OBSERVATIONS ON MICHIGAN OIL OF PEPPERMINT

by

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Next to turpentine oil, peppermint oil is commercially the most important volatile oil distilled. While large quantities of this oil are distilled in several European countries and particularly in Japan, the United States is probably the largest producer of this oil as well as oil of turpentine.

The cultivation of peppermint and the distillation of its oil began on a small scale in New England and thence immigrated westward. In New York, especially in Wayne County, this agricultural industry assumed considerable proportions during the second half of the ninteenth century only to be outstripped in the course of time as was also the salt industry, by Michigan. A former lake bottom, the thousand acres of which, sold for a few dollars an acre, after having been drained, and deprived of timber and underbrush at the rate of one hundred acres per winter, may even today be seen in the process of evolution into a peppermint farm of great financial promise. While this change may not be quite as striking as that produced by oil wells or shafts sunk into the earth, the social and economical changes wrought, are not as disastrous to human society.

The chemistry of such a commodity ought to be of interest other than that which may delight the plant chemist.

As in so many other instances however, Americans do not appear to have fully appreciated the bearing of science on this subject in a commercial sense. There was a time when Michigan peppermint oil was synonymous with poor peppermint oil, but this state of affairs is rapidly changing, yet the agricultural improvements have been more rapid than increased scientific knowledge of the chemical changes in the plant, as the laboratory in which the oil is manufactured. In this connection it might be of interest to note that it was a French chemist who in 1832 made the first elementary analysis of peppermint camphor or menthol, which crystalizes more readily from American oil than from the European oils, and therefore was the first to attract attention. The study of this substance and its derivatives opened up new paths in the fields of both organic and physical chemistry. Yet for more than half a century, the scientific interest in this oil was entirely overshadowed by its commercial importance.

It was in 1894 that oil of peppermint became one of the best known oils chemically speaking, owing to the investigations of Power and Kleber*, the examination

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* Pharm. Rundschau, 12, p. 157.

having been made in the American branch laboratory of a German firm. The chemical composition of this oil as revealed by the two chemists mentioned above is given in the following table.

1.	Acetaldehyde	CH_3CHO	.044%
2.	Isovaleraldehyde	$(CH_3)_2.CH.CH_2CHO$	.048%
3.	Free acetic acid	CH_3COOH	
4.	Free isovalerianic acid	$(CH_3)_2CH.CH_2COOH$	
5.	Pinene	$C_{10}H_{16}$	
6.	Phellandren	$C_{10}H_{16}$	
7.	Cincol	$C_{10}H_{18}O$	
8.	l-Limonene	$C_{10}H_{16}$	
9.	Menthone	$C_{10}H_{18}O$	
10.	Menthol	$C_{10}H_{20}O$	
11.	Menthyl acetate	$C_{10}H_{19}O.CH_3CO$	
12.	Menthyl isovalerianate	$C_{10}H_{19}O.C_4H_9CO$	
13.	Menthyl esters of	$C_9H_{11}COOH$, $C_{10}H_{19}O.C_8H_{11}O$	
14.	α-Lactone	$C_{10}H_{16}O_2$	
15.	Cadinene	$C_{15}H_{24}$	
16.	Amyl alcohol	$C_5H_{11}OH$ (acetate)	
17.	Dimethyl sulphide	$S(CH_3)_2$	

Minor examinations preceeding this seemingly exhaustive study were made by F. B. Power in Flückigers laboratory in 1880* and by R. I. Halsey in this laboratory** The

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* Pharm. Jour., 40, p. 219.

**Proc. W.P.A., 1894, p. 88.

The former obtained results indicating the presence of a terpene or its polymers. The latter a little later identified l-pinene whereas Power and Kleber a year later enumerated inactive pinene, perhaps a mixture of d- and l-pinene* in their list of constituents.

While in a sense peppermint oil haw been exhaustively examined chemically by the two investigators mentioned, this should not discourage further investigation but should rather encourage it, since it really makes possible a better phyto-chemical study of the subject.

Investigation along plant physiological lines have already been begun. Results of such investigation s have been reported by Roure,-Bertrand Fil cf Grasse, France, while it is well known that the German firm of Schimmel & Co. at Miltitz has had similar investigations in progress for a number of years. In the United States however, the largest producer of peppermint oil, no similar investigations are known of.

