The Chemistry of the Triterpenes and Related Compounds. Part XXV. Some Stereochemical Problems concerning Polyporenic Acid C.*

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The $C_{(16)}$-hydroxyl group of polyporenic acid C is shown to have the α-configuration. The configuration at $C_{(20)}$ of polyporenic acid C is discussed and shown to be the same as that of eburicoic acid. The formation and chemistry of a number of derivatives of 20-*iso*eburicane are described.

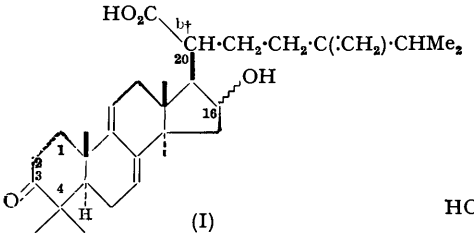
Polyporenic acid C is a 16-hydroxy-derivative of 3-oxoeburico-7 : 9(11) : 24(28)-trien-21-oic acid (cf. I †) and it has been suggested that the hydroxyl group has the β-configuration (Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2548). The only assumption made in arriving at this structure, apart from that concerning the configuration of the hydroxyl group, was that no stereochemical inversion occurred at $C_{(20)}$ during the conversion of polyporenic acid C into an eburicoic acid derivative. Biogenetic evidence supports this

* Part XXIV, *J.*, 1954, 2385.

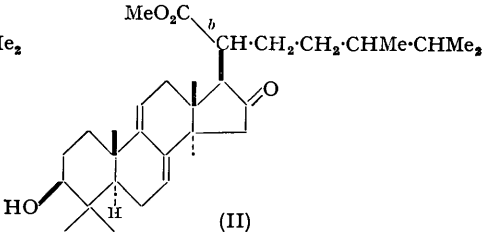
† The placing of a letter " b " against a bond attached to $C_{(20)}$ indicates that the substituent attached by the bond to $C_{(20)}$ is in the same relative configuration to $C_{(20)}$ as is the $C_{(21)}$-methyl group of lanostane. The placing of a letter " a " against a bond attached to $C_{(20)}$ indicates that the substituent attached by the bond to $C_{(20)}$ is in the same relative configuration to $C_{(20)}$ as is $C_{(22)}$ of lanostane.

assumption. Its chemical validity, and also the configuration of the hydroxyl group, are now discussed.

Reduction of the 3β-hydroxy-16-oxo-derivative (II) (Bowers *et al.*, *loc. cit.*) with lithium aluminium hydride gave two triols in approximately equal amounts. These must differ

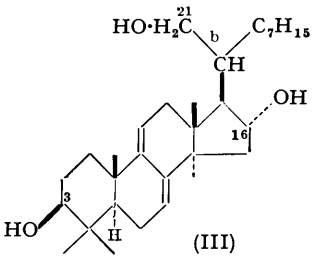


(I)



(II)

at $C_{(16)}$, one being the 3β : 16α : 21- and the other the corresponding 3β : 16β : 21-derivative (cf. III and IV). One of the triols was identical with that obtained by reduction of methyl dihydropolyporenate C successively with sodium borohydride and lithium aluminium hydride and hence must have the same configuration at $C_{(16)}$ as polyporenic acid C. This triol had a molecular rotation $[M]_D$ in pyridine of +179° whilst the other triol had $[M_D]$ +429°. Fukushima and Gallagher (*J. Amer. Chem. Soc.*, 1951, **73**, 196) have calculated molecular-rotation differences between 16α- and 16β-hydroxy-steroids and the corresponding deoxy-compounds. They found for the 16α-OH group $\Delta[M_D] = -44°$ to −77° and for the 16β-OH group $\Delta[M_D] = +33°$ to +40°. Hence $[M_D]$ 16β-OH minus $[M_D]$ 16α-OH is +77° to +111°, with the 16β-hydroxy-steroids more dextrorotatory (cf. Klyne and Stokes, *J.*, 1954, 1979). By analogy, therefore, the more dextrorotatory triol described above should be (IV), and the other, which is also obtained from methyl dihydropolyporenate C, should be the 3β : 16α : 21-triol (III). The molecular-rotation



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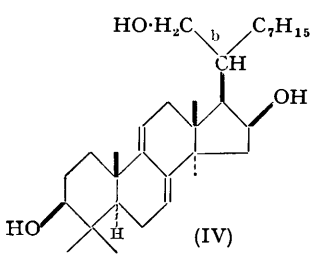

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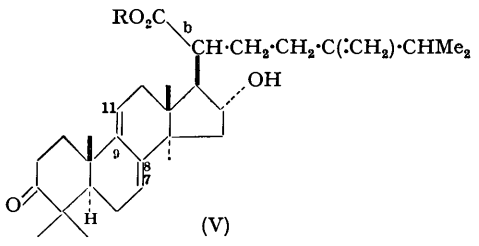


(V)

difference ($\Delta[M_D]$ 250°) between the triols is greater than that found for the steroids, but this is probably due to a vicinal effect between the oxygen functions at $C_{(16)}$ and $C_{(21)}$. This interpretation of the data leads to the α-configuration for the hydroxyl group of methyl dihydropolyporenate C and to structure (V) for polyporenic acid C. This conclusion is opposite to that previously suggested.

