726. *Colensenone.*

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A nor-diterpene oxide isolated from *Dacrydium colensoi* is shown to have structure (II). This has been confirmed by the synthesis of its dihydro-derivative from 2-oxomanoyl oxide.

THE neutral fraction of the heartwood extractives of *Dacrydium colensoi* contains the diterpene oxides manoyl oxide [1] (I) and 2-oxomanoyl oxide,[2] together with a tricyclic tetrahydroxy-diterpene, dacrydol.[3] A re-investigation of this wood has led to the isolation of a ketonic nor-diterpene oxide $C_{19}H_{30}O_2$, for which the name colensenone is suggested (cf. below).

Colensenone is a colourless highly crystalline compound, stable to alkali. Because of its co-occurrence with the known diterpene oxides it was initially thought to be an isomer of 2-oxomanoyl oxide, but mass spectrometry showed a molecular weight of 290 which, together with the elemental analyses of the compound and its derivatives, proved that it has a formula $C_{19}H_{30}O_2$, *i.e.*, is probably a nor-diterpene. The infrared spectrum shows no hydroxyl absorption, a strong carbonyl band (1733 cm.$^{-1}$), and bands (3190, 1643, 991, and 911 cm.$^{-1}$) characteristic of a vinyl group. Strong bands in the C–O stretching region (1088 and 1115 cm.$^{-1}$) indicate that the second oxygen atom is present in an oxide ring. This was confirmed by conversion of colensenone by hydrogen chloride in acetic acid into two diastereoisomers, $C_{19}H_{31}Cl_3O$. A *gem*-dimethyl group in colensenone absorbs at 1387 and 1376 cm.$^{-1}$. The absence of high-intensity absorption above 220 mμ in the ultraviolet spectrum of colensenone precludes the presence of a conjugated double bond. Hydrogenation (1 mol.) produces colensanone which is fully saturated, showing no end-absorption

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[1] Hosking and Brandt, *Ber.*, 1935, **68**, 37.
[2] Hosking and Brandt, *Ber.*, 1935, **68**, 286.
[3] Grant, *J. New Zealand Inst. Chem.*, 1959, **23**, 121.

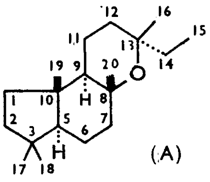
in the ultraviolet spectrum. It follows that colensenone contains two carbocyclic rings, an oxide ring (probably six-membered), and one double bond.

The hindered nature of the carbonyl group is shown by its failure to form carbonyl derivatives and the failure of the strongly positive Cotton effect curve to show any reduction in amplitude under conditions of ketal formation. The carbonyl group, however, is reduced by sodium borohydride, which leads to colensenol, $C_{19}H_{32}O_2$, showing strong hydroxyl absorption and no carbonyl absorption in the infrared region. The ketone group also reacts slowly with methylmagnesium halide, to give the methyl-substituted alcohol, $C_{20}H_{34}O_2$, in low yield, with a trace of its dehydration product. Wolff–Kishner reduction of colensenone under Huang-Minlon conditions gives colensen $C_{19}H_{32}O$, and colensan, $C_{19}H_{34}O$.* This reaction shows that the ketonic group in colensenone cannot be excessively hindered (cf. 6-oxocativic acid[4]). Colensenone gives a negative Zimmermann test. Colensanone is stable to acid, thus eliminating a β-alkoxy-ketone structure.

The high frequency of the carbonyl infrared absorption and the maximum of the ultraviolet low-intensity band (299 mμ, ε 31) suggest that the keto-group of colensenone is present either as a cyclopentanone or as an α-alkoxy-ketone. The second possibility was eliminated by the preparation of the diastereoisomeric trichloro-compounds whose carbonyl group absorbs at 1738 cm.$^{-1}$ and whose ultraviolet maximum is unchanged. The α-halogen atom of an α-alkoxy-ketone would occupy the more stable equatorial conformation[5] with a resultant lowering of the ultraviolet maximum.[6] Nuclear magnetic resonance evidence (see below) eliminates position 12 for the ketone group. Hence, the compound contains a cyclopentanone unit. The infrared spectra of the two trichloro-compounds were superimposable, which proves that they are diastereoisomeric at position 13 and are not 8-epimers.

