose of removing completely the ethyl alcohol, and dried with anhydrous sodium sulphate. By means of acetylation the menthol content of the original as well as that of the reduced oil is ascertained, thus revealing the amount of menthol produced by the reduction. From this the amount of menthone contained in the original oil can be computed. If the original oil contained m_1 % total menthol, and the reduced oil m_2 %, the percentage of menthone of the original oil follows from the formula

$$\frac{(m_2 - m_1) \cdot 154}{156}.$$

Ionone. For the quantitative determination of ionone see p. 468.

PHENOL DETERMINATION.

For the determination of phenols the method of shaking out with dilute sodium hydroxide solution has proven satisfactory.

[1]) Pharm. Rundsch. (New York) 12 (1894), 162; Arch. der Pharm. 232 (1894), 655.

[2]) Absolute alcohol is preferable to such containing water, since the reduction is more complete and the sodium alcoholate formed is kept better in solution. Beckmann, Journ. f. prakt. Chem. II. 55 (1897), 18.

It was first applied by Gildemeister[1]) to oil of thyme, is readily carried out and for practical purposes is sufficiently accurate. In as much as all phenols yield water-soluble compounds with the alkalies, the method is quite generally applicable for volatile oils. However, as has been pointed out by Schimmel & Co.,[2]) the concentration of the alkali[3]) has to be chosen with reference to the phenol to be determined. For thymol or carvacrol-containing oils (oils of ajowan, thyme, Cretian origanum oil) a five percent, solution is employed as originally suggested by Gildemeister *(loc. cit.)*. Eugenol-containing oils (oils of clove, clove stems, pimenta, bay and cinnamon leaves), however, are to be shaken out with a three percent. solution. If in the latter case a stronger solution is used, the results obtained are too high, for the excess of alkali together with the eugenol alkali exercice a solvent capacity on the nonphenol constituents, more particularly those containing oxygen. It may happen that oils with a high eugenol content are completely dissolved in the alkali. For this reason Umney's[4]) proposition to use a 10 to 12 p. c. caustic potash solution is to be rejected, for the results obtained are always too high. The idea might readily suggest itself always to use a three percent solution. However, it has been shown that thymol and carvacrol are not quantitatively removed by such a solution.

The assay is conducted in the following manner: To 10 cc. of oil contained in a cassia flask that has a capacity of at least 100 cc. (fig. 75, p. 583) enough three or five percent. caustic soda solution is added to fill the flask about four-fifths. The mixture is thoroughly and repeatedly shaken. That portion of the oil which has not entered into reaction is driven into the neck of the flask by the addition of more lye. Gentle tapping or rotation of the flask are resorted to, if necessary, to cause any oily drops that adhere to the glass walls to rise into the neck. After all of the nonphenols have risen into the neck, a process that usually

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[1]) Hager, Fischer and Hartwich, *Kommentar zum Arzneibuch für das Deutsche Reich. 3. Ausgabe.* Berlin 1892. 1. Ed., Vol. II, p. 377.

[2]) Report of Schimmel & Co. April 1907, 118.

[3]) It should be specially mentioned that it makes no difference whether soda lye or potash lye be used. Because of the higher molecular weight of the latter, somewhat more solution, however, will have to be used.

[4]) Pharmaceutical Journ. III. 25 (1895), 951.

requires several hours, their volume is read off by means of the calibration. Substracting this number from 10 yields the amount of oil dissolved and multiplication of this number with 10 the phenol content of the oil expressed in volume percent.

In the case of oil of cloves, the mixture is heated in a water bath for 10 minutes. The object of this is to saponify the aceteugenol, which is of equal value in the assay of the oil, and to determine it together with the free eugenol.

In place of the cassia flask a large burette can be used. In as much as these burettes, as a rule, have a capacity of but 60 cc., they should be used only where a five percent lye is applicable. Otherwise it might occur that the amount of alkali should prove insufficient for the complete solution of the phenol. In the case of oil of cloves a cassia flask will be used for the reason that the mixture is to be heated on a water bath.

If for the purpose of identification the phenol is to be isolated, the phenol-containing lye is separated from the oil, filtered through a moist, hardened filter, and the phenol regenerated by means of dilute sulphuric acid. The liberated phenol is shaken out with ether, the solution transferred to an evaporating dish, and the ether evaporated. The residual phenol can be identified by means of suitable derivatives. Thymol is identified readily since it solidifies upon cooling either by itself or when inocculated with a fragment of thymol.

Other methods for the quantitative determination of phenols have been worked out by Schryver, by Verley and Boelsing, and by Hesse. However, they are not used as commonly as the one described. Under special circumstances, however, the one or the other method may prove useful, more particularly if only little oil is available.

Schryver[1]) makes use of the property of sodium amide, $NaNH_2$, to react with the phenols in such a way that the phenol hydrogen is replaced by the sodium and ammonia is set free. The latter is combined with acid and titrated.

The process is carried out in the following manner: About 1 g. of sodium amide is reduced to a fine powder, washed two or three times by decantation with benzene, and transferred to

[1]) Journ. Soc. chem. Industry 18 (1899), 553.

a 200 cc. flask with a wide neck, which is provided with a separating funnel and a condenser. 50 to 60 cc. of benzene free from thiophene are then transferred to the flask and boiled on a water bath. At the same time air free from carbon dioxide is drawn into the flask by means of a suction pump and through the separating funnel, the stem of which passes beneath the surface of the benzene. After boiling for ten minutes the last traces of ammonia adhering to the sodium amide have been drawn off. 20 cc. of normal sulphuric acid are then given into a receiver and this connected with the condenser. Now a solution of 1 to 2 g. of the phenol or of the volatile oil are allowed to flow slowly from the separating funnel into the boiling mixture of sodium amide and benzene. The separating funnel is washed with some benzene and air is sucked through the apparatus until all of the ammonia has been absorbed by the acid in the receiver. This usually requires one and a quarter hours. Finally, the excess of sulphuric acid in the receiver is titrated with sodium carbonate solution, methyl orange being used as indicator. The result is expressed as percent of phenol or, in the case of unknown phenols, as hydroxyl number. The "hydroxyl value" is defined by Schryver as the number of cc. of normal sulphuric acid necessary to neutralize the ammonia set free by 1 g. of substance if the conditions described above are followed.

This method, which determines only free phenols, is appliciable only for such oils that are free from alcohols, aldehydes and ketones, to those oils that are mixtures of phenols and terpenes.[1]) On account of the great capacity of the amide to react with water, the oils must be, in addition, absolutely free from moisture.

The method of Verley and Bœlsing[2]) is based on the observation that the phenols react energetically in the cold with acetic acid anhydride provided pyridine be present. The acetic acid resulting combines directly with pyridine. In as much as pyridine is neutral towards phenolphthalein, the acetic acid not combined with phenol can be determined titrimetrically. For the assay about 3 g. of oil are heated for 15 minutes with 25 cc. of a mixture of 120 g. acetic acid anhydride and 880 g. pyridine

[1]) Report of Schimmel & Co. October 1904, 129.

[2]) Berl. Berichte 34 (1901), 3354.

in a 200 cc. flask without condenser on a water bath. Upon cooling an equal volume of water is added to convert any unchanged acetic acid anhydride into acetic acid, *i. e.*, into pyridine acetate. The acetic acid not combined with phenol is then titrated back, using phenolphthalein as indicator. In like manner the acetic acid content of 25 cc. of the mixture is established. Subtraction reveals the amount of acetic acid combined with the phenol, whence the phenol content of the oil can be computed.

Phenol present as ester, *e. g.*, aceteugenol in oil of cloves, is not determined by this method. However, it should be noted that the oils to be examined should contain no alcohols since these react like the phenols.

According to the method proposed by Hesse,[1]) phenols and more particularly phenol carboxylic esters, such as salicylic acid, can be determined. The oil to be examined is dissolved as such, or after previous dilution with an indifferent solvent (benzyl alcohol) in three parts of anhydrous ether. To the cooled solution half-normal alcoholic potassium hydroxide is carefully added, when the potassium compound of the phenol or phenolcarboxylic ester separates in crystalline form. The crystals are filtered off, washed with anhydrous ether, and decomposed with carbonic acid. The amount of phenol or ester set free can be determined by weight. If, in the case of small amounts, the alkali formed is to be determined titrimetrically, a considerable excess of potassium hydroxide should be avoided, otherwise it may occur that solid alkali as well as potassium phenylate may separate out.

In addition to these general methods several special methods are known which may here be described.

For the determination of thymol and carvacrol in volatile oils Kremers and Schreiner[2]) have worked out a method. It is a modification of the method recommended by Messinger and Vortmann[3]) and depends upon the property of these phenols to combine, in alkaline solution, with iodine to a red iodine thymol

[1]) Chem. Zeitschr. **2** (1903), 434.
[2]) Pharm. Review **14** (1896), 221.
[3]) Berl. Berichte **23** (1890), 2753.

compound which is precipitated. The excess of iodine, after acidulation of the liquid, can be titrated back with sodium thiosulphate solution. Every molecule of thymol, respectively carvacrol, requires 4 atoms of iodine for precipitation.

The process for thymol, which differs slightly from that for carvacrol, is as follows:

5 cc. of the oil to be assayed are weighed, transferred to a glass-stoppered burette that is calibrated into $^1/_{10}$ cc., and diluted with about an equal volume of petroleum ether. Five p. c. soda solution is added, the mixture well shaken and then allowed to separate. Complete separation having resulted, the alkaline solution is allowed to flow into a 100 cc. measuring flask and the shaking out with alkali solution repeated as often as a diminution of volume results.

The alkaline thymol solution is diluted with 5 p. c. sodium hydroxide solution to 100 cc. or, if necessary, to 200 cc.

To 10 cc. of this solution, transferred to a 500 cc. measuring flask, a slight excess of $\frac{N}{10}$ iodine solution is added causing the thymol to be precipitated as a dark brown iodine compound. In order to test whether sufficient iodine has been added, a few drops are transferred to a test tube and several drops of hydrochloric acid added. If a sufficient amount of iodine has been added, the solution is colored brown by free iodine, otherwise it becomes milky due to precipitated thymol. An excess of iodine having been added, the solution is acidified with dilute hydrochloric acid and diluted to 500 cc. In 100 cc. of the filtrate the excess of iodine is titrated by means of $\frac{N}{10}$ sodium thiosulphate solution.

The number of cc. of thiosulphate solution are deducted from the volume of iodine used and the resultant multiplied by five, this product indicating the total amount of iodine used by the thymol.

Each cc. of $\frac{N}{10}$ iodine solution consumed corresponds to 0,0037528 g. thymol.

From the amount of thymol found in the alkaline solution the percentage of phenol in the original oil can readily be computed.

The reaction can be expressed by means of the following equation:

$$C_{10}H_{14}O + 4I + 2NaOH = C_{10}H_{12}I_2O + 2NaI + 2H_2O.$$

In the assay of carvacrol a slight modification becomes necessary because the carvacrol iodide separates milky. In order to cause the formation of a precipitate the mixture is shaken thoroughly after the iodine has been added and then filtered. It is only then that the solution is acidified with hydrochloric acid. The process after that is the same as for thymol. The computation is likewise the same.

A method for the assay of eugenol in caraway oil has been suggested by Thoms.[1]) The method is based on the separation of eugenol as benzoyl eugenol. It enjoys the advantage that a melting point determination reveals identity as well as purity of the separated phenol. Somewhat later Thoms[2]) modified this method by removing the sesquiterpenes, which interfere at times, before adding the benzoyl chloride. He enlarged upon it by taking into consideration the eugenol acetate occurring in the oil.

Assay of total eugenol. 5 g. of oil of cloves, contained in a 150 cc. beaker, are saponified with 20 g. of 15 p. c. caustic soda solution by heating on a water bath for half an hour. When still warm the contents of the beaker are transferred to a separating funnel with a short tube. After complete separation of the two layers, the solution of eugenol sodium is transferred back to the beaker. The sesquiterpenes remaining in the separating funnel are washed twice, each time with 5 cc. of 15 p. c. caustic soda solution and the lye in each case added to the eugenol sodium solution. 6 g. of benzoyl chloride are now added and the mixture shaken thoroughly until a uniform mixture has been obtained. In a few minutes the ester formation has taken place with appreciable rise of temperature. Any excess of benzoyl chloride is destroyed by brief heating on the water bath. After cooling 50 cc. of water are added, the mixture heated until the crystalline ester has been liquified, and again allowed to cool. The supernatant, clear liquid is removed by filtration, allowing the crystalline cake to remain in the beaker. Again 50 cc. of

[1]) Berichte d. deutsch. pharm Ges. **1** (1891), 278.

[2]) Arch. der Pharm. **241** (1903), 592.

water are added, heated on a water bath until the ester has melted, cooled and filtered. Finally, the ester is washed a third time in like manner with 50 cc. of water. The excess of caustic soda and sodium salts are then regarded as having been removed.

Any crystalline particles that have been cought in the filter are retransferred to the beaker. The benzoyl eugenol, while still moist, is dissolved in 25 cc. of alcohol (90 p. c. by weight) with the aid of the heat of the water bath and gentle agitation. Even after the beaker has been removed from the water bath, the shaking is continued until the benzoyl eugenol has crystallized out. This takes place within several minutes. The temperature of the mixture is lowered to 17°, the precipitate collected on a filter 9 cm. in diameter, and the filtrate collected in a graduated cylinder. About 20 cc. of filtrate are thus obtained. The alcoholic solution that has been retained by the crystalline magma in the filter is displaced by 90 p. c. (by weight) alcohol until the filtrate amounts to 25 ccm. The moist filter and precipitate are then transferred to a weighing dish (the latter together with the filter dried at 101° having been weighed previously), and dried at 101° until of constant weight. In as much as 25 cc. of 90 p. c. alcohol dissolve 0,55 g. of pure benzoyl eugenol at 17°, this amount should be added to the amount weighed.

