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THE DITERPENES OF *DACRYDIUM COLENSOI*—III[1]

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Abstract—An oxidoditerpene, isolated from the heartwood of *Dacrydium colensoi*, has been shown to be 18-hydroxy-2-ketomanoyl oxide (V).

PREVIOUS investigators of the heartwood extractives of *Dacrydium colensoi* have isolated the oxidoditerpenes manoyl oxide (I),[2] 2-ketomanoyl oxide,[3] the noroxidoditerpene colensen-2-one,[4] and a tricarbocyclic diterpene, dacrydol.[5] An examination of the higher boiling fractions has led to the isolation of a further five terpenoid compounds: 2-keto-3-oxamanoyl oxide,[1] 2α-hydroxymanoyl oxide,[1] 2,3-secomanoyl oxide dioic acid,[1] a hydroxy-ketomanoyl oxide designated as compound A, m.p. 113–114°, and compound B, $C_{20}H_{32}O_3$, m.p. 169–170°. The structure and stereochemistry of compound A is reported below.

Compound A analysed for $C_{20}H_{32}O_3$. The IR spectrum showed a hydroxyl band (3470 cm^{-1}), a strong carbonyl band (1699 cm^{-1}), and bands characteristic of a vinyl group (3095, 1640, 985, 920 cm^{-1}). Strong bands in the C—O stretching region (1115, 1075 cm^{-1}) indicated that the third oxygen was present in an oxide ring. From this spectral evidence compound A was assigned the same basic structure as the co-occurring manoyl oxide. This was confirmed by the isolation of manoyl oxide as a product of a degradation reaction (see later). The carbonyl frequency of the dihydro derivative (1709 cm^{-1}) and the UV maximum (291 mμ) indicated that the keto group was present as a cyclohexanone system. This was confirmed by the perturbed methylene band[6] at 1426 cm^{-1} which also showed the presence of at least one —CH_2— adjacent to the keto group.

The NMR spectrum of compound A showed the typical α-vinyl pattern[7] (H_A 4·05, H_B 5·03, H_C 4·83τ; J_{AB} 10·5, J_{BC} 1·8, J_{AC} 17·5 c/s). The position of the keto group was indicated by the two AB systems centred at 7·56τ (J_{AB} 13·3 c/s) and 7·93τ (J_{AB} 9·8 c/s) due to two methylene groups adjacent to the keto group, thus fixing the keto group at C-2. Furthermore, the optical rotatory dispersion curve of compound A exhibited a strong positive Cotton effect, almost superimposable on that of 2-ketomanoyl oxide.

An attempt to confirm the position of the keto group in compound A chemically by the hydrogenolysis of the tosyl ester,[8] although unsuccessful, was informative. Under tosylation conditions compound A gave a highly crystalline product, $C_{20}H_{30}O_2$, which was formulated as the 3,18-cyclopropyl-2-ketomanoyl oxide (II) from spectral

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measurements. The absence of a hydroxyl band in the IR spectrum and the carbonyl band at 1678 cm^{-1}, together with the UV absorption (λ_{max} 215 mμ, ε 2100) were in good agreement with those reported for the cyclopropyl ketones of the maaliol series.[9] In the NMR spectrum, the cyclopropyl protons (forming the AB part of an ABX system) occurred as a multiplet at 9·01–9·36τ under a methyl signal (total area of five protons) similar to those reported for thujopsene.[10] LAH reduction of the cyclopropyl ketone (11) gave manoyl oxide (in 15% yield) and so established the absolute configuration of the ring junctions in compound A. We can find no analogy for this unexpected reaction which is being investigated further.

The presence of a primary hydroxyl in compound A was established by the NMR spectrum which showed only four methyl signals (9·17, 8·84, 8·70, 8·70τ) together with an AB system at 6·50τ (J_{AB} 11·5 c/s). Thus one of the methyl groups of the manoyl oxide skeleton had been replaced by a hydroxymethyl group. The AB system is a consequence of the non-equivalence of the methylene protons due to C-4 being asymmetric,[11] and not as some workers have suggested, due to the restricted rotation. Furthermore the hydroxymethyl group can only be at C-17, C-18, or C-19 since the C-16 and C-20 methyl groups, β to the ether oxygen, can be assigned to the low field methyl signal (8·70τ).

