Dimethyldithiolanes in the Anal Sac Secretion of the Weasel, Mustela nivalis

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Several dimethyl-1,2-dithiolanes are identified in the anal sac secretion of the weasel. We compare and contrast the results with previously published work.

The volatile components of the anal sac secretion of the weasel, and of other mustelids, have been the subject of several investigations in recent years. Sulphur-containing compounds are important constituents of these secretions, and their use in pest deterrence has been investigated [1]. Here we present initial results from our own studies of the anal sac secretion of the weasel, in order to reassess the status in the secretion of a family of sulphur-containing heterocyclic compounds: the dimethyl-1,2-dithiolanes. The compounds of particular concern are: 3,3-dimethyldithiolane (1), cis-3,4-dimethyldithiolane (2), trans-3,4-dimethyldithiolane (3), cis-3,5-dimethyldithiolane (4) and trans-3,5-dimethyldithiolane (5) (Fig. 1).

Some or all of these dithiolanes have been reported in the anal sac secretions of the weasel and other mustelids. Compound (1) has been identified in the mink [2–5], the polecat [5, 6], the ferret [6], and the weasel [6], and it has been claimed to be a major component of weasel secretion [5]. The 3,4- and 3,5-dimethyldithiolanes have been tentatively identified in the weasel, polecat and ferret [6]. The presence of compounds (1), (2) and (3) in the anal sac secretion of the ferret was confirmed by matching GC retention times of the independently synthesized compounds with retention times of the components of the secretion [7]. The presence of dimethyldithiolanes in the weasel, however, appears to have been inferred only by mass spectral analysis of compounds of molecular weight 134. It was clear to us during our work, and indeed it has been previously stated [8], that the mass spectra of these compounds are too similar to allow unambiguous identification. We therefore synthesized compounds (1)–(5) and co-injected them with the volatile extracts of the anal sac secretion in order to determine whether or not they are present in the secretion.

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Fig. 1. Structures of dimethyl-1,2-dithiolanes reported in the anal sac secretions in mustelids.

Compound 1 was prepared using the method of Crump [7] from 1,3-dibromo-3-methylbutane. Application of Crump’s method to the preparations of cis/trans isomers 4 and 5 failed, but a successful synthesis was achieved via the ditosylate 6 in place of the dibromide. Cis/trans isomers 2 and 3 were prepared similarly (Fig. 2). We were unable to separate the cis isomers from the trans isomers in the two synthetic mixtures of 2 plus 3 and of 4 plus 5; however, separation of the isomers was not necessary in order to investigate the presence of each isomer in the secretion. All that was required was to determine which peak in the gas chromatogram of each synthetic mixture belonged to the cis isomer and which to the trans. This was achieved with

Notes
the aid of the high resolution (400 MHz) proton NMR spectrum of each of the synthetic mixtures. From the chemical shifts and splitting patterns in each NMR spectrum, it was possible to assign peaks to both the cis and trans isomers; and the relative intensities of the NMR peaks, compared with those of the GC peaks, allowed us to identify unambiguously the cis and trans isomer peaks in the chromatograms of the two product mixtures.

GC analyses were carried out either on solutions of the whole secretion in dichloromethane ('direct injection', method a), or on dichloromethane solutions of headspace volatiles collected on an activated charcoal disc using Grob's method [9]. Headspace volatiles were collected from the secretion directly ('dry headspace', method b) or from a suspension of the secretion in saturated sodium sulphate solution ('salted-out headspace', method c) – see Table I. The resulting solutions were co-injected with each of the synthetic dimethyl-dithiolanes in turn into a Hewlett Packard gas chromatograph, equipped with a J+W DB-1 capillary column and connected to a 5970 Hewlett Packard mass spectrometer detector. Full details of the analytical method are given elsewhere [10].

Table I. Results of GC co-injection.

<table>
<thead>
<tr>
<th>Weasel</th>
<th>Sex</th>
<th>Analytical method</th>
<th>Dimethyl-dithiolanes identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>F</td>
<td>a</td>
<td>1, 2, 3</td>
</tr>
<tr>
<td>B</td>
<td>M</td>
<td>c</td>
<td>2, 3</td>
</tr>
<tr>
<td>C</td>
<td>M</td>
<td>b</td>
<td>2, 3</td>
</tr>
<tr>
<td>D</td>
<td>F</td>
<td>a</td>
<td>2, 3</td>
</tr>
<tr>
<td>E</td>
<td>M</td>
<td>a</td>
<td>1, 2, 3</td>
</tr>
</tbody>
</table>

a = 'direct injection'; b = 'dry headspace'; c = 'salted-out headspace'.

ent in all, but in lesser amounts. 3,3-Dimethyl-dithiolane (1) was found in two of the weasels at a relatively low level. Neither cis- nor trans-3,5-dimethyl-dithiolane (4) and (5) were found in any of the weasels. These results are in contrast to earlier work, which suggested that 3,3-dimethyl-dithiolane was a major component of weasel secretion [5, 6]. As these earlier identifications seemed to be by mass spectroscopy alone, we suggest that what was observed was in fact trans-3,4-dimethyl-dithiolane, the presence of which was not reported at all. Our results also conflict with the suggestion, based on mass spectral evidence alone, that 3,5-dimethyl-dithiolane is in the anal sac secretion of the weasel [6]. In fact, our GC profiles of the dimethyl-dithiolanes in the weasel are almost identical to the profile from the ferret [8].

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