If a stands for the amount of benzoic ester found, b for the amount of clove oil employed (about 5 g.), and if 25 cc. of alcoholic solution of ester are removed by filtration in accordance with the above directions, then the percentage of eugenol in clove oil is indicated by the formula

$$\frac{4100 \cdot (a + 0{,}55)}{67 \cdot b}.$$

This formula results from the two equations:

(Benzoyl eugenol) (Eugenol)

$$268 : 164 = (a + 0{,}55) : \text{the amount of eugenol found.}$$

$$\text{Eugenol} = \frac{164 \cdot (a + 0{,}55)}{268}.$$

$$\text{Hence } b\text{: } \frac{164 \cdot (a + 0{,}55)}{268} = 100 : x.$$

$$x = \frac{164 \cdot (a + 0{,}55) \cdot 100}{268 \cdot b} = \frac{4100 \cdot (a + 0{,}55)}{67 \cdot b}.$$

Assay of free eugenol. 5 g. of clove oil dissolved in 20 g. ether are quickly shaken out in a separating funnel with 20 g. of 15 p. c. caustic soda solution. The eugenol sodium solution is transferred to a beaker and the ethereal solution of sesquiterpenes is washed twice with 5 g. each of caustic soda solution of like strength. The united alkaline solutions are heated on a water bath for the purpose of driving off the ether and the benzoylation carried out in the manner described above.

Thus the free eugenol as well as that present as ester can be determined quantitatively. Thom's method can be applied equally well to other eugenol-containing oils provided they contain no free alcohols.

METHYL NUMBER.

A number of volatile oils contain as important constituents methyl and ethyl ethers of phenols and acids, the alkyl groups of which can be determined according to Zeisel's method.[1]) Benedikt and Grüssner[2]) have recommended the quantitative methoxyl determination for the practical and scientific investigation of volatile oils, and have shown its usefulness by a series of illustrations. They designate as methyl number that number which tells how many mg. of methyl 1 g. of substance splits off when boiled with hydriodic acid. Ethyl or propyl and *iso*propyl are here considered as having been replaced by the equivalent amount of methyl. The weighed amount of silver iodide is therefore in all cases calculated as methyl.

The vapors of methyl iodide formed by boiling from 0,2 to 0,3 g. of the oil to be investigated with hydriodic acid (sp. gr. 1,70, to which, according to Herzig[3]) 8% of acetic acid are added) are first passed through some warm water in which some phosphorus is suspended, so as to retain any iodine vapors which may have been carried over. After the methyl iodide has passed through this apparatus it is passed into an alcoholic solution of silver nitrate and the separated silver iodide weighed.

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[1]) Monatsh. f. Chem. **6** (1885), 989.
[2]) Chem. Ztg. **13** (1889), 872, 1087.
[3]) Monatsh. f. Chem. **9** (1888), 544.

A very convenient apparatus has been designed by L. Ehmann[1]) for carrying out this determination.

Gregor[2]) has recently suggested to replace the phosphorus suspended in water by a solution of one part each of potassium bicarbonate and arsenous acid in 10 parts of water, by which not only the iodine vapors but also any hydriodic acid carried over is retained. For collecting the methyl iodide Gregor uses a $^1/_{10}$ normal silver nitrate solution which has been acidified with nitric acid and titrates back the silver not used for the precipitation of the silver iodide with $^1/_{10}$ normal potassium sulphocyanate solution according to Volhard.

Of the oils investigated by Benedikt and Grüssner the following gave no methyl numbers: the oils of wormwood, bitter almond, angelica, bergamot, caraway, lemon, copaiba-balsam, coriander, cubeb, elemi, eucalyptus, geranium, juniper, cherry laurel, lavender, spearmint, peppermint, olibanum, oil of *Pinus montana,* savin, East Indian and West Indian sandalwood, turpentine and valerian.

High methyl numbers were given by anise oil, star anise oil and fennel oil on account of their content of anethol and methyl chavicol, by clove oil, clove stem oil and oil of cinnamon leaves on account of their content of eugenol. In wintergreen oil the high methyl number is due to the methyl salicylate, in parsley oil to the apiol, and in calamus oil to its asarone[3]) content.

The determination is applicable only to oils absolutely free from alcohol, as ethyl alcohol itself gives a methyl number, from which it follows, that this method may also be used for the quantitative estimation of alcohol in those oils which in their pure condition do not contain any methoxyl groups.[4])

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[1]) Description and illustration of the apparatus are to be found in Chem. Ztg. **14** (1890), 1767.

[2]) Monatsh. f. Chem. **19** (1898), 116.

[3]) Thoms and Beckstrœm, Berl. Berichte **35** (1902), 3191.

[4]) The methyl numbers of some of the oils examined by Benedikt and Grüssner can be explained only by assuming the presence of alcohol. It is to be regretted that the physical constants of the oils were not recorded so that some judgement might be passed on their purity. For the Ceylon cinnamon oil marked No. 22 in the paper of Benedikt and Grüssner they find 25,7 as methyl number and compute therefore a 28,1 p. c. eugenol content. In as much as pure Ceylon cinnamon oil contains only 4 to 8 p. c. eugenol, it would seem to follow (provided the methyl number found was due only

CINEOL DETERMINATION.

In addition to fractional distillation, several methods for the assay of cineol have been recommended. They all depend on the capacity of cineol to form addition products with certain other compounds. The description of the individual method is here given.

1. *Distillation method.*[1]) The oil to be examined is fractionated, fractions of two degrees each being collected, placed in a freezing mixture and their temperature reduced to — 15 to — 18°. Attempts are then made to cause them to congeal by shaking or by introducing a cineol crystal. After having stood in the freezing mixture for an hour, the liquid portion is drawn off by means of a pipette drawn out to a fine point. With some experience a well nigh dry mass of crystals can be obtained, from which the last traces of liquid can be removed by shaking the crystals. The liquified cineol of all fractions is united and weighed.

In as much as a portion of the cineol remains dissolved in the terpenes, all of the cineol is not obtained by this method. Hence the method is applicable only then when it is desired to ascertain which of a number of oils is richest in cineol.

2. *Hydrogen bromide method.* Into a solution of 10 cc. of oil in 40 cc. of low boiling petroleum ether (b. p. 35 to 40°), thoroughly chilled in a freezing mixture, absolutely dry hydrogen bromide is passed so long as a precipitate continues to be formed. The purely white cineol hydrobromide ($C_{10}H_{18}O \cdot HBr$) is quickly separated with the aid of a suction pump and washed with cold petroleum ether. Into the filtrate more hydrogen bromide is passed and, if additional precipitate results, this is collected separately and combined with the bulk of precipitate first obtained and separated.

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to eugenol) that the oil had been adulterated with cinnamon leaf oil rich in eugenol. This example reveals that the methyl numbers reported should be adopted cautiously. It would be desirable indeed to repeat the determinations in connection with oils the purity of which has previously been established by other means. Only thus can desirable data be obtained which will give this method practical value. For the scientific investigation of volatile oils the methoxyl determination should prove exceedingly valuable since it reveals the presence or absence of phenol ethers or acid esters containing methyl, ethyl or propyl groups.

[1]) Helbing's Pharmacological Record No. VIII. London 1892.

In order to remove the petroleum ether, the cineol hydrobromide is left in a vacuum desiccator for a quarter of an hour. It is then transferred to a cassia flask with the aid of a little alcohol and decomposed with water. By the addition of more water the cineol is raised into the neck of the flask and its volume read off by means of the graduated scale. Multiplication with 10 yields the percentage of cineol by volume in the oil.

3. *Phosphoric acid method,*[1]) adopted by the U. S. Pharmacopœia, 8th decennial revision. To a solution of 10 cc. of oil in 50 cc. petroleum ether, which is thoroughly chilled in a freezing mixture, concentrated phosphoric acid is gradually added while stirring until the white precipitate ($C_{10}H_{18}O \cdot H_3PO_4$) attains a yellowish or reddish tint. The crystalline mass is removed with the aid of a force filter, washed with petroleum ether, dried by pressing between porous plates, and decomposed with water. The regenerated cineol is measured and the volume percentage computed.

Both the hydrobromic acid and phosphoric acid methods suffer form the drawback that their addition products with cineol are readily decomposible thus rendering difficult a quantitative separation. In consequence the results, as shown by Schimmel & Co.[2]) in connection with trial assays of mixtures of known cineol content, are unreliable. In part they deviate very materially from the true composition. Nevertheless, the hydrogen bromide method may prove useful in cases where the cineol content is low since then all other methods fail.

4. *Resorcinol method.* Recently a method has been worked out in the laboratory of Schimmel & Co.[3]) which depends on the

[1]) The method was first suggested by Helbing and Passmore who, however, employed no diluent. Helbing's Pharmacological Record No. XXIV. London 1893. Kebler attempted to introduce an improvement by titrating the phosphoric acid set free from the regenerated cineol after the cineol phosphate had been expressed. Americ. Journ. Pharm. **70** (1898), 492. If one, however, recalls how difficult it is to remove the sirupy phosphoric acid from the tough cineol phosphate cake, this change is not likely to enjoy the confidence of the analyst.

[2]) Report of Schimmel & Co. October **1907**, 47.

[3]) Report of Schimmel & Co. October **1907**, 47; Wiegand and Lehmann, Chem. Ztg. **32** (1908), 109; Report of Schimmel & Co. April **1908**, 52.

property of cineol to form an addition product with resorcinol which is soluble in an excess of concentrated resorcinol solution. Method of procedure: To 10 cc. of oil contained in a 100 cc. cassia flask (fig. 75, p. 583) enough 50 p. c. resorcinol solution is added to fill the flask about four-fifths. For five minutes the mixture is thoroughly shaken, then that portion of the oil which has not gone into solution is driven into the neck with resorcinol solution. Any oily particles adhering to the walls of the flask are caused to rise to the surface by rotating the flask or gently tapping it. After the resorcinol solution has become perfectly clear, which usually requires several hours, the volume of oil remaining is read off, the cineol content ascertained by subtracting this amount from 10 and the resultant multiplied with 10 in order to obtain the percentage by volume. Oils very rich in cineol are advantageously diluted with an equal volume of turpentine oil since the cineolresorcinol occasionally crystallizes from concentrated solutions thus rendering futile the entire process.

The method as described above is to be applied only to such oils that contain no appreciable amounts of oxygenated compounds (alcohols, aldehydes) since resorcinol dissolves these also, thus causing the results to be too high. In all other cases the assay is carried out, not with the original oil but with the cineol fraction. For this purpose 100 cc. of oil are distilled from a Ladenburg fractionating flask with three bulbs (fig. 71, p. 566) at such a rate that a drop is collected each second. Fraction 170 to 190°, which contains all of the cineol of the oil, is collected separately and its volume ascertained. The cineol content of this fraction is then determined as described above and the percentage of cineol in the original oil computed. In the examination of mixtures of known cineol content, Wiegand and Lehmann have shown that the error is at most 2%.

If only small amounts of oil are available the method can be modified so as to separate the solid resorcinol compound and to decompose the latter. With some practice acceptable results can thus also be obtained though not with the same certainty as with the fractionation method just described. Nevertheless, it is preferable to the phosphoric acid addition method since the additionproduct of cineol with resorcinol is more stable than that with phosphoric acid.

10 cc. of oil are mixed with 20 cc. of a 50 p. c. resorcinol solution. If necessary, a crystal of cineol resorcinol is added and the resulting crystalline mass is stirred to form a uniform mixture. The crystalline mass is separated by means of a force filter, pressed between filter paper to remove the last traces of oil, and transferred to a beaker. Caustic alkali is then added, the mixture gently heated and the liquid transferred to a cassia flask by means of a funnel the tube of which passes to the bottom of the flask. The flask is finally filled to the mark, the amount of separated cineol read off and multiplied by 10 to obtain percentage by volume.

For the regeneration of the resorcinol used for these determinations steam is passed through the solution from which the non-cineol portions of the oil has been previously separated. The cineol distills over and the aqueous solution is evaporated for the recovery of the resorcinol which can be used again for another assay.

HYDROCYANIC ACID ASSAY.

The qualitative test for hydrogen cyanide has already been referred to on p. 533. Quantitatively it is best determined gravimetrically: About 1 g. of oil is accurately weighed and dissolved in 10 to 20 times its volume of alcohol. To this solution 10 cc. of alcoholic ammonia free from chlorine are added to decompose the phenylhydroxyacetonitrile since otherwise only a part of the hydrocyanic acid is determined.[1]) After standing for a short time an aqueous solution of silver nitrate is added and the mixture acidulated with nitric acid.[2]) After the solution has become clear, the silver cyanide is is collected on a filter, that has been previously dried and weighed, is carefully washed with water and dried at 100° until of constant weight. If *s* represents the number of grams of oil used, and *a* the number of grams

[1]) Kremers and Schreiner, Pharm. Review 14 (1896), 196.

[2]) If much hydrogen cyanide be present, the addition of silver nitrate to the ammoniacal solution soon causes the precipitation of a finely crystalline precipitate of silver cyanide ammonia, NH_3AgCN. In order to prevent this the nitric acid should be added immediately after the addition of the silver nitrate solution.

of silver cyanide obtained, the percentage of hydrogen cyanide in the oil results from the following formula:

$$\% \text{ HCN} = \frac{a \cdot 20{,}179}{s}.$$

More convenient, but less accurate, because the end reaction is ascertainable with difficulty and uncertainty, is the titrimetric method according to Vielhaber.[1]) Liebigs' method, which is frequently applied to bitter almond water, is not at all applicable to the oil.

The assay is carried out according to the following directions: About 1 g. of oil is weighed accurately and shaken with 10 cc. of water. In order to split up the cyanhydrin, some freshly precipitated magnesium hydroxide is added, then 2 to 3 drops of a 10 p. c. potassium chromate solution as indicator. While constantly shaking — in order to insure the intimate contact of the oil with the mixture — the titration is carried out by slowly adding $\frac{N}{10}$ silver nitrate solution until the red color of the silver chromate indicates the end of the reaction. Every cc. of $\frac{N}{10}$ silver nitrate solution corresponds to 0,0027018 g. of hydrocyanic acid. The percentage can be computed with the aid of the following formula:

$$\% \text{ HCN} = \frac{0{,}27018 \cdot b}{s}$$

in which b represents the number of cc. of $\frac{N}{10}$ silver nitrate solution and s the number of grams of oil used.

For practical purposes the titrimetric method may suffice. It has been adopted by the U. S. Pharmacopœia for the hydrocyanic acid assay of bitter almond oil. The U. S. P. gives 0,002684 as factor. The difference is due to the fact that the factor given above is based on $O = 16$ whereas the factor of the U. S. P. is based on $H = 1$.

Reference should here also be made to a critical discussion by Runne[2]) of all gravimetric and volumetric methods for the determination of hydrocyanic acid in bitter almond water.

