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

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Abstract—The dihydro derivative (**1**; R = Et) of the homo-diterpene lactone, colensen-2β-ol-1α-hydroxymethyl-2α-carboxylactone (**1**; R = CH=CH_2) described in the preceding paper, has been synthesized by two independent routes. The stereochemistry of some disubstituted ring A derivatives which could not be established by spectroscopic techniques was determined by chemical methods.

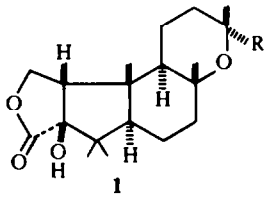
2,3-DICARBOXY-2,3-SECOMANOYL oxide (**2**; R = H, R′ = CH=CH_2) from the heartwood of *Dacrydium colensoi* was converted to dihydro dimethyl 2,3-secomanoyl oxide 2,3-dioate (**2**; R = Me, R′ = Et). Dieckmann condensation[2] of the dimethyl ester gave the epimeric β-keto esters, 1α-methoxycarbonylcolensan-2-one (**3**) and 1β-methoxycarbonylcolensan-2-one (**4**) in a 1:4 ratio. The stereochemistry of the products was established by an examination of the 1-H resonance in the NMR spectra. In **4** the 1α-H exhibited long range coupling (4 σ) with the C-10 angular Me group.[3] This was confirmed by double resonance experiments when the W/2 for the 1-H reverted to the same order as in the epimeric derivative (**3**). In addition the α-substituted derivative could be epimerised to **4** under acid conditions. LAH reduction of the keto ester (**3**) gave the epimeric 1,3 diols (**5**; R = H and **6**; R = H) identical in all respects (m.m.p.; IR) with the 1,3 diols obtained from the LAH reduction of 1α-hydroxymethylcolensan-2-one,[1] a degradation product of the lactone. Preferential acetylation of the primary alcohol in the 1,3-diols gave the epimeric hydroxy-acetates (**5**; R = Ac and **6**; R = Ac) respectively which gave the same β-keto-acetate (**7**) on oxidation.

A similar sequence of reactions was carried out for the β-keto ester (**4**). LAH reduction gave the epimeric 1,3-diols (**8**; R = H and **9**; R = H) in a 2:1 ratio. Unlike the 1α-hydroxymethyl-2-hydroxy epimers,[3] the absolute configurations of the 1β-hydroxymethyl-2-hydroxy epimers could not be established from the carbinol proton signals, a coupling of 6–8 c/s being predicted for both epimers. The structure assignments were made on chemical evidence. Preferential tosylation of the primary OH group gave the epimeric monotosyl derivatives (**8**; R = Ts and **9**; R = Ts) which could be readily distinguished by the base catalysed elimination products.[4] Base treatment of the *trans* monotosyl derivative (**8**; R = Ts) gave the expected ring opened product (**10**) while the *cis* isomer (**9**; R = Ts) gave the predicted oxetan derivative (**11**).

It is interesting to note that these assignments were opposite to those predicted (a) on a yield basis—where the predominance of hydride reduction from the less hindered α-face would be expected to produce a greater proportion of 1β-hydroxymethylcolensan-2β-ol (**9**; R = H) (b) from H-bonding studies. Table 1 gives the minimum distances for H-bonding in the three possible conformations of the epimeric 1β-hydroxymethylcolensan-2-ols as measured from Dreiding models. Although both epimeric 1,3-diols exhibited H-bonding, it would be predicted that the *trans* 1,3-diol,

having the larger OH—O distance, would be associated with the weaker H-bond. Table 1 shows this was not the case.

