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CHARACTERISATION OF PYRAZINES IN GALBANUM OIL

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Recent investigations of the composition of the essential oil of Galbanum have led to the isolation and identification of the geometrical isomers of 1,3,5-undecatriene (1,2,3), one of which, according to Teisseire (3), possesses an odour characteristic of the oil. During our own studies, we have isolated from a distillation fraction possessing the characteristic odour of the oil, the afore mentioned trienes and a novel constituent, 2-methoxy-3-sec-butylpyrazine, which possesses an intense odour. Its structure was suggested by spectroscopic techniques and confirmed by synthesis. In a recent publication (4) by Buttery and co-workers the characterisation of an isomeric compound, 2-methoxy-3-isobutylpyrazine, isolated from green bell pepper oil has been described, which prompts us to report our own findings with respect to Galbanum oil.

Distillation of the oil afforded a fraction b.p. 78-83°/10 mm. from which the unknown compound was obtained in a pure state, by means of preparative scale g.l.c. Its mass spectrum (A.E.I. MS 902, 70 e.v.) above mass 40 showed the following characteristics (intensities in parentheses with base peak taken as 100); molecular ion 166 (5), major ions 151 (50), 138 (100), 137 (35), 124 (68), 123 (10), 105 (12), 41 (8). At high resolution the mass of the molecular ion was found to be 166·11024 which is consistent with the molecular formula $C_9H_{14}N_2O$. The infrared absorption spectrum showed maxima at 1544, 1464, 1449, 1396, 1356, 1171, 1014 and 844 $cm.^{-1}$ The 60MHz proton n.m.r. spectrum (CCl_4 solvent) indicated the presence of a sec-butyl group; δ 0.82 (triplet, J = 7Hz, 3H) 1.19 (doublet, J = 7Hz, 3H) ca. 1.3-2.1 (complex multiplet, 2H) 3.13 (sextet, J = 7Hz, 1H); a methoxyl group δ 3.94 (3H) and two aromatic ring protons forming an AB system at δ 7.83 and 7.99 (J = 2.75Hz).

The spectroscopic data suggested the unknown compound to be a disubstituted pyrazine, the substituents being methoxy and sec-butyl at the 2- and 3- positions (5). This conclusion was corroborated by the synthesis of the compound as follows: 2-methoxy-3-methylpyrazine was prepared from commercially available (6) 2-chloro-3-methylpyrazine by reaction

with sodium methoxide, followed by careful fractionation to remove the 2,6-isomer (7). In practice 2-methoxy-3-methylpyrazine was obtained in 95 % purity (n.m.r.). Successive alkylations (8) at the α carbon atom with methyl iodide and ethyl bromide, in each case via the sodium derivative of the pyrazine in liquid ammonia, gave 2-methoxy-3-sec-butylpyrazine. A pure (by g.l.c.) sample, obtained by preparative scale g.l.c., had i.r., n.m.r. and mass spectra identical with those of the unknown compound isolated from Galbanum oil. No impurity signals could be observed in the n.m.r. spectra of both the natural and synthetic materials.

The concentration of 2-methoxy-3-sec-butylpyrazine in Galbanum oil is estimated to be less than 0.05 % from the gas-liquid chromatogram of the oil. On the evidence of g.l.c.-mass spectrometry, other pyrazines are also present, and one of these has been tentatively identified as 2-methoxy-3-isobutylpyrazine, on the basis of the mass spectral details reported (4) for this compound. Further work is in progress to confirm this assignment and to characterise other pyrazines in Galbanum oil.

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