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The Chemistry of the Metasternal Gland Secretion of the Eucalypt Longicorn *Phoracantha synonyma* (Coleoptera: Cerambycidae)

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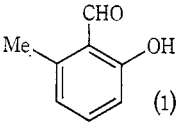
Abstract

The metasternal gland secretion of *Phoracantha synonyma* contains a diversity of volatile components, one of which, 2-hydroxy-6-methylbenzaldehyde (1), is of widespread occurrence in the genus. Three major components and several minor components are macrocyclic lactones, of which the following have been positively identified: decan-9-olide (2), (*Z*)-dec-4-en-9-olide (3) and 11-hydroxytetradec-5-en-13-olide (4). The methyl and ethyl esters of 2-methylbutyric and related acids are also present and are responsible for the characteristic odour of the fresh secretion.

In an earlier paper[1] we discussed the chemistry of the metasternal gland secretion of the common eucalypt longicorn, *Phoracantha semipunctata* (F.), and we now present our findings concerning the secretion of a closely related (but chemically very distinct) species, *P. synonyma* Newman. The latter secretion, which was obtained in the same manner as before, had a strong and distinctive pineapple-like odour.

Gas chromatographic analyses on OV-1 (columns 1 and 2) and Carbowax-20M (columns 3 and 4) of the CS_2-extractives from fresh secretion showed the presence of three major components [(I), (J), (K)] and a number of minor ones [(E), (M), (N), (O), (P) etc.], although the pairs (I)+(J) and (O)+(P) were not resolved on the OV-1 columns. The proportions varied somewhat between individual beetles and (E) was sometimes a major component, occasionally even exceeding (I) in abundance. However, in all of the many tens of analyses performed, (K) was consistently the largest component.

Component (E) was apparently identical with the most abundant constituent of the *P. semipunctata* secretion, which had earlier been identified[1] as 2-hydroxy-6-methylbenzaldehyde (1); this identification was confirmed by correspondence of gas chromatographic retention times (columns 4 and 5) and by close agreement of the mass spectra. Component (E) has also been detected in other species of the genus.



(1)

Of the other components of the *P. synonyma* secretion, only (K) was affected by a boric acid subtraction column[2] but it was apparently dehydrated, rather than absorbed, for a large broad peak at much shorter retention time resulted. None of the components was absorbed by an *o*-dianisidine column. These findings suggested that

[1] Moore, B. P., and Brown, W. V., *Aust. J. Chem.*, 1972, **25**, 591.
[2] Bierl, B. A., Beroza, M., and Ashton, W. T., *Mikrochim. Acta*, 1969, 637.

components (I), (J), (M), (N), (O) and (P) were neither alcohols nor aldehydes and that component (K) contained a secondary or tertiary alcoholic function.

Consideration of retention indices[3] suggested carbon numbers of about 10 for components (I) and (J), and indicated moderate polarity, with (J) the more polar of the two.

The mass spectrum of component (I) (g.c.-coupled, column 3) showed the molecular ion at *m/e* 170·13086 (4·6%), indicating an empirical formula of $C_{10}H_{18}O_2$. Important fragments occurred at *m/e* 155 (7%, $M-CH_3$), 152 (15%, $M-H_2O$), 98 (base peak, $C_6H_{10}O$), 84 (58%), 83 (29), 69 (36), 55 (83), 43 (53), 42 (31) and 41 (61). The mass spectrum of component (J) (taken under the same conditions) showed the molecular ion at *m/e* 168·11430 (26%) ($C_{10}H_{16}O_2$) and important fragmentation peaks at 150 (16%, $M-H_2O$), 126 (28%, $C_7H_{10}O_2$), 113 (56%), 108 (42), 85 (60), 81 (40), 71 (base peak), 68 (50), 67 (67), 55 (71), 54 (57), 43 (54) and 41 (66).

Component (I) was not affected by Pt/H_2 in acetic acid but it appeared to result when component (J) was reduced in this way. This conclusion was supported by comparisons of retention times and of mass spectra.

Both components (I) and (J) were reduced by lithium aluminium hydride to highly polar products which resembled decane-1,10-diol in retention behaviour but were a little less polar. Mass spectra were recorded from the coupled system, with column 1. The reduction product from (I) gave no molecular ion, the largest detectable fragment being at *m/e* 123 (6%), with the base peak at *m/e* 45. However, the corresponding product from (J), in which the unsaturated centre provided a stabilizing influence, yielded a more informative spectrum. In this case a molecular ion was detectable at *m/e* 172 (3·3%) ($C_{10}H_{20}O_2$), together with important fragments at 154 (2·2%, $M-H_2O$), 136 (2·2%, $M-2H_2O$), 94 (34%), 79 (base peak), 71 (61), 68 (56), 67 (54), 55 (41), 45 (45), 43 (40) and 41 (45). The high polarity of the compound and its loss of two molecules of water in the mass spectrometer indicated that the reduction product from (J) was a diol and since its formation entailed no loss of carbon, it was presumably derived from a (monounsaturated) lactone. Component (I) was evidently the corresponding saturated lactone.

