

MAMMALIAN EXOCRINE SECRETIONS. XII:
CONSTITUENTS OF INTERDIGITAL SECRETIONS OF
BONTEBOK, *Damaliscus dorcas dorcas*, AND BLESBOK,
D. d. phillipsi

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Abstract—In addition to the nine compounds identified in the interdigital secretion of the bontebok, *Damaliscus dorcas dorcas*, in a previous study, 76 compounds belonging to different compound types, were identified in the interdigital secretions of the bontebok and the blesbok, *D. d. phillipsi*. These compounds include alkanes, alcohols, aldehydes, ketones, fatty acids, terpenoids, γ -lactones, an isopropyl ester, long-chain hydroxyesters, 2-substituted pyridines, phenols, steroids, and dimethylsulfone. No qualitative differences were found between secretions from the two sexes or from animals from different habitats. Although no attempt was made to correlate territorial behavior or other behavioral phenomena with the qualitative composition of interdigital secretions from individual animals, available information seems to indicate that quantitative differences probably do not have a major semiochemical function. Only two species of bacteria, *Bacillus brevis* and *Planococcus citreus*, were found in the interdigital pouches of male and female members of the two subspecies, regardless of the habitat of the animals.

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B. brevis synthesized, among other unidentified constituents, (Z)-3-penten-2-ol, 2-hexanone, 2-octanone, 2-nonanone, tetradecanoic acid, pentadecanoic acid, heptadecanoic acid, octadecanoic acid, (Z)-9-hexadecenoic acid, and isopropyl hexadecanoate in vitro, while *P. citreus* produced, among others, the γ -lactones dodecan-4-olide and (Z)-6-dodecen-4-olide, which is one of the major constituents of the interdigital secretions of both subspecies. Some components of the interdigital secretions are not present in the interdigital glandular tissue, and the possibility is discussed that these compounds could be produced by microbiological activity in the interdigital pouch.

Key Words—*Damaliscus dorcas*, mammalian semiochemicals, mammalian pheromones, exocrine secretions, interdigital secretions, chemical communication, mass spectrometry, NMR.

INTRODUCTION

Damaliscus dorcas is a member of the alcelaphine group of antelope (Family Bovidae, Tribe Alcelaphini) and is endemic to South Africa. The nominate subspecies *D. dorcas dorcas*, the bontebok, occupied a limited range on the coastal plains of the southwestern Cape Province. Populations were severely depleted and the subspecies narrowly averted extinction (Bigalke, 1955). Its status has improved considerably, although bontebok are still listed as rare in the South African Red Data Book (Smithers, 1986). The blesbok *D. dorcas phillipsi* was one of the dominant antelope of the central plateau grasslands of South Africa, and although it too suffered a considerable decline, it has been widely translocated and is now common and widespread on farms and reserves.

Both subspecies are of medium size (males approx. 60 kg). The bontebok has a more richly purplish brown body, with more white on the legs than the blesbok, and the large rump-patch is pure white. Both have $2n = 38$ chromosomes (Wurster and Benirschke, 1968), and they are capable of interbreeding (Fabricius et al., 1989). The social structure is similar to that of many African plains antelope, with territorial males, groups of bachelor males, and female (nursery or harem) herds. Blesbok also form mixed aggregations, mainly in winter (Lynch, 1974), but David (1973) did not find this to be the case in the bontebok population studied.

Some adult males establish territories that are most consistently occupied and defended around the time of the autumn rut in blesbok (Lynch, 1974) but occupied year-round by bontebok (David, 1973). Territorial advertising involves visual display, defecation on a limited number of dung sites on which animals often lie, and scent marking. Both sexes have preorbital glands, larger in males than in females, and interdigital or pedal glands on the forefeet. Lynch (1974) describes the interdigital gland secretion of blesbok as a yellow, odorous substance that adheres to the hairs between the digits. Territorial males occasionally

pawed their dung patches three or four times, either with one foot or alternately with both, when they returned to the patches, before lying down on them. David (1973) never observed bontebok pawing the ground in any context. Lynch presumed that blesbok males pawed to demarcate the territory but considered this an unimportant function since so little of the secretion could be rubbed off. The secretion adhering to the hair was thought to be more significant in marking the animal itself. Bigalke et al. (1980) tested the reaction of a captive male bontebok to interdigital secretion and its two major chemical components. The test substances were offered at a food trough on gauze swabs or in an airstream. Mean length of feeding bouts was not significantly affected. The test elicited irregular brief bouts of sniffing at the scent sources, which also occurred during some control runs. There were, in addition, a few shows of aggression, but these were also performed fairly regularly outside the test situation. The limited response to interdigital secretion, and the fact that its chemical composition shows little individual variation, was taken to indicate that the scent may only be species-specific. Spread about an inhabited area, it would merely indicate use by conspecifics and would not elicit particular reactions.

In two previous studies (Burger et al., 1976, 1977) only nine of the constituents of the complex interdigital secretion of the bontebok, *Damaliscus dorcas dorcas*, could be identified, largely due to the complexity of the secretion and a lack of expertise in this field of research. The evolution of capillary column technology and the accumulation of mass spectral data on the long-chain compounds that are typically found in mammalian exocrine secretions prompted us to reinvestigate this secretion. In this communication we wish to report the confirmation of the structures proposed for the previously identified compounds and the identification of an additional 77 constituents of the interdigital secretions of the bontebok and the related subspecies, *D. d. phillipsi*, the blesbok.

METHODS AND MATERIALS

General

All Pyrex glassware and the porcelain mortar and pestle used in the preparation and handling of biological material and extracts were heated to 500°C in an annealing oven to remove any traces of organic material. Dichloromethane (Merck, Residue Analysis Grade) was used for extraction purposes. Syringes, stainless-steel needles, and other apparatus were cleaned with this solvent.

Analytical Methods

Gas chromatographic (GC) analyses were carried out with a Carlo Erba 5300 gas chromatograph equipped with a flame ionization detector, Grob split-

splitless injector, and the following glass capillary columns: (1) 50 m \times 0.3 mm, coated with PS-089 (polarity equivalent to SE-52) at a film thickness of 0.25 μm ; (2) 40 m \times 0.3 mm, coated with OV-1701-OH at a film thickness of 0.375 μm ; and (3) 40 m \times 0.25 mm coated with Superox 4 at a film thickness of 0.20 μm . All analyses were done with helium as carrier gas at a linear velocity of 28.6 cm/sec (column temperature 40°C). The flame ionization detector was operated at 280°C and the injector at 220°C. Samples were injected in the split mode, the analytes thermally focused on the column at ca. 30°C, and analyzed with a temperature program of 2°C/min from 40°C to 250°C (hold).

Electron impact (EI) mass spectra were recorded at 70 eV on a Carlo Erba QMD 1000 gas chromatograph—mass spectrometer (GC-MS system), with the columns and conditions described above. An interface temperature of 250°C was used. The ion source temperature was set at 180°C and the pressure in the source housing was ca. 2×10^{-5} torr at a column temperature of 40°C, decreasing to ca. 1×10^{-5} torr towards the end of the temperature program. Accurate mass measurements on synthetic reference compounds were done with a Varian MAT 311A high-resolution mass spectrometer and a Kratos DS 50 data system. ^1H and ^{13}C NMR spectra were recorded at 299.905 MHz and 75.42 MHz, respectively, at 25°C on a Varian VXR 300 NMR spectrometer.

Sample Collection and Preparation

Interdigital secretions were collected from bontebok captured in the Bontebok National Park, Swellendam, from a few blesbok captured in the Mountain Zebra National Park, Cradock, and from blesbok culled on the experimental farm of the University of Stellenbosch in the district of Heidelberg, Cape Province. Samples were taken from both sexes.

Surgical gauze squares (ca. 25 \times 25 mm) consisting of several layers of surgical gauze were extracted for 5 hr with dichloromethane (Residue Analysis Grade), dried in an atmosphere of purified N_2 (activated charcoal), and stored in glass-stoppered bottles. Interdigital secretion was collected by rolling a gauze square around the tip of dressing forceps, inserting the forceps with gauze into the interdigital cavity, and collecting the secretion by rotating the forceps while removing it from the cavity. The gauze pads with the yellowish secretion were stored at -30°C in glass bottles with Teflon-lined screw caps until used for analysis.

Initially the secretion was extracted from the gauze with a minimum of dichloromethane in the smallest possible Soxhlet extractor. The problem with this method is that the extract has to be concentrated for further work by the evaporation of a considerable volume of dichloromethane, possibly resulting in the loss of some of the more volatile constituents of the secretion. The solvent was evaporated by placing the vial containing the extract in a 2-liter glass

beaker covered with aluminum foil and the solvent vapor purged from the beaker with purified N₂ (purified by activated charcoal) without blowing the purge gas directly into the vial containing the extract. Depending on the concentration of the extract and the size of the vial, the removal of 5 ml of dichloromethane took up to 10 hr.

To avoid the use of large volumes of solvent, the following method was also used: A glass vial containing dichloromethane (<5 ml) and the gauze pads on which the secretions of two animals had been collected were centrifuged for 1 min at 1500 rpm to improve contact between the gauze and the small volume of solvent by compressing the gauze in the vial. The material in the vial was sonicated in the ultrasonic bath for 2 min, and the extract was separated from the gauze by centrifuging the gauze in a sintered glass filter insert suspended in a 5-ml Reacti-Vial. The extract was concentrated as described above. A comparison of this extract and an extract obtained by extracting any residual material from the gauze in a Soxhlet extractor showed that only negligible quantities of the carboxylic acids present in the secretion were left unextracted by this cold extraction method, and it was adopted for the extraction of the secretions of individual animals. Larger quantities of gauze were extracted in a Soxhlet extractor.

An interdigital gland was excised from the foreleg of a culled male bontebok. The gland, resembling a pouch with a depth of about 60 mm, a width of 20 mm and a wall thickness of about 3 mm, weighed 6.25 g. The few hairs on the inner glandular surface were removed with a razor blade and the gland was thoroughly washed with several quantities of pure dichloromethane, cut into small pieces, frozen with liquid N₂, and ground to a fine powder with a mortar and pestle cooled with liquid N₂. The glandular material was extracted with dichloromethane in a small Soxhlet extractor and the extract concentrated as described above. An extract of the interdigital gland of a blesbok was prepared in a similar manner.

