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

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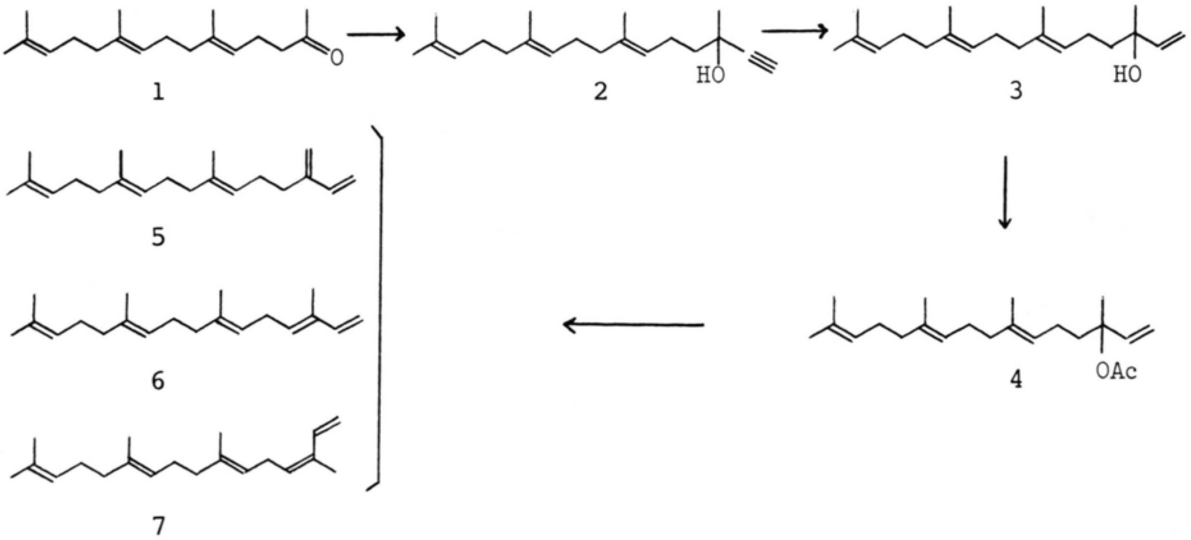
Acyclic terpenoid compounds, aldehydes, ketones, hydroxy esters, and dimethyl sulphone were identified in the dorsal exudate of the antelope *Antidorcas marsupialis.* The novel diterpenes α- and β-springene, found in this exudate, were synthesised from farnesyl acetone.

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 occurence 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-



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* 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.

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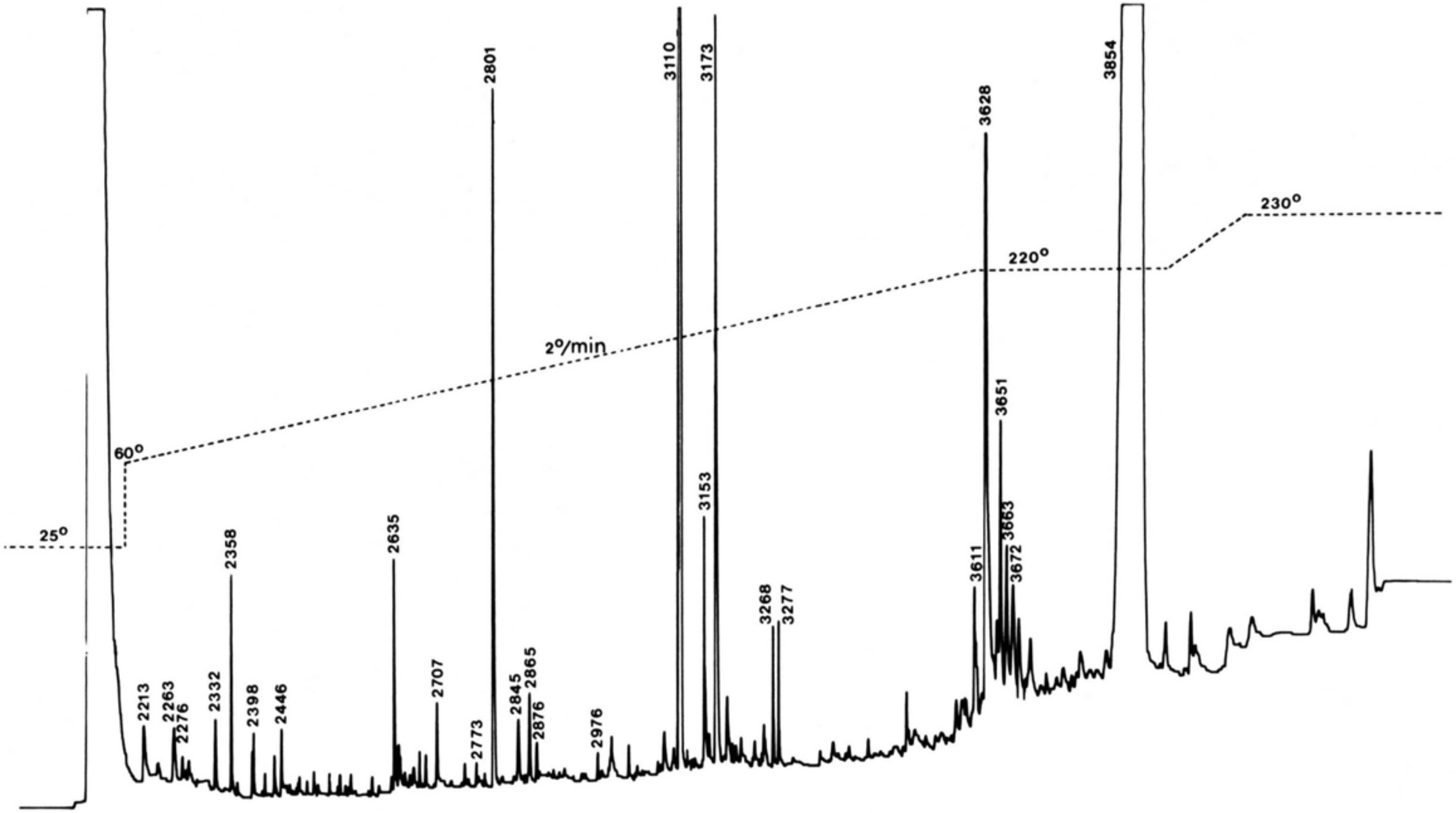

