Studies on Mammalian Pheromones, I

Ketones from the Pedal Gland of the Bontebok (*Damaliscus dorcas dorcas*)

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The significance of pheromones in olfactory communication in mammals, and the possibility of using synthetic pheromones to influence the behaviour of problem animals, are briefly discussed. The isolation, identification and synthesis of the principal volatile component contained in the pedal gland exudate of the bontebok, *Damaliscus dorcas dorcas, viz.* (Z)-5-undecen-2-one, are reported. Some of the other major constituents of the secretion have been identified as 2-heptanone, 2-nonanone, 2-undecanone and 2,5-undecanedione.

Cutaneous glands which secrete odoriferous substances of importance in olfactory communication occur in many groups of mammals. They are common in carnivores and rodents and in most ungulate groups, but are also found in some primates and in many other orders. The glands may be situated in many different parts of the body. Among antiodactyls, for example, pedal, inguinal, preputial and preorbital glands are especially common, but tarsal, metatarsal, carpal, dorsal, caudal, postcomual and occipital glands are also present in some species[1].

Volatile compounds contained in the glandular secretion serve as chemical signals which are generally known as pheromones if they trigger responses in conspecific receivers[2]. Mykytowycz[3] reviewed the role of glands in communication and Eisenberg and Kleiman[4] have dealt with olfactory communication in mammals.

The volatile substances which act as pheromones may be released into the air by diffusion from the gland. Secretions may also be spread upon the animal's own body or upon that of a social partner. In most cases which have been described, however, objects are marked, and signals must be presumed to be transmitted for some time thereafter by evaporative release of pheromones from the glandular exudate. Scent marking of this kind is often associated with territorial behaviour[4].

Eisenberg and Kleiman[4] showed that pheromones may transmit information on the identity of individuals, races and species, on sex, age, mood and on sexual state. A variety of physiological and behavioural responses to such information have been demonstrated.

The chemical identity of the active components of mammalian gland secretions has only been determined in a few cases. Known pheromones are of widely differing chemical nature and little is known of their precise functions. The first recorded cases of the isolation of mammalian scent material, are those of civetone from the civet, *Viverra civetta*, and muskone from musk deer, *Moschus moschiferus*, by Ruzicka[5] in 1926. An unsaturated γ-lactone, *cis*-4-hydroxydodec-6-enoic acid lactone, is an active component in the tarsal gland secretion of black-tailed deer, *Odocoileus hemionus columbianus*[6]. Eight compounds secreted by the subauricular gland in prong-

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horn antelope, *Antilocapra americana,* have been identified as two acids, two alcohols and their four esters [7]. A series of short chain aliphatic acids have been suggested to be the active components of the vaginal secretion in the rhesus monkey, *Macaca mulatta* [8], while similar acids have also been identified in the anal scent of both the red fox, *Vulpes vulpes* [9], and the small Indian mongoose, *Herpestes auropunctatus* [10]. It is suggested that they are the products of bacterial metabolism. In contrast to these compounds of relatively simple chemical nature, 5α-androst-16-en-3-one has been isolated as a boar taint-producing substance in the pig, *Sus scrofa* [11]. The interesting natural product, 5-thiomethylpentane-2,3-dione, has recently been isolated from the anal scent gland of the striped hyena, *Hyaena hyaena* [12].

The rich African mammal fauna offers a fruitful and unexploited field for pheromone research. Additional motivation stems from the fact that several bovid species, notably the grey duiker, *Sylvicapra grimmia,* and the grysbok, *Raphicerus melanotis,* cause damage of economic significance in vineyards, orchards and timber plantations in parts of South Africa. The grey duiker employs the preorbital gland in territorial marking [13] and Manson [14] describes similar behaviour in the male grysbok. A research program was initiated to isolate and identify the pheromones produced in these preorbital glands, and to investigate the feasibility of reducing damage by the use of synthetic pheromones.

It was soon found that preorbital exudates are only produced in very small quantities. Extremely low concentrations of compounds volatile enough to be considered pheromonal, are present. The secretion of the more productive pedal gland of the bontebok, *Damaliscus dorcas dorcas,* was therefore employed to develop and perfect suitable analytical techniques.

