Tetrahedron Letters No. 30, pp. 2837-2838, 1971. Pergamon Press. Printed in Great Britain.

CHARACTERISATION OF THIOL ESTERS IN GALBANUM OIL

J.W.K.Burrell, R.A.Lucas, D.M.Michalkiewicz and G.Riezebos

Proprietary Perfumes Limited, Ashford, Kent.

(Received in UK 14 June 1971; accepted in UK for publication 24 June 1971)

In previous publications (1) from this laboratory, the isolation and identification of pyrazine derivatives present in the essential oil of Galbanum has been reported. A further investigation into the composition of the distillation fractions which contribute most to the characteristic odour of the oil, has led to the identification of S-iso-propyl 3-methylbutanethioate, S-sec-butyl 3-methylbutanethioate, S-sec-butyl 2-methylbutanethioate, S-iso-propyl 3-methylbut-2-enethioate and S-sec-butyl 3-methylbut-2-enethioate. The occurrence in nature of any of these compounds has not been previously reported.

A coupled g.l.c./m.s. analysis of a fraction of the oil (b.p.74°/10mm) (A.E.I. MS 902, 70 e.v.) showed the presence of a compound of molecular weight 160. The presence of sulphur in this compound was indicated by the isotope pattern of the molecular ion and certain of the fragment ions. The comparison of this spectrum m/e (abundance) 57 (100), 85 (97), 43 (50), 41 (47), 160 (16), 117 (4) with published spectra of thioesters (2), together with the high resolution mass spectrum of this component (observed 160.09224 $C_8H_{16}SO$ calculated 160.09218, observed 117.03694 C_5H_9SO calculated 117.03740, observed 85.06507 C_5H_9O calculated 85.06533) suggested that this constituent was S-iso-propyl 3-methylbutanethioate. This structure was confirmed by the synthesis of the ester from the corresponding mercaptan by one of the methods described by Wenzel and Reid (3).

Similarly from other fractions (b.p. 74°/10mm - 82°/3mm) four other materials were characterised on the basis of their spectra namely: S-sec-butyl 3-methylbutanethioate (2) m.s. 57 (100), 85 (96), 41 (58), 43 (23), 119 (10), 174 (8); S-sec-butyl 2-methylbutanethioate m.s. 57 (100), 85 (34), 174 (7), 56 (6), 119 (4); S-iso-propyl 3-methylbut-2-enethioate m.s. 83 (100), 55 (44), 41 (16), 43 (13), 115 (5), 158 (1), i.r. (4) 1675 cm^{-1} (s) -C=O str., 1635 cm^{-1} (s) -C=C- str. conjugated to carbonyl, 1015 cm^{-1} (s) $-\overset{|}{C}-S-$ str., 1090 cm^{-1} (m) $-C-\overset{||}{C}-$ str., 810 and 850 cm^{-1} (s) $-C=\overset{|}{C}-$ def.; S-sec-butyl 3-methylbut-2-enethioate m.s. 83 (100), 55 (24), 41 (7), 115 (3), 172 (1), i.r. 1670 cm^{-1} (s) -C=O str., 1630 cm^{-1} (s) -C=C- str. conjugated

to carbonyl, 1010 cm^{-1} (s) $-\overset{\|}{C}-S-$ str., 1090 cm^{-1} (m) $-C-\overset{\|}{C}-$ str., 805 and 850 cm^{-1} (s) $-C=\dot{C}-$ def.

Final proof of the structures was obtained by the synthesis of authentic samples of these materials.

Naves (5) has previously reported the isolation of isobutyl and cis and trans propenyl disulphides from fractions of Galbanum oil similar to the ones we investigated. In our hands, disulphides could only be detected after the fractions had been chromatographed on alumina or under adverse gas chromatographic conditions which suggests that these sulphides might be artefacts and not genuine constituents of the oil.

Acknowledgement

The authors wish to thank Dr. J.C. Belsten for assistance in the preparation of the materials.

References

1. A.F. Bramwell, J.W.K. Burrell and G. Riezebos, Tetrahedron Letters, 1969, No. 37, 3215 - 3216.
J.W.K. Burrell, R.A. Lucas, D.M. Michalkiewicz and G. Riezebos, Chem. and Ind., 1970, 1409.
2. W.H. McFadden, R.M. Seifert and Jan Wasserman, Anal. Chem., 1965, 37, 560 - 566.
3. F.W. Wenzel Jr., E. Emmet Reid, J.A.C.S., 1937, 59, 1089 - 1090.
4. R.A. Nyquist and W.J. Potts, Spectrochimica Acta., 1959, 7, 514 - 538.
5. Y.R. Naves, Parf. Cosm. Sav., 1969, 12, (12), 586 - 589.