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[1]) Arch. der Pharm. **213** (1878), 408.

[2]) Apotheker Ztg. **24** (1909), 288, 297, 306, 314, 325, 333, 344, 356.

MUSTARD OIL ASSAY.

Mustard oil can be assayed by weighing it as thiosinamine, or better by double decomposition with ammoniacal silver nitrate solution. In this case also thiosinamine is first obtained as intermediate product but, as soon as formed, it is decomposed with the precipitation of silver sulphide. According to the second method distinction is made between the gravimetric process (weighing of the precipitated silver sulphide) and the titrimetric process (in which $\frac{N}{10}$ silver nitrate solution is used and the excess of silver nitrate is titrated back). In actual practice the titrimetric method is used well nigh exclusively. For the sake of completeness, however, the other two methods are also described.

Thiosinamine method.[1]) If in a flask 3 g. of mustard oil and 3 g. of alcohol are shaken together with 6 g. of ammonia water the mixture becomes clear after standing several hours in the cold (quickly at 50°) and as a rule separates crystals of thiosinamine without coloration. The mother liquid having been separated from the crystals is evaporated in such a manner that only a part thereof is transferred to the evaporating dish on a water bath and new portions added only then when the odor of ammonia has disappeared. Finally the crystals are also transferred to the evaporating dish the last traces being transferred with the aid of a little alcohol. The dish is heated on the water bath until of constant weight. The 3,25 or at most 3,5 g. of thiosinamine (corresponding to from 92,6 to 100% of *iso*thiocyan allyl) thus obtained constitute an brownish crystalline mass melting at 70° with a leek-like but by no means penetrating odor. It dissolves in 2 parts of warm water to a solution that does not change blue litmus paper, and possesses a bitter but not persistent taste.

It should be remembered, however, that any carbon disulphide present is likewise determined as thiosinamine, since with ammonia it undergoes the following reaction:

$$\underset{\text{Carbon disulphide}}{CS_2} + \underset{\text{Ammonia}}{4NH_3} = \underset{\text{Ammonium thiocyanate}}{(NH_4)SCN} + \underset{\text{Ammonium sulphide}}{(NH_4)_2S}$$

[1]) Direction according to the German Pharmacopœia, 3rd ed. 1890.

and since the resulting products remain largely behind upon evaporation. If the residue amounts to more than 3,5 g. an impermissible amount of carbon disulphide is very likely present, especially if it has the odor of ammonium sulphide.

The percentage of *iso*thiocyan allyl can be computed with the aid of the formula:

$$\frac{a \cdot 85{,}34}{s}$$

in which a represents the amount of thiosinamine obtained and s the amount in grams of mustard oil used.

Kremel[1]) has suggested the use of ammonia of definite strength and to titrate back with half-normal hydrochloric acid the amount not used. No results of practical experience with this method appear to have been recorded.

Determination with ammoniacal silver solution.

a) *Titrimetric method.* To about 5 g. (accurately weighed) of a solution of 1 g. mustard oil in 49 g. alcohol and contained in a 100 cc. measuring flask, 50 cc. of $\frac{N}{10}$ silver nitrate solution and 10 cc. ammonia water ($d_{15°}$ 0,960) are added; the flask, provided with a tube 1 meter long that serves as reflux condenser, and the mixture heated for 1 hour on a water bath that is in active ebullition. After the temperature of the mixture has been reduced to that of the room, water is added to the 100 cc. mark, the contents shaken and filtered. To 50 cc. of the filtrate 6 cc. of nitric acid ($d_{15°}$ 1,153) and a few drops of ferric ammonium sulphate are added and titrated with ammonium thiocyanate until the red color remains permanent. In order to ascertain the total amount of silver solution that has entered into the reaction, the number of cc. of ammonium thiocyanate solution used should be multiplied by 2 and the product subtracted from 50. If s grams of the alcoholic solution of mustard oil have required a cc. of $\frac{N}{10}$ silver nitrate solution the percentage of *iso*thiocyan allyl in the oil is

$$\frac{a \cdot 24{,}78}{s}.$$

[1]) Pharm. Post **21** (1888), 828.

The reactions that take place can be represented by the following equations. First of all, the ammonia acts with the formation of thiosinamine:

$$CSNC_3H_5 + NH_3 = \begin{matrix} \diagup NHC_3H_5 \\ C:S \\ \diagdown NH_2 \end{matrix} .$$

Ammoniacal silver nitrate breaks up this compound into allylcynamide aud sulphuretted hydrogen:

$$\begin{matrix} \diagup NHC_3H_5 \\ C:S \\ \diagdown NH_2 \end{matrix} = CN \cdot NHC_3H_5 + H_2S .$$

The sulphuretted hydrogen combines with the silver oxide to form silver sulphide.

The end reactions can be represented by the following empirical equation:

$$CSNC_3H_5 + 3NH_3 + 2AgNO_3 = Ag_2S + CNNHC_3H_5 + 2NH_4NO_3.$$

The principle of this method dates back to E. Dieterich[1]) who, however, suggested that the silver sulphide be weighed (see below). Gadamer[2]) then modified the method by making it titrimetric. Following the directions of E. Dieterich the mixture was not heated but set aside for 24 hours. K. Dieterich[3]) as well as Firbas[4]) pointed out that the decomposition of the thiosinamine with silver nitrate is not complete even after 24 hours at room temperature and that accurate values are received only then when the mixture is heated for a short time after the period of standing. Kuntze[5]) determined somewhat later that at room temperature more or less of the silver compound of allylsulphocarbaminic acid ethylester is formed as well as silver sulphide. For every molecule of mustard oil this demands but one atom of silver, whereas the formation of silver sulphide demands two

[1]) Helfenberger Annalen **1886**, 59.

[2]) Arch. der Pharm. **237** (1899), 110. Comp. also Arch. der Pharm. **246** (1908), 59, footnote 2.

[3]) Pharm. Ztg. **45** (1900), 768.

[4]) Zeitschr. d. allg. österr. Apoth. Ver. **58** (1904), 222.

[5]) Arch. der Pharm. **246** (1908), 58.

atoms of silver. The result is that less silver nitrate solution is used than is necessary for the complete decomposition, hence the results are too low.

The precipitation of thiourethane silver is avoided if the process is carried out at higher temperature. According to Kuntze the best results are obtained if the process is carried out as described above with the exception, however, that the mixture is immediately heated on a water bath for 1 hour. According to experiments made by Kuntze, the reduction of the silver solution when boiled with alcohol need not be feared.

b) *Gravimetric method.* As already pointed out, the method of determining the amount of *iso*thiocyanallyl by means of ammoniacal silver solution was first suggested by E. Dieterich *(loc. cit.),* who, however, weighed the precipitated silver sulphide. Somewhat later K. Dieterich[1]) modified the method somewhat. One proceeds, first of all, as in the titrimetric method, but naturally it is not necessary to employ a standardized silver solution. After the precipitate has subsided, it is collected by passing the hot liquid through a filter that has previously been washed successively with ammonia, hot water, alcohol, and ether, dried and weighed. The collected precipitate is washed with hot water, the water displaced by strong alcohol and this in turn by ether. The precipitate thus treated is dried at about 80° until of constant weight. The percentage of *iso*thiocyanallyl in the oil follows from the formula

$$\frac{a \cdot 39{,}995}{s}$$

in which a = the amount in grams of silver sulphide,
s = the amount in grams of mustard oil used.

According to Kuntze *(loc. cit.)* useful results are likewise obtained according to this method if the mixture is set aside at room temperature for 24 hours. Although, as previously indicated, thiourethane silver as well as silver sulphide may result, this effects the result but little, since the molecular weights of both compounds (248 and 252) are almost the same. As already pointed out, the side reaction may cause appreciable differences when proceeding according to the titrimetric method.

[1]) Helfenberger Annalen **1900**, 182.

TEST FOR CHLORINE.

The test for chlorinated products is an important one in the examination of bitter almond oil, cherry laurel oil and a number of chemical preparations. In the case of the two oils mentioned, the test serves as a means to detect adulteration with common, technical benzaldehyde; in the case of chemical preparations it affords a clue as to their purity. The principal chemicals of this group are benzylalcohol, benzaldehyde, phenylacet aldehyde, cinnamic aldehyde, synthetic camphor, and benzyl acetate.

Socalled *Beilstein test.* A piece of copper oxide fastened to a platinum wire is moistened with the oil to be tested and held in the outer zone of a Bunsen flame. As soon as the carbon has burned away, the presence of chlorine is indicated by the greenish or greenish-blue color of the flame. This color is produced by volatilizing copper chloride and its intensity and duration depends on the amount of chlorine present.

Lime test. The oil to be tested is mixed intimately with about ten times its amount of burnt marble[1]) free from chlorine and the mixture heated to a low red heat in a crucible for a short time. Any chlorine that may be present combines with the calcium. The powder is dissolved in nitric acid and the filtered solution tested for chlorine in the ordinary manner.

Combustion method.[2]) This method consists in burning the oil and testing the combustion products for hydrogen chloride. A piece of filter paper about 5×6 cm. is folded, saturated with the oil, the excess of oil thrown off, and the paper placed in a small porcelain capsule which in turn rests within a larger porcelain evaporating dish about 20 cm. in diameter. The paper is ignited and immediately covered with a beaker of 2 liter capacity the inner surface of which is moistened with water. The sizes of the implements should be so selected that the rim of the larger porcelain dish projects somewhat beyond that of the beaker. After the flame has become extinguished, the beaker

[1]) In place of the marble, calcined soda free from chlorine may be taken.

[2]) Comp. Schimmel's Bericht April **1890**, 99; also Report October **1904**, 7.

is allowed to remain in its position for several minutes. The products of combustion which have condensed on the inner surface of the beaker are then washed into a filter with about 10 cc. of distilled water. The filtrate, rendered acid with a drop of nitric acid, should not be rendered turbid upon the addition of silver nitrate test solution.

This method has proven especially effecient in the testing of volatile oils. Even the minutest traces of chlorine compounds can thus be detected. For the sake of absolute certainty a blank test should be made with a pure oil, since deceptions may occur if the water and the implements used have not been absolutely free from chlorine compounds. Compared with the lime test it has the advantage of being more convenient, especially if a large number of oils have to be tested.

In the case of oils containing hydrocyanic acid, deceptions may occur if unoxidized hydrogen cyanide is deposited on the inner surface of the beaker and washed out with the water. In such cases silver nitrate may produce a turbidity although the oil was pure. Such turbidity is due to AgCN and not to AgCl. This turbidity, however, differs from that produced by silver chloride in its disappearance when the liquid is heated carefully not quite to the boiling point.

Whereas the combustion method is much more delicate and reliable than Beilstein's method when applied to volatile oils, the latter is better adapted, according to Stephan,[1]) as a test for chlorine in artificial camphor.

The quantitative determination of chlorine can be carried out according to the well known method of Carius. A definite amount of oil is heated with fuming nitric acid in the presence of silver nitrate in a sealed tube and the silver chloride thus produced is weighed.

[1]) Comp. Lohmann, Berichte d. deutsch. pharm. Ges. 19 (1909), 222.

THE DETECTION OF SOME OF THE MORE COMMON ADULTERANTS.

TURPENTINE OIL.

Turpentine oil may be considered as the adulterant most often used. Very often it can be recognized by its characteristic odor, especially in those oils which contain no pinene, as this is the main constituent of turpentine oil. In general, its presence causes changes in the specific gravity, solubility, boiling temperature and optical rotation. It must here be remembered that there are dextro- as well as lævogyrate turpentine oils.

The positive proof of the presence of turpentine oil in oils, which in their pure state contain no pinene, is furnished by the isolation of and characteristic derivates of pinene. The constituents boiling in the neighborhood of 160°, are fractionated out and, according to the method described on page 296, the pinene nitrosochloride, as well as pinene nitrolbenzylamine or pinene nitrolpiperidine are prepared. If the fraction is strongly optically active, it is better to identify the pinene by oxidation to pinonic acid (see p. 297), for the yield of pinene nitrosochloride decreases as the optical activity of pinene increases.

If pinene is a normal constituent of the oil, the addition of turpentine oil can be recognized by a comparison of the physical properties of the lowest boiling fractions of the adulterated oil with the corresponding portions of the pure oil. The detection of turpentine oil in rosemary oil furnishes an example (see this).

CEDAR WOOD, COPAIBA AND GURJUN BALSAM OILS.

On account of their cheapness and faint odor, these three oils belong to the most favored and the most dangerous of adulterants. They may, however, be detected without difficulty in most cases by means of their physical properties, which differ from those of many of the volatile oils, namely their difficult solubility in 70 to 90 percent or even stronger alcohol, their high

specific gravity (above 0,900), their high boiling temperature, above 250°, and finally their rotatory power.

All three oils turn the plane of polarized light more or less to the left. With copaiba balsam oil the angle of rotation α_D lies between -7 and $-35°$,[1]) with cedar wood oil between -25 and $-44°$, and with gurjun balsam oil between -35 and $-130°$ (!).

At present only cedar wood oil and copaiba balsam oil can be detected in a chemical way. For this purpose the oil is subjected to fractional distillation and the fraction that passes over at about 260° examined. The cedrene contained in cedar wood oil can be oxidized in acetone solution with potassium permanganate to a glycol $C_{15}H_{26}O_2$ which melts at 160°, whereas caryophyllene can be characterized by means of its hydrate (m. p. 94 to 96, see p. 333 and 334). For the detection of gurjun balsam oil the observation of Deussen and Philipp[2]) can possibly be utilized. If oxidized in acetone solution with potassium permanganate, the indifferent components yield a fraction 170 to 180° under 12 mm. pressure, which in turn yields a semicarbazone, $C_{16}H_{27}N_3O$, that melts at 234°.

ALCOHOL.

The addition of alcohol to a volatile oil always results in a lowering of the specific gravity. When an oil containing alcohol is dropped into water, the drops do not remain clear and transparent, as is the case with pure oils, but become opaque and milky.

For the definite identification of alcohol the suspected oil is heated until it just begins to boil,[3]) and the first few drops that come over are collected in a test tube and filtered, to remove any oil globules which may also have come over, through a filter moistened with water. The filtrate is made strongly alkaline with dilute potassa solution, and treated, after heating to 50 to 60°,

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[1]) African copaiba balsam oils, the presence of which can be ascertained by the identification of cadinene (see p. 329), are dextrogyrate. According to the observations thus far recorded, the angle varies between $+16°51'$ and $+22°26'$. Dextrogyrate gurjunbalsam oils are also said to occur.