Colensanone shows a perturbed methylene band at 1415 cm.$^{-1}$, which indicates the presence of at least one methylene group adjacent to the ketone group and provides further proof of a cyclopentanone system since this band is nearer the range reported for perturbed methylene groups in cyclopentanone systems in the di- and tri-terpenoids.[7,8] Deuteration of colensenone followed by mass spectrometry shows the presence of two exchangeable hydrogens α to the carbonyl group.

The nuclear magnetic resonance spectrum of colensenone shows eleven of the twelve bands in the ethylenic region (3·85—5·19 τ) expected for a vinyl group. At higher field five sharp, unsplit peaks, due to methyl groups attached to quaternary centres, occur at 9·18, 9·03, 9·01, 8·71, and 8·68 τ, each integrated area corresponding to three protons. The two methyl peaks at lowest field are assigned to the 16- and 20-methyl groups which are adjacent to the ether-oxygen atom. These peak values exclude position 12 for the keto-group since the 16-methyl group would be deshielded and so afford a peak at a lower field than 8·71 or 8·68 τ. At the same time, by comparison with manoyl oxides, the stereochemistry of these methyl groups can be assigned as β.[9] In view of the effect of an adjacent



(A)

* The compound, $C_{19}H_{34}O$, which is shown below to have structure (A), is named colensan and forms the basis of the other names. The natural product colensenone, shown below to have structure (II), is specifically colens-14-en-2-one.

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[4] Halsall and Moyle, *J.*, 1960, 1324.

[5] Barton, Campos-Neves, and Cookson, *J.*, 1956, 3500.

[6] Cookson, *J.*, 1954, 282.

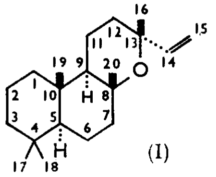
[7] Bottomley, Cole, and White, *J.*, 1955, 2624.

[8] Cole and Thornton, *J.*, 1956, 1007.

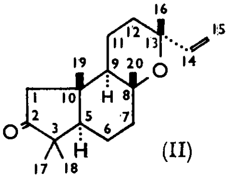
[9] Wenkert, Beak, and Grant, *Chem. and Ind.* 1961, 1574.

keto-group[10] and ring fusion[11] on angular methyl groups the individual assignment of the remaining methyl groups is still in doubt. A two-proton peak quadruplet at 7·96 τ (*J* 15·8 c./sec.) is also consistent with a methylene adjacent to a ketone group in a five-membered ring.

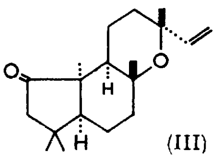
On the basis of this evidence, alternative structures (II) and (III) can be proposed for colensenone, with the 2-keto-formulation (II) favoured on biogenetic grounds. The positive Cotton effect of colensenone requires the A/B ring junction to be *trans* in (II) and antipodal *cis* in (III).



(I)



(II)



(III)

To distinguish between these two structures, Demjanow ring-enlargement of colensenone oxide and Bayer–Villiger oxidation of colensenone were attempted under a variety of conditions, but in each case the starting material was recovered unchanged.

