Studies on Mammalian Pheromones, II

Further Compounds from the Pedal Gland of the Bontebok *(Damaliscus dorcas dorcas)*

B. V. Burger, Maritha le Roux, C. F. Garbers, H. S. C. Spies

Department of Chemistry, University of Stellenbosch, South Africa

R. C. Bigalke

Department of Nature Conservation, University of Stellenbosch, South Africa

K. G. R. Pachler, P. L. Wessels

N. C. R. L., C. S. I. R., Pretoria, South Africa

and

V. Christ and K. H. Maurer

Varian MAT, Bremen

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Dedicated to Prof. Dr. L. Birkofer *on His 65th Birthday*

Olfactory Communication, Pheromones, Mass Spectrometry, NMR Spectra Simulation, γ-Lactone Synthesis

The identification of four further major constituents of the pedal gland exudate of the bontebok, *Damaliscus dorcas dorcas*, *viz.* α-terpineol, 2-*n*-heptylpyridine, *m*-cresol and (Z)-6-dodecen-4-olide and the investigation of the stereochemistry of the double bond in (Z)-6-dodecen-4-olide by means of iterative computer analysis are described. An improved synthesis of this compound is outlined.

The identification of 2-heptanone, 2-nonanone, 2-undecanone, 2,5-undecanedione and (Z)-5-undecen-2-one as some of the major volatile constituents of the pedal gland exudate of the bontebok *(Damaliscus dorcas dorcas)* has been discussed in the preceding paper [1] in this series on mammalian pheromones. Further investigation also revealed the presence of compounds other than ketones, as major constituents of this glandular secretion. The present report deals with the structural characterisation of these compounds and the synthesis of one of them, an unsaturated long chain γ-lactone.

Material and Methods

A. General

The methodology adopted for the isolation of the secretion of the pedal gland of the bontebok, the gas chromatographic techniques employed for the preparative purification of the volatile fraction and some of the individual constituents, and the instrumentation with which NMR and IR spectra and gc-ms-analyses were obtained, have been described in detail in the previous report [1] in this series.

Requests for reprints should be sent to Dr. B. V. Burger, University of Stellenbosch, *Stellenbosch 7600*, South Africa.

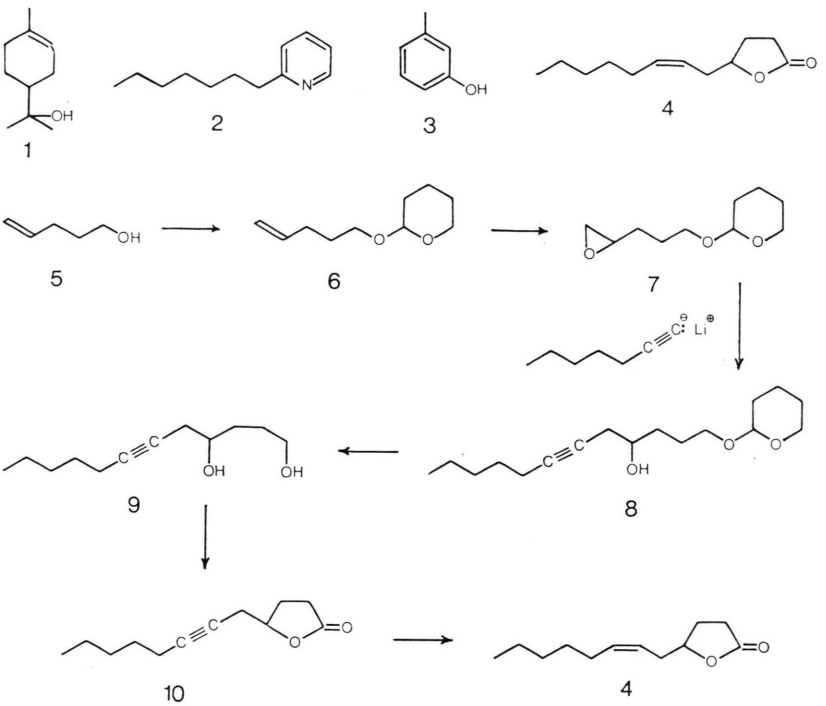
B. Synthesis of 2-n-heptylpyridine (**2**)