The failure of H-bonding studies to give the correct structure assignment emphasises the limitations of this method as pointed out by Fetizon.[6]



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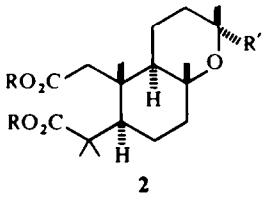

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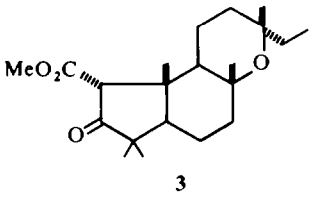

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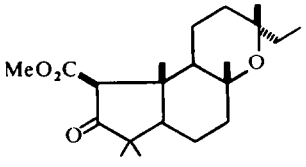

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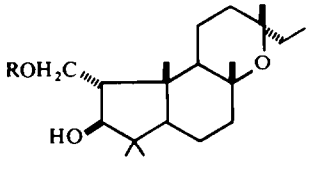

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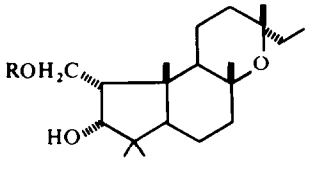

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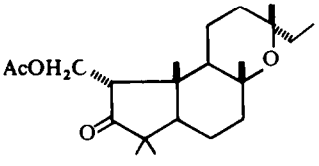

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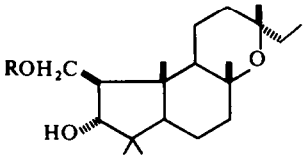

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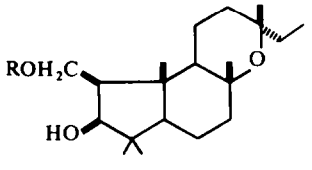

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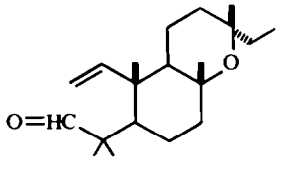

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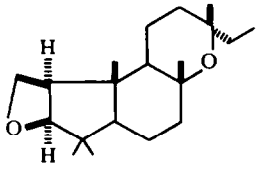

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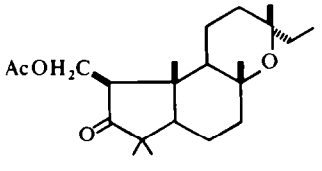

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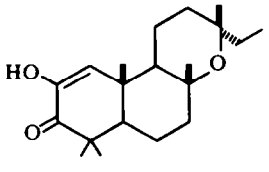

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Preferential acetylation of the primary alcohol grouping of the 1,3 diols gave the epimeric hydroxyacetates (**8**; R = Ac and **9**; R = Ac) respectively. Oxidation of the hydroxy-acetates gave the same β-ketoacetate (**12**) and established that no epimerization at C-1 had occurred in any of the conversions in the formation of the epimeric β-keto-acetate (**7**).

The β-keto-acetate (**7**) failed to form a cyanohydrin under several modified conditions. It is well established that cyclopentane systems form carbonyl derivatives with

TABLE 1

Config.	α-Envelope	β-Envelope	½-Chair	OH Absorption	Δν	OH—H calc[c]
cis 1βCH$_2$OH,2βOH	< 1·4[a]	< 1·4	< 1·4	3620, 3581 cm^{-1}	59	2·08
trans 1βCH$_2$OH,2α—OH	> 2·7[b]	2·4	2·6	3634, 3557 cm^{-1}	83	1·89

[a] For distances below 1·4Å the covalent bond distance is approached.
[b] No H-bonding is observed for distances greater than 2·7Å.
[c] Calculated according to Klyne's equation,[5] assuming bonded primary H, with a standard value of 3640 cm^{-1}.

much less ease than the corresponding cyclohexanones due to developing torsional strain and Van der Waals eclipsing interactions. By minimising the solvation of the nucleophile by use of a dipolar aprotic solvent, cyanohydrin formation was achieved. It is envisaged that the bulky CN^- nucleophile approached from the less hindered α-face of the molecule to give the 2α-cyano-2β-hydroxy derivative. Immediate alkaline hydrolysis of the reaction mixture gave the dihydro derivative (**1**; R = Et)) of the lactone in 20% yield. The other product of the reaction was colensan-2-one, the result of a reverse aldol reaction[7] under the alkaline conditions on the β-keto-acetate (unreacted or present in equilibrium with the cyanohydrin).

