

**94.** *The Chemistry of the Triterpenes. Part XV.\* The Environment of the Unreactive Double Bond of Polyporenic Acid A.*

By T. G. HALSALL, E. R. H. JONES, and A. J. LEMIN.

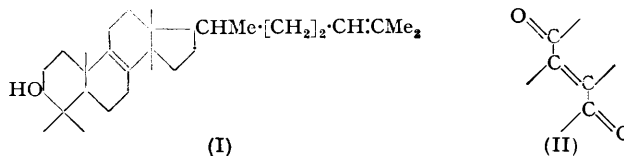
Oxidation of derivatives of methyl polyporenic acid A has given products containing characteristic chromophoric systems. Detailed examination of these compounds has permitted the elucidation of the environment of the unreactive double bond and the formulation of a partial structure for polyporenic acid A. A close relationship exists between this partial structure and the structure now proposed for lanosterol; it is emphasized by the isolation of 1 : 2 : 8-trimethylphenanthrene from the selenium dehydrogenation products from polyporenic acid A.

The unreactive hydroxyl group has been shown to be in the  $\beta$ -position to the inert double bond.

IN the preceding two papers polyporenic acid A has been characterised as a tetracyclic dihydroxy-carboxylic acid with two double bonds. One of these has been shown to be present in a vinylidene group, and to be in the  $\beta\gamma$ -position to the carboxyl group. The other is unreactive and the infra-red spectra of derivatives of polyporenic acid A indicate that it is fully substituted. In other non-steroid tetracyclic compounds an unreactive tetrasubstituted double bond has also been found and has been shown to lie between two rings as in lanosterol (I) (Barnes, Barton, Cole, Fawcett, and Thomas, *Chem. and Ind.*, 1952, 426; Cavalla, McGhie, and Pradhan, *J.*, 1951, 3142; Barton, Fawcett, and Thomas, *J.*,

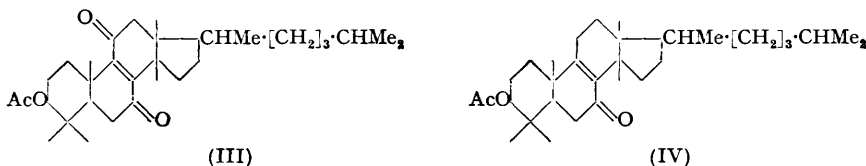
\* Part XIV, preceding paper.

1951, 3147; Voser, Montavon, Gunthard, Jeger, and Ruzicka, *Helv. Chem. Acta*, 1950, **33**, 1893; Curtis, Fridricksons, and Mathieson, *Nature*, 1952, **170**, 321).



In lanosterol the environment of the unreactive double bond has been elucidated largely by a study of the behaviour of lanostenyl acetate on oxidation. A similar study of the oxidation of derivatives of polyporenic acid A has now been carried out.

Oxidation of methyl polyporeenate A *a* : *b*-diacetate with chromic acid in acetic acid gave a diketone (methyl *c* : *d*-diketopolyporeenate A *a* : *b*-diacetate),  $C_{35}H_{50}O_8$ , the ultra-violet spectrum of which showed a maximum at 2730 Å characteristic of the system (II) in the fully transoid arrangement. Similar light-absorption properties are shown by 8 : 11-diketolanost-9-en-2-yl acetate (III) (Cavalla and McGhie, *J.*, 1951, 834). The formula of the diketone indicated that the reactive double bond was still present and this was confirmed by the presence of a band at  $900\text{ cm.}^{-1}$  in the infra-red spectrum of the diketone determined in carbon tetrachloride.

