The Chemistry of the Triterpenes and Related Compounds. Part XXIV. The Conversion of Polyporenic Acid A into a Lanosterol Derivative.*

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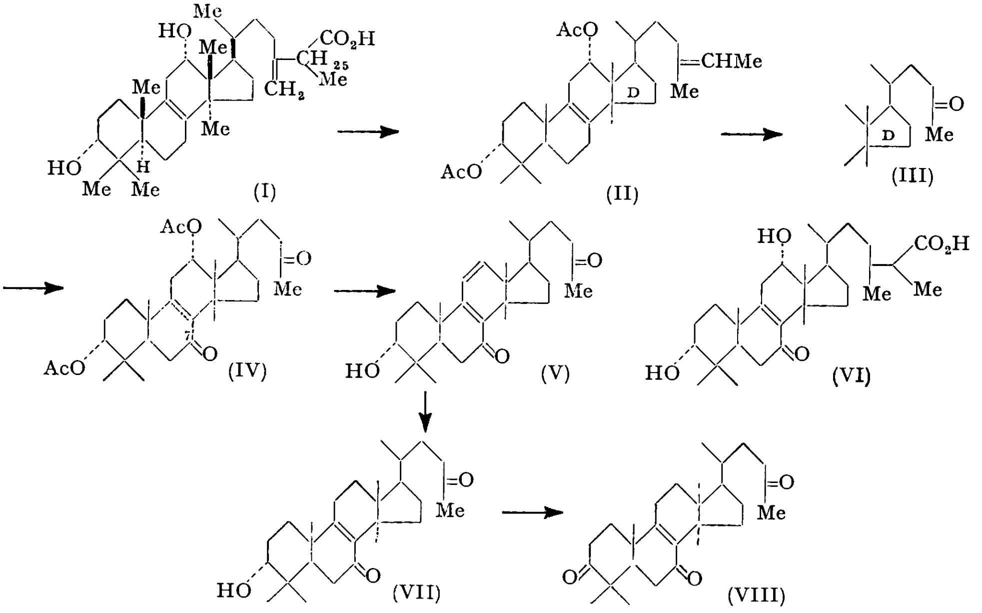
[Reprint Order No. 5148.]

Following extensive degradative investigations a structure for polyporenic acid A, $C_{31}H_{50}O_4$, was proposed (Halsall, Hodges, and Jones, *J.*, 1953, 3019). The proof of the structure has now been completed by the conversion of the acid and of lanosterol into a common C_{28} degradation product.

Structure (I) for polyporenic acid A was suggested by Halsall, Hodges, and Jones (*J.*, 1953, 3019) on the basis of degradative evidence and a probable biogenetic relationship with eburicoic acid and polyporenic acid C. Final proof of the correctness of (I) has now been obtained by the conversion of polyporenic acid A into a compound of known structure derived from lanosterol. Roth, Saucy, Anliker, Jeger, and Heusser (*Helv. Chim. Acta*, 1953, **36**, 1908) have also recently carried out the conversion of polyporenic acid A and lanosterol into a common, but different, degradation product.



Ozonolysis of the diacetate of decarboxylated polyporenic acid A (II) has already been shown to give a methyl ketone (III) (Halsall *et al.*, *loc. cit.*). Oxidation of this ketone with chromic acid for a short time introduced a second oxo-group at $C_{(7)}$ giving (IV). (Oxidation for a longer time gave the 7 : 11-diketone.) Treatment of (IV) with methanolic potassium hydroxide gave the dienone (V). This reaction is analogous to that with (VI), already described by Halsall, Jones, and Lemin (*J.*, 1953, 468), in which the corresponding dienone is formed. Reduction of (V) with zinc dust in acetic acid gave the αβ-unsaturated ketone (VII) which was oxidised to the triketone (VIII).

" Isocholesteryl acetate " which contains lanostadienyl acetate (IX) was ozonised, the crude product was treated directly with methylmagnesium iodide and the resulting diol (X) was oxidised with chromic acid in acetone to the corresponding diketone (XI). After purification and characterisation (XI) was oxidised with chromic acid in acetic acid giving

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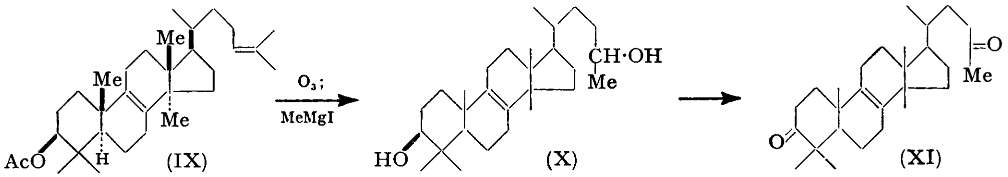
* Part XXIII, *J.*, 1954, 1905.

the triketone (VIII), identical (mixed m. p.; infra-red spectra in carbon tetrachloride) with that prepared from polyporenic acid A.

