Isolation and X-Ray Crystal Structure of Mintsulphide, a Novel Sulphur-containing Sesquiterpene

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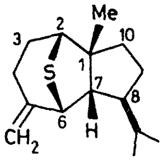
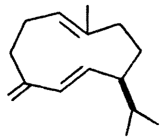
Summary A sulphur-containing sesquiterpene, mintsulphide, was isolated from peppermint oil and its structure was determined by X-ray crystallographic analysis.

PEPPERMINT OIL has attracted much attention from natural product chemists, and many of its chemical components have been characterised. It has thus been demonstrated that the oil is a rich source of mono- and sesqui-terpenoids.[1] However, all the chemical components of the oil have not yet been completely identified, particularly those with higher b.p.s.



(1)



(2)

As part of our research on natural perfumery compounds, we have undertaken a detailed investigation of minor components of the oil and have now characterized a novel sulphur-containing sesquiterpene, which we have named mintsulphide (**1**). The volatile part of the oil {d_{25}^{25} 0·9010, $[\alpha]_D$ −25·50° and n_D^{20} 1·4605} of *Mentha piperita* L. (2·5 kg) was removed and the residue (80 g) (b.p. > 100 °C at 8 mmHg) was separated by repeated SiO_2 column chromatography followed by preparative g.l.c. (FFAP 10% on Celite 545 (80—100 mesh) resulting in the isolation of white needles of compound (**1**) (300 mg) {m.p. 59—61 °C (from MeOH) $[\alpha]_D^{25}$ −61·1° (n-hexane)}.

The mintsulphide (**1**), $C_{15}H_{24}S$, M^+ 236·1584 (calc. 236·1598), showed no hydroxy or carbonyl i.r. absorption; its complete structure and stereochemistry were elucidated by an X-ray crystallographic study. *Crystal data*: monoclinic, space group $P2_1$, $a = 10{\cdot}554(2)$, $b = 6{\cdot}443(1)$, $c = 10{\cdot}236(2)$ Å, $\beta = 90{\cdot}55(6)^\circ$, $Z = 2$. 1377 independent reflections with $2\theta < 140^\circ$ (Cu-K_α radiation) were collected and least-squares refinement gave a final R value of 0·078.†

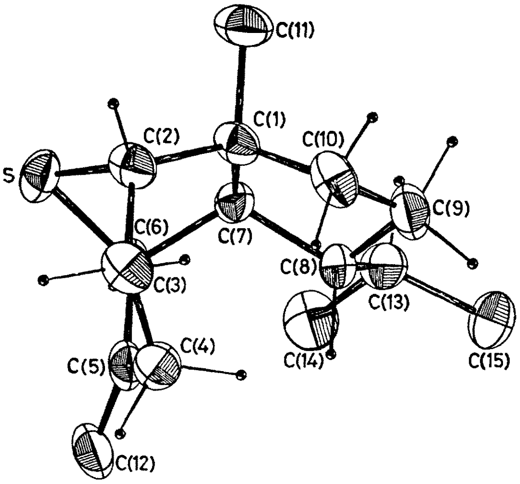


FIGURE. A perspective view of the enantiomer of the mintsulphide molecule (**1**).

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as a supplementary publication no. Sup. 22597 (6 pp.) from the British Library, Lending Division. For details of obtaining this material, see Notice to Authors No. 7, *J.C.S. Dalton* or *Perkin I* and *II*, 1979, Index Issues.

The following spectral evidence supports the assigned structure of (**1**): ^{1}H n.m.r. spectrum ($CDCl_3$) δ 0·85 and 0·90 (d, d, 6 and 4 Hz, -CH*Me*$_2$), 1·35 (s, 1 -Me), 2·86 (t, 3 Hz, 2-H), 3·68 (d, 6 Hz, 6-H), and 4·6 (m, C=C*H*$_2$); ^{13}C n.m.r. spectrum ($CDCl_3$) δ 57·82 (s, C-1), 55·62 (d, C-2), 66·73 (d, C-6), 54·02 (d, C-7), 47·66 (d, C-8), 34·50 (d), 21·47 and 21·42 (q, q, *C*H*Me*$_2$), 32·38 (q, C-1-*Me*), 146·89 and 107·96 (s, t, *C*=*C*H$_2$) and 31·53, 27·78, 32·48, and 36·69 (each t, C-3, C-4, C-9, and C-10) p.p.m.

The absolute configuration was confirmed by the photochemical conversion of (−)-germacrene D (**2**)[2] in the presence of sulphur into the mintsulphide (**1**). This suggests that (**1**) may be biogenetically related to (**2**).‡ It is thus shown that the mintsulphide is (1*R*)-*cis*-2,6-epithio-*cis*-8-isopropyl-1-methyl-5-methylene-*cis*-bicyclo-[5.3.0]decane.

(*Received*, 9*th January* 1979; *Com.* 023.)

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‡ Our preliminary survey indicated that (**1**) was also present in other plants which are known to metabolize (**2**).

[1] B. M. Lawrence, J. W. Hogg, and S. J. Terhune, *Flavour Ind.*, 1972, 467 and references cited therein.
[2] M. Niwa, M. Iguchi, and S. Yamamura, *Tetrahedron Letters*, 1978, 4043 and references cited therein.