Microbiological Experiments

The interdigital pouches of a male bontebok were swabbed with sterile gauze and the swabs placed into sterile McCartney bottles containing 0.89% saline solution. The samples were mixed thoroughly on a vortex mixer, after which 0.5 ml from each was enriched in Hutner's mineral salts medium (Bøvre and Hendriksen, 1976) containing 0.5% acetate as carbon source. The enrichments were incubated at 37°C for four days. The enriched cultures were vortexed and 10⁻¹–10⁻⁶ dilutions were spread-plated onto Hutner's mineral salts agar and incubated at 37°C for four days. Only two types of bacterial colonies were observed: white and yellow–orange. Several of these colonies were purified on Hutner's mineral salts agar, inoculated on Hutner's mineral salts agar

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slants, and incubated until visible growth was observed. These cultures were then subjected to phenotypic tests (Bøvre and Hendriksen, 1976; Cruickshank et al., 1975; Sneath et al., 1986). According to Sneath et al. (1986) the bacterial isolates could be classified as *Bacillus brevis* (white colony) and *Planococcus citreus* (yellow–orange colony).

The bacterial isolates were grown statically in 2 liters of liquid Hutner's mineral salts medium (Bøvre and Hendriksen, 1976) at 37°C for four days. After centrifugation, the supernatant containing the bacterial extracellular metabolites were decanted and concentrated from 2 liters to 15 ml under reduced pressure. The organic metabolic products were extracted with dichloromethane, but too little material was obtained for a satisfactory GC-MS analysis. From the bacteriological results, it could be seen that the bacterial isolates had a respirative metabolism requiring oxygen for rapid growth. The experiments were therefore repeated by supplementing Hutner's medium with 0.3% yeast extract and aerating the cultures during incubation. After dilution of the supernatants to facilitate proper extraction, the organic volatiles were extracted with dichloromethane in a liquid–liquid extractor. The dichloromethane extracts were carefully concentrated to 50 ml for GC-MS analysis by slow evaporation of the solvent at room temperature (see above). During concentration, the characteristic pleasant odor of (Z)-6-dodecen-4-olide was clearly detectable in the extract obtained from *P. citreus*.

Reference Compounds

Some of the compounds identified in the interdigital secretions of the bon-tebok and blesbok were available from previous research projects in this series, while others are commercially available from Merck (Darmstadt, Germany), Fluka (Buchs, Switzerland), Aldrich (Milwaukee, Wisconsin), Sigma (St. Louis, Missouri), and BASF (Ludwigshafen, Germany). The following compounds were synthesized during the present investigation. Boiling points are uncorrected.

4-Octanone. Condensation of butylmagnesium bromide with butanoyl chloride in tetrahydrofuran, hydrolysis of the resulting magnesium alcoholate with water, and conventional isolation procedures, gave 4-octanone (**11**) in 48% yield, bp 55–57°C (18 mm Hg). HR-MS: m/z M^+ = 128.121, calcd. for $C_8H_{16}O$ 128.120. 1H NMR ($CDCl_3$): δ = 2.39 (2H, t, $CH_3-CH_2-CH_2-CO-$, $^3J_{H3,H2}$ 7.4 Hz), 2.38 (2H, t, $-CO-CH_2-(CH_2)_2-$, $^3J_{H5,H6}$ 7.4 Hz), 1.2–1.7 (6H, m, $CH_3-CH_2-CH_2-CO-$, $-CO-CH_2-(CH_2)_2-CH_3$), 0.91 (6H, t, CH_3 , $^3J_{H1,H2} \approx ^3J_{H8,H7}$ 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ = 211.48 (s, C-4), 44.77 (t, C-3), 42.60 (t, C-5), 26.08 (t, C-6), 22.46 (t, C-7), 17.40 (t, C-2), 13.88 (q, C-8), 13.79 (q, C-1).

4-Nonanone. Condensation of pentylmagnesium bromide and butanoyl chloride according to the general procedure described for 4-octanone, gave

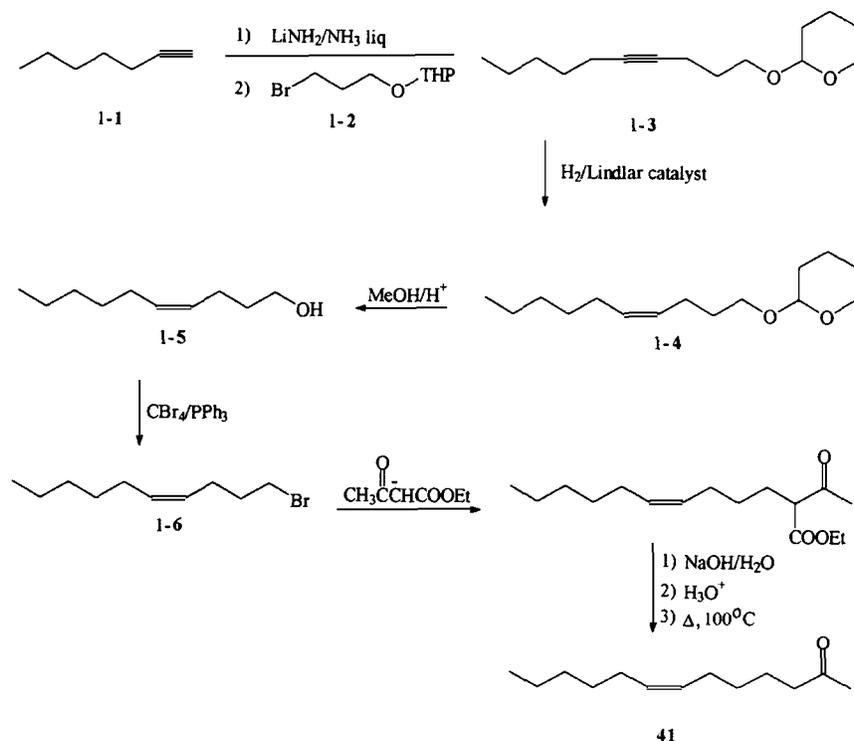
4-nonanone (**22**) in 50% yield, bp 75–77°C (20 mm Hg). HR-MS: m/z M^+ = 142.33, calcd. for $C_9H_{18}O$ 142.136. 1H NMR ($CDCl_3$): δ = 2.38 (4H, t, $—CH_2—CO—CH_2—$), 1.2–1.7 (8H, m, $CH_3—CH_2—CH_2—CO—CH_2—(CH_2)_3—CH_3$), 0.91 (6H, t, CH_3 , $^3J_{H1,H2} \approx ^3J_{H9,H8}$ 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ = 211.69 (s, C-4), 44.78 (t, C-3), 42.87 (t, C-5), 31.67 (t, C-7), 23.76 (t, C-6), 22.48 (t, C-8), 17.48 (t, C-2), 13.81 (q, C-9), 13.70 (q, C-1).

7-Octen-2-one. Base-catalyzed condensation of 5-bromo-1-pentene with ethyl acetoacetate (Marvel and Hager, 1944), saponification of the condensation product, and decarboxylation of the corresponding β -ketoacid (Johnson and Hager, 1944) gave 7-octen-2-one (**13**) in 47% yield; bp 56–58°C (20 mm Hg). HR-MS: m/z M^+ = 126.102, calcd. for $C_8H_{14}O$ 126.104. 1H NMR ($CDCl_3$): δ = 5.80 (1H, ddt, $CHaHb=CH—$, $^3J_{H7,H8a}$ 10.3 Hz, $^3J_{H7,H8b}$ 17.0 Hz), 5.00 (1H, ddt, $CHaHb=CH—$, $^3J_{H8b,H8a}$ 2 Hz, $^3J_{H8b,H7}$ 17.0 Hz, $^4J_{H8b,H6}$ 1.4 Hz), 4.97 (1H, ddt, $CHaHb=CH—$, $^2J_{H8b,H8a}$ 2 Hz, $^3J_{H8a,H7}$ 10.2 Hz), 2.43 (2H, t, $CH_3—CO—CH_2—$, $^3J_{H4,H3} \approx ^3J_{H4,H5}$ 7.4 Hz), 2.13 (3H, s, $CH_3—CO—$), 2.06 (2H, ddt, $CHaHb=CH—CH_2—$, $^3J_{H6,H5} \approx ^3J_{H6,H7}$ 7.4 Hz, $^4J_{H6,H8b}$ 1.4 Hz), 1.60 (2H, quint. $—CO—CH_2—CH_2—$, $^3J_{H4,H3} \approx ^3J_{H4,H5}$ 7.4 Hz), 1.39 (2H, quint. $—CO—(CH_2)_2—CH_2—$, $^3J_{H5,H4}$ 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ = 209.0 (s, C-2), 138.5 (d, C-7), 114.7 (t, C-8), 43.6 (t, C-3), 33.5 (t, C-6), 29.8 (q, C-1), 28.4 (t, C-5), 23.3 (t, C-4).

(Z)-7-Tridecen-2-one (4I). This was synthesized according to Scheme 1. 1-Heptyne (**1-1**) (20.22 g, 0.21 mol) was added dropwise to a suspension of lithium amide in liquid NH_3 , prepared by allowing a solution of lithium (1.59 g, 0.23 mol) to react with liquid NH_3 in the presence of a catalytic quantity of Fe(III) nitrate. 1-Bromo-3-tetrahydropyranyloxypropane (**1-2**) (43.91 g, 0.20 mol) was added to the suspension of lithium amide over a period of 20 min, the reaction mixture was stirred for a further 1.5 hr, diluted with ether (300 ml), and left overnight to allow evaporation of the liquid NH_3 . A mixture of NH_4Cl and $MgSO_4$ was added to the reaction mixture, the solids were removed by filtration, and the solvent evaporated to give 1-tetrahydropyranyloxy-4-decyne (**1-3**) in an undistilled yield of 91%. The product was used without purification for the preparation of the corresponding ethylenic compound (**1-4**).