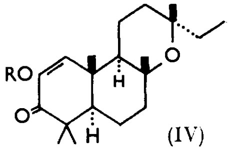
It was then decided to synthesise the 2-ketone (II) from 2-oxomanoyl oxide. Autoxidation of 2-oxomanoyl oxide by the method of Barton *et al.*[12] was unsatisfactory in that the vinyl group was also attacked, but it proceeded smoothly with dihydro-oxomanoyl oxide to give, in good yield, the diosphenol (IV; R = H) characterised as its acetate (IV; R = Ac) and as its quinoxaline derivative. The diosphenol was insoluble in hot aqueous alkali but formed its salt in alcoholic alkali. In addition to the diosphenol, the 2,3-seco-acid (V) was isolated. On alkali-treatment the diosphenol underwent a benzilic acid rearrangement to give the ring-contracted hydroxy-acid (VI). The stereoselective nature of the benzilic acid contraction of diosphenols[13] requires a β-hydroxyl configuration. The acid (VI) was reduced with lithium aluminium hydride to the 1,2-diol (VII), cleavage of which gave the ketone (II) identical (m. p., mixed m. p. and infrared spectrum) with colensanone.

Treatment of the diosphenol with alkaline hydrogen peroxide gave the seco-acid (V); pyrolysis of this afforded an anhydride ($\nu_{max.}$ 1792 and 1756 cm.$^{-1}$) rather than the expected cyclopentanone (II). Catalytic reduction of the diosphenol (IV) over Adams catalyst gave the 2α,3β-diol (VIII), as did reduction with lithium aluminium hydride and then sodium borohydride. Cleavage of this diol, followed by chromic acid oxidation, gave the seco-acid (V).

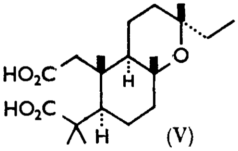
This synthesis of colensanone was not entirely specific in that the initial autoxidative step could have proceeded in the opposite direction, involving C-1 and affording the isomeric diosphenol (IX). To prove that this was not the case both dihydro-1- and dihydro-3-oxomanoyl oxide were prepared (essentially by Hodges's method[14]) and were autoxidised. Dihydro-2-oxomanoyl oxide was reduced with lithium aluminium hydride to an alcohol, m. p. 81°, identical with that obtained by sodium borohydride reduction[15] and considered to be the β-epimer. Repetition of the sodium borohydride reduction failed to give the two epimers isolated previously, only the higher-melting epimer, m. p. 81°, being isolated. As a result, this product must now be regarded as the equatorial α-alcohol. Dehydration with phosphoryl oxychloride gave the hydrocarbon (X). Dihydro-1-oxomanoyl oxide was prepared *via* the αβ-unsaturated ketone (XI). Autoxidation of dihydro-1-oxomanoyl oxide was very slow and gave in good yield the

[10] Shoolery and Rogers, *J. Amer. Chem. Soc.*, 1958, **80**, 5121.
[11] Musher, *J. Amer. Chem. Soc.*, 1961, **83**, 1146.
[12] Barton, Pradham, Sternhell, and Templeton, *J.*, 1961, 255.
[13] Georgian and Kundu, *Chem. and Ind.*, 1958, 1322.
[14] Hodges, *Tetrahedron*, 1961, **12**, 215.
[15] Grant, *J.*, 1959, 860.

diosphenol (IX). Epoxidation of the hydrocarbon (X) gave the 2α,3α-epoxide (XII) whence lithium aluminium hydride afforded the 3α-alcohol (XIII). Oxidation of this alcohol gave dihydro-3-oxomanoyl oxide which underwent rapid autoxidation to the diosphenol (IV) derived also from dihydro-2-oxomanoyl oxide.



(IV)



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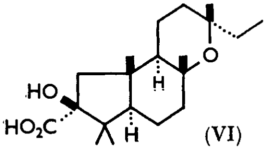

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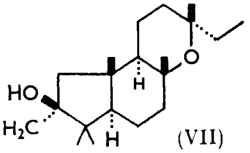

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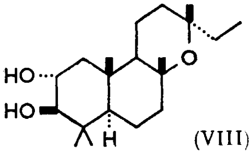

