

V.—*On the Camphor of Peppermint.*

By A. OPPENHEIM, Ph.D.

THE camphor of peppermint, known as constituting the stearoptene of the essential oil of *Mentha piperita*, has lately been obtained in larger quantities, so as to allow of a closer examination being instituted than has hitherto been possible. It arrives from Japan in coarse earthenware jars, merely protected by paper covers, and consists of a mass of small, white, fragrant, prismatic crystals, resembling sulphate of magnesia, which salt, in fact, seems to be constantly used for the purpose of adulterating the Japanese peppermint-camphor, as from ten to twenty per cent. of that salt may be separated from the camphor by washing it with water. When washed with warm water, the peppermint-camphor melts, and,

on congealing, forms itself into a hard crystalline mass. It melts at 36 C, and distils, without decomposition, at 210°. These properties very nearly coincide with those established by Dumas,\* for the stereoptene of American oil of peppermint. The composition of these two substances is exactly the same, viz. :

0.260 grm. of Japanese camphor of peppermint, dried at 100°, gave 0.732 grm. of carbonic acid, and 0.315 grm. of water, or in 100 parts.

	Japan camphor of peppermint.	Dumas American camphor.	Calculated.
C	76.93	76.5	76.92
H	13.40	13.1	12.82
O	„	„	10.26

This corresponds with the formula established by Dumas,  $C_{10}H_{20}O$ .† Walter verified this formula in 1830, by determining the vapour-density of the corresponding hydrocarbon,  $C_{10}H_{18}$ .

The nature of this body which, on many grounds, claims our attention, has not been determined by either of these chemists. Whether it be an alcohol, an aldehyde, a ketone, or of a nature less distinct (like the hydrates of oil of turpentine), it possesses particular interest, from the fact of its bordering on the two great groups of organic chemistry, the group of fatty and that of aromatic bodies. To the former it is related by being isomeric with capric aldehyde, and to the latter, by differing from a number of aromatic bodies, merely in the number of its hydrogen-equivalents.

The camphol of Berthelot,  $C_{10}H_{18}O$ , differs from it by two equivalents of hydrogen; common camphor,  $C_{10}H_{16}O$ , by four; the cuminic alcohol of Rossi,  $C_{10}H_{14}O$ , also thymol and carvacrol, by six; and cuminol,  $C_{10}H_{12}O$ , by eight equivalents of hydrogen.

The relation of camphol and camphor being that of an alcohol and its aldehyde,‡ the position which the camphor of peppermint holds towards them, will call for our particular attention from their being related, not only as regards their composition, but also with respect to their physical properties. The peppermint-camphor turns the plane of polarization to the left.

\* Gerhardt, *Traité de Chimie Organique*, vol. iv. p. 357.

† C = 12; H = 1; O = 16.

‡ Berthelot, "La Chimie Organique fondue sur la Synthèse."

A preliminary determination of its rotatory power has been arrived at by the aid of Dubosc's saccharometer. A tube 22mm. in length was filled with a 10 per cent. solution of peppermint-camphor in alcohol, when it was found to deflect the plane of polarization as much as a plate of quartz 0.44mm. thick. This corresponds to an angle of  $10.56^\circ = a$ , and to a molecular rotatory power,—

$$[a] = \frac{a}{l\epsilon\delta} = 59.6.$$

Peppermint-camphor is but slightly soluble in water, although it imparts to the liquid a strong odour and taste. It is very soluble in alcohol, ether, sulphide of carbon, and in fatty and essential oils; insoluble in aqueous solutions of alkalies. From an alcoholic solution of soda, it crystallizes in long needles. A current of sulphurous acid or of hydrochloric acid gas dissolves it. By evaporation, the acids pass off, leaving the peppermint-camphor unaltered. Concentrated acids, especially nitric, sulphuric, hydrochloric, formic, acetic, and butyric acid, dissolve it very freely. From these solutions it is separated by water as well as by alkalies, as an oil which soon solidifies and then exhibits the original properties of the camphor.

When concentrated acetic acid is heated with peppermint-camphor in a sealed tube, for ten or twelve hours, at about  $120^\circ\text{C}$ ., these two bodies combine into a light oil, no longer decomposable by water or by cold solutions of alkalies. After washing with carbonate of soda, and drying over chloride of calcium, it boils between  $222^\circ$  and  $224^\circ\text{C}$ . without decomposition.

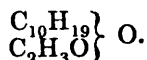
I. 0.303 grm. of this distillate yielded, by analysis, 0.314 grm. of water and 0.827 grm. of carbonic acid.

The same body is obtained by the action of anhydrous acetic acid on peppermint-camphor.

II. 0.310 grm. thus prepared, gave 0.303 grm. of water and grm. of carbonic acid.

	I.	II.	Calculated.
C	73.06	72.58	72.73
H	11.04	11.18	11.11

This agrees with the formula,—



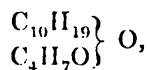
That is, peppermint-camphor in which one equivalent of hydrogen has been substituted by acetyl, so as to form a compound ether.

This body is highly refractive, and deflects the plane of polarization to the left more strongly than the camphor from which it is derived. By preliminary observation with the saccharometer, its molecular rotatory power  $[\alpha]$  has been found =  $114^\circ$ . Hydrate of baryta does not seem to decompose it; but, by heating it with an alcoholic solution of soda, to  $120^\circ$  C. for three hours, it is perfectly decomposed into acetate of soda, and an oil which soon congeals into a crystalline mass, not unlike common camphor. After being pressed between blotting-paper, it distils at  $210^\circ$  C., fuses at  $34^\circ$ , and exhibits otherwise the original properties of peppermint-camphor.

