Mammalian Pheromone Studies, VI*. Compounds from the Preorbital Gland of the Blue Duiker, *Cephalophus monticola*

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Forty five volatile compounds, mostly straight- and branched-chain alcohols and ketones, as well as derivatives of two of these alcohols, two γ-lactones, an aromatic thiol ester and other simple aromatic compounds, have been identified in the preorbital secretion of the blue duiker, *Cephalophus monticola*.

The blue duiker, *Cephalophus monticola*, is the most widespread of all the duiker species found in Africa. It inhabits forests all over the eastern parts of the continent, but prefers forests with relatively open undergrowth which allows visual communication as well as movement. The blue duiker is strongly territorial and males as well as females mark out their home range continuously by means of urine, dung and preorbital secretions [1]. The preorbital gland appears to be equally productive in both sexes yielding about 0.5 ml of secretion per animal when it is scooped from the opening of a normally productive gland with the rim of a small vial. Normally the secretion is an inhomogeneous mixture of a clear, colourless liquid and white mucous material which, in the female, tends to have a bluish-grey colour. The characterization of the volatile components in this secretion was undertaken as part of a comprehensive study of the relationship between the chemical composition of the preorbital gland secretions and their semiochemical function in the territorial behaviour of South African antelope species. In this communication we wish to report the identification of 45 of the volatile compounds present in the secretion of the blue duiker.

Preorbital gland secretion was collected individually from sexually mature males and females by scooping the material from the opening of the gland with Reacti-Vials (Pierce Chemical Co., Rockford, IL, USA.). The organic volatiles were extracted by vigorously shaking the collected material with 1.0 ml of dichloromethane in a mechanical flask shaker for 2 h, centrifuging the resulting emulsion for 30 min and removing the dichloromethane extract from underneath the supernatant water layer with a 1000-μl syringe. To avoid distorting the quantitative ratio of the organic volatiles present in the extract, it was used for GC analysis without further purification or evaporation of the solvent. For GC-MS analysis, however, the extract was concentrated by slow evaporation of the solvent at room temperature. The resulting total ion current trace is shown in Fig. 1.

In contrast with the preorbital gland secretion of the grysbok, *Raphicerus melanotis*, which almost exclusively contains compounds with long, unbranched structures having relatively uninformative mass spectra [2], the organic fraction of the secretion of the blue duiker contains only relatively small molecules. With the exception of 4-methoxy-2-methyl-1-butene all of these compounds could be identified, albeit tentatively in some cases, by comparison of their mass spectra with published data [3].

As is shown in Table I, the majority of the volatile organic compounds present in the secretion can be classified into four distinct compound groups, *viz.* unbranched alcohols, unbranched ketones, branched alcohols and branched ketones. Whereas many of the 2-, 3- and 4-alkanols in the first group are structurally related to the 2-, 3- and 4-alkanones in the second group, such a simple relationship does not exist between members of the third and fourth compound groups. No aldehydes related to the branched primary alcohols of the third group were thus far found in the secretion and although it contains one secondary alcohol, this alcohol is structurally not related to any of the ketones in group four. One of the major constituents in the extract is the methyl ether (689) of 3-methyl-3-buten-1-ol (739), which is also a major constituent of the secretion. Only one further derivative of one of the alcohols, prenyl alcohol (918), was found in the secretion, but this derivative, prenyl acetate (1630), is present only in a minute quantity. Finally, a number of minor aromatic constituents, including the thiol ester (3763), were identified in the secretion.

* For the preceding paper in this series see B. V. Burger, Maritha le Roux, H. S. C. Spies, Verona Truter, R. C. Bigalke, and P. A. Novellie, Z. Naturforsch. **36c**, 344 (1981).

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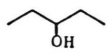
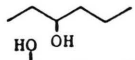
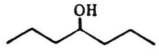
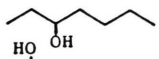
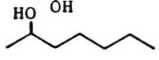
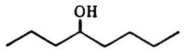
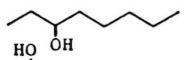
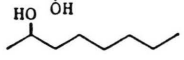
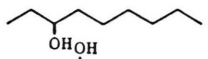
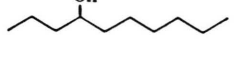
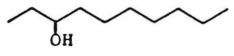
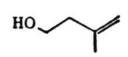
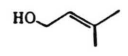
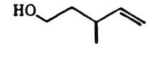
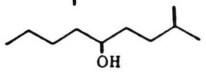
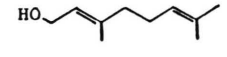
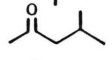
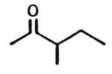
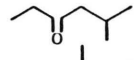
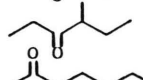
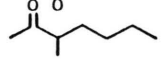
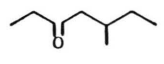
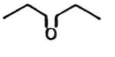
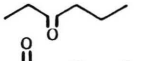
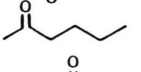
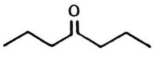
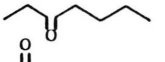
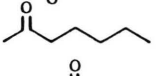
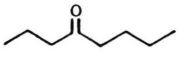
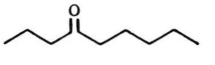
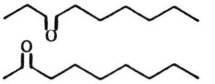
Table I. Compounds identified in the preorbital gland secretion of the blue duiker, *Cephalophus monticola*. (a) Numbering as in Fig. 1; (b) low resolution EI/MS; (c) mass spectral and retention time comparison with synthetic material.