Fig. 1. Gas chromatogram (total ion current, Carbowax 20 M) of the dorsal secretion of the springbok, *Antidorcas marsupialis.*

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

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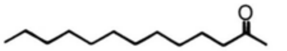
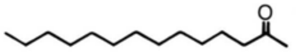
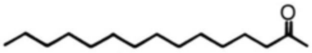
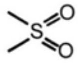
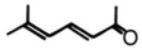
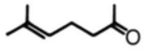
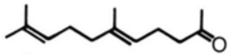
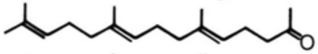
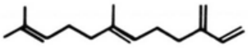
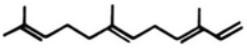
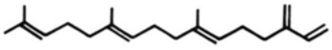
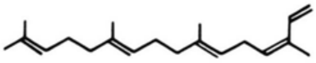
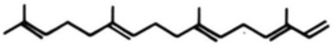
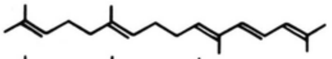
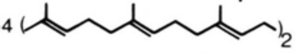
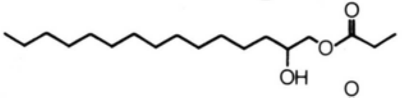
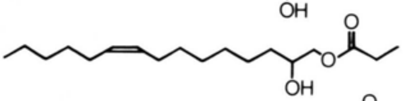
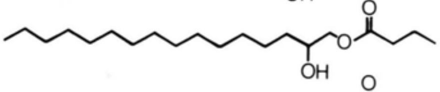
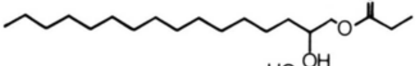
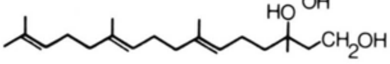
2773			ae
2876			a
2976			ae
2845			abce
2263			abe
2358			abe
2801			abe
3268			abe
2635			abcde
2707			ab
3110		ß-SPRINGENE	abcde
3153			ae
3173		α-SPRINGENE	abe
3277		?	ab
3854			abcd
3628			abcde
3651			abcf
3663			ac
3672			a
3611		?	a

pentaene (α-springene) (**6**) (17%) and (3*Z*,6*E*,10*E*)-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×4.3 mm) for spectral (^{13}C NMR and MS) structure verification. Although the (3*Z*)-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×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 ^{1}H and ^{13}C NMR, as well as mass spectrometric data, and was confirmed by comparison 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 ^{1}H NMR spectrum of the isolated material with olefinic patterns simulated with E and Z coupling constants [11].

Acknowledgements

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