Additional Sulfur Compounds from the Anal Glands of the Striped Polecat, *Ictonyx striatus* (Mustelidae, Mammalia)

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Two sulfur compounds have been identified in the anal gland secretions of captive-raised adults of the striped polecat (*Ictonyx striatus*), an African mustelid. 3-Ethyl-1,2-pentanedithiolane was observed in the secretions of an adult male and an adult female. 1,3-Pentanedithiol was observed in the male; this compound has not previously been reported from mustelid anal glands.

Introduction

The paired anal glands of skunks, ferrets, and other mustelids are known to produce volatile, sulfur-containing compounds that are thought to repel predators (e.g., Andersen and Bernstein, 1980), mark territories (Gorman, 1980), and/or signal alarm (Brinck *et al.*, 1978). A headspace analysis of the glandular exudate of a free-ranging male striped polecat (*Ictonyx striatus*), a large African mustelid, revealed 2-ethylthiacyclobutane as the major volatile component (Apps *et al.*, 1988). Nine other sulfur-containing compounds, some tentatively characterized by their mass spectra, were indicated. We report here on the identification of two additional compounds in the anal gland secretions of *I. striatus,* 3-ethyl-1,2-pentanedithiolane and 1,3-pentanedithiol.

Material and Method

Anal gland secretions were obtained from a 11.3-year-old male and a 12.5-year-old female *I. striatus,* born and raised at the National Zoological Park, Washington, D.C. Animals were fed Feline Diet (Zu-Preem Nutritional Products, Topeka, KS), mice, fish, rib bone, eggs, and fruit. Secretions were obtained by palpating the anal glands and collecting the exuded fluids in glass vials with Teflon-lined caps. A few milliliters of CH_2Cl_2 were added to the vials before they were placed on dry ice. The secretions were extracted in *n*-hexane and kept frozen (–4 °C) until analysis.

Samples were analyzed by capillary GC/MS using a 30 m × 32 mm SPB-1 column (1.0 μm coating) connected to a 5890 Hewlett-Packard gas chromatograph programmed from 50° to 300 °C at 12 °C/min. The gas chromatograph was connected to a Hewlett-Packard 5971A mass spectrometer. One drop of secretion extract was diluted in 3 ml of hexane, and 1 μl of this solution was injected onto the column. Compounds were identified by their mass spectra.

To confirm the identity of 3-ethyl-1,2-pentanedithiolane in the secretions, it was synthesized by reducing 1-chloro-3-pentanone to its corresponding alcohol with $NaBH_4$, brominating the alcohol with PBr_3, and treating this product with sulfur and Na_2S. Details of the synthesis follow. A solution of 1.4 g of $NaBH_4$ in 25 ml of cold water was added drop-wise to 15 ml of 1-chloro-3-pentanone solution in 25 ml of water, which was cooled in an ice bath. The mixture was stirred for 30 min and allowed to rise to room temperature. Thirteen ml of 2.5 N HCl were added to the mixture which was then extracted with 30 ml of diethyl ether. The ether extract was washed once with water, dried over $MgSO_4$, and concentrated on a rotary evaporator to yield 13.9 g of 1-chloro-3-pentanol, the identity of which was confirmed by IR spectroscopy.

1-Chloro-3-pentanol was placed in a flask immersed in a mixture of crushed ice and Na_2SO_4 (–7 °C). Fifteen ml of PBr_3 were added dropwise to the flask and the mixture was allowed to sit overnight at room temperature. The flask was fitted with a fractionating column and condenser and

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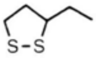
then distilled under reduced pressure by water aspiration. The distillate collected at 98–101 °C was cooled to 0 °C, washed with a 50% aqueous H_2SO_4 (0 °C), and then dried over anhydrous K_2CO_3. A total of 7.3 g of 3-bromo-1-chloropentane was collected.

In the last step, 13 ml of 3-bromo-1-chloropentane obtained in the previous step were placed into a flask with 60 ml of N,N-dimethylformamide (DMF) and the mixture was stirred. Sulfur (1.3 g) and sodium sulfide nonahydrate (9.6 g) were suspended in 40 ml of DMF and added to the reaction mixture, which was stirred at room temperature for two days. The mixture was then heated at 80–85 °C for 24 h. The hot solution was poured into a beaker filled with 100 g of ice and 50 ml of water. The mixture was extracted twice with 40 ml portions of hexane. The combined organic layer was washed with water, dried over $MgSO_4$, and concentrated on a rotary evaporator. The odorous, yellow product was transferred to a flask fitted with a distillation column. The mixture was heated and 3.5 ml of 3-ethyl-1,2-pentanedithiolane were collected at 127–130 °C.

A 1.7 ml sample of the synthesized 3-ethyl-1,2-pentanedithiolane was used to synthesize 1,3-pentanedithiol. The former compound was added dropwise to a slurry of 1.8 g of $LiAlH_4$ in 32 ml of anhydrous diethyl ether. The mixture was stirred at room temperature for 2 h, and then refluxed for 30 min. The reaction was cooled to room temperature and 3 ml of water were slowly added. Excess 10% aqueous H_2SO_4 was added to dissolve the aluminum salts. An additional 15 ml of diethyl ether were added and the two ether layers were collected. The aqueous layer was washed with two additional 15 ml portions of diethyl ether. The combined organic layers were washed with 20 ml of water, dried over anhydrous $MgSO_4$, and concentrated on a rotary evaporator. The product was characterized by GC/MS and IR spectroscopy.

Results and Discussion

GC chromatograms of the male and the female secretions indicated at least ten components each. Compound **1,** which was observed in both sexes, displayed the following *m/z* (rel. int.) values: 134(93), 119(5), 105(30), 101(13), 69(100), 64(37), 55(32), 45(69) and 41(20). These values are consistent with 3-ethyl-1,2-pentanedithiolane (Fig. 1), as confirmed by comparison with the synthetic compound. Compound **2,** which was observed only in the male, displayed the following *m/z* (rel. int.) values: 136(93), 107(3), 102(80), 87(30), 84(28), 75(48), 73(100), 69(90), 61(58), 60(98), 55(70), 47(98), and 45(90). These values are the same as those observed for synthetic 1,3-pentanedithiol (Fig. 1).



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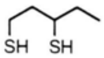

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Fig. 1. The structural formulae of (**1**) 3-ethyl-1,2-pentanedithiolane and (**2**) 1,3-pentanedithiol.

Apps *et al.* (1988) observed that an isomer of ethyldithiacyclopentane was abundant in the anal gland secretions of a free-ranging male *I. striatus,* but the structural details of this component were not resolved. We identified this compound as 3-ethyl-1,2-pentanedithiolane. Dithiolanes are known from the anal glands of several other mustelids, most notably *Mustela* spp. (Crump, 1980a, b; Buglass *et al.*, 1991; Brinck *et al.*, 1983; Schildknecht and Birkner, 1983). 3-Ethyl-1,2-pentanedithiolane, however, has previously been reported only in the stoat (*M. erminea*) (Crump, 1980a, b; Buglass *et al.*, 1991; Brinck *et al.* 1983), where it was indicated as a minor component in the females' secretions (compound **8** in: Crump, 1980a), and in the mink (*M. vison*) (Schildknecht *et al.*, 1981). 1,3-Pentanedithiol, which we observed only in our male *I. striatus*, has not previously been reported from mustelid anal glands. Further studies are needed to determine whether this compound arises from the reduction of 3-ethyl-1,2-pentanedithiolane.

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