

**Mammalian Pheromone Studies, IV*.
Terpenoid Compounds and Hydroxy Esters
from the Dorsal Gland of the Springbok,
*Antidorcas marsupialis***

B. V. Burger, Maritha le Roux, H. S. C. Spies,
Verona Truter

Department of Chemistry, University of Stellenbosch,
Stellenbosch 7600, South Africa

and

R. C. Bigalke

Department of Nature Conservation, University of
Stellenbosch, South Africa

Z. Naturforsch. **36 c**, 340–343 (1981);
received November 26, 1980

Olfactory Communication, Pheromones, GC-MS-Analysis,
Terpenoids, Springene

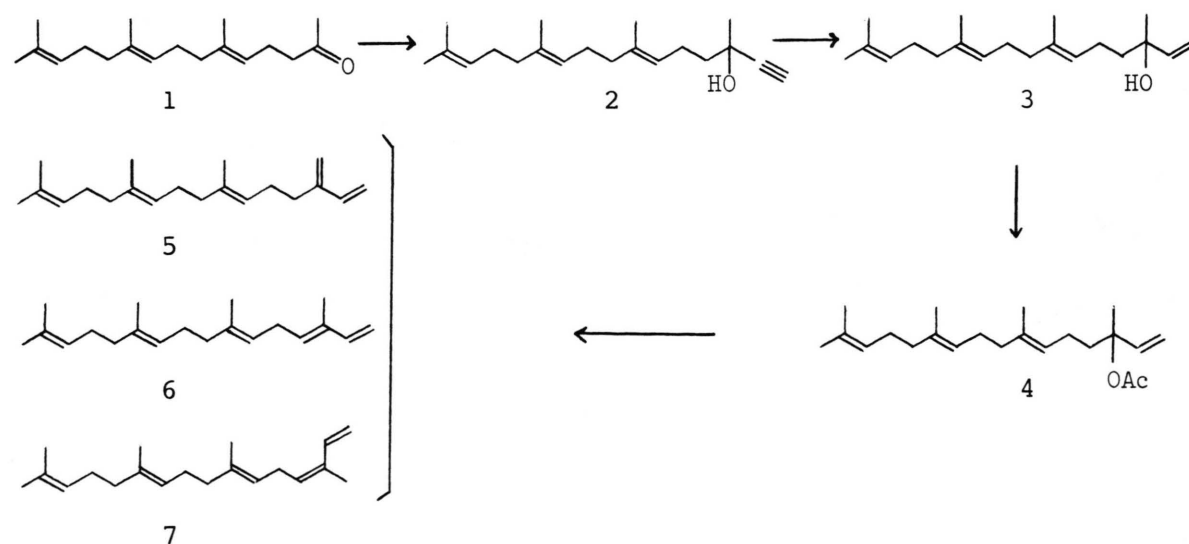
Acyclic terpenoid compounds, aldehydes, ketones, hydroxy esters, and dimethyl sulphone were identified in the dorsal exudate of the antelope *Antidorcas marsupialis*. The novel diterpenes α - and β -springene, found in this exudate, were synthesised from farnesyl acetone.

It is generally accepted that the secretions produced by specialised cutaneous glands of mammals play an important role in the social and reproductive

behaviour of mammals. The biological function of the dorsal cutaneous exudate of the antelope *Antidorcas marsupialis*, commonly known as the springbok, is still under investigation, but it is most likely employed as a conspecific alarm signal. No significant differences were found in the exudate produced by the apparently equally productive dorsal gland in male, female, and sexually immature animals. In contrast to the limited occurrence of terpenoid compounds in mammalian exocrine secretions, the dorsal exudate of the springbok contains a series of C_8 to C_{30} isoprenoid and terpenoid hydrocarbons and ketones.

The isolation and structure determination of one of these compounds, the novel diterpene (*E,E*)-7,11,15-trimethyl-3-methylenehexadeca-1,6,10,14-tetraene (β -springene) (**5**) have been reported in a previous communication [1]. We now wish to report the synthesis of β -springene and of two isomeric α -farnesene-analogous diterpenes, as well as the identification of these compounds and a number of other compounds in the dorsal exudate of the springbok.

Condensation of (*E,E*)-farnesyl acetone (**1**) with lithium acetylide ethylene diamine complex [2], selective hydrogenation of the resulting ethynyl alcohol **2** to the corresponding ethenylalcohol **3** [3] and 4-dimethylaminopyridine catalysed acetylation of **3** with acetic anhydride [4], followed by palladium acetate catalysed elimination of acetic acid [5] from **4** according to the following scheme, gave a mixture of diterpenes containing β -springene (**5**) (78%), (*E,E,E*)-3,7,11,15-tetramethylhexadeca-1,3,6,10,14-



* For the preceding paper in this series see B. V. Burger, Maritha le Roux, H. S. C. Spies, Verona Truter and R. C. Bigalke, Tetrahedron Letters **1978**, 5221.

Reprint requests to Prof. B. V. Burger.