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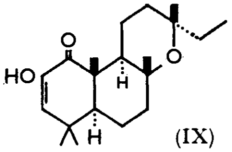
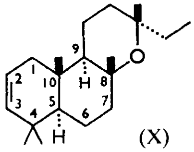
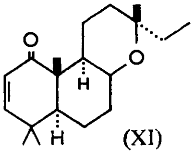


(IX)

The very slow autoxidation of dihydro-1-oxomanoyl oxide parallels the anomalous behaviour of the 1-keto-group in optical rotatory dispersion studies [16] and in bromination.[17] The unidirectional autoxidation of dihydro-2-oxomanoyl oxide proceeds in the same direction as the enolisation of 2-oxo-steroids.[18]



(X)



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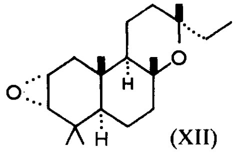
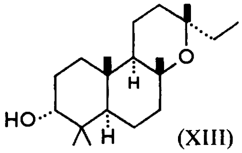


(XII)



(XIII)

Ceanothic acid, a ring-contracted triterpenoid,[19] represents an excellent biosynthetic analogy for colensenone. In the latter, however, biogenesis has proceeded two stages beyond the β-hydroxy-carboxylic acid structure of ceanothic acid, namely, oxidation to the β-keto-carboxylic acid and subsequent decarboxylation.

EXPERIMENTAL

M. p.s were taken on the Kofler block and are corrected. Ultraviolet absorption spectra are for EtOH solutions unless otherwise stated. Infrared spectra are taken for Nujol mulls unless stated to the contrary. Light petroleum refers to the fraction of b. p. 60—80°. Merck's standardised aluminium oxide was used in chromatography.

Isolation of Colensenone.—*Dacrydium colensoi* chips were extracted with acetone, the acetone removed under a vacuum, and the extract taken up in ether and treated with sodium hydroxide to remove acids and phenols. After precipitation of dacrydol by the addition of light petroleum and removal of the solvent under a vacuum, the neutral oily residue was fractionated up a helix-packed column [20] with magnetic take-off, and the fraction of b. p. 125—135°/0·15 mm. was collected. Chromatography of this oil on alumina from light petroleum gave, on elution with light petroleum, manoyl oxide having m. p. 27—28° after recrystallisation from aqueous acetone. Further elution with light petroleum–ether (9 : 1) gave *colensenone*, having m. p. 99—100° after recrystallisation from aqueous methanol and vacuum-sublimation (Found: C, 78·8; H, 10·7. $C_{19}H_{30}O_2$ requires C, 78·6; H, 10·4%), $\nu_{max.}$ 1733 (C=O); 3070, 1643, 1414, 991, and 911 (CH:CH$_2$), 1118 and 1088 (C–O) cm.$^{-1}$, $\lambda_{max.}$ 299 mμ (ε 31), ε_{210} 140. Positive Cotton effect curve, 317·5 mμ (peak), [α] +3900°.

Colensanone.—Colensenone (200 mg.) in methanol (20 ml.) was hydrogenated over Adams

[16] Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co. Inc., New York, 1960, p. 42.
[17] Sigg and Tamon, *Helv. Chim. Acta*, 1960, **43**, 1402.
[18] Djerassi and Nakano, *Chem. and Ind.*, 1960, 1385.
[19] de Mayo and Starratt, *Tetrahedron Letters*, 1961, 259.
[20] Shorland, *J. Appl. Chem.*, 1951, **2**, 438.

catalyst. One mol. of hydrogen was absorbed. Recrystallisation from aqueous methanol and vacuum-sublimation gave *colensanone* (180 mg.), m. p. 105—106° (Found: C, 78·4; H, 11·3. $C_{19}H_{32}O_2$ requires C, 78·0; H, 11·0%), $\nu_{max.}$ (in CCl_4) 1743 (C=O), 1415 (perturbed CH_2), 1387 and 1376 (*gem*-Me_2) cm.$^{-1}$, $\lambda_{max.}$ 298·5 mμ (ε 33), ε_{210} 80.

