OBSERVATIONS ON AMERICAN MENTHOL.

By J. H. Long.

As is well known, the menthol from the American oil of peppermint differs much in its physical appearance from that obtained from the English or Japanese oil. The common Japanese menthol appears in commerce in the form of small prismatic crystals, while the American products appear as long, slender needles. This difference is evidently not accidental, depending on the method of distillation and purification followed by the different producers, as it is observed in the products which have been recrystallized by the same person under the same general conditions. A distinct difference in the odor of the two products may also be noted, even after several crystallizations and distillation in vacuo.

The American menthol is produced chiefly from the oil distilled in New-York and Michigan, but owing to its relatively high cost is not commonly found in the market at the present time.

A grade of very great purity is produced by the well known distiller of essential oils, Albert M. Todd, Esq., of Nottawa, Mich., to whom I am indebted for samples used in this investigation.

The peculiarities of this menthol were explained in the *American Journal of Pharmacy* for June, 1884, and the name *pipmenthol* then suggested. A fuller description of the product was given by Prof. Henry Trimble in the August, 1884, number of the same journal.

To obtain the menthol from the oil the latter is placed in a vessel with double walls, the space between being packed with a mixture of ice and salt. After a time crystallization takes place, from 20 to 40 per cent. of the menthol present separating out. The solvent oil is then allowed to drain out through a tube leading from the bottom of the inner vessel. By exposure to the air the crystals soon dry and are practically pure, as shown by tests of numerous samples made at different times. From oil very rich in the camphor crystals separate out at a temperature near 0° C. A specimen secured in this way was dried by simply passing between folds of filter paper when it was found to be nearly pure.

In a preliminary examination of a number of samples obtained from several sources, solutions were made by dissolving 10 grms. of the commercial product in alcohol of 95 per cent. strength and making up to 100 cc. These solutions were polarized in a 300 mm. tube of the large Landolt apparatus with the following result:

No. a_D
1—14.805.
2—14.741.
3—14.745.
4—14.660.
5—14.690.
6—14.760.

Samples 4 and 5 were quite moist. After drying higher results were obtained, each showing

$$a_D = - 14.73.$$

From this it appears that the commercial product is nearly constant in composition, if the polarization can be taken as a criterion.

I had at my disposal a large amount of sample No. 6, which was purified as follows:

About 500 grms. was melted and poured into warm water in a beaker on a water bath. The two liquids were repeatedly mixed by stirring and kept at a temperature of 60–70° C half an hour. In this way a slight amount of some insoluble body was separated from the menthol, and collected at the bottom of the beaker. The menthol layer was then poured off and allowed to stand until it crystallized, the crystals being afterwards dried between porous plates in the air. An attempt was made to distil these dried crystals under the ordinary atmospheric pressure, but without perfect success, as a slight decomposition took place. This was indicated by a change of color in the boiling liquid, it becoming yellowish brown, and also by a lowered rotation in the distillate. A solution of 10 grms. made to 100 cc. with alcohol, as before, gave now

$$a_D = - 14.^\circ 51.$$

However, distilling under reduced pressure gave a much better result. Some specimens were distilled several times under a pressure of 50–100 mm. and when polarized under the same conditions as before gave uniformly $a_D = -14.°820$.

The whole sample was purified in this way and used for a number of experiments chiefly in the line of polarization phenomena.

DENSITY, MELTING POINT AND BOILING POINT.

The density of the solid menthol in compact form was found by weighing in water to be

$$d\frac{20}{4} = .890.$$

This is the value given by Moriya (Jour. Chem. Soc. xxxix, 77) for the crystals at 15°.

For the density of the melted menthol I find

$$d\frac{44.6}{4} = .8810,$$

which is somewhat higher than the value given by Gladstone and Dale for the Japanese. My own determination for the Japanese is

$$d\frac{47}{4} = .878.$$

The melting point of the distilled American menthol I find as 42.°3, while that of the single Japanese sample was a trifle higher, viz: 42°.6. These are somewhat higher than the values usually given, which were probably obtained from the undistilled product. With crystals dried in the air or between paper I find lower values. Moriya (loc. cit.) gives 39°, Atkinson & Yoshida (Jour. Chem. Soc. xli, 50) give low values for the air dried crystals, but find 42.°2 as the melting point of a sample purified by distillation. The boiling point of the distilled American menthol I find to be 212.°5 (corr.) with Bar. = 742. The values given by various observers for the Japanese range between 210° and 213°.

SPECIFIC ROTATION.