A solution of the acetylenic compound (**1-3**) (43.12 g, 0.18 mol) in heptane/ethyl acetate (1:1, 106 ml) was partially hydrogenated in the presence of Lindlar catalyst (1.62 g, Fluka) and quinoline (1.5 ml) to give *(Z)*-1-tetrahydropyranyloxy-4-decene (**1-4**) in quantitative yield. The product was not distilled. MS: m/z (%) = 138(5), 110(3), 101(3), 95(3), 85(100), 84(22), 67(25), 55(33), 41(55).

Methanol was added slowly to a stirred suspension of *(Z)*-1-tetrahydropyranyloxy-4-decene (**1-4**) (43 g, 0.18 mol) in hydrochloric acid (2 M, 104 ml) until a homogenous solution was obtained. The solution was stirred at 40°C for 20 hr, and the largest part of the methanol was removed under reduced pressure.



SCHEME 1. Synthesis of (Z)-7-tridecen-2-one.

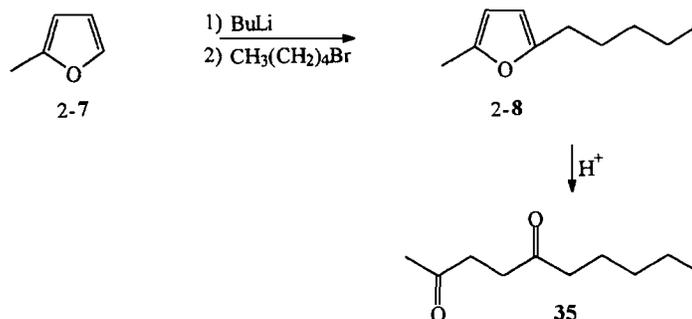
The residue was diluted with water (50 ml) and extracted with ether. The combined ether extracts were washed with NaHCO_3 solution, dried over MgSO_4 , and the solvent evaporated to give (Z)-4-decen-1-ol (1-5) in a yield of 96%. MS: m/z (%) = 138(5), 110(9), 95(24), 81(77), 67(77), 55(75), 41(100).

Tetrabromomethane (36.81 g, 0.111 mol) was added to a solution of (Z)-4-decen-1-ol (1-5) (17.32 g, 0.111 mol) and triphenylphosphine (32.62 g, 0.124 mol) in dry acetonitrile (60 ml) at 0°C . The reaction mixture was stirred for 6 hr at room temperature, diluted with pentane (116 ml) and cooled to 5°C to allow the triphenylphosphine oxide to crystallize. The solid material was removed by filtration. The residual triphenylphosphine oxide was diluted with pentane, cooled to -30°C , and the triphenylphosphine oxide was removed. Evaporation of the solvent under reduced pressure and distillation of the residue gave (Z)-1-bromo-4-decene (1-6) in a yield of 85%; bp $107\text{--}108^\circ\text{C}$ (5 mm Hg). MS: m/z (%) 220(26), 118(25), 192(1), 178(2), 176(2), 164(23), 162(23), 150(43), 148(43), 137(9), 135(20), 121(7), 119(5), 109(27), 107(13),

97(69), 95(30), 83(74), 81(77), 69(95), 67(76), 57(30), 55(100), 41(100), 39(96).

In a synthesis similar to that of 7-octen-2-one (**13**), the alkylation of ethyl acetoacetate (11.1 g, 85 mmol) with (*Z*)-1-bromo-4-decene (**1-6**) (20.71 g, 95 mmol), hydrolysis of the condensation product, and decarboxylation of the corresponding β -ketoacid gave (*Z*)-7-tridecen-2-one (**41**) in 43% yield; bp 132–134°C (4 mm Hg). HR-MS: m/z M^+ = 196.181, calcd. for $C_{13}H_{24}O$ 196.183. 1H NMR ($CDCl_3$): δ = 5.35 (4H, m, $-\text{CH}=\text{CH}-$, $^3J_{H7,H8}$ 10.8 Hz), 2.43 (2H, t, $-\text{CO}-\text{CH}_2-$, $^3J_{H4,H3} \approx ^3J_{H4,H5}$ 7.6 Hz), 2.13 (1H, s, $\text{CH}_3-\text{CO}-$), 2.02 (4H, dt, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$, $^3J_{H6,H7} \approx ^3J_{H6,H5} \approx ^3J_{H9,H8} \approx ^3J_{H9,H10}$ 7.5 Hz), 1.59 (2H, quint. $-\text{CO}-\text{CH}_2-\text{CH}_2-$, $^3J_{H4,H3} \approx ^3J_{H4,H5}$ 7.6 Hz), 1.2–1.4 [8H, m, $-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-(\text{CH}_2)_3-$], 0.89 (2H, t, CH_3-CH_2- , $^3J_{H13,H12}$ 6.9 Hz). ^{13}C NMR ($CDCl_3$): δ = 208.5 (s, C-2), 130.4 (d, C-8), 129.1 (d, C-7), 43.7 (t, C-3), 31.6 (t, C-11), 29.8 (q, C-1), 29.4 (t, C-5*), 29.3 (t, C-10*), 27.2 (t, C-9), 26.9 (t, C-6), 23.5 (t, C-4), 22.6 (t, C-12), 14.1 (q, C-13) (*assignments interchangeable).

Decane-2,5-dione (**35**). This was synthesized according to Scheme 2. A solution of butyl lithium (0.30 mol) in tetrahydrofuran (140 ml) was cooled to -15°C and treated with 2-methylfuran (**2-7**). The resulting product, 2-lithio-5-methylfuran, was alkylated (Ramanathan and Levine, 1962; Büchi and Wüest, 1996) with 1-bromopentane (4.53 g, 0.30 mol) in tetrahydrofuran (48 ml) at -15°C . The reaction mixture was stirred at this temperature for 1 hr, left overnight at room temperature, and poured on ice. Conventional work-up procedures gave 5-methyl-2-pentylfuran (**2-8**) in a yield of 77%. 1H NMR ($CDCl_3$): δ = 5.59 (2H, d, $=\text{CH}-\text{CH}=\text{CH}$), 2.08 (3H, s, CH_3), 2.54 [2H, t, $-\text{CH}_2-(\text{CH}_2)_3-\text{CH}_3$], ca. 1.28 [6H, m, $-\text{CH}_2-(\text{CH}_2)_3-\text{CH}_3$], 0.98 [3H, t, $-\text{CH}_2-(\text{CH}_2)_3-\text{CH}_3$]. The product was used without purification for the preparation of decane-2,5-dione, in the following procedure.



SCHEME 2. Synthesis of decane-2,5-dione.

Dilute H_2SO_4 (1%, 19 ml) was added to a solution of 5-Methyl-2-pentylfuran (2-8) (35 g, 0.23 mol) in acetic acid (36 ml) and the reaction mixture was stirred at an oil bath temperature of 120°C for 3 hr (Büchi and Wüest, 1966). The reaction mixture was cooled to room temperature and poured into water. Isolation of the organic product in the normal manner gave a brown oil, which was fractionated to give decane-2,5-dione (35) in a yield of 78%; bp $77\text{--}78^\circ\text{C}$ (0.1 mm Hg). HR-MS: m/z M^+ = 170.130, calcd. for $\text{C}_{10}\text{H}_{18}\text{O}_2$ 170.131. ^1H NMR (CDCl_3): δ = 2.69 (4H, m, $\text{CO}-\text{CH}_2-\text{CH}_2-\text{CO}$), 2.45 [2H, t, $\text{CO}-\text{CH}_2-(\text{CH}_2)_3-\text{CH}_3$, $^3J_{\text{H}_6,\text{H}_7}$ 7.5 Hz], 2.18 (3H, s, CH_3-CO), 1.58 [2H, quint. $\text{CO}-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_2-$, $^3J_{\text{H}_7,\text{H}_6} \approx ^3J_{\text{H}_7,\text{H}_8}$ 7.4 Hz], 1.2–1.4 [4H, m, $\text{CO}-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$], 0.89 [3H, t, $\text{CO}-(\text{CH}_2)_4-\text{CH}_3$, $^3J_{\text{H}_{10},\text{H}_9}$ 6.9 Hz] ^{13}C NMR (CDCl_3): δ = 209.52 (s, C-5), 207.13 (s, C-2), 42.79 (t, C-6), 36.10 and 36.93 (t, C-3, C-4, assignment ambiguous), 31.42 (t, C-8), 29.89 (q, C-1), 23.57 (t, C-7), 22.48 (t, C-9), 13.91 (q, C-10).

Isopropyl Hexadecanoate (52). This was prepared by esterification of isopropyl alcohol and hexadecanoic acid with perchloric acid as catalyst, benzene as solvent, and azeotropic water removal. HR-MS: m/z M^+ = 298.286, calcd. for $\text{C}_{19}\text{H}_{38}\text{O}_2$ 298.287. ^{13}C NMR (CDCl_3) δ = 173.4 (s, C-1), 67.3 (d, C-1'), 34.8 (t, C-2), 32.0 (t, C-14), 29.2–29.7 (10t, C-4–C-13), 25.1 (t, C-3), 22.7 (t, C-15), 21.9 (2q, C-2'), 14.1 (q, C-16).

3-Propylphenol (31). This was prepared according to the method of Carvalho and Sargent (1984) with a yield of 52%; bp 114°C (20 mm Hg). HR-MS: m/z M^+ = 136.088, calcd. for $\text{C}_9\text{H}_{12}\text{O}$ 136.089. ^1H NMR (CDCl_3): δ = 7.12 (1H, m, $=\text{CR}-\text{CH}=\text{CH}-$, $^3J_{\text{H}_5,\text{H}_6}$ 7.7 Hz, $^5J_{\text{H}_5,\text{H}_2}$ 0.85 Hz), 6.74 (1H, m, $=\text{CR}-\text{CH}=\text{CH}-$, $^3J_{\text{H}_4,\text{H}_5}$ 7.6 Hz, $^4J_{\text{H}_4,\text{H}_6}$ 1.1 Hz, $^4J_{\text{H}_4,\text{H}_2}$ 1.6 Hz), 6.66 (1H, m, $-\text{CH}=\text{CR}-$), 6.65 (1H, m, $\text{OH}-\text{C}=\text{CH}-$, $^4J_{\text{H}_6,\text{H}_2}$ -2.7 Hz), 5.6 (1H, s, OH), 2.51 (2H, t, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$, $^3J_{\text{H}_{1'},\text{H}_{2'}}$ 7.6 Hz), 1.60 (2H, m, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$, $^3J_{\text{H}_{2'},\text{H}_{1'}}$, $^3J_{\text{H}_{2'},\text{H}_{3'}}$, 7.5 Hz), 0.91 (3H, t, CH_3-). ^{13}C NMR (CDCl_3): δ = 155.31 (s, C-1), 129.44 (d, C-5), 121.20 (d, C-4), 115.59 (d, C-2), 112.71 (d, C-6), 144.76 (s, C-3), 37.95 (t, $\text{CH}_2-\text{CH}_2-\text{CH}_3$), 24.35 (t, $\text{CH}_2-\text{CH}_2-\text{CH}_3$), 13.79 (q, $\text{CH}_2-\text{CH}_2-\text{CH}_3$).