As a preliminary step toward such an investigation, the by-products resulting in the fractionation of refined oil by the A. U. Todd Company of Kalamazoo, Mich., have been studied as to their physical constants and their menthol and menthyl ester contents. The results of this first study are herewith recorded.

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* G.-H.-K., The Vol. Oils, p. 645.

Three fractions of five pounds each of peppermint oil, obtained as byproducts in the preparation of twice rectified oil from the crude oil, from A. W. Todd of Kalamazoo, Michigan.

The oil, labelled as the first fraction was of a light yellow color, the second fraction, nearly colorless and the last fraction of a lemon yellow color. These facts lead one to the belief that the fractions were labelled inaccurately, that is, the first and second fractions. Additional facts will be furnished to substantiate this belief.

Determination of Physical Constants.

The first physical constants to be determined were the specific gravities of the different fractions by means of the specific gravity bottle or pycnometer, and also the Mohr - Westphalt specific gravity balance for comparison. The results obtained are found in the tabulation of physical constants. By this table it is seen that the specific gravities do not agree as to accuracy in that the specific gravity taken with the specific gravity balance are in each case a little greater than the results obtained by means of the specific gravity bottle or pycnometer. In both cases, however, the first fraction has a greater specific gravity than the second fraction, which results confirm the belief that a mistake in labeling the fractions has been made. The difference in the results obtained would indicate either that the specific gravity balance was not sensitive enough or that a mistake in weighing had been made. A difference in the specific gravities of one oil might infer that a mistake in the operation of weighing had occurred. As a difference in all three fractions was obtained however, it would indicate that the specific gravity balance was inaccurate.

The next physical constants determined were the observed and specific rotatory powers of each fraction. The Laurent half shadow apparatus was used for this purpose. From eight to ten observations were taken for each fraction with both the 50 and 100 mm. tubes. The averages of these results and the calculated specific rotatory powers* of each fraction, are found in the following tabulation of physical constants.

Tabulation of Physical Constants.

	1st Fraction	2nd Fraction	3rd Fraction
Specific gravity at 20° C. by means of pycnometer.	0.8861	0.8859	0.9154
Specific gravity at 20° C. by means of the Mohr-Westphalt balance.	0.8931	0.8901	0.9177
α_D in 50 mm. tube	10° 30'	7° 22'	23° 52'
α_D in 100 mm. tube	22° 31'	15° 14'	47° 44'

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* U. S. P. 1900, p. 580.

Tabulation of Physical Constants. (Continued).

	1st Fraction	2nd Fraction	3rd Fraction
$(\alpha)_D$ in 50 mm. tube	23° 42'	16° 37'	52° 8'
$(\alpha)_D$ in 100 mm. tube	25° 24'	17° 12'	52° 8'

The results obtained are very close and vary to any extent in only one instance and that of only about 2° in the first fraction. From the results obtained it is seen that the third fraction has the greatest rotatory power, while presumably the first fraction has a greater rotatory power than the second fraction. These figures confirm the suspicion that the oil labelled as the second fraction, is really the first fraction obtained in the distillation of the oil of peppermint. Not only the physical constants but also the chemical constants, as we shall see, will confirm this belief.

Determination of Chemical Constants.

The experiments performed in estimating the chemical constants consisted merely in determining the menthol and menthyl content, and also the acid number and saponification numbers of each fraction. The operations undergone in the determination of the chemical constants were as follows.

About 10 cc. - 15 cc. of oil were weighed in a tared 150 cc. - 200 cc. flask. The acid number was then obtained by titrating this oil with an alcoholic potassium hydroxide solution of known strength, using phenolphthalein as indicator. As the indicator will not readily mix with the oil, a little alcohol was added. Care must be taken however, to use neutral alcohol otherwise a higher acid number will be obtained owing to the small amount of free acetic acid found in nearly all commercial alcohol. As this fact was not taken into consideration in the first few experiments, the difference can be readily seen from the results in the tabulation. In titrating the oil with the alkaline solution, a twenty-five cc. burette was filled with the standard alkali, and when the oil became neutral, the readings were taken and the acid number calculated. The remainder of the twenty-five cc. of standard alkali solution, was then added to the oil and the mixture heated with a reflux condenser from one to two hours on a water bath at 100° C. After being thoroughly saponified, the mixture was cooled and then titrated with N/2 H_2SO_4 V. S. with about 1/2 cc. of phenolphthalein as indicator. In titrating with the standard acid, it will be found advantageous to add about 15 - 20 cc. of distilled water , which will dissolve the potassium sulphate, insoluble in alcohol, and also be of aid in determining the end of the reaction as it takes up the phenolphthalein and also the first traces of excess of acid. This method was found especially advantageous in working with the third fraction which becomes a very dark color during the process of saponification even without the presence of phenolphthalein. It would thus be found impossible to distinguish the end of the reaction if distilled water were not used.