Material and Methods

A. General

Dichloromethane (Merck, GR) was analysed gas-chromatographically and found to be pure enough for extraction purposes. The surgical gauze, dressing forceps, syringes, scissors, teflon stoppers, vials, etc., that were used to collect, isolate and handle material, were cleaned by extraction for 24 h with methanol and then dichloromethane in a Soxhlet apparatus. NMR sample tubes were cleaned in an adapted Soxhlet apparatus with, alternatively, boiling solvent and hot solvent vapour, using methanol, benzene and dichloromethane in succession. Teflon stoppers were used on these tubes. All Pyrex glassware used in the handling of material and for the distillation of synthetic compounds, was heated to 500 °C in an annealing oven to remove any traces of organic material. Analytical and preparative gas-chromatographic separations were carried out with a Perkin Elmer 990 gas-chromatograph, using helium as carrier gas. A Perkin Elmer SCOT column coated with FFAP (30 m × 0.5 mm, ca. 70 000 theoretical plates) was used for analytical work and for gc-ms analyses. Packed glass columns were used for preparative gas-chromatographic separations. By using a pressure insensitive integrated effluent splitter with a small dead volume, as well as an aerosol precipitator, distinct separations, with an excellent recovery of material, were achieved. Gc-ms analyses were carried out on a Varian MAT CH7 mass spectrometer, equipped with a Varian gas-chromatograph and a single stage Biemann-Watson helium separator, and also with a Varian MAT 311A mass spectrometer and Varian gas-chromatograph, employing direct coupling of the capillary column to the spectrometer. Both gc-ms systems were used in combination with a Varian MAT Spectro-System 100 MS data system. ^{1}H-NMR spectra were recorded in 99.98% isotopically pure deuterochloroform as solvent, using the deuterium of the solvent as the internal lock signal on a Varian XL 100 instrument (with Fourier transform averaging). Solution IR spectra were recorded in deuterochloroform with a Perkin Elmer 21 spectrophotometer, equipped with a beam condenser (Barnes Engineering Co.) and 0.1 mm ultra micro NaCl cavity cells.

B. Isolation

Initially material was collected from a captive male bontebok. The gas-chromatographic separations achieved with the volatile fraction were unsatisfactory, possibly because of impurities. These may have been introduced through contamination of the interdigital cavity, in which the gland is situated, with urine or faeces from the floor of the pen. To exclude this possibility, all other samples were taken from free-ranging animals, freshly captured in the Bontebok National Park, Swellendam, C.P., and the De Hoop Nature Reserve near Bredasdorp, C.P., South Africa. Material was collected from thirty animals over a period of approximately nine months.

A preliminary gas-chromatographic analysis of volatile material, isolated from several samples taken from individual animals, showed no significant seasonal or regional variation, either qualitatively or quantitatively. Similarly, only relatively small quantitative differences were found between males and females. All available material was therefore pooled for analysis.

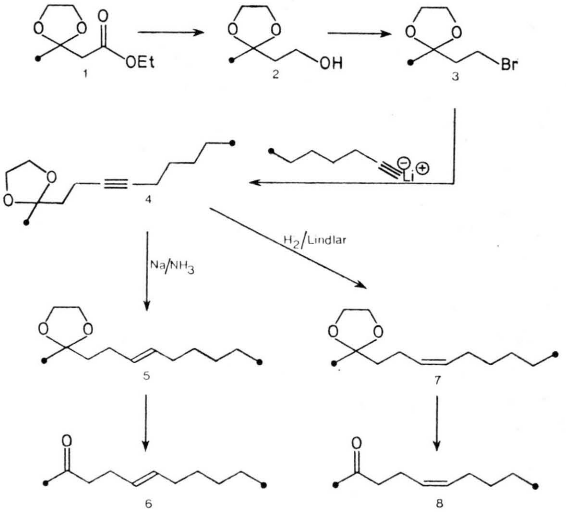
The Bontebok were netted, trapped or immobilised with a mixture of Fentanyl and flupyridol (Azaperone, Janssen). The yellow, waxy pedal gland exudate was removed from the interdigital cavity by means of clean surgical gauze and dressing forceps. Organic material was extracted from the gauze with dichloromethane in a small Soxhlet apparatus and the extract concentrated in an inert gas atmosphere to yield approx. 5 ml of a yellow viscous oil, consisting mainly of non-volatile lipids. The concentrate was subjected to preparative gas-chromatography in 0.5 ml batches [1.7 m × 8 mm glass, 6% OV 25 on 60 – 80 mesh Chromosorb WAW DMCS, 47 ml He/min, temperature program 100 – 185 °C (8 °C/min)]. Contrary to expectation, a well-defined difference was found between the volatile and non-volatile material which made it possible to isolate the volatile fraction by condensing it from the column effluent up to a retention time corresponding to that of methyl stearate, while the non-volatile material remained in the column inlet. The resulting volatile fraction was transferred to a Reacti-Vial (Pierce Chemical Co.) with dichloromethane. Slow evaporation of the solvent in an inert gas atmosphere at room temperature gave approx. 25 μl of a approx. 50% solution of the volatile components in dichloromethane. The non-volatile lipids and inorganic matter remaining in the inlet of the gas-chromatograph were rinsed out with dichloromethane, following which the inlet and column were conditioned for a few hours at 280 °C with reversed gas flow before the following separation was carried out.

