Tetrahedron Letters No. 14, pp 1253 - 1254, 1974. Pergamon Press. Printed in Great Britain.

S-PRENYL THIOISOBUTYRATE FROM SOME AGATHOSMA OILS

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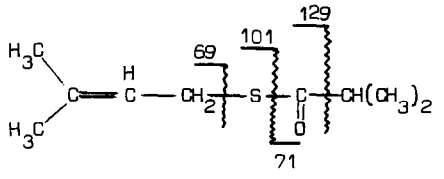
(Received in UK 29 January 1974; accepted for publication 20 February 1974)

Several years ago we reported that the essential oils of A. apiculata[1] and of A. puberula (Rutaceae)[2,3] contained considerable amounts of sulphur, 8-11% in the former and 2.5% in the latter. Distillation of the oil of A. apiculata afforded a fraction (b.p. 100-101°/17 mm) rich in sulphur which was considered to be a mixture of butyl 1-pentenyl disulphide and an unsaturated ester, $C_{10}H_{16}O_2$. The oil of A. puberula gave a similar boiling fraction which was thought to be a mixture of 2-pentenyl tetrasulphide and linalyl isobutyrate.

We have recently examined a few Agathosma oils by g.l.c. on both Apiezon and FFAP columns; it was clear that a single compound was responsible for most of the sulphur in both of the above oils as well as for that in A. clavisepela (4.0% S).[4] A fraction, b.p. 100°/15 mm, obtained by repeated distillation of A. apiculata oil through a 1 m spinning band column, was shown to be gas-chromatographically homogeneous. The mass spectrum showed that it was S-prenyl thioisobutyrate (observed m/e 172.090 (60%), calculated for $C_9H_{16}SO$ 172.092). As expected the base peak at m/e 69 (it overlapped with the internal standard and could not be accurately determined) is due to the 3,3-dimethylallyl ion. Accurate measurements agreed with the proposed fragmentations: found m/e 129.038 (5%), C_6H_9SO requires 129.037; found m/e 101.041 (9%), C_5H_9S requires 101.042; found m/e 71.046 (50%), C_4H_7C requires 71.050.



The above fraction showed ν_{max} 1680 cm^{-1}, and λ_{max} 234 (ε 5300) and 206 nm (ε 6800). The 100 MHz NMR spectrum in deuterochloroform agreed with the proposed structure: δ 1.18, d (J 7 Hz), 6H, $-CH(CH_3)_2$; δ 1.70, broad s, 6H, $=C(CH_3)_2$; δ 2.71, septet, 1H, (J 7 Hz), 1H, $-CH(CH_3)_2$; δ 3.50, d (J 8 Hz), 2H, $-CH_2-$; δ 5.20, triplet of quintets, (J 1 Hz and 8 Hz) 1H, $-CH=$. The structure was confirmed by synthesis of the thioester from 3-methylbut-2-enthiol[5] and isobutyroyl chloride in the presence of pyridine.

Fractions of identical b.p. to the above were obtained by distillation of oils from A. puberula and A. clavisepela; from their IR and NMR spectra these were also S-prenyl

thioisobutyrate. Burrell et al.[6] have recently characterized five thiol esters in galbanum oil which are closely related to this ester.

Although 3-methylbut-2-enthiol has been found in nature,[7,8] naturally occurring derivatives have not been reported previously. Such an omission is surprising in view of the central role played by energy-rich prenyl compounds in biosynthesis; this report suggests that S-prenyl thioesters may be more abundant (c.f. ref. 9).

Commercial buchu oil (from A. betulina) contains about 0.7% sulphur and two groups[10,11] have recently shown that this is present as a mixture of two stereoisomeric p-menthane-8-thiol-3-ones.

I am grateful to Dr. K. G. R. Pachler of the National Chemical Research Laboratory, Pretoria, for the NMR spectra, Dr. E. E. Bartel of the University of Stellenbosch for the mass spectra, and the Council for Scientific and Industrial Research for a grant.

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