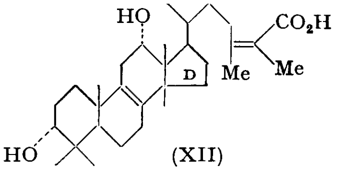
These results finally prove the correctness of structure (I) for polyporenic acid A, which is therefore 3α : 12α-dihydroxyeburico-8 : 24(28)-dien-26-oic acid. The only feature of the structure which remains to be elucidated is the stereochemistry of $C_{(25)}$.



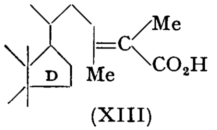
(IX) Lanosteryl acetate. (X) (XI)

In the preparation of decarboxylated polyporenic acid A, it was found that, when the crude acid obtained by the hydrolysis of methyl polyporenate A was decarboxylated, some ether-insoluble acid (20%) was obtained, besides the expected decarboxy-compound. This acid had an ultra-violet spectrum characteristic of an αβ-unsaturated acid. Its methyl ester could be acetylated to give both a monoacetate and a diacetate. Ozonolysis of the latter gave the same methyl ketone (III) as is obtained from the ozonolysis of both the diacetate of the decarboxylated acid (II) and methyl *iso*polyporenate diacetate (Halsall, Hodges, and Jones, *loc. cit.*). The acid must therefore be a geometrical isomer of *iso*polyporenic acid A. It has been given the trivial name, ψ-polyporenic acid A. The *iso*- and ψ-acids must each be represented by one of the two structures (XII) and (XIII) but it has not been possible to decide conclusively which is which, although, as indicated below, it is likely that (XII) represents the *iso*-acid. To distinguish systematically between *iso*polyporenic acid A and ψ-polyporenic acid A, the former is designated as 3α : 12α-dihydroxyeburico-8 : 24-dien-26-oic acid and the latter as 3α : 12α-dihydroxyeburico-8 : 24-dien-27-oic acid.

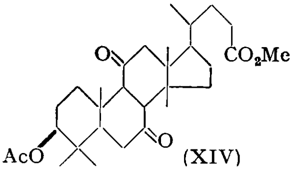
ψ-Polyporenic acid A was only obtained from "polyporenic acid A" prepared by hydrolysis of methyl polyporenate. It was not formed when pure acid A (obtained from the fungus extract without methylation and hydrolysis) was decarboxylated, although when this acid was methylated, the resulting ester hydrolysed, and the hydrolysis product decarboxylated some ψ-polyporenic acid A was again isolated. It has already been shown that during the hydrolysis of methyl polyporenate A, methyl *iso*polyporenate A is formed (Halsall, Hodges, and Jones, *loc. cit.*). The formation of the ψ-acid is best explained by assuming that the hydrolysis product from methyl polyporenate A contained, in addition to acid A, some *iso*polyporenic acid A formed by hydrolysis of methyl *iso*polyporenate, and that the *iso*-acid is thermally isomerised to the ψ-acid.



(XII)



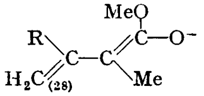
(XIII)

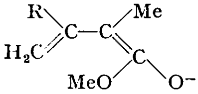


(XIV)

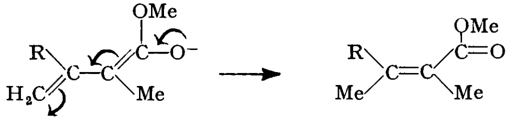
It is likely that *iso*polyporenic acid A has structure (XII) for the following reasons. When methyl polyporenate A is isomerised to methyl *iso*polyporenate A the intermediate ion in the reaction will exist mainly in the ***transoid*** form (A) rather than in the ***cisoid*** form (B) since the repulsion between the partial negative charges on the $C_{(28)}$ carbon atom and the carbonyl oxygen will be less in (A) than in (B). If proton attack occurs at $C_{(28)}$ to complete the isomerisation (cf. C) then the spatial distribution of atoms represented by (A) should also be present in methyl *iso*polyporenate A (cf. D). Structure (D) has the two largest groups *cis* to one another and therefore would be expected to be slightly less stable than structure (E). If methyl *iso*polyporenate A is represented by (D) then (E) must be methyl ψ-polyporenate A. The thermal isomerisation of the *iso*- to the *ψ*-acid is in agreement with this conclusion as it corresponds to the isomerisation of the less stable (D) to the more stable (E).