A mixture of 6.54 g anhydrous, oxygen-free pyridine and 90 ml of a 0.92 M solution of heptyl lithium [2] in benzene was sealed off in an argon atmosphere in a glass vial and heated at 97 °C for 5 h [3]. The resulting reaction mixture was shaken with anhydrous Na_2SO_4 and filtered through a layer of anhydrous $MgSO_4$ to remove the lithium hydride formed in the reaction. After removal of the solvent from the clear, almost colourless filtrate, the residue was distilled and the distillate ($b.p._{16}$ 128–134 °C) carefully fractionated to yield 9.7 g (66%) 2-*n*-heptylpyridine (**2**); $b.p._{3.5}$ 108 °C.

Mass spectrum (gc inlet) *m/e* 65 (4); 66 (4); 78 (4); 79 (3); 92 (6); 93 (100); 94 (8); 106 (23); 107 (5); 118 (2); 120 (16); 134 (4); 148 (3); 162 (0.8); 176 (1.2); 177 (1.2); 178 (0.3%).

$C_{12}H_{19}N$

Calcd:	C 81.28	H 10.80;
Found:	C 81.20	H 11.13.



C. Synthesis of (Z)-6-dodecen-4-olide (**4**)

The unsaturated γ-lactone **4**, which was found to be the second most abundant constituent of the volatile fraction of the pedal gland exudate, was synthesised for biological evaluation according to the given reaction scheme.

2-(Pent-4′-en-1′-yloxy)-tetrahydropyran (**6**)

To a stirred and cooled mixture of 26 g 4-penten-1-ol (**5**) and 0.5 ml conc. HCl, 30.5 g (20% excess) 2,3-dihydro-4H-pyran was added with an infusion pump at such a rate that the temperature did not exceed 15 °C. After completion of the addition the mixture was stirred for approx. 6 h, Na_2SO_4 was then added and the reaction mixture left overnight, whereupon 100 ml ether was added, followed by a mixture of $NaHCO_3$ and Na_2SO_4. The suspension was stirred for 2 h, whereafter the solid material was filtered off, the solvent evaporated and the resulting residue distilled to yield 48.7 g (94.5%) 2-(pent-4′-en-1′-yloxy)-tetrahydropyran (**6**); $b.p._{.16}$ 91 – 96 °C.

2-(4′,5′-Epoxypent-1′-yloxy)-tetrahydropyran (**7**)

To a stirred mixture of 4.9 g 2-(pent-4′-en-1′-yloxy)-tetrahydropyran (**6**) and 60 mg 4,4′-thio-bis-(6-t-butyl-3-methylphenol) [4] in approx. 60 ml alcohol-free $CHCl_3$ [5], 7.15 g *m*-chloroperbenzoic acid [6, 7] was added in small quantities in an argon atmosphere. After completion of the addition the reaction vessel was darkened with foil and the reaction mixture stirred for approx. 21 h at room temperature. The reaction was followed by TLC. The *m*-chlorobenzoic acid formed in the reaction was then filtered off and excess peracid destroyed by addition of 10% sodium sulfite until a negative starch-iodide reaction was obtained. The reaction mixture was washed successively with 5% $NaHCO_3$ solution, water and saturated NaCl solution. The organic layer was dried over Na_2SO_4 and concentrated at reduced pressure. Distillation of the residue gave 4.87 g (90.5%) 2-(4′,5′-epoxypentan-1′-yloxy)-tetrahydropyran (**7**); $b.p._{0.95}$ 69 – 71 °C.

$C_{10}H_{18}O_3$

Calcd:	C 64.49	H 9.74;
Found:	C 64.85	H 9.70.

2-(4′-Hydroxydodec-6′-yn-1′-yloxy)-tetrahydropyran (**8**)

In an argon atmosphere, 7.18 ml of a 14.35% solution of butyl lithium [8] in hexane was added dropwise to a stirred and cooled (0 °C) solution of 1.55 g 1-heptyne in 5 ml freshly distilled dioxane [9] and the mixture stirred for 30 min, whereafter 2.88 g 2-(4′,5′-epoxypentan-1′-yloxy)-tetrahydro-

pyran (**7**) in a small volume of dioxane was added during 20 min. The reaction mixture was stirred at 60 °C and the reaction followed by TLC. After completion of the reaction, ether was added, followed by solid NH_4Cl, and the resulting ether solution washed with water until neutral, dried (Na_2SO_4) and concentrated under reduced pressure at 40 °C. Distillation of the residue gave 0.58 g unreacted epoxide **7** and 3.16 g (72.3%; approx. 90% corrected for recovered starting material) 2-(4′-hydroxydodec-6′-yn-1′-yloxy)-tetrahydropyran (**8**); b.p.$_{0.02}$ 119 – 121 °C.