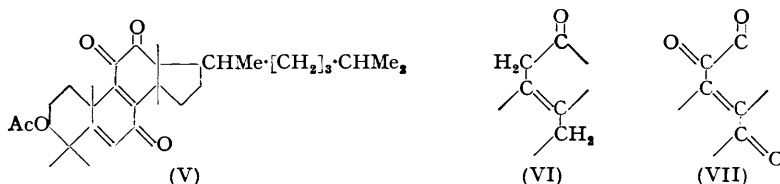


Similar oxidation of methyl dihydro-II-polyporeenate A *a* : *b*-diacetate gave the corresponding methyl dihydro-II-*c* : *d*-diketopolyporeenate A *a* : *b*-diacetate, which again absorbed at 2730 Å. The use of milder conditions resulted in the introduction of only one keto-group, giving methyl dihydro-II-*c*-ketopolyporeenate A *a* : *b*-diacetate. The ultra-violet spectrum had a peak at 2510 Å, characteristic of an  $\alpha\beta\beta$ -trisubstituted  $\alpha\beta$ -unsaturated ketone, and was similar to that of 8-ketolanost-9-en-2-yl acetate (IV) (Birch-enough and McGhie, *J.*, 1950, 1249; Barton, Fawcett, and Thomas, *loc. cit.*). The infra-red spectrum of the monoketo-oxidation product, determined in Nujol, showed a strong band at  $1658\text{ cm.}^{-1}$ , indicative of an  $\alpha\beta$ -unsaturated carbonyl group on a six-membered ring. In addition to the monoketone, a conjugated dienone containing only one acetoxy group was obtained as a by-product. Its nature is discussed later.

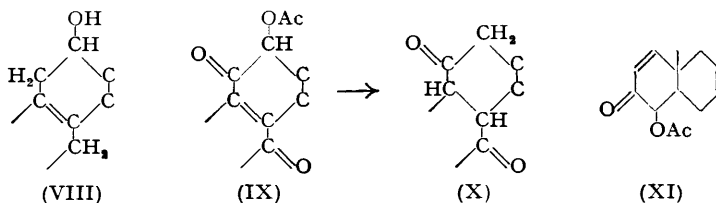
When methyl *a* : *b*-diketopolyporeenate A was oxidised with chromic acid in acetic acid two further keto-groups were again introduced giving methyl *a* : *b* : *c* : *d*-tetraketopolyporeenate A and the reactive double bond was again unattacked. The position of the ultra-violet absorption maximum (2830 Å) differed from that observed with methyl *c* : *d*-diketopolyporeenate A *a* : *b*-diacetate and the corresponding dihydro-II-derivative. Absorption at about this wave-length has been observed with 8 : 11 : 12-triketolanosta-6 : 9-dien-2-yl acetate (V) by Dorée, McGhie, and Kurzer (*J.*, 1949, 570) ( $\lambda_{\text{max.}}$ , 2800 Å) and by Voser, Montavon, Gunthard, Jeger, and Ruzicka (*loc. cit.*) ( $\lambda_{\text{max.}}$ , 2850 Å). It is probable therefore that one of the keto-groups in methyl *a* : *b*-diketopolyporeenate A is in the  $\alpha$ -position to one of the methylene groups undergoing oxidation, *i.e.*, in the  $\beta$ -position to the unreactive double bond. Methyl *a* : *b*-diketopolyporeenate A would then possess partial structure (VI) and the tetraketone oxidation product would be represented by (VII), the chromophoric system being very similar to that present in (V). The presence of an  $\alpha$ -diketone grouping in the tetraketone was confirmed by oxidation with alkaline hydrogen peroxide whereupon the monomethyl ester of a tricarboxylic acid was formed without loss of carbon atoms. This result further proves that the  $\alpha$ -diketone system is present in a ring.

Oxidation of methyl *b*-ketopolyporeenate A *a*-acetate with chromic acid in acetic acid gave a triketone monoacetate, methyl *b* : *c* : *d*-triketopolyporeenate A *a*-acetate, which also

showed absorption at 2830 Å, indicative of the chromophore (VII). The presence of a cyclic  $\alpha$ -diketone grouping was again demonstrated by oxidation with alkaline hydrogen peroxide. These results prove that the *b*-keto-group of the original keto-acetate is in the

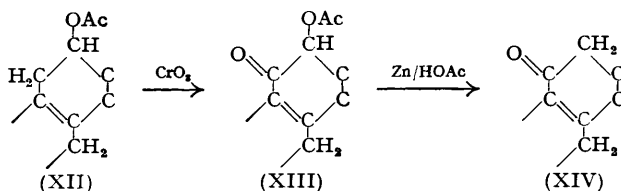


$\beta$ -position to the unreactive double bond, and hence that in polyporenic acid the *b*-(*i.e.*, unreactive) hydroxyl group is similarly situated (cf. VIII). Confirmation of the partial structure (VIII) was provided by the zinc-acetic acid reduction of methyl dihydro-II-*c* : *d*-diketopolyporeenate A *a* : *b*-diacetate which should contain the grouping (IX) if (VIII) is a correct partial structure for polyporenic acid A.