(A)

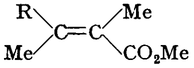




(B)



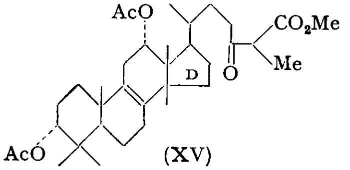
H+ (C) (D)



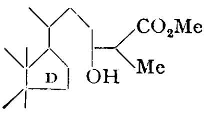
(E)

Although the relationship between polyporenic acid A and lanosterol was established by the formation from both of (VIII) as described above, our original intention had been to establish a relationship by the conversion of polyporenic acid A into a derivative of (XIV), which had already been prepared from lanosterol (Voser, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1952, **35**, 497). The formation of C_{27} acid derivatives was attempted by three different routes. The first was the oxidation of the methyl triketone (VIII) with sodium hypobromite or sodium hypoiodite, but both reagents failed to yield any acidic products.

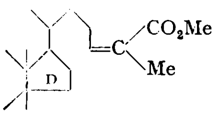
The second route involved the ozonolysis of methyl polyporenate A diacetate to the β-oxo-ester (XV). This was reduced to the β-hydroxy-ester (XVI) with sodium borohydride, but an attempt by heating with acetic anhydride to dehydrate (XVI) to the αβ-unsaturated ester (XVII), which would have given a C_{27} acid on ozonolysis, gave only an uncrystallisable gum.



(XV)

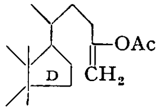


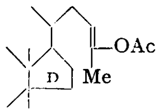
(XVI)



(XVII)

(XVIII)





(XIX)

Finally, attempts were made to prepare from the methyl ketone (IV) the enol acetate (XVIII), ozonolysis of which would give the required C_{27} acid structure. When (III) was heated under reflux for 15 hours in chloroform with dimethylaniline and acetyl chloride a mixture of the enol acetate (XVIII) and the isomeric acetate (XIX) was obtained. The latter compound was the only product when the above reagents were heated under reflux for 3 days and also when the methyl ketone (III) was acetylated with *iso*propenyl acetate. Ozonolysis of the mixture of enol acetates gave the required C_{27} acid but the yield by this route did not encourage us to make use of it further.

EXPERIMENTAL

Rotations were determined in chloroform at room temperature unless otherwise stated. M. p.s were determined on a Kofler block and are corrected. Alumina of activity I—II was employed for all chromatograms, and the light petroleum used for elution had b. p. 60—80°. Crystallisations were from methanol unless stated otherwise.

3α : 12α-Diacetoxy-7 : 24-dioxo-26 : 27-bisnorlanost-8-ene (IV).—3α : 12α-Diacetoxy-24-oxo-26 : 27-bisnorlanost-8-ene (III) (Halsall, Hodges, and Jones, *loc. cit.*) (500 mg.) in acetic acid

(25 c.c.) was treated with chromic acid (225 mg.) at 80—90° for 10 min. Dilution with water and ether-extraction yielded a product which was adsorbed from benzene on alumina (50 g.). The fraction eluted with benzene–ether (9 : 1) gave 3α : 12*α-diacetoxy*-7 : 24-*dioxo*-26 : 27-*bisnorlanost*-8-*ene* as needles (330 mg.), m. p. 228—230°, [α]$_D$ +73° (*c*, 0·71) (Found : C, 72·65; H, 9·4. $C_{32}H_{48}O_6$ requires C, 72·7; H, 9·15%). Light absorption in ethanol : Max., 2540 Å; ε = 9800. The infra-red spectrum in carbon tetrachloride had bands at 1735—1745 and 1673 cm.$^{-1}$ and a shoulder at 1730 cm.$^{-1}$.

