X.—*On Peppermint Camphor (Menthol) and some of its Derivatives.*

By R. W. Atkinson, B.Sc. and H. Yoshida.

Peppermint camphor, as found in commerce, even when not expressly adulterated with magnesium sulphate, is almost invariably contaminated with oily matter, which accompanies it in the plant, and on account of the difficulty of removing this impurity, most of the previous determinations of the melting point are too low. The specimens upon which we worked came from Dewa, in the north of Japan, and were found to melt at about 35° C., and to boil at 210—211° (uncorr.). This menthol was purified by distillation, the first and last portions being rejected, after which the cooled and solidified product was well pressed between filtering paper, and exposed repeatedly in thin layers to the air. By several repetitions of this process the melting point was finally raised to 42·2°, the solidifying point to 40·3°, and the boiling point to

212° (corr.). These numbers agree most nearly with those of Beckett and Wright (*Chem. Soc. J.*, 1876, **1**, 1). The melting points were determined by enclosing the capillary tube, containing the menthol, together with a delicate thermometer, in a test-tube immersed in water, which was slowly heated, a process originally described by Anschütz and Schultz (*Ber.*, **10**, 1800).

Menthone, $C_{10}H_{18}O$.

Mr. Moriya has shown (*Chem. Soc. J.*, 1881, Trans., 77) that when menthol is heated in sealed tubes with acid bichromate solution at 120°, for about 10 hours, an oil boiling at 204—205° is obtained, having a composition which agrees with the formula $C_{10}H_{18}O$. We have repeated this experiment, preparing larger quantities, and have made determinations of some of the principal physical properties of the compound, believing that this knowledge will be of assistance in elucidating the structure of the menthol derivatives.

Weak chromic acid liquor has very little action upon menthol at 100°. To prepare menthone, about 30 grams of purified menthol were placed in a narrow-necked bottle, together with 10 grams of potassic dichromate, and about an equal weight of sulphuric acid; on shaking the mixture much heat was liberated, and the menthol was changed into a black spongy mass. The bottle was then heated in a digester to a temperature of 135°, for about four hours. At the end of that time the light oily layer was separated from the solution of chromic sulphate, and subjected several times to the same treatment with fresh oxidising mixtures. The optical activity of the oil was examined after each treatment, and it was observed that it gradually decreased from — 59° to 0° for the transition tint, but did not stop there, the rotation becoming positive and increasing till it rose to $[\alpha]_j = +21°$.

Purified by distillation, menthone is a colourless mobile liquid, neutral to test-papers, soluble in almost all proportions in alcohol, chloroform, benzene, and carbon disulphide, but insoluble in water.

On combustion the following numbers were obtained :—

(1.) 0·5918 gram gave 1·6884 gram CO_2 and 0·6296 gram H_2O.
(2.) 0·4362 ,, 1·2415 ,, ,, 0·4625 ,,
(3.) 0·3472 ,, 0·9902 ,, ,, 0·3659 ,,

	1.	2.	3.	Mean.	Theory $C_{10}H_{18}O$.
Carbon	77·81 p.c.	77·62 p.c.	77·78 p.c.	77·73	77·92
Hydrogen	11·82 ,,	11·78 ,,	11·71 ,,	11·77	11·69

Mr. Moriya's numbers (not published in his paper) were—

	Mean.
Carbon	77·59 per cent.
Hydrogen	11·87 ,,

Two determinations of the vapour-density of the compound gave the numbers 77·45 and 76·69, the number calculated for $C_{10}H_{18}O$ being 77·0.

Menthone boils at 206·3° (corr.), and smells like much diluted peppermint. It does not combine with acid sodium sulphite; concentrated oil of vitriol has scarcely any action on it in the cold.