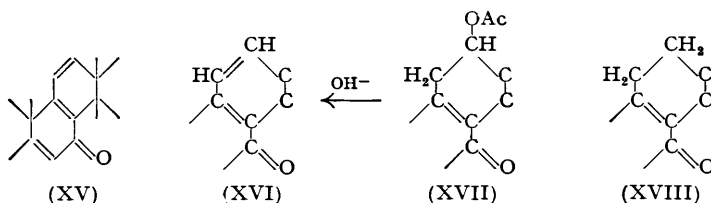
The similar unsaturated diketone system in 8 : 11-diketolanostenyl acetate (III) is reduced by zinc and acetic acid to the saturated 1 : 4-diketone (Dorée, McGhie, and Kurzer, *J.*, 1948, 988). Further examples are known in which the acetoxy group is eliminated from  $\alpha$ -acetoxy-ketones by the action of zinc, *e.g.*, in (XI) (Woodward, Sondheimer, Taub, Heusler, and McLamore, *J. Amer. Chem. Soc.*, 1952, **74**, 4223). Therefore, if partial structure (IX) is present in methyl dihydro-II-*c* : *d*-diketopolyporeenate A *a* : *b*-diacetate, reduction with zinc and acetic acid should lead to methyl *b*-deoxytetrahydro-II-*c* : *d*-diketopolyporeenate A *a*-acetate, containing the grouping (X). The reduction product was indeed the methyl ester of a saturated monoacetoxy-diketo-acid. The infra-red spectrum of this compound, determined in carbon tetrachloride, showed strong bands at 1708  $\text{cm}^{-1}$  and 1738  $\text{cm}^{-1}$ . The first band is due to the unconjugated keto-groups and the second to the ester groups.

Reduction of the partial oxidation product, methyl dihydro-II-*c*-ketopolyporeenate A *a* : *b*-diacetate, with zinc and acetic acid led to the replacement of the *b*-acetoxy group by hydrogen giving methyl *b*-deoxydihydro-II-*c*-ketopolyporeenate A *a*-acetate, showing an absorption maximum at 2540 Å. At first it was thought that these results implied that the introduction of the first keto-group (group *c*) had taken place between the double bond and the acetoxy group, giving an  $\alpha$ -acetoxy-ketone, the reactions being represented by the partial structures (XIII) and (XIV). However, this view was rendered untenable



by the discovery that very mild alkali treatment of methyl dihydro-II-*c*-ketopolyporeenate A *a* : *b*-diacetate gave a conjugated dienone still containing one acetoxy group, one carbomethoxyl group, and no hydroxyl group (infra-red spectrum). The absorption maximum at 3180 Å is indicative of the conjugation of the carbonyl group with the two double bonds in the *same* ring.

Although it is well known that a homoannular diene absorbs at a longer wave-length than the correspondingly substituted heteroannular diene, there is apparently no reference to a similar bathochromic shift in conjugated dienones possessing a homoannular diene system. Thus Fieser and Fieser ("Natural Products related to Phenanthrene," 3rd Edn., 1949, Reinhold Publ. Corp., p. 192) imply that no such shift occurs since their calculated maximum of 3180 Å for a  $\Delta^{8(14),9(11)}$ -dien-15-one in the steroid series makes no allowance for the homoannular bathochromic shift. The absorption maximum of cholesta-2:4-dien-6-one was found some years ago by the senior author (cf., Ross, *J.*, 1946, 735) to lie at 3160 Å (see also Reich, Walker, and Collins, *J. Org. Chem.*, 1951, **16**, 1753, who give 3140 Å). The latter, probably more accurate figure corresponds to a bathochromic shift of 360 Å comparable with that of *ca.* 410 Å in the homoannular diene series. In the tetracyclic triterpene group a cross-conjugated trienone (8-ketolanosta-6:9:11-trien-2-yl acetate) containing the chromophore (XV) has been described by Birchenough and McGhie (*J.*, *loc. cit.*). This compound shows maxima at 2560 and 3270 Å; the latter, due to the dienone system, again indicates a pronounced bathochromic shift.