Colensenol.—Colensenone (250 mg.) in methanol (20 ml.) was treated with an excess of sodium borohydride, and the mixture worked up in the usual manner. Chromatography of the product (265 mg.) on alumina from light petroleum gave, on elution with light petroleum–ether (4 : 1), *colensenol*, m. p. 98—99° after vacuum-sublimation (Found: C, 78·4; H, 11·1. $C_{19}H_{32}O_2$ requires C, 78·0; H, 11·0%), $\nu_{max.}$ 3420 (OH); 3080, 1643, 1411, 991, and 916 ($CH{:}CH_2$) cm.$^{-1}$.

Wolff–Kishner Reduction.—Colensenone (350 mg.), in redistilled diethylene glycol (30 ml.) and 50% hydrazine hydrate (2·7 ml.), was heated to effect dissolution, and the temperature lowered and kept at 110—130° for 1 hr. Potassium hydroxide (2 g.) was added and the temperature maintained at 120—130° for 1 hr. The whole was then heated under distillation conditions until the temperature reached 215° and then maintained under reflux at 215° for 6 hr. After cooling, the mixture was poured into ice–water and extracted with ether. The product (340 mg.) was chromatographed on alumina from light petroleum. Elution with light petroleum gave *colensan* (100 mg.), m. p. 49·5—50·5° (from aqueous acetone) (Found: C, 81·9; H, 12·1. $C_{19}H_{34}O$ requires C, 81·95; H, 12·3%). Further elution of the column with light petroleum gave *colensen* (90 mg.), m. p. 32—33° (from aqueous acetone) (Found: C, 82·2; H, 11·4. $C_{19}H_{32}O$ requires C, 82·6; H, 11·6%), $\nu_{max.}$ (film) 3080, 1644, 1401, 991, and 918 ($CH{:}CH_2$) cm.$^{-1}$. Hydrogenation of colensen over Adams catalyst gave colensan, m. p. and mixed m. p. 49°.

Reaction with Methylmagnesium Halide.—Colensenone (625 mg.) in dry ether (20 ml.) was added dropwise to ethereal methylmagnesium iodide [from magnesium (0·5 g.) and methyl iodide (5·22 g.)] and refluxed for 10 hr., then cooled. The complex was decomposed with saturated aqueous ammonium chloride, and the product (665 mg.) was extracted with ether and chromatographed on alumina from light petroleum. Elution with light petroleum gave semicrystalline material (20 mg.). $\nu_{max.}$ (film) 3096, 1650, 990 and 909 ($CH{:}CH_2$), 880 ($>C{=}CH_2$) cm.$^{-1}$. Elution of the column with light petroleum–ether (9 : 1) gave unchanged colensenone (210 mg.). Light petroleum–ether (4 : 1) eluted *2-methylcolensen-2-ol* (175 mg.), having m. p. 146—147° after recrystallisation from aqueous acetone and vacuum-sublimation (Found: C, 78·6; H, 11·4. $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·2%), $\nu_{max.}$ 3440 (OH), 3075, 1639, 1409, 989 and 913 ($CH{:}CH_2$) cm.$^{-1}$.

Colensone Trihydrochloride.—Dry hydrogen chloride was bubbled through a solution of colensenone (450 mg.) in glacial acetic acid (25 ml.) for 14 hr. After standing overnight the reaction mixture was poured into water and ether extracted and the product (550 mg.) chromatographed on alumina from light petroleum. Elution with light petroleum–ether (2 : 1) gave an oil (220 mg.) followed by crystalline *5-chloro-4β-(3,5-dichloro-3-methylpentenyl)-(8α)perhydro-1,1,5β,9β-tetramethylindenone*,[21] which on fractional crystallisation from light petroleum gave two *diastereoisomers*, m. p. 69—70° and m. p. 97—98° (Found: C, 60·3; H, 8·0; Cl, 28·1. $C_{19}H_{31}Cl_3O$ requires C, 59·8; H, 8·2; Cl, 27·9%). The infrared spectra of the diastereoisomers were practically identical: $\nu_{max.}$ (in KBr) 1740 (C=O), 1414 (perturbed CH_2), 833 and 736 (CCl) cm.$^{-1}$; $\lambda_{max.}$ was at 298 mμ (ε 38).