Small samples (approx. 0.1 – 1.0 μl) of the volatile fraction (50% CH_2Cl_2 solution) were used for gc and gc-ms analyses [Perkin Elmer SCOT column, 30 m × 0.5 mm, FFAP as stationary phase, 5 ml He/min, temperature program 60 – 180 °C (1 or 2 °C/min)]. Low resolution spectra were recorded with a Varian MAT CH7 mass spectrometer, but as the use of a Biemann-Watson helium separator had an adverse effect on the gas-chromatographic separation, direct coupling of the column to a Varian MAT 311A mass spectrometer was resorted too for element mapping. An element map was thus obtained for each peak visible in the gas-chromatogram (TIC trace) shown in Fig. 1.

The typically uninformative mass spectra of the terpene alcohols, unsaturated long-chain ketones and unsaturated long-chain γ- and δ-lactones presumed to be present in the volatile fraction, necessitated the isolation of these constituents for IR and NMR analysis. Preparative separation of the individual constituents was carried out with a packed glass column [15 m × 3 mm glass, 2.5% FFAP on 60 to 80 mesh Chromosorb WAW DMCS, 21 ml He/min, temperature program 80 – 190 °C (1 °C/min)]. Eight of the 44 constituents isolated in high purity by preparative gas-chromatography were obtained in sufficient quantities (20 – 450 μg) for the recording of IR and proton FT-NMR spectra with the available instrumentation.

C. Synthesis of (E)- and (Z)-5-undecen-2-one

The principal constituent of the volatile fraction was characterised as (Z)-5-undecen-2-one (**8**). This compound and its (E)-isomer **6**, were synthesised for spectroscopic comparison according to the following scheme:



2,2-Ethylenedioxybutanol-4 (**2**)

To a stirred and cooled solution of 14.4 g $LiAlH_4$ (20% excess) in 1600 ml absolute ether, a solution of 110 g ethyl 3,3-ethylenedioxybutanoate (**1**) [15] in 100 ml ether was added during 30 min. The temperature of the reaction mixture was kept below 2 °C during the addition and for 10 min thereafter. The speed of stirring was increased and 100 ml saturated tartaric acid solution was added dropwise, with cooling of the reaction mixture. Vigorous stirring was continued for a further 15 min, after which the crystalline tartrates were removed by filtration through cotton wool. The filtrate was stirred with a mixture (1 : 1) of anhydrous Na_2SO_4 and $NaHCO_3$ to remove traces of tartaric acid and water, the solid material was filtered off, the solvent evaporated, and the resulting residue distilled to yield 72.5 g (95%) 2,2-ethylenedioxybutanol-4 (**2**); b. p. $_{12}$88 – 91 °C.

2,2-Ethylenedioxy-4-bromobutane (**3**)

To 150 ml absolute ether at – 20 °C, 59.1 g 2,2-ethylenedioxybutanol-4 (**2**) and 42.7 g PBr_3 (diluted with ether to the same volume as the hydroxycompound **2**) were added simultaneously with an infusion pump at such a rate that the temperature remained between – 10 and – 20 °C. After completion of the addition, the reaction mixture was stirred for a further 15 minutes, following which 20 g $NaHCO_3$ powder was added, followed by approx. 15 ml saturated $NaHCO_3$ solution. The organic layer was separated, washed at 0 °C with small portions of water to pH 7 and dried (Na_2SO_4). Removal of the solvent and distillation of the residue gave 56.8 g (65%) 2,2-ethylendioxy-4-bromobutane (**3**); b. p. $_{12}$75 – 81 °C.