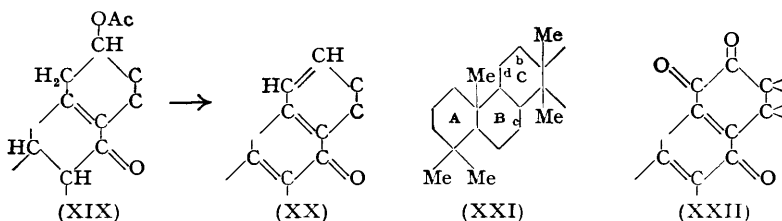


The conjugated dienone resulting from the alkali treatment described above is formulated as (XVI). By using the value of 360 Å for the bathochromic shift due to the homoannular diene, the calculated absorption maximum for (XVI) is 3210 Å which agrees well with the observed figure of 3180 Å. The ready formation of the dienone indicates that the introduction of the first keto-group into methyl dihydro-II-polyporene A *a*:*b*-diacetate occurs at the  $\alpha$ -methylene group on the opposite side of the double bond from the *b*-acetoxy group, the product being an  $\alpha\beta$ -unsaturated  $\delta$ -acetoxy-ketone (XVII). This, on alkali treatment, is readily converted into the dienone (XVI).

With the partial formulation of methyl dihydro-II-*c*-ketopolyporene A *a*:*b*-diacetate as (XVII) it became clear that its reduction by zinc dust in acetic acid was not a simple reaction. In fact it takes place in two steps. The first is the elimination of acetic acid from the keto-diacetate with boiling acetic acid. This reaction occurs in the absence of zinc and the resultant conjugated dienone is identical with that obtained by alkali treatment and also with that described earlier as a by-product in the preparation of methyl dihydro-II-*c*-ketopolyporene A *a*:*b*-diacetate. In the latter case the dienone must arise from the monoketone as in the acetic acid reaction described above. The second step is the reduction of the  $\gamma\delta$ -double bond of the dienone, and this has been carried out independently. The product of this reaction (methyl *b*-deoxydihydro-II-*c*-ketopolyporene A *a*-acetate; partial structure XVIII) is not identical with methyl acetyldihydro-monoketoeburicoate (personal communication from Professor A. Robertson) and methyl acetylmonoketoelemenolate (Ruzicka, Rey, Spillman, and Baumgartner, *Helv. Chim. Acta*, 1943, **26**, 1695). Oxidation of the above *b*-deoxy-compound with chromic acid in acetic acid gave methyl *b*-deoxydihydro-II-*c*:*d*-diketopolyporene A *a*-acetate, not identical with either methyl acetyldihydrodiketoeburicoate (Lahey and Strasser, *J.*, 1951, 873) or methyl acetyldiketoelemenolate (Ruzicka, Rey, Spillman, Baumgartner, *loc. cit.*).

The acid- and alkali-catalysed dehydrations described above have a ready parallel in Greenhalgh, Henbest, and Jones's finding (*J.*, 1952, 2375) that the  $\alpha\beta$ -unsaturated  $\delta$ -hydroxy-ketone, 7 $\alpha$ -hydroxycholest-4-en-3-one, undergoes dehydration very readily in the presence of mild acidic and alkaline reagents to the conjugated dienone, cholesta-4:6-dien-3-one. The ease of dehydration in the present case suggests that the *b*-hydroxyl group is polar.

Oxidation of methyl dihydro-II-*c*-ketopolyporeenate A *a*:*b*-diacetate with selenium dioxide in acetic acid gave a trienone containing only one acetoxy group, and showing absorption maxima at 2600 and 3270 Å. These values correspond to the chromophore (XV) found in 8-ketolanosta-6:9:11-trien-2-yl acetate and indicate that the reaction (XIX) → (XX) has occurred. The very close similarity of the carbon skeleton of the partial structure (XIX) to that of lanosterol (I) suggests that the grouping (XXI) may be present in polyporenic acid A. In support of this partial formulation is the isolation of 1:2:8-trimethylphenanthrene from the products of the dehydrogenation of polyporenic acid A with selenium. Further oxidation of the trienone gave an impure product, the absorption spectrum of which indicated the presence of the partial structure (XXII). The absence of



any evidence of oxidation beyond this stage suggests that no hydrogen atoms occur at positions  $\alpha$  to any of the unsaturated centres of the grouping (XXII). If the partial formulation of polyporenic acid A as (XXI) is correct, then the position of the *b*-hydroxyl group corresponds to the C<sub>(12)</sub>-position in the steroids. The lack of reactivity of the *b*-keto-group compared with that of the 12-keto-group of the steroids is worthy of comment. (For a discussion of the reactivity of the 12-keto-group of the steroids see Fieser and Fieser, *op. cit.*, p. 124.) The lack of reactivity is almost certainly due to the presence of the additional methyl group at the position corresponding to C<sub>(14)</sub> in the steroids.