When menthone is repeatedly cohobated with zinc chloride, a hydrocarbon is obtained, which smells like that of the hydrocarbon to be afterwards described, obtained from menthol by the action of hydric iodide with subsequent treatment with caustic soda and sodium. A pasty somewhat opalescent mass is formed from which the oil is liberated by treatment with water. The amount of the hydrocarbon obtained was, however, too small to permit of its identification; it was probably a mixture of several bodies.

That menthone stands to menthol in a similar relation to that in which camphor stands to borneol, is shown by the fact that menthol can be reproduced from its ketone, $C_{10}H_{18}O$, by a reaction quite similar to that by which borneol is produced from camphor. When a solution of menthone in petroleum of somewhat high boiling point, is heated with metallic sodium, the latter is quickly dissolved; and on decomposing the solution by carbonic acid, shaking up the product with water, rapidly separating the water from the oily layer, and setting it aside, it deposits minute crystals of peppermint camphor, which can be obtained in a coherent mass, best by distilling in a current of steam. When purified by the process adopted for the natural menthol, it was found to melt at 42·2°, solidfying at 40·3°, but to have a less energetic lævorotatory power than the natural product, viz., — 39°. It may be remembered that synthesised borneol differs in its specific rotatory power from the natural substance, but the present instance is perhaps more remarkable, seeing that the intermediate body possesses a rotation opposite both to the natural and to the artificial menthol.

Specific Rotatory Power.—Not having at our command any other kind of polarimeter, we were obliged to be content with the results given by a Soleil-Ventzky saccharimeter, although, as is well known, its indications are not exact for other substances than sugar.

Mr. Moriya (*loc. cit.*) stated that this body was inactive to polarised light, but as his experiments were made upon solutions of the oil, which further was probably not completely freed from menthol, the rotatory effect was imperceptible. We found that the pure oil in a decimeter tube gave an average rotation of 49·73 divisions, from which the specific rotatory power is calculated.

$$[\alpha]_j = + \frac{49{\cdot}73 \times 38{\cdot}34}{100 \times 0{\cdot}901} = + 21{\cdot}16^{\circ}.$$

Specific Gravity and Rate of Expansion.—The specific gravity was determined by the use of a carefully calibrated specific gravity bottle, and the weights reduced to a vacuum; the numbers give the density at the temperature mentioned, compared with that of water at 4° C. Each number is the mean of five experiments.

Temperature.	D_4^t	Volume.
0°	0·9126	1·00000
10	0·9048	1·00862
20	0·8972	1·01716
40	0·8819	1·03481
60	0·8665	1·05320
80	0·8511	1·07226
100	0·8355	1·09228

When combined, these numbers lead to the formula for the expansion—

$$V_t = 1 + 0{\cdot}00085037t + 0{\cdot}0000004156t^2 + 0{\cdot}00000000314 15t^3.$$

Molecular Refraction.—The refractive index was determined with the aid of a delicate spectrometer belonging to the physical laboratory of the University of Tôkiô, and fully described by Prof. Mendenhall in the Eighth Memoir of the Science Department of the University ("On the Wave-lengths of some of the Principal Fraunhofer Lines).

The sources of light employed were the red and green lines of the hydrogen spectrum having the wave-lengths 6562 and 4682 respectively. The temperature of the air at the time of the observations was 8—9°, and the specific gravity of the liquid at 8·5° was 0·90602.

The index of refraction for $H_\alpha = 1{\cdot}45283$
" " " $H_\beta = 1{\cdot}46094$

Using Cauchy's formula for an infinite wave-length (Brühl, *Annalen*, **200**, 139, we get—

$$A = 1{\cdot}442998$$
$$B = 0{\cdot}425268$$

The molecular refaction is, therefore,

$$R = P\left(\frac{A - 1}{d}\right) = 154\left(\frac{1{\cdot}442998 - 1}{0{\cdot}90602}\right) = 75{\cdot}3.$$

Using the values given by Brühl for carbon, hydrogen, and oxygen, the calculated molecular refraction for $C_{10}H_{18}O$, the carbon-atoms not

being doubly combined, is 75·1, a result agreeing so well with the observed number, that we may conclude that the carbon-atoms are all singly united.

