Reduction of Oil of Peppermint with Lithium Aluminum Hydride.

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The widespread use of lithium aluminum hydride suggested the treatment of oil of peppermint with this reducing agent to determine the effect of this reagent on the menthyl acetate and menthone contents in the oil.

Menthone is a cyclic ketone, $C_{10}H_{18}O$, which occurs with the related alcohol, 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. The biogenesis of menthone and the other components in the oil has been discussed by Hall (1), Strauss (2), Rutovskii and Travain (3). Usually, the sum of the menthol and menthone contents in oil of peppermint will be within the range of 75 to 85 per cent. It is believed that the menthone is responsible for the bitter after-taste when the oil is used for flavoring purposes. Even though it might be commercially feasible to reduce the menthone to menthol, it is not certain that the resulting product would be satisfactory for drug or flavoring purposes. Since there are two centers of asymmetry in menthone and three in menthol, the reduction of menthone will give rise to a mixture of menthol isomers which may alter appreciably the flavor of the product, and which may have different pharmacological activities.

Experimental Procedure

The oil of peppermint used in this work was a composite sample collected in the Michigan-Indiana mint territory during the 1954 season. The sample was divided into five portions, four to be reduced, and one to serve as a control.

The reduction of the samples was carried out by the following procedures:

A) Sample 1. Lithium aluminum hydride (14.25 g., 0.375 moles) was suspended in 300 ml. of anhydrous ether in a one-liter, three-necked, round-bottom flask fitted with a stirrer, a condenser fitted with a soda-lime drying tube, and an addition funnel. With constant stirring, the peppermint oil (88.6 g.), dissolved in 100 ml. of anhydrous ether, was added slowly over a period of one hour. After the addition was completed, the reaction mixture was refluxed for twenty-four hours. The excess lithium aluminum hydride was decomposed with 60 ml. of 50% ethanol, and the aluminum salts dissolved in 450 ml. of dilute hydrochloric acid (3 parts water to one part of concentrated hydrochloric acid). The ether layer was separated and the aqueous portion extracted three times with 100 ml. of ether. The combined ether layers were washed twice with 200 ml. of water and then dried over sodium sulfate, anhydrous. After

the ether was removed by distillation, the resulting yellow oil was heated at a temperature between 60-70° C. at 12-15 mm. for a period of one hour. The yield of reduced peppermint oil was 84.9 g.

Sample 2. In a second experiment, 9.50 g. (0.25 moles) of lithium aluminum hydride was used, and the reaction mixture was refluxed for a period of forty-eight hours. The yield of reduced peppermint oil was 84.0 g.

B) Sample 3. An ether solution of lithium aluminum hydride was prepared as described in "Organic Reactions" (4), and standardized according to the procedure of Felkin (5). The molarity of the lithium aluminum hydride was 0.72 M.

In treating the third sample, the same apparatus and procedure as in Samples 1 and 2 were used, with the following modification. A solution of 60 g. of peppermint oil in 100 ml. of anhydrous ether was added to 200 ml. of 0.72 M (0.144 moles) lithium aluminum hydride over a period of forty minutes, and the mixture refluxed for four hours. The product was isolated and purified as described above. The yield was 56.8 g.

Sample 4. The experiment described for Sample 3 was repeated with a one-hour refluxing period instead of four. The yield of reduced peppermint oil was 56.9 g.

Analytical Data

The four reduced samples and the control sample were analyzed using the procedure of the United States Pharmacopoeia for menthol and menthyl acetate. The menthone was determined by a method described previously by Baldinger (6), in which hydroxylamine hydrochloride was used as the reagent in a volumetric procedure.

The infra-red spectrum of the control sample exhibited characteristic absorption frequencies for a carbonyl (5.88μ), and a hydroxyl (2.9μ) function. After reduction, the spectra of the samples showed the disappearance of the carbonyl absorption and an increase in intensity of the hydroxyl absorption. These observations are consistent with the analytical data of the samples.

TABLE 1. Analytical Data for Reduced Samples and the Control Sample of Peppermint Oil.

	Control Sample	Sample 1	Sample 2	Sample 3	Sample 4
Optical Rotation @ 25° C.	—24.3°	—22.9°	—22.9°	—22.5°	—23.0°
Refractive Index @ 26° C.	1.4584	1.4630	1.4631	1.4635	1.4635
Menthyl Acetate	7.06%	1.02%	0.95%	1.17%	1.02%
Menthol	50.45%	79.05%	81.60%	81.56%	81.38%
Menthone	28.84%	2.44%	2.25%	2.66%	3.42%

Conclusion

Reduction of oil of peppermint with lithium aluminum hydride shows a marked effect upon the menthone and menthyl acetate contents. A color change which occurred in each of the samples except No. 1 is a possible factor against treatment of the oil for commercial uses.

Literature Cited

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