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2-PROPYLTHIETANE, THE MAJOR MALODOROUS SUBSTANCE FROM THE ANAL GLAND OF THE STOAT (MUSTELA ERMINEA)

D.R. Crump
Chemistry Division, D.S.I.R., Private Bag, Petone, New Zealand.

Recently several sulphur containing constituents of mammalian scent materials have been identified including 5-thiomethylpentane-2,3-dione from the striped hyena[1], 3-methyl-1-thiomethylbut-3-ene and 2-phenyl-1-thiomethylethane from the red fox[2], and 2,2-dimethylthietane, 3,3-dimethyl-1,2-dithiolane, and di-(3-methylbutyl) disulphide from the mink[3]. We now report the structure of the major malodorous component from the anal gland secretion of the male stoat (Mustela erminea L.).

Gas chromatographic analysis of a diethyl ether extract of the viscous yellow fluid obtained from the anal glands of male stoats[4] revealed four volatile components. G.C.-M.S.[5] showed the major (50%) and most volatile of these to have the composition $C_6H_{12}S$ (m/e 116,101,87,82,74,73,69,67). The presence of one sulphur atom was confirmed by the characteristic relative intensities of the M+1 and M+2 peaks in the spectrum. The component of molecular weight 116, which was separated by preparative g.c.(0.2mg), exhibited the p.m.r. spectrum shown in the figure[6].

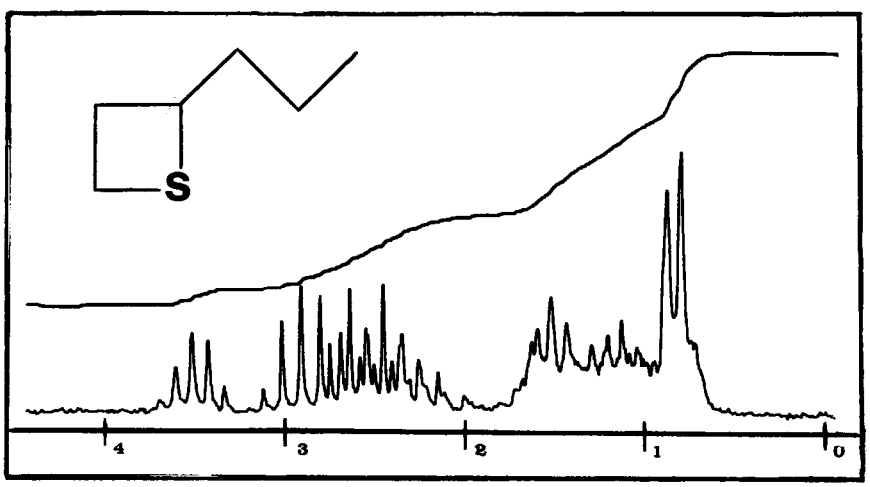

Figure. P.M.R. Spectrum of 2-propylthietane

This spectrum is consistent with that of a substituted thietane containing a tertiary hydrogen adjacent to the sulphur atom (δ3.5) and four other hydrogens on the ring (δ2-3). The mass spectral fragmentation (loss of methyl, ethyl, propenyl) and the lack of defined structure in the methylene region (δ0.5-2) of the p.m.r. spectrum implied a n-propyl chain. These data lead to the conclusion that this compound is 2-propylthietane(1).

Synthesis of (1) was achieved by desulphurisation[7] of 3-propyl-1,2-dithiolane(2) with tris(diethylamino) phosphine. The dithiolane(2) was prepared from 1,3-dibromo-hexane by treatment with the disulphide anion in DMF[8]. The mass spectrum, retention times, and p.m.r. spectra of synthetic (1), purified by preparative g.c., were identical with those of the natural substance.

The sulphur containing constituents of the anal gland secretion from the mink (Mustela vison) probably result from biosynthesis via an isoprenoid pathway[9]; however 2-propylthietane from the closely related stoat (Mustela erminea) does not appear to be so derived. The nature of the remaining components and those from the female stoat are under investigation.

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4. Material (ca 30mg per stoat) was removed from anal glands excised from animals that had been frozen soon after trapping. I thank Dr P.J. Moors, Wildlife Service, Department of Internal Affairs, for providing the glands.
5. An AEI MS30 combined with a Varian 2800 gas chromatograph was used for analysis. A Varian 2700 gas chromatograph was used for preparative g.c. A 5% OV101 and 10% EGSSX were used for analysis and a 0.5% OV101 column for collecting.
6. P.m.r. spectra were obtained on a Varian FT-80A instrument in benzene-d_6 with a 1.7mm tube.
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