A very simple two step synthesis of the dihydro derivative of the lactone was achieved in high yield using the co-occurring 2-oxomanoyl oxide as the starting material. 2-oxomanoyl oxide was hydrogenated to the dihydro derivative and autoxidized to the previously described diosphenol[8] (**13**). Hydroxymethylation[9] of the diosphenol with alkaline, aqueous formaldehyde solution (M KOH or 0·05 M $NaHCO_3$) resulted in concurrent benzilic acid ring contract. It is considered that as in bromination[10] axial attack from the less hindered α-face of the molecule would give the kinetically controlled product, dihydro-1α-hydroxymethyl-2,3-dioxomanoyl oxide.

As reported by Hanna and Ourisson[10] for the analogous 1α-bromo-4,4-dimethylcholestan-2,3-dione, the 1α-substituent cannot epimerise under the alkaline conditions to the thermodynamically stable epimer due to steric interaction between the 11α-H and the enol form and steric hindrance to the removal of the 1β-H. This also accounts for the nonformation of the α-disubstituted derivative. Levisalles[11] has shown by radioactive tracer experiments that the benzilic acid ring contraction of 4,4-dimethylcholestan-2,3-dione gives exclusively the 2α-carboxy derivative. In lactone synthesis the benzilic acid ring contraction could proceed by an intermolecular or an intramolecular mechanism. The intermolecular mechanism via nucleophilic attack at C-3 through a chair transition (94%)[11] could be inhibited by the axial 1α-hydroxymethyl group and so increase the percentage of attack at C-2 via a boat transition. However an intramolecular mechanism predetermines the stereochemistry of the lactone, as the axial 1α-hydroxymethyl anion (primary conformation) is well placed for nucleophilic α-face attack at C-3 via a chair transition state. An intramolecular mechanism is also supported by the ease of the reaction—$NaHCO_3$ at room temperature. Relative rate studies of the diosphenol in 0·05 M $NaHCO_3$ solution with and without added formaldehyde showed only ring contraction in the presence of formaldehyde, i.e. the

reaction under these conditions being intramolecular, the base strength being sufficient to generate the 1α-hydroxymethyl anion in the intermediate hydroxy diketone but the [OH^-] being insufficient for intermolecular addition at the C-3 carbonyl carbon.

EXPERIMENTAL

For general experimental details, see Part VI.

Dihydro dimethyl 2,3-secomanoyl oxide 2,3-dioate (**2**; R = Me, R′ = Et). Compound **2** (R = H, R′ = CH=CH_2; 10 g in AcOEt (200 ml) was hydrogenated over Adams catalyst to the dihydro derivative which was methylated with an ethereal soln of diazomethane to give **2** (R = Me, R′ = Et; 7·5 g) m.p. 54–56° (from aq acetone, lit.[8] 54·5–56·5°).