3α : 12*α-Diacetoxy*-7 : 11 : 24-*trioxo*-26 : 27-*bisnorlanost*-8-*ene*.—3α : 12α-Diacetoxy-24-oxo-26 : 27-bisnorlanost-8-ene (III) (1·06 g.) in acetic acid (45 c.c.) was treated with chromic acid (1·85 g.) at 80—90° for 90 min. Dilution with water and ether-extraction yielded a product which was adsorbed from benzene on alumina (100 g.). The fraction eluted with ether gave 3α : 12*α-diacetoxy*-7 : 11 : 24-*trioxo*-26 : 27-*bisnorlanost*-8-*ene* as yellow prisms (65 mg.), m. p. 201—203°, [α]$_D$ +94° (*c*, 0·63) (Found : C, 70·55; H, 8·5. $C_{32}H_{46}O_7$ requires C, 70·8; H, 8·55%). Light absorption in ethanol : Max., 2730 Å; ε = 7300.

7 : 24-*Dioxo*-26 : 27-*bisnorlanosta*-8 : 11-*dien*-3*α-ol* (V).—3α : 12α-Diacetoxy-7 : 24-dioxo-26 : 27-bisnorlanost-8-ene (1·61 g.) was heated under reflux for 30 min. with 1% methanolic potassium hydroxide (160 c.c.). Dilution with water and ether-extraction afforded a product which was adsorbed from benzene on alumina (150 g.). Elution with benzene–ether (3 : 2) yielded a fraction, giving 7 : 24-*dioxo*-26 : 27-*bisnorlanosta*-8 : 11-*dien*-3*α-ol* as plates (1·013 g.), m. p. 204—205°, [α]$_D$ −4° (*c*, 1·0) (Found : C, 78·7; H, 9·85. $C_{28}H_{42}O_3$ requires C, 78·8; H, 9·9%). Light absorption in ethanol : Max., 3180 Å; ε = 8450. The infra-red spectrum in carbon tetrachloride had bands at 1657 and 1718 cm.$^{-1}$.

Zinc-dust Reduction of 7 : 24-*Dioxo*-26 : 27-*bisnorlanosta*-8 : 11-*dien*-3*α-ol* (V).—Zinc dust (4 g.) was added in small portions during 2 hr. to a boiling solution of 7 : 24-dioxo-26 : 27-bisnorlanosta-8 : 11-dien-3α-ol (1·96 g.) in acetic acid (200 c.c.). Dilution with water and ether-extraction afforded a product which was adsorbed from benzene on alumina (150 g.). Elution with benzene–ether (19 : 1) yielded a fraction which gave 7 : 24-*dioxo*-26 : 27-*bisnorlanost*-8-*en*-3*α-yl acetate* as plates (146 mg.), m. p. 159—161°, [α]$_D$ −42° (*c*, 1·21) (Found : C, 76·85; H, 9·9. $C_{30}H_{46}O_4$ requires C, 76·55; H, 9·85%). Light absorption in ethanol : Max., 2540 Å; ε = 8900. Further elution with benzene–ether (1 : 1) yielded a fraction which gave 7 : 24-*dioxo*-26 : 27-*bisnorlanost*-8-*en*-3*α-ol* (VII) as plates (1·05 g.), m. p. 195—197°, [α]$_D$ 0° (*c*, 0·72) (Found : C, 78·75; H, 10·25. $C_{28}H_{44}O_3$ requires C, 78·45; H, 10·35%). Light absorption in ethanol : Max., 2540 Å; ε = 9700. The infra-red spectrum in carbon tetrachloride had bands at 1665 and 1719 cm.$^{-1}$.

3 : 7 : 24-*Trioxo*-26 : 27-*bisnorlanost*-8-*ene* (VIII).—7 : 24-Dioxo-26 : 27-lanost-8-en-3α-ol (1·05 g.) in acetone (30 c.c.) was oxidised with chromic acid solution (8N) in the usual manner (cf. Bowers *et al. J.*, 1953, 2555). The product was adsorbed from benzene on alumina (100 g.), eluted with benzene–ether (19 : 1), and crystallised giving 3 : 7 : 24-*trioxo*-26 : 27-*bisnorlanost*-8-*ene* as plates (894 mg.), m. p. 171—172°, [α]$_D$ +13° (*c*, 0·87) (Found : C, 78·65; H, 10·05. $C_{28}H_{42}O_3$ requires C, 78·8; H, 9·9%). Light absorption in ethanol : Max., 2530 Å; ε = 8900. The infra-red spectrum in carbon tetrachloride had bands at 1670 and 1713 cm.$^{-1}$ and a shoulder at 1718 cm.$^{-1}$.