I find nothing in the literature on the specific rotation of the liquid (melted) menthol. Some results are found for the Japanese menthol based on an examination of alcoholic solutions, but the date seems to be, in several instances, inaccurate. The value given by Oppenheim (Jour. Chem. Soc. xv, 26) is

$$[a]_D = -59.^\circ6,$$

deduced from a 10 per cent. solution in alcohol. Moriya (loc. cit.) gives

$$[a]_j = -59.^\circ3$$

which corresponds approximately to

$$[a]_D = -49.^\circ4$$

for a 10 per cent. solution.

For a 10 per cent. alcoholic solution, Arth (Ann. de Chim. et de Phys. [6], vii, 438) gives

$$[a]_D = -50.^\circ1,$$

while for one of 5 per cent. he gives

$$[a]_D = -49.^\circ4.$$

I have made a direct determination of the rotation in a sample of the melted American menthol. A 200 mm. jacketed tube was employed and a temperature of 46° was maintained during the time of the experiment by means of a current of warm water. This temperature is high enough to keep the substance in a state of perfect fluidity, and is the temperature at which the specific gravity was found.

The mean of a number of closely agreeing readings was

$$a_D = -87.^\circ716,$$

and this gives, after introducing a slight correction for length of tube at the higher temperature,

$$[a]_D = -49.^\circ86.$$

To determine how this value agrees with those deduced from the rotation of solutions was the object of a lengthy series of experiments, the main details of which are here given. Solutions were made in alcohol, benzene and glacial acetic acid, the menthol used being all taken from the same distilled sample.

SOLUTIONS IN ALCOHOL.

For these tests a pure redistilled alcohol of approximately 95 vol. per cent. was used. This was taken in preference to absolute alcohol where change of strength by exposure to air is unavoidable.

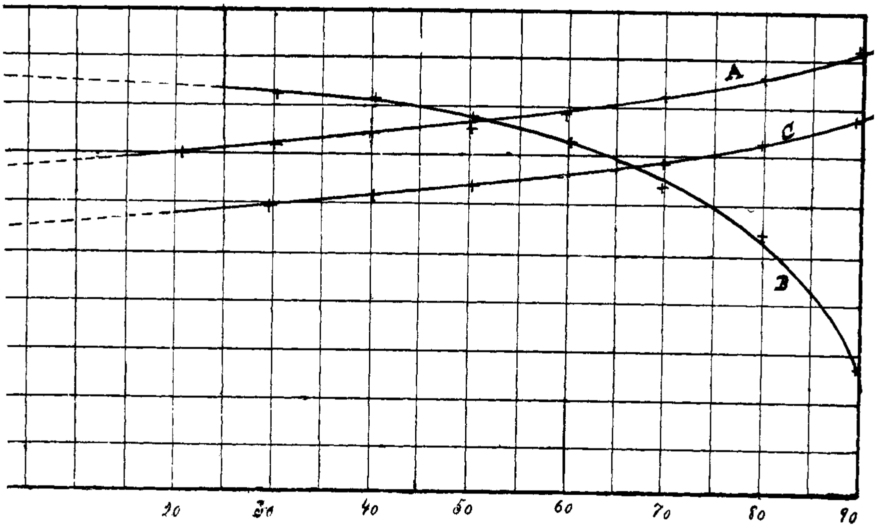
The actual strength of the alcohol employed in all the tests is given by the specific gravity,

$$d\frac{20}{4} = .81441.$$

Eight solutions were made with approximately 10, 20, 30, 40, 50, 60, 70 and 80 per cent. of menthol, all weights being reduced to vacuo. A portion of each solution was used for a specific gravity determination in a small pyknometer, brought always to a temperature of 20° in a vessel of water. This temperature was maintained with an error of less than 0.°1 in all the experiments. The remainder of each solution was used for polarization in a 300 mm. tube, kept at 20° by a current of water.

The variation of the length of the tube from 300 is inappreciable, and can be neglected.

The results of the experiments are shown in tabular form, as follows:



No.	Per Cent. of Menthol.	Per Cent. of Alcohol.	Sp. Gr. of Solution.	Observed Rotation.• a.
1	10.1228	89.8772	.82271	— 12.°385
2	20.0126	79.9874	.83010	— 24.°585
3	30.0904	69.9096	.83845	— 37.°186
4	40.3447	59.6553	.84732	— 50.°218
5	49.8839	50.1161	.85560	— 62.°540
6	60.0664	39.9336	.86391	— 75.°856
7	69.9443	30.0557	.87401	— 89.°141
8	78.9552	21.0448	.88283	— 101.°398

From the observed values of the above table the specific rotations given below were calculated according to the usual formula.

$$[a] = \frac{10^4\ a}{l\ c} = \frac{10^4\ a}{l\ p\ d}$$

Where a is the observed angle of rotation, l the length of tube in millimeters, c the concentration, or grms. in 100 cc. of solution, p the percentage strength of the solution and d its density.