Meanwhile a blank test is performed by titrating 25 cc. of the standard alkali solution, with the N/2 H_2SO_4V.S. The number of cc. of acid used in titrating the excess of alkali used in the saponification of the oil, is then subtracted from the amount of acid used to neutralize 25 cc. of the KOH solution and the result obtained will represent the number of cc. of N/2 KOH V. S. necessary to saponify the esters and acids in the oil. This result is then mulitplied by 0.02787, the KOH factor, and the result obtained will be the amount of KOH necessary to saponify the esters and neutralize the acids in the oil. On dividing this result by the weight of the oil used, the saponification number of the oil is obtained. As the saponification number of the oil, is the sum of the acid and ester numbers, the ester number can then be obtained by subtracting the acid number which was obtained in the beginning of the process, from the saponification number. The amount or percentage of ester and its equivalent as menthol was then obtained from prepared tables,*which are the accurate results of experiments. The amount and percentage of esters may also be calculated by multiplying the number of cc. of N/2 KOH necessary to saponify, by 9.834, giving the amount of esters present, and dividing this result by the weight of the oil, thus obtaining the percentage of esters in the oil. The amount of menthol can thus be calculated by the following proportion:

9.834 : 7.749 :: amount or percentage of ester : X. "X" will be the amount or percentage of ester equivalent of free menthol in the oil.

The saponificatied oil was then repeatedly washed with distilled water in a separatory funnel, until freed from potassium sulphate. After separating out all the water possible, the oil was transferred to an acetylization flask containing about 1 gram of anhydrous sodium acetate and about 10 cc. of acetic acid anhydride, and then boiled gently for about one to two hours in order that all the menthol might be obtained as the acetate. The mixture was then allowed to cool and then washed with distilled water and afterwards with a 1% solution of sodium carbonate until the mixture is only slightly alkaline to phenolphthalein T. S. The acetylized oil is then dried with the aid of fused calcium chloride after which it was filtered into a tared 150 -

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* G. & H., The Vol. oils, p. 202.

200 cc. flask and about 50 - 75 cc. of standard alcoholic alkali added, depending upon the amount of acetylized oil, and also on the fraction as the third fraction requires more than the other two fractions, owing to a greater percentage of menthol content. This mixture was then boiled with a reflux condenser, on a water bath for at least an hour in order to affect complete saponification.
The mixture was then titrated with N/2 H_2SO_4 V. S. in same manner as in the preceeding experiment, adding a little water for the same reasons.

The saponification number is then calculated in same manner as before. From this result, the amount and percentage of total free and combined menthol have been obtained by referring to the tables* mentioned in the former experiment. The free menthol content orrigionally in the oil, was then acertained by subtracting the menthol equivalent as ester, already obtained, from the total menthol content. The following tabulation contains the results obtained by experiments performed on the different fractions of the oil, including also the amount of potassium hydroxide to neutralize acid and also to saponify the oil in the different experiments.

Tabulation of Chemical Constants.