Butyric acid combines with peppermint-camphor on being heated with it to  $200^\circ$  C. for about thirty hours.

The product was separated into two parts, distilling from  $230^\circ$  to  $240^\circ$ , and from  $240$  to  $250^\circ$  respectively. The former of these portions gave the following analytical results:—

0.287 grm. of the liquid gave 0.303 grm. water, and 0.792 grm. of carbonic acid, corresponding to the formula,



which is that of butyrate of menthyl; in 100 parts,—

	Found.	Calculated.
C	74.84	74.33
H	11.74	11.50

A preliminary determination of its rotatory power gave  $[\alpha] = 88.80^\circ$ .

A concentrated solution of hydrochloric acid acts on peppermint-camphor at  $100^\circ$  C. But it is necessary to heat them together for a week in order to obtain a considerable quantity of chloride of menthyl. At a temperature of  $120^\circ$  C., twenty-four hours suffice to complete this reaction.

The chloride of menthyl may be washed with carbonate of soda, but it does not bear distillation. The following analyses were made with non-distilled portions of the liquid dried over chloride of calcium:—

I. 0.323 grm. gave 0.332 grm. of water and 0.794 grm. of carbonic acid.

II. 0.382 grm. gave 0.296 of chloride of silver.

III. 0.310 grm. gave 0.206 grm. of chloride of silver.

This corresponds to the formula  $C_{10}H_{19}Cl$ , or, in 100 parts,

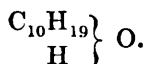
	i.	ii.	iii.	Calculated.
C	67.06	„	„	68.62
H	11.32	„	„	10.89
Cl	„	19.16	19.67	20.34

The same body was obtained by Walter, by the action of perchloride of phosphorus on peppermint-camphor.

Iodide and bromide of phosphorus react very strongly on this body; but, as the resulting bodies bear distillation as little as the chloride of menthyl, these methods are not advisable for obtaining them. Hydriodic acid combines with peppermint-camphor at about  $120^{\circ}C$ .

Sodium acts very strongly on peppermint-camphor. It dissolves therein when fused; and disengages hydrogen. By raising the temperature, about one equivalent of sodium may be made to unite with the fused camphor, forming a vitreous, transparent mass, white originally, but becoming brown and moist when exposed to the air. It is decomposed by water, but soluble in absolute alcohol and in iodide of ethyl. The reaction of this body on the sodium-compound is not so simple as might be expected. When heated to  $100^{\circ}$ , the transparent liquid solidifies, but continues to be soluble in a mixture of ether and alcohol. From this solution, deliquescent crystals may be obtained, which contain iodine, sodium, carbon, and hydrogen; but continued evaporation decomposes these crystals into iodide of sodium and an oily substance, which does not appear to be the mixed ether expected to be formed by such reaction. The products of this and of similar reactions form the subject of the continuation of these researches.

From the compound ethers and the sodium-compound hitherto obtained, it is already evident that the camphor of peppermint is a monatomic alcohol having the formula—



It belongs to the general type  $C_nH_{2n}O$ , and is, therefore, homo-

logous with the allylic alcohol of Hofman and Cahours, and with the acetylic alcohol of Berthelot. As it is isologous with campholic alcohol, the name *mentholic alcohol*, or *menthol*, may perhaps be advantageously substituted for that of camphor of peppermint.

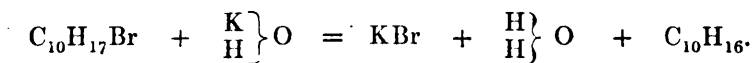
The corresponding hydrocarbon, menthene,  $C_{10}H_{18}$ , which Walter obtained by the action of phosphoric acid, may likewise be produced in various other ways. It has been found among the products of the reaction of chloride of menthyl on ethylate of sodium. The most advantageous way of preparing it seems to be to react on menthol with chloride of zinc. Prepared in this way, the menthene has no action on polarized light. It boils at  $163^{\circ}C$ .

0.227 grm. yielded, by analysis, 0.282 grm. of water, and 0.733 grm. carbonic acid; in 100 parts—

	Found.	Calculated.
C	86.59	86.94
H	13.65	13.05

Bromine does not combine directly with this hydrocarbon. It reacts on it very violently, disengaging currents of hydrobromic acid, and forming various products of substitution, of no stability whatever, even at ordinary temperatures.

By adding, drop by drop, two equivalents of bromine to one of menthene, monobrominated menthene  $C_{10}H_{17}Br$  must be formed, which, by the action of oxide of silver, or of hydrate of soda, might be transformed into camphol. But this reaction gives rise to a hydrocarbon  $C_{10}H_{16}$ , boiling between  $170^{\circ}$  and  $175^{\circ}C$ .



The acid corresponding to menthol is identical or isomeric with the campholic acid of Delalande,  $C_{10}H_{18}O_2$ .

The ordinary oxidizing agents, such as nitric acid, chromic acid, &c., do not produce this acid. They at once attack the carbon of the mentholic alcohol. I hope, however, to be able to produce it by a less direct method of oxidation.