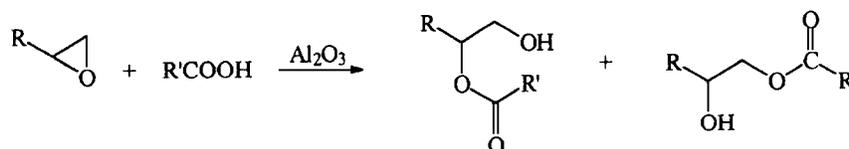
2-[(E)-4-Heptenyl]pyridine (37). 2-Picoline (10.99 g, 118 mmol) was added to a solution of phenyllithium (125 mmol) in ether (100 ml), and the mixture was stirred for 30 min at room temperature. (*Z*)-1-Chloro-3-hexene (7 g, 59 mmol) was added dropwise to the resulting solution of picolyl-lithium, and the reaction mixture was refluxed for 4 hr. A solution of ammonium chloride in dilute ammonia was added and the organic material isolated in the usual manner, with ether as a solvent. Fractionation of the organic product gave a mixture of isomeric pyridine derivatives in a yield of 70%, containing 7% 2-[(*Z*)-4-heptenyl]pyridine and 93% 2-[(*E*)-4-heptenyl]pyridine (GC); bp $82\text{--}86^\circ\text{C}$ (5 mm Hg). HR-MS: m/z M^+ = 175.138, calcd. for $\text{C}_{12}\text{H}_{17}\text{N}$ 175.136. ^1H NMR (CDCl_3): δ = 8.5 (1H, ddd, $^5J_{\text{H}_6,\text{H}_3}$ 0.9 Hz,

$^3J_{H_6,H_5}$ 5.0 Hz, $^4J_{H_6,H_4}$ 1.8 Hz), 7.58 (1H, ddd, $^3J_{H_4,H_5}$ 7.7 Hz, $^3J_{H_4,H_3}$ 7.7, $^4J_{H_4,H_6}$ 1.8 Hz), 7.13 (1H, m, $^3J_{H_3,H_4}$ 7.7 Hz, $^4J_{H_3,H_5}$ 1.3 Hz, $^5J_{H_3,H_6}$ 0.9 Hz), 7.11 (1H, m, $^3J_{H_5,H_6}$ 5.0 Hz, $^3J_{H_5,H_4}$ 7.7 Hz, $^4J_{H_5,H_3}$ 1.3 Hz), 5.38 (2H, m, —CH=CH—, $^3J_{H_4',H_3'}$ 8.1 Hz, $^3J_{H_4',H_5'}$ 15.7 Hz, $^4J_{H_4',H_6'}$ 1.1 Hz, $^3J_{H_5',H_6'}$ 6.3 Hz), 2.80 [2H, t, CH₂—(CH₂)₂—CH=CH—, $^3J_{H_1',H_2'}$, 7.8 Hz], 2.09 [2H, m, —(CH₂)₂—CH₂—CH=CH—], 1.99 (2H, quint, —CH₂—CH₂—CH=CH—CH₂—CH₃, $^3J_{H_2',H_1'}$ ≈ $^3J_{H_2',H_3'}$ 7.9 Hz), 1.79 (2H, m, —CH₂—CH₃, $^3J_{H_6',H_7'}$ 7.5 Hz), 0.95 (3H, t, —CH₂—CH₃, $^3J_{H_7',H_6'}$ 7.5 Hz). ¹³C NMR (CDCl₃): δ = 162.21 (s, C-2), 149.15 (d, C-6), 136.22 (d, C-4), 132.17 (d, C-4'), 128.53 (d, C-5'), 122.73 (d, C-3*), 120.91 (d, C-5*), 37.89 (t, C-2'), 29.91 (t, C-1'), 26.82 (t, C-3'), 20.57 (t, C-6'), 14.34 (q, C-7'). (*assignments interchangeable).

2-Heptanoylpyridine (42). A solution of 2-cyanopyridine (25.4 g, 0.24 mol) in ether (175 ml) was added over a period of 10 min to hexylmagnesium bromide (0.30 mol) in ether (100 ml) and the reaction mixture refluxed for 4 hr (Shaw et al., 1978). The practically black reaction mixture was carefully treated with cold water (25 ml) followed by dilute sulfuric acid (2.5 M, 300 ml) to give an orange solution. The ether was separated from the acidic aqueous phase containing most of the product and extracted twice with dilute sulfuric acid (1 M). The combined aqueous phases were heated on a steam bath for 15 min, cooled in an ice bath, and neutralized with Na₂CO₃. Extraction with ether and the usual isolation procedures gave 2-heptanoylpyridine (**42**) in a yield of 60%; bp 114–116°C (1 mm Hg). HR-MS: m/z M⁺ = 191.131, calcd. for C₁₂H₁₇NO 191.131. ¹H NMR (CDCl₃): δ = 8.68 (1H, ddd, $^3J_{H_6,H_5}$ 4.8 Hz, $^4J_{H_6,H_4}$ 1.7 Hz, $^5J_{H_6,H_3}$ 0.9 Hz), 8.04 (1H, ddd, $^3J_{H_3,H_4}$ 7.8 Hz, $^4J_{H_3,H_5}$ ≈ $^5J_{H_3,H_6}$ 1.1 Hz), 7.82 (1H, ddd, $^3J_{H_4,H_5}$ = 6.0 Hz, $^3J_{H_4,H_3}$ ≈ 7.5 Hz, $^4J_{H_4,H_6}$ 1.7 Hz), 7.46 (1H, ddd, $^3J_{H_5,H_4}$ 6.0 Hz, $^3J_{H_5,H_6}$ 4.8 Hz, $^4J_{H_5,H_3}$ 1.3 Hz), 3.22 (2H, t, —CO—CH₂—CH₂—), 1.74 (2H, quint., —CO—CH₂—CH₂—CH₂—), 1.4–1.2 [6H, m, —(CH₂)₃—CH₃], 0.89 [3H, t, —(CH₂)₃—CH₃]. ¹³C NMR (CDCl₃): δ = 202.13 (s, CO), 153.73 (s, C-2), 148.97 (d, C-6), 136.82 (d, C-4), 126.93 (d, C-5), 121.75 (d, C-3), 37.76 (t, CO—CH₂—CH₂—), 31.78 (t, —CH₂—CH₂—CH₃), 29.09 [t, CO—(CH₂)₂—CH₂—], 24.03 (t, CO—CH₂—CH₂) 22.61 (t, CH₂—CH₃), 14.08 (q, —CH₃).

1-Hydroxyalk-2-yl and 2-Hydroxyalk-1-yl Carboxylic Acid Esters. These were prepared by the Al₂O₃-catalyzed reaction of long-chain 1,2-epoxyalkanes with the appropriate carboxylic acids according to the general reaction scheme shown in Scheme 3.

A solution of butanoic acid (4.08 g, 46 mmol) in dry ether (10 ml) was added to Al₂O₃ (84.71 g, neutral, activity I) in dry ether (90 ml). The suspension was stirred for 15 min, treated with a solution of 1,2-epoxyoctadecane (3.04 g, 11 mmol) in ether (30 ml), and the reaction mixture stirred for a further 3 hr. After addition of CH₃OH (100 ml), the reaction mixture was stirred for 2 hr,



SCHEME 3. Synthesis of hydroxyesters.

