A STUDY OF PEPPERMINT OIL

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
Richard W. Thompson
1938

R. C. Marston

A STUDY OF

PEPPERMINT OIL

A thesis submitted to the faculty of Michigan
State College in partial fulfillment of the
requirements for the degree of Master of
Science

Richard Walter Thompson

Department of Chemistry

1938

6-29-54
3
C

A Study of Peppermint Oil

1. Introduction

Mints have been known to the Western World since the earliest times. Several, the identity of which is uncertain, were used as spices or in medicine by the Egyptians(1), Hebrews (2), and Romans (3). They seem to have been put to similar uses by the barbarous tribes dwelling east of the Rhine(4). Charlemagne mentions in his Capitulare three mints as worthy of cultivation.

---

(1) Schweinfurth, Berichte deutsch. botan. Gesellschaft 2 (1884), 368.

(2) Math.,23:23; Luke, 11:43.

(3) Plinii, Naturalis historiae libri.Lib.19, cap.8.

(4) Gildemeister and Hoffmann, The Volatile Oils, Vol. 1, p. 190.

References to mints occur in the writings of the abbess Hildegard, c.1160. The Berlin ordinance of 1574 mentions Oleum Menthae, and the Frankfort list of 1582 mentions Oleum Menthae, Oleum Polemii, and Oleum Pulegii.(1) Whether or not peppermint corresponds to any of these is a matter that can no longer be elucidated. The earliest known specimens of Mentha piperita are those in the British Museum in London, obtained by John Ray in Hertfordshire in 1696(2).

Cultivation of peppermint began in England about 1750, and reached its height a century later, after which a decline set in because of severe American competition. Cultivation on the Continent began not earlier than in England.

Peppermint was grown in Japan much earlier than in any other country, flourishing there long before the

(1) Gildemeister and Hoffmann, The Volatile Oils, Vol.I, p.191.

(2) John Ray, Historia Plantarum, Vol.III, p.284.

Christian era(1). Fluckiger asserts that menthol was extracted and used in medicine two thousand years ago(2). When the distillation of peppermint oil began is not known.

The production and distillation of peppermint oil in the United States began in Wayne County, New York, early in the nineteenth century. Later the industry spread to Michigan, Indiana, Oregon, and California. The United States is now the world's principal producer, outside of Japan, and eighty to ninety percent of the crop is grown in Michigan.

Peppermint oils from different parts of the world vary widely in their composition. Indeed, so many factors are operative, soils, weather, fertilizers, varieties, strains, time of harvesting, etc., that oils from a single area may show striking differences. In general, however, English oil commands top prices, with American oil second, and Japanese oil at the bottom of the list. The last usually has a menthol con-

---

(1) Imperial Encyclopedia, 8th edition, Vol. 68, p.326

(2) Pharmakognosie, (1891), p. 726

tent of eighty to ninety percent and is deficient or totally lacking in those components, especially the esters, which impart that fine flavor so prized in the candy and gum industries.

The first thoroughgoing study of American peppermint oil was carried out by Power and Kleber near the end of the last century(1). They examined an oil distilled from the dry herb and identified the following compounds:

Acetaldehyde
Acetic acid
A-pinene
L-limonene
Menthone
Menthyl acetate
Cadinene
Isovalerianic aldehyde
" acid
Phellandrene
Cineole
Menthol
Menthyl isovalerianate
A menthyl ester, $C_{10}H_{19}.C_2H_3O_2$
A lactone, $C_{10}H_{16}O_2$

---

(1) Pharm. Rundeschau 12, (1894), 157

Amyl acetate (trace)
Dimethyl sulphide (trace)

For the present study, which was purely qualitative and restricted to the isolation of the components, and their identification, an oil was chosen which was produced on a muck soil in 1937 in Ingham County, near Lansing, Michigan.

2. Experimental

To separate the oil into its components, samples were distilled in three ways: in vacuo, at atmospheric pressure, and with steam. Some of the menthol was removed by cooling and crystallization, but this was possible only when the more volatile compounds had been distilled off. Atmospheric and steam distillation were used but little, since these methods caused too much decomposition of the hydrocarbons present. When distilling in vacuo, five degree fractions were collected, and the apparatus was so designed that each fraction could be removed without breaking the vacuum. A fractionating column over four feet long was used, and it was wrapped with nichrome wire so that it could be heated electrically.