Autoxidation of Dihydro-oxomanoyl Oxide.—Dihydro-oxomanoyl oxide (finely powdered; 2·5 g.), suspended in t-butyl-alcoholic N-potassium t-butoxide (80 ml.) was shaken with oxygen in a standard hydrogenation apparatus for ¾ hr. (1 mol. of oxygen uptake). Water (200 ml.) was added and then 6N-hydrochloric acid (50 ml.). The solution was extracted with chloroform (2 × 100 ml.), and the extracts were washed with saturated aqueous sodium hydrogen carbonate (2 × 35 ml.) and then water (100 ml.). Removal of the solvent under a vacuum gave a product (2·26 g.) from which the *diosphenol* (IV; R = H) crystallised. Recrystallised from light petroleum and finally aqueous methanol, this had m. p. 105—107°, $\lambda_{max.}$ 271 mμ (ε 9010), shifted reversibly in alkali to $\lambda_{max.}$ 316 mμ (ε 6430), $\nu_{max.}$ 3395 (OH), 1658 and 1642 (diosphenol) cm.$^{-1}$ (Found: C, 74·9; H, 10·3. $C_{20}H_{32}O_3$ requires C, 75·0; H, 10·1%). The compound gave an immediate ferric chloride test. This diosphenol (170 mg.) was treated with an excess of pyridine-acetic anhydride (1 : 1) overnight at room temperature. Crystallisation of the product from aqueous methanol gave the *diosphenol acetate* (IV; R = Ac) (150 mg.) m. p.

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[21] Carman, *Tetrahedron*, 1962, **18**, 285.

86—87°, $\lambda_{max.}$ 325—327 and 237·5 mμ (ε 43 and 8870, respectively), $\nu_{max.}$ 1762 (diosphenol acetate), 1690 (αβ-unsaturated ketone), 1645 (conjugated ethylenic linkage), 1208 (C–O of acetate) cm.$^{-1}$ (Found: C, 72·8; H, 9·2. $C_{22}H_{34}O_4$ requires C, 72·9; H, 9·45%). The diosphenol (125 mg.) and freshly sublimed *o*-phenylenediamine (100 mg.) in ethanol (3 ml.) and glacial acetic acid (0·5 ml.) were refluxed for 3 hr. The *quinoxaline derivative* (150 mg.), recrystallised from aqueous methanol, had m. p. 145·5—146·5°, $\lambda_{max.}$ 322 and 238 mμ (ε 11,720 and 31,970, respectively), $\lambda_{infl.}$ 313 and 242 mμ (ε 9180 and 25,700, respectively) (Found: C, 79·5; H, 9·3; N, 6·7. $C_{26}H_{36}N_2O$ requires C, 79·5; H, 9·2; N, 7·1%). The sodium hydrogen carbonate extract from the autoxidation, on acidification and ether-extraction, gave the *seco-acid* (V), m. p. 187—189° (from light petroleum), $\nu_{max.}$ 1704 and 1695 (C=O of carboxylic acids) cm.$^{-1}$ (Found: C, 67·8; H, 9·9. $C_{20}H_{34}O_5$ requires C, 67·8; H, 9·7%).