Direct gas chromatographic comparisons of components (I) and (J) with the known δ-lactones isoiridomyrmecin, nepetolactone and decan-5-olide showed the beetle components to be less polar, with appreciably shorter retention times. In this regard, (I) and (J) were thus intermediate between small-ring lactones and C_{10} open-chain esters, a finding that suggested the presence of a macrolide system.

Microhydrogenolysis[2] of either (I) or (J) yielded n-nonane (i.e., with normal loss of the oxygen-substituted terminal carbon) as the major product and indicated an unbranched carbon skeleton, a conclusion which was supported by the close similarity between the mass spectrum of (I) and that reported[4] for the lactone of 11-hydroxydodecanoic acid. Component (I) therefore appeared to be the lactone (2) of 9-hydroxydecanoic acid and this was supported by the apparent identity between its lithium aluminium hydride reduction product and decane-1,9-diol (agreement of retention times on columns 4 and 5 and close matching of mass spectra).

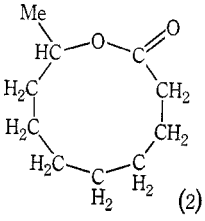
Final confirmation of the structure (2) for component (I) resulted from the synthesis of this material from 9-bromodecanoic acid, by application of the general method of

[3] Kováts, E. Sz., *Adv. Chromatogr.*, 1965, **1**, 229.

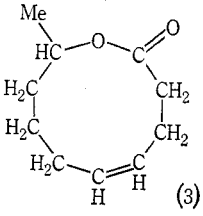
[4] Vesonder, R. F., Stodola, F. H., Wickerham, L. J., Ellis, J. J., and Rohwedder, W. K., *Can. J. Chem.*, 1971, **49**, 2029.

Hunsdiecker and Erlbach[5] for cyclization of ω-bromo acids. As might be expected on stereochemical grounds, the yield of lactone was very low and its purification proved difficult but this was finally achieved by successive, small-scale gas chromatographic separations on columns 2 and 4. Decan-9-olide (2) thus prepared proved identical with component (I) in gas chromatographic behaviour (columns 2, 4 and 5) and the mass spectra of the two materials were in close agreement.

The location of the double bond in component (J) was achieved by application of an ozonolysis technique first proposed[6] for macrocyclic hydrocarbons. In the present work, substitution of lithium aluminium hydride for the original hydride led to simultaneous reduction of the ozonide and lactone moieties to alcohols and the resulting diols were then identified gas chromatographically, directly, or after conversion into their acetates. In the case of component (J), butane-1,4-diol, and hexane-1,5-diol were identified as the major reaction products, and (J) therefore appeared to be the lactone of a 9-hydroxydec-4-enoic acid.



(2)



(3)

(*E*)-Dec-4-ene-1,9-diol was prepared by reducing (*E*)-10-hydroxydec-6-en-2-one[7] with sodium borohydride in ethanol. The mass spectrum of the diol was very similar to that of the diol derived from (J) but the two compounds showed slightly but consistently different retention times on columns 4 and 5. However, (*Z*)-dec-4-ene-1,9-diol, prepared in an analogous manner, appeared to be identical with the insect-derived diol. Component (J) was thus identified as (*Z*)-dec-4-en-9-olide (3).

The transformations leading to the structures of components (I) and (J) are shown diagrammatically in Scheme 1, p. 1368.

The largest component of the *P. synonyma* metasternal gland secretion, (K), showed much longer retention times than did components (I) and (J), particularly on Carbowax, and consideration of retention indices suggested the presence of an additional functional group, together with a higher carbon number.