the Al_2O_3 filtered off, and the filtrate concentrated on a rotary evaporator. The residue was taken up in ether and the solution washed with NaHCO_3 solution and water. Normal work-up methods gave a mixture of isomeric hydroxyesters in a yield of 76%. According to GC analysis on an apolar capillary column, the product contained 63% of 2-hydroxyoctadec-1-yl butanoate (**65**) and 37% of 1-hydroxyoctadec-2-yl butanoate (**64**). HR-MS (mixture of isomers): m/z $M^+ = 356.328$, calcd. for $\text{C}_{22}\text{H}_{44}\text{O}_3$ 356.329. NMR data were obtained from an analysis of the ^1H and ^{13}C spectra of the mixture of isomers. *Major component (65)*: ^1H NMR (CDCl_3): $\delta = 4.15$ (1H, dd, $\text{CHH}-\text{O}$, $^2J_{\text{H1}'\text{B},\text{H1}'\text{A}} -11.4$ Hz, $^3J_{\text{H1}'\text{B},\text{H2}'}$ 3.3 Hz), 3.96 (1H, dd, $\text{CHH}-\text{O}$, $^2J_{\text{H1}'\text{A},\text{H1}'\text{B}} -11.4$ Hz, $^3J_{\text{H1}'\text{A},\text{H2}'}$ 7.3 Hz), 3.84 (1H, m, $-\text{CH}-\text{OH}$, $^3J_{\text{H2}',\text{H3}'}$ 6.3 Hz), 2.34 (2H, t, $-\text{CH}_2-\text{CO}$, $^3J_{\text{H2},\text{H3}}$ 7.5 Hz), 1.89 (1H, s, OH), 1.67 (2H, m, CH_3-CH_2 , $^3J_{\text{H3},\text{H4}} \approx ^3J_{\text{H3},\text{H2}}$ 7.5 Hz), 1.2–1.6 [30H, m, $\text{CH}_3-(\text{CH}_2)_{15}$], 0.96 [3H, t, $\text{CH}_3-(\text{CH}_2)_2$, $^3J_{\text{H4},\text{H3}}$ 7.5 Hz], 0.88 [3H, t, $\text{CH}_3-(\text{CH}_2)_{16}$, $^3J_{\text{H18}',\text{H17}'}$ 7.0 Hz]. ^{13}C NMR (CDCl_3): $\delta = 173.87$ (s, C-1), 70.09 (d, C-2'), 68.55 (t, C-1'), 36.10 (t, C-2), 33.38 (t, C-3'), 31.94 (t, C-16'), 29.3–29.7 (11t, C-5'–C15'), 25.39 (t, C-4'), 22.70 (t, C-17'), 18.46 (t, C-3), 14.12 (q, C-18'), 13.67 (q, C-4). *Minor component (64)*: ^1H NMR (CDCl_3): $\delta = 4.92$ (1H, m, $\text{CH}-\text{O}$, $^3J_{\text{H1}',\text{H2}'}$ 6.3 Hz), 3.72 (1H, dd, $\text{CHH}-\text{OH}$, $^2J_{\text{H,H}} -12.0$ Hz, $^3J_{\text{H,H1}'}$ 3.3 Hz), 3.62 (1H, dd, $\text{CHH}-\text{OH}$, $^2J_{\text{H,H}} -12.0$ Hz, $^3J_{\text{H,H1}'}$ 6.3 Hz), 2.34 (2H, t, $-\text{CH}_2-\text{CO}$, $^3J_{\text{H2},\text{H3}}$ 7.5 Hz), 1.89 (1H, s, OH), 1.67 (2H, m, CH_3-CH_2 , $^3J_{\text{H3},\text{H4}} \approx ^3J_{\text{H3},\text{H2}}$ 7.5 Hz), 1.2–1.6 [30H, m, $\text{CH}_3-(\text{CH}_2)_{15}$], 0.96 [3H, t, $\text{CH}_3-(\text{CH}_2)_2$, $^3J_{\text{H4},\text{H3}}$ 7.5 Hz], 0.88 [3H, t, $\text{CH}_3-(\text{CH}_2)_{15}$, $^3J_{\text{H17}',\text{H16}'}$ 7.0 Hz]. ^{13}C NMR (CDCl_3): $\delta = 173.87$ (s, C-1), 75.49 (d, C-1'), 64.99 (t, CH_2OH), 36.44 (t, C-2), 31.94 (t, C-15'), 30.55 (t, C-2'), 29.3–29.7 (11t, C-4'–C-14'), 25.38 (t, C-3'), 22.70 (t, C-16'), 18.46 (t, C-3), 14.12 (q, C-17'), 13.67 (q, C-4).

Treatment of 1,2-epoxyoctadecane (3.04 g, 11 mmol) with 2-methyl propanoic acid (4.08 g, 46 mmol) in ether and in the presence of Al_2O_3 , as described in the foregoing synthesis of the hydroxyesters (**64** and **65**) gave 2.66 g (66%) of a mixture of 71% of 2-hydroxyoctadec-1-yl 2-methylpropanoate (**63**) and 29% of 1-hydroxyoctadec-2-yl 2-methyl propanoate. HR-MS (mixture of isomers): m/z $M^+ = 356.332$, calcd. for $\text{C}_{22}\text{H}_{44}\text{O}_3$ 356.329. *Major component (63)*: ^1H NMR (CDCl_3): $\delta = 4.14$ (1H, dd, $\text{CHH}-\text{O}$, $^2J_{\text{H1}'\text{B},\text{H1}'\text{A}} -11.3$ Hz, $^3J_{\text{H1}'\text{B},\text{H2}'}$ 3.2 Hz), 3.97 (1H, dd, $\text{CHH}-\text{O}$, $^2J_{\text{H1}'\text{A},\text{H1}'\text{B}} -11.4$ Hz, $^3J_{\text{H1}'\text{A},\text{H2}'}$ 7.2 Hz), 3.83 (1H, m, $^3J_{\text{H2}',\text{H3}'}$ 6.4 Hz), 2.60 (1H, m, $(\text{CH}_3)_2-\text{CH}-\text{CO}$,

$^3J_{H_2,H_3} \approx ^3J_{H_2,CH_3}$ 14 Hz), 2.00 (1H, s, OH), 1.2–1.6 [30H, m, $CH_3-(CH_2)_{15}$], 1.85 [6H, m, $(CH_3)_2-CH$, $^4J_{H_3,CH_3} -6.8$ Hz, $^3J_{H_3,H_2} \approx ^3J_{CH_3,H_2}$ 13.6 Hz], 0.88 [3H, t, $CH_3-(CH_2)_{16}$, $^3J_{H_{18'},H_{17'}}$ 6.7 Hz]. ^{13}C NMR ($CDCl_3$): δ = 177.47 (s, C-1), 70.11 (d, C-2'), 68.58 (t, C-1'), 33.95 (d, C-2), 33.37 (t, C-3'), 31.95 (t, C-16'), 29.3–29.7 (11t, C-5'–C-15'), 25.39 (t, C-4'), 22.71 (t, C-17'), 19.01 (q, C-3), 14.12 (q, C-18'). *Minor component* (1-hydroxyoctadec-2-yl 2-methylpropanoate): 1H NMR ($CDCl_3$): δ = 4.89 (1H, m, $CH-O$, $^3J_{H_{1'},H_{2'}}$ 6.4 Hz), 3.75 (1H, dd, $CHH-OH$, $^3J_{H,H} -11.9$ Hz, $^3J_{H,H_{1'}}$ 3.4 Hz), 3.64 (1H, dd, $CHH-OH$, $^2J_{H,H} -11.9$ Hz, $^3J_{H,H_{1'}}$ 6.2 Hz), 2.58 [1H, m, $(CH_3)_2-CH-CO$, $^3J_{H_2,H_3} \approx ^3J_{H_2,CH_3}$ 14.0 Hz], 2.00 (1H, s, OH), 1.85 [6H, t, $(CH_3)_2-CH$, $^4J_{H_3,CH_3} -6.8$ Hz, $^3J_{H_3,H_2} \approx ^3J_{CH_3,H_2}$ 13.6 Hz], 1.2–1.6 [30H, m, $CH_3-(CH_2)_{15}$], 0.88 [3H, t, $CH_3-(CH_2)_{15}$, $^3J_{H_{17'},H_{16'}}$ 6.7 Hz]. ^{13}C NMR ($CDCl_3$): δ = 177.47 (s, C-1), 75.40 (d, C-1'), 65.03 (t, CH_2OH), 34.18 (d, C-2), 31.91 (t, C-15'), 30.53 (t, C-2'), 29.3–29.7 (11t, C-4'–C-14'), 25.36 (t, C-3'), 22.69 (t, C-16'), 19.03 (q, C-3), 14.12 (q, C-17').

A mixture of 1-hydroxyoctadec-2-yl pentanoate (**66**) (32%) and 2-hydroxyoctadec-1-yl pentanoate (**67**) (68%) was prepared from 1,2-epoxyoctadecane and pentanoic acid as described above. HR-MS (mixture of isomers): m/z M^+ = 370.347, calcd. for $C_{23}H_{46}O_3$ 370.345.

The reaction of 1,2-epoxynonadecane (3.0 g, 11 mmol) and butanoic acid (3.84 g, 44 mmol) in ether with Al_2O_3 as catalyst, gave (2.92 g, 74%) of a mixture of 2-hydroxynonadec-1-yl butanoate (**68**) (67%) and 1-hydroxynonadec-2-yl butanoate (33%). HR-MS (mixture of isomers): m/z M^+ 370.345, calcd. for $C_{23}H_{46}O_3$ 370.345. *Major component* (**68**): 1H NMR ($CDCl_3$): δ = 4.16 (1H, dd, $CHH-O$, $^2J_{H_{1'B},H_{1'A}} -11.3$ Hz, $^3J_{H_{1'B},H_{2'}}$ 3.0 Hz), 3.96 (1H, dd, $CHH-O$, $^2J_{H_{1'A},H_{1'B}} -11.4$ Hz, $^3J_{H_{1'A},H_{2'}}$ 7.4 Hz), 3.85 (1H, m, $-CH-OH$, $^3J_{H_{2'},H_{3'}}$ 6.2 Hz), 2.34 (2H, t, $-CH_2-CO$, $^3J_{H_2,H_3}$ 7.4 Hz), 1.73 (1H, s, OH), 1.67 (2H, m, CH_3-CH_2 , $^3J_{H_3,H_4} \approx ^3J_{H_3,H_2}$ 7.4 Hz), 1.2–1.6 [32H, m, $CH_3-(CH_2)_{16}$], 0.96 [3H, t, $CH_3-(CH_2)_2$, $^3J_{H_4,H_3}$ 7.4 Hz], 0.88 [3H, t, $CH_3(CH_2)_{16}$, $^3J_{H_{19'},H_{18'}}$ 6.7 Hz]. ^{13}C NMR ($CDCl_3$): δ = 177.35 (s, C-1), 70.10 (d, C-2'), 68.56 (t, C-1'), 36.10 (t, C-2), 33.38 (t, C-3'), 31.94 (t, C-17'), 29.3–29.7 (12t, C-5'–C-16'), 25.38 (t, C-4'), 22.71 (t, C-18'), 18.46 (t, C-3), 14.12 (q, C-19'), 13.67 (q, C-4). *Minor component* (1-hydroxynonadec-2-yl butanoate): 1H NMR ($CDCl_3$): δ = 4.92 (1H, m, $CH-O$, $^3J_{H_{1'},H_{2'}}$ 6.8 Hz), 3.72 (1H, dd, $CHH-OH$, $^2J_{H,H} -12.0$ Hz, $^3J_{H,H_{1'}}$ 3.0 Hz), 3.62 (1H, dd, $CHH-OH$, $^2J_{H,H} -12.0$ Hz, $^3J_{H,H_{1'}}$ 6.3 Hz), 2.33 (2H, t, $-CH_2-CO$, $^3J_{H_2,H_3}$ 7.4 Hz), 1.73 (1H, s, OH), 1.67 (2H, m, CH_3-CH_2 , $^3J_{H_3,H_4} \approx ^3J_{H_3,H_2}$ 7.4 Hz), 1.2–1.6 [32H, m, $CH_3-(CH_2)_{16}$], 0.96 [3H, t, $CH_3-(CH_2)_2$, $^3J_{H_4,H_3}$ 7.4 Hz], 0.88 [3H, t, $CH_3-(CH_2)_{16}$, $^3J_{H_{18'},H_{17'}}$ 6.7 Hz]. ^{13}C NMR ($CDCl_3$): δ = 177.35 (s, C-1), 75.43 (d, C-1'), 64.93 (t, CH_2OH), 36.30 (t, C-2), 31.94 (t, C-16'), 30.55 (t, C-2'), 29.3–29.7 (12t, C-4'–C-15'), 25.38 (t, C-3'), 22.71 (t, C-17'), 18.46 (t, C-3), 14.12 (q, C-18'), 13.67 (q, C-4).