Acetaldehyde

When a sample was distilled at atmospheric pressure, a small portion came over between 30° and 110°. A part of this was treated with sodium bisulphite. A precipitate formed, but too little for identification. Probably it was due to the presence of acetaldehyde or valerianaldehyde or both. The possibility that the precipitate was due to a combination with traces of menthone in this fraction is excluded, because menthone does not combine with sodium bisulphite(1).

Dimethyl sulphide

This fraction possessed a strong, disagreeable odor, like that of dimethyl sulphide. When superimposed upon a .5 N. solution of mercuric chloride in a testtube, a white precipitate quickly formed at the interface. This is the standard test for dimethyl sulphide in peppermint oil(2).

(1) Heusler and Pond, The Chemistry of the Terpenes, p.298.

(2) U.S.Pharmacopeia

Pinene

The fraction boiling at50-55°/10mm. was purified by repeated distillation, then distilled at atmospheric pressure, and that portion boiling from 154 to 158° collected, the boiling point of pinene being 156°. Many attempts were made to prepare the hydrochloride after the method of Wallach(1), but no solid derivative could be obtained. The sample was carefully dried with anhydrous copper sulphate or calcium chloride. Then hydrochloric acid gas, prepared by dropping sulphuric acid into a mixture of salt and concentrated hydrochloric acid, and dried by passing through sulphuric acid,was passed into the sample, which was well cooled by a freezing mixture.

It may be of interest to note in passing that metallic sodium was tried as a dehydrating agent on a few samples. In every case polymerization to an orange jelly-like mass was the result. This is similar to the action of sodium on isoprene,of which pinene may be regarded as the bimolecular compound.

Pinene was finally identified by converting it to the nitrosochloride(2). Equal parts of sample, ethyl

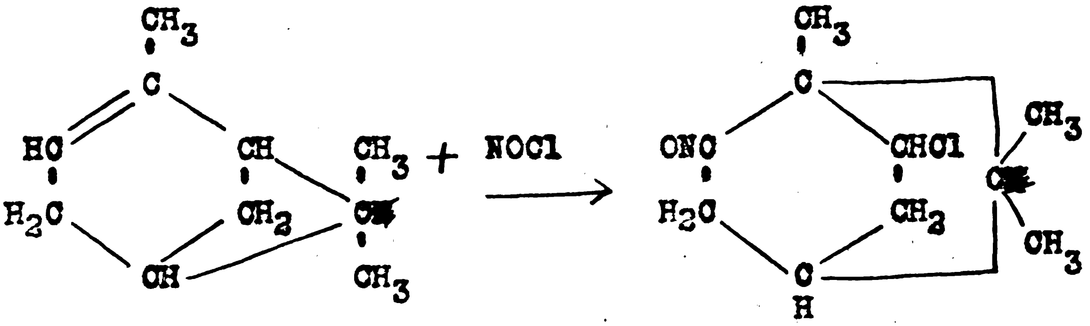
---

(1) Wallach, Annalen, 239, 4.

(2) Wallach and Otto, Annalen, 253, 251.

nitrite, and acetic acid were mixed and thoroughly cooled. Then concentrated hydrochloric acid was added little by little. The crystals of pinene nitrosochloride which quickly formed were filtered off by suction, recrystallized from alcohol, washed with cold alcohol, and dried at 50°. The melting found was 100-102°. That given is 109-111°(1).

Equation for the reaction:



Pinene

Pinene nitrosochloride

The ethyl nitrite used in this derivative was prepared by dissolving twenty-five grams of sodium nitrite in a mixture of one hundred cc. of water and ten grams of alcohol contained in a three-neck flask. From a dropping funnel a solution of twenty grams of sulphuric acid in one hundred fifty cc. of water and ten grams of alcohol was added in a thin stream. The ethyl nitrite distilled off as it formed and was collected in a flask cooled with ice. It was then ready for use without fur-

---

(1) Annalen, 253, 251.

ther purification.

Menthene

A menthene boiling at 167-8° has been found in Russian peppermint oil by Andres and Andreef. To determine if it occurred in American oil, the fraction boiling at55-58°/10mm. was taken. Two cc. of hydrochloric acid in two cc. of glacial acetic acid was added slowly to a well cooled mixture of five cc. of sample, five cc. of glacial acetic acid, and four cc. of ethyl nitrite(1). But no crystalline derivative could be obtained.