No conclusive evidence has yet been obtained about the position of the *a*-hydroxyl group. Dehydration experiments at present in progress suggest however that it is on the carbon atom adjacent to a *gem*-dimethyl group on ring A.

#### EXPERIMENTAL

M. p.s were determined on a Kofler block and are corrected. Rotations were determined in chloroform. Light petroleum refers to the fraction with b. p. 40–60° unless otherwise stated. The alumina used for chromatography had an activity of I–II. The derivatives of polyporenic acid A used as starting materials were prepared according to the methods described in the preceding two papers.

*Methyl c*:*d*-Diketopolyporeenate A *a*:*b*-Diacetate.—Methyl polyporeenate A *a*:*b*-diacetate (1.7 g.) was oxidised in acetic acid (70 c.c.) with chromic acid (3 g.) at 80–90°. After 90 minutes, dilution with water and isolation with ether yielded an oil (1.0 g.). This in ether was purified by chromatography on alumina (100 g.) to give an oily solid, crystallisation of which from methanol gave *methyl c*:*d*-diketopolyporeenate A *a*:*b*-diacetate as pale yellow needles (0.5 g.), m. p. 141–142°,  $[\alpha]_D^{20} +40.5^\circ$  (*c*, 0.60) (Found: C, 70.4; H, 8.75. C<sub>35</sub>H<sub>50</sub>O<sub>8</sub> requires C, 70.3; H, 8.4%). Light absorption in ethanol: Max., 2730 Å;  $\epsilon = 9500$ .

*Methyl Dihydro-II-c*:*d*-diketopolyporeenate A *a*:*b*-Diacetate.—Methyl dihydro-II-polyporeenate A *a*:*b*-diacetate (1.5 g.) was oxidised in acetic acid (70 c.c.) with chromic acid (2.4 g.) at 80–90°. After 50 minutes, dilution with water and isolation with ether yielded an oil (0.65 g.) which was adsorbed from benzene (20 c.c.) on alumina (100 g.). Elution with benzene-ether (4:1; 400 c.c.) gave an oil (60 m.g.), which crystallised in contact with methanol. Recrystallisation from the same solvent gave *methyl dihydro-II-b*:*c*:*d*-triketopolyporeenate A *a*-acetate as yellow prisms, m. p. 150–151.5° (Found: C, 71.7; H, 9.0. C<sub>35</sub>H<sub>48</sub>O<sub>7</sub> requires C, 71.2; H, 8.7%). Light absorption in ethanol: Max., 2840 Å;  $\epsilon = 8150$ . Further elution with benzene-ether (7:3; 500 c.c.) gave a fraction (0.5 g.) which formed pale yellow needles (from methanol) of *methyl dihydro-II-c*:*d*-diketopolyporeenate A *a*:*b*-diacetate (0.45 g.), m. p. 148–149.5°,  $[\alpha]_D^{20} +176^\circ$  (*c*, 0.15) (Found: C, 69.9; H, 8.95. C<sub>35</sub>H<sub>52</sub>O<sub>8</sub> requires C, 69.95; H, 8.7%). Light absorption in ethanol: Max., 2730 Å;  $\epsilon = 9500$ .

*Methyl Dihydro-II-c*-ketopolyporeenate A *a*:*b*-Diacetate.—Methyl dihydro-II-polyporeenate A *a*:*b*-diacetate (2 g.) was oxidised in acetic acid (100 c.c.) with chromic acid (0.9 g.) at 80–90°.