RESULTS AND DISCUSSION

A typical total ion chromatogram of an extract of the interdigital secretion of a male bontebok is shown in Figure 1. The secretions of male and female members of both subspecies were qualitatively identical, regardless of the habitat of the animals. Many of the constituents of the interdigital secretions were tentatively identified by comparison of their low-resolution electron impact mass spectra with those in NBS and Wiley mass spectra libraries. Further diagnostic information was obtained from the chemical ionization mass spectra of some of the constituents. The electron impact mass spectra of certain long-chain compound classes contain so little information in the higher mass ranges that it is impossible to detect certain types of chain branching. The structures of the majority of the compounds identified were therefore confirmed by gas chromatographic comparison (coelution) with authentic commercially available or synthesized material. Some compound classes were represented by several members of the respective homologous series of compounds, in which case representative compounds only were synthesized for comparison. The compounds identified in the interdigital secretions are listed in Table 1 together with the relevant mass spectral data, information on the analytical techniques employed in their identification, and some quantitative data on the major constituents present in the secretions in quantities higher than 1 ng/animal.

Members of the homologous series of alkanes, 1-alkanols, 2-alkanols, alkanals, 2-, 3- and 4-alkanones, and alkanic acids were all found to have unbranched structures. Of these constituents (*Z*)-3-penten-2-ol, 2-nonanol, pentanal, (*E*)-2-hexenal, (*E*)-2-nonenal, (2*Z*,4*Z*)-2,4-heptadienal, and (2*Z*,4*Z*)-2,4-decadienal were detected and identified with a capillary column coated with OV-1701-OH. 2-Decanone was detected by using a capillary column coated with Superox 4. The secretions contain several terpenoid compounds, of which squalene had previously been identified in the dorsal secretion of the springbok, *Antidorcas marsupialis* (Burger et al., 1981). In addition to the diketone, undecane-2,5-dione, identified in the secretion of the bontebok in a previous study (Burger et al., 1976), decane-2,5-dione was found in the secretions in the present study.

The interdigital secretions of the two subspecies also contain various long-chain hydroxyesters of the type previously identified in the dorsal secretion of the springbok, *Antidorcas marsupialis* (Burger et al., 1981) and in the pre-orbital secretion of the grysbok, *Raphicerus melanotis* (Burger et al., 1996), and steenbok, *R. campestris* (Burger et al., unpublished results). So far no information is available on the stereochemistry and possible function of long-chain hydroxyesters in the secretions in which they have been identified. These aspects have not been investigated in the present study and will be subjected to further investigation. Phenol, 3-methylphenol, 3-ethylphenol, and 3-propylphenol are responsible for the faint but distinctive cresollike smell of the secretions

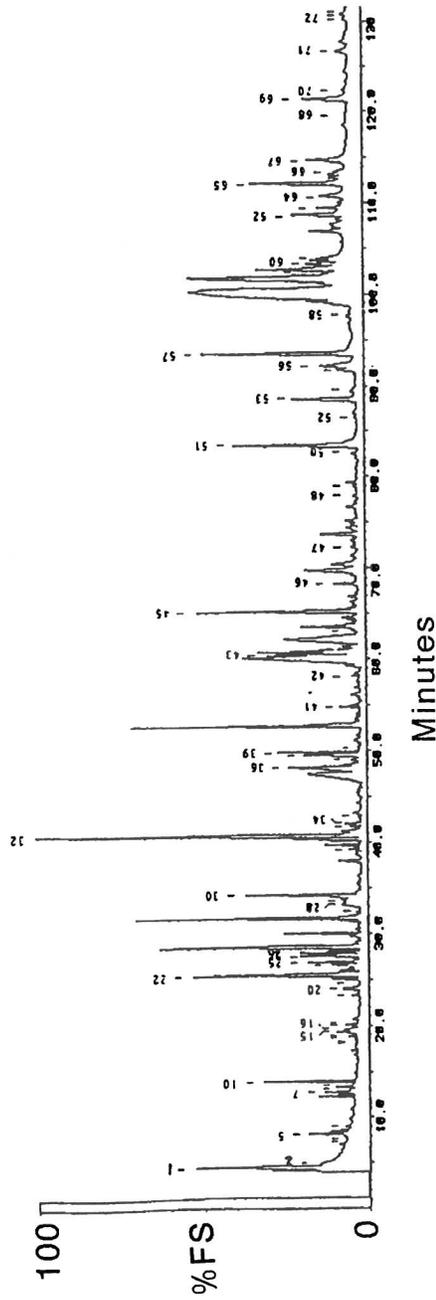


FIG. 1. Total ion chromatogram of an extract of the interdigital secretion of a male bontebok, *Damaliscus dorcas dorcas*. Gas chromatographic conditions as given in the experimental part.

TABLE 1. COMPOUNDS IDENTIFIED IN INTERDIGITAL SECRETION OF BONTÉBOK AND BLESBOK

No. in Figure 1	Compounds	Quantity (ng/animal) ^a				EI mass spectral data [m/z (%)]
		Bontébok		Blesbok		
		Male	Female	Male	Female	
4	Alkanes Octane ^{b,c}					114(7), 85(40), 71(30), 57(44), 43(100), 41(40)
10	Nonane ^{b,c}	35	2	1	1	128(8), 99(8), 85(35), 71(28), 57(87), 43(100), 41(55)
40	Tetradecane ^{b,c}			3	1	198(4), 155(1), 141(3), 127(3), 113(5), 99(10), 85(36), 71(55), 57(100), 43(81), 41(50)
44	Hexadecane ^{b,c}				7	226(4), 169(1), 155(1), 141(3), 127(3), 113(5), 99(10), 85(36), 71(55), 57(100), 43(81), 41(55)
21	Terpenoids γ -Terpinene ^{b,c}					136(30), 121(32), 105(11), 93(100), 91(56), 79(27), 77(44), 43(20), 41(24)
26	Linalool ^{b,c}	33	2			136(18), 121(25), 93(100), 91(41), 80(21), 79(30), 77(27), 71(35), 69(38), 67(28), 55(24), 43(43), 41(72)
28	<i>p</i> -Cymen- α -ol ^{b,c}	1	3	13	7	150(10), 135(79), 91(28), 65(10), 43(100)
30	α -Terpineol ^{b,c,d}	80	14	66	8	136(45), 121(45), 107(7), 93(60), 81(45), 73(28), 67(26), 60(35), 59(100), 43(67)
72	Squalene ^{b,c}					175(1), 161(1), 149(4), 136(6), 121(8), 107(6), 95(12), 81(46), 69(100), 55(4), 41(23)
6	Alcohols (<i>Z</i>)-3-Penten-2-ol ^{b,c,e}					86(6), 71(100), 58(4), 53(15), 45(36), 43(90), 41(46)
20	2-Hexanol ^{b,c} 1-Heptanol ^{b,c}	5				87(6), 71(5), 69(9), 45(100), 43(20), 41(18) 98(2), 83(5), 70(95), 56(100), 41(89)

	2-Nonanol ^{b,c,e}					129(3), 98(4), 69(8), 57(18), 56(8), 55(5), 45(100), 43(25), 41(14)
49	1-Hexadecanol ^{b,c}					196(1), 168(1), 154(1), 140(2), 125(5), 111(18), 97(50), 83(70), 69(75), 57(70), 55(100), 43(85), 41(70)
54	1-Octadecanol ^{b,c}					111(18), 97(33), 83(61), 69(38), 57(73), 55(67), 43(94), 41(100)
58	1-Icosanol ^{b,c}					167(3), 153(2), 139(4), 125(10), 111(24), 97(46), 83(57), 69(55), 57(88), 55(70), 43(100), 41(70)
61	1-Henicosanol ^{b,c}	18	5			125(18), 111(35), 97(75), 83(85), 69(75), 57(100), 55(99), 43(90), 41(85)
62	1-Docosanol ^{b,c}	55	14	8	19	181(1), 167(2), 153(3), 139(5), 125(16), 111(37), 97(65), 83(76), 69(60), 57(70), 55(75), 43(100), 41(69)
69	1-Tetracosanol ^{b,c}	82	6	17	33	181(2), 167(4), 153(4), 139(7), 125(5), 111(29), 97(63), 83(76), 69(59), 57(78), 55(75), 43(100), 41(65)
75	1-Hexacosanol ^{b,c}					181(4), 167(5), 153(5), 139(6), 125(14), 111(33), 97(48), 83(55), 69(48), 57(85), 55(65), 43(100), 41(61)
	Aldehydes					
	Pentanal ^{b,c,e}					86(12), 71(5), 58(33), 57(25), 44(100), 43(92), 42(18), 41(50)
5	Hexanal ^{b,c,f}	13	11		7	82(14), 72(23), 67(13), 57(63), 56(89), 44(100), 43(65), 41(95)
	(E)-2-Hexenal ^{b,c,e}					98(18), 83(43), 80(13), 70(18), 69(49), 57(40), 55(74), 41(100)
8	Heptanal ^{b,c,f}	11	5	4	5	96(10), 86(15), 81(20), 71(24), 70(90), 57(62), 55(65), 44(100), 43(78), 42(60), 41(94)
15	(E)-2-Heptenal ^{b,c,f}					112(7), 111(2), 97(10), 94(1), 84(12), 83(69), 70(38), 69(39), 68(35), 57(54), 56(48), 55(68), 41(100)
	(2Z,4Z)-2,4-Heptadienal ^{b,c,e}					110(20), 95(10), 81(100), 67(21), 53(30), 41(33)