2,2-Ethylenedioxyundec-5-yne (**4**)

To a stirred suspension of lithamide, prepared from 1.84 g Li in redistilled liquid NH_3, 27.3 g (23% excess) heptyne-1 was added during 15 min. The reaction mixture was stirred for 1 h, and then 44.9 g 2,2-ethylenedioxy-4-bromobutane (**3**) was added with stirring over a period of 20 min. Stirring was continued for a further 15 min, whereupon the reaction mixture was diluted with 500 ml ether. After the liquid NH_3 had evaporated the ether solution was decanted from the solid material, washed to pH 10 with small quantities of water, dried and concentrated at reduced pressure. Distillation of the residue gave 9.25 g (23%) 2,2-ethylenedioxyundec-5-yne (**4**); b. p. $_{1.2}$88 – 89 °C.

$C_{13}H_{22}O_2$
Calcd: C 74.24 H 10.54;
Found: C 74.48 H 10.75.

(Z)-2,2-Ethylenedioxyundec-5-ene (**7**)

A solution of 4 g 2,2-ethylenedioxyundec-5-yne (**4**) in *n*-heptane/ethyl acetate (1 : 1), was partially hydrogenated in the presence of Lindlar catalyst[16] and three drops of quinoline. Isolation of the product in the usual manner, followed by distillation gave 4.02 g (100%) (Z)-2,2-ethylenedioxyundec-5-ene (**7**); b. p. $_{1.2}$80 – 80.5 °C.

$C_{13}H_{24}O_2$
Calcd: C 73.53 H 11.39;
Found: C 74.29 H 11.89.

(Z)-5-Undecen-2-one (**8**)

A solution of 3.49 g (Z)-2,2-ethylenedioxyundec-5-ene (**7**) in 50 ml dioxane was stirred with 17 ml saturated tartaric acid solution at 80 °C for 5$^1/_2$ h in an argon atmosphere. After completion of the an argon atmosphere. After completion of the hydrolysis, the reaction mixture was carefully concentrated at 10 °C and reduced pressure on a rotary evaporator to yield approx. 15 ml of viscous residue. To this 100 ml light petroleum (40 – 60 °C) was added, followed by sufficient anhydrous Na_2SO_4 to give, on vigorous shaking, a homogeneous suspension of the solid inorganic material in the petroleum. The solid material was filtered off and washed with petroleum. The combined filtrate and washings were dried (Na_2SO_4) and concentrated at reduced pressure. Distillation of the resulting residue gave 2.55 g (95%) (Z)-5-undecen-2-one (**8**); b. p. $_5$87 – 89 °C.

NMR δ (100 MHz, $CDCl_3$) 0.88 (CH_3, t); 1.08 – 1.52 (3 CH_2, m); 2.03 (CH_2, allyl., q); 2.13 (CH_3), s; 2.20 – 2.62 (4 H, $=CH(C\underline{H}_2)_2CO-$, m); 5.10 – 5.62 (2 H, olefin., m); IR (CS_2) 1708, 1150 (CO); 1350 ($-COCH_3$); 710 cm^{-1} ($-CH=C$, *cis*-subst.).

$C_{11}H_{20}O$
Calcd: C 78.51 H 11.98;
Found: C 78.29 H 12.22.

(E)-2,2-Ethylenedioxyundec-5-ene (**5**)

By means of an infusion pump, 3 g 2,2-ethylenedioxyundec-5-yne (**4**) was added to a stirred solution of 0.99 g Na in 100 ml purified liquid NH_3, cooled to – 68 °C in a dry-ice bath. The acetylenic compound was introduced below the surface of the reaction mixture over a period of 20 min, *i. e.* at such a rate as to prevent crystallisation of the compound in the delivery needle of the infusion pump. The reaction mixture was stirred for a further 2 h after completion of the addition, and then diluted with 130 ml ether. After stirring for another 45 min, the reaction mixture was treated with 5 g NH_4Cl, stirred for 1$^1/_2$ h and then treated with 10 ml methanol to remove coagulated pieces of Na. Thereafter the mixture was stirred for a further 30 min with 10 g Na_2SO_4. All the solid material was removed by filtration, the filtrate concentrated under reduced pressure, and the residue distilled to give 3.0 g (99%) (E)-2,2-ethylenedioxyundec-5-ene (**5**); b. p. $_{1.1}$80 – 81 °C.