0341-0382/81/0300-0340 \$ 01.00/0

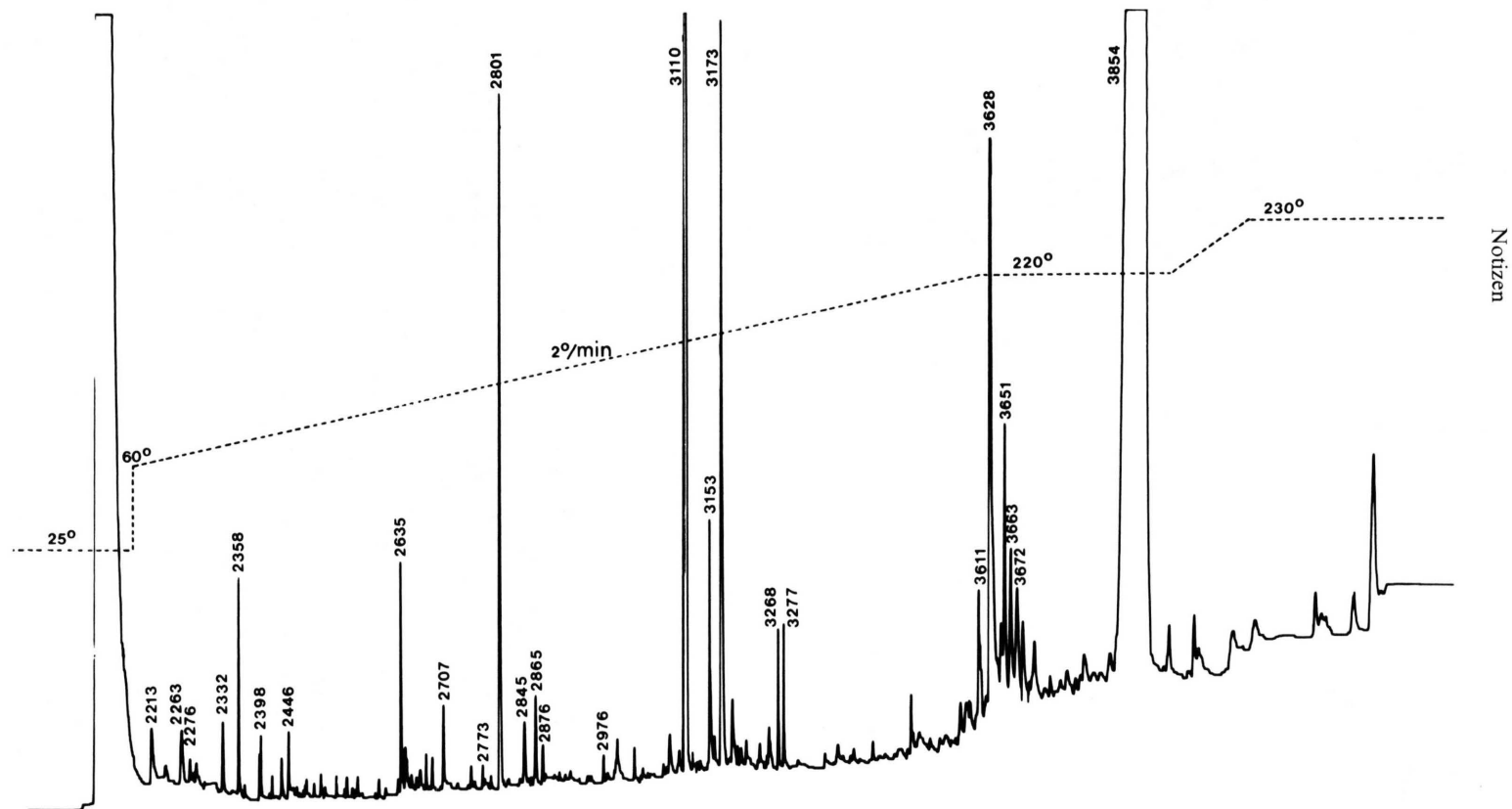
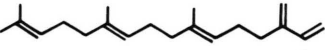
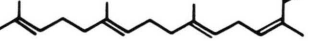
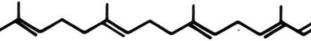
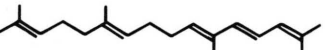
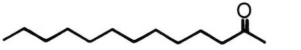
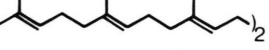
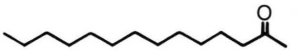
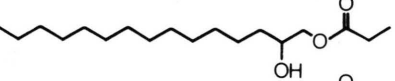
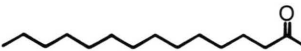
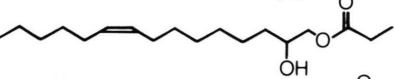
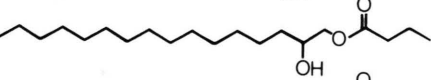
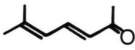
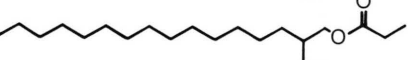
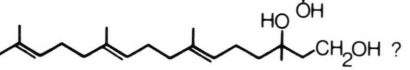
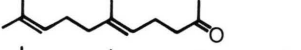
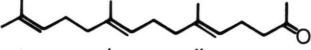
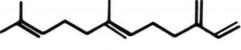
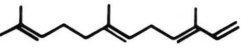


Fig. 1. Gas chromatogram (total ion current, Carbowax 20 M) of the dorsal secretion of the springbok, *Antidorcas marsupialis*.