[2]) Liebig's Annalen **369** (1909), 56.

[3]) Not all of the alcohol is driven over by heating on the water bath.

with a solution of iodine in potassium iodide, until the solution remains slightly yellow. If alcohol is present small crystals of iodoform will separate in a short time at the bottom of the liquid. It must here be remembered that other bodies, such as aldehydes, acetone and acetic ether also yield iodoform under the conditions given.

Larger amounts of alcohol may be removed from volatile oils by shaking with water, from which the alcohol may be again removed by distillation and identified by the iodoform reaction. If the shaking out is done in a graduated cylinder, the increase of the aqueous layer corresponds approximately to the amount of the alcohol.

It is better, however, to use sodium chloride solution or glycerin, because with these the two layers separate better, and a more accurate reading is possible.

The alcohol content may also be approximately calculated if the specific gravity is determined before and after shaking with water.

If d is the specific gravity of the oil (at 15°),
D the specific gravity of the oil shaken with water, and
s the specific gravity of the alcohol,[1])
the alcohol content of the oil in percent follows from the formula

$$\frac{(D-d)\cdot 100}{D-s}.$$

As already mentioned on page 599 the amount of the alcohol in an oil which in itself does not give a methyl number, may be determined quantitatively by Zeisel's methoxyl method.

FATTY OIL.

The volatile oils adulterated with fatty oil leave a permanent fatty stain when evaporated on paper. With high boiling and difficultly volatile oils, however, similar residues are left, which may give rise to mistakes. Fatty oil is insoluble in 90 percent alcohol.[2]) For the separation of the fatty oil from the volatile

[1]) The specific gravities of alcohols of varying strengths are given on p. 568.

[2]) Castor oil only is soluble in 90 p. c. alcohol, but is insoluble in 70 p. c. alcohol and in petroleum ether. Mention should also be made of the slight optical activity of castor oil, α_D about $+5°$.

oil, the latter is distilled off by steam distillation or removed by evaporation in an open dish on the water bath. However, it should be remembered that some volatile oils, such as bergamot, lemon, orange, anise and star-anise oil, leave a residue of several percent even when they are not adulterated. This is also true of resinified oils.

The presence of the fat may be shown qualitatively in the residue by heating with potassium bisulphate in a test tube. Penetrating odors of acrolein show its presence. By igniting the residue on a platinum foil the characteristic odor of burning fat is noticed.

As the fatty oils give saponification numbers which lie between 180 and 200, the amount of the fat added can be determined quantitatively by saponification either directly in the volatile oil itself or in the distillation residue.

Oils that have been adulterated with cocoa nut oil solidify wholly or in part in a freezing mixture. Cocoa nut oil has been found in cananga oil, citronella oil and palmarosa oil and detected in this manner.

MINERAL OIL, PETROLEUM.

Mineral oil, paraffin oil, kerosene, petroleum and petroleum fractions are insoluble in alcohol and can therefore be detected without difficulty in volatile oils; besides, they are often easily recognized by their low specific gravity. Palmarosa oil to which some mineral oil has been added is only partly soluble in 70 percent alcohol. If the insoluble portion is successively treated with 90 percent and absolute alcohol, an oil remains, which in the beginning it is true is colored brown by sulphuric or nitric acids, but in general resists the action of these acids and also of alkalies, and on saponification with alcoholic potassa gives no saponification number.

The mineral oils have different boiling points. The hydrocarbons of illuminating oil boil at about the same temperature as the terpenes. Lower boiling fractions are said to be sometimes used for adulterating turpentine oil. A higher boiling mineral oil, about 250°, has been found in citronella and in gingergrass oils. The petroleum fractions of lower boiling temperatures are

easily volatile with water vapor, the higher fractions not at all, or at least to a small degree only.

A method for the quantitative estimation of mineral oils consists in weighing the residue left after having removed the volatile oil by oxidation with fuming nitric acid, as described under turpentine oil. According to Herzfeld[1]) concentrated sulphuric acid is better adapted to the separation of mineral oil than nitric acid. However, the investigators are very much divided in their opinions on this subject. (For details see under turpentine oil in the second volume). Attention should be called to the fact that some volatile oils, such as rose oil, chamomile oil, orange flower oil and others, contain larger or smaller amounts of paraffins as natural constituents.

CHLOROFORM.

This body, which has been found occasionally in volatile oils (for instance, in cognac oil), can be isolated by distillation on a water bath and identified by the *iso*nitrile reaction. This consists in that a small amount of the suspected distillate is treated with a few drops of aniline and alcoholic caustic soda solution, and gently heated. In the presence of chloroform the noxious and exceedingly disagreeable smelling vapors of phenyl-*iso*nitrile are formed.

ADDITIONS TO INCREASE THE ESTER CONTENT.

The valuation of such oils as bergamot and lavender according to their ester content has led to the occasional adulteration of such oils with cheaper esters or organic acids for the purpose of increasing their apparent ester content. Among the substances added for this purpose the following have been observed thus far: benzoic acid, salicylic acid, oleic acid, diethylsuccinate, triethylcitrate, glycerylmonacetate, ethyltartrate and terpinylacetate.

The presence of acids can be detected by means of an increase in the acid value, which, in most oils, is very small. For this reason the advice was given on p. 571 to determine

[1]) Zeitschr. f. öff. Chem. 9 (1903), 454. Comp. Chem. Zentralbl. **1904**, I. 548.

the acid value and the ester value separately. The acids can be isolated by shaking the oil containing them with dilute soda solution, separating the latter and decomposing the salt formed with a mineral acid.

The identification of the esters may be carried out in various ways. In most instances the oil is fractionated, the fraction to be examined saponified, and the attempt made to characterize the components. However, special methods are also employed varying with the kind of ester. Thus *e. g.* fractional saponification may lead to the detection of added terpinyl acetate. In consequence of the high specific gravity of the esters used for adulteration, such adulterated oils become suspicious in many instances because of their increased density. Details as to such adulterations will be found in the second volume under the respective oils.

Table I

for Calculating the Percentage Content of Alcohols of the Formulas $C_{10}H_{18}O$, $C_{10}H_{20}O$, $C_{15}H_{24}O$ and $C_{15}H_{26}O$ from the Saponification Values before and after Acetylation, also the Percentage Content of the Acetic Esters of these Alcohols.

Table II

for Determining the Ester Value (Acid Value, Saponification Value), also the Percentage Content of Alcohol and Ester directly from the Number of cc. $\frac{n}{2}$ Potassium Hydroxide when 1,50 g. of Oil are used.

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for Calculating the Percentage Content of Alcohols of the Formul before and after Acetylation, also the Percenta

$C_{10}H_{18}O$				$C_{10}H_{20}O$			
E. V.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	E. V.
1	0,35	0,28	0,28	0,35	0,28	0,28	1
2	0,70	0,55	0,55	0,71	0,56	0,56	2
3	1,05	0,83	0,83	1,06	0,84	0,84	3
4	1,40	1,10	1,10	1,41	1,11	1,12	4
5	1,75	1,38	1,38	1,77	1,39	1,40	5
6	2,10	1,65	1,66	2,12	1,67	1,68	6
7	2,45	1,93	1,94	2,47	1,95	1,96	7
8	2,80	2,20	2,21	2,83	2,23	2,24	8
9	3,15	2,48	2,49	3,18	2,51	2,52	9
10	3,50	2,75	2,77	3,54	2,79	2,81	10
11	3,85	3,03	3,05	3,89	3,06	3,09	11
12	4,20	3,30	3,33	4,24	3,34	3,37	12
13	4,55	3,58	3,61	4,60	3,62	3,66	13
14	4,90	3,85	3,89	4,95	3,90	3,94	14
15	5,25	4,13	4,17	5,30	4,18	4,23	15
16	5,60	4,40	4,45	5,66	4,46	4,51	16
17	5,95	4,68	4,74	6,01	4,74	4,80	17
18	6,30	4,95	5,02	6,36	5,01	5,08	18
19	6,65	5,23	5,30	6,72	5,29	5,37	19
20	7,00	5,50	5,58	7,07	5,57	5,66	20
21	7,35	5,78	5,87	7,42	5,85	5,94	21
22	7,70	6,05	6,15	7,78	6,13	6,23	22
23	8,05	6,33	6,44	8,13	6,41	6,52	23
24	8,40	6,60	6,72	8,49	6,69	6,81	24
25	8,75	6,88	7,01	8,84	6,96	7,10	25
26	9,10	7,15	7,29	9,19	7,24	7,39	26
27	9,45	7,43	7,58	9,55	7,52	7,68	27
28	9,80	7,70	7,87	9,90	7,80	7,97	28
29	10,15	7,98	8,15	10,25	8,08	8,26	29
30	10,50	8,25	8,44	10,61	8,36	8,55	30

e I

$_{}H_{18}O$, $C_{10}H_{20}O$, $C_{15}H_{24}O$ and $C_{15}H_{26}O$, from the Saponification Values ıntent of the Acetic Esters of these Alcohols.

$C_{15}H_{24}O$				$C_{15}H_{26}O$			
E. V.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	E. V.
1	0,47	0,39	0,39	0,47	0,40	0,40	1
2	0,94	0,79	0,79	0,94	0,79	0,79	2
3	1,40	1,18	1,18	1,41	1,19	1,19	3
4	1,87	1,57	1,58	1,89	1,59	1,59	4
5	2,34	1,96	1,97	2,36	1,98	1,99	5
6	2,81	2,36	2,37	2,83	2,38	2,39	6
7	3,28	2,75	2,76	3,30	2,78	2,79	7
8	3,74	3,14	3,16	3,77	3,17	3,19	8
9	4,21	3,53	3,56	4,24	3,57	3,59	9
10	4,68	3,93	3,96	4,71	3,96	3,99	10
11	5,15	4,32	4,36	5,19	4,36	4,40	11
12	5,61	4,71	4,76	5,66	4,76	4,80	12
13	6,08	5,11	5,16	6,13	5,15	5,20	13
14	6,55	5,50	5,56	6,60	5,55	5,61	14
15	7,02	5,89	5,96	7,07	5,95	6,01	15
16	7,49	6,29	6,36	7,54	6,34	6,42	16
17	7,95	6,68	6,77	8,01	6,74	6,83	17
18	8,42	7,07	7,17	8,49	7,14	7,23	18
19	8,89	7,46	7,57	8,96	7,53	7,64	19
20	9,36	7,86	7,98	9,43	7,93	8,05	20
21	9,83	8,25	8,38	9,90	8,33	8,46	21
22	10,29	8,64	8,79	10,37	8,72	8,87	22
23	10,76	9,03	9,19	10,84	9,12	9,28	23
24	11,23	9,42	9,60	11,31	9,51	9,69	24
25	11,70	9,82	10,01	11,79	9,91	10,10	25
26	12,16	10,21	10,42	12,26	10,30	10,51	26
27	12,63	10,60	10,83	12,73	10,70	10,92	27
28	13,10	11,00	11,24	13,20	11,10	11,34	28
29	13,57	11,39	11,65	13,67	11,49	11,75	29
30	14,04	11,79	12,06	14,14	11,89	12,17	30

Table I

$C_{10}H_{18}O$				$C_{10}H_{20}O$			
E. V.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	E. V.
31	10,85	8,53	8,73	10,96	8,64	8,84	31
32	11,20	8,80	9,02	11,31	8,91	9,13	32
33	11,55	9,08	9,31	11,67	9,19	9,43	33
34	11,90	9,35	9,59	12,02	9,47	9,72	34
35	12,25	9,63	9,88	12,37	9,75	10,01	35
36	12,60	9,90	10,17	12,73	10,03	10,31	36
37	12,95	10,18	10,47	13,08	10,31	10,60	37
38	13,30	10,45	10,76	13,44	10,59	10,90	38
39	13,65	10,73	11,05	13,79	10,86	11,19	39
40	14,00	11,00	11,34	14,14	11,14	11,49	40
41	14,35	11,28	11,63	14,50	11,42	11,78	41
42	14,70	11,55	11,93	14,85	11,70	12,08	42
43	15,05	11,83	12,22	15,20	11,98	12,38	43
44	15,40	12,10	12,51	15,56	12,26	12,68	44
45	15,75	12,38	12,81	15,91	12,54	12,97	45
46	16,10	12,65	13,10	16,26	12,81	13,27	46
47	16,45	12,93	13,40	16,62	13,09	13,57	47
48	16,80	13,20	13,69	16,97	13,37	13,87	48
49	17,15	13,48	13,99	17,32	13,65	14,17	49
50	17,50	13,75	14,29	17,68	13,93	14,47	50
51	17,85	14,03	14,58	18,03	14,21	14,77	51
52	18,20	14,30	14,88	18,39	14,49	15,07	52
53	18,55	14,58	15,18	18,74	14,76	15,38	53
54	18,90	14,85	15,48	19,09	15,04	15,68	54
55	19,25	15,13	15,77	19,45	15,32	15,98	55
56	19,60	15,40	16,07	19,80	15,60	16,28	56
57	19,95	15,68	16,38	20,15	15,88	16,59	57
58	20,30	15,95	16,68	20,51	16,16	16,89	58
59	20,65	16,23	16,98	20,86	16,44	17,20	59
60	21,00	16,50	17,28	21,21	16,71	17,50	60
61	21,35	16,78	17,58	21,57	16,99	17,81	61
62	21,70	17,05	17,88	21,92	17,27	18,11	62
63	22,05	17,33	18,18	22,27	17,55	18,42	63
64	22,40	17,60	18,49	22,63	17,83	18,73	64
65	22,75	17,88	18,79	22,98	18,11	19,04	65
66	23,10	18,15	19,10	23,34	18,39	19,34	66
67	23,45	18,43	19,40	23,69	18,66	19,65	67
68	23,80	18,70	19,70	24,04	18,94	19,96	68
69	24,15	18,98	20,01	24,40	19,22	20,27	69
70	24,50	19,25	20,32	24,75	19,50	20,58	70