Although biogenetically C-17 or C-18 are the most likely positions of the hydroxymethyl group, the C-19 position cannot be ruled out. It has been shown[4] that dihydro-2-ketomanoyl oxide is autoxidized to the diosphenol (III) exclusively. Autoxidation of a 17- or 18-hydroxymethyl-2-keto compound would produce a diosphenol containing a β-hydroxy-ketone system which would undergo a reverse aldol[12] under the alkaline conditions of the autoxidation to give a nor-diosphenol and formaldehyde. Similarly the diosphenol from the autoxidation of a 19-hydroxymethyl-2-keto compound would also undergo a reverse aldol cleavage since the hydroxyl group is vinylogously β to the carbonyl.* However the alternative nor-diosphenol products would show most distinctive NMR spectra and be readily distinguished. The NMR spectrum of the autoxidation product of dihydro compound A is consistent only with the nor-diosphenol (IV), $C_{19}H_{30}O_3$, derived from a C-17 or C-18 hydroxymethyl group. The spectrum showed the absence of an olefinic proton, a low field signal (4·17τ) which disappeared on deuteration being assigned to the enol proton. The allylic methyl at C-4 appeared as a doublet (8·2τ, J 1·7 c/s, secondary coupling with C-5 H), and the C-1 methylene as an AB system centred at 7·64τ (J_{AB} 16·8 c/s). Enolization has now been directed towards C-4 as would be expected from stability considerations since C-4 is no longer blocked as a quaternary centre. The ultraviolet absorption spectrum of the nor-diosphenol at 282 mμ (ε 9020) (shifted bathochromically to 333 mμ (ε 7600) in alkali) confirmed the substitution[13] of the nor-diosphenol as —C(=O)—C(OH)=C—, i.e. no βH.

* We thank the referee for drawing our attention to this point.

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In many cases it has been possible to assign the stereochemistry of hydroxymethyl groups from a consideration of the chemical shifts of the hydroxymethyl group and its derivatives.[14] However, compound A and its derivatives showed chemical shifts which were intermediate in value between those reported for axial and equatorial orientations, though the value for the formyl derivative (0·30τ) would suggest an axial orientation.[15]

The stereochemistry of compound A at C-4 can be established by comparing the chemical shifts of the methyl groups of dihydro compound A and its epimeric C-2 alcohols with dihydro-2-ketomanoyl oxide, dihydro-2α-hydroxymanoyl oxide, and dihydro-2β-hydroxymanoyl oxide. Of the three methyls attached to ring A in dihydro-2-ketomanoyl oxide and its derivatives, the C-18 and C-19 methyls are axial and symmetrically placed with respect to C-2 and so exhibit similar changes in chemical shift with a change of functional group at C-2, and are thus readily identified. The third methyl (C-17) is not effected by changes at C-2 and this is reflected by its relatively stable shift, which enables it to be identified (Table 1). Dihydro compound A has only two methyl groups in ring A, the third methyl being replaced by the hydroxymethyl group. By comparing the methyl shifts for dihydro compound A and its C-2 alcohol derivatives with dihydro-2-ketomanoyl oxide and its C-2 alcohol derivatives

TABLE 1. CHEMICAL SHIFTS OF RING A METHYL GROUPS OF COMPOUND A AND 2-KETOMANOYL OXIDE DERIVATIVES

Dihydro derivative of	C-17 Me	Axial C-18, C-19 Me
2-Ketomanoyl oxide	8·95	9·22, 9·14
18-Hydroxy-2-ketomanoyl oxide	8·87	9·21
2α-Hydroxymanoyl oxide	9·06	9·18, 9·15
2α,18-Dihydroxymanoyl oxide	8·96	9·17
2β-Hydroxymanoyl oxide	8·95	9·05, 9·01
2β,18-Dihydroxymanoyl oxide	8·92	8·98