Dieckmann condensation. Dihydro dimethyl 2,3-secomanoyl 2,3-dioate (0·6 g) in dry benzene (40 ml) was refluxed with dry t-BuOK (0·1 g) for 72 hr. The reaction mixture was cooled, diluted with water, and the organic layer dried (Na_2SO_4). Removal of the solvent gave a product which was separated by PLC (2 × ether/hexane 1:3 development). The upper band gave 1α-*methoxycarbonylcolensan-2-one* (**3**; 100 mg) (m.p. 103–105° repeated sublimation 90°/0·02 mm); ν_{max}^{Nujol} 1742 (ester C=O), 1712 cm^{-1} (C=O); NMR Me signals at 0·83, triplet (*J* 6 c/s), 0·86, 0·99, 1·16, 1·18, 1·31; C—1 H 2·98 ($W_{\frac{1}{2}}$ 1 c/s); C$\underline{H}_3$OCO 3·62δ. (Found: C, 71·8; H, 9·8. $C_{21}H_{34}O_4$ requires: C, 72·0; H, 9·7%). The lower band gave 1β-*methoxycarbonylcolensan-2-one* (**4**; 420 mg) as an oil, b.p. 80°/0·02 mm; ν_{max}^{film} 1752 (ester C=O), 1720 cm^{-1} (C=O); NMR Me signals at 0·85, triplet (*J* 6 c/s), 0·99, 1·01, 1·05, 1·17, 1·31; C-1, H, 3·06 ($W_{\frac{1}{2}}$ 1·8 c/s, reducing to 1 c/s on irradiation of the Me signal at 1·05; CH$\underline{H}_3$OCO 3·67δ. (Found: C, 71·9; H, 10·0. $C_{21}H_{34}O_4$ requires: C, 72·0; H, 9·7%).

Epimerization of 1α-*methoxycarbonylcolensan-2-one* (**3**). Compound **3** (10 mg) in benzene (10 ml) was refluxed with *p*-toluenesulphonic acid (3 mg) for 1½ hr. Dilution with water and ether extraction gave an oil (9 mg) identified (IR, TLC) as **4**.

LAH reduction of 1α-*methoxycarbonylcolensan-2-one* (**3**). Compound **3** (100 mg) in dry ether (20 ml) was refluxed with LAH for 1½ hr. Excess LAH was destroyed by the addition of wet ether and the soln exhaustively extracted with ether. Removal of the solvent gave a product which was separated into two bands by PLC (ether/hexane 2:1 development). The upper band gave **6**, (R = H; 30 mg) m.p. 174–176° from aq MeOH and sublimation 120°/0·02 mm) (lit.[1] 174–176°) identical in all respects (IR, NMR, m.m.p.) with a degradation product of the lactone. The lower band gave the epimeric **5** (R = H; 55 mg) m.p. 178–180° (from aq MeOH and vacuum sublimation 150°/0·02 mm) identical (IR, NMR, m.m.p.) with a degradation product of the lactone.

Partial acetylation. Compound **5** (R = H; 50 mg) in pyridine (2 ml) and Ac_2O (0·02 ml) was allowed to stand at room temp for 14 hr. Dilution with water and ether extraction, followed by PLC (ether/hexane 1:1 development) gave 1α-*acetoxymethylcolensan-2β-ol* (**5**; R = Ac; 40 mg) as an oil b.p. 75°/0·02 mm; ν_{max}^{film} 3460 (OH), 1733, 1223 cm^{-1} (acetate); NMR Me signals at 0·85, triplet (*J* 7 c/s), 0·94, 1·03, 1·07, 1·21, 1·32; C$\underline{H}_3$COO 2·06; C$\underline{H}$OH 3·90, singlet ($W_{\frac{1}{2}}$ 2·2 c/s); C$\underline{H}$OAc as AB part of ABX system H_B 3·94, H_A 4·16δ (J_{AB} 10·8, J_{AX} 5·1, J_{BX} 10·7 c/s). (Found: C, 72·4; H, 10·5. $C_{22}H_{38}O_4$ requires: C, 72·1; H, 10·4%). Similarly **6** (R=H; 50 mg) on partial acetylation gave 1α-*acetoxymethylcolensan-2α-ol* (**6**; R = Ac; 40 mg) as an oil b.p. 75°/0·02 mm; ν_{max}^{film} 3460 (OH), 1728, 1239 cm^{-1} (acetate); NMR Me signals at 0·84, triplet (*J* 6 c/s), 0·87, 0·93, 0·96, 1·21, 1·32; C$\underline{H}_3$COO 2·03; C$\underline{H}_2$OAc as AB part of ABX system H_B 4·16, H_A 4·41 (J_{AB} 11·7, $J_{AX} = J_{BX}$ 5·7 c/s); C$\underline{H}$OH 4·34δ, doublet (*J* 7·0 c/s). (Found: C, 72·55; H, 10·5. $C_{22}H_{38}O_4$ requires: C, 72·1; H, 10·4%).

