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MAMMALIAN PHEROMONE STUDIES - III[1]. (E,E)-7,11,15-TRIMETHYL-3-METHYLENEHEXADECA-1,6,10,14-TETRAENE, A NEW DITERPENE ANALOGUE OF β-FARNESENE 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, South Africa
and
R.C. Bigalke
Department of Nature Conservation, University of Stellenbosch, South Africa

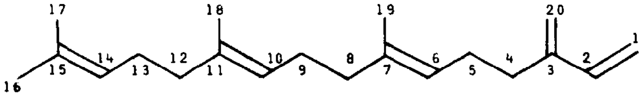
The secretions produced by the cutaneous glands of mammals are generally considered to be involved in conspecific chemical communication, acting as pheromones. From a review[2] of mammalian chemical ecology it appears that, although the known mammalian pheromones are of widely differing chemical nature, only a few terpenoid compounds have been identified in cutaneous secretions. In contrast to this apparently limited occurrence of terpenoids, we have now found the dorsal cutaneous secretion of the antelope *Antidorcas marsupialis*, which is commonly known as the springbok, to contain a series of C_8 to C_{30} isoprenoid and terpenoid hydrocarbons and ketones, such as α- and β-farnesene, geranylacetone, farnesylacetone and squalene. The isolation and identification of these, mostly known, compounds will be communicated in a forthcoming paper. In addition, however, the secretion also contains five C_{20} compounds which, from their mass spectra, appear to be isomeric analogues of α- and β-farnesene. In this communication we wish to report the isolation and structure elucidation of one of these new diterpenes, (E,E)-7,11,15-trimethyl-3-methylenehexadeca-1,6,10,14-tetraene, the major volatile constituent of the dorsal secretion, which we have named β-springene (1).[3]

Collection of the dorsal secretions of 310 trapped male and female animals[4] on clean, pre-extracted gauze, extraction of the organic material with CH_2Cl_2 (residue analysis grade) and evaporation of the solvent at a low temperature, gave a pale yellow oil (*ca*. 4.7 ml) from which the volatile constituents were isolated severally by preparative gas chromatography (Carbowax 20M, 3%, glass column). This procedure gave the major volatile constituent, β-springene (3 mg) in 98%

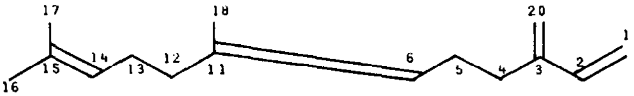
purity; $^{m}/e$ (%) 272 (M^+, $C_{20}H_{32}$, 3), 257(1), 229(1), 203(2), 201(1), 190(2), 187(3), 177(1), 175(1), 161(6), 159(3), 147(5), 137(3), 135(6), 133(14), 120(13), 119(9), 109(7), 107(12), 95(15), 93(39), 81(39), 79(16), 69(100), 67(20), 55(20), 53(8), 44(10), and 41(54).

Below $^{m}/e$ 133 the mass spectrum of this compound closely resembles that of β-farnesene and as a working hypothesis we therefore assumed β-springene to be the acyclic diterpene (1). This structure was confirmed by comparison of its ^{13}C NMR spectrum with the spectra of two model compounds, β-farnesene (2) and squalene (4), which are also present in, and were isolated from the springbok dorsal secretion. β-Farnesene (1 mg) was isolated in 98% purity; $^{m}/e$ (%) 204 (M^+, $C_{15}H_{24}$, 6), 189(2), 162(2), 161(11), 148(2), 147(3), 134(5), 133(23), 120(18), 119(9), 109(8), 107(10), 105(8), 93(55), 91(16), 81(21), 79(21), 69(100), 67(19), 55(21), 53(11), 44(15), and 41(75), in close agreement with published data.[5] By comparison of the gas chromatographic retention times and ^{13}C NMR spectral properties of the isolated material and synthetic (E)-β-farnesene,[6] E-configuration was established for this model compound. Squalene (1.5 mg) was obtained from the secretion in an absolutely pure state with spectral properties identical with published data.[5,7]

The ^{13}C NMR spectra of β-springene and the model compounds (2) and (4) were recorded at 20 MHz with proton noise decoupling using 12 μl of $CDCl_3$ as solvent in 1.7 mm micro sample tubes. Deuterium lock was provided by the solvent. Resonances were assigned by referring to published values for myrcene (3)[8] and squalene (4)[7] (Table 1).



