Iodine Number of Oil of Peppermint

LAWRENCE H. BALDINGER, University of Notre Dame

Introduction

In the analysis of essential or volatile oils, little or no importance is attached to the determination of the iodine number, inasmuch as other chemical constants for these oils seem to be of more importance in establishing standards of purity and identity. The decoloration of an iodine in chloroform solution by a sample of oil of peppermint in a chance qualitative test suggested the problem of the determination of the iodine values for several samples of this essential oil as a possible aid in determining the purity and commercial value of the oil.

The usual chemical constants which are determined for oil of peppermint include the ester value, expressed as menthyl acetate, total menthol content, free and combined in the form of menthyl acetate, and the menthone content. The United States Pharmacopoeia[1] sets standards for the first two values, requiring not less than 5% of esters, expressed as menthyl acetate ($C_{10}H_{19}.C_2H_3O_2$), and not less than 50% total menthol ($C_{10}H_{19}.OH$), free and as esters, but specifies no purity rubric for menthone content. Arbitrary values for this substance have been suggested by the large-scale users of this essential oil since it is believed that some of the characteristic odor and flavor of peppermint oil is due to the menthone ($C_{10}H_{18}O$).

Inasmuch as chemical and physical constants had been determined for a number of samples of peppermint oil, it seemed desirable to calculate the possible relationships between the iodine values and the other constants for these oils. While it must be admitted that these relationships are usually of theoretical interest only, it frequently happens that practical ratios do exist between various constants.

Experimental Procedure

For the determination of the iodine values of the oils, a method suggested by F. W. Rosenmund and W. Ruhnhenn[2] was used, a method similar to but faster than the Hanus procedure. Strictly speaking, because of the substitution of bromine for iodine in the reagent, the value might be considered as a bromine value, except for the fact that the milli-equivalent for iodine instead of bromine is used in the calculations.

The reagent is prepared by mixing 8 g. of pyridine and 10 g. of concentrated sulfuric acid with 20 ml. of glacial acetic acid, and to this solution adding 12 g. of bromine in 20 ml. of glacial acetic acid. After thorough mixing, the solution is diluted to one liter with glacial acetic acid.

[1] The United States Pharmacopoeia, 11th. Dec. Rev., Mack Printing Co., 1936, p. 259.

[2] Rosenmund and Ruhnhenn. Pharm. Weekblad. 61:76 (1924); through Year Book of the American Pharmaceutical Association 13:428 (1924).

To determine the iodine number for a sample, 0.5 ml. of oil, accurately weighed, is treated with 25 ml. of the reagent and allowed to stand for 30 minutes. Two grams of potassium iodide is then added and the mixture is diluted with 50 ml. of water. The mixture is allowed to stand for 10 minutes and the iodine liberated by the excess bromine is titrated with N/10 sodium thiosulfate solution. With each group of samples a blank is run under similar conditions. The iodine value is calculated using the following formula:

$$\text{Iodine Value} = \frac{(B - A)(0.01269)100}{W}$$

where B is the number of milliliters of N/10 sodium thiosulfate solution required for the blank, A is the number of milliliters of N/10 sodium thiosulfate solution for back titration, 0.01269 is the iodine factor for N/10 iodine solution, W is the weight of sample. No marked variation of iodine values with length of exposure of oils to the bromine solution was observed (Table I).

The menthol and ester values were determined using the methods of the United States Pharmacopoeia.[3] The menthone values were determined, using hydroxylamine hydrochloride in a method formulated from a number of references[4]. The chemical constants are tabulated in Table II. In Table III ratios between the iodine values and the other chemical constants are listed.

Discussion and Summary

The results of the investigation indicate that the iodine number may be of theoretical interest in the examination of peppermint oil samples. Data for a larger number of samples, however, is necessary before the practicability of this constant can be demonstrated. From the data as listed in Table II it will be observed that those oils with high iodine

TABLE I.—Variation of Iodine Values with Length of Exposure of Oil to Bromine Solution

Weight of Oil	Time in Minutes	Iodine Value
0.4470	10	65.7
0.4410	10	66.0
0.4812	15	65.8
0.4401	15	66.4
0.4812	20	66.6
0.3442	20	67.1
0.4771	25	66.6
0.3412	25	67.3
0.3440	30	67.1
0.3414	30	67.2

[3] The United States Pharmacopoeia, 11th. Dec. Rev., Mack Printing Co., 1936, p. 259.
[4] Schimmel Report, **1928**:22, 23; **1929**:143; **1932**:104; **1933**:12, 92.

values have low menthol and high menthone contents, whereas those samples with normal menthol and menthone contents have iodine values which vary between 62 and 72. The ratio of the iodine value to the combined ester and menthone values for the latter samples is practically constant, while the samples with low menthol and high menthone values show a slightly lower ratio than the normal samples. With additional data from a large number of samples of all grades it may be possible to propose a range for the iodine value as an aid in establishing the quality of peppermint oil. The investigation is being continued using other iodinating solutions.

TABLE II.—Chemical Constants for Peppermint Oil Samples

Sample Number	Ester %	Menthol %	Menthone %	Iodine Value
1	6.43	53.60	24.32	62.5
2	5.46	52.50	26.86	67.5
3	5.41	50.94	27.47	68.1
4	6.36	52.76	24.98	66.1
5	5.76	49.35	26.77	67.3
6	7.94	50.53	30.08	75.5
7	4.46	39.37	43.11	82.8
8	5.22	39.50	42.31	82.7
9	4.73	41.05	38.02	79.0
10	6.44	51.94	29.88	74.2
11	4.76	49.49	30.28	72.1

TABLE III.—Ratios of Chemical Constants of Peppermint Oil Samples

Sample Number	Iodine Value	Iodine Value
	Ester + Menthone	Menthol
1	2.03	1.17
2	2.09	1.29
3	2.07	1.34
4	2.11	1.25
5	2.08	1.36
6	1.98	1.49
7	1.74	2.10
8	1.74	2.09
9	1.85	1.92
10	2.04	1.43
11	2.00	1.46