TABLE 2. CHEMICAL SHIFTS OF SOME MANOYL OXIDE DERIVATIVES

Compound	C-17	C-19	C-16	C-20	$\underline{CH_2}OR$	Jc/s	C-18
18-Hydroxy-2-KMO	8·84	9·17	8·70	8·70	6·50	11·0	—
Dihydro-18-hydroxy-2-KMO	8·87	9·21	8·82	8·75	6·51 s		—
Dihydro-2α,18-dihydroxyMO	8·96	9·17	8·81	8·73	6·42	10·8	—
Dihydro-2β,18-dihydroxyMO	8·92	8·98	8·81	8·73	6·28	10·4	—
Dihydro-18-hydroxyMO	9·08	9·23	8·86	8·78	6·53	10·3	—
Dihydro-18-acetoxy-2-KMO	8·85	9·16	8·78	8·70	6·03 s		—
Dihydro-2β,18-diacetoxyMO	8·90	8·96	8·80	8·70	5·79	11·0	—
Dihydro-18-acetoxyMO	9·06	9·22	8·83	8·75	6·00	11·3	—
18-Formyl-2-KMO	8·77	9·33	8·70	8·70	—		—
3,18-Cyclopropyl-2-KMO	8·83	9·25	8·71	8·71	—		—
Dihydro-2-KMO	8·95	9·22	8·81	8·72	—		9·14
Dihydro-2α-hydroxyMO	9·06	9·18	8·84	8·75	—		9·15
Dihydro-2β-hydroxyMO	8·95	9·05	8·79	8·70	—		9·01

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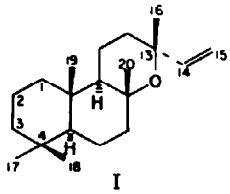
[15] T. J. King and J. P. Yardley, *J. Chem. Soc.* 4308 (1961).

it is apparent that compound A has only one axial methyl group, the other having been replaced by the hydroxymethyl group. Hence compound A is 18-hydroxy-2-ketomanoyl oxide (V). The assignment of the methyl groups of 18-hydroxy-2-keto-manoyl oxide derivatives and dihydro-2-ketomanoyl and its derivatives follows readily (Table 2).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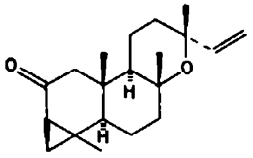
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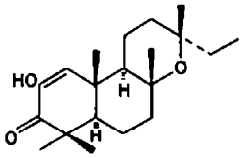
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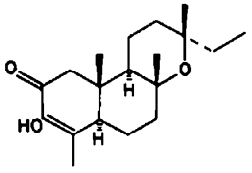
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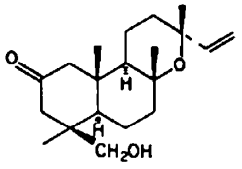
V

EXPERIMENTAL

M.ps are corrected and were taken on a Kofler block. UV spectra, measured on a Shimadzu RS27 instrument, are for EtOH solutions. IR spectra, measured on a Perkin–Elmer 421 instrument, are for Nujol mulls, unless otherwise stated. Light petroleum refers to the fraction b.p. 60–80°. Merck's standardized aluminium oxide and Light's silicic acid were used in chromatography. The NMR spectra were measured at 60 Mc in $CDCl_3$ solution using tetramethylsilane and $CHCl_3$ as internal standards.

Isolation of 18-*hydroxy-2-ketomanoyl oxide. Dacrydium colensoi* chips were extracted with acetone, the acetone removed under vacuum, and the extract taken up in ether and treated with NaOH to remove acids and phenols. After the precipitation of dacrydol by the addition of light petroleum, and removal of the solvent under vacuum, the neutral oily residue was distilled and all fractions to b.p. 160°/0·15 mm collected. The distillation residue was chromatographed from light petroleum–ether (1 : 1) on alumina. Elution with this solvent gave manoyl oxide, 2-ketomanoyl oxide, colensen-2-one, and 2-keto-3-oxamanoyl oxide. Continued elution of the column with ether gave 18-*hydroxy-2-ketomanoyl oxide* (V), m.p. 113–114° after recrystallization from light petroleum. (Found: C, 75·4; H, 10·1. $C_{20}H_{32}O_3$ requires: C, 75·0; H, 10·1%); ν_{max} 3470 (—OH), 1699 (C=O), 3095, 1639, 986, 920 (CH:CH_2), 1115, 1075 (C—O) cm^{-1}; λ_{max} 291 mμ (ε 35). Positive Cotton effect curve 310 mμ (peak), a −64. Proton resonance: methyl peaks at 9·17, 8·84, 8·70, 8·70τ; C-1 and C-3 methylenes as AB systems centred at 7·56τ (J_{AB} 13·0 c/s) and 7·93τ (J_{AB} 9·8 c/s); C$\underline{H_2}$OH as an AB system centred at 6·50τ (J_{AB} 11·5 c/s); vinyl protons H_A 4·05, H_B 5·03, H_Q 4·83τ (J_{AB} 10·5, J_{BQ} 1·8, J_{AC} 17·5 c/s). Continued elution of the column with ether gave *compound* B, m.p. 169–170° after recrystallization from aqueous MeOH and vacuum sublimation. (Found: C, 78·9; H, 10·4. $C_{20}H_{32}O_2$ requires: C, 78·9; H, 10·6%) ν_{max} 3280 (—OH), 3080, 1634, 991, 924 (CH:CH_2), 1658 (C:CH) cm^{-1}.