TABLE 1. CONTINUED

No. in Figure 1	Compounds	Quantity (ng/animal) ^a				Blesbok	EI mass spectral data [m/z (%)]
		Bontebok		Blesbok			
		Male	Female	Male	Female		
18	Octanal ^{b,c}	5	4	14	3	110(5), 100(12), 85(19), 84(50), 69(38), 57(78), 56(73), 44(80), 43(100), 42(40), 41(97)	
19	(E)-2-Octenal ^{b,c,f}	3	3	2	3	111(4), 98(8), 97(10), 83(40), 70(58), 69(30), 57(65), 55(100)	
	(E)-2-Nonenal ^{b,c,e}					122(6), 112(3), 111(8), 97(11), 96(15), 83(48), 70(68), 69(52), 57(50), 55(93), 43(100), 41(60)	
	(2Z,4Z)-2,4-Decadienal ^{b,c,e,f}					152(10), 123(6), 95(17), 83(13), 81(100), 67(27), 55(35), 53(22), 41(60)	
	Ketones						
1	2-Pentanone ^{b,c,f}	24	19	16	4	86(12), 71(34), 57(9), 43(100), 41(18)	
2	3-Methyl-2-butanone ^{b,c}					86(13), 71(4), 43(100), 41(18)	
3	2-Hexanone ^{b,c,f}	2	1			100(10), 85(7), 71(5), 58(65), 43(100), 41(15)	
7	2-Heptanone ^{b,c,f,g}	17	4	3	3	114(4), 99(3), 85(3), 71(12), 59(12), 58(63), 43(100)	
11	4-Octanone ^{b,c,f}					128(33), 99(5), 85(80), 71(100), 58(65), 57(93), 43(87), 41(65)	
13	7-Octen-2-one ^{b,c}	3	3	1	2	126(3), 111(2), 108(3), 99(10), 97(5), 83(3), 71(19), 68(16), 58(4), 55(9), 43(100), 41(25)	
14	3-Octanone ^{b,c,f}	1	8	1	4	128(5), 99(39), 85(8), 72(58), 71(48), 57(62), 43(100), 41(15)	
16	2-Octanone ^{b,c,f}	16	8	10	6	128(4), 113(2), 85(5), 71(16), 59(14), 58(65), 43(100)	
22	4-Nonanone ^{b,c,f}	86		2	9	142(4), 99(75), 86(37), 71(100), 58(68), 55(22), 43(95), 41(55)	

25	2-Nonanone ^{b,c,f,g}	29	13	11	12	142(3), 127(3), 113(1), 99(2), 85(5), 71(46), 59(22), 58(96), 43(100), 41(15)
	2-Decanone ^{b,c,h}					156(4), 85(6), 71(30), 59(37), 58(99), 43(100), 41(22)
32	(Z)-5-Undecen-2-one ^{b,c,g}	48	23	70	101	168(2), 150(2), 139(2), 125(5), 110(26), 97(20), 81(44), 68(33), 58(15), 54(43), 43(100), 41(55)
33	(Z)-7-Undecen-2-one ^b	5	1	1	1	150(1), 125(6), 110(8), 97(6), 81(14), 71(17), 69(15), 58(9), 55(16), 43(100), 41(33)
34	2-Undecanone ^{b,c,f,g}	8	1	3	3	170(2), 127(2), 112(3), 110(3), 85(8), 71(30), 59(28), 58(100), 43(80), 41(20)
35	Decane-2,5-dione ^{b,c}	1	1	1	1	127(14), 114(36), 99(54), 71(70), 43(100)
39	Undecane-2,5-dione ^{b,c,f,g}	46	36	7	10	141(3), 127(4), 114(44), 99(38), 85(15), 71(60), 43(100), 41(20)
41	(Z)-7-Tridecen-2-one ^{b,c,f}	12	1	3	7	178(2), 138(7), 125(9), 110(10), 97(14), 96(15), 81(23), 71(39), 67(25), 58(9), 55(26), 54(20), 43(100), 41(38)
17	Carboxylic acids					
	Hexanoic acid ^{b,c}	62	1	6	2	87(15), 73(50), 60(100), 55(20), 43(35), 41(45)
24	Heptanoic acid ^{b,c}	11	6	6	5	101(6), 87(22), 73(43), 60(100), 55(36), 43(50), 41(64)
29	Octanoic acid ^{b,c}					115(8), 101(22), 85(20), 73(73), 60(100), 55(37), 43(48), 41(38)
36	Decanoic acid ^{b,c}	51	17	21	32	172(3), 154(2), 143(7), 129(40), 115(12), 101(6), 87(15), 73(92), 71(40), 60(100), 57(42), 55(62), 43(65), 41(77)
43	Dodecanoic acid ^{b,c,f}	89	61		22	200(20), 171(1), 157(20), 143(6), 129(38), 115(10), 87(18), 73(96), 60(100), 57(47), 55(47), 43(78), 41(70)
47	Tetradecanoic acid ^{b,c,f}	6	2	2	3	228(17), 185(22), 171(12), 157(7), 143(14), 129(38), 115(14), 97(17), 85(36), 73(90), 71(35), 69(35), 60(68), 57(55), 55(54), 43(100), 41(91)

TABLE 1. CONTINUED

No. in Figure 1	Compounds	Quantity (ng/animal) ^a				EI mass spectral data [m/z (%)]
		Bontebok		Blesbok		
		Male	Female	Male	Female	
48	Pentadecanoic acid ^{b,c}	3	1	3	1	242(12), 213(2), 199(12), 185(8), 171(7), 157(8), 143(15), 129(30), 115(10), 97(18), 83(28), 73(83), 71(37), 69(39), 60(60), 57(62), 55(60), 43(100), 41(92)
50	(Z)-9-Hexadecenoic acid ^{b,c}					236(2), 194(1), 151(1), 138(3), 123(8), 111(14), 97(35), 83(47), 69(84), 55(100), 41(90)
51	Hexadecanoic acid ^{b,c,f}	127	42	66	92	256(17), 227(3), 213(15), 199(4), 185(9), 171(11), 157(13), 143(6), 129(32), 115(11), 97(19), 83(23), 73(80), 60(61), 57(57), 55(57), 43(100), 41(85)
53	Heptadecanoic acid ^{b,c}	59	15	29	31	270(4), 241(3), 227(13), 213(3), 199(2), 185(11), 171(12), 157(3), 143(4), 129(35), 115(15), 97(23), 85(28), 83(29), 73(70), 60(55), 57(59), 55(56), 43(100), 41(83)
55	(9Z,12Z)-9,12-Octadecadienoic acid ^{b,c}	12	19	9	48	280(5), 196(1), 164(2), 150(5), 136(8), 123(15), 109(34), 95(68), 81(88), 67(100), 55(89), 43(58), 41(89)
56	(Z)-9-Octadecenoic acid ^{b,c}	25	5	8	32	264(5), 222(2), 180(2), 165(2), 137(4), 123(9), 111(13), 97(36), 83(45), 81(35), 69(72), 67(40), 55(100), 43(73), 41(80)
57	Octadecanoic acid ^{b,c,f}	156	56	67	87	284(5), 255(3), 241(18), 227(4), 213(2), 199(5), 185(15), 171(6), 157(3), 143(4), 129(39), 115(12), 101(7), 97(27), 85(28), 73(100), 60(88), 55(87), 43(95), 41(68)
59	Icosanoic acid ^{b,c,f}					312(15), 269(5), 255(3), 241(2), 227(3), 213(2), 199(3), 185(7), 171(4), 157(4), 143(3), 129(38), 115(14), 101(6), 97(27), 85(21), 73(100), 60(73), 55(58), 43(96), 41(60)

45	Lactones (Z)-6-Dodecen-4- olide ^{b,c,d,f}	17	6	3	4	196(1), 136(4), 121(2), 105(1), 96(8), 85(100), 79(8), 67(8), 55(10), 41(17)
46	Dodecan-5-olide ^{b,c,f}	129	96	70	75	155(3), 136(4), 114(10), 99(100), 83(8), 71(44), 70(30), 55(45), 43(34), 42(31), 41(34)
52	Ester Isopropyl hexadecanoate ^{b,c,f}					257(14), 256(19), 239(12), 213(5), 199(2), 185(4), 171(4), 157(5), 143(3), 129(15), 111(7), 102(44), 97(15), 83(20), 73(34), 71(31), 69(29), 60(67), 57(55), 55(48), 43(100), 41(50)
60	Hydroxyesters 2-Hydroxyoctadec-1-yl ethanoate ^b	23	9	2	6	255(3), 125(4), 111(10), 103(11), 97(18), 83(19), 74(32), 69(16), 57(22), 55(20), 43(100)
63	2-Hydroxyoctadec-1-yl 2-methylpropanoate ^{b,c}	21	8	3	21	255(3), 131(7), 111(5), 102(38), 87(24), 71(100), 57(27), 55(27), 43(56)
64	1-Hydroxyoctadec-2-yl butanoate ^{b,c}	35	9	4	15	255(3), 131(5), 111(4), 102(17), 87(15), 71(100), 57(23), 55(18), 43(36)
65	2-Hydroxyoctadec-1-yl butanoate ^{b,c}	101	39	7	61	255(3), 131(6), 111(5), 102(27), 87(24), 71(100), 57(20), 55(20), 43(41)
66	1-Hydroxyoctadec-2-yl pentanoate ^{b,c}	10	8	4	9	255(1), 145(3), 116(15), 101(20), 85(100), 69(20), 57(90), 43(42)
67	2-Hydroxyoctadec-1-yl pentanoate ^{b,c}	37	36	13	26	255(2), 145(5), 116(30), 101(41), 85(100), 69(20), 57(100), 43(34)
68	2-Hydroxynonadec-1-yl butanoate ^{b,c}					269(2), 131(4), 111(5), 102(25), 87(19), 71(100), 57(23), 55(25), 43(52)
70	2-Hydroxyicos-1-yl 2-methylpropanoate ^b					283(1), 131(5), 111(5), 102(28), 87(16), 71(100), 57(40), 55(25), 43(67)
71	2-Hydroxyicos-1-yl butanoate ^b	27	8	2	6	283(2), 131(6), 111(7), 102(23), 87(20), 71(100), 57(29), 55(28), 43(46)
73	2-Hydroxyicos-1-yl pentanoate ^b	10	5	3	3	283(1), 145(5), 116(28), 101(37), 85(100), 69(19), 57(100), 43(32)