Constituent[a]	Compound	
629		b,c
1016		b,c
1036		b,c
1490		b,c
1520		b,c
1540		b,c
2023		b,c
2062		b,c
2079		b,c
2586		b
3062		b
3098		b
739		b,c
918		b,c
1201		b
2551		b
3349		b,c
497		b,c
752		b,c
810		b,c
1190		b
1700		b
1757		b
1979		b,c

Constituent[a]	Compound	
601		b,c
944		b,c
955		b,c
1374		b,c
1441		b,c
1454		b,c
1908		b,c
2441		b,c
2510		b,c
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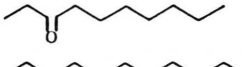
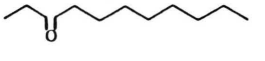
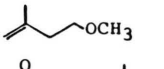
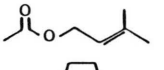
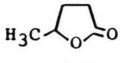
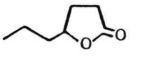
3026		b,c
3514		b
689		b,c
1630		b
848		b
1890		b
3154		b,c
2336		b,c
2656		b,c
2874		b,c
3763		b

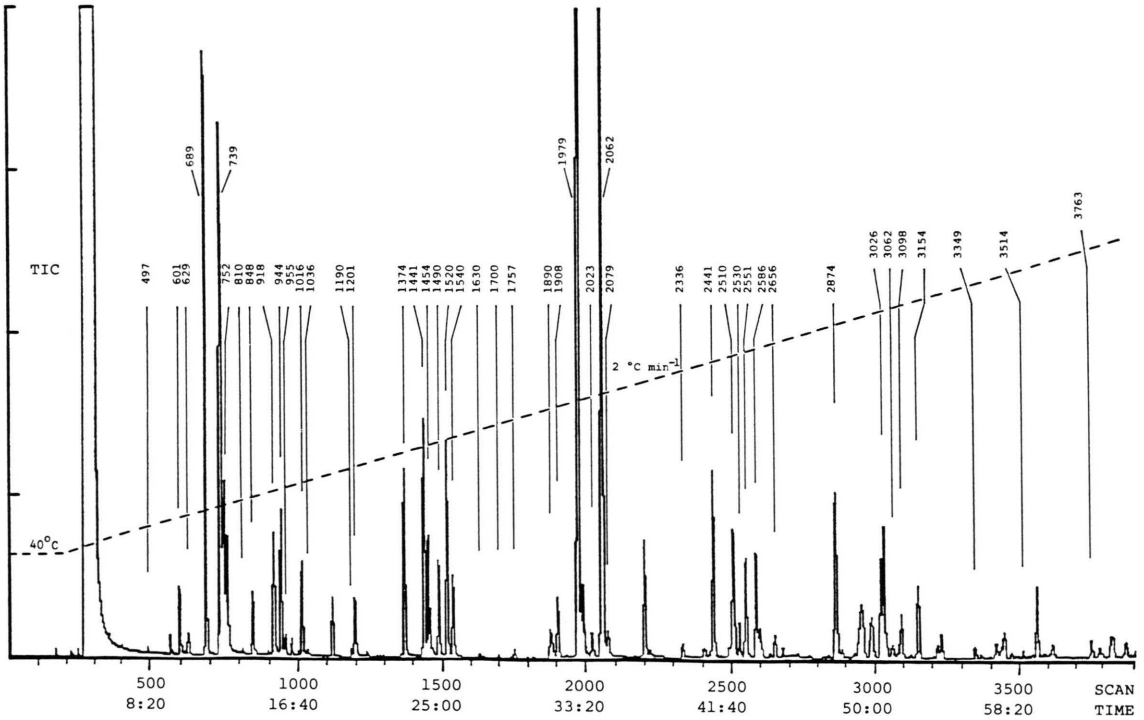


Fig. 1. Gas chromatogram (total ion detection) of a dichloromethane extract of the preorbital gland secretion of the blue duiker, *Cephalophus monticola*. Glass capillary column coated with SE-30 (40 m × 0.3 mm, film thickness 1.0 μm); 40 (3 min) – 200 °C at 2 °C/min.

Most of the proposed structures listed in Table I were verified by mass spectral and gas chromatographic retention time comparison with authentic synthetic material. As indicated in Table I, however, the identification of a few compounds was based solely on mass spectral evidence in those cases where either the mass spectra left no doubt as to the structures of the compounds, or their mass spectra, in conjunction with the spectra of other homologues present in the secretion, afforded sufficient evidence to support the proposed structure.

Further work to substantiate the identification of these compounds, and to characterize the still unidentified constituents, is being carried out.

Acknowledgements

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[1] J. Kingdon, East African Mammals – An Atlas of Evolution in Africa, Vol. 3, Part C (Bovids), pp. 281–285, Academic Press, London 1982.

[2] B. V. Burger, M. le Roux, H. S. C. Spies, V. Truter, R. C. Bigalke, and P. A. Novellie, Z. Naturforsch. **36c,** 344 (1981).

[3] E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Registry of Mass Spectral Data, John Wiley & Sons, New York 1974.