Table I

$C_{15}H_{24}O$				$C_{15}H_{26}O$			
E. V.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	E. V.
31	14,51	12,18	12,47	14,61	12,28	12,58	31
32	14,98	12,57	12,88	15,08	12,68	13,00	32
33	15,45	12,96	13,29	15,55	13,08	13,41	33
34	15,91	13,35	13,71	16,02	13,48	13,83	34
35	16,38	13,75	14,12	16,50	13,88	14,25	35
36	16,85	14,14	14,54	16,97	14,27	14,67	36
37	17,32	14,54	14,95	17,44	14,66	15,09	37
38	17,79	14,93	15,37	17,91	15,06	15,51	38
39	18,25	15,32	15,78	18,38	15,46	15,93	39
40	18,71	15,71	16,20	18,86	15,86	16,35	40
41	19,18	16,10	16,62	19,33	16,25	16,77	41
42	19,65	16,50	17,04	19,80	16,65	17,19	42
43	20,12	16,89	17,46	20,27	17,05	17,61	43
44	20,59	17,28	17,88	20,74	17,44	18,04	44
45	21,05	17,68	18,30	21,21	17,84	18,46	45
46	21,52	18,07	18,72	21,69	18,24	18,89	46
47	21,99	18,46	19,14	22,16	18,63	19,32	47
48	22,46	18,85	19,56	22,63	19,03	19,74	48
49	22,93	19,25	19,98	23,10	19,43	20,17	49
50	23,39	19,64	20,41	23,57	19,82	20,59	50
51	23,86	20,03	20,83	24,04	20,22	21,02	51
52	24,33	20,42	21,26	24,51	20,62	21,45	52
53	24,80	20,82	21,68	24,99	21,01	21,88	53
54	25,26	21,21	22,11	25,46	21,41	22,31	54
55	25,73	21,60	22,54	25,93	21,81	22,74	55
56	26,20	22,00	22,96	26,40	22,20	23,17	56
57	26,67	22,39	23,39	26,87	22,60	23,61	57
58	27,14	22,78	23,82	27,34	23,00	24,04	58
59	27,61	23,17	24,25	27,81	23,39	24,47	59
60	28,07	23,57	24,68	28,29	23,79	24,91	60
61	28,54	23,96	25,11	28,76	24,19	25,34	61
62	29,01	24,35	25,54	29,23	24,58	25,77	62
63	29,48	24,75	25,97	29,70	24,98	26,21	63
64	29,95	25,14	26,41	30,17	25,38	26,65	64
65	30,41	25,53	26,84	30,64	25,77	27,09	65
66	30,88	25,93	27,27	31,11	26,17	27,53	66
67	31,35	26,32	27,71	31,59	26,57	27,97	67
68	31,81	26,71	28,14	32,06	26,96	28,41	68
69	32,28	27,10	28,58	32,53	27,35	28,85	69
70	32,75	27,50	29,02	33,00	27,75	29,29	70

Table I

$C_{10}H_{18}O$				$C_{10}H_{20}O$			
E. V.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	E. V.
71	24,85	19,53	20,62	25,10	19,78	20,89	71
72	25,20	19,80	20,93	25,46	20,06	21,20	72
73	25,55	20,08	21,24	25,81	20,34	21,51	73
74	25,90	20,35	21,55	26,16	20,61	21,83	74
75	26,25	20,63	21,85	26,52	20,89	22,14	75
76	26,60	20,90	22,16	26,87	21,17	22,45	76
77	26,95	21,18	22,47	27,22	21,45	22,77	77
78	27,30	21,45	22,78	27,58	21,73	23,08	78
79	27,65	21,73	23,09	27,93	22,01	23,39	79
80	28,00	22,00	23,40	28,29	22,29	23,71	80
81	28,35	22,28	23,72	28,64	22,56	24,02	81
82	28,70	22,55	24,03	28,99	22,84	24,34	82
83	29,05	22,83	24,34	29,35	23,12	24,66	83
84	29,40	23,10	24,65	29,70	23,40	24,97	84
85	29,75	23,38	24,97	30,05	23,68	25,29	85
86	30,10	23,65	25,28	30,41	23,96	25,61	86
87	30,45	23,93	25,60	30,76	24,24	25,93	87
88	30,80	24,20	25,91	31,11	24,51	26,25	88
89	31,15	24,48	26,23	31,47	24,79	26,57	89
90	31,50	24,75	26,54	31,82	25,07	26,89	90
91	31,85	25,03	26,86	32,17	25,35	27,21	91
92	32,20	25,30	27,18	32,53	25,63	27,53	92
93	32,55	25,58	27,49	32,88	25,91	27,85	93
94	32,90	25,85	27,81	33,24	26,19	28,17	94
95	33,25	26,13	28,13	33,59	26,46	28,49	95
96	33,60	26,40	28,45	33,94	26,74	28,82	96
97	33,95	26,68	28,77	34,30	27,02	29,14	97
98	34,30	26,95	29,09	34,65	27,30	29,47	98
99	34,65	27,23	29,41	35,00	27,58	29,79	99
100	35,00	27,50	29,73	35,36	27,86	30,11	100
101	35,35	27,78	30,05	35,71	28,14	30,44	101
102	35,70	28,05	30,37	36,06	28,41	30,77	102
103	36,05	28,33	30,70	36,42	28,69	31,09	103
104	36,40	28,60	31,02	36,77	28,97	31,42	104
105	36,75	28,88	31,34	37,12	29,25	31,75	105
106	37,10	29,15	31,67	37,48	29,53	32,08	106
107	37,45	29,43	31,99	37,83	29,81	32,41	107
108	37,80	29,70	32,32	38,19	30,09	32,74	108
109	38,15	29,98	32,64	38,54	30,36	33,07	109
110	38,50	30,25	32,97	38,89	30,64	33,40	110

$C_{15}H_{24}O$				$C_{15}H_{26}O$			
E. V.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	E. V.
71	33,22	27,89	29,46	33,47	28,15	29,73	71
72	33,69	28,28	29,90	33,94	28,54	30,17	72
73	34,15	28,67	30,34	34,41	28,94	30,61	73
74	34,62	29,07	30,78	34,89	29,34	31,06	74
75	35,09	29,46	31,22	35,36	29,73	31,50	75
76	35,56	29,85	31,66	35,83	30,13	31,95	76
77	36,03	30,25	32,10	36,30	30,53	32,40	77
78	36,49	30,64	32,54	36,77	30,92	32,84	78
79	36,96	31,03	32,98	37,24	31,31	33,29	79
80	37,43	31,43	33,43	37,71	31,71	33,74	80
81	37,90	31,82	33,87	38,19	32,11	34,19	81
82	38,37	32,21	34,32	38,66	32,50	34,64	82
83	38,84	32,60	34,77	39,13	32,90	35,09	83
84	39,30	33,00	35,22	39,60	33,30	35,54	84
85	39,77	33,39	35,66	40,07	33,69	35,99	85
86	40,24	33,78	36,11	40,54	34,09	36,44	86
87	40,70	34,18	36,56	41,01	34,49	36,90	87
88	41,17	34,57	37,01	41,49	34,88	37,35	88
89	41,64	34,96	37,46	41,96	35,28	37,80	89
90	42,11	35,36	37,92	42,43	35,68	38,26	90
91	42,57	35,75	38,37	42,90	36,08	38,71	91
92	43,04	36,14	38,82	43,37	36,47	39,17	92
93	43,51	36,53	39,27	43,84	36,87	39,63	93
94	43,98	36,92	39,73	44,31	37,26	40,09	94
95	44,45	37,32	40,18	44,79	37,66	40,55	95
96	44,92	37,71	40,64	45,26	38,05	41,01	96
97	45,39	38,10	41,10	45,73	38,45	41,47	97
98	45,85	38,50	41,55	46,20	38,85	41,93	98
99	46,32	38,89	42,01	46,67	39,24	42,39	99
100	46,79	39,29	42,47	47,14	39,64	42,86	100
101	47,26	39,68	42,93	47,61	40,04	43,32	101
102	47,72	40,07	43,39	48,09	40,43	43,78	102
103	48,19	40,46	43,85	48,56	40,83	44,24	103
104	48,66	40,85	44,32	49,03	41,23	44,71	104
105	49,13	41,25	44,78	49,50	41,63	45,18	105
106	49,59	41,64	45,24	49,97	42,02	45,65	106
107	50,06	42,04	45,70	50,44	42,42	46,12	107
108	50,53	42,43	46,16	50,91	42,81	46,59	108
109	51,00	42,82	46,63	51,39	43,21	47,06	109
110	51,46	43,21	47,10	51,86	43,61	47,53	110

Table I

$C_{10}H_{18}O$				$C_{10}H_{20}O$			
E. V.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig oil	E. V.
111	38,85	30,53	33,30	39,25	30,92	33,73	111
112	39,20	30,80	33,62	39,60	31,20	34,06	112
113	39,55	31,08	33,95	39,95	31,48	34,39	113
114	39,90	31,35	34,28	40,31	31,76	34,73	114
115	40,25	31,63	34,61	40,66	32,04	35,06	115
116	40,60	31,90	34,94	41,01	32,31	35,39	116
117	40,95	32,18	35,27	41,37	32,59	35,73	117
118	41,30	32,45	35,60	41,72	32,87	36,06	118
119	41,65	32,73	35,93	42,07	33,15	36,40	119
120	42,00	33,00	36,26	42,43	33,43	36,73	120
121	42,35	33,28	36,60	42,78	33,71	37,07	121
122	42,70	33,55	36,93	43,14	33,99	37,41	122
123	43,05	33,83	37,26	43,49	34,26	37,75	123
124	43,40	34,10	37,60	43,84	34,54	38,08	124
125	43,75	34,38	37,93	44,20	34,82	38,42	125
126	44,10	34,65	38,27	44,55	35,10	38,76	126
127	44,45	34,93	38,60	44,90	35,38	39,10	127
128	44,80	35,20	38,94	45,26	35,66	39,44	128
129	45,15	35,48	39,27	45,61	35,94	39,78	129
130	45,50	35,75	39,61	45,96	36,21	40,13	130
131	45,85	36,03	39,95	46,32	36,49	40,47	131
132	46,20	36,30	40,29	46,67	36,77	40,81	132
133	46,55	36,58	40,63	47,02	37,05	41,16	133
134	46,90	36,85	40,97	47,38	37,33	41,50	134
135	47,25	37,13	41,31	47,73	37,61	41,84	135
136	47,60	37,40	41,65	48,09	37,89	42,19	136
137	47,95	37,68	41,99	48,44	38,16	42,53	137
138	48,30	37,95	42,33	48,79	38,44	42,88	138
139	48,65	38,23	42,67	49,15	38,72	43,23	139
140	49,00	38,50	43,02	49,50	39,00	43,58	140
141	49,35	38,78	43,36	49,85	39,28	43,92	141
142	49,70	39,05	43,71	50,21	39,56	44,27	142
143	50,05	39,33	44,05	50,56	39,84	44,62	143
144	50,40	39,60	44,39	50,91	40,11	44,97	144
145	50,75	39,88	44,74	51,27	40,39	45,32	145
146	51,10	40,15	45,09	51,62	40,67	45,67	146
147	51,45	40,43	45,44	51,97	40,95	46,02	147
148	51,80	40,70	45,78	52,33	41,23	46,38	148
149	52,15	40,98	46,13	52,68	41,51	46,73	149
150	52,50	41,25	46,48	53,04	41,79	47,08	150

Table I

$C_{15}H_{24}O$				$C_{15}H_{26}O$			
E. V.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	E. V.
111	51,93	43,60	47,57	52,33	44,00	48,00	111
112	52,40	44,00	48,04	52,80	44,40	48,47	112
113	52,87	44,39	48,50	53,27	44,80	48,94	113
114	53,34	44,78	48,97	53,74	45,19	49,42	114
115	53,81	45,17	49,44	54,21	45,59	49,89	115
116	54,28	45,57	49,91	54,69	45,99	50,36	116
117	54,74	45,96	50,39	55,16	46,38	50,84	117
118	55,21	46,35	50,86	55,63	46,78	51,32	118
119	55,68	46,74	51,33	56,10	47,18	51,80	119
120	56,14	47,14	51,81	56,57	47,57	52,28	120
121	56,61	47,53	52,28	57,04	47,97	52,76	121
122	57,08	47,92	52,76	57,51	48,36	53,24	122
123	57,55	48,32	53,23	57,99	48,76	53,72	123
124	58,01	48,71	53,71	58,46	49,16	54,20	124
125	58,48	49,10	54,18	58,93	49,55	54,68	125
126	58,95	49,50	54,66	59,40	49,95	55,17	126
127	59,42	49,89	55,14	59,87	50,35	55,65	127
128	59,89	50,28	55,62	60,34	50,74	56,13	128
129	60,36	50,67	56,11	60,81	51,14	56,62	129
130	60,82	51,07	56,59	61,28	51,54	57,10	130
131	61,29	51,46	57,07	61,75	51,93	57,59	131
132	61,76	51,85	57,55	62,22	52,33	58,08	132
133	62,23	52,25	58,03	62,70	52,73	58,57	133
134	62,70	52,64	58,52	63,17	53,12	59,06	134
135	63,16	53,03	59,00	63,64	53,52	59,55	135
136	63,63	53,42	59,49	64,11	53,92	60,04	136
137	64,10	53,82	59,98	64,59	54,31	60,53	137
138	64,57	54,21	60,47	65,06	54,71	61,02	138
139	65,04	54,60	60,96	65,53	55,11	61,51	139
140	65,50	55,00	61,45	66,00	55,50	62,01	140
141	65,97	55,39	61,94	66,47	55,90	62,50	141
142	66,44	55,78	62,43	66,94	56,30	63,00	142
143	66,90	56,18	62,93	67,41	56,69	63,50	143
144	67,37	56,57	63,42	67,89	57,09	64,00	144
145	67,84	56,96	63,92	68,36	57,49	64,50	145
146	68,31	57,35	64,41	68,83	57,88	65,00	146
147	68,78	57,75	64,91	69,30	58,28	65,50	147
148	69,25	58,14	65,40	69,77	58,68	66,00	148
149	69,72	58,53	65,90	70,24	59,07	66,50	149
150	70,18	58,93	66,40	70,71	59,46	67,00	150