NMR δ (60 MHz, $CDCl_3$) 0.85 (CH_3, t); 1.1 – 1.5 (3 CH_2, m); 1.5 – 1.9 (5 CH_2, m); 2.0 – 2.5 (2 $CH_2-C\equiv C$, m); 2.32 (OH, s); 3.2 – 4.1 ($>CH-OH$, 2 CH_2-O, m); 4.6 ($O-CH-O$, br. s.); IR (film) 3440 cm^{-1} (OH).

$C_{17}H_{30}O_3$

Calcd: C 72.30 H 10.71;
Found: C 72.74 H 10.81.

1,4-Dihydroxydodec-6-yne (**9**)

Methanol was added to a stirred suspension of 2.0 g 2-(4′-hydroxydodec-6′-yn-1′-yloxy)-tetrahydropyran (**8**) in 5.5 ml 2 N HCl until it became homogeneous. The mixture was then stirred at 40 °C while the reaction was followed by TLC. After approx. 10 h the reaction mixture was added to 20 ml water and the product extracted thoroughly with ether. The combined extracts were treated with a 10% solution of $NaHCO_3$, washed with water, dried (Na_2SO_4) and concentrated under reduced pressure. The small quantity of unhydrolysed pyranyl ether (**8**) which was still present in the residue was removed by means of chromatography on a silica gel column. Distillation of the product of hydrolysis gave 1.35 g (96.5%) 1,4-dihydroxydodec-6-yne (**9**); b.p.$_{0.022}$ 108 – 110 °C (air bath).

NMR δ (60 MHz, $CDCl_3$) 0.9 (CH_3, t); 1.1 – 1.5 (3 CH_2, m); 1.5 – 1.9 ($HO-CH-CH_2-CH_2-CH_2OH$, m); 2.0 – 2.6 (2 $CH_2-C\equiv C$, m); 2.55 (2 OH, s); 3.5 – 4.0 ($>CH-OH$, $-CH_2-OH$, m); IR (film) 3350 cm^{-1} (OH).

$C_{12}H_{22}O_2$

Calcd: C 72.66 H 11.18;
Found: C 72.66 H 11.32.

6-Dodecyn-4-olide (**10**)

The oxidizing agent, Ag_2CO_3 on Celite[10], was prepared beforehand according to the method of Fétizon[11] and dried azeotropically with benzene directly before use. The reagent, having been prepared in this way, contained approx. 1 mmol Ag_2CO_3 per 0.57 g reagent. In a reaction vessel darkened with foil, 17 g Ag_2CO_3/Celite was added to 0.6 g 1,4-dihydroxydodec-6-yne (**9**) in approx. 200 ml benzene, whereupon the reaction mixture was refluxed overnight. After completion of the oxidation, the solid material was filtered off and the filtrate concentrated under reduced pressure. After removal, by distillation, of by-products resulting from oxidation of the secondary alcohol group in the diol **9**, redistillation of the desired product gave 0.43 g (73%) 6-dodecyn-4-olide (**10**); b.p.$_{0.05}$ 79 – 81 °C (air bath).

NMR δ (60 MHz, $CDCl_3$) 0.9 (CH_3, t); 1.1 – 1.6 (3 CH_2, m); approx. 2.0 – 2.6 (2 $CH_2-C\equiv C$, m); approx. 1.9 – 2.4 ($-CH-CH_2-CH_2-COO$, m); 4.6 ($>CH-O$, quintet); IR (film) 1780 cm^{-1} ($C=O$, γ-lactone).

$C_{12}H_{18}O_2$

Calcd: C 74.19 H 9.34;
Found: C 73.94 H 9.52.