*Dihydro-*18-*hydroxy-2-ketomanoyl oxide.* 18-Hydroxy-2-ketomanoyl oxide (0·31 g) in MeOH (20 ml) was hydrogenated over Adams catalyst. One mole H_2 was absorbed to give dihydro-18-hydroxy-2-ketomanoyl oxide (0·29 g), m.p. 102–103°. (Found: C, 74·3; H, 10·8. $C_{20}H_{34}O_3$ requires: C, 74·5; H, 10·6%); ν_{max} (CCl_4) 1708 (C=O), 1426 (perturbed methylene) cm^{-1}.

18-*Formyl-2-ketomanoyl oxide.* 18-Hydroxy-2-ketomanoyl oxide (146 mg) in acetone (10 ml) was oxidized with 8N chromic-sulphuric acid. The product (103 mg) after recrystallization from aqueous acetone gave 18-*formyl-2-ketomanoyl oxide*, m.p. 154–156°. (Found: C, 75·4; H, 9·5. $C_{20}H_{30}O_3$

requires: C, 75·4; H, 9·5%); ν_{max} 1709 (C=O) cm^{-1}. Proton resonance: methyl peaks at 9·33, 8·77, 8·70, 8·70τ; C-1 and C-3 methylenes as AB systems at 7·47 (J_{AB} 15·0 c/s) and 7·81τ (J_{AB} 13·2 c/s); aldehyde 0·30τ.

Wolff-Kishner reduction. Hydrazine hydrate (6 ml) was added to dihydro-18-hydroxy-2-ketomanoyl oxide (1·12 g) in diethylene glycol (100 ml) and the temp maintained at 120° for ½ hr. Potassium hydroxide (5 g) was added and the temp kept at 120° for 1 hr. The whole was then heated under distillation conditions until the temp reached 215°, and then maintained under reflux at 215° for 5 hr. After cooling, the solution was diluted with water (1:1) and the product (0·91 g) filtered off. Recrystallization from aqueous MeOH gave dihydro-18-hydroxymanoyl oxide, m.p. 104–105°. (Found: C, 77·7; H, 11·9. $C_{20}H_{36}O_2$ requires: C, 77·9; H, 11·8%); ν_{max} 3300 (—OH) cm^{-1}. Proton resonance: methyl peaks at 9·23, 9·08, 9·08 (triplet, J 5·8 c/s), 8·86, 8·78τ; C$\underline{H}_2$OH as AB system centred at 6·45τ (J_{AB} 11·2 c/s).

18-*Acetoxy-2-ketomanoyl oxide.* 18-Hydroxy-2-ketomanoyl oxide (100 mg) in pyridine–acetic anhydride (1:1; 5 ml) was allowed to stand overnight. Crystallization of the product (105 mg) from aqueous MeOH gave 18-*acetoxy-2-ketomanoyl oxide*, m.p. 114–115°. (Found: C, 72·6; H, 9·5. $C_{22}H_{34}O_4$ requires: C, 72·9; H, 9·45%); ν_{max} (CCl_4) 1748 (acetate C=O), 1715 (C=O), 1245 (acetate C—O) cm^{-1}. Proton resonance: methyl peaks at 9·15, 8·85, 8·69, 8·69τ; acetate methyl 7·96τ; C$\underline{H}_2$OH 6·01τ (singlet).