The values of [a] are not quite constant, but vary slightly with the concentration, decreasing as the latter increases. In other words [a] increases with q, expressing by this the percentage amount of the inactive solvent present.

By plotting the values of the specific rotation as ordinates with the amounts of solvent as abscissas we get a curve nearly straight at first but finally slightly concave upward, as shown below in the figure at A.

The deviation from a straight line is so little, however, that the values of [a] can be very well expressed by the simple interpolation formula:

$$[a] = A + Bq. + Cq^2.$$

From solutions 4, 6 and 8 I find

$$[a] = 48.216 + .013237\ q. - .00001041\ q^2.$$

From 6, 7 and 8,

$$[a] = 48.191 + .014974\ q. - .00003886\ q^2.$$

From 3, 6 and 8,

$$[a] = 48.239 + .011510\ q. + 00001795\ q^2.$$

From 2, 5 and 8,

$$[a] = 48.312 + .006840\ q. + .00007501\ q^2.$$

The mean of the last three is,

$$[a] = 48.247 + .011108\ q. + .00001870\ q^2.$$

I employed this last equation in the calculation of the values given in the table below, under : "[a] cal."

No.	pd. = c.	[a] obs.	[a] cal.	diff.
1.....	8.3281	49.°571	49.°396	— .175
2.....	16.6124	49.°330	49.°255	— .075
3.....	25.2293	49.°131	49.°115	— .016
4.....	34.1848	48.°968	48.°976	+ .008
5.....	42.6807	48.°843	48.°851	+ .008
6.....	51.8920	48.°727	48.°720	— .007
7.....	61.1320	48.°606	48.°598	— .008
8.....	69.7040	48.°489	48.°488	— .001

The calculated and observed values agree very closely except for the two most dilute solutions, where the specific rotations by observation is higher.

In Arth's experiments, referred to above, the strength of the alcohol is not given, nor is the density of his solutions, but it is evident that the value for the 10 per cent. solution is too high. This value is inconsistent when taken in connection with that of the 5 per cent. solution.

From the above observations it is seen that the specific rotation of the pure substance, as deduced from tests of solutions, must be about 48.°25 at 20°. In order to compare this value with that obtained by observations on the melted menthol I polarized solutions at higher temperatures. One such solution contained 17.37 per cent. of menthol and had the specific gravity :

$$d\,\frac{46}{4} = .798.$$

In the 200 mm. tube it gave $a = -21.^\circ05$, from which

$$[a] = -50.^\circ62.$$

That is, the specific rotation increases with the temperature. Assuming that the increase is approximately the same for all concentrations the specific rotation deduced from strong solutions at this temperature should be about — 49.°5. This agrees satisfactorily with the observed value — 49.°89.

SOLUTIONS IN BENZENE.

Several tests were made with pure recrystallized benzene as a menstruum, in which the menthol is very readily soluble. The chief results of these experiments are given in this table :

No.	Per Cent. of Menthol.	Per Cent. of Benzene.	Sp. Gr. of Solution.	Observed Rotation, a.
9.....	10.0326	89.9674	.88016	— 12.°282
10.....	20.0163	79.9837	.88131	— 25.°265
11.....	30.4343	69.5657	.88276	— 38.°928
12.....	39.8777	60.1223	.88435	— 51.°437
13.....	49.3899	50.6101	.88575	— 64.°206
14.....	59.8799	40.1201	.88778	— 78.°300
15.....	69.6514	30.3486	.89025	— 91.°510

Calculating the specific rotations from the above observations and plotting them as functions of the dilution, q, we obtain a curve which deviates greatly from a straight line. The deviation at the points corresponding to weak solutions is so great that a simple interpolation formula will not satisfy the whole curve.

For the stronger solutions this equation gives results which can be used :

$$[a] = 49.^\circ511 - .025634\,q. + .0008403\,q^2. - .00001102\,q^3.$$

Nearly the same constant is given by the equation :

$$[a] = 49.^\circ495 - \frac{28.614\,q.}{2836.8 + q.}$$

The true specific rotation of the menthol as found from the benzene solutions appears, therefore, to be higher than that found from the solutions in alcohol. The specific rotation of the melted menthol lies between that deduced from the benzene and alcohol solutions.

Owing to the greater volatility of the benzene it is probable that the rotations observed are a trifle high because of a slight loss of the menstruum by evaporation, even when great care was taken in the manipulation.