$C_{13}H_{24}O_2$
Calcd: C 73.53 H 11.39;
Found: C 73.97 H 11.53.

(E)-5-Undecen-2-one (**6**)

Hydrolysis of 2.85 g (E)-2,2-ethylenedioxyundec-5-ene (**5**), according to the method described above for the preparation of (Z)-5-undecen-2-one (**8**), gave 2.13 g (94.5%) (E)-5-undeceen-2-one (**6**); b.p. $_5$91 – 95 °C.

NMR δ (100 MHz, $CDCl_3$) 0.88 (CH_3, t); 1.08 to 1.52 ($3\,CH_2$, m); 1.94 (CH_2, allyl., q); 2.12 (CH_3, s); 2.16 – 2.64 (4 H, $=CH(C\underline{H}_2)_2CO-$, m); 5.12 – 5.62 (2 H, olefin., m); IR (CS_2) 1708, 1150 (CO); 1350 ($-COCH_3$); 970 cm^{-1} ($-CH=C$, *trans*-subst.).

$C_{11}H_{20}O_2$

Calcd:	C 78.51	H 11.98;
Found:	C 78.23	H 11.94.

NMR, IR and mass spectra recorded for the synthetic compounds confirmed their structures. The stereochemical identity of the ketones **6** and **8** was confirmed by their IR spectra. No gc separation of these isomers could be effected with the available SCOT column.

Results and Discussion

An unsaturated methyl ketone was identified as the principal constituent of the volatile fraction of the gland secretion. In addition, three saturated methyl ketones and a saturated diketone were found among the other major constituents.

The molecular formula of the principal constituent (scan numbers 875 to 890, Fig. 1) was $C_{11}H_{20}O$ (element map). The base peak at *m/e* 43 ($C_2H_3O^+$) in the mass spectrum of this compound (Fig. 2), and a singlet resonance at δ 2.15 in its NMR spectrum (Fig. 3), were characteristic of a methyl ketone. Due to a proton background in the probe of the NMR spectrometer (affecting the δ 1 – 3 region), the integral trace of the proton spectrum (Fig. 3) was of only limited diagnostic value. However, the multiplet at δ 5.35 could be assigned to two olefinic protons, and the triplet at δ 0.9 to a single methyl group. The absence of resonances which could be ascribed to methyl groups in a saturated environment, led to the conclusion that this particular methyl ketone had an unbranched structure. An IR carbonyl absorption at 1708 cm^{-1} excluded the possibility of α,β-unsaturation. Furthermore, the absence of the characteristic resonance of an α-methylene group in a β,γ-unsaturated ketone, between δ 2.7 and δ 3.5, indicated no β,γ-unsaturation. The resonance pattern at δ 2.43 could, however, be assigned to two methylene groups between the ethylenic and carbonyl functions in a γ,δ-unsaturated ketone, while the resonance at δ 2.05 could be assigned to the remaining allylic methylene group in such a system.

The high resolution mass spectrometric data revealed that oxygen-containing species, resulting from the loss of C_nH_{2n+1} fragments from the molecular