Benzilic Acid Rearrangement of the Diosphenol.—The diosphenol (IV; R = H) (1 g.) in ethanol (35 ml.) was added to 8% aqueous sodium hydroxide (35 ml.) and refluxed under nitrogen for $5\frac{1}{2}$ hr. The solution was diluted, acidified with dilute sulphuric acid, and extracted with ether. The ether extract was shaken with saturated aqueous sodium hydrogen carbonate, and the acidic material isolated, giving the *2-hydroxycolensan-2α-carboxylic acid* (VI), m. p. 179—180° (from light petroleum), $\nu_{max.}$ 3510 (OH), 1702 (C=O of carboxylic acid) cm.$^{-1}$ (Found: C, 70·7; H, 10·3. $C_{20}H_{34}O_4$ requires C, 71·0; H, 10·1%).

Reduction of Acid (VI) *by Lithium Aluminium Hydride.*—The acid (0·6 g.) in dry ether (10 ml.) was added dropwise to an excess of lithium aluminium hydride in ether (50 ml.), and the solution refluxed for $1\frac{1}{2}$ hr. The excess of hydride was destroyed with water, 10% sulphuric acid added (50 ml.), and the solution extracted with ether, to give *2-hydroxymethylcolensan-2β-ol* (VII) (0·5 g.), m. p. 74—75° (from aqueous methanol), $\nu_{max.}$ 3510, 3415, 3250 (OH) cm.$^{-1}$ (Found: C, 73·85; H, 10·8. $C_{20}H_{36}O_3$ requires C, 74·0; H, 11·2%).

Cleavage of Diol (VII) *by Periodic Acid.*—The diol (90 mg.) in ethanol (7 ml.) was added to periodic acid (350 mg.) in water (3 ml.), the solution left overnight at room temperature, then diluted, and the product (65 mg.) was extracted with ether. Recrystallised from aqueous methanol and sublimed *in vacuo*, this had m. p. 105—106°, undepressed on admixture with colensanone. The infrared spectra of the synthetic ketone and colensanone were identical.

Oxidation of Diosphenol (IV; R = H) *by Alkaline Peroxide.*—The diosphenol (0·91 g.) in methanol (70 ml.) at 0° was added to a 10% solution (70 ml.) of potassium hydroxide. 30% Hydrogen peroxide (50 ml.) was added with stirring but so that the temperature did not rise above 5°. The solution was stirred at room temperature overnight, diluted, and extracted with ether, and the acidic fraction isolated as usual. This had m. p. 187—189° after recrystallisation from light petroleum, undepressed on admixture with the seco-acid (V) from the autoxidation of dihydro-2-oxomanoyl oxide.

Reduction of Diosphenol (IV; R = H).—(*a*) The diosphenol (0·3 g.) in glacial acetic acid (20 ml.) was hydrogenated over Adams catalyst. Two mol. of hydrogen were absorbed. Recrystallisation of the product from aqueous methanol followed by vacuum-sublimation gave the 2α,3β-*diol* (VIII), m. p. 138—139°, $\nu_{max.}$ 3510, 3375 (OH) cm.$^{-1}$ (Found: C, 73·8; H, 11·5. $C_{20}H_{36}O_3$ requires C, 74·0; H, 11·2%). (*b*) The diosphenol (0·2 g.) was reduced with lithium aluminium hydride in the usual way. The crude product showed hydroxyl absorption and carbonyl absorption at 3435 and 1708 cm.$^{-1}$, respectively, and was reduced with sodium borohydride in methanol to the diol (VIII), m. p. 138—139°.

Cleavage of Diol (VIII) *by Periodic Acid.*—The diol (170 mg.) was treated with periodic acid (650 mg.) as previously described. The crude product (180 mg.), which showed typical aldehyde absorption at 2700 and 1717 cm.$^{-1}$, was oxidised in glacial acetic acid with chromic acid to the seco-acid (V), m. p. 187—189°, undepressed on admixture with the acid from the autoxidation of dihydro-2-oxomanoyl oxide.