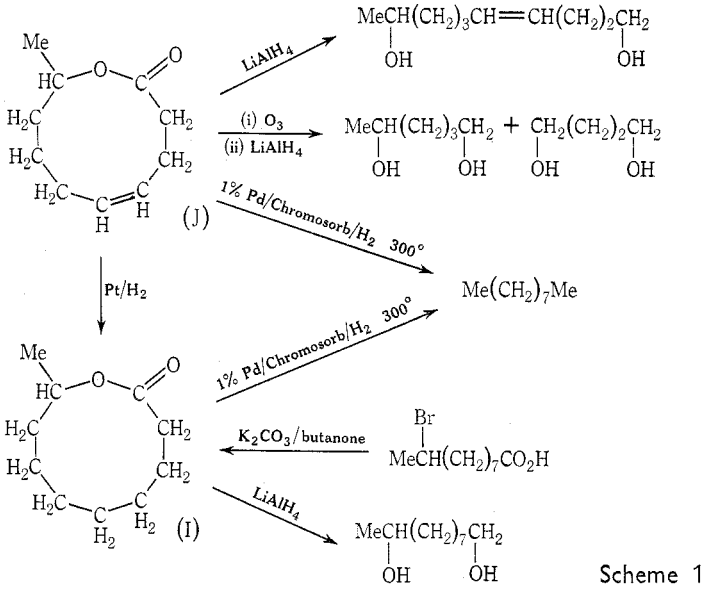
The mass spectrum of component (K) (g.c.-coupled, column 3) showed the molecular ion at *m/e* 240·17068 (3·4%) ($C_{14}H_{24}O_3$), together with important fragmentation peaks at 222 (9·3%, $M-H_2O$), 204 (2·6%), 180 (22), 136 (30), 98 (51), 97 (53), 84 (81), 81 (70), 80 (62), 67 (78), 55 (80), 45 (52), 43 (95) and 41 (base peak). This spectrum was consistent with that to be expected from an hydroxyl-substituted four-carbon homologue of (J).

Microhydrogenolysis of (K) yielded n-tridecane as the major product and indicated an unbranched carbon chain of 14 atoms in the original lactone.

In view of the ready dehydration suffered by (K) on the boric acid subtraction column, use was made of the reaction for small-scale preparative purposes. Material

[5] Hunsdiecker, H., and Erlbach, H., *Chem. Ber.*, 1947, **80**, 129.
[6] Hubert, A. J., *J. Chem. Soc.*, 1963, 4088.
[7] Grob, C. A., and Moesch, R., *Helv. Chim. Acta*, 1959, **79**, 728.

corresponding with the broad peak produced under such conditions was collected and, when rerun on column 4 (at 160°), showed two peaks of similar size (at 8·48 and 9·42 min). A mass spectrum obtained from these components combined was weak but showed what was assumed to be a molecular ion at m/e 222 (i.e., $K-H_2O$). Catalytic reduction (Pt/H_2/ethanol) of the combined components yielded a single product, which was shown to be identical with tetradecan-13-olide prepared by direct synthesis. Further reduction of this lactone derived from (K), with lithium aluminium hydride, gave a product which, after acetylation, was identified as 1-methyltridecane-1,13-diyl diacetate by direct comparison of retention times (on columns 1 and 4) with those of a synthetic specimen. Thus component (K) was shown to be a tetradecen-13-olide with an additional hydroxyl substituent in the ring.



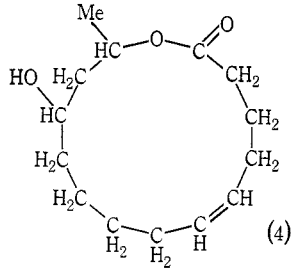
Scheme 1

In order to locate the position of the double bond a sample of component (K) was ozonized in carbon disulphide, the solvent removed and replaced with ether, and an aliquot of the solution injected directly into the microhydrogenolyser. The only significant peak detected corresponded with n-octane. The remaining ozonide was reduced with lithium aluminium hydride and the product(s) acetylated. Gas chromatographic analysis revealed pentane-1,5-diyl diacetate as the only significant product of its class. These data served to locate the double bond at position 5.

Catalytic reduction (Pt/H_2/aq. acetic acid) of component (K) gave a product (assumed to be a dihydro derivative) with a slightly shorter retention time on column 4 (12·49 compared with 14·49 min at 180°). This material was dehydrated on the boric subtraction column to give two major products (retention times 8·13 and 8·86 min, column 4, 155°). When these combined products were ozonized and the products were reduced with lithium aluminium hydride as above, decane-1,10-diol was identified as the major degradation product. This would locate the original hydroxyl substituent of component (K) on C 10 or C 11, according to the direction of dehydration. On biosynthetic grounds, and assuming component (K) to be derived from head-to-tail

linkage of acetate units, the C 11 position appeared the more probable. This was tested by direct application of the above train of reactions (ozonolysis, reduction, acetylation) to component (K). Two significant products were detected, namely the above pentane-1,5-diyl diacetate and a compound matching the first-eluting component of synthetic 1-methyloctane-1,3,8-triyl triacetate in chromatographic (columns 4 and 5) and mass spectral behaviour. The second component of the synthetic product (which was a mixture of two isomers) also gave a matching mass spectrum.

Thus the free hydroxyl group of component (K) was located on C 11 and the position of a double bond between C 5 and C 6 was further confirmed. Component (K) was therefore an 11-hydroxytetradec-5-en-13-olide (4) of undetermined stereochemistry but, by analogy with component (J), a (*Z*)-configuration of the double bond appeared probable.