Table I. Compounds identified in the dorsal secretion of the springbok. (a) Low resolution MS; (b) high resolution MS; (c) ^1H NMR (down to 1 μg sample size). (d) ^{13}C NMR (down to 80 μg sample size); (e) retention time comparison; (f) micro-ozonolysis.

2213		ae	3110		β -SPRINGENE	abcde
2276		ae	3153			ae
2332		ae	3173		α -SPRINGENE	abe
2398		ae	3277		?	ab
2773		ae	3854			abcd
2876		a	3628			abcde
2976		ae	3651			abcf
2845		abce	3663			ac
2263		abe	3672			a
2358		abe	3611			a
2801		abe				
3268		abe				
2635		abcde				
2707		ab				

pentaene (α -springene) (**6**) (17%) and (3Z,6E,10E)-3,7,11,15-tetramethylhexadeca-1,3,6,10,14-pentaene (**7**) (5%) in an overall yield of 70% (calculated on the farnesyl acetone), b. p. 90 °C (air bath)/ 4×10^{-5} mm. α -Springene (**6**) and β -springene (**5**) were isolated by preparative gas chromatography (3% Carbowax 20M, glass column, 14 m $\times$ 4.3 mm) for spectral (^{13}C NMR and MS) structure verification. Although the (3Z)- α -springene **7** could not be isolated due to incomplete separation from the β -isomer, its presence was established by comparison of the ^{13}C NMR spectra of the mixture, the two isolated springene isomers, and (Z)-ocimene.

As the α -springene isomers **6** and **7** are readily autoxidised, the small quantities of these two compounds present in the dorsal exudate could not be isolated in a pure state from the exudate by preparative gas chromatography. However, their presence in the exudate could be established unequivocally by gas chromatographic retention time comparison and by comparison of the mass spectra of the synthetic

α -springene isomers **6** and **7** with the spectra of components (3173) and (3153) obtained by GC-MS-analysis of the exudate (Carbowax 20M, glass capillary column, 40 m $\times$ 0.3 mm) (Figure 1).

Other compounds identified in the dorsal exudate are given in Table I, together with the respective analytical methods employed. Assignment of Z or E configuration to the double bonds in the unsaturated compounds was based on retention time comparison with authentic samples and/or on ^{13}C NMR data [6].

Preparative gas chromatographic separation of the volatile constituents in the secretion, did not yield the components (3277) and (3611) in sufficient quantities for NMR analysis. The structures proposed for these compounds are based on mass spectrometric information alone and must therefore be considered as tentative in the absence of further spectrometric corroboration.

The structure of the hydroxy ester (3628) was deduced from ^1H and ^{13}C NMR, as well as mass spectrometric data, and was confirmed by compari-

son of the isolated material with synthetic 2-hydroxypentadec-1-yl propanoate. The synthetic material was prepared by epoxidation of 1-pentadecene [7, 8] and nucleophilic ring opening of the epoxide with propanoic acid in the presence of activated aluminium oxide [9]. The resulting hydroxy ester also served as model compound in the identification of the other hydroxy esters. The position of the double bond in component (3651) was determined by micro-ozonolysis [10] and *Z* configuration was assigned

to this double bond by comparison of the olefinic resonance in the ^1H NMR spectrum of the isolated material with olefinic patterns simulated with *E* and *Z* coupling constants [11].

Acknowledgements

Support by the University of Stellenbosch and the C. S. I. R. of the research reported in this paper is gratefully acknowledged.

- [1] B. V. Burger, Maritha le Roux, H. S. C. Spies, Verona Truter, and R. C. Bigalke, *Tetrahedron Letters* **1978**, 5221.
- [2] O. F. Beumel and R. F. Harris, *J. Org. Chem.* **29**, 1872 (1964).
- [3] D. J. Cram and N. L. Allinger, *J. Amer. Chem. Soc.* **78**, 2518 (1956).
- [4] G. Höfle and W. Steglich, *Synthesis* **1972**, 619.
- [5] J. Tsuji, T. Yamakawa, M. Kaito, and T. Mandai, *Tetrahedron Letters* **1978**, 2075.
- [6] M. W. Duch and D. M. Grant, *Macromolecules* **3**, 165 (1970).
- [7] Y. Kishi, M. Aratani, H. Tanio, T. Fukuyama, and T. Goto, *Chem. Comm.* **1972**, 64.
- [8] H. Kropf and M. R. Yazdanbachs, *Tetrahedron* **30**, 3455 (1974).
- [9] G. H. Posner and D. Z. Rogers, *J. Amer. Chem. Soc.* **99**, 8208 (1977).
- [10] M. Beroza and B. A. Bierl, *Anal. Chem.* **39**, 1131 (1967).
- [11] C. W. Haigh and J. M. Williams, *J. Mol. Spectrosc.* **32**, 398 (1969).