

SOME OBSERVATIONS ON THE CONSTANTS OF OIL OF
SPEARMINT.*BY L. E. WARREN.¹

Several years ago criticisms were received that the U. S. P. standard for carvone in oil of spearmint (not less than 43%) was too low. Likewise the lower limit for optical rotatory power (-38°) was said to be too low. It was claimed that the low carvone limit and the low rotatory requirements of the Pharmacopœia permitted adulteration. It was also claimed that the U. S. P. X method for the assay of carvone in oil of spearmint was unworkable. The fault was said to lie in the use of a 5% solution of sodium acid sulphite as a neutralizing reagent instead of a concentrated solution. By the use of the weaker solution the volume of the reacting mixture becomes so great that it exceeds the capacity of the cassia flask in which the reaction is directed by the Pharmacopœia to be carried out, and the assay cannot be completed. Since these allegations were of considerable importance from the standpoint of the enforcement of the Food and Drugs Act, a study of the situation was undertaken.

Very little information concerning the constants of oil of spearmint has appeared in the literature during the last 10 years. Christensen and Hiner² examined four specimens of oil of spearmint grown in Florida during the years of 1929 and 1930, inclusive. They found that the specific gravity varied between 0.9215 and 0.9253; the refractive index from 1.4825 to 1.4897; the optical rotation from -56.09° to -59.075° ; and the carvone content from 69.5 to 80.2%.

Oil of caraway, oil of cinnamon and oil of spearmint are directed by the U. S. Pharmacopœia to be assayed by the same method. As applied to oil of spearmint, the method is as follows:

Place 10 cc. of oil of spearmint, measured from a pipette, in a 100-cc. cassia flask and add 50 cc. of a saturated solution of sodium sulphite which has been carefully rendered neutral to 2 drops of phenolphthalein T.S. by means of a 5 per cent sodium bisulphite solution. Heat the mixture in a bath containing boiling water and shake the flask repeatedly, neutralizing the mixture from time to time by the addition of a few drops of the 5 per cent sodium bisulphite solution. When no coloration appears upon the addition of a few more drops of phenolphthalein T.S. and heating for fifteen minutes, cool to room temperature and, when the liquids have separated completely, add sufficient sodium sulphite solution to raise the lower limit of the oily layer within the graduated portion of the neck. Note the volume of the residual liquid. This measures not more than 5.7 cc., indicating the presence of not less than 43 per cent by volume of carvone.

Eight specimens of oil of spearmint were procured from five dealers in this country,³ each specimen being supposed to be of good quality. In addition, a laboratory specimen known to be at least 15 years old was rectified by steam distillation and the product included in the examination. Two of the specimens studied were stated by the dealer to be what are known as "Scotch Spearmint" oils. That is, they were produced from a variant of *Mentha spicata* grown in this

* Scientific Section, A. Ph. A., Toronto meeting, 1932.

¹ Food and Drug Administration.

² JOUR. A. PH. A., 21 (1932), 147.

³ Practically no oil of spearmint is imported, all of the supply being produced in this country. Southern Michigan and northern Indiana are the principal producing localities.

country, the original stocks of which were brought from Scotland. The U. S. P. X assay was applied to several of the specimens, but without success, owing to the fact that the volume of the reacting solution became in each case too great to be contained in the cassia flask.¹ The method was modified by the use of a concentrated solution (about 35 per cent) of sodium acid sulphite as a reagent for neutralizing the solution instead of the 5 per cent strength as directed by the Pharmacopœia. A 30 per cent solution also works well. With this modification the method was found to work satisfactorily. In addition to the assay for carvone, the optical rotatory values of the oils at 20°, the indices of refraction at or near 20°, and the densities at $\frac{25^\circ \text{C.}}{25^\circ \text{C.}}$ were determined. Some of the specimens were assayed by the U. S. P. IX method. This procedure is the same as the U. S. P. X process except that acetic acid is used instead of sodium acid sulphite to maintain an acid reaction. Some of the specimens contained so much carvone that the assay could not be completed with diluted acetic acid as prescribed by the U. S. P. IX. In these 20% acetic acid was used. The findings are recorded in the accompanying table.

TABLE I.—ANALYSES OF SEVERAL SPECIMENS OF OIL OF SPEARMINT.

Sample.	Density 25° C./25° C.	Refractive Index.	Optical Rotatory Power 20° C.	Carvone (U. S. P. X Method Modified).	Carvone U. S. P. IX Assay (Modified).
A	0.9270	1.4870	-51.83	60.1	61.1
B	0.9248	1.4860	-58.13	60.5	
				59.5	59.5
C		1.4850	-59.65	61.4	58.6
D	0.9232	1.4860	-55.36	63.10	63.9
E*	0.9368	1.4875	-49.99	61.4	
F	0.9245	1.4860		66.1	65.50
G	0.9207	1.4855	-57.12	60.9	59.1
H	0.9221	1.4860	-55.20	57.5	
I	0.9212	1.4810	-45.05	53.6	
				54.1	
U. S. P. Requirements	0.917 to 0.934	1.482 to 1.490	-38° to -56°	Not less than 43%	

* Old specimen rectified. It conforms to the U. S. P. X in all particulars except that its specific gravity is slightly high.

An examination of the findings shows that none of the oils approach the U. S. P. X lower limits in optical rotatory power (-38°) or in carvone content (43%). Since most of the oils assay over 60% of carvone it would appear that the U. S. P. limit for carvone (not less than 43%) might be raised with propriety. However, in order to secure further information the aid of dealers in oil of spearmint was sought.