(Z)-6-dodecen-4-olide (**4**)

A solution of 0.35 g 6-dodecyn-4-olide (**10**) in methanol was partially hydrogenated in the presence of 8.5mg 5% Pd/$BaSO_4$ catalyst and 8.5 mg quinoline. Isolation of the product in the usual manner, followed by distillation, gave 0.35 g (99%) (Z)-6-dodecen-4-olide (**4**); b.p.$_{0.06}$ 64 – 65 °C (air bath) [Lit.[12] b.p.$_{0.5}$ 110 – 120 °C].

$C_{12}H_{20}O_2$

Calcd: C 74.00 H 10.16;
Found: C 73.43 H 10.27.

Results and Discussion

Gc-ms-analysis of the volatile fraction of the field collected pedal gland exudate of the bontebok gave the trace of total ion current *vs* scan number (TIC trace) depicted in Fig. 1.

The mass spectrum of the compound denoted by scan number 909 in the TIC trace, exhibited prominent peaks at *m/e* 27 (25); 41 (42); 43 (74); 59 (100); 67 (39); 68 (39); 81 (69); 93 (85); 121 (60) and 136 (63%) (intensities in parenthesis as percentages of the base peak). Although all the previously identified compounds[1] contained in the pedal gland secretion of the bontebok, have un-

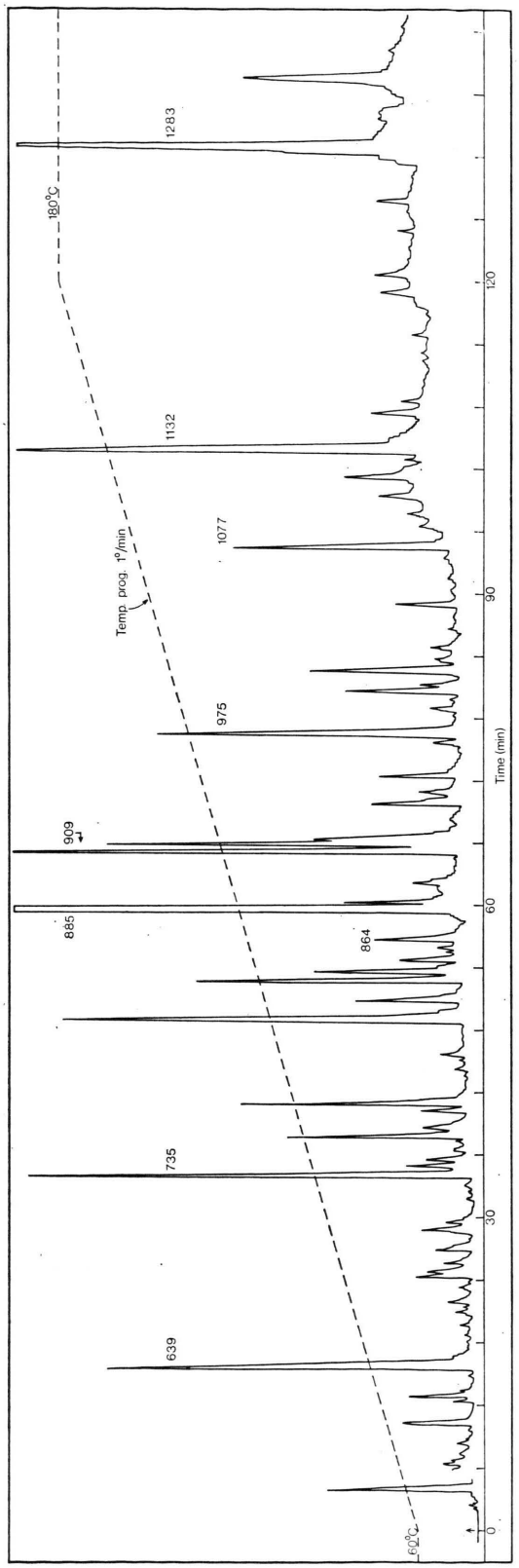
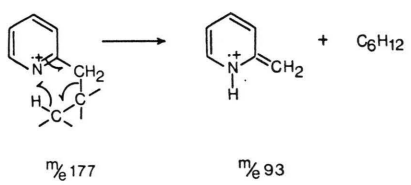