(4)

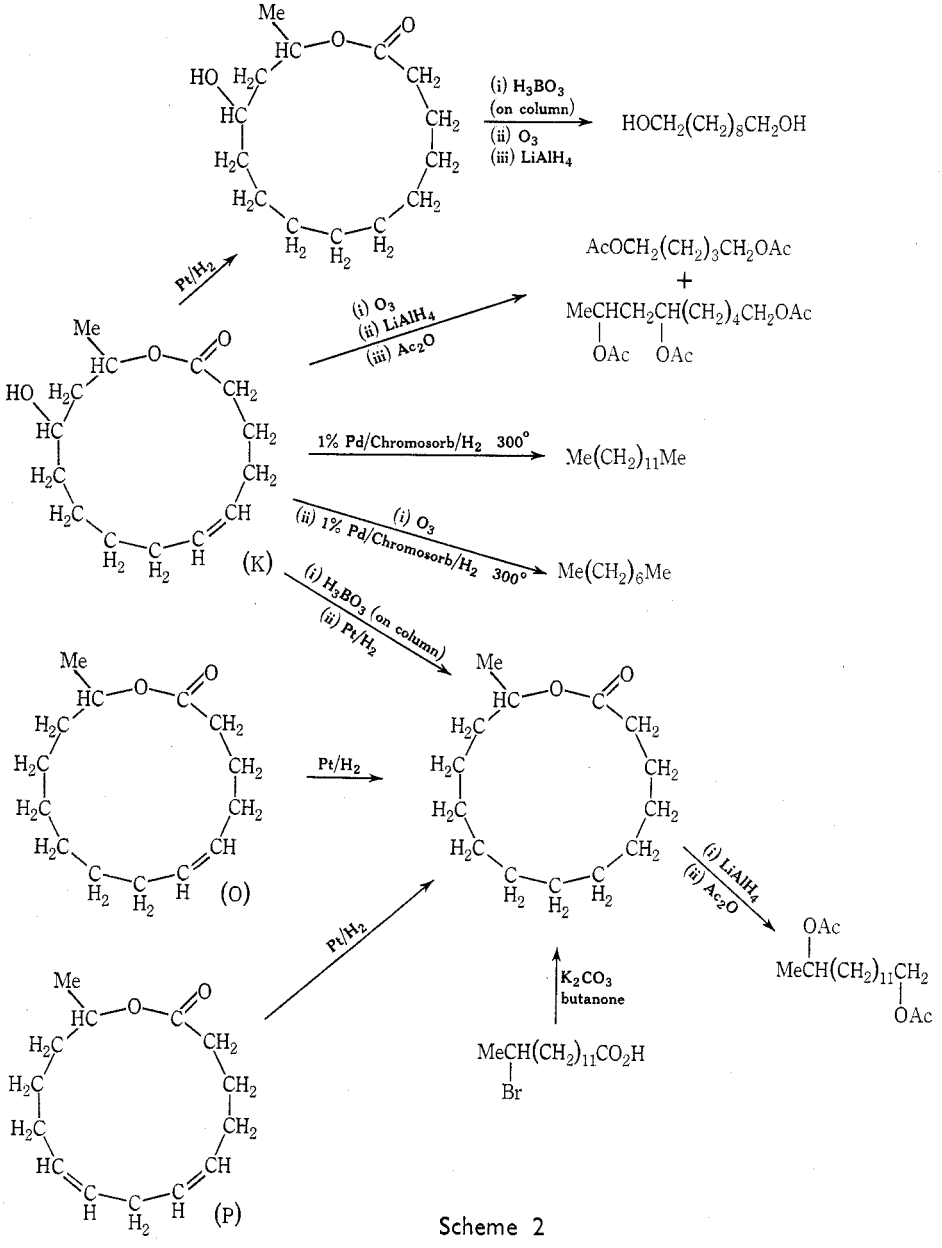
Consideration of retention indices (on columns 2 and 4) of the minor components of the secretion suggested that (M), (N) and (O) were homologues of (J), with two, three and four additional carbon atoms, respectively. Component (P) was apparently analogous to (O) but with an additional double bond, but it did not match either of the dehydration products of component (K). Component (N) was the least abundant of all and could not be characterized further.