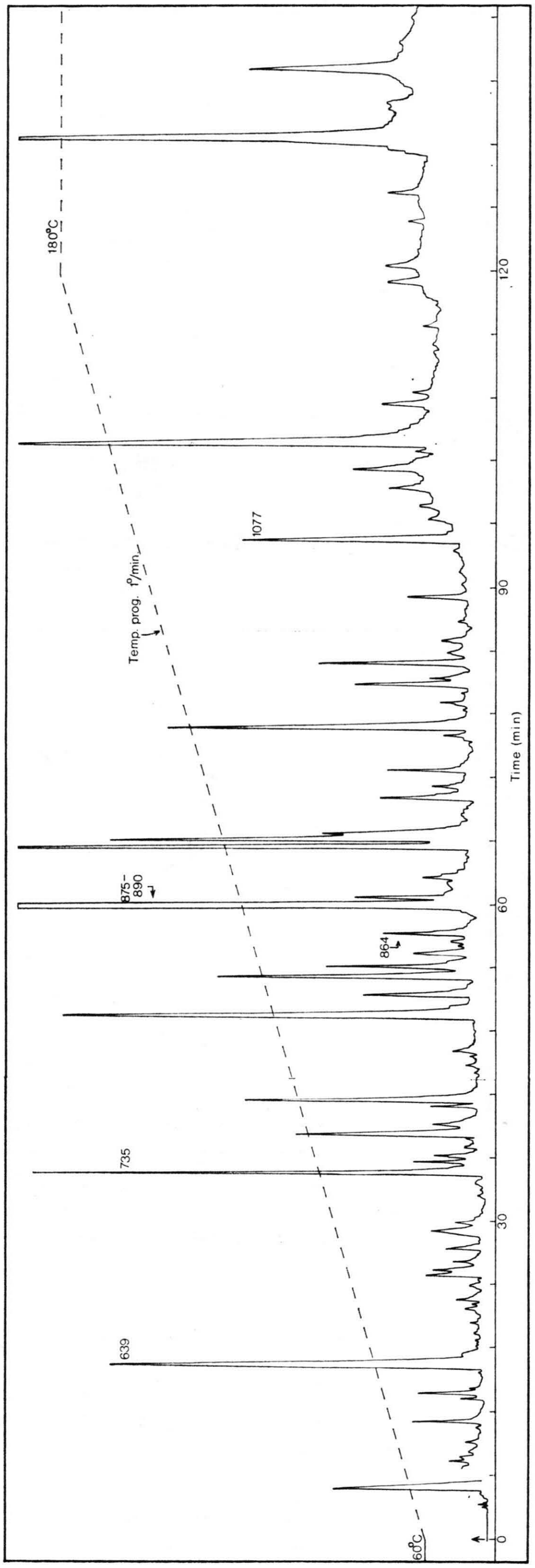


Fig. 1. Gas chromatogram (TIC trace, Varian MAT 311 A) of the volatile fraction of the pedal gland exudate of the bontebok *(Dadaliscus dorcas dorcas)*.

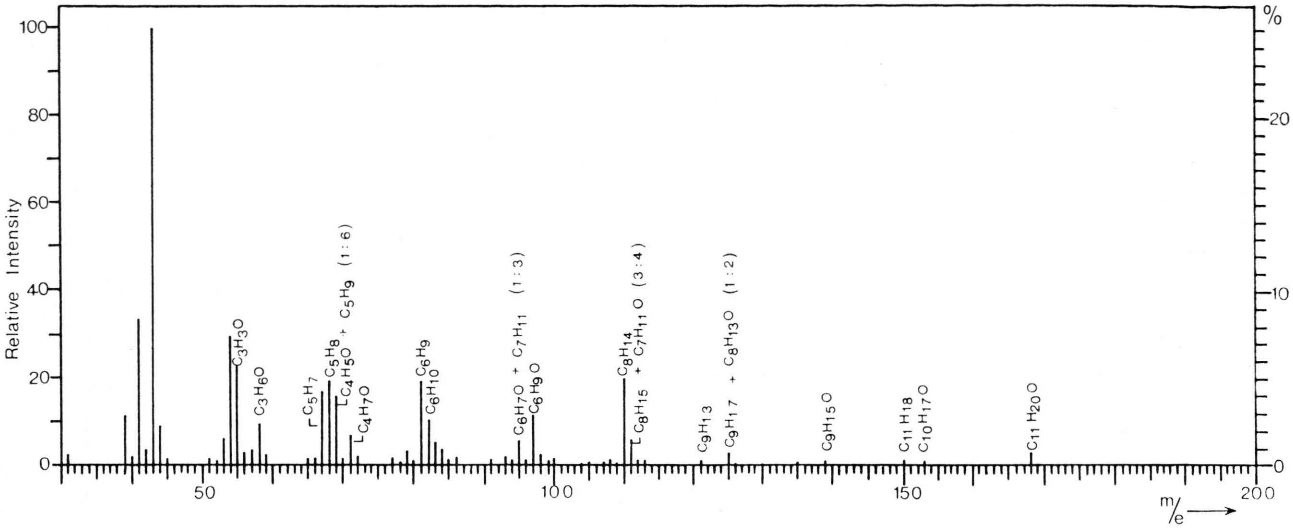


Fig. 2. Mass spectrum of the principal constituent contained in the volatile fraction of the pedal gland exudate of the bontebok (Scan numbers 875 to 890, Fig. 1).