Cineole

The fraction boiling at 58-63°/10mm . , was distilled repeatedly in vacuo, and finally a portion boiling at 175-178°(atmospheric) was tested for cineole. Pure cineole boils at 176°(2). An attempt was made to prepare the addition product of cineole and iodol(3).

---

(1) Sicker and Kremers, Amer. Chem. Journ., 14, 292.

(2) Heusler and Pond, The Chemistry of the Terpenes, p.324.

(3)Hirschsohn, Pharm. Zeitschr.f. Russl., 32,49.

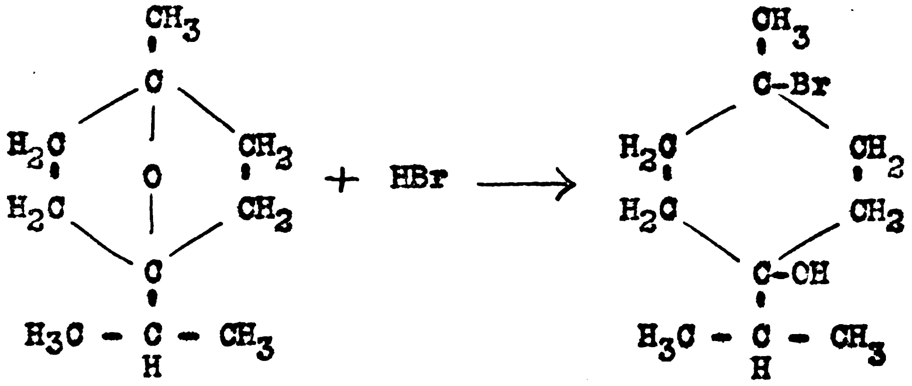
As no iodol was available, it was necessary to prepare it from pyrrole. But only a gram or two of this was on hand, and the yield of iodol was so small that no crystals of the derivative were obtained.

The hydrobromide was then resorted to. Into a Wurtz flask fitted with a dropping funnel were placed one part of red phosphorus and two parts of water. Bromine was then added dropwise from the funnel and the hydrobromic acid gas formed was passed through a U-tube containing red phosphorus to remove bromine vapor and through a U-tube containing calcium chloride to remove moisture. When the dried gas was admitted to a flask containing a petroleum ether of sample, well cooled by a freezing mixture, a heavy white precipitate formed immediately. This was filtered, washed with petroleum ether,and dried with suction. Decomposition was so rapid that it was never possible to recrystallize the product and very difficult to dry it properly. The melting points found for different samples were 48°, 52-54°, 56-58°, and 58-60°. That recorded in the literature is 56-57°(1).

---

(1) Heusler and Pond, The Chemistry of the Terpenes, p. 326.

Equation for the reamtion:



L-limonene

The cineole fraction was tested also for limonene, in three ways. Limonene boils at 175-177°(1).

The nitrosochloride method of Wallach(2) was not successful. To a mixture of five cc. of sample, eleven cc. of ethyl nitrite, and twelve cc. of glacial acetic acid, cooled with ice and salt, was added a mixture of six cc. of hydrochloric acid and six cc. of glacial acid, slowly and in small portions. Finally five cc. of ethyl alcohol was added, and the mixture was allowed to stand for some time in a freezing mixture. But no crystals formed.

An attempt to prepare the tetrabromide using the procedure of Power and Kleber was likewise unsuccessful(3).

(1) Heusler and Pond, The Chemistry of the Terpenes, p.72.

(2) Annalen, 252, 106; 270, 174.