After 10 minutes, dilution with water and isolation with ether yielded an oil (1.95 g.). This was dissolved in benzene-ether (7 : 3; 500 c.c.); chromatography on alumina (100 g.) gave a solid, several recrystallisations of which from methanol gave *methyl dihydro-II-c-ketopolyporene A a : b-diacetate* as prisms (1.3 g.), m. p. 172—174°,  $[\alpha]_D^{20} + 60^\circ$  (*c*, 0.94) (Found : C, 71.85; H, 9.5.  $C_{35}H_{52}O_7$  requires C, 71.6; H, 9.2%). Light absorption in ethanol; Max., 2510 Å;  $\epsilon = 10,000$ . In a second preparation on the same scale the reaction mixture was allowed to cool to room temperature before dilution with water. The oil (1.97 g.) isolated with ether was adsorbed from benzene (50 c.c.) on alumina (200 g.). Elution with benzene-ether (9 : 1; 300 c.c.) gave a fraction (0.4 g.), several recrystallisations of which from methanol gave the *dienone* (XVI) as prisms, m. p. 194—195°,  $[\alpha]_D^{20} - 27^\circ$  (*c*, 0.61) (Found : C, 75.45; H, 9.8.  $C_{33}H_{50}O_5$  requires C, 75.25; H, 9.6%). Light absorption in ethanol: Max., 3180 Å;  $\epsilon = 7600$ . Further elution with benzene-ether (7 : 3; 800 c.c.) yielded a fraction (1.5 g.) which gave the monoketo-diacetate, described above, as prisms (from methanol), m. p. 172—174°,  $[\alpha]_D^{20} + 60^\circ$  (*c*, 0.85).

*Methyl a : b : c : d-Tetraketopolyporene A*.—Methyl *a : b*-diketopolyporene A (1.5 g.) was oxidised in acetic acid (70 c.c.) with chromic acid (2.4 g.) at 80—90°. After 30 minutes, dilution with water and isolation with ether yielded an oily solid (0.55 g.). This was dissolved in benzene (20 c.c.); chromatography on alumina (60 g.) and crystallisation from methanol gave *methyl a : b : c : d-tetraketopolyporene A* as bright orange plates (0.4 g.), m. p. 141—142°,  $[\alpha]_D^{20} + 34^\circ$  (*c*, 0.8) (Found : C, 73.3; H, 8.5.  $C_{31}H_{42}O_6$  requires C, 72.9; H, 8.1%). Light absorption in ethanol: Max., 2830 Å;  $\epsilon = 9000$ .

*Action of Alkaline Hydrogen Peroxide on Methyl a : b : c : d-Tetraketopolyporene*.—The tetraketone (170 mg.) was dissolved in dioxan (20 c.c.), and methanolic potassium hydroxide (10%; 8 c.c.) and hydrogen peroxide (100-vol.; 4 c.c.) were added. After 10 minutes at 50° the yellow colour of the reaction mixture had almost disappeared. More hydrogen peroxide (1 c.c.) was added and then, after 10 minutes at 20°, the solution was poured into water. The product, isolated with ether, was divided into a neutral and an acidic fraction. The neutral ester (40 mg.) crystallised from methanol as needles, m. p. 173.5—174.5°,  $[\alpha]_D^{20} + 59.5^\circ$  (*c*, 0.78) (Found : C, 74.5; H, 9.4.  $C_{31}H_{48}O_5$  requires C, 74.7; H, 9.25%). Light absorption in ethanol: Max., 2410 Å;  $\epsilon = 9200$ . The acidic fraction gave a tricarboxylic acid monomethyl ester as a colourless glass (120 m.g.),  $[\alpha]_D^{20} - 22.5^\circ$  (*c*, 1.77). Light absorption in ethanol: Max., 2390—2400 Å;  $\epsilon = 8300$ . The glass was dissolved in acetone (5 c.c.), treated with an excess of diazomethane in ether, and kept at 20° for 30 minutes. After decomposition of the excess of diazomethane the *trimethyl* ester was isolated as a colourless, uncrystallisable amorphous solid (100 mg.),  $[\alpha]_D^{20} - 23^\circ$  (*c*, 0.55) (Found : C, 68.85; H, 8.8.  $C_{33}H_{48}O_8$  requires C, 69.2; H, 8.45%). Light absorption in ethanol; Max., 2360—2380 Å;  $\epsilon = 8500$ .

*Methyl b : c : d-Triketopolyporene A a-Acetate*.—Methyl *b*-ketopolyporene A *a*-acetate (1.4 g.) was oxidised in acetic acid (70 c.c.) with chromic acid (2.14 g.) at 80—90°. After 10 minutes, dilution with water and isolation with ether yielded a neutral fraction, which gave *methyl b : c : d-triketopolyporene A a-acetate* as bright orange needles (0.6 g.) (from methanol), m. p. 158—159°,  $[\alpha]_D^{20} - 103^\circ$  (*c*, 1.0) (Found : C, 71.5; H, 8.7.  $C_{35}H_{46}O_7$  requires C, 71.5; H, 8.4%). Light absorption in ethanol: Max., 2840 Å;  $\epsilon = 9250$ .