Dihydro-18-*acetoxymanoyl oxide.* Dihydro-18-hydroxymanoyl oxide (0·15 g) on acetylation (as above) gave *dihydro*-18-*acetoxymanoyl oxide*, m.p. 73–74·5° after recrystallization from aqueous acetone. (Found: C, 75·4; H, 11·1. $C_{22}H_{38}O_3$ requires: C, 75·4; H, 10·9%); ν_{max} 1743 (acetate C=O), 1238 (acetate C—O) cm^{-1}. Proton resonance: methyl peaks at 9·22, 9·06, 9·06 (triplet, J 5·9 c/s), 8·83, 8·75τ; acetate methyl 7·98τ; C$\underline{H}_2$OAc 6·00τ (J_{AB} 11·3 c/s).

2β, 18-*Dihydroxymanoyl oxide.* 18-Hydroxy-2-ketomanoyl oxide (153 mg) in dry ether (15 ml) was added dropwise to an excess of LAH in dry ether (50 ml), and the solution refluxed for 2 hr. The excess of LAH was destroyed with water, 10% H_2SO_4 added (20 ml) and the solution extracted with ether to give 2β, 18-*dihydroxymanoyl oxide*, m.p. 154–155° from aqueous MeOH. (Found: C, 74·7; H, 11·0. $C_{20}H_{34}O_3$ requires: C, 74·5; H, 10·6%); ν_{max} 3430 (—OH), 1036 (C—O of secondary alcohol). Proton resonance: methyl signals at 8·99, 8·90, 8·71, 8·71τ; C$\underline{H}_2$OH as AB system centred at 6·28τ (J_{AB} 11·0 c/s); C$\underline{H}$OH 5·85τ (multiplet).

2β, 18-*Diacetoxymanoyl oxide*, 2β, 18-Dihydroxymanoyl oxide (100 mg) was acetylated (as above) to give 2β, 18-*diacetoxymanoyl oxide*, m.p. 96–97° (from aqueous MeOH). (Found: C, 70·5; H, 9·5. $C_{24}H_{38}O_5$ requires: C, 70·9; H, 9·4%); ν_{max} 1732 (acetate C=O), 1249 (C—O of acetate) cm^{-1}. Proton resonance: methyl peaks at 8·95, 8·95, 8·71, 8·71τ; acetate methyls 7·89, 7·93τ; C$\underline{H}_2$OAc as AB system centred at 5·75τ (J_{AB} 11·3 c/s); C$\underline{H}$OAc 4·84τ (Triplet, J 4·1 c/s).

Dihydro-2α, 18-*dihydroxymanoyl oxide.* Dihydro-18-hydroxy-2-ketomanoyl oxide (0·37 g) in propan-1-ol (25 ml) was refluxed with the addition of small pieces of Na for 3 hr. The product (0·33 g) was chromatographed on alumina (10 g) from benzene. Elution with $CHCl_3$ gave a mixture of dihydro-2β and 2α, 18-dihydroxymanoyl oxide, followed by *dihydro*-2α, 18-*dihydroxymanoyl oxide*, m.p. 205–207° after recrystallization from aqueous acetone and sublimation (120°/0·05 mm). (Found: C, 73·9; H, 11·2. $C_{20}H_{36}O_3$ requires: C, 74·0; H, 11·2%); ν_{max} 3300 (—OH) cm^{-1}. Proton resonance: methyl peaks at 9·17, 9·15 (triplet, J 7·0 c/s), 8·96, 8·81, 8·73τ; C$\underline{H}_2$OH as AB system centred at 6·42τ (J_{AB} 10·8 c/s).

3,18-*Cyclopropyl-2-ketomanoyl oxide.* 18-Hydroxy-2-ketomanoyl oxide (0·53 g) and *p*-toluenesulphonyl chloride (1·5 g) in pyridine (2·5 ml) were refluxed for 1½ hr. The solution was poured into ice-water (100 ml) and extracted with ether. The ethereal extract was washed with 1N HCl, then water, and dried over anhyd. Na_2SO_4. The product (0·63 g) was chromatographed on alumina (16 g) from light petroleum. Elution with light petroleum–ether (19:1) gave the 3,18-*cyclopropyl*-2-*ketomanoyl oxide* (11, 0·49 g). m.p. 154–156° from aqueous MeOH. (Found: C, 79·4; H, 10·2. $C_{20}H_{30}O_3$ requires: C, 79·4; H, 10·0%); ν_{max} 3040 (cyclopropane), 1680 (C=O) cm^{-1}. λ_{max} 215 mμ (ε 2,100), 284 mμ (ε 70). Proton resonance: methyl peaks at 9·25, 8·83, 8·71, 8·71τ; cyclopropane protons (AB part of ABX system) 9·01–9·36τ.