The values of the specific rotation are given in the following table, while the plotted curve, showing variations in some, is given at B in the figure.

No.	pd. = c.	[α] obs.	[a] cal.	diff.
9......	8.8303	46.°366		
10......	17.6405	47.°741		
11......	26.8662	48.°299	48.°085	— .214
12......	35.2658	48.°619	48.°613	— .006
13......	43.7472	48.°922	48.°940	+ .018
14......	53.1602	49.°097	49.°125	+ .028
15......	62.0071	49.°193	49.°199	+ .006

SOLUTIONS IN ACETIC ACID.

A third series of experiments was carried out, using pure recrystallized acetic acid as the solvent.

The solutions were made in all cases without the application of heat and were not allowed to go above 22°. The table below gives the results of the individual tests:

No.	Per Cent. of Menthol.	Per Cent. of Acid.	Sp. Gr. of Solution.	Observed Rotation, a.
16......	10.2488	89.7512	1.03099	— 15.°482
17......	20.1108	79.8892	1.01298	— 29.°744
18......	30.1956	69.8044	.99615	— 43.°739
19......	40.4986	59.5014	.98010	— 57.°559
20......	49.5124	50.4876	.96606	— 69.°201
21......	59.8591	40.1409	.95161	— 82.°164
22......	70.0220	29.9780	.93757	— 94.°454

The results of the calculated specific rotations, when plotted as before, give a very regular curve resembling that found from the alcohol solution. This curve is shown at C in the figure.

The points on this curve are given by equations as follows:

From 20, 21 and 22,

$$[a] = 47.663 + .007638\ q. + .00006929\ q^2.$$

From 17, 20 and 22,

$$[a] = 47.615 + .010226\ q. + .00003712\ q^2.$$

From 16, 18 and 21,

$$[a] = 47.856 + .001293\ q. + + .00010784\ q^2.$$

The mean of these gives,

$$[a] = 47.711 + .006386\ q. + .00007142\ q^2.$$

from which the calculated specific rotations in the table below were found. These agree very well with the results of direct experiment:

No.	pd. = c.	[a] obs.	[a] cal.	diff.
16.....	10.5665	48.°840	48.°859	+ .019
17.....	20.3718	48.°668	48.°676	+ .008
18.....	30.0792	48.°471	48.°505	+ .034
19.....	39.6928	48.°338	48.°343	+ .005
20.....	47.8320	48.°225	48.°215	— .010
21.....	56.9625	48.°081	48.°082	+ .001
22.....	65.6506	47.°954	47.°966	+ .012

It is apparent that acetic acid is not a good menstruum in this case, although the values given are very regular. The specific rotation in the concentrated solutions falls below that observed with the liquid menthol. At high temperatures menthol and acetic acid act on each other with production of acetate, and it is possible that some of the same product is formed at a temperature of 20° even.

But Oppenheim has shown (loc. cit.) that the acetate has a much higher specific rotation than the original menthol, which result I have confirmed by recent experiments. However, with the ether formed at the ordinary temperature I should have found a higher rather than a lower specific rotation with the solutions experimented on. An observation having some bearing on the question was made during the tests in this manner. Several solutions, first polarized immediately after preparation, were kept ten days in well stoppered bottles and polarized again. In the second test a higher result was always found, which would correspond to the behavior of ether produced in the interval.

Apparently, the first effect of the acid with the menthol is to produce a combination characterized by slightly lower specific rotation, which later gives place to the ether with higher than normal rotation.

Several experiments were tried with a single sample of Japanese menthol dissolved in alcohol and acetic acid. The results found were slightly higher than those obtained from any one of the American samples. This Japanese product was clean and dry and apparently a pure commercial specimen. I redistilled it under low pressure and used this product for the test.

In the 300 mm. tube it gave,

$$a = -14.^\circ 840$$

for a solution containing exactly 10 grms. in 100 cc., the same alcohol employed in the other test being used here.

The purified American sample gave under the same conditions,

$$a = -14.^\circ 820.$$

The slight differences in physical properties between the two varieties of menthol are not important enough to point to a difference in chemical structure. It is possible that they may be due to the presence of traces of associated products in the original oil which cannot be perfectly separated by the simple methods employed in purification. It appears from the investigations of Beckett and Wright (Jour. Chem. Soc., XXIX., 1) and Trimble (loc. cit.) that the oil of peppermint contains, besides menthol, another oxidized product in small amount, probably menthone. This is a body with high boiling point, only slightly lower than that of menthol and + rotation. A trace of it could easily remain with the menthol and exert an appreciable influence on the specific rotation, sufficient, probably, to account for the trifling differences noted above.

CHICAGO, May, 1892.