¹ In 1930, Kassner [JOUR. A. PH. A., 19 (1920), 138] had observed that the U. S. P. X method for the assay of cinnamon oil was unworkable. However, the fact had been noted by the chemists in the Import Office of the Food & Drug Administration considerably earlier (unpublished).

MEMORANDA ON OIL OF SPEARMINT.

The following memoranda were obtained from the records of a dealer in certain essential oils. The two values found in each space represent the highest and the lowest findings for what were considered to be genuine oils for the several different years mentioned. In some cases a third value has been given and the expression "Redist." given after the factor. This means that the oil had been redistilled. It will be noted that the year 1928 is vacant. This is due to the fact that the company had no data for that year, or that the records had been misplaced.

TABLE II.

Year.	Optical Rotatory Value (Degrees).	Refractive Index.	Carvone %.	Specific Gravity.
1921	-42.32	1.4803	44.5	0.9133
	-58.39	1.4895	65.0	0.9260
1922	-49.50	1.4862	57.0	0.9212
	-55.30	1.4905	71.0 Redist.	0.9340 Redist.
			66.0	0.9287
1923	-46.75	1.4870	57.0	0.9225
	-55.50	1.4880	65.0	0.9270
1924	-50.75	1.4875	60.0	0.9258
	-55.20 Redist.	1.4910 Redist.	72.0 Redist.	0.9360 Redist.
	-54.60	1.4895	71.0	0.9350
1925	-44.15	1.4860	56.0	0.9253
	-51.50 Redist.	1.4895 Redist.	66.0 Redist.	0.9340 Redist.
	-52.50	1.4885	64.0	0.9300
1926	-48.00	1.4870	60.5	0.9230
	-53.75 Redist.	1.4910 Redist.	72.0 Redist.	0.9355 Redist.
	-52.00	1.4890	65.0	0.9300
1927	-50.10	1.4845	54.0	0.9213
	-54.25 Redist.	1.4896 Redist.	59.0	0.9332 Redist.
	-52.25	1.4900	59.0	0.9346
1928	No information available			
1929	-47.50	1.4854	51.0	0.9170
	-51.75 Redist.	1.4919 Redist.	70.0 Redist.	0.9380 Redist.
	-53.50	1.4865	60.0	0.9220
1930	-48.50	1.4850	53.0	0.9180
	-55.85 Redist.	1.4900 Redist.	68.0 Redist.	0.9255 Redist.
	-55.50	1.4878	58.0	0.9260
1931	-53.25	1.4870	54.0	0.9226
	-54.25 Redist.	1.4868 Redist.	62.0 Redist.	0.9221 Redist.
1932	-48.75		52.0	
	-60.25		58.0	

An examination of the values in Table II reveals that optical rotatory values of less than -48° were encountered in but four of the eleven years covered by the census. Concerning the carvone content, the dealer stated:

"... we have never seen any genuine American Oils which contain as low as 43% of carvone and it is very seldom we assay a genuine sample where the carvone content, when assayed by the method prescribed in the U. S. P. X, is much under 50. Reference to our records indicates

that in 1921, when growing conditions were normal and the yield per acre particularly high, we assayed two samples, one of which indicated a carvone content of 44.5% and one a carvone content of 47.5%. Without exception, these are the lowest assays we have ever encountered in genuine oil. . . . It is our opinion the minimum limit of carvone content [in the U. S. P. XI] may be raised with perfect safety and with considerable propriety."

Since the chief controversy concerning the constants of spearmint oil had reference to the optical rotatory power and the carvone content another dealer was requested to furnish information concerning his experience with these two values. He gave the highest and lowest findings which had been recorded in his laboratory in each year since 1915. This information is given in Table III.

TABLE III.

Year.	Optical Rotatory Power. Degrees.		Low. %	Carvone.	High. %
	Low.	High.			
1915	-35.48	-50.40	51.0		64.5
1916	-41.70	-59.16	52.5		58.0
1917	-43.93	-50.40	46.0		65.5
1918	-43.83	-46.71	48.0		57.0
1919	-39.90	-53.60	43.0		66.0
1920	-42.80	-49.66	44.0		58.0
1921	-46.41	-53.53	52.0		61.0
1922	-45.33	-53.53	52.0		66.5
1923	-47.08	-57.61	53.0		68.0
1924	-36.21	-56.80	41.5		69.0
1925	-41.30	-55.91	50.0		68.0
1926	-40.71	-51.50	61.0		62.0
1927	-39.95	-55.87	50.0		65.5
1928	-35.27	-56.21	51.0		67.0
1929	-46.91	-50.30	60.0		63.0
1930	-43.10	-57.97	52.0		60.0
1931		-58.45			62.5
1932	-53.50	-58.33	59.5		67.5

It will be noted that the minimum values are sometimes lower than those in Table II. Inquiry was made of the dealer whether in his opinion the two recent specimens having low optical rotatory values (-46.91° for 1929 and -43.10° for 1930) were of poor quality. He replied that both specimens were normal in odor and taste, although the rotation was lower than usually observed. He thought that the variant was probably due to variation in the soil and climatic conditions. Apparently he considered the specimens unadulterated.

So far as these studies indicate, it appears that the minimum standards for optical rotatory power and carvone content in the U. S. P. X for Oil of Spearmint are lower than the market quality of the product warrants. It is believed that an optical rotation of from -48° to -59° and a minimum requirement for carvone content of not less than 50% would be warranted.

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