*Dihydro-*1*-oxomanoyl Oxide.*—Dihydro-2-oxomanoyl oxide (2 g.) was reduced by refluxing with lithium aluminium hydride in ether for $1\frac{1}{2}$ hr., to give dihydro-2α-hydroxymanoyl oxide (1·8 g.), m. p. 80—81°. This product could not be separated into epimers by chromatography over alumina. Dehydration of this alcohol with phosphoryl chloride as previously described [15] gave the hydrocarbon (X), m. p. 84—85°. By using Hodges's method [14] this hydrocarbon (1·0 g.) was refluxed with selenium dioxide (2·2 g.) in glacial acetic acid (20 ml.) for $\frac{1}{4}$ hr. The crude product (1·1 g.) was hydrolysed by heating it with sodium hydroxide (10 g.) in 1 : 4 aqueous methanol (20 ml.) for $1\frac{1}{2}$ hr. The product (0·95 g.) was oxidised in acetone with 8N-chromic acid–sulphuric acid to the αβ-unsaturated ketone (XI), m. p. 134—135°, $\lambda_{max.}$ 330 and 224 mμ (ε 65 and 9200, respectively), $\nu_{max.}$ 1677 (αβ-unsaturated ketone), 1630 (conjugated ethylenic linkage) cm.$^{-1}$. Hydrogenation in ethyl acetate over Adams catalyst gave dihydro-1-oxomanoyl oxide, m. p. 80—81° (from aqueous methanol), $\nu_{max.}$ 1706 (cyclohexanone) cm.$^{-1}$.

*Autoxidation of Dihydro-*1-*oxomanoyl Oxide*.—Dihydro-1-oxomanoyl oxide (0·45 g.) was autoxidised as described earlier, to give the *diosphenol* (IX) (0·41 g.). Autoxidation was very slow, 20 hr. being required for the uptake of 1 mol. of oxygen. Recrystallised from aqueous methanol, the diosphenol had m. p. 97—99° [mixed m. p. with diosphenol (IV) was ~85°], $\lambda_{max.}$ 267 mμ (ε 3980) shifted reversibly in alkali to $\lambda_{max.}$ 310—312 mμ (ε 2470), $\nu_{max.}$ 3425 (OH), 1681, and 1657 (diosphenol) cm.$^{-1}$ (Found: C, 75·3; H, 10·4. $C_{20}H_{32}O_3$ requires C, 75·0; H, 10·1%).

*Dihydro-*3-*oxomanoyl Oxide*.—The hydrocarbon (X) (0·73 g.) was allowed to react with a solution of perbenzoic acid in chloroform at room temperature for 2 days. The excess of perbenzoic acid was removed and the product chromatographed on alumina from light petroleum. Elution with light petroleum–ether (25 : 1) gave the 2α,3α-*epoxide* (XII) (0·62 g.), m. p. 77—78° (from aqueous methanol) (Found: C, 78·2; H, 11·1. $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·2%). The epoxide (0·45 g.) was refluxed with lithium aluminium hydride in ether for 2 hr. The product crystallised, and recrystallisation from aqueous methanol gave *dihydro-*3α-*hydroxymanoyl oxide* (XIII) m. p. 111—112°, $\nu_{max.}$ 3400 (OH) cm.$^{-1}$ (Found: C, 77·7; H, 11·6. $C_{20}H_{36}O_2$ requires C, 77·9; H, 11·8%). The alcohol was dissolved in acetone and oxidised with 8N-chromic acid–sulphuric acid to dihydro-3-oxomanoyl oxide (0·3 g.), m. p. 69—70° (from aqueous methanol), $\nu_{max.}$ 1701 (cyclohexanone) cm.$^{-1}$.

*Autoxidation of Dihydro-*3-*oxomanoyl Oxide*.—Dihydro-3-oxomanoyl oxide (0·65 g.) was autoxidised as above; the oxidation was complete in 20 min. The product (0·55 g.), after recrystallisation from light petroleum and finally aqueous methanol, had m. p. 105—107° undepressed on admixture with diosphenol (IV; R = H) from the autoxidation of dihydro-2-oxomanoyl oxide.

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