3 : 24-*Dioxo*-26 : 27-*bisnorlanost*-8-*ene* (XI).—" Isocholesteryl acetate " (8·4 g.) in ethyl acetate (200 c.c.) was treated with ozonized oxygen (6%) for 6½ hr. The solution was then washed repeatedly with ferrous sulphate solution. The residue obtained by evaporation of the ethyl acetate was dissolved in ether (500 c.c.) and heated under reflux with methylmagnesium iodide (15 g.) in ether (300 c.c.) for 30 min. From the mixture the crude diol was isolated in the usual manner and was oxidised in acetone (200 c.c.) with chromic acid solution (8N). The neutral fraction formed was separated, adsorbed from benzene–light petroleum (1 : 1) on alumina (500 g.), and eluted with benzene–ether (19 : 1) giving 3 : 24-*dioxo*-26 : 27-*bisnorlanost*-8-*ene* as platelets (1·97 g.), m. p. 178—184°, [α]$_D$ +77° (*c*, 0·77) (Found : C, 81·55; H, 10·8. $C_{28}H_{44}O_2$ requires C, 81·5; H, 10·75%).

Oxidation of 3 : 24-*Dioxo*-26 : 27-*bisnorlanost*-8-*ene from " Isocholesteryl Acetate*."—The diketone (850 mg.) in acetic acid (50 c.c.) was oxidised with chromic acid (350 mg.) at 80—90° for 13 min. Dilution with water and extraction with ether afforded a product which was adsorbed from benzene on alumina (100 g.). Elution with benzene–ether (1 : 1) yielded a fraction which on crystallisation gave 3 : 7 : 24-trioxo-26 : 27-bisnorlanost-8-ene as plates (391 mg.), m. p. 171·5—173° (undepressed on admixture with a sample prepared from polyporenic acid A), [α]$_D$ +12° (*c*, 0·48). Light absorption in ethanol : Max., 2540 Å; ε = 8600. The infra-red spectrum in carbon tetrachloride was identical with that of a sample prepared from polyporenic acid A.

ψ-Polyporenic Acid A (3α : 12α-*Dihydroxyeburico*-8 : 24-*dien*-27-*oic Acid*).—Methyl polyporenate A (37 g.) was heated under reflux for 10 hr. with methanolic potassium hydroxide (3%; 300 c.c.). The solution was then diluted with water and acidified with acetic acid. The precipitated acid was crystallised once from aqueous *iso*propanol, giving a mixture of polyporenic acid A and *iso*polyporenic acid A (30 g.). The mixed acids (40 g.) were kept at 220° for 1 hr. under nitrogen, and the product was then separated into an acidic (7 g.) and a neutral fraction. Repeated crystallisation of the former from aqueous methanol, *iso*propanol, dioxan, and acetic acid gave *ψ-polyporenic acid A* (3α : 12α-*dihydroxyeburico*-8 : 24-*dien*-27-*oic acid*) as fine needles, m. p. 265—266°, $[\alpha]_D$ +51° (*c*, 1·0 in pyridine) (Found: C, 76·7; H, 10·45. $C_{31}H_{50}O_4$ requires C, 76·5; H, 10·35%). Light absorption in ethanol: Max., 2260 Å; ε = 10,500. Methylation of the acid with ethereal diazomethane in the usual manner gave *methyl ψ-polyporenate A* (*methyl* 3α : 12α-*dihydroxyeburico*-8 : 24-*dien*-27-*oate*) as needles (from nitromethane), m. p. 180—181°, $[\alpha]_D$ +65° (*c*, 0·97) (Found: C, 76·5; H, 10·5. $C_{32}H_{52}O_4$ requires C, 76·75; H, 10·45%). Light absorption in ethanol: Max., 2260 Å; ε = 10,800.

Methyl ψ-Polyporenate A Diacetate.—Methyl ψ-polyporenate A (300 mg.) was heated under reflux for 1 hr. with acetic anhydride (5 c.c.) and sodium acetate (100 mg.). The product was adsorbed from benzene on alumina (30 g.) and eluted with benzene–ether (9 : 1), giving *methyl ψ-polyporenate A diacetate* (*methyl* 3α : 12α-*diacetoxyeburico*-8 : 24-*dien*-27-*oate*) as needles (260 mg.), m. p. 154—155°, $[\alpha]_D$ +68° (*c*, 1·58) (Found: C, 73·85; H, 9·75. $C_{36}H_{56}O_6$ requires C, 73·95; H, 9·65%). Light absorption in ethanol: Max., 2260 Å; ε = 10,100.

