

Some Low Boiling Constituents of Peppermint Oil

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Isobutyraldehyde and *trans*-2-hexenal (leaf aldehyde) have been identified among the low boiling constituents of peppermint oil.

THE IDENTIFICATION of trace low-boiling constituents of peppermint oil has been studied using a forerun fraction normally discarded in the commercial rectification of peppermint oil.¹ It is necessary to remove this small forerun to improve the taste and odor of the finished oil and to comply with the U.S.P. requirement that the dimethyl sulfide be removed. This forerun represents approximately one-tenth of 1% of the throughput of peppermint oil in the distillery and the oil originates from peppermint grown in the states of Washington and Oregon. This forerun is known to contain dimethyl sulfide, a complex mixture of aliphatic aldehydes and alcohols and monoterpene hydrocarbons.

In this study, isobutyraldehyde has been identified in the fraction which distilled at 60–64°, and *trans*-2-hexenal (leaf aldehyde), a common constituent of volatile oils derived from green leaf sources, was identified in the fraction which distilled at 138–142°. Polarimetric data has indicated the presence of (+)- α -methylbutyraldehyde in the fraction which distilled at 91°.

The presence of isovaleraldehyde, previously reported as a constituent of peppermint oil (1), has been confirmed in the fraction collected at 91°. From the optical rotation of this fraction, +3.7° in a 1-dm. tube, one might conclude that it contains about 80% isovaleraldehyde and 20% (+)- α -methylbutyraldehyde.²

Thus, the ratio of these two isomers appears to be similar to the corresponding isoamyl alcohol: active-amyl alcohol ratio in fusel oil. Ehrlich (2) has reported that samples of commercial valeraldehyde

made by oxidation of fusel oil showed rotations of +2.82° and +3.37°, measured in 1-dm. tubes.

EXPERIMENTAL

The peppermint oil forerun was first fractionated by distillation through a column 20 mm. in inside diameter and 20 ft. high, packed with single turn glass helices, 1/8 in. in diameter.

The fraction which boiled at 60–64°, n_D^{25} 1.3775, was identified as isobutyraldehyde by conversion to its 2,4-dinitrophenylhydrazone derivative, m.p. 183–184°, no depression upon admixture with an authentic specimen.

The fraction which distilled at a constant 91°, n_D^{25} 1.3930, α_D + 3.7°, was shown to contain the previously recorded (1) isovaleraldehyde by conversion to its 2,4-dinitrophenylhydrazone derivative, m.p. 120–121°, no depression upon admixture with an authentic specimen.

The fraction which boiled at 138–142° was shown to contain *trans*-2-hexenal by the preparation of three crystalline derivatives.

The 2,4-dinitrophenylhydrazone derivative, red needles, melted at 146–147°.

Anal.—Calcd. for $C_{12}H_{14}N_4O_4$: C, 51.79; H, 5.07; N, 20.14. Found: C, 51.66; H, 4.80; N, 20.38. This derivative of 2-hexenal is reported to melt at 144° (3), 145 to 145.4° (4), and 147° (5).

The semicarbazone derivative melted at 175°. This derivative of 2-hexenal is reported to melt at 173° (3, 5), 175–176° (6), and 176.4 to 177.2° (4).

The acid (obtained by alkaline silver oxide oxidation of the aldehyde) melted at 32 to 32.5°, after recrystallization from petroleum ether and from dilute alcohol.

Anal.—Calcd. for $C_8H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 63.23; H, 8.84. The melting point of 2-hexenoic acid has been reported as 32° (7), 32–33° (6), and 33° (8).

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² Attempts to separate this fraction into two components by fractional distillation were not successful. The work reported herein was done in 1956–1959, before preparative gas chromatography was generally available. This technique would likely be a valuable method today for the separation of such valeraldehyde isomers in sufficient quantities for further investigation.

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