Table I

$C_{10}H_{18}O$				$C_{10}H_{20}O$			
E. V.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	E. V.
151	52,85	41,53	46,83	53,39	42,06	47,44	151
152	53,20	41,80	47,18	53,74	42,34	47,79	152
153	53,55	42,08	47,53	54,10	42,62	48,15	153
154	53,90	42,35	47,88	54,45	42,90	48,50	154
155	54,25	42,63	48,23	54,80	43,18	48,86	155
156	54,60	42,90	48,58	55,16	43,46	49,21	156
157	54,95	43,18	48,94	55,51	43,74	49,57	157
158	55,30	43,45	49,29	55,86	44,01	49,93	158
159	55,65	43,73	49,65	56,22	44,29	50,29	159
160	56,00	44,00	50,00	56,57	44,57	50,65	160
161	56,35	44,28	50,36	56,92	44,85	51,01	161
162	56,70	44,55	50,71	57,28	45,13	51,37	162
163	57,05	44,83	51,07	57,63	45,41	51,73	163
164	57,40	45,10	51,42	57,99	45,69	52,09	164
165	57,75	45,38	51,78	58,34	45,96	52,46	165
166	58,10	45,65	52,14	58,69	46,24	52,82	166
167	58,45	45,93	52,50	59,05	46,52	53,18	167
168	58,80	46,20	52,86	59,40	46,80	53,55	168
169	59,15	46,48	53,22	59,75	47,08	53,91	169
170	59,50	46,75	53,58	60,11	47,36	54,28	170
171	59,85	47,03	53,94	60,46	47,64	54,64	171
172	60,20	47,30	54,31	60,81	47,91	55,01	172
173	60,55	47,58	54,67	61,17	48,19	55,38	173
174	60,90	47,85	55,03	61,52	48,47	55,75	174
175	61,25	48,13	55,40	61,87	48,75	56,12	175
176	61,60	48,40	55,76	62,23	49,03	56,48	176
177	61,95	48,68	56,13	62,58	49,31	56,85	177
178	62,30	48,95	56,49	62,94	49,59	57,23	178
179	62,65	49,23	56,86	63,29	49,86	57,60	179
180	63,00	49,50	57,22	63,64	50,14	57,97	180
181	63,35	49,78	57,59	64,00	50,42	58,34	181
182	63,70	50,05	57,96	64,35	50,70	58,71	182
183	64,05	50,33	58,33	64,70	50,98	59,09	183
184	64,40	50,60	58,70	65,06	51,26	59,46	184
185	64,75	50,88	59,07	65,41	51,54	59,84	185
186	65,10	51,15	59,44	65,76	51,81	60,21	186
187	65,45	51,43	59,81	66,12	52,09	60,59	187
188	65,80	51,70	60,19	66,47	52,37	60,97	188
189	66,15	51,98	60,56	66,82	52,65	61,35	189
190	66,50	52,25	60,93	67,18	52,93	61,72	190

Table I

$C_{15}H_{24}O$				$C_{15}H_{26}O$			
E. V.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	E. V.
151	70,65	59,32	66,90	71,19	59,86	67,51	151
152	71,12	59,71	67,40	71,66	60,26	68,01	152
153	71,58	60,10	67,90	72,13	60,65	68,52	153
154	72,05	60,50	68,40	72,60	61,05	69,02	154
155	72,52	60,89	68,90	73,07	61,45	69,53	155
156	72,99	61,28	69,41	73,54	61,84	70,04	156
157	73,46	61,68	69,91	74,01	62,24	70,55	157
158	73,92	62,07	70,42	74,49	62,64	71,06	158
159	74,39	62,46	70,92	74,96	63,03	71,57	159
160	74,86	62,86	71,43	75,43	63,43	72,08	160
161	75,33	63,25	71,93	75,90	63,83	72,59	161
162	75,80	63,64	72,44	76,37	64,22	73,10	162
163	76,26	64,03	72,95	76,84	64,62	73,62	163
164	76,73	64,42	73,46	77,31	65,02	74,13	164
165	77,20	64,82	73,97	77,78	65,41	74,65	165
166	77,67	65,21	74,49	78,26	65,81	75,16	166
167	78,14	65,60	75,00	78,73	66,21	75,68	167
168	78,60	66,00	75,52	79,20	66,60	76,20	168
169	79,07	66,39	76,03	79,67	67,00	76,72	169
170	79,54	66,79	76,55	80,14	67,39	77,24	170
171	80,01	67,18	77,06	80,61	67,79	77,76	171
172	80,48	67,57	77,58	81,08	68,19	78,28	172
173	80,94	67,96	78,10	81,56	68,58	78,81	173
174	81,41	68,35	78,62	82,03	68,98	79,33	174
175	81,88	68,75	79,14	82,50	69,38	79,85	175
176	82,35	69,14	79,66	82,97	69,77	80,38	176
177	82,81	69,54	80,18	83,44	70,17	80,91	177
178	83,28	69,93	80,70	83,91	70,57	81,43	178
179	83,75	70,32	81,23	84,38	70,96	81,96	179
180	84,21	70,71	81,75	84,86	71,36	82,49	180
181	84,68	71,10	82,28	85,33	71,76	83,02	181
182	85,15	71,50	82,80	85,80	72,15	83,55	182
183	85,62	71,89	83,33	86,27	72,55	84,09	183
184	86,09	72,28	83,86	86,74	72,95	84,62	184
185	86,56	72,68	84,39	87,21	73,34	85,15	185
186	87,03	73,07	84,92	87,68	73,74	85,69	186
187	87,49	73,46	85,45	88,16	74,14	86,22	187
188	87,96	73,86	85,98	88,63	74,53	86,76	188
189	88,43	74,25	86,51	89,10	74,93	87,30	189
190	88,89	74,64	87,05	89,57	75,32	87,84	190

Table I

$C_{10}H_{18}O$				$C_{10}H_{20}O$			
E. V.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	E. V.
191	66,85	52,53	61,31	67,53	53,21	62,10	191
192	67,20	52,80	61,68	67,89	53,49	62,48	192
193	67,55	53,08	62,06	68,24	53,76	62,86	193
194	67,90	53,35	62,43	68,59	54,04	63,24	194
195	68,25	53,63	62,81	68,95	54,32	63,63	195
196	68,60	53,90	63,19	69,30	54,60	64,01	196
197	68,95	54,18	63,57	69,65	54,88	64,39	197
198	69,30	54,45	63,95	70,01	55,16	64,78	198
199	69,65	54,73	64,33	70,36	55,44	65,16	199
200	70,00	55,00	64,71	70,71	55,71	65,55	200
201	70,35	55,28	65,09	71,07	55,99	65,93	201
202	70,70	55,55	65,47	71,42	56,27	66,32	202
203	71,05	55,83	65,85	71,77	56,55	66,71	203
204	71,40	56,10	66,23	72,13	56,83	67,09	204
205	71,75	56,38	66,62	72,48	57,11	67,48	205
206	72,10	56,65	67,00	72,84	57,39	67,87	206
207	72,45	56,93	67,39	73,19	57,66	68,26	207
208	72,80	57,20	67,77	73,54	57,94	68,65	208
209	73,15	57,48	68,16	73,90	58,22	69,04	209
210	73,50	57,75	68,55	74,25	58,50	69,44	210
211	73,85	58,03	68,93	74,60	58,78	69,83	211
212	74,20	58,30	69,32	74,96	59,06	70,22	212
213	74,55	58,58	69,71	75,31	59,34	70,62	213
214	74,90	58,85	70,10	75,66	59,61	71,01	214
215	75,25	59,13	70,49	76,02	59,89	71,41	215
216	75,60	59,40	70,88	76,37	60,17	71,80	216
217	75,95	59,68	71,28	76,72	60,45	72,20	217
218	76,30	59,95	71,67	77,08	60,73	72,60	218
219	76,65	60,23	72,06	77,43	61,01	73,00	219
220	77,00	60,50	72,45	77,79	61,29	73,40	220
221	77,35	60,78	72,85	78,14	61,56	73,80	221
222	77,70	61,05	73,25	78,49	61,84	74,20	222
223	78,05	61,33	73,64	78,85	62,12	74,60	223
224	78,40	61,60	74,04	79,20	62,40	75,00	224
225	78,75	61,88	74,44	79,55	62,68	75,40	225
226	79,10	62,15	74,84	79,91	62,96	75,81	226
227	79,45	62,43	75,23	80,26	63,24	76,21	227
228	79,80	62,70	75,63	80,61	63,51	76,62	228
229	80,15	62,98	76,03	80,97	63,79	77,02	229
230	80,50	63,25	76,44	81,32	64,07	77,43	230

Table I

$C_{15}H_{24}O$				$C_{15}H_{26}O$			
E. V.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	E. V.
191	89,36	75,03	87,58	90,04	75,72	88,38	191
192	89,83	75,42	88,12	90,51	76,12	88,92	192
193	90,30	75,82	88,65	90,98	76,51	89,46	193
194	90,77	76,21	89,19	91,46	76,91	90,00	194
195	91,24	76,60	89,73	91,93	77,31	90,54	195
196	91,70	77,00	90,27	92,40	77,70	91,09	196
197	92,17	77,39	90,81	92,87	78,10	91,64	197
198	92,64	77,78	91,35	93,34	78,50	92,18	198
199	93,11	78,17	91,89	93,81	78,89	92,73	199
200	93,57	78,57	92,44	94,28	79,29	93,28	200
201	94,04	78,96	92,98	94,76	79,68	93,83	201
202	94,51	79,35	93,53	95,23	80,08	94,38	202
203	94,98	79,75	94,07	95,70	80,48	94,93	203
204	95,44	80,14	94,62	96,17	80,87	95,48	204
205	95,91	80,53	95,17	96,64	81,26	96,03	205
206	96,38	80,92	95,72	97,11	81,66	96,59	206
207	96,85	81,32	96,27	97,58	82,06	97,14	207
208	97,32	81,71	96,82	98,05	82,45	97,70	208
209	97,79	82,10	97,37	98,52	82,85	98,25	209
210	98,25	82,50	97,92	99,00	83,25	98,81	210
211	98,72	82,89	98,48	99,47	83,64	99,37	211
212	99,19	83,28	99,03	99,94	84,04	99,93	212
213	99,66	83,67	99,59	100,41	84,44	100,49	213
214	100,12	84,07	100,14				214

Table I

$C_{10}H_{18}O$				$C_{10}H_{20}O$			
E. V.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	E. V.
231	80,85	63,53	76,84	81,67	64,35	77,83	231
232	81,20	63,80	77,24	82,03	64,63	78,24	232
233	81,55	64,08	77,64	82,38	64,91	78,65	233
234	81,90	64,35	78,05	82,74	65,19	79,06	234
235	82,25	64,63	78,45	83,09	65,46	79,47	235
236	82,60	64,90	78,86	83,44	65,74	79,88	236
237	82,95	65,18	79,27	83,80	66,02	80,29	237
238	83,30	65,45	79,67	84,15	66,30	80,71	238
239	83,65	65,73	80,08	84,50	66,58	81,12	239
240	84,00	66,00	80,49	84,86	66,86	81,53	240
241	84,35	66,28	80,90	85,21	67,14	81,95	241
242	84,70	66,55	81,31	85,56	67,41	82,36	242
243	85,05	66,83	81,72	85,92	67,69	82,78	243
244	85,40	67,10	82,13	86,27	67,97	83,20	244
245	85,75	67,38	82,54	86,62	68,25	83,61	245
246	86,10	67,65	82,96	86,98	68,53	84,03	246
247	86,45	67,93	83,37	87,33	68,81	84,45	247
248	86,80	68,20	83,78	87,69	69,09	84,87	248
249	87,15	68,48	84,20	88,04	69,36	85,29	249
250	87,50	68,75	84,62	88,39	69,64	85,71	250
251	87,85	69,03	85,03	88,75	69,92	86,14	251
252	88,20	69,30	85,45	89,10	70,20	86,56	252
253	88,55	69,58	85,87	89,45	70,48	86,98	253
254	88,90	69,85	86,29	89,81	70,76	87,41	254
255	89,25	70,13	86,71	90,16	71,04	87,83	255
256	89,60	70,40	87,13	90,51	71,31	88,26	256
257	89,95	70,68	87,55	90,87	71,59	88,69	257
258	90,30	70,95	87,97	91,22	71,87	89,11	258
259	90,65	71,23	88,40	91,57	72,15	89,54	259
260	91,00	71,50	88,82	91,93	72,43	89,97	260
261	91,35	71,78	89,25	92,28	72,71	90,40	261
262	91,70	72,05	89,67	92,64	72,99	90,83	262
263	92,05	72,33	90,10	92,99	73,26	91,27	263
264	92,40	72,60	90,52	93,34	73,54	91,70	264
265	92,75	72,88	90,95	93,70	73,82	92,13	265
266	93,10	73,15	91,38	94,05	74,10	92,57	266
267	93,45	73,43	91,81	94,40	74,38	93,00	267
268	93,80	73,70	92,24	94,76	74,66	93,44	268
269	94,15	73,98	92,67	95,11	74,94	93,87	269
270	94,50	74,25	93,10	95,46	75,21	94,31	270

Table I

$C_{10}H_{18}O$				$C_{10}H_{20}O$			
E. V.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcool in the orig. oil	E. V.
271	94,85	74,53	93,54	95,82	75,49	94,75	271
272	95,20	74,80	93,97	96,17	75,77	95,19	272
273	95,55	75,08	94,40	96,52	76,05	95,63	273
274	95,90	75,35	94,84	96,88	76,33	96,07	274
275	96,25	75,63	95,28	97,23	76,61	96,51	275
276	96,60	75,90	95,71	97,59	76,89	96,96	276
277	96,95	76,18	96,15	97,94	77,16	97,40	277
278	97,30	76,45	96,59	98,29	77,44	97,84	278
279	97,65	76,73	97,03	98,65	77,72	98,29	279
280	98,00	77,00	97,47	99,00	78,00	98,73	280
281	98,35	77,28	97,91	99,35	78,28	99,18	281
282	98,70	77,55	98,35	99,71	78,56	99,63	282
283	99,05	77,83	98,80	100,06	78,84	100,08	283
284	99,40	78,10	99,24	—	—	—	—
285	99,75	78,38	99,68	—	—	—	—
286	100,10	78,65	100,13	—	—	—	—

Tiglinate of geraniol: $C_4H_7COOC_{10}H_{17}$.