Fig. 1. Gas chromatogram (TIC trace, Varian MAT 311A) of the volatile fraction of the pedal gland exudate of the bontebok (*Damaliscus dorcas dorcas*).

branched structures, this compound was identified as α-terpineol (**1**) on account of the excellent correspondence of its mass spectrum to published mass spectral data [13]. Unfortunately, owing to incomplete separation on a packed column, preparative gas chromatographic isolation of the compound did not yield sufficient material for the confirmation of this structural assignment by NMR and IR spectrometry. However, the identification of the compound as α-terpineol was substantiated by proving the isolated compound and synthetic α-terpineol [14] to be gas chromatographically identical using a 25 m FFAP glass capillary column.

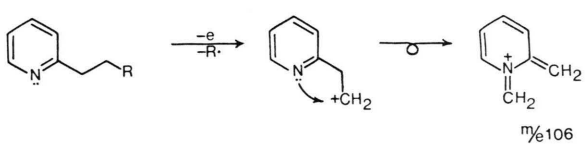
Owing to the fact that those compounds which are volatile enough to be considered pheromonal, occur in such low concentrations that isolation of sufficiently pure samples proved impracticable, the determination of the optical rotation of compounds with asymmetrical centres was not attempted.

The mass spectrum of the constituent represented by scan number 975 in the TIC trace (Fig. 1) exhibited a molecular ion at an odd mass number corresponding to the molecular formula $C_{12}H_{19}N$ (element map). The base peak appearing at *m/e* 93 could be interpreted in terms of the loss of C_6H_{12} from a heptyl side chain attached to a pyridine nucleus in the 2-position by a McLafferty rearrangement [15]:



m/e 177 m/e 93

Furthermore, the ion at *m/e* 106 (20%, $C_7H_8N^+$) could be attributed to cleavage of the carbon-carbon bond γ to the pyridine ring, which in such an alkyl-substituted pyridine, yields an ion of relatively high abundance due to stabilisation of the alkyl carbonium site by the electron pair on the nitrogen atom [16]:



m/e 106

The appearance of these two most abundant ions at *m/e* 93 and 106 was consistent with a monosubstituted pyridine nucleus with, furthermore, no

substituents in positions 1′ and 2′ in the side chain. In view of the relative intensities of the ions at *m/e* 106 ($C_7H_8N^+$, 20); 120 ($C_8H_{10}N^+$, 14); 134 ($C_9H_{12}N^+$, 4); 148 ($C_{10}H_{14}N^+$, 3); 162 ($C_{11}H_{16}N^+$, 1%), and the absence of a significant peak at *m/e* 43, the remaining C_5H_{11} group in the side chain could be assumed to be unbranched. This structural assignment, namely 2-*n*-heptylpyridine (**2**), was confirmed by comparison of its mass spectrum with the fully identical spectrum of **2**, synthesised by alkylation of pyridine[3]. On a 25 m glass capillary column with FFAP as stationary phase, the retention time of this component corresponded to that of the synthetic material.

Computer comparison of the mass spectrum of the compound denoted by scan number 1132 in the TIC trace (Fig. 1) with a library of standard spectra, produced the correlation factors 48, 69 and 51% for *m*-cresol, *p*-cresol and ethyl *p*-cresyl ether respectively. The cresyl ether could, however, be eliminated as an IR spectrum of the compound indicated the presence of an OH group. By comparing its NMR spectrum, recorded with 40 μg of gas chromatographically isolated material, with the spectra of authentic samples of *o*-, *m*-, and *p*-cresol, it could be proved that this constituent was *m*-cresol (**3**).