1α-*Acetoxymethylcolensan*-2-one (**7**). Compound **5** (R = Ac; 35 mg) in acetone (4 ml) was oxidized with Jones reagent (0·6 ml) for 3 min. Dilution with 5% $NaHCO_3$ aq and ether extraction, followed by PLC (ether/hexane 1:3 development) gave **7** (28 mg) m.p. 63–64° (sublimation 55°/0·02 mm) (lit.[1] 63–64°) identical in all respects (IR, m.m.p.) with a degradation product of the lactone. Similarly oxidation of the epimeric **6** (R = Ac) gave the same product (**7**).

LAH reduction of 1β-*methoxycarbonylcolensan-2-one* (**4**). Compound **4** (100 mg) in dry ether (20 ml) was reduced with LAH as described earlier. The product was separated into two components by PLC (8 × ether/hexane 2:1 development). The upper band gave **9** (R = H; 25 mg) m.p. 118–120° (sublimation 90°/0·02 mm); $\nu_{max}^{CCl_4}$ 3630 (non-bonded OH), 3581 cm^{-1} (bonded OH); NMR Me signals at 0·85, triplet (*J* 7 c/s), 0·87, 0·89, 1·05, 1·16, 1·25; C$\underline{H}$-C$\underline{H}_2$OH as ABX system $H_A = H_B$ 3·96, H_X 1·82 ($\frac{1}{2}|J_{AX} + J_{BX}|$ 7·7 c/s); C$\underline{H}$OH 4·13δ, doublet (*J* 7·4 c/s). (Found: C, 73·55; H, 10·9. $C_{20}H_{36}O_3$ requires: C, 74·0; H, 11·15%).

The lower band gave 1β-*hydroxymethylcolensan-2α-ol* (**8**; R = H; 60 mg) m.p. 126·5–127·5° (sublimation 95°/0·02 mm) $\nu_{max}^{CCl_4}$ 3634, 3613 (non-bonded OH), 3557 cm^{-1} (bonded OH); NMR Me signals at 0·85, triplet (*J* 6 c/s), 0·73, 0·92, 0·94, 1·16, 1·26; C$\underline{H}_2$OH as AB part of ABX system H_B 3·75, H_A 4·15 (J_{AB} 10·1, J_{AX} 4·1, J_{BX} 10·0 c/s); C$\underline{H}$OH 3·94δ, doublet (*J* 8·5 c/s) (Found: C, 73·8; H, 11·1. $C_{20}H_{36}O_3$ requires: C, 74·0; H, 11·15%).

Partial tosylation. Compound **8** (R = H; 60 mg) in dry redistilled pyridine (2 ml) was cooled to 5° and and a soln of freshly recrystallized tosyl chloride (70 mg) in pyridine (2 ml) added. After standing at room temp for 12 hr the soln was diluted and ether extracted. PLC (ether/hexane 1:1 development) of the product gave 1β-*tosyloxymethylcolensan-2α-ol* (**8**; R = Ts) as a colourless oil, ν_{max}^{film} 3540 cm^{-1} (OH); NMR Me signals at 0·72, 0·84, triplet (*J* 7 c/s), 0·88, 0·92, 1·16, 1·24; C$\underline{H}_3$Ar 2·45; C$\underline{H}$OH 3·75, doublet (*J* 8 c/s); C$\underline{H}_2$OTs as AB part of ABX system H_B 4·16, H_A 9·0, J_{AX} 4·5, J_{BX} 7·5 c/s; aromatic protons as AB system H_B 7·33, H_A 7·79 (J_{AB} 8, meta coupling 2 c/s). Similarly partial tosylation of **9** (R = H) gave 1β-*tosyloxymethylcolensan-2β-ol* (**9**; R = Ts) as an oil, ν_{max}^{film} 3530 cm^{-1} (OH); NMR Me signals at 0·80, 0·85, 0·85, triplet (*J* 7 c/s), 1·02, 1·16, 1·23; C$\underline{H}_3$Ar 2·44; C$\underline{H}$OH 3·96, doublet (*J* 7 c/s); C$\underline{H}_2$OTs 4·20, multiplet; aromatic protons as AB system H_B 7·32, H_A 7·80δ (J_{AB} 8, meta coupling 2 c/s).

