THIETANES AND DITHIOLANES FROM THE ANAL GLAND OF THE STOAT (*Mustela erminea*)

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Abstract—2-Propylthietane (1), 2-pentylthietane (3), and 3-propyl-1, 2-dithioliolane (4) were identified as the sulfur-containing components of the male stoat anal gland secretion. Additional sulfur containing compounds identified in female stoat anal gland secretions were 2-ethylthietane (7) and 3-ethyl-1,2-dithioliolane (8).

Key Words—Stoat, ermine, *Mustela erminea*, mustelid, thietane, dithioliolane, sulfur containing compounds, anal gland secretion.

INTRODUCTION

The chemical composition of a number of sulfur-containing compounds from mammalian scent gland secretions has recently been elucidated (Wheeler et al., 1975; Jorgenson et al., 1978; Schildknecht et al., 1976). In mustelids the anal gland secretion of the mink, *Mustela vison* has been investigated by Schildknecht et al. (1976), who have identified the major sulfur-containing component as 2,2-dimethylthietane (9). Minor sulfur-containing compounds are 3,3-dimethyl-1,2-dithioliolane (10) and di-(3-methylbutyl)disulfide (11). Brinck et al. (1978) have confirmed the presence of thietane (9) as the major component of the secretion taken from living minks. Two further sulfur-containing compounds were detected, but structures could not be assigned from the available spectral data. No specific sex differences were found in the mink secretions even during the reproductive period.

In this paper the structures of the sulfur-containing compounds from the anal glands of male and female stoats, *Mustela erminea*, are reported.
The proton magnetic resonance (PMR) spectra were obtained using a Varian FT-80A instrument and a 1.7-mm tube. An AEI MS30 mass spectrometer combined with a Varian 2800 gas chromatograph and a data system was used for high-resolution GCMS analysis. A Varian 2700 gas chromatograph was used for preparative, and a Pye GCV for analytical gas chromatography. The glass columns (6 ft. x 1/4 in.) used for gas chromatography were (1) 5% OV-101 on Gas-Chrom Q 100/120, (2) 3% SE52 on Chromosorb G 60/80, and (3) 10% EGSSX on Chromosorb W AW DMCS 100/120. A Perkin Elmer 241 polarimeter was used for the optical rotation measurement.

**Collection and Separation of Volatile Compounds.** Male and female stoats, *Mustela erminea*, were caught in Fenn traps, as reported by King and Edgar (1977), by National Park Rangers in Fiordland National Park, New Zealand, and the whole animals were frozen soon after trapping. The anal glands were dissected later and were kept at -10°C until analyzed. The viscous yellow fluid (two or three drops per gland) was removed from the glands with a Pasteur pipette and was extracted with an equal volume of diethyl ether by agitation in a vortex mixer. GC of the extract on the 5% OV-101 column gave the chromatograms in Figure 1 for the male stoat and in Figure 3 for the female stoat.

Sufficient material (0.2 mg) of the major compound (1) was collected by preparative GC, using the OV-101 column, from 20 male stoats for a FTPMR spectrum and an optical rotation.

Examination of the extracts by combined gas chromatography-mass spectrometry (GCMS) on the OV-101 column afforded mass spectra of each of the components.

**Synthesis of Dithiolanes and Thietanes.** The synthetic thietanes used in this work were prepared by desulfurization of the corresponding dithiolanes with tris-diethylaminophosphine as previously described (Crump, 1978). The dithiolanes were prepared from the appropriate 1,3-dibromides by treatment with the disulfide anion in dimethyl formamide.

**RESULTS**

The gas chromatogram of the diethyl ether extract of the anal gland secretion of the male stoat is shown in Figure 1. The relative proportions of these compounds (51, 12, 8, 6, and 22%, respectively) varied little between individuals except for compound 2 which varied widely and was frequently absent. The peak labeled 5 in Figure 1 was separated into two components (5 and 6), as shown in Figure 2, by use of the SE52 column. Quantitative