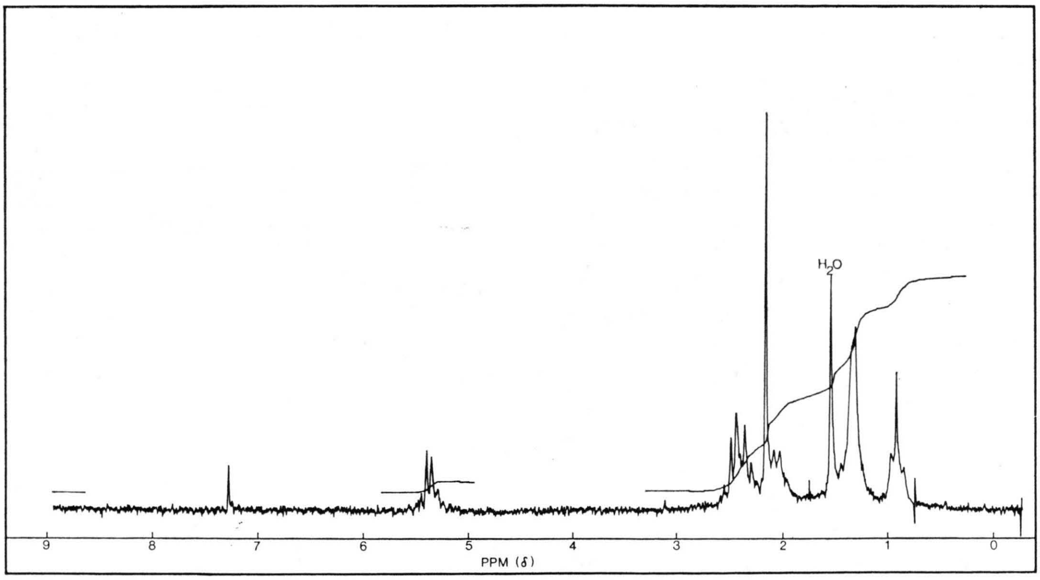


Fig. 3. ^1H FT-NMR spectrum (100 MHz) of the principal volatile constituent of the pedal gland exudate of the bontebok (450 μg in 99.98% isotopically pure $CDCl_3$, deuterium as internal lock signal).

ion, occurred with gradually increasing abundance for $n = 1, 2, -, 5$. This rising trend was interrupted when $n = 6$, but resumed when $n = 7$. Although it is known that hydrogen shifts, resulting in double bond migration, can take place in the molecular ion[17], this break in the gradual incline was interpreted as additional evidence in favour of γ,δ-unsaturation. The absence of a m/e 58 ion ($C_3H_6O^+$) in the mass spectrum (high resolution data) of an unbranched, unsaturated ketone of this type, was attributed to suppression of the expected McLafferty rearrangement by the fact that the γ-carbon atom is attached to a double bond. These observations, and the additional evidence provided by NMR against a possible β,γ-double bond, could only be interpreted in terms of γ,δ-unsaturation.

On account of the absence of an absorption band at 980 – 960 cm^{-1} and the presence of a band at 700 cm^{-1} in the IR spectrum, a *cis*-configuration of the double bond was assumed. The compound was therefore (Z)-5-undecen-2-one (**8**).

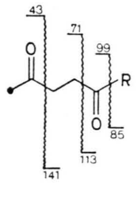
With a view to spectroscopic comparison and biological evaluation, both the (E)- and (Z)- isomers, **6** an **8** respectively, were synthesised according to the above reaction scheme.

In $LiAlH_4$ reductions dilute mineral acid is usually employed to hydrolyse the alkoxide complex. However, in order to avoid simultaneous hydrolysis of the ketal group and to restrict loss of product owing to its solubility in water, a cold, saturated tartaric acid solution was used in the preparation of the alcohol **2**, instead of mineral acid.

On the other hand, by using the same reagent, viz. tartaric acid, at 80 °C, the ketals **5** and **7** could easily be hydrolysed [18]. This procedure afforded excellent yields of the ketones **6** and **8**, without the occurrence of double bond migration, which was found to be considerable in preliminary experiments in which the conventional acid reagent was employed. The IR, NMR, and mass spectra of the synthetic ketone (Z)-5-undecen-2-one (**8**) proved identical to those of the isolated compound.

Three of the major components contained in the volatile fraction, namely those denoted by scan numbers 639, 735 and 864 respectively in the TIC trace (Fig. 1), were identified as the saturated methyl ketones 2-heptanone, 2-nonanone and 2-undecanone, by comparing their mass spectra with published data [19]. The identification of component 735 as 2-nonanone was confirmed by comparing the IR and NMR spectra recorded on 40 μg of the isolated compound, with those of an authentic synthetic sample.