The molecular formula of the second most abundant constituent of the volatile fraction of the pedal gland exudate of the bontebok (scan number 1283, Fig. 1) was found to be $C_{12}H_{20}O_2$ (element map). The base peak at *m/e* 85 ($C_4H_5O_2^+$) in the mass spectrum of this compound (Fig. 2) was typical of an γ-alkylsubstituted γ-lactone. The presence of a γ-lactone ring was confirmed by the carbonyl absorption at 1763 cm^{-1} (in $CDCl_3$) in its IR spectrum. These observations and the presence of a multiplet at δ approx. 5.5 in the NMR spectrum of the compound (Fig. 3 a) were indicative of a long-chain γ-lactone with a double bond in the side chain. The triplet at δ 0.9 in the NMR spectrum was assigned to a single methyl group, while the absence of other methyl resonances led to the conclusion that the side chain had an unbranched structure. This left the position and stereochemistry of the double bond to be determined. The observed chemical shift and splitting pattern of the methyl resonance at δ 0.9 and of the γ-hydrogen resonance at δ 4.38 could be accommodated by three possible isomers, 6-dodecen-4-olide, 7-dodecen-4-olide and 8-dodecen-4-olide. No conclusive evidence concerning the position of the double bond could be obtained from either the NMR spectrum or from the typically uninformative mass spectrum of the isolated γ-lactone. By spectrometric and gas chromatographic comparison (*cf.* Fig. 3) of the isolated compound with authentic synthetic material[17] this constituent could, however, be characterised as a 6-dodecen-4-olide.

Since only a relatively weak shoulder appeared at approx. 995 cm^{-1} in the IR spectrum of the isolated compound, (Z)-configuration was provisional-

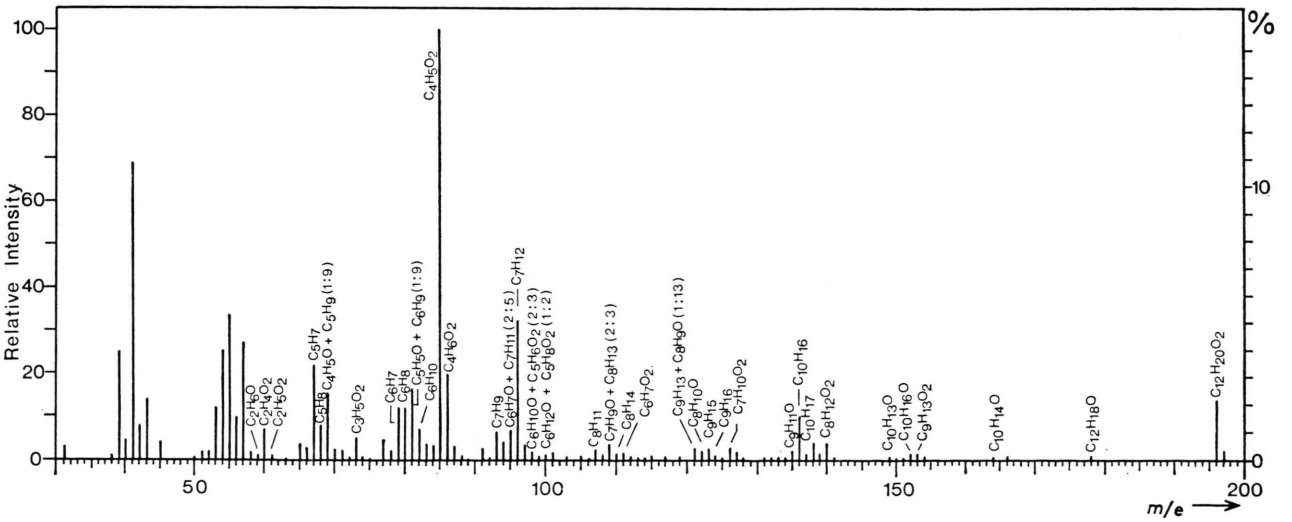


Fig. 2. Mass spectrum of the constituent appearing at scan number 1283 in the TIC trace (Fig. 1) of the volatile fraction of the pedal gland exudate of the bontebok.