	1st Fraction	2nd Fraction	3rd Fraction
Weight of the oil	8.8427 gms.	10.661 gms.	10.986 gms.
Amount of KOH to neutralize free acid	0.0031105"	0.00674454	0.0241248"
Acid number	0.347	0.632	2.196
Amt. of KOH to sapon.	0.1912578 gms.	0.144924 gms.	0.404115 gms.
Saponification No.	21.507	13.59	36.78
Ester number	21.16	12.958	34.584
Percentage of menthyl acetate	7.477%	4.585%	12.224%
Percentage of menthol as ester	5.885%	3.608%	9.6335%

Weight of oil	14.698 gms.	13.132 gms.
Amount of KOH to neutralize free acid	0.0037122	0.00261976
Acid number	0.252	0.199
Amt. of KOH to sapon.	0.241352 gms.	0.258474 gms.
Saponification No.	16.168	19.68
Ester number	16.168	19.481
Percentage of menthol acetate	5.73%	6.888%
Percentage of menthol as ester	4.84%	5.4246%

	1st Fraction	2nd Fraction	3rd Fraction
Weight of oil	13.0225 gms.	10.1106 gms.	21.903 gms.
Amount of KOH to neutralize acid	0.0052395	0.00259978	0.04021641
Acid number	0.402	0.257	1.836
Amount of KOH to saponify	0.298766 gms.	0.19360825 gms.	.8071152 gm.
Saponification No.	22.942	19.14	36.84
Ester number	22.54	18.883	35.004
Percentage of menthol acetate	7.969%	6.679%	12.3714%
Percentage of menthol as ester	6.28%	5.257%	9.751%
Weight of acetylized oil	7.81 gms.	5.233 gms.	11.0511 gms.
Amount of KOH to saponify	1.14685 "	0.629862 "	1.93278 "
Saponification No.	146.84	120.36	174.89
Percentage of total menthol	45.96%	36.85%	56.07%
Percentage of free menthol	39.68%	31.593%	46.319%

This tabulation of results shows that the second fraction contains less menthol as well as menthyl ester content, than the first fraction, which facts confirm the suspicion that the fractions are labelled inaccurately.

Agnelli, P. J. 1900

Uber den Anbau der Mentha Piperita und eine neue Sorte derselben.

Pharmaceutische Post, 33, p. 263; (Jahresbericht, p. 69; Proc. A. Ph. A., 49, p. 680.)

An account of an improved peppermint plant, the Mentha piperita Agnelliana.

Charabot, E. 1900

Chemie Vegetals. - Recherches sur la genese des composed da la serie du menthol dans les plantes.

Comptes Rendus, 130, p. 518; (Year Book of Pharmacy, 1900, p. 170; Chem. Central., 71, i, p. 728; Pharm. Jour., p. 277; Proc. A. Ph. A., 48, p. 750; Jahresbericht, 36, p. 318.)

Plant physiological investigations.

Eliel, L. 1900

On Peppermint.

Proc. Ind. Pharm. Ass., 1900, p. 58; (Proc. A. Ph. A., 49, p. 480.)

An account of the peppermint cultivation in northern Indiana.

Gerrard, A. W. 1900

The Recovery of Waste Menthol.

Yearbook, 37, p. 436; (Proc. A. Ph. A., 49, p. 831.)

The author prefers recrystallization from ether, to sublimation.

Lifshitz, 1900

Ueber Pfeffermintzöle verschiedener Herkuntf.

(Chem. Ztg., 1900, Ref. p. 366; Jahresbericht, 36, p. 318.)

A comparison of physical constants, (sp. gr., congealing point, boiling point, Maumene's test, solubility in 90% alcohol) and chemical constants, (acid number, ester number, saponification number, iodine number) and menthol and menthone content of different Russian, English, German, American and Japanese oils.

Charabot, Eugene 1901

Die Bildung des aetherischen Oiles in Mentha Piperita.

Chem. Ztg., 1901, p. 130; (Jahresbericht, 36, p.74.)

Welmans, P. 1901

Ueber Pfeffermintzöle D. A. B. IV und die Farbreactionem deselben.

Pharm. Ztg., 46, p. 532 u. 591; (Jahresbericht, 36, p. 318; Proc. A. Ph. A., 50, p. 982.)

A critical discussion of the pharmacopoeial requirements and tests.

Charabot, E. and Herbert, A. 1902

Mecanisme des variations chemequez chez la plante soumise a l'influence du nitrate de sodium.

Bull. Soc. Chim. (3), 27, p. 914 and Compt. Rend., 134, p. 1228;* (Pharm. Jour., 1902, p. 549; Proc. A. Ph. A., 50, p. 831.)

On the influence of sodium nitrate as a fertilizer on the developement of the peppermint plant and its oil.

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* The communication to the Acad. des Sc. appears to be an abridged account of the paper presented to the Bull. Soc. Chim.