(1)



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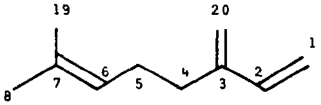

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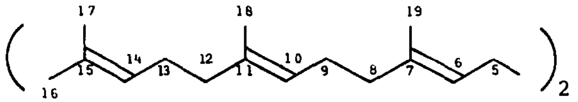

(4)

Table 1: Comparison of ^{13}C chemical shift data (δ_C in ppm from TMS) for β-springene, (E)-β-farnesene (2), myrcene (3), and squalene (4)

Carbon atom[a]	Springene[b] (± 0.05 ppm)	β-Farnesene		Myrcene published values[8]	Squalene	
		natural[b] (± 0.05 ppm)	synthetic[c] (± 0.06 ppm)		natural[b] (± 0.06 ppm)	published values[7]
1	115.63	115.68	115.62	115.5		
2	139.07	139.07	139.09	139.0		
3	146.21	146.26	146.24	145.9		
4	31.52	31.55	31.56	30.8		
5	26.69	26.73	26.78	26.1	28.25	28.40
6	124.09	124.12	124.14	124.4	124.31	124.60
7	134.93			131.0	134.78	134.60
8	39.75			25.1	39.72	39.90
9	26.69				26.67	26.90
10	124.29				124.31	124.60
11	135.41	135.46	135.38		135.01	134.80
12	39.75	39.76	39.77		39.72	39.70
13	26.82	26.80	26.78		26.77	27.00
14	124.48	124.45	124.46		124.42	124.80
15	131.21	131.28	131.23		131.08	130.60
16	25.66	25.70	25.67		25.60	25.50
17	17.67	17.71	17.67		17.60	17.50
18	16.03	16.07	16.03		15.97	15.90
19	16.03			17.1	15.97	15.90
20	113.00	113.05	112.98	112.6		

[a] Numbering of carbon atoms shown in formulae (1) - (4).

[b] $CDCl_3$ with δ_C 77.04 ppm from TMS as internal reference.

[c] 0.1 Molar $CDCl_3$ solution with TMS as internal reference. The signals of C-5 and C-13 were not separated due to the presence of *ca*. 13% of (Z)-β-farnesene in the synthetic material.

The excellent agreement of the ^{13}C shifts of C-1 to C-6 and C-20 in β-farnesene (2) and the C-7 to C-19 shifts in squalene (4) with the shifts of these carbon atoms in (1), unequivocally confirms the proposed structure (1) for β-springene. The shifts of the methyl carbon atoms C-18 and C-19 (δ *ca*. 16.0) and the methylene carbon atoms C-8 and C-12 (δ *ca*. 39.7) furthermore provide evidence that the 6,7- and 10,11-double bonds in β-springene and the two model compounds (2) and (4), which were isolated from the dorsal secretion, possess E-configuration. The ^{13}C resonance of these carbon atoms are expected at δ *ca*. 23.2 and 32.3 respectively for the corresponding Z-compounds

Subjection of a sample of farnesol to gas chromatographic separation under the conditions employed for the isolation of β-springene, did not result in the formation of any α- or β-farnesene and it is therefore unlikely that β-springene is an artefact formed from a C_{20} farnesol analogue during gas chromatographic separation.

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REFERENCES AND NOTES:

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2. E. Albone, *Chem. Br.* 13, 92 (1977).
3. The title compound may also be named for example, 6,10,14-hexadehydroneophytadiene or geranylmyrcene. However, as the springbok dorsal secretion apparently contains several analogues of α- and β-farnesene, β-springene seemed to be an appropriate name for the diterpene described in this paper. A name derived from the generic name of the animal would have been a misnomer for this compound.
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