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METHYLTHIOMETHYL 2-METHYLBUTANETHIOLATE IN ESSENTIAL OIL OF HOP

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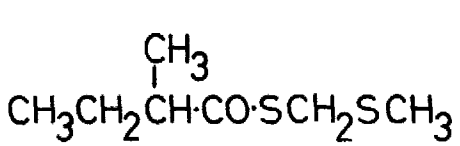
Summary: Methylthiomethyl 2-methylbutanethiolate, a new flavour-potent thioester, has been identified in the essential oil of hops.

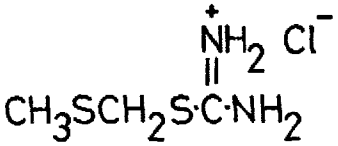
The essential oil of hops is an extremely complex mixture in which over 200 compounds have been identified.[1] These include about two dozen sulphur compounds which are generally dominated by a group of methyl thiolesters.[2] We now report the identification of a thioester (1) formally derived from 2-methylbutanoic acid and methylthiomethanethiol.

In chemical tests,[3] (1) behaved both as a sulphide and a thioester; thus it was quantitatively removed from hop oil by shaking either with aqueous hydrogen peroxide or hydroxylamine. GC-MS studies on (1) were carried out on a fraction (prep. GC on 10% Carbowax 20M) of hop oil distilled from a batch of 1978 Wye Northdown hops. The molecular formula of (1), $C_7H_{14}OS_2$, was obtained by HR mass measurement of the molecular ion (M^+ 178.0481). Fragments with m/e 57 (100%), 85, and 41 in the mass spectrum suggested the presence of a branched pentanethiolate moiety[4] and the only other ion of significant abundance m/e 61 was consistent with a $CH_3SCH_2\cdot$ group in (1).

The identity of the new thioester with (1) was confirmed by synthesis. Reaction of the isothiuronium salt (2)[5] (5 mmol) with 5N NaOH at room temperature afforded methylthiomethanethiol[6] which was treated with 2-methylbutanoyl chloride (5 mmol) and pyridine (5 mmol) at 0°C. After work-up by ether extraction, methylthiomethyl 2-butanethiolate (1) was isolated by prep. GC as a colourless oil,[7] ν_{max} (film) 1700 cm^{-1} (C=O); δ (CCl_4, 60MHz) 0.91 (3H, t, J = 7Hz, $C\underline{H}_3CH_2$), 1.16 (3H, d, J = 7Hz, $C\underline{H}_3CH$), 1.52 (2H, m, $CH_3C\underline{H}_2$), 2.10 (3H, s, CH_3S), 2.55 (1H, m, CH), 3.93 (2H, s, SCH_2S); m/e (%) 178 (M^+, 44), 85 (36), 61 (29), 57 (100), 41 (17). The synthetic material had identical GC[8] and GC-MS characteristics to the natural product. Further studies suggest that 2-methylbutanethiolate may be accompanied by a smaller amount of the 3-methylbutanethiolate as is the case in the S-methyl thioester series.[2(c)] Thioester (1) possesses an intense cabbagy, oniony aroma and its presence in some hop growths may be detrimental to hop flavour in beer.



(1)



(2)

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7. Satisfactory elemental analyses have been obtained for this compound.

8. Polar (Carbowax 20M) and non-polar (SE 30) columns.

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