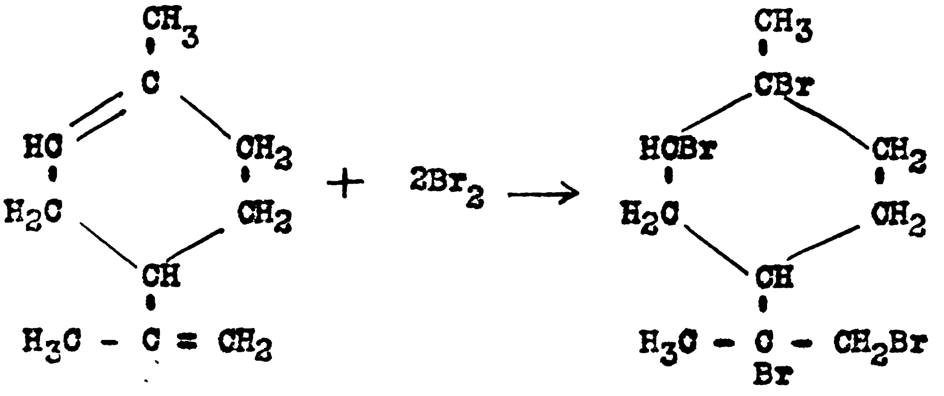
(3) Pharm. Rundschau, 12, (1894), 160.

The sample was added dropwise to a cooled mixture of bromine and acetic acid until only a slight excess of bromine remained. The solution was then decolorized with an aqueous solution of sulphur dioxide, and water was added to precipitate the bromide. But again no crystals developed. Power and Kleber claimed that in this way the formation of hydrobromic acid and of uncrystallizable bromides of isomeric terpenes was inhibited.

The only method found which would yield a solid derivative was that of Wallach, and this was successful but once. The sample was purified as much as possible and diluted with four times its volume of glacial acetic acid. To the solution, cooled with ice, bromine was added from a medicine dropper as long as it was absorbed with decolorization. After standing for several days, a few crystals were observed, the melting point of which was 98-100°, no attempt being made to recrystallize them. The melting point recorded is 104 to 105°(1).

(1) Heusler and Pond, The Chemistry of the Terpenes, p.73.

Equation for the reaction:



L-limonene Limonene tetrabromide

Phellandrenes

The cineole and limonene fraction was further tested for the presence of phellandrenes, the α-modification boiling at 175°, and the β-form at 171°. A solution of five grams of sodium nitrite in eight grams of water was placed beneath a layer of five cc. of sample in ten cc. of petroleum ether contained in a testtube. Then five cc. of glacial acetic acid was added with shaking to release nitrous acid(1). Although this procedure was repeated on many samples, no crystals of nitrosite were ever obtained. The nitrosite is the only solid derivative of phellandrene known.

(1) Wallach and Gildemeister, Annalen, 246, 283.

These results would seem to indicate that phellandrene was not present in the oil examined. Yet whenever a fraction boiling at 58-63°/10mm. was afterward distilled at atmospheric pressure, it rapidly turned from colorless to a deep red. As cineole and limonene are stable compounds and can be distilled at ordinary pressures without decomposition, while phellandrene with its conjugated system of double bonds is among the most unstable of the terpenes(1), it may be assumed that this compound was present. Probably the failure to prepare the nitrosite was due to insufficient purification.

Menthone

Next to menthol, menthone is the most abundant constituent of peppermint oil, occurring in amounts as high as twenty percent. As it boils at 207-208°, and menthol at 212-215°, the two cannot be separated by distillation. However by cooling the fraction boiling within this range to a point well below freezing, it was possible to crystallize out a large part of the menthol, which was removed by filtering with suction as rapidly as possible.

(1) Heusler and Pond, The Chemistry of the Terpenes, p. 109.

Many attempts were made to prepafe the oxime of menthone, using the method of,Beckmann(1). A menthone sample was dissolved in three times its weight of ninety percent alcohol, and powdered hydroxylamine hydrochloride was added in an amount about 1.3 times that required by the equation. Then during ten minutes a little more than the theoretical amount of sodium bicarbonate was added in small portions to neutralize the acid and release the hydroxylamine. After standing thirty minutes with occasional stirring the mixture was poured into cold water and stirred vigorously. But nocrystals of the oxime were ever obtained by this method or variations of it. Nor could the ox ime be gained by shaking out of ethereal solution with dilute sulphuric acid. The references on this procedure, however, were not available(2).

The dibromo derivative was tried(3). Two mols of bromine was added to one mol of the menthone fraction dissolved in chloroform at room temperature. But

---

(1) Annalen, 350, 329.

