Assay for Menthone in Oil of Peppermint

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For the estimation of menthone in oil of peppermint, as well as for the quantitative determination of aldehydes and ketones in other essential oils, oximation with hydroxylamine hydrochloride in an alcohol medium with subsequent titration of the liberated hydrochloric acid appears to give the best results. Variations in menthone content of a sample of oil submitted to different laboratories may result from a number of factors, i.e., type of indicator, concentration of hydroxylamine solution, method of addition of solution, and temperature.

Kremers[1] was the first to publish a gravimetric method for the estimation of aldehydes and ketones with hydroxylamine hydrochloride. Walther[2] first used a volumetric procedure with hydroxylamine hydrochloride for determining citral in oil of lemon. Stillman and Reed[3] have published a summary of methods employed for the determination of aldehydes and ketones, as well as a method of their own invention.

Menthone is a ketone, $C_{10}H_{18}O$, which occurs with menthol, $C_{10}H_{19}OH$, in oil of peppermint. Also present in the oil are menthyl acetate, $C_{10}H_{19}C_2H_3O_2$, a mixture of terpenes, and small amounts of organic compounds related to or derived from these four essential components.[4]

Concerning the biogenesis of these compounds in peppermint, the reader is referred to a discussion by Hall[5] who has also included a brief history of the theories to explain the formation of these substances by the plant. Earlier investigators advanced the theory that menthone was formed in the plant by the oxidation of menthol and that oils distilled late in the season would show a high menthone content. Recently, however, Strauss[6] has stated: "Peppermint for oil production is best cut after full bloom has been reached, not at the beginning of flowering. In this way it is possible to obtain a maximum yield of oil with a menthone content not exceeding 15 per cent. According to Rutovskii and Travain[7] the menthol content of the plant increases during growth, whereas the menthone content decreases. It appears that, under the influence of the sunlight during the growth of the plant up to the time of full bloom, menthol is slowly formed from menthone, to which the bitter aftertaste of peppermint oil is due.

The author's observation on the menthone content of numerous samples of oil collected at different stages of growth agree with the find-

[1] Kremers, Pharm. Rev. **14**:76, 244 (1896); Pharm. Arch. **2**:81 (1899); **3**:9 (1900); J. Soc. Chem. Ind. **20**:16 (1901).

[2] Walther, Pharm. Zentralh., **40**:621 (1899); **41**:614 (1900).

[3] Stillman and Reed, Perfumery Essent. Oil Record, **23**:278 (1932).

[4] Power and Kleber, Pharm. Rundschau, **12**:157 (1894).

[5] Hall, Chem. Rev., **13**:479 (1933).

[7] Rutovskii and Travain, Riechstoff, Ind. **4**:124 (1929).

[6] Strauss, IV Congr. interna. plantes medicinals plantes essences, Paris, p. 270 (1931); through Schimmel Report, p. 45 (1933).

ings of Strauss. Apparently the biogenetic processes in the plant synthesize menthone as well as menthol and a phytochemical reduction changes the former substance into the corresponding alcohol menthol, as the plant matures. Although the significance of the observation can be questioned, it is interesting to note that the sum of the menthol and menthone percentage in oil of peppermint will be within the range of 75 to 85 per cent.

Experimental Procedure

The particular problem which constituted the basis for this report was to determine whether the constituents of oil of peppermint, other than menthone, would react with hydroxylamine hydrochloride to cause a variation in menthone content. For this purpose an artificial oil of peppermint was prepared by combining accurately-weighed amounts of alpha-pinene, 13.87%, menthyl acetate 4.71%, menthol 51.16%, and menthone 30.26%, in proportions commonly found in natural oil of peppermint. The menthone was prepared by the oxidation of menthol with dichromic acid, the menthyl acetate by acetylation of menthol, the alpha-pinene by purification and distillation of oil of turpentine; the menthol was U. S. P. grade and was not subjected to further purification. The artificial oil as well as the pure components were subjected to oximation by two methods as listed below. The results are tabulated in Table I.

Method I. Weigh the dried substance to be analyzed into a glass-stoppered flask containing 10 ml. of alcohol. Add 30 ml. of N/2 KOH and 10 ml. of 1 N hydroxylamine hydrochloride solution. Repeat on a blank omitting the oil. Shake vigorously at frequent intervals for one hour. Titrate the excess KOH with N/2 H_2SO_4, using 8 drops of brom-phenol-blue indicator (0.4% solution). Color change is from blue to green to yellow. Titrate the blank to full yellow and match the sample to the blank. Back-titrate the blank to a pale-green with KOH. Match the sample with this. Subtract the amount used for the back-titration from the original titration as a basis for the calculation. Subtract the number of ml. of H_2SO_4 used for the blank. This represents the number of ml. of KOH used to neutralize the HCl liberated. One ml, of N/2 KOH is equivalent to 0.077 grams of ketone.

$$\% \text{ Menthone} = (7.7 \times \text{ml. N/2 KOH}) \div \text{weight of sample}$$

Method II. Weigh the dried substance to be analyzed into a glass-stoppered flask containing 5 ml. of alcohol; add 20 ml. of 1 N hydroxylamine hydrochloride, 0.4 ml. dimethyl yellow indicator, and add N/2 KOH until the red color changes to yellow. Place the flask in a water bath at 75°-80° C. and neutralize the liberated HCl with N/2 KOH at five-minute intervals; after forty minutes, complete the titration to the full yellow color of the indicator and record the burette reading.

Two determinations are carried on side by side, using separate burettes, and the first one completed, plus an excess of one ml. of N/2 KOH is used as the color standard for the end point of the duplicate. A correction factor is necessary because the end-point of the titration

occurs at a pH different from that of normal hydroxylamine hydrochloride. The percentage composition is determined from the duplicate. An additional correction factor must be used if the KOH used is not exactly N/2.

$$\% \text{ Menthone} = (7.7 \times 1.008 \times \text{ml. N/2 KOH}) \div \text{weight of sample}$$

If the apparent menthone content for the amount of each of the constituents of the artificial oil of peppermint is calculated, based on the values given in Table I, it will be observed that the sum of these apparent menthone contents will agree fairly well with the menthone assay for the artificial oil, as shown in the following example.

As determined by the two methods, the average per cent of apparent ketone shown by alpha-pinene is 4.42%, by menthone 98.55%, by menthol 2.3%, and by menthyl acetate 60.25%. Using these figures, the apparent menthone in the artificial oil of peppermint is calculated to be 34.45%.

The average experimental value for the menthone content obtained in the analysis of the artificial oil is 34.15%.

Conclusion

It is apparent that the presence of various components in oil of peppermint definitely affects the apparent menthone per cent, that the percentages of ester, menthol, and terpene must be considered in determining the pure menthone content. Other essential oils or mixtures of organic compounds on which oximation procedures may be performed will undoubtedly show the same variations in ketone or aldehyde content, depending upon the reactivity of the different constituents with hydroxylamine hydrochloride.

TABLE I. Apparent Menthone Content of Artificial Oil of Peppermint and of the Constituents of Artificial Oil of Peppermint.

Constituent	Per Cent Menthone Method I	Method II
Alpha-pinene	4.2	4.5
	4.4	4.3
	4.6	4.5
Menthyl Acetate	62.3	59.4
	60.1	61.5
	59.0	59.1
Menthone	99.3	98.3
	97.6	98.5
	98.4	98.7
Menthol	2.3	2.3
	2.3	2.3
	2.4	2.2
Artificial Oil of Peppermint. Calculated Menthone Content 30.26%	34.0	34.2
	33.9	34.1
	33.4	34.3