Menthene, $C_{10}H_{18}$.

This substance was prepared by heating menthol with zinc chloride. The purified peppermint camphor was cohobated with about twice its weight of zinc chloride, in a flask provided with a vertical condenser. After heating for about half a day, the hydrocarbon was separated and then digested with sodium for some time at a gentle heat. The product was carefully fractionated several times, and the main portion which passed over at 165—166° (uncorr.) was preserved for examination. It was found necessary to purify it from small quantities of polymerised bodies, and for this purpose the liquid was digested with clean pieces of sodium, and occasionally separated by distillation from a reddish-brown precipitate. After about a month the production of the reddish precipitate ceased; the liquid was again fractionated; and that portion which distilled at 167·4° (corr.) served for the following determinations:—The observed boiling point, 167·4°, is higher than that usually given for menthene, but the greater part of the product obtained distilled constantly at that temperature.

Specific Rotatory Power.—At 15° the liquid contained in a tube 1 decimeter long, gave a rotation equal to 10·73°, the specific gravity at the same temperature being 0·8102, and the specific rotatory power $[\alpha]_j = .+ 13{\cdot}25°$. This observation differs from that of previous observers, who have regarded menthene as an optically inactive body. In Mr. Moriya's case this was perhaps caused by the menthene used containing a little unaltered menthol, as well as from the circumstance that he used dilute alcoholic solutions, whilst the above determinations were made with the undiluted liquid.

Specific Gravity and Rate of Expansion.—The specific gravity at the various temperatures was determined, as in the case of menthone, each number being the average of five experiments.

Temperature.	$D\frac{t}{4}$	Volume.
0°	0·8226	1·00000
10	0·8145	1·00994
20	0·8073	1·01899
40	0·7909	1·04008
60	0·7761	1·06000

These results lead to the formula for the volumes—

$$V_t = 1 + 0{\cdot}00099183t + 0{\cdot}000000592t^2 + 0{\cdot}0000000075t^3.$$

Molecular Refraction.—The indices of refraction were found to be—

$$\text{for } H_\alpha = 1{\cdot}448997$$
$$\text{and for } H_\beta = 1{\cdot}459200.$$

from which we find—

$$B = 0{\cdot}534289$$
$$A = 1{\cdot}43664$$

The specific gravity at 8·5° is 0·8137: hence the molecular refraction is—

$$R = 138 \times \frac{1{\cdot}43664 - 1}{0{\cdot}8137} = 74{\cdot}045.$$

The number calculated for $C_{10}H_{18}$ from the values for carbon (in single union) and hydrogen given by Brühl, is 71·82. A closer agreement is obtained by assuming the existence of one pair of carbon-atoms doubly united, the rest being in single union, viz.,—

$$C''_2 + C'_8 + H_{18} = 73{\cdot}82.$$

Menthene is a colourless mobile liquid, of an agreeable odour, recalling that of cymene; moderately soluble in ether or alcohol, more so in benzene, turpentine, and petroleum. When heated with fuming hydrochloric acid for some time it yields hydrochloride of menthene, $C_{10}H_{19}Cl$, an oil more or less coloured yellow, which after washing with water and drying over potassic carbonate, contained, in two experiments, 20·25 and 20·3 per cent. of chlorine, the theoretical percentage being 20·34.

Heated with hydriodic acid at the ordinary pressure of the air, menthene takes up the elements of the acid, forming an unstable brown oil, having an odour resembling that of the iodide formed by the action of hydriodic acid on menthol.

Action of Hydriodic Acid on Menthol.