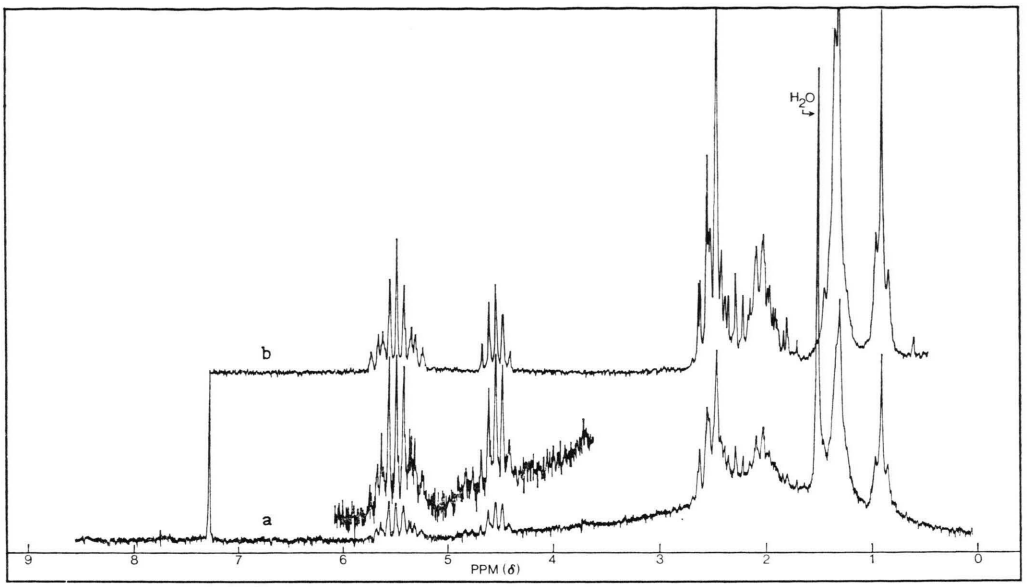


Fig. 3. (a) ^{1}H FT-NMR spectrum (100 MHz) of the unsaturated long-chain γ-lactone isolated from the pedal gland exudate of the bontebok (80 μg in 99.98% isotopically pure $CDCl_3$, deuterium as internal lock signal); (b) ^{1}H NMR spectrum of synthetic (Z)-6-dodecen-4-olide in $CDCl_3$.

ly assigned to the double bond. However, it had to be taken into consideration that an IR spectrum recorded with such a small sample could be unreliable, especially in the lower frequency range. As the (E)-isomer of the γ-lactone had not been synthesised, it was impossible to determine whether the available SCOT column was capable of separating the (E)- and (Z)-isomers. The fact that the retention times of the synthetic (Z)-isomer and isolated compound were identical, could therefore not be used as conclusive evidence in favour of (Z)-configuration of the latter compound. As, furthermore, the olefinic resonances in NMR spectra of the isolated and synthetic samples seemed to differ slightly, it was considered necessary to undertake a more detailed investigation of the stereochemistry of the double bond.

The problem was approached by obtaining values for chemical shifts and coupling constants from a 220 MHz spectrum [17] of the synthetic sample for the $ABMPX_2$ spin system in question (depicted in the formula below). These parameters were used to simulate olefinic resonances at 100 MHz for different values of the coupling constant J_{AB}, which could then be compared with that of the isolated material.

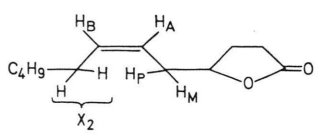


Table I. Final parameter values used for simulation of the olefinic resonance pattern at 100 MHz for (Z)-6-dodecen-4-olide (4).

Chemical shift δ [ppm]		Coupling constant J [Hz]			
H_A	5.3503	J_{AB}	10.94	J_{BP}	−1.53
H_B	5.5619	J_{AM}	7.29	J_{BX}	7.32
H_M	2.353	J_{AP}	7.55	J_{MP}	−15.0
H_P	2.463	J_{AX}	−1.59	J_{MX}	0.1
H_X	2.036	J_{BM}	−1.54	J_{PX}	0.1

A modified version of the computer program LAME [18] was used for this purpose. The most satisfactory fit, as shown in Fig. 4, was obtained with the parameter values given in Table I, *i. e.* with a *cis*-coupling J_{AB} of 10.94 Hz. As illustrated in Fig. 4, a noticeable deviation from the olefinic pattern of the isolated material already existed with a relatively small *trans*-coupling J_{AB} of 13.8 Hz, thus