Action of alkali on the tosyloxy derivatives. (a) Compound **8** (R = Ts; 60 mg) in t-BuOH was added to a 1N solution of t-BuOK (0·3 ml). TLC showed that the reaction was complete in 5 min. Dilution with water and ether extraction gave the 2,3-*seco unsaturated aldehyde* (**10**; 32 mg), m.p. 65·5–66·5° (from aq EtOH) ν_{max}^{Nujol} 2720, 1720 (CHO); 3085, 1633, 1407, 1000, 910 cm^{-1} (CH=CH_2); NMR Me signals at 0·83 triplet (*J* 7 c/s), 0·94, 1·01, 1·05, 1·17, 1·30; CH=CH_2 as an ABX system H_B 4·85, H_A 5·15, H_X 5·46 (J_{AX} 11, J_{AB} 2, J_{BX} 17 c/s); C$\underline{H}$O 9·46δ. (Found: C, 78·6; H, 11·2. $C_{20}H_{34}O_2$ requires: C, 78·4; H, 11·2%). (b) Compound **9** (R = Ts; 60 mg) in t-BuOH (2 ml) was treated with t-BuOK as above. After 5 min the reaction mixture was diluted with water and ether extracted to give the *oxetan derivative* (**11**; 32 mg) m.p. 131–133° (sublimation 60°/0·01 mm) NMR Me signals at 0·83, triplet (*J* 7 c/s), 0·93, 1·01, 1·19, 1·24, 1·36; the oxetan methylene, C-1, and C-2 protons formed an ABXC system C-1 H, 2·47, six lines, H_A 4·71, triplet, H_B 4·03, quartet, C-2 H 4·91δ, doublet (J_{AB} 6, $J_{A,1}$ 6, $J_{B,1}$ 2, $J_{1,2}$ 6 c/s) (Found: C, 78·2; H, 11·2. $C_{20}H_{34}O_2$ requires: C, 78·4; H, 11·2%).

Partial acetylation. Compound **8**; (R = H; 20 mg) in pyridine (3 ml) and Ac_2O (0·02 ml) was allowed to stand for 14 hr. PLC (ether/hexane 1:1) gave 1β-*acetoxymethylcolensan-2α-ol* (**8**; R = Ac; 15 mg) as an oil b.p. 80°/0·02 mm ν_{max}^{film} 3460 (OH), 1730, 1240 cm^{-1} (acetate); NMR Me signals at 0·80, 0·86, triplet (*J* 7 c/s), 0·94, 0·96, 1·18, 1·28; C$\underline{H}_3$COO 2·05, C$\underline{H}$OH 3·84, doublet (*J* 8·3 c/s), C$\underline{H}_2$OAc as AB part of ABX system H_B 4·20, H_A 4·52 δ (J_{AB} 11·3, J_{AX} 4·8, J_{BX} 6·8 c/s). (Found: C, 71·7; H, 10·4. $C_{22}H_{38}O_4$ requires: C, 72·1; H, 10·4%). Similarly preferential acetylation of **9** (R = H) gave 1β-*acetoxymethylcolensan-2β-ol* (**9**; R = Ac) as an oil b.p. 80°/0·02 mm ν_{max}^{film} 3440 (OH), 1730, 1240 cm^{-1} (acetate); NMR Me signals at 0·84, triplet (*J* 7 c/s), 0·87, 0·87, 1·04, 1·16, 1·26; C$\underline{H}_3$COO 2·05; C$\underline{H}$OH 3·95, doublet (*J* 7·0 c/s); C$\underline{H}$OAc as AB part of ABX system H_B 4·40, H_A 4·44 δ (J_{AB} 11·2, J_{AX} 3·0, J_{BX} 11·1 c/s). (Found: C, 72·3; H, 10·2. $C_{22}H_{38}O_4$ requires: C, 72·1; H. 10·4%).