Methyl ψ-Polyporenate A Monoacetate.—Methyl ψ-polyporenate A (200 mg.) in pyridine (3 c.c.) was treated with acetic anhydride (1 c.c.) and kept at 20° for 3 days. The product was adsorbed from benzene on alumina (20 g.) and eluted with benzene–ether (3 : 2), giving *methyl ψ-polyporenate A monoacetate* (*methyl* 3α-*acetoxy*-12α-*hydroxyeburico*-8 : 24-*dien*-27-*oate*) as needles (152 mg.), m. p. 164·5—165·5°, $[\alpha]_D$ +21° (*c*, 1·19) (Found: C, 75·45; H, 10·2. $C_{34}H_{54}O_5$ requires C, 75·25; H, 10·05%). Light absorption in ethanol: Max., 2260 Å; ε = 10,900. After one year the monoacetate melted at 190—192°. This melting point was undepressed on admixture with a sample of the monoacetate which was prepared by the same method in a later experiment and crystallised as plates.

Oxidation of Methyl ψ-Polyporenate A.—Methyl ψ-polyporenate A (250 mg.) in acetone (20 c.c.) was oxidised with chromic acid (8N) in sulphuric acid (25% v/v) at 30°. The product was adsorbed from benzene on alumina (25 g.) and eluted with benzene–ether (1 : 1), giving *methyl* 3 : 12-*dioxoeburico*-8 : 24-*dien*-27-*oate* as needles (206 mg.), m. p. 191—192°, $[\alpha]_D$ +94° (*c*, 1·49) (Found: C, 77·35; H, 9·65. $C_{32}H_{48}O_4$ requires C, 77·35; H, 9·75%). Light absorption in ethanol: Max., 2260 Å; ε = 11,150.

Ozonolysis of Methyl ψ-Polyporenate A Diacetate.—Methyl ψ-polyporenate A diacetate (380 mg.) in acetic acid (10 c.c.) was treated with ozonised oxygen for 20 min. The solution was then heated under reflux with water (20 c.c.) for 10 min. The product, isolated by ether-extraction, was adsorbed from benzene on alumina (30 g.), and eluted with ether, giving 3α : 12α-diacetoxy-24-oxo-26 : 27-bisnorlanost-8-ene (III) as needles (200 mg.), m. p. 199—201° (undepressed on admixture with an authentic sample), $[\alpha]_D$ +82° (*c*, 0·50).

Attempted Oxidation of 26 : 27-*Bisnorlanost*-8-*ene*-3 : 7 : 24-*trione* (VIII).—3 : 7 : 24-Trioxo-26 : 27-bisnorlanost-8-ene (300 mg.) in methanol (50 c.c.) was treated with a mixture of bromine (300 mg.) and sodium hydroxide (250 mg.) in water (10 c.c.). After 24 hr. the solution was diluted with water, extracted with ether, acidified with acetic acid, and re-extracted with ether. No acidic fraction was obtained. Attempts to oxidise the triketone to a C_{27}-acid with sodium hypoiodite were also unsuccessful.

Ozonolysis of Methyl Polyporenate A Diacetate [*Methyl* 3α : 12α-*Diacetoxyeburico*-8 : 24(28)-*dien*-26-*oate*].—Methyl polyporenate A diacetate (2·5 g.) in acetic acid (40 c.c.) was treated with ozonised oxygen (6%) for 80 min. The solution was then heated under reflux with water (80 c.c.) for 10 min. The product, isolated with ether, was adsorbed from benzene–light petroleum (6 : 4) on alumina (200 g.) and eluted with benzene, giving *methyl* 3α : 12α-*diacetoxy*-24-*oxolanost*-8-*en*-26-*oate* (XV) as needles (1·50 g.), m. p. 142—143°, $[\alpha]_D$ +104° (*c*, 0·83) (Found: C, 72·0; H, 9·1. $C_{35}H_{54}O_7$ requires C, 71·65; H, 9·3%). Light absorption in ethanol: Max., 2480 Å; ε = 5900. Light absorption in ethanol with a trace of alkali present: Max., 2860 Å; ε = 14,400. The infra-red spectrum in carbon tetrachloride exhibited a band at 1733 cm.$^{-1}$ with a shoulder at 1740 cm.$^{-1}$.