E. V.	Ester	E. V.	Ester	E. V.	Ester	E. V.	Ester	E. V.	Ester
1	0,42	21	8,85	41	17,28	61	25,71	81	34,13
2	0,84	22	9,27	42	17,70	62	26,13	82	34,55
3	1,26	23	9,69	43	18,12	63	26,55	83	34,98
4	1,69	24	10,11	44	18,54	64	26,97	84	35,40
5	2,11	25	10,54	45	18,96	65	27,39	85	35,82
6	2,53	26	10,96	46	19,38	66	27,81	86	36,24
7	2,95	27	11,38	47	19,80	67	28,23	87	36,66
8	3,37	28	11,80	48	20,23	68	28,65	88	37,09
9	3,79	29	12,22	49	20,65	69	29,08	89	37,51
10	4,21	30	12,64	50	21,07	70	29,50	90	37,93
11	4,63	31	13,06	51	21,49	71	29,92	91	38,35
12	5,05	32	13,49	52	21,91	72	30,34	92	38,77
13	5,47	33	13,91	53	22,33	73	30,76	93	39,19
14	5,90	34	14,33	54	22,75	74	31,18	94	39,62
15	6,32	35	14,75	55	23,18	75	31,61	95	40,04
16	6,74	36	15,17	56	23,60	76	32,03	96	40,46
17	7,16	37	15,59	57	24,02	77	32,45	97	40,88
18	7,58	38	16,01	58	24,44	78	32,87	98	41,30
19	8,01	39	16,44	59	24,87	79	33,29	99	41,72
20	8,43	40	16,86	60	25,29	80	33,71	100	42,14

Tal

for Determining the Ester Value (Acid Value, Saponification Value), al

cc. $\frac{n}{2}$ Potassium Hydroxi

cc. $\frac{n}{2}$ KOH	E. V. (A. V.; S. V.)	$C_{10}H_{18}O$				$C_{10}H_{20}O$		
		Tiglate	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcoho in the orig. o
0,1	*1,87*	0,79	0,65	0,51	0,51	0,66	0,52	0,52
0,2	*3,73*	1,57	1,30	1,02	1,02	1,32	1,04	1,04
0,3	*5,60*	2,36	1,96	1,54	1,54	1,98	1,56	1,57
0,4	*7,47*	3,15	2,61	2,05	2,06	2,64	2,08	2,09
0,5	*9,33*	3,93	3,26	2,56	2,58	3,30	2,60	2,61
0,6	*11,20*	4,72	3,92	3,08	3,10	3,96	3,12	3,14
0,7	*13,07*	5,50	4,57	3,59	3,63	4,62	3,64	3,68
0,8	*14,93*	6,29	5,22	4,10	4,15	5,28	4,16	4,21
0,9	*16,80*	7,08	5,88	4,62	4,68	5,94	4,68	4,74
1,0	*18,67*	7,86	6,53	5,13	5,21	6,60	5,20	5,27
1,1	*20,53*	8,65	7,18	5,64	5,73	7,26	5,72	5,81
1,2	*22,40*	9,44	7,84	6,16	6,25	7,92	6,24	6,35
1,3	*24,27*	10,23	8,49	6,67	6,79	8,58	6,76	6,89
1,4	*26,13*	11,01	9,14	7,18	7,32	9,24	7,28	7,43
1,5	*28,00*	11,80	9,80	7,70	7,86	9,90	7,80	7,97
1,6	*29,87*	12,59	10,45	8,21	8,40	10,56	8,32	8,51
1,7	*31,73*	13,37	11,10	8,72	8,94	11,22	8,84	9,05
1,8	*33,60*	14,16	11,76	9,24	9,48	11,88	9,36	9,60
1,9	*35,47*	14,95	12,41	9,75	10,02	12,54	9,88	10,15
2,0	*37,33*	15,73	13,06	10,26	10,56	13,20	10,40	10,70
2,1	*39,20*	16,52	13,72	10,78	11,11	13,86	10,92	11,25
2,2	*41,07*	17,31	14,37	11,29	11,65	14,52	11,44	11,80
2,3	*42,93*	18,09	15,02	11,80	12,20	15,18	11,96	12,36
2,4	*44,80*	18,88	15,68	12,32	12,75	15,84	12,48	12,91
2,5	*46,67*	19,67	16,33	12,83	13,30	16,50	13,00	13,47
2,6	*48,53*	20,45	16,98	13,34	13,85	17,16	13,52	14,03
2,7	*50,40*	21,24	17,64	13,86	14,41	17,82	14,04	14,59
2,8	*52,27*	22,03	18,29	14,37	14,96	18,48	14,56	15,15
2,9	*54,13*	22,81	18,94	14,88	15,51	19,14	15,08	15,72
3,0	*56,00*	23,60	19,60	15,40	16,07	19,80	15,60	16,28

e II

e Percentage Content of Alcohol and Ester directly from the Number of ien 1,50 g. of Oil are used.

$C_{15}H_{24}O$			$C_{15}H_{26}O$			E. V. (A. V.; S. V.)	cc. $\frac{n}{2}$ KOH
Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil		
0,87	0,73	0,73	0,88	0,74	0,74	*1,87*	**0,1**
1,74	1,46	1,47	1,76	1,48	1,48	*3,73*	**0,2**
2,62	2,20	2,21	2,64	2,22	2,22	*5,60*	**0,3**
3,49	2,93	2,95	3,52	2,96	2,97	*7,47*	**0,4**
4,36	3,66	3,69	4,40	3,70	3,72	*9,33*	**0,5**
5,24	4,40	4,44	5,28	4,44	4,48	*11,20*	**0,6**
6,11	5,13	5,19	6,16	5,18	5,23	*13,07*	**0,7**
6,98	5,86	5,94	7,04	5,92	5,98	*14,93*	**0,8**
7,86	6,60	6,69	7,92	6,66	6,74	*16,80*	**0,9**
8,73	7,33	7,44	8,80	7,40	7,50	*18,67*	**1,0**
9,60	8,06	8,19	9,68	8,14	8,26	*20,53*	**1,1**
10,48	8,80	8,95	10,56	8,88	9,03	*22,40*	**1,2**
11,35	9,53	9,71	11,44	9,62	9,80	*24,27*	**1,3**
12,22	10,26	10,47	12,32	10,36	10,57	*26,13*	**1,4**
13,10	11,00	11,24	13,20	11,10	11,34	*28,00*	**1,5**
13,97	11,73	12,00	14,08	11,84	12,11	*29,87*	**1,6**
14,84	12,46	12,77	14,96	12,58	12,88	*31,73*	**1,7**
15,72	13,20	13,54	15,84	13,32	13,66	*33,60*	**1,8**
16,59	13,93	14,32	16,72	14,06	14,45	*35,47*	**1,9**
17,46	14,66	15,09	17,60	14,80	15,23	*37,33*	**2,0**
18,34	15,40	15,87	18,48	15,54	16,01	*39,20*	**2,1**
19,21	16,13	16,65	19,36	16,28	16,80	*41,07*	**2,2**
20,08	16,86	17,43	20,24	17,02	17,58	*42,93*	**2,3**
20,96	17,60	18,21	21,12	17,76	18,37	*44,80*	**2,4**
21,83	18,33	19,00	22,00	18,50	19,17	*46,67*	**2,5**
22,70	19,06	19,79	22,88	19,24	19,97	*48,53*	**2,6**
23,58	19,80	20,58	23,76	19,98	20,76	*50,40*	**2,7**
24,45	20,53	21,37	24,64	20,72	21,56	*52,27*	**2,8**
25,32	21,26	22,16	25,52	21,46	22,36	*54,13*	**2,9**
26,20	22,00	22,96	26,40	22,20	23,17	*56,00*	**3,0**

Table II

cc. $\frac{n}{2}$ KOH	E. V. (A. V.; S. V.)	$C_{10}H_{18}O$				$C_{10}H_{20}O$		
		Tiglate	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcoh in th orig.
3,1	57,87	24,39	20,25	15,91	16,63	20,46	16,12	16,8
3,2	59,73	25,17	20,90	16,42	17,20	21,12	16,64	17,4
3,3	61,60	25,96	21,56	16,94	17,76	21,78	17,16	17,9
3,4	63,47	26,75	22,21	17,45	18,33	22,44	17,68	18,5
3,5	65,33	27,53	22,86	17,96	18,90	23,10	18,20	19,1
3,6	67,20	28,32	23,52	18,48	19,46	23,76	18,72	19,7
3,7	69,07	29,11	24,17	18,99	20,03	24,42	19,24	20,2
3,8	70,93	29,89	24,82	19,50	20,60	25,08	19,76	20,8
3,9	72,80	30,68	25,48	20,02	21,18	25,74	20,28	21,4
4,0	74,67	31,47	26,13	20,53	21,75	26,40	20,80	22,0
4,1	76,53	32,25	26,78	21,04	22,32	27,06	21,32	22,7
4,2	78,40	33,04	27,44	21,56	22,90	27,72	21,84	23,2
4,3	80,27	33,83	28,09	22,07	23,48	28,38	22,36	23,7
4,4	82,13	34,61	28,74	22,58	24,06	29,04	22,88	24,3
4,5	84,00	35,40	29,40	23,10	24,65	29,70	23,40	24,9
4,6	85,87	36,19	30,05	23,61	25,24	30,36	23,92	25,5
4,7	87,73	36,97	30,70	24,12	25,82	31,02	24,44	26,1
4,8	89,60	37,76	31,36	24,64	26,41	31,68	24,96	26,7
4,9	91,47	38,55	32,01	25,15	27,01	32,34	25,48	27,3
5,0	93,33	39,33	32,66	25,66	27,60	33,00	26,00	27,9
5,1	95,20	40,12	33,32	26,18	28,19	33,66	26,52	28,5
5,2	97,07	40,91	33,97	26,69	28,79	34,32	27,04	29,1
5,3	98,93	41,69	34,62	27,20	29,39	34,98	27,56	29,7
5,4	100,80	42,48	35,28	27,72	29,99	35,64	28,08	30,3
5,5	102,67	43,27	35,93	28,23	30,59	36,30	28,60	30,9
5,6	104,53	44,05	36,58	28,74	31,19	36,96	29,12	31,5
5,7	106,40	44,84	37,24	29,26	31,80	37,62	29,64	32,2
5,8	108,27	45,63	37,89	29,77	32,40	38,28	30,16	32,8
5,9	110,13	46,41	38,54	30,28	33,01	38,94	30,68	33,4
6,0	112,00	47,20	39,20	30,80	33,62	39,60	31,20	34,0
6,1	113,87	47,99	39,85	31,31	34,24	40,26	31,72	34,6
6,2	115,73	48,77	40,50	31,82	34,85	40,92	32,24	35,3
6,3	117,60	49,56	41,16	32,34	35,47	41,58	32,76	35,9
6,4	119,47	50,35	41,81	32,85	36,09	42,24	33,28	36,5
6,5	121,33	51,13	42,46	33,36	36,71	42,90	33,80	37,1
6,6	123,20	51,92	43,12	33,88	37,33	43,56	34,32	37,8
6,7	125,07	52,71	43,77	34,39	37,96	44,22	34,84	38,4
6,8	126,93	53,49	44,42	34,90	38,58	44,88	35,36	39,0
6,9	128,80	54,28	45,08	35,42	39,20	45,54	35,88	39,7
7,0	130,67	55,07	45,73	35,93	39,83	46,20	36,40	40,3

Table II

$C_{15}H_{24}O$			$C_{15}H_{26}O$			E. V. (A. V.; S. V.)	cc. $\frac{n}{2}$ KOH
Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oli		
27,07	22,73	23,76	27,28	22,94	23,98	*57,87*	3,1
27,94	23,46	24,56	28,16	23,68	24,79	*59,73*	3,2
28,82	24,20	25,37	29,04	24,42	25,60	*61,60*	3,3
29,69	24,93	26,17	29,92	25,16	26,41	*63,47*	3,4
30,56	25,66	26,98	30,80	25,90	27,23	*65,33*	3,5
31,44	26,40	27,79	31,68	26,64	28,05	*67,20*	3,6
32,31	27,13	28,61	32,56	27,38	28,88	*69,07*	3,7
33,18	27,86	29,43	33,44	28,12	29,70	*70,93*	3,8
34,06	28,60	30,25	34,32	28,86	30,52	*72,80*	3,9
34,93	29,33	31,07	35,20	29,60	31,35	*74,67*	4,0
35,80	30,06	31,89	36,08	30,34	32,18	*76,53*	4,1
36,68	30,80	32,72	36,96	31,08	33,02	*78,40*	4,2
37,55	31,53	33,55	37,84	31,82	33,86	*80,27*	4,3
38,42	32,26	34,38	38,72	32,56	34,70	*82,13*	4,4
39,30	33,00	35,22	39,60	33,30	35,54	*84,00*	4,5
40,17	33,73	36,05	40,48	34,04	36,38	*85,87*	4,6
41,04	34,46	36,89	41,36	34,78	37,23	*87,73*	4,7
41,92	35,20	37,73	42,24	35,52	38,07	*89,60*	4,8
42,79	35,93	38,58	43,12	36,26	38,92	*91,47*	4,9
43,66	36,66	39,42	44,00	37,00	39,78	*93,33*	5,0
44,54	37,40	40,27	44,88	37,74	40,64	*95,20*	5,1
45,41	38,13	41,13	45,76	38,48	41,50	*97,07*	5,2
46,28	38,86	41,98	46,64	39,22	42,36	*98,93*	5,3
47,16	39,60	42,84	47,52	39,96	43,23	*100,80*	5,4
48,03	40,33	43,70	48,40	40,70	44,09	*102,67*	5,5
48,90	41,06	44,56	49,28	41,44	44,96	*104,53*	5,6
49,78	41,80	45,42	50,16	42,18	45,83	*106,40*	5,7
50,65	42,53	46,29	51,04	42,92	46,71	*108,27*	5,8
51,52	43,26	47,16	51,92	43,66	47,59	*110,13*	5,9
52,40	44,00	48,04	52,80	44,40	48,47	*112,00*	6,0
53,27	44,73	48,91	53,68	45,14	49,35	*113,87*	6,1
54,14	45,46	49,79	54,56	45,88	50,24	*115,73*	6,2
55,02	46,20	50,67	55,44	46,62	51,13	*117,60*	6,3
55,89	46,93	51,55	56,32	47,36	52,02	*119,47*	6,4
56,76	47,66	52,44	57,20	48,10	52,92	*121,33*	6,5
57,64	48,40	53,32	58,08	48,84	53,82	*123,20*	6,6
58,51	49,13	54,21	58,96	49,58	54,72	*125,07*	6,7
59,38	49,86	55,11	59,84	50,32	55,62	*126,93*	6,8
60,26	50,60	56,01	60,72	51,06	56,52	*128,80*	6,9
61,13	51,33	56,91	61,60	51,80	57,43	*130,67*	7,0