The mass spectrum from component (M) (cooled probe inlet) showed a molecular ion at *m/e* 196 (16%) ($C_{12}H_{20}O_2$) and important fragments at 178 (7%, $M-H_2O$), 136 (21%), 96 (22), 95 (22), 84 (28), 82 (26), 81 (41), 80 (40), 79 (32), 67 (72), 55 (67), 54 (33) and 41 (base peak). This spectrum provided further evidence that component (M) was a double homologue of (J). Ozonolysis of component (M), followed by reduction of the ozonide with lithium aluminium hydride, gave pentane-1,5-diol and heptane-1,6-diol, indicating that (M) was almost certainly dodec-5-en-11-olide. Again by analogy with (J), the configuration of the double bond was considered likely to be (*Z*). Thus component (M) is closely related to the fungal lactone isolated by Vesonder *et al.*[4] but it differs in the position (and perhaps also in the configuration) of the double bond.

The mass spectrum of component (O) (cooled probe inlet) was too weak for accurate assessment but it clearly showed a molecular ion at *m/e* 224 ($C_{14}H_{24}O_2$) and important fragments at 209 ($M-CH_3$), 206 ($M-H_2O$), 195, 181, 168, 164, 140, 137, 126, 124, 110, 96, 81, 67 and 55. The mass spectrum of component (P) (g.c.-coupled, column 3) was even weaker but it appeared to show a molecular ion at *m/e* 222 ($C_{14}H_{22}O_2$).

Catalytic reduction of either (O) or (P) gave a single product which was identified gas chromatographically as tetradecan-13-olide. Application of the ozonolysis–reduction–acetylation train of reactions to component (O) gave a mixture of which the

main components were identified gas chromatographically as pentane-1,5-diyl diacetate and 1-methyloctane-1,8-diyl diacetate, whereas (P) gave pentane-1,5-diyl diacetate, 1-methylpentane-1,5-diyl diacetate and possibly a little hexane-1,6-diyl diacetate (peak very small). Component (O) therefore appeared to be tetradec-5-en-13-olide



Scheme 2

and component (P) was probably the corresponding 5,8-dienolide, but there was no information concerning the configurations of the unsaturated centres. However, the postulated dispositions of the double bonds would be in keeping with those generally occurring in insect lipids.

Transformations leading to the structures of components (K), (O) and (P) are shown diagrammatically in Scheme 2.

None of the above identified components would account for the distinctive pine-apple-like odour of the fresh secretion. This odour, which was gradually lost from secretion stored in unsealed containers, was evidently due to much more volatile substances and its quality was strongly suggestive of esters of short-chain fatty acids which in normal gas chromatography would be masked by solvent peaks.

In an attempt to locate these very volatile components, the fresh aqueous secretion was injected neat onto column 3, at 75°, equipped with an effluent splitter. One portion of the effluent was monitored by the detector in the usual way and the other by the human nose. In this manner two small peaks were detected on the trace concurrently with the emergence of the distinctive fruity odour. High-sensitivity analysis on column 4 showed the presence of two relatively large and three minor components in this region, that matched the retention times of methyl 2-methylbutyrate, ethyl 2-methylbutyrate, ethyl isobutyrate, methyl isovalerate and ethyl isovalerate, respectively. The identifications of the two major esters were supported by retention times on column 6 but shortages of material precluded the recording of mass spectra.

Experimental

General Procedures

Melting points are uncorrected. Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. Mass spectra were determined on an AEI MS902 mass spectrometer with an on-line Raytheon 706 computer. Inlets used were a cooled probe or a silicone membrane separator coupled to a Philips gas chromatograph. P.m.r. spectra were measured in carbon tetrachloride on a Varian A60 instrument.

Analytical and small-scale preparative gas chromatography was conducted on a Varian 2100 instrument with a Hewlett–Packard 3370A digital integrator, and with flame ionization detectors, a nitrogen flow of 25 ml/min, and the following glass columns.

Column 1.—2 m by 4 mm of 5% OV-1 on Gas-chrom Q.
Column 2.— 4 m by 4 mm of 5% OV-1 on Gas-chrom Q.
Column 3.—2 m by 3 mm of 5% Carbowax-20M on Gas-chrom Z.
Column 4.—4 m by 3 mm of 5% Carbowax-20M on Gas-chrom Z.
Column 5.—2 m by 3 mm of 5% EGSS-X on Gas-chrom Z.
Column 6.— 2 m by 3 mm of Poropak P.

Columns for the Philips gas chromatograph were constructed of stainless steel.

Larger-scale preparative gas chromatography was conducted on a Loenco Prep-matic machine, with thermal conductivity detectors and 2 m by 10 mm stainless steel columns, packed with 20% OV-1 on Gas-chrom Z. Helium was the carrier gas.

Supplies of living beetles were obtained from a light trap operated nightly throughout the summer months at Black Mountain, A.C.T. The secretion was collected in micropipettes as described in an earlier paper[1] and, in cases of individual analyses, was treated with a little carbon disulphide and subjected to gas chromatography without delay. However, pooled secretion intended for later preparative work could be stored without serious deterioration for several weeks in sealed tubes under refrigeration.