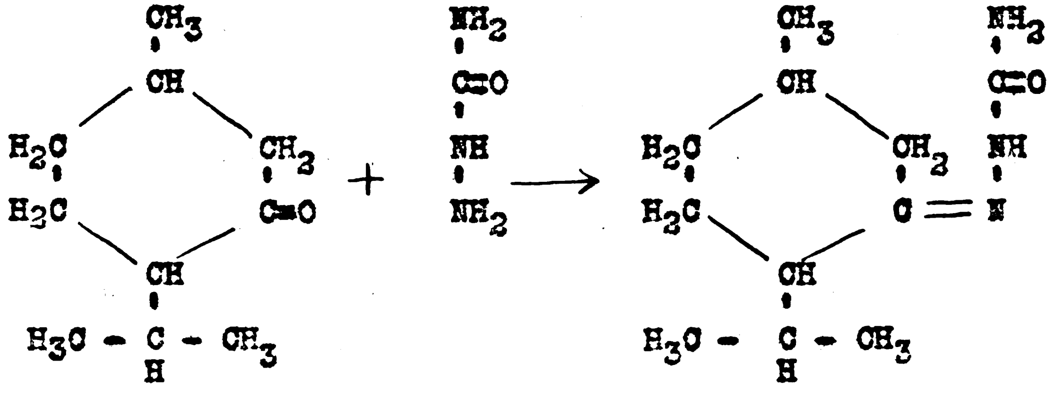
(2) Beckmann, Journ.f.Prakt.Chem.,II, 55,(1897), 17.
C., (1887), 1375, 1461.

(3) Beckmann and Eichelberg, Ber.,29, 418.

addition of alcohol did not cause any precipitation. If too much bromine was used, other crystalline products should have formed, but none was observed.

Finally Flatau's method for the preparation of the semicarbazone was tried(1). Assuming the sample to be two-thirds menthone, the theoretical amount of semicarbazi~~d~~ne was dissolved in a little water. Corresponding amounts of sample and of potassium acetate were then dissolved in a mixture of alcohol and water. The two solutions were then mixed and filtered. In the filtrate, small needles of the semicarbazone were soon observed. These were removed and recrystallized three times from boiling alcohol. After drying, the melting point was found to be 175°. Five more recrystallizations raised the melting point to 177-178°. The value recorded is 178°(2).

Equation for the reaction:



Menthone Menthone semicarbazone

---

(1) Bulletin de la Societe Chimique, 3, 19, 783.

(2) Heusler and Pond, The Chemistry of the Terpenes, p.303.

L-menthol

Menthol costituted about fifty percent of the oil examined, and was readily obtained by freezing oil from which the more volatile components had been removed. When recrystallized from chloroform,,it melted at 42-43°, which is the value recorded in the literature(1). For a derivative the benzoate, melting at 53-54°, was chosen. Menthol and benzoic anhydride were heated together in a bomb tube for three hours at 160°(2). After cooling, the reaction mixture solidified to a yellow, crystalline mass according to expectations. Unfortunately, after boiling with sodium carbonate solution to neutralize excess benzoic anhydride; dissolving in ether and shaking with cold, dilute sodium hydroxide solution; separation; and evaporation of the ether, the benzoate did not crystallize again, and only a yellow oil remained.

Dimenthyl sulphite was then tried(3). Unlike almost all other solid derivatives of menthol, this does not

---

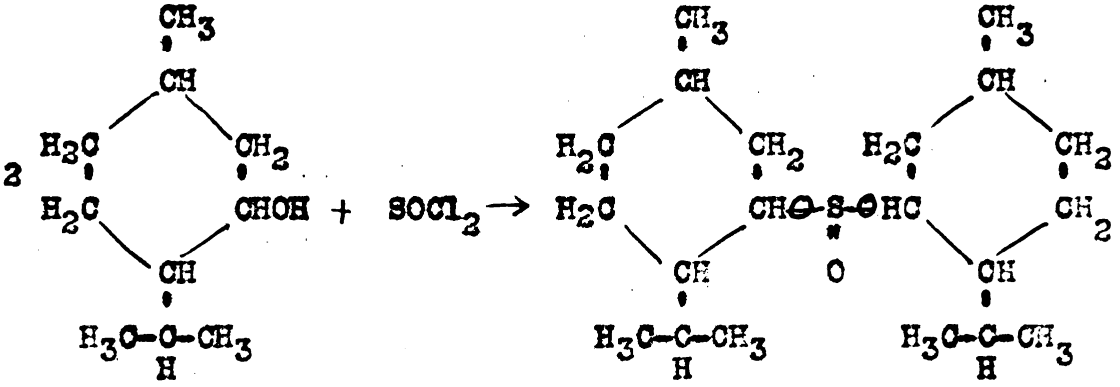
(1) Heusler and Pond, The Chemistry of the Terpenes, p.309.