1β-*Acetoxymethylcolensan-2-one* (**12**). Compound **8** (R = Ac; 10 mg) in acetone (12 ml) was oxidized with Jones reagent (0·02 ml) for 3 min as previously described. PLC (ether-hexane 1:3 development) of the product gave 1β-*acetoxymethylcolensan-2-one* (**12**; 8 mg) as an oil b.p. 85°/0·02 mm ν_{max}^{film} 1730, 1233 cm^{-1} (C = O, acetate); NMR Me signals at 0·74, 0·87, triplet (J 7 c/s), 0·94, 1·06, 1·20, 1·33; C$\underline{H}_3$COO 2·04; C-1 H 2·30, multiplet; C$\underline{H}_2$OAc 4·25 δ, multiplet. (Found: C, 72·5; H, 9·9. $C_{22}H_{36}O_4$ requires: C, 72·5; H, 10·0%). Oxidation of the epimer **9** (R = Ac) gave the same product (**12**).

Lactone formation

(a) *From compound* **7**. Dry HCN gas was bubbled into a soln of **7** (25 mg) in dry redistilled DMF (15 ml) for 1½ hr. The reaction mixture was hydrolysed immediately by the addition of methanolic KOH (20%, 20 ml) and refluxing for ½ hr. Acidification and ether extraction gave a product which was separated by PLC (ether/hexane 1:1 development) into two components. The upper band gave colensan-2-one (16 mg), identified by IR and m.m.p. The lower band gave **1** (R = Et; 5 mg) m.p. 203–205° (vacuum sublimation 110°/0·02 mm) identical in all respects (IR, m.m.p.) with the dihydro derivative of the naturally occurring lactone.

(b) *From 2-oxomanoyl oxide.* 2-Oxomanoyl oxide (5 g) in EtOAc (30 ml) was hydrogenated over Adams catalyst to give dihydro-2-oxomanoyl oxide. Finely powdered dihydro-2-oxomanoyl oxide was suspended

in t-butyl alcoholic N t-BuOK (100 ml) and shaken in an atmosphere of O_2 for ½ hr (1 mol propn. O_2 absorbed). Dilution with water, acidification, followed by ether extraction gave **13** (3 g) m.p. 105–107° (from aq MeOH) (lit.[8] 105–107°). KOH (50 mg) was added to a solution of the diosphernol (100 mg) in MeOH (20 ml) and 37% CH_2O (0·5 ml) and the reaction mixture refluxed for 1 hr. Dilution with water, acidification, and ether extraction gave a product which was purified by PLC (ether/hexane 1:1 development) to give the dihydroderivative of the lactone (60 mg; IR, NMR, m.m.p.).

$NaHCO_3$ (50 mg) was added to a soln of the diosphenol (80 mg) in MeOH (10 ml) and 37% CH_2O (0·5 ml) added. Another soln identical to this, but without the addition of CH_2O was prepared. Both solns were heated to 60° for 2 hr. After this time the CH_2O containing soln showed 90% conversion to the dihydrolactone while the soln without CH_2O showed only unchanged diosphenol, no benzilic acid rearrangement product being detected.

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