Charabot, E. and Herbert, A. 1902

Contribution a l'stude des modifications chimiques chez la plante soumise a l'influense du chlorure de sodium.

Bull. Soc. Chim. (3), 27, p. 204 and Comp. Rend., 134, p. 181;* (Sch. & Co. Report April 1902, p. 54; Proc. A. Ph. A., 50, p. 831; Yearbook, 1902, p. 120.)

On the influence of sodium chloride as a fertilizer in the developement of the peppermint plant and its oil.

Denniston, R. H. 1902

A Michigan Peppermint Still.

Pharm. Rev., 20, p. 108; (Proc. A. Ph. A., 50, p. 979.)

Description of still with reproduction of photographs taken by the author.

Kebler, L. F. 1902

The adulteration of drugs.

Am. Jour. of Pharm., 74, p. 12; (Proc. of A. Ph. A., 50, p. 983.)

Oil of peppermint; adulteration with oil of turpentine

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*The communication to the Acad. des Sc. appears to be an abridged account of the paper to the Bull. Soc. Chim.

Beckman, E. 1903

Increase of menthol by chemical means.

Pharm. Ztg., 48, No. 77, (Sept. 1903) p. 780; (Proc. A. Ph. A., 52, p. 876.)

The menthol content of the oil can be increased by reduction of the menthone.

Bennett, C. T. 1903

Oil of peppermint; a new adulterant.

Chem. & Drug., 62, p. 591; (Proc. A. Ph. A., 51, p. 909; Yearbook, 1903, p. 130; Jahresbericht, 1903, p. 204.)

Adulteration with "acetine", a mixture of the three acetic esters of glycerine

Charabot, E. and Herbert, A. 1903

Influence de la nature du milien exterieur sur l'etat d'hydratum de la plants.

Bull. Soc. Chim. (3), 29, p. 1239 and Compt. Rend., 136, p. 160;* (Proc. A. Ph. A., 51, p. 752; ibidem, 52, p. 665; C. & D., 64, p. 578.)

On the effect of mineral salts on the developement of the peppermint plant.

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* The communication to the Acad. des Sc. appears to be an abridged account of the paper to the Bull. Soc. Chim.

Parry, E. J. and Bennett, C. T. 1903

Adulterated peppermint oil.

Chem. & Drug., 63, p. 154; (Yearbook 1904, p. 133; Proc. A. Ph. A., 52, p. 876.)

A heavy oil, presumably that from African copaiba, as adulterant of Wayne Co. oil. See also note, Chem. & Drug., 62, p. 998.

Todd, A. M. 1903

The purity of peppermint oil.

Chem. & Drug., 63, p. 369; (Proc. A. Ph. A., 52, p. 877.)

Further discussion of the wholesale adulteration of "Wayne Co." peppermint oil brought out by Parry.

Weilen, 1903

Die Prüfung des Pfefferminztöles auf den Geschmach.

Pharm. Weehbl. 1903, No. 18; Pharm. Ztg., 1903, p. 416; (Jahresbericht, 38, p. 305.)

The author points out the important role played by the menthyl esters in so far as the taste e.g. in peppermint lozengers is concerned.

Herbert, A. et Truffaut, Geo. 1904

Influence de la nature du milien exterieur sur la composition de la plante minerale.

Bull. Soc. Chim., 29, p. 1235; (Chem. & Drug., 64, p. 578; Proc. A. Ph. A., 52, p. 665.)

On the influence of surroundings on the inorganic components of plants (incl. Mentha.)

Panchaud, Adalbert 1904

Ueber die Wertbestimmung ätherischer oele.

Schweiz. Wehschr. f. Chem. und Phar., 42, p. 126; (Jahresberciht, 39, p. 374.)

Oleum Mentha (p.177). The ester determination is to be ignored, the determination of the total menthol only is to be made official.

Parry und Bennett, C. T. 1904

The adulteration of peppermint oil.

Chem. & Drug., 64, p. 854; (Jahresbericht 1904, p. 375; Proc. A. Ph. A., 52, p. 877.)

Characteristics of genuine Wayne Co. oil and of oil adulterated with "triacetin," African copaiba oil, and cedarwood oil.

Approved Edward Kremers

Prof. of Pharm. Chem.