(2) Beckmann, Annalen, 262,31.

(3) Kenyon and Pickard, J. Chem. Soc., 107, p.45.

require a high temperature for its preparation, and in fact must be prepared at a temperature below 6°. Equivalent amounts of thionyl chloride and menthol, each diluted with a large volume of petroleum ether, were slowly mixed and allowed to react at alow temperature. The product was then separated from unchanged menthol by fractional distillation in vacuo. Dimenthyl sulphite boils at 210°/9mm. and solidifies to a white mass, which crystallizes readily from dilute alcohol in needles which melt at 52°. The value found was 50-52°.

Equation for the reaction:



Menthol Dimenthyl sulphite

Esters

An effort was made to obtain the saponification numbers of the fractions boiling at 107-112°/10mm. and at 124-130°/10mm., as menthyl acetate boils at 109°/10mm. and menthyl isovalerianate at 125-127°/10mm. These fractions were redistilled many times, but as is shown by the data were even then far from pure. Yet, as these fractions were not acid to litmus or phenolphthalein before saponification, the data reveals that esters were present.

Normality of H_2SO_4 solution	.2545
" " KOH "	.4510

Fraction	Acetate	Isovalerianate
Gm. of sample	1.0326	0.9993
Cc. " KOH	25.24	26.21
Cc. " H_2SO_4 to neutralize	38.68	37.86
Gm.millieqt. KOH	11.38	11.82
" H_2SO_4	9.83	9.64
" KOH to saponify	1.55	2.18
Saponification No. found	84.1	123.2
" " calcd.	280	231

In order to identify the acid radicals, about one gram of the potassium salt was placed in a small flask with the theoretical amount of thionyl chloride and heated gently for thirty minutes under a reflux condenser. The cooled residue was then treated with two mols of p-toluidine dissolved in thirty cc. of benzene and refluxed a few minutes. Finally the benzene solution was washed with water, dilute acid, dilute alkali, and again with water, filtered, and evaporated to dryness(1). But the recrystallizing medium, methyl alcohol, yielded no crystals for either ester, and so the presence of neither was proved.

Cadinene

The highest boiling fraction, from 130 to 148°/mm. was tested for cadinene, $C_{15}H_{24}$, a sesquiterpene containing two conjugated double bonds, the exact position of which has never been determined. The compound boils at 274-275°/atmospheric(2). It oxidizes very rapidly in the air, and when distilling in vacuo a stream of inert gas, rather than air, should be used to prevent bumping. Many attempts were made to obtain the dihydrochloride of this compound(3), one volume of sample being mixed with two volumes of glacial acetic acid, a fairly rapid stream of hydrochloric acid gas passed in, and the mixture kept at or near 0° for two days, but a crystalline derivative was never obtained. Yet the boiling point of

---

(1) Kamm, Qualitative Organic Analysis, p.177.

(2) Heusler and Pond, Chemistry of the Terpenes, p.415.

(3) J. Chem. Soc., 1924, p.1993.

the fraction and the fact that a large amount of decomposition occurred whenever it was distilled in the air suggest that cadinene was probably present.

Residue

The residue, after all the aforementioned fractions were collected, was a resinous mass of a deep orange-red color, consisting largely of oxidation products and polymers of phellandrene and cadinene.

3. Conclusion

A qualitative study of Michigan peppermint oil proved the presence of several chemical compounds. Evidence was found of the presence of several others.

References

Heusler and Pond, The Chemistry of theTerpenes

Gildemeister and Hoffmann, The Volatile Oils

Parry, The Chemistry of the Essential Oils

Fisher, Laboratory Manual of Organic Chemistry

Kamm, Qualitative Organic Analysis

Schimmel & Co., Annual Reports on Essential Oils

U.S.Pharmacopeia

Annalen Chemie

American Chemical Journal

Bulletin de la Societe Chimique

Journal fur Praktische Chemie

Berichte

Journal of the Chemical Society