LAH reduction of the cyclopropyl ketone (11). The cyclopropyl ketone (0·5 g) in tetrahydrofuran (20 ml) was added to an excess of LAH in tetrahydrofuran (70 ml), refluxed for 6 hr and worked up as usual. The product (0·48 g) was oxidized with 8N chromic acid–sulphuric acid and then chromatographed on alumina (14 g) from light petroleum. Elution with light petroleum gave manoyl oxide (1),

(70 mg), the IR spectrum of which was identical with that of an authentic specimen. Further elution with light petroleum–ether (19:1) gave the unchanged cyclopropyl ketone (mixed m.p.).

Autoxidation of dihydro-18-hydroxy-2-ketomanoyl oxide. Dihydro-18-hydroxy-2-ketomanoyl oxide (1·15 g) suspended in t-butyl alcoholic N-potassium t-butoxide (40 ml) was shaken with oxygen in a standard hydrogenation apparatus for 35 min. (1 mole O_2 uptake). The solution was diluted with water (400 ml) and 6N HCl (30 ml) added. The solution was extracted with $CHCl_3$ (2 × 100 ml), the extracts washed with saturated $NaHCO_3$aq (2 × 35 ml), and then water (100 ml). Removal of the solvent under vacuum gave a product (675 mg) which was chromatographed on silicic acid (40 g) from light petroleum. Elution with light petroleum–ether (9:1) gave the *nor-diosphenol* (IV; 150 mg), m.p. 149–150° after recrystallization from aqueous MeOH and vacuum sublimation. (Found: C, 74·75; H, 9·9. $C_{19}H_{30}O_3$ requires: C, 74·5; H, 9·9%); ν_{max} 3410 (—OH), 1655 1624 (diosphenol) cm^{-1}. λ_{max} 282 mμ (ε 9200) shifted bathochromically in alkali to λ_{max} 333 mμ (ε 7600). Proton resonance: methyl peaks at 9·29, 9·20 (triplet, J 5·9 c/s), 8·87, 8·78τ; allylic methyl 8·23τ (doublet, J 1·7 c/s); enolic proton 4·17τ.

Dihydro-2α-hydroxymanoyl oxide. Dihydro-2-ketomanoyl oxide (0·77 g) in propan-1-ol (50 ml) was refluxed with Na as described earlier. The product (0·72 g) was chromatographed on alumina (30 g) from light petroleum–ether (4:1). Elution with the same solvent gave a mixture of dihydro-2β and 2α-hydroxymanoyl oxides (0·18 g), followed by *dihydro-2α-hydroxymanagh oxide* (0·41g), m.p. 59–62° from aqueous EtOH. (Found: C, 78·2; H, 12·0. $C_{20}H_{36}O_3$ requires: C, 77·9; H, 11·8%); ν_{max} 3300 (—OH) cm^{-1}. Proton resoance: methyl peaks at 9·18, 9·15, 9·15 (triplet, J 5·9 c/s), 9·06, 8·84, 8·75τ; C<u>H</u>OH (poorly resolved) 6·13τ.

Dihydro-2β-hydroxymanoyl oxide. 2-Ketomanoyl oxide (2·7 g) in dry ether (40 ml) was reduced with LAH as previously described. The product (2·61 g), contaminated with traces of 2α-hydroxymanoyl oxide, was chromatographed on alumina (80 g) from light petroleum–ether (7:3). Elution with the same solvent gave 2β-hydroxymanoyl oxide which was dissolved in ethyl acetate (30 ml) and hydrogenated over Adams catalyst. Recrystallization from aqueous acetone gave dihydro-2β-hydroxymanoyl oxide, m.p. 81·5–83·5°. (Found: C, 77·5; H, 11·8. Calc. for $C_{30}H_{36}O_3$: C, 77·9; H, 11·8%); ν_{max} 3420 (—OH) cm^{-1}. Proton resonance: methyl peaks at 9·15 (triplet, J 5·8 c/s), 9·05, 9·01, 8·95, 8·79, 8·70τ; C<u>H</u>OH 5·85τ (multiplet).

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