The mass spectrum (Fig. 4) of the compound denoted by scan number 1077 in the TIC trace (Fig. 1) showed prominent peaks at *m/e* 71 ($C_4H_7O^+$), 99 ($C_5H_7O_2^+$), 85 ($C_6H_{13}^+$), 113 ($C_7H_{13}O^+$) and 141 ($C_9H_{17}O^+$), which were interpreted in terms of α-fragmentation in a 2,5-diketone:



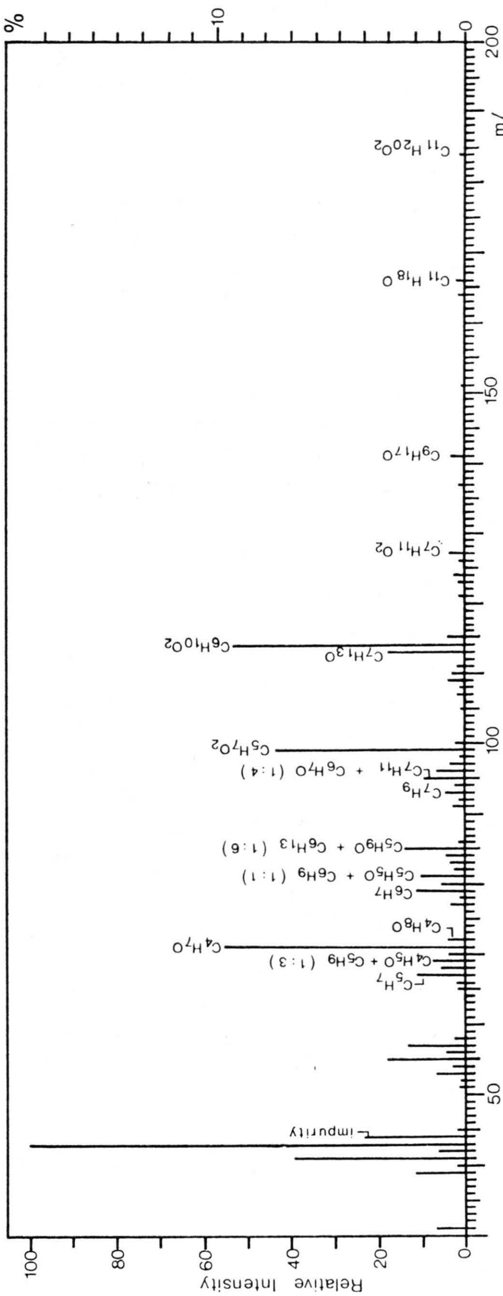
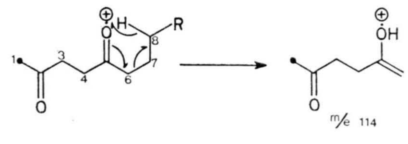


Fig. 4. Mass spectrum of the component appearing at scan number 1077 in the TIC trace (Fig. 1) of the volatile fraction of the pedal gland exudate of the bontebok.

The molecular formula of the *m/e* 114 ion ($C_6H_{10}O_2^+$), formed by a McLafferty rearrangement, indicated the absence of branching at C-6:



A galvanometrically recorded spectrum of this compound exhibited peaks of low intensity at M-15, M-29, M-43, M-57 and M-71 (absent in the bar graphs obtained from the data system as an 1% threshold was used), and it was therefore assumed that the ketone had a straight-chain structure. Although 10 μg of the pure compound was isolated, IR and NMR spectra could not be recorded with the available instrumentation. However, by comparing its mass spectrum with that of an authentic synthetic sample[20], this diketone was identified unequivocally as 2,5-undecanedione.

For comparison, pedal gland extracts from the blesbok, *Damaliscus dorcas phillipsi*, were analysed and found to contain the same constituents as those of the bontebok. A chemotaxonomic comparison with other species of the genus *Damaliscus* is planned.

Work is continuing on the identification and synthesis of other constituents of bontebok pedal gland secretion. The pheromones already synthesised have been subjected to a preliminary biological test, with encouraging results. Intense interest was evinced by two captive animals, one of them a normally aggressive and unapproachable male. A thorough evaluation of the biological significance of these pheromones is planned.

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