*Action of Alkaline Hydrogen Peroxide on Methyl b : c : d-Triketopolyporene A a-Acetate*.—Methyl *b : c : d-triketopolyporene A a-acetate* (1.14 g.) was dissolved in dioxan (60 c.c.), and methanolic potassium hydroxide (10%; 40 c.c.) and hydrogen peroxide (100-vol.; 15 c.c.) were added. After 10 minutes at 50° more hydrogen peroxide (10 c.c.) was added and the mixture was kept at 20° for 10 minutes, by which time the yellow colour had almost disappeared. Dilution with water and extraction with ether yielded a neutral glass (0.03 g.) which was not investigated further. Acidification of the extracted alkaline solution and isolation with ether yielded a tricarboxylic acid monomethyl ester as a colourless glass (1.0 g.),  $[\alpha]_D^{20} - 37^\circ$  (*c*, 1.0). Light absorption in ethanol: Max., 2360—2380 Å;  $\epsilon = 8500$ . The glass (0.89 g.) was dissolved in acetone (5 c.c.), treated with an excess of diazomethane in ether, and kept at 20° for 30 minutes. After decomposition of the excess of diazomethane the *trimethyl* ester was isolated as an amorphous solid (0.88 g.). This was dissolved in ether (5 c.c.) and chromatographed on alumina (60 g.), but only an uncrystallisable gum was obtained, having  $[\alpha]_D^{20} - 37.5^\circ$  (*c*, 1.23) (Found : C, 67.7; H, 8.2.  $C_{35}H_{52}O_9$  requires C, 68.1; H, 8.5%).

*Zinc Dust Reduction of Methyl Dihydro-II-c : d-Diketopolyporene A a : b-Diacetate*.—To a boiling solution of methyl dihydro-II-c : d-diketopolyporene A *a : b-diacetate* (80 mg.) in acetic acid (10 c.c.), zinc dust (500 mg.) was added in small portions during 45 minutes; the solution became colourless on the first addition. After cooling, the solution was filtered into water, extraction of which with ether led to the isolation of a crystalline neutral fraction (75 mg.).

Several recrystallisations of this from methanol gave *methyl b-deoxytetrahydro-II-c: d-diketopolyporene A a-acetate* as plates, m. p. 164—165°,  $[\alpha]_D^{20} + 39.5^\circ$  (*c*, 0.34) (Found: C, 73.05; H, 9.85.  $C_{35}H_{52}O_6$  requires C, 72.75; H, 9.6%). Light absorption in ethanol: 2730 ( $\epsilon = 5$ ) and 2100 Å ( $\epsilon = 490$ ).

*Zinc Dust Reduction of Methyl Dihydro-II-c-ketopolyporene A a: b-Diacetate.*—To a boiling solution of methyl dihydro-II-c-ketopolyporene A a: b-diacetate (400 mg.) in acetic acid (20 c.c.), zinc dust (1.5 g.) was added in small portions during 1 hour. The cooled solution was filtered into water, extraction of which with ether led to the isolation of a solid neutral fraction (360 mg.) which was adsorbed from benzene (20 c.c.) on alumina (100 g.). Elution with benzene-ether (19:1; 600 c.c.) gave a fraction, crystallisation of which from methanol-chloroform gave *methyl 6-deoxydihydro-II-c-ketopolyporene A a-acetate* as long needles, m. p. 210—212.5°,  $[\alpha]_D^{20} - 67.5^\circ$  (*c*, 0.48) (Found: C, 75.35; H, 10.05.  $C_{33}H_{52}O_5$  requires C, 75.05; H, 9.9%). Light absorption in ethanol: Max., 2540 Å;  $\epsilon = 10,000$ .

*Alkali Treatment of Methyl Dihydro-II-c-ketopolyporene A a: b-Diacetate.*—Methyl dihydro-II-c-ketopolyporene A a: b-diacetate (230 mg.) was refluxed with methanolic potassium hydroxide (20 c.c.; 1%) for 30 minutes. After dilution with water the neutral and the acidic products were separated. The yield of the latter was negligible, but the former (200 mg.), after several recrystallisations from methanol, gave (XVI) as prisms, m. p. 192—193° undepressed when the dienone was mixed with that obtained in the preparation of methyl dihydro-II-c-ketopolyporene A a: b-diacetate,  $[\alpha]_D^{20} - 31^\circ$  (*c*, 0.53) (Found: C, 75.0; H, 9.6. Calc. for  $C_{33}H_{50}O_5$ : C, 75.25; H, 9.6%). Light absorption in ethanol: Max., 3180 Å;  $\epsilon = 7500$ .