Table II

cc. $\frac{n}{2}$ KOH	E. V. (A. V.; S. V.)	$C_{10}H_{18}O$				$C_{10}H_{20}O$		
		Tiglate	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcoh in th orig.
7,1	132,53	55,85	46,38	36,44	40,47	46,86	36,92	40,9
7,2	134,40	56,64	47,04	36,96	41,10	47,52	37,44	41,6
7,3	136,27	57,43	47,69	37,47	41,73	48,18	37,96	42,2
7,4	138,13	58,21	48,34	37,98	42,37	48,84	38,48	42,9
7,5	140,00	59,00	49,00	38,50	43,02	49,50	39,00	43,5
7,6	141,87	59,79	49,65	39,01	43,66	50,16	39,52	44,2
7,7	143,73	60,57	50,30	39,52	44,30	50,82	40,04	44,8
7,8	145,60	61,36	50,96	40,04	44,95	51,48	40,56	45,5
7,9	147,47	62,15	51,61	40,55	45,60	52,14	41,08	46,1
8,0	149,33	62,93	52,26	41,06	46,25	52,80	41,60	46,8
8,1	151,20	63,72	52,92	41,58	46,90	53,46	42,12	47,5
8,2	153,07	64,51	53,57	42,09	47,55	54,12	42,64	48,1
8,3	154,93	65,29	54,22	42,60	48,20	54,78	43,16	48,8
8,4	156,80	66,08	54,88	43,12	48,86	55,44	43,68	49,5
8,5	158,67	66,87	55,53	43,63	49,53	56,10	44,20	50,1
8,6	160,53	67,65	56,18	44,14	50,19	56,76	44,72	50,8
8,7	162,40	68,44	56,84	44,66	50,85	57,42	45,24	51,5
8,8	164,27	69,23	57,49	45,17	51,51	58,08	45,76	52,1
8,9	166,13	70,01	58,14	45,68	52,18	58,74	46,28	52,8
9,0	168,00	70,80	58,80	46,20	52,86	59,40	46,80	53,5
9,1	169,87	71,59	59,45	46,71	53,54	60,06	47,32	54,2
9,2	171,73	72,37	60,10	47,22	54,21	60,72	47,84	54,9
9,3	173,60	73,16	60,76	47,74	54,89	61,38	48,36	55,6
9,4	175,47	73,95	61,41	48,25	55,57	62,04	48,88	56,2
9,5	177,33	74,73	62,06	48,76	56,25	62,70	49,40	56,9
9,6	179,20	75,52	62,72	49,28	56,93	63,36	49,92	57,6
9,7	181,07	76,31	63,37	49,79	57,61	64,02	50,44	58,3
9,8	182,93	77,09	64,02	50,30	58,30	64,68	50,96	59,0
9,9	184,80	77,88	64,68	50,82	59,00	65,34	51,48	59,7
10,0	186,67	78,67	65,33	51,33	59,69	66,00	52,00	60,4
10,1	188,53	79,45	65,98	51,84	60,38	66,66	52,52	61,1
10,2	190,40	80,24	66,64	52,36	61,08	67,32	53,04	61,8
10,3	192,27	81,03	67,29	52,87	61,78	67,98	53,56	62,5
10,4	194,13	81,81	67,94	53,38	62,48	68,64	54,08	63,2
10,5	196,00	82,60	68,60	53,90	63,19	69,30	54,60	64,0
10,6	197,87	83,39	69,25	54,41	63,90	69,96	55,12	64,7
10,7	199,73	84,17	69,90	54,92	64,61	70,62	55,64	65,4
10,8	201,60	84,96	70,56	55,44	65,32	71,28	56,16	66,1
10,9	203,47	85,75	71,21	55,95	66,03	71,94	56,68	66,8
11,0	205,33	86,53	71,86	56,46	66,75	72,60	57,20	67,6

$C_{15}H_{24}O$			$C_{15}H_{26}O$			E. V. (A. V.; S. V.)	cc. $\frac{n}{2}$ KOH
Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil		
62,00	52,06	57,81	62,48	52,54	58,34	*132,53*	7,1
62,88	52,80	58,71	63,36	53,28	59,25	*134,40*	7,2
63,75	53,53	59,62	64,24	54,02	60,17	*136,27*	7,3
64,62	54,26	60,53	65,12	54,76	61,09	*138,13*	7,4
65,50	55,00	61,45	66,00	55,50	62,01	*140,00*	7,5
66,37	55,73	62,36	66,88	56,24	62,93	*141,87*	7,6
67,24	56,46	63,28	67,76	56,98	63,86	*143,73*	7,7
68,12	57,20	64,21	68,64	57,72	64,80	*145,60*	7,8
68,99	57,93	65,14	69,52	58,46	65,74	*147,47*	7,9
69,86	58,66	66,07	70,40	59,20	66,67	*149,33*	8,0
70,74	59,40	67,00	71,28	59,94	67,61	*151,20*	8,1
71,61	60,13	67,93	72,16	60,68	68,55	*153,07*	8,2
72,48	60,86	68,87	73,04	61,42	69,50	*154,93*	8,3
73,36	61,60	69,81	73,92	62,16	70,45	*156,80*	8,4
74,23	62,33	70,75	74,80	62,90	71,40	*158,67*	8,5
75,10	63,06	71,69	75,68	63,64	72,35	*160,53*	8,6
75,98	63,80	72,64	76,56	64,38	73,31	*162,40*	8,7
76,85	64,53	73,60	77,44	65,12	74,27	*164,27*	8,8
77,72	65,26	74,56	78,32	65,86	75,23	*166,13*	8,9
78,60	66,00	75,52	79,20	66,60	76,20	*168,00*	9,0
79,47	66,73	76,48	80,08	67,34	77,17	*169,87*	9,1
80,34	67,46	77,44	80,96	68,08	78,14	*171,73*	9,2
81,22	68,20	78,41	81,84	68,82	79,12	*173,60*	9,3
82,09	68,93	79,38	82,72	69,56	80,10	*175,47*	9,4
82,96	69,66	80,35	83,60	70,30	81,08	*177,33*	9,5
83,84	70,40	81,33	84,48	71,04	82,06	*179,20*	9,6
84,71	71,13	82,31	85,36	71,78	83,05	*181,07*	9,7
85,58	71,86	83,30	86,24	72,52	84,05	*182,93*	9,8
86,46	72,60	84,28	87,12	73,26	85,04	*184,80*	9,9
87,33	73,33	85,27	88,00	74,00	86,04	*186,67*	10,0
88,20	74,06	86,26	88,88	74,74	87,04	*188,53*	10,1
89,08	74,80	87,26	89,76	75,48	88,05	*190,40*	10,2
89,95	75,53	88,26	90,64	76,22	89,06	*192,27*	10,3
90,82	76,26	89,26	91,52	76,96	90,07	*194,13*	10,4
91,70	77,00	90,27	92,40	77,70	91,09	*196,00*	10,5
92,57	77,73	91,28	93,28	78,44	92,11	*197,87*	10,6
93,44	78,46	92,29	94,16	79,18	93,13	*199,73*	10,7
94,32	79,20	93,31	95,04	79,92	94,16	*201,60*	10,8
95,19	79,93	94,33	95,92	80,66	95,19	*203,47*	10,9
96,06	80,66	95,35	96,80	81,40	96,22	*205,33*	11,0

Table II

cc. $\frac{n}{2}$ KOH	E. V. (A. V.; S. V.)	$C_{10}H_{18}O$				$C_{10}H_{20}O$		
		Tiglate	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcoh in th orig.
11,1	207,20	87,32	72,52	56,98	67,46	73,26	57,72	68,3
11,2	209,07	88,11	73,17	57,49	68,18	73,92	58,24	69,0
11,3	210,93	88,89	73,82	58,00	68,90	74,58	58,76	69,8
11,4	212,80	89,68	74,48	58,52	69,63	75,24	59,28	70,5
11,5	214,67	90,47	75,13	59,03	70,36	75,90	59,80	71,2
11,6	216,53	91,25	75,78	59,54	71,09	76,56	60,32	72,0
11,7	218,40	92,04	76,44	60,06	71,82	77,22	60,84	72,7
11,8	220,27	92,83	77,09	60,57	72,56	77,88	61,36	73,5
11,9	222,13	93,61	77,74	61,08	73,30	78,54	61,88	74,2
12,0	224,00	94,40	78,40	61,60	74,04	79,20	62,40	75,0
12,1	225,87	95,19	79,05	62,11	74,79	79,86	62,92	75,7
12,2	227,73	95,97	79,70	62,62	75,53	80,52	63,44	76,5
12,3	229,60	96,76	80,36	63,14	76,27	81,18	63,96	77,2
12,4	231,47	97,55	81,01	63,65	77,02	81,84	64,48	78,0
12,5	233,33	98,33	81,66	64,16	77,77	82,50	65,00	78,7
12,6	235,20	99,12	82,32	64,68	78,53	83,16	65,52	79,5
12,7	237,07	99,91	82,97	65,19	79,29	83,82	66,04	80,3
12,8	238,93	—	83,62	65,70	80,05	84,48	66,56	81,0
12,9	240,80	—	84,28	66,22	80,81	85,14	67,08	81,8
13,0	242,67	—	84,93	66,73	81,57	85,80	67,60	82,6
13,1	244,53	—	85,58	67,24	82,34	86,46	68,12	83,4
13,2	246,40	—	86,24	67,76	83,12	87,12	68,64	84,2
13,3	248,27	—	86,89	68,27	83,89	87,78	69,16	84,9
13,4	250,13	—	87,54	68,78	84,67	88,44	69,68	85,7
13,5	252,00	—	88,20	69,30	85,45	89,10	70,20	86,5
13,6	253,87	—	88,85	69,81	86,23	89,76	70,72	87,3
13,7	255,73	—	89,50	70,32	87,01	90,42	71,24	88,1
13,8	257,60	—	90,16	70,84	87,80	91,08	71,76	88,9
13,9	259,47	—	90,81	71,35	88,60	91,74	72,28	89,7
14,0	261,33	—	91,46	71,86	89,39	92,40	72,80	90,5
14,1	263,20	—	92,12	72,38	90,18	93,06	73,32	91,3
14,2	265,07	—	92,77	72,89	90,98	93,72	73,84	92,1
14,3	266,93	—	93,42	73,40	91,78	94,38	74,36	92,9
14,4	268,80	—	94,08	73,92	92,58	95,04	74,88	93,7
14,5	270,67	—	94,73	74,43	93,39	95,70	75,40	94,6
14,6	272,53	—	95,38	74,94	94,20	96,36	75,92	95,4
14,7	274,40	—	96,04	75,46	95,01	97,02	76,44	96,2
14,8	276,27	—	96,69	75,97	95,83	97,68	76,96	97,0
14,9	278,13	—	97,34	76,48	96,65	98,34	77,48	97,9
15,0	280,00	—	98,00	77,00	97,47	99,00	78,00	98,7

$C_{15}H_{24}O$			$C_{15}H_{26}O$			E. V. (A. V.; S. V.)	cc. $\frac{n}{2}$ KOH
cetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil		
96,94	81,40	96,38	97,68	82,14	97,25	*207,20*	11,1
97,81	82,13	97,41	98,56	82,88	98,29	*209,07*	11,2
98,68	82,86	98,44	99,44	83,62	99,33	*210,93*	11,3
99,56	83,60	99,48	100,32	84,36	100,38	*212,80*	11,4
00,43	84,33	100,51	—	—	—	*214,67*	11,5
—	—	—	—	—	—	*216,53*	11,6
—	—	—	—	—	—	*218,40*	11,7
—	—	—	—	—	—	*220,27*	11,8
—	—	—	—	—	—	*222,13*	11,9
—	—	—	—	—	—	*224,00*	12,0
—	—	—	—	—	—	*225,87*	12,1
—	—	—	—	—	—	*227,73*	12,2
—	—	—	—	—	—	*229,60*	12,3
—	—	—	—	—	—	*231,47*	12,4
—	—	—	—	—	—	*233,33*	12,5
—	—	—	—	—	—	*235,20*	12,6
—	—	—	—	—	—	*237,07*	12,7
—	—	—	—	—	—	*238,93*	12,8
—	—	—	—	—	—	*240,80*	12,9
—	—	—	—	—	—	*242,67*	13,0
—	—	—	—	—	—	*244,53*	13,1
—	—	—	—	—	—	*246,40*	13,2
—	—	—	—	—	—	*248,27*	13,3
—	—	—	—	—	—	*250,13*	13,4
—	—	—	—	—	—	*252,00*	13,5
—	—	—	—	—	—	*253,87*	13,6
—	—	—	—	—	—	*255,73*	13,7
—	—	—	—	—	—	*257,60*	13,8
—	—	—	—	—	—	*259,47*	13,9
—	—	—	—	—	—	*261,33*	14,0
—	—	—	—	—	—	*263,20*	14,1
—	—	—	—	—	—	*265,07*	14,2
—	—	—	—	—	—	*266,93*	14,3
—	—	—	—	—	—	*268,80*	14,4
—	—	—	—	—	—	*270,67*	14,5
—	—	—	—	—	—	*272,53*	14,6
—	—	—	—	—	—	*274,40*	14,7
—	—	—	—	—	—	*276,27*	14,8
—	—	—	—	—	—	*278,13*	14,9
—	—	—	—	—	—	*280,00*	15,0

Table II

cc. $\frac{n}{2}$ KOH	E. V. (A. V.; S. V.)	$C_{10}H_{18}O$				$C_{10}H_{20}O$		
		Tiglate	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcoh in th orig.
15,1	*281,87*	—	98,65	77,51	98,29	99,66	78,52	99,5
15,2	*283,73*	—	99,30	78,02	99,12	100,32	79,04	100,4
15,3	*285,60*	—	99,96	78,54	99,95	—	—	—

Table II

$C_{15}H_{24}O$			$C_{15}H_{26}O$			E. V. (A. V.; S. V.)	cc. $\frac{n}{2}$ KOH
cetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil		
—	—	—	—	—	—	*281,87*	**15,1**
—	—	—	—	—	—	*283,73*	**15,2**
—	—	—	—	—	—	*285,60*	**15,3**

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