About 10 oz. of hydriodic acid solution, of sp. gr. 1·7, were heated with about 6 oz. of menthol in a flask with an inverted condenser; the heating was continued for three days, at the end of which time the dark oily liquid was separated from the aqueous portion. The oil decomposes on distillation between 170° and 200°. The distillate was lighter than water, and had a pleasant odour; when it was boiled with caustic soda solution, the dark colour which it assumed on standing, by the decomposition of some iodo-compound, was removed; but again on standing the dark colour reappeared. Nothing distilled below 160°: hence no decane was present. Berthelot (*Bull. Soc. Chim.*, **11**, 102) states that a small quantity of amyl hydride and of decyl hydride, together with terpilene hydride ($C_{10}H_{20}$), which formed

three-fourths of the total liquid, are produced in this reaction. The strength of the hydriodic acid used in his experiments was, however, higher than in ours.

When the above liquid is cohobated with caustic soda-solution, then with sodium, and distilled, it yields a clear colourless hydrocarbon of an agreeable odour. It polymerises on heating, and can only be purified by long digestion with sodium. The corrected boiling point was found to be 168·6°. Combustion showed that it consisted mainly of a hydrocarbon, $C_{10}H_{16}$, mixed with a small quantity of a more highly hydrogenised body, $C_{10}H_{18}$, or $C_{10}H_{20}$.

(1.) 0·3642 gram gave 1·1714 gram CO_2 and 0·3989 gram H_2O.
(2.) 0·4212 „ 1·3517 „ „ 0·4769 „
(3.) 0·4034 „ 1·3024 „ „ 0·4400 „

	1.	2.	3.	Mean.
Carbon	87·72 p.c.	87·52 p.c.	88·05 p.c.	87·76
Hydrogen ..	12·17 „	12·58 „	12·12 „	12·29
				100·05

	Calculated for	
	$C_{10}H_{16}$	$C_{10}H_{18}$
Carbon.....	88·235	86·96
Hydrogen ..	11·765	13·04
	100·000	100·00

Two determinations of the vapour-density made with Victor Meyer's apparatus, gave the numbers 66·1 and 68·4; mean 67·25. The number calculated for $C_{10}H_{18}$ is 68·0.

Specific Rotatory Power.—As a mean of five observations, the liquid contained in a decimeter tube was found to rotate the ray of polarised light through 4·23°: hence, density at 18° = 0·8137,

$$[\alpha]_j = \frac{4{\cdot}23}{0{\cdot}8137} = + 5{\cdot}2°.$$

Specific Gravity and Rate of Expansion.—The specific gravity was determined as before.

Temperature.	$D_{\frac{4}{4}}^{t}$	Volume.
0°	0·8254	1·00000
10	0·8178	1·00929
20	0·8111	1·01763
40	0·8001	1·03162
60	0·7924	1·04165

These numbers lead to the following equation, expressing the volumes at different temperatures:—

$$V_t = 1 + 0{\cdot}000976768t - 0{\cdot}00000479t^2 + 0{\cdot}00000000133t^3.$$

Molecular Refraction.—The indices of refraction were found to be for $H_\alpha = 1{\cdot}4481614$, and for $H_\beta = 1{\cdot}457148$, from which we find—

$$A = 1{\cdot}43723$$
$$\text{and } B = 0{\cdot}47059$$

The specific gravity at 18° being 0·8115, the molecular refraction for $C_{10}H_{16}$ is $R = 136 \times \frac{1{\cdot}43723 - 1}{0{\cdot}8115} = 73{\cdot}28$.

The number calculated for $C_{10}H_{16}$, all the carbons being in single union, is 69·24, but if we assume the presence of two pairs doubly united, we get the number—

$$C'_6 + C''_4 + H_{16} = 73{\cdot}24.$$

This hydrocarbon is a clear, colourless, mobile liquid, easily soluble in petroleum or benzene, less so in ether and alcohol, and insoluble in water. Its odour resembles that of cymene. Bromine acts strongly upon it, about two atoms being taken up, with evolution of some hydrobromic acid; the resulting bromo-compound is as unstable as the iodo-compound.