Degradative Techniques

(A) Hydrogenations were carried out on a micro-scale in septum-sealed Reacti-vials with hydrogen and a trace of Adams platinic oxide catalyst. Ethanol or 80% aqueous acetic acid served as solvent and the products in solution were removed by means of a syringe and applied directly to the gas chromatograph.

(B) Hydrogenolyses were performed in an apparatus similar to that described by Bierl *et al.*[2] but modified to fit directly onto the inlet of a Carlo–Erba Fractovap gas chromatograph. Hydrogen was

the carrier gas and the products were identified from their retention times on a glass column of 2 m by 4 mm of 10% OV-101 on Gas-chrom Z. The catalyst used was 1% palladium on Chromosorb P and was maintained at 300°.

(C) Subtraction columns were 10% boric acid/5% Carbowax-20M (for alcohols), and 5% *o*-dianisidine/5% Carbowax-20M (for aldehydes), prepared as described,[2] with the reagent in the top 150 mm of the column. The boric acid column was further used to effect small-scale dehydrations of secondary alcohols, the products (indicated by characteristically broad peaks) being trapped from the effluent by passage through glass capillaries cooled with solid carbon dioxide.

(D) Micro-ozonolyses were conducted in carbon disulphide solution, according to the general directions of Moore and Brown.[8]

(E) Lithium aluminium hydride reductions were carried out in ether solution, followed by quenching with ethanol and water. When the only expected products were diols, the reaction mixture was saturated with sodium chloride and extracted three times with ether. The concentrated ethereal extract was either analysed directly by gas chromatography (columns 4 and 5) or alternatively freed from ether and treated with a little acetic anhydride in pyridine and heated at 100° for 15 min and the reaction mixture analysed directly on columns 1, 4 and 5.

When triols were to be expected from the reduction, the reaction mixture was centrifuged and the mother liquor recovered; the residue was washed with ethanol and centrifuged, successively, twice and the washings combined with the mother liquor. The residue from the combined liquors was then treated with the acetylation mixture as above and the reaction mixture analysed directly on columns 4 and 5.

10-Hydroxydec-6-yn-2-one

Crude 7-(2-tetrahydropyranyloxy)hept-3-yn-1-ol[7] (18·8 g) was subjected to the same series of reactions as described by Grob and Moesch[7] for the conversion of (*E*)-7-(2-tetrahydropyranyloxy)-hept-3-en-1-ol into (*E*)-10-hydroxydec-6-en-2-one and yielded a mixture (13 g) containing the required 10-hydroxydec-6-yn-2-one. This mixture was distilled under vacuum (0·5 mmHg) and a fraction, b.p. 105–140°, (3·5 g) was collected. Gas chromatography and mass spectroscopy (column 3 at 140°) indicated that the desired product was largely located in this fraction and further refinement was achieved by treatment with Girard's reagent-T, followed by recovery from the adduct under standard conditions. The yield of *10-hydroxydec-6-yn-one* thus obtained was 1 g (9%) and re-analysis as above indicated a purity of better than 90%. A pure specimen collected from the gas chromatographic column formed a colourless oil, n_D^{25} 1·4739 (Found: *m/e* 168·11497. $C_{10}H_{16}O_2$ requires *m/e* 168·11503).

(Z)-*10-Hydroxydec-6-en-2-one*

10-Hydroxydec-6-yn-2-one (0·5 g) was dissolved in pyridine (5 ml) and hydrogenated over 5% palladium on barium sulphate (0·1 g) for 1 h. The solution was then decanted, dissolved in 2 N aqueous hydrochloric acid and extracted with ether. The product (0·4 g), recovered from the ethereal extract, was shown by gas chromatography (column 3, 140°) to contain more than 90% of a single component. A pure sample of (Z)-*10-hydroxydec-6-en-2-one* collected from the column formed a colourless oil, n_D^{25} 1·4650 (Grob and Moesch[7] report 1·4658 for the (*E*) isomer) (Found: *m/e* 170·13072. $C_{10}H_{18}O_2$ requires *m/e* 170·13068). The p.m.r. spectrum showed δ 2·4, s, 3H (CH_3CO); 2·96, s, 1H (OH); 3·55, t, 2H (CH_2); 5·32, m, 2H (HC=CH) and was consistent with the postulated structure.

(Z)-*Dec-4-ene-1,9-diol*

A stirred solution of (*Z*)-10-hydroxydec-6-en-2-one (0·36 g) in ethanol (5 ml) was treated with small amounts of sodium borohydride and progress of the reduction was monitored by gas chromatographic analyses of aliquots withdrawn at intervals. When reduction appeared to be complete water (10 ml) was added and the mixture was extracted with ether. The product, recovered in standard fashion from the ethereal extract, was shown by gas chromatography to be about 90% pure (yield: 0·34 g, 92%). A pure specimen of (Z)-*dec-4-ene-1,9-diol* was collected from column 3 (140°) and formed a colourless oil, n_D^{25} 1·4707 (Found: *m/e* 172·14671. $C_{10}H_{20}O_2$ requires *m/e* 172·14633).