TABLE I. CONTINUED

No. in Figure 1	Compounds	Quantity (ng/animal) ^a				EI mass spectral data [m/z (%)]
		Bontebok		Blesbok		
		Male	Female	Male	Female	
74	2-Hydroxyhencicos-1-yl butanoate ^b					297(1), 131(5), 111(6), 102(24), 87(20), 71(100), 57(38), 55(27), 43(39)
76	2-Hydroxydocos-1-yl butanoate ^b					311(1), 131(6), 111(8), 102(25), 87(19), 71(100), 57(42), 55(35), 43(50)
37	Pyridines 2-[(E)-4-Hepten-1-yl] pyridine ^{b,c,f}	4	5	2	1	160(6), 146(4), 133(10), 118(6), 106(14), 93(100), 78(6), 65(6), 51(5), 41(7)
38	2-Heptypyridine ^{b,c,d,f}	32	48	22	16	177(1), 148(4), 134(5), 120(16), 106(25), 93(100), 78(6), 65(5), 51(3), 41(6)
42	2-Heptanoylpyridine ^{b,c}	5	4	1	1	191(8), 163(7), 148(14), 134(48), 120(27), 106(42), 93(19), 79(100), 78(78), 51(17), 43(21), 41(21)
12	Phenols Phenol ^{b,c}					94(100), 66(40), 65(28), 55(4)
23	3-Methylphenol ^{b,c,d}	59	42	5	124	108(94), 107(100), 90(15), 80(15), 79(46), 77(46), 65(5), 63(8), 53(13), 51(15), 50(10)

27	3-Ethylphenol ^{b,c}	2	5	6	122(30), 108(9), 107(100), 91(7), 77(21), 65(5), 53(4)
31	3-Propylphenol ^{b,c}	7	3	27	136(56), 121(22), 108(59), 107(100), 98(19), 94(12), 91(16), 78(19), 77(40), 65(13), 51(9)
	Steroids				
	Cholesterol ^{b,c,i}				386(18), 368(13), 353(15), 326(4), 301(23), 275(31), 255(19), 231(14), 213(34), 199(14), 185(12), 173(18), 159(37), 145(58), 133(38), 119(42), 105(71), 95(64), 81(73), 67(52), 55(82), 43(100)
	Desmostero ^{b,c,i}				384(5), 369(8), 351(6), 300(8), 271(37), 253(12), 213(15), 199(7), 185(7), 173(9), 159(22), 145(28), 133(22), 119(21), 105(41), 95(42), 81(42), 69(100), 55(58), 41(60)
	Other				
9	Dimethylsulfone ^{b,c,f}				94(61), 79(100), 65(3), 64(4), 63(7), 48(8), 45(25)

^aQuantities lower than 1 ng/animal not given.

^bLow-resolution mass spectrum.

^cRetention-time comparison with authentic synthetic material.

^dIdentified in previous study (Burger et al., 1977).

^eDetected using OV-1701-OH column.

^fLow-resolution CI(CH₄)-MS.

^gIdentified in previous study (Burger et al., 1976).

^hDetected using Superox 4 column.

ⁱElutes beyond retention time range shown in Figure 1.

to the human nose. Although aromatic compounds are fairly common in mammalian exocrine secretions, the pyridine derivatives 2-heptylpyridine, 2-[(*E*)-4-heptenyl]pyridine, and 2-heptanoylpyridine are noteworthy because nitrogen-containing aromatic heterocyclic compounds are relatively rare in mammalian exocrine secretions. Pyridine and pyrazine derivatives have been found in male rabbit fecal pellets (Goodrich et al., 1981) and muscopyridine in the secretion of the scent gland of the musk deer (Biemann et al., 1957). Dimethylsulfone also has been found in the dorsal secretion of the springbok (Burger et al., 1981) and in the preorbital secretion of the suni, *Neotragus moschatus* (Burger et al., unpublished results). Finally, cholesterol and desmosterol are present in the secretions in small quantities (retention times beyond range shown in Figure 1).

The possibility exists that the carboxylic acids could be artifacts formed by autoxidation of aldehydes. Although this is a valid argument, and autoxidation could possibly make some contribution to the production of carboxylic acids, there does not seem to be a definite correlation between the quantities of the aldehydes and carboxylic acids present in the secretion. It is, for example, very unlikely that hexanal and heptanal could be oxidized to the corresponding acids whereas octanal is not.

Although a further 76 constituents were identified in the present study, many compounds, including several terpenoids, remained unidentified, mostly because of their uninformative and/or impure mass spectra. Comprehensive two-dimensional gas chromatography, preparative gas chromatography in conjunction with NMR analysis, and techniques such as HPLC-GC will have to be used in future projects to obtain further structural information on these constituents.

On principle, experimental animals were not sacrificed to obtain material for the present study and it was, therefore, not possible to collect material at regular intervals in order to determine whether the composition of the secretions is influenced by seasonal changes or other factors. Nevertheless, a relatively large number of samples of animals of different ages and from different regions of the country were analyzed over many years. Although the research was concentrated mainly on the qualitative composition of the secretions, very similar gas chromatographic profiles were obtained throughout. Some quantitative data on the major constituents present in the secretions of randomly selected individual male and female bontebok and blesbok in quantities higher than 1 ng/animal are given in Table 1. It must be pointed out that it is not possible to remove secretion quantitatively from the interdigital pouch, and the results are therefore based only on the fraction collected from the interdigital pouch. The secretion from the male bontebok referred to in Table 1 was observed to have a lower than normal viscosity and the higher values obtained for this animal can therefore probably be attributed to more efficient removal of the secretion from the interdigital cavity. Secretions from some of the older animals were more viscous than those of young ones to the extent that they were quite difficult to remove from the interdigital pouch in some cases.

This difference appeared to be due to the absence of low-viscosity oils or waxes in older animals. Since this waxy material probably acts as a controlled-release substance, the secretions of the older animals are released from the secretion at a higher rate in the absence of the waxy material and therefore appear to have a stronger, more pungent smell to the human nose than those of the younger animals. At this stage it is not clear whether this difference in viscosity has any semiochemical significance or whether it is merely a consequence of the slower production of secretion in older animals.

The possibility was investigated that some of the constituents of the secretions may be produced by microorganisms in the interdigital cavity and are not secreted by the animal itself. A GC-MS analysis of an extract of the glandular tissue from the interdigital pouch (Figure 2) revealed the presence of very small quantities of some of the major constituents of the secretion. This is a somewhat inconclusive result as the presence of components of the secretion in the glandular tissue could be ascribed either to the impregnation of the tissue with compounds produced by microorganisms, production of the compounds by the gland, or to production of some of the compounds by the gland and the others by microorganisms. Comparison of the ratios in which the major compounds are present in the secretion and in extracts of the glandular tissue shows that the carboxylic acids are present in much higher concentrations in the glandular tissue than in the secretion. Although this result is again not conclusive, it was considered to be an indication that at least some of the compounds could be produced by microorganisms.

Two aerobic bacteria, *Bacillus brevis* (Dubos and Cattaneo, 1939) and *Planococcus citreus* (Sneath et al., 1986), were found to be present in the interdigital secretions of male and female animals from different populations of both subspecies. The absence of any other bacteria in the interdigital cavity can possibly be attributed to the production of the antibacterial agents gramicidine and tyrocidine by *B. brevis*. (Dubos and Cattaneo, 1939). The production of a yellow water-soluble pigment by *P. citreus* (Sneath et al., 1986) may explain the yellow coloration of the lower parts of the white hair surrounding the interdigital cavity.

The two bacterial species were grown on modified Hutner medium, and the metabolites produced by the bacteria analyzed in the normal manner. Complete qualitative analysis of the bacterial products lies outside the scope of the present research, but preliminary results indicate that the long-chain carboxylic acids, isopropyl hexadecanoate, and some of the ketones are produced in vitro by *B. brevis*. (Z)-6-Dodecen-4-olide is one of the major compounds produced by *P. citreus*. It is therefore not unlikely that some of the other constituents of the interdigital secretions of the bontebok and blesbok could also be produced by mutual metabolism by the bacteria of each other's metabolites. This possibility will be investigated in further work on the interdigital secretions of the bontebok and blesbok.

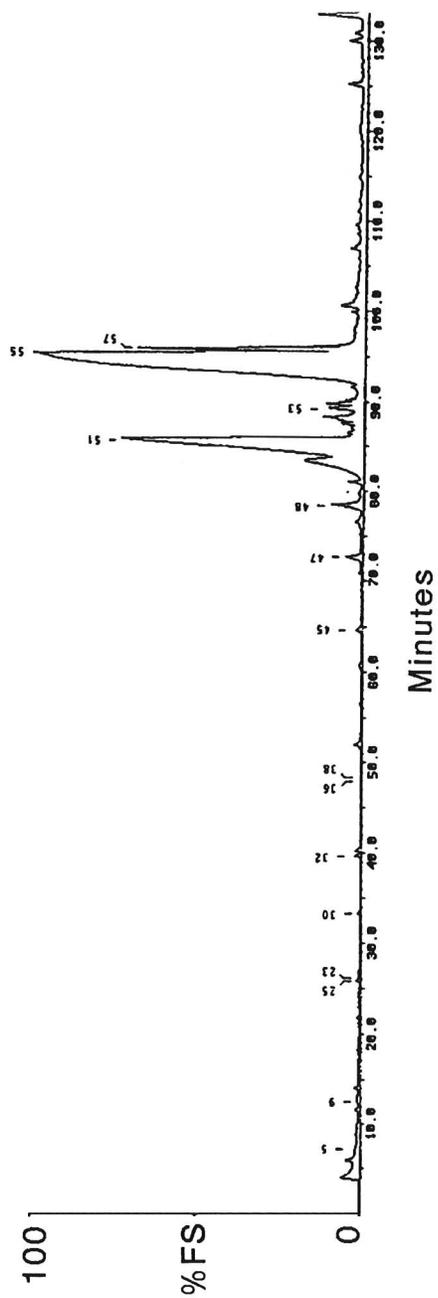


FIG. 2. Total ion chromatogram of an extract of interdigital glandular tissue from a male bontebok. Gas chromatographic conditions as in Figure 1.

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