*Action of Boiling Acetic Acid on Methyl Dihydro-II-c-ketopolyporene A a: b-Diacetate.*—Methyl dihydro-II-c-ketopolyporene A a: b-diacetate (275 mg.) was refluxed with acetic acid (20 c.c.) for 2 hours. The acetic acid was then evaporated under reduced pressure, leaving an oily solid. Two recrystallisations from methanol gave (XVI) as prisms, m. p. and mixed m. p. 192—194°,  $[\alpha]_D^{20} - 30^\circ$  (*c*, 0.65). Light absorption in ethanol: Max., 3180 Å;  $\epsilon = 6650$ .

*Reduction of the Dienone (XVI) with Zinc Dust in Acetic Acid.*—To a boiling solution of (XVI) (115 mg.) in acetic acid (15 c.c.), zinc dust (2 g.) was added in small portions during 1 hour. The cooled solution was filtered into water, and extraction with ether led to the isolation of a solid neutral fraction (100 mg.). Several recrystallisations from chloroform-methanol gave methyl b-deoxydihydro-II-c-ketopolyporene A a-acetate as needles, m. p. 209—210°,  $[\alpha]_D^{20} - 66^\circ$  (*c*, 0.66). Light absorption in ethanol: Max., 2540 Å;  $\epsilon = 8950$ . The infra-red spectrum was identical with that of a specimen prepared by zinc dust reduction of methyl dihydro-II-c-ketopolyporene A a: b-diacetate in acetic acid.

*Oxidation of Methyl Dihydro-II-c-ketopolyporene A a: b-Diacetate with Selenium Dioxide.*—Methyl dihydro-II-c-ketopolyporene A a: b-diacetate (320 mg.) in acetic acid (100 c.c.) was refluxed with selenium dioxide (200 mg.) for 3 hours. The selenium was filtered off and the solution poured into water. The neutral product was then isolated as an oil (300 mg.), chromatographed in ether on alumina (30 g.), and crystallised from methanol, giving the *trienone* (XX) (260 mg.) as plates, m. p. 171—174°,  $[\alpha]_D^{20} + 29^\circ$  (*c*, 0.52) (Found: C, 75.2; H, 9.25.  $C_{33}H_{48}O_5$  requires C, 75.5; H, 9.2%). Light absorption in ethanol: Max., 2600 ( $\epsilon = 9600$ ) and 3270 Å ( $\epsilon = 9600$ ).

*Dehydrogenation of Polyporenic Acid A with Selenium.*—Polyporenic acid A (20 g.) was heated at 220—230° (bath-temp.) in nitrogen until decarboxylation was complete. Precipitated selenium (10 g.) was then added and the bath-temperature raised to 320°. Selenium (5 g.) was added at hourly intervals until a total quantity of 30 g. had been used. The heating was continued for a further 30 hours, and then the product was cooled, powdered, and extracted with ether and benzene. The extract was dried ( $Na_2SO_4$ ) and evaporated, giving a dark brown oil (14 g.). This was distilled under reduced pressure (2 mm.) to give the following fractions: (i) colourless mobile liquid (0.4 g.), b. p. 40—60° (bath-temp.); (ii) pale brown viscous oil (1.1 g.), b. p. 170—230° (bath-temp.); residue—a dark brown oily solid (12 g.).

Fraction (ii) was chromatographed on alumina (100 g.), and the solid fractions obtained by elution with light petroleum-benzene (9.1) gave 1:2:8-trimethylphenanthrene (0.6 g.) as plates, m. p. 145—146°, after many recrystallisations from ethanol (Found: C, 92.2; H, 7.0. Calc. for  $C_{17}H_{16}$ : C, 92.7; H, 7.3%). The picrate and the *s*-trinitrobenzene adduct had m. p.s. 163—164° and 190—191°, respectively. No depressions in m. p. were observed when these three compounds were admixed with corresponding authentic samples. The absorption spectrum of the hydrocarbon,  $\lambda_{max}$  2630, 2840, 2950, 3080, 3400, and 3560 Å ( $\epsilon_{max}$  58,900, 13,200, 11,700, 14,100, 350, and 170 respectively), was also characteristic of 1:2:8-trimethylphenanthrene.

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