[8] Moore, B. P., and Brown, W. V., *J. Chromatogr.*, 1971, **60**, 157.

Methyl 6,8-Dioxononanoate

This was prepared by application of the general method of Hauser and Linn[9] to the monomethyl ester–acid chloride (2·7 g) of adipic acid, but the reaction temperature was −10°. The crude product was distilled in a vacuum (1 mmHg) and a fraction, b.p. 120–170° (bath temperature), was collected. Gas chromatographic analysis (column 4, 185°) showed this material to be about 90% pure (yield: 1 g, 33%). A pure sample of *methyl 6,8-dioxononanoate* collected from the column formed a colourless oil, n_D^{25} 1·4682 (Found: *m/e* 200·10475. $C_{10}H_{16}O_4$ requires m/*e* 200·10486).

1-Methyloctane-1,3,8-triyl Triacetate

Methyl 6,8-dioxononanoate (0·5 g) was warmed with ethanolic sodium borohydride (0·3 g) for 15 min. The mixture was then diluted with water and the ethanol removed under vacuum. The residue was extracted repeatedly with ether and the combined extracts were dried over anhydrous sodium sulphate. The crude methyl 6,8-dihydroxynonanoate remaining after removal of the solvent was dissolved directly in butan-1-ol (15 ml) and the mixture refluxed with metallic sodium (0·85 g) for 1 h (when all the metal had dissolved). The mixture was then cooled, diluted with saturated aqueous sodium chloride and the butanolic layer separated, washed with further brine and dried over anhydrous sodium sulphate. After removal of the butanol under vacuum, the residual crude nonane-1,3,8-triol was dissolved in pyridine (5 ml) and treated with acetic anhydride (2·5 ml). The mixture was heated on a water bath for 15 min, then cooled, diluted with water and extracted with ether. The extract was washed with aqueous sodium bicarbonate and water, then dried over anhydrous sodium sulphate. The crude product (0·3 g, 40% overall yield) was purified by preparative-scale gas chromatography (at 205°) to give *1-methyloctane-1,3,8-triyl triacetate* as a colourless oil, n_D^{25} 1·4427. The mass spectrum showed no molecular ion but fragments at *m/e* 287 (M−15, 0·2%), 242 (M−60, 1·6), 200 (9), 182 (9), 173 (27), 159 (11), 140 (12), 131 (25), 128 (20), 122 (22), 113 (27), 99 (21), 81 (20), 71 (27), 61 (21), 43 (base peak) (Found: *m/e* 242·15251. $C_{13}H_{22}O_4$ (M−CH_3CO_2H) requires *m/e* 242·15181). Satisfactory elementary analyses could not be obtained from this substance, owing to its ready pyrolysis, but the p.m.r. spectrum showed δ 1·15, d, 3H (CH_3); 1·9, s, 9H (3 × CH_3CO); 3·95, t, 2H (CH_2O); 4·85, q, 2H (2 × CH–O) and was consistent with the postulated structure.

Saturated Diols

Hexane-1,5-diol and heptane-1,6-diol were prepared from cyclopentanone and cyclohexanone, respectively, by reaction with methylmagnesium iodide, dehydration of the resulting carbinols with sodium bisulphate, and then ozonolysis and reduction according to the general technique of Sousa and Bluhm.[10] Nonane-1,8-diol, decane-1,9-diol and tetradecane-1,13-diol were prepared by reduction of the methyl esters of the appropriate keto acids with lithium aluminium hydride. Hexane-1,5-diol, n_D^{25} 1·4478 (lit.[11] 1·4492); heptane-1,6-diol, n_D^{25} 1·4522 (lit.[12] 1·453); *nonane-1,8-diol*, n_D^{25} 1·4553 (Found: C, 67·7; H, 12·9. $C_9H_{20}O_2$ requires C, 67·5; H, 12·6%). Decane-1,9-diol, n_D^{25} 1·4572 (lit.[13] n_D^{20} 1·4583); tetradecane-1,13-diol, nacreous plates (from cyclohexane), m.p. 51° (lit.[14] 49–50°).