Reduction of Methyl 3α : 12α-*Diacetoxy*-24-*oxolanost*-8-*en*-26-*oate* (XV) *with Sodium Borohydride.*—The β-keto-ester (586 mg.) in dioxan (35 c.c.) was treated with sodium borohydride (50 mg.) in water (5 c.c.) and kept at 20° for 1 hr. The product, isolated with ether, was adsorbed from benzene on alumina (50 g.) and eluted with ether, giving *methyl* 3α : 12α-*diacetoxy*-24-*hydroxylanost*-8-*en*-26-*oate* as needles (261 mg.), m. p. 124—125°, $[\alpha]_D$ +76° (*c*, 0·93) (Found : C, 70·9; H, 9·5. $C_{35}H_{56}O_7$ requires C, 71·4; H, 9·6%).

Attempted Dehydration of Methyl 3α : 12α-*Diacetoxy*-24-*hydroxylanost*-8-*en*-26-*oate*.—The ester (115 mg.) was heated under reflux with acetic anhydride (5 c.c.) for 1 hr. The product, isolated with ether, was adsorbed from light petroleum on alumina (10 g.) and eluted with benzene, giving an uncrystallisable gum (102 mg.). Light absorption in ethanol: Max., 2480 Å; ε = *ca.* 700.

Methyl 3α : 12α-*Dihydroxy*-24-*oxolanost*-8-*en*-26-*oate*.—Methyl polyporenate A (3·0 g.) in acetic acid (50 c.c.) was treated with ozonised oxygen (6%) for 3 hr. The solution was then heated under reflux with water (100 c.c.) for 10 min. The product, isolated with ether, was adsorbed from benzene on alumina deactivated with water (5%), and eluted with benzene–ether (4 : 1), giving *methyl* 3α : 12α-*dihydroxy*-24-*oxolanost*-8-*en*-26-*oate* as fine needles (920 mg.) (from nitromethane), m. p. 115—116°, $[\alpha]_D$ +64° (*c*, 1·10) (Found : C, 74·3; H, 10·2. $C_{31}H_{50}O_5$ requires C, 74·05; H, 10·05%). Light absorption in ethanol : Max., 2560 Å; ε = 240. Light absorption in ethanol with a trace of alkali present : Max., 2860 Å; ε = 14,500.

Enol Acetylation of 3α : 12α-*Diacetoxy*-26 : 27-*bisnorlanost*-8-*en*-24-*one* (III).—(*a*) 3α : 12α-Diacetoxy-26 : 27-bisnorlanost-8-en-24-one (500 mg.) in chloroform (5 c.c.) was heated under reflux with dry dimethylaniline (6 c.c.) and acetyl chloride (4 c.c.) for 15 hr. The product, isolated in the usual manner, was adsorbed from light petroleum on alumina (50 g.) and eluted with benzene, giving crystals (110 mg.), m. p. 114—120°, of a mixture of 3α : 12α : 24-triacetoxy-26 : 27-bisnorlanosta-8 : 23-diene (XIX) and 3α : 12α : 24-triacetoxy-26 : 27-bisnorlanosta-8 : 24-diene (XVIII). The infra-red spectrum in carbon tetrachloride had bands at 1735, 1669, and 873 cm.$^{-1}$. The band at 873 cm.$^{-1}$ indicates the presence of the grouping $>C = CH_2$.

(*b*) 3α : 12α-Diacetoxy-26 : 27-bisnorlanost-8-en-24-one (2·4 g.) in chloroform (13 c.c.) was heated under reflux for 3 days with dimethylaniline (15 c.c.) and acetyl chloride (10 c.c.). The product, isolated in the usual manner, was adsorbed from light petroleum on alumina (200 g.) and eluted with benzene–light petroleum (3 : 2), giving 3α : 12α : 24-*triacetoxy*-26 : 27-*bisnorlanosta*-8 : 23-*diene* (XX) as needles (920 mg.) (repeated crystallisation), m. p. 148—150°, $[\alpha]_D$ +64° (*c*, 0·93) (Found : C, 73·65; H, 9·4. $C_{34}H_{52}O_6$ requires C, 73·35; H, 9·4%). Acetylation with *iso*propenyl acetate yielded the same product. The infra-red spectrum in carbon tetrachloride had a band at 1735 cm.$^{-1}$.