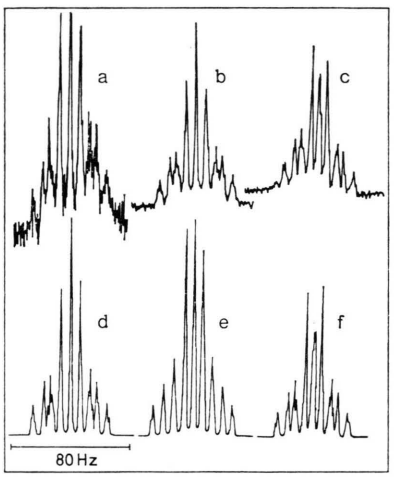


Fig. 4. Comparison of observed and simulated olefinic NMR resonances at 100 MHz. Observed: (a) for isolated 6-dodecen-4-olide, $CDCl_3$ as solvent; (b) for synthetic (Z)-6-dodecen-4-olide, $CDCl_3$ as solvent; (c) for synthetic (Z)-6-dodecen-4-olide, CCl_4 as solvent. Simulated: (d) with the parameter values given in Table I (*i.e.* J_{AB} 10.94 Hz, δ_A 5.3503, δ_B 5.5619); (e) with J_{AB} 13.8 Hz, δ_A 5.3503 and δ_B 5.5619; (f) with J_{AB} 10.94 Hz, δ_A 5.3345 and δ_B 5.5161.

furnishing conclusive evidence in favour of the Z-configuration of the double bond. Thus, the isolated γ-lactone could finally be characterised as (Z)-6-dodecen-4-olide (**4**).

It is significant to observe that the slight difference between the NMR spectra of the synthetic and isolated compounds mentioned previously, was due to differences in concentration and solvent polarity. The use of CCl_4, for example, led to an upfield shift of 0.016 and 0.046 ppm of the olefinic protons H_A and H_B respectively (*cf.* Fig. 4 c and f).

Mention has been made in the literature of the isolation of the unsaturated γ-lactone **4** from butterfat [19, 20], from the cultured broth of *Sporobolomyces odorus* [21], and from the meat of lambs fed on a supplementary lipid diet of high linoleic acid content [22], while it has also been found to be the major pheromonal component of the tarsal tuft scent of the black-tailed deer *(Odocoileus hemionus columbianus)* [23].

The first reported synthesis of (Z)-6-dodecen-4-olide (**4**), in which a Grignard coupling of methyl-4-oxobutanoate with 1-bromo-2-octyne was employed, gave this γ-lactone in a very low yield, and furthermore required gas chromatographic separation of two isomeric products [24]. A more convenient synthesis utilising *inter alia* the condensation of 1,2-epoxy-4-decyne with diethyl malonate, gave (Z)-6-dodecen-4-olide in an overall yield of almost 30% [12]. Recently another synthesis exploiting thermolytical or photochemical cyclisation of a chloroamide and hydrolysis of the resulting iminolactone hydrochloride for the construction of the γ-lactone ring, has been reported [25]. This synthesis gave (Z)-6-dodecen-4-olide (**4**) in an overall yield of approx. 6%.

As the envisaged biological evaluation of (Z)-6-dodecen-4-olide is expected to require considerable quantities of material, another promising approach to the synthesis of this compound, as formulated in the accompanying reaction scheme, was investigated.

Commercially available 4-penten-1-ol was converted into its tetrahydropyranyl ether **6**, whereafter the terminal double bond was epoxidised with *m*-chloroperbenzoic acid to give 2-(4′,5′-epoxypent-1′yloxy)-tetrahydropyran (**7**). Coupling this epoxide with 1-heptyne, gave 2-(4′-hydroxydodec-6′-yn-1′-yloxy)-tetrahydropyran (**8**) in a satisfactory yield, which could, however, be adversely affected by traces of moisture. Hydrolysis of the acetylenic tetrahydropyranyl ether **8** gave, 1,4-dihydroxydodec-6-yne (**9**). The recently reported oxidation with Ag_2CO_3 on Celite [10], which was selected as the most promising of several methods [26–29] considered for the selective oxidation of the primary alcohol moiety of the diol **9**, gave the acetylenic γ-lactone **10** in 73% yield. However, the reagent had to be carefully prepared and the reaction carried out in a darkened vessel to ensure a satisfactory yield. Partial hydrogenation over Lindlar catalyst gave the required γ-lactone (Z)-6-dodecen-4-olide (**4**) in an overall yield of 54% (based on 4-penten-1-ol).

Methods are at present being developed for physiological screening under laboratory conditions of all compounds identified in the pedal gland exudate of the bontebok, which will be followed up by field evaluation of those compounds eliciting positive response in test animals.

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