Decan-9-olide

9-Hydroxydecanoic acid (2 g) in glacial acetic acid (10 ml) was treated with concentrated aqueous hydrobromic acid (20 ml) and the mixture was warmed on a water bath. Small aliquots of the reaction mixture were removed at intervals, treated with excess ethereal diazomethane, and the resulting esters examined gas chromatographically (column 4, 160°). After 3 h the transformation of the initially formed 9-acetoxydecanoic acid to the corresponding bromo acid(s) appeared to be complete. The mixture was then diluted with cold water, extracted with ether, and the extract washed with water and dried over anhydrous sodium sulphate. Evaporation of the extract left crude bromo acid (2·3 g) which, after distillation under vacuum, afforded a colourless oil, b.p. 80–95° (bath temperature)/

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0·05 mmHg. A low-resolution mass spectrum showed the expected molecular ion at *m/e* 250 but gas chromatographic analysis of a methylated sample showed the presence of two major components (*c.* 34% and 65%, respectively) and indicated that some migration of the bromine atom had taken place. Attempts to avoid this migration by varying reaction conditions or by treatment of the hydroxy acid in pyridine with thionyl bromide were unsuccessful and yielded inferior products.

Lactonization of the mixed bromo acids was carried out in high dilution by treatment with potassium carbonate, according to the general directions of Hunsdiecker and Erlbach,[5] but with butanone (rather than acetone) as solvent. The yield of non-acidic material amounted to some 50% of the weight of mixed bromo acids taken but this included condensation products from the solvent which, in gas chromatography (column 4, 125°), emerged earlier than did the lactones of interest. The latter comprised one major component, corresponding in retention time with the natural component (I), together with minor components of shorter and longer retention times. A small sample of pure *decan-9-olide* was obtained, as a colourless oil, after refinement on columns 2 and 4 (Found: *m/e* 170·13050. $C_{10}H_{18}O_2$ requires *m/e* 170·13068). The yield of synthetic lactone was of the order of 1%.

Methyl 13-Oxotetradecanoate

Monomethyl brassylate[15] (14 g) in light petroleum (b.p. 40–60°, 20 ml) was refluxed for 1 h with thionyl chloride (13 ml). Solvent was then removed on a water bath and unreacted thionyl chloride under vacuum. The resulting crude acid chloride was taken up in dry ether (30 ml) and the solution added dropwise, with stirring, to a cooled ethereal solution of cadmium methyl, previously prepared by adding dry cadmium chloride (10 g) to the Grignard reagent from magnesium (3·8 g) and methyl iodide (21 g) in ether (100 ml). The reaction mixture was allowed to stand overnight at room temperature and then decomposed with crushed ice. The neutral products were isolated (in ether) in a standard manner and, when recovered, formed an oil (10·3 g) which soon solidified. Recrystallization from cooled pentane afforded *methyl 13-oxotetradecanoate* as colourless plates, m.p. 52–55° (Found: *m/e* 256·20383. $C_{15}H_{28}O_3$ requires *m/e* 256·20385).

13-Hydroxytetradecanoic Acid

The above crude keto ester (6 g) was dissolved in 95% ethanol (20 ml) and the stirred solution treated at intervals, at 25°, with small quantities of powdered sodium borohydride. Progress in the reduction of the keto group was monitored by gas chromatography (column 4, 195°) on aliquots withdrawn at intervals and the addition of reducing agent was terminated as soon as the process appeared complete (prolonged treatment, particularly at elevated temperatures, resulted in attack on the ester group). The reaction mixture was then treated with excess ethanolic sodium hydroxide (for hydrolysis purposes) and allowed to stand overnight. *13-Hydroxytetradecanoic acid* was recovered by standard means in nearly quantitative yield and, upon recrystallization from hexane, formed colourless plates, m.p. 60° (Found: C, 68·6; H, 11·5. $C_{14}H_{28}O_3$ requires C, 68·8; H, 11·5%).

Tetradecan-13-olide

This was prepared, in very limited quantity, from 13-hydroxytetradecanoic acid in a manner analogous to that described for the C_{10} homologue and was similarly purified by gas chromatography (column 4, 160°); it formed a colourless *oil* (Found: *m/e* 226·19306. $C_{14}H_{26}O_2$ requires *m/e* 226·19329). The low-resolution mass spectrum showed the molecular ion at *m/e* 226 (15%) and important fragments at 208 (45), 182 (42), 111 (37), 98 (65), 83 (50), 69 (66), 55 (base peak), 43 (51), 41 (61). This spectrum matched closely that from a sample derived by degradation of component (K) and retention times of the two samples (on columns 2, 4 and 5) were also in close agreement.

Methyl 8-Oxononanoate

This was prepared in a manner entirely analogous to that described for the C_{15} homologue and was characterized as its 2,4-dinitrophenylhydrazone, m.p. 99° (from methanol) (lit.[16] 92·5–93·5°) (Found: *m/e* 366·15262. Calc. for $C_{16}H_{22}N_4O_6$: *m/e* 366·15394).

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