Methyl 3α : 12α-*Diacetoxy*-4 : 4 : 14α-*trimethyl*allo*chol*-8-*en*-24-*oate*.—The mixed enol acetates (443 mg.; m. p. 114—120°), described in the cognate paragraph above, in ethyl acetate were treated with ozonised oxygen (6%) for 20 min. The solution was then washed with ferrous sulphate solution and separated into an acid (190 mg.) and a neutral fraction. The former was methylated with ethereal diazomethane, and the resulting ester was adsorbed from benzene on alumina (20 g.) and eluted with benzene–ether (1 : 1), giving *methyl* 3α : 12α-*diacetoxy*-4 : 4 : 14α-*trimethyl*allo*chol*-8-*en*-24-*oate* as plates (85 mg.), m. p. 196—198°, $[\alpha]_D$ +88° (*c*, 0·89) (Found : C, 72·3; H, 9·45. $C_{32}H_{50}O_6$ requires C, 72·4; H, 9·5%).

3α : 12α-*Dihydroxy*-26 : 27-*bisnorlanost*-8-*en*-24-*one*.—3α : 12α-Diacetoxy-26 : 27-bisnorlanost-8-en-24-one (1·58 g.) was heated under reflux with 1% methanolic potassium hydroxide (50 c.c.) for 18 hr. The product, isolated in the usual manner, was adsorbed from benzene on alumina (150 g.) and eluted with ether–methanol (19 : 1), giving 3α : 12α-*dihydroxy*-26 : 27-*bisnorlanost*-8-*en*-24-*one* as plates (726 mg.), m. p. 209—210·5°, $[\alpha]_D$ +73° (*c*, 0·99) (Found : C, 78·45; H, 10·7. $C_{28}H_{46}O_3$ requires C, 78·1; H, 10·75%). The infra-red spectrum in carbon disulphide had a band at 1713 cm.$^{-1}$.

Methyl 4 : 4 : 14α-*Trimethyl*-3-*oxo*allo*chol*-8-*en*-24-*oate*.—" Isocholesterol " (3·0 g.) in acetic acid (200 c.c.) was treated with ozonised oxygen for 2½ hr. The product, isolated by extraction with ether, was oxidised in acetone (200 c.c.) with chromic acid solution (8N) in the usual way. The acid formed (1·18 g.) was separated and methylated with ethereal diazomethane, and the product adsorbed from benzene–light petroleum (4 : 1) on alumina (150 g.). Elution with benzene gave *methyl* 4 : 4 : 14α-*trimethyl*-3-*oxo*allo*chol*-8-*en*-24-*oate* as needles (720 mg.), m. p. 141—143°, $[\alpha]_D$ +76° (*c*, 0·97) (Found : C, 78·0; H, 10·45. $C_{28}H_{44}O_3$ requires C, 78·45; H, 10·35%).

Methyl 4 : 4 : 14α-*Trimethyl*-3 : 7-*dioxo*allo*chol*-8-*en*-24-*oate*.—Methyl 4 : 4 : 14α-trimethyl-3-oxo*allo*chol-8-en-24-oate (400 mg.) in acetic acid (35 c.c.) was treated with chromic acid (180 mg.) and kept at 80—90° for 10 min. Extraction with ether yielded a product which was adsorbed from benzene on alumina (40 g.). Elution with benzene–ether (9 : 1) gave *methyl* 4 : 4 : 14α-*trimethyl*-3 : 7-*dioxo*allo*chol*-8-*en*-24-*oate* as needles (271 mg.), m. p. 154—155°,

$[\alpha]_D$ +5° (*c*, 0·78) (Found: C, 75·8; H, 9·6. $C_{28}H_{42}O_4$ requires C, 75·95; H, 9·55%). Light absorption in ethanol: Max., 2520 Å; ε = 8,800.

The authors thank Professor E. R. H. Jones, F.R.S., for his interest and advice. One of the authors (R. H.) is indebted to the University of Manchester for a Research Studentship and to the Royal Commissioners of the 1851 Exhibition for the award of an Overseas Scholarship. Thanks are also proffered to Mr. E. S. Morton and Mr. H. Swift for the microanalyses.

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[*Received, February 23rd*, 1954.]