Acetylation of 16α-hydroxy-steroids results in a large negative shift in the molecular rotation while 16β-hydroxy-steroids give a positive shift (cf. Fukushima and Gallagher, *loc. cit.*; Klyne and Stokes, *loc. cit.*). Inspection of Table 1 shows that acetylation of the $C_{(16)}$ hydroxyl group of polyporenic acid C and its derivatives is accompanied by a large

negative shift in the molecular rotation, confirming the assignment of the α-configuration to this group.

The formation of two epimeric 16-hydroxy-derivatives on reduction of the 16-oxo-derivative (II) with lithium aluminium hydride is in contrast to the almost exclusive

TABLE 1.

	$[M_D]$ ($CHCl_3$)		
		Acetate	$\Delta Ac(C_{(16)})$
Polyporenic acid C	(+ 29°)†	−114°	[−143°]
Methyl polyporenate C	+ 49	−156	−205
Methyl dihydropolyporenate C	+ 50	−130	−180
Methyl 3β : 16α-dihydroxyeburico-7 : 9(11) : 24(28)-trien-21-oate	+138	+143	−150
Methyl 3β : 16α-dihydroxyeburico-7 : 9(11)-dien-21-oate	+136	+117	−174 *

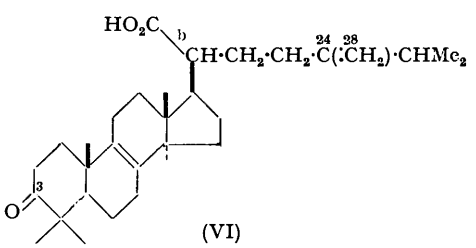
* Calculated by assuming that $\Delta Ac(3\beta\text{-OH})$ is +155°. This value is the mean of the ΔAc values quoted for the 3β-OH group of methyl dehydroeburicoate and methyl dehydrodihydroeburicoate (Gascoigne, Robertson, and Simes, *J.*, 1953, 1833). The ΔAc (3β-OH) for methyl 16β-chloro-3β-hydroxyeburico-7 : 9(11)-dien-21-oate (Bowers *et al.*, *loc. cit.*) is +171°. If this value is used instead of +155° then the $\Delta Ac(C_{(16)})$ values for the last two compounds become −166° and −190°.

† Measurements in pyridine solution. Ref.: Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2548.

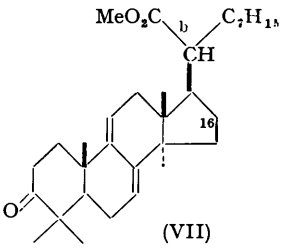
formation of the 16β-alcohol from 16-oxo-steroids (Hirshmann, *J. Biol. Chem.*, 1949, **178**, 751).

To study further the properties of the $C_{(16)}$ hydroxyl group of polyporenic acid C derivatives the carbonyl group of methyl dihydropolyporenate C was reduced by the Wolff–Kishner method.

Only one product was expected since similar reduction of eburiconic acid (VI) (Gascoigne, Holker, Ralph, and Robertson, *J.*, 1951, 2346), methyl 3β-acetoxy-16-oxoeburico-7 : 9(11)-dien-21-oate (Bowers *et al.*, *loc. cit.*), and methyl 24-oxo-28-noreburico-8-en-21-oate



(VI)



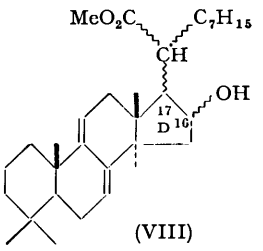
(VII)

(Holker, Powell, Robertson, Simes, Wright, and Gascoigne, *J.*, 1953, 2422) leads to only one reported product in each case. Further, reduction of (VII), differing from the dihydro-ester only in the absence of a hydroxyl group at $C_{(16)}$, followed by methylation of the product with diazomethane, gave only methyl eburico-7 : 9(11)-dien-21-oate. This was also formed, along with two nitrogenous compounds (see below), from the corresponding 3 : 16-dioxo-derivative. Compound (VII) was obtained by oxidation of the deacetylation product from methyl 3β-acetoxyeburico-7 : 9(11)-dien-21-oate prepared from polyporenic acid C as described by Bowers *et al.* (*loc. cit.*).

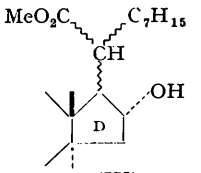
Reduction of the dihydro-ester and methylation of the product gave, however, two compounds which were readily separated by chromatography. Both were methyl monohydroxy-esters, $C_{32}H_{52}O_3$. For discussion they are designated "ester A" and "ester B," the yield of "B" being about twice that of "A." The most likely difference between them appeared to be in configuration at one or more of the carbon atoms 16, 17, and 20, owing to partial inversion brought about by alkali during the reduction (cf. VIII).

At first we were inclined to discount inversion at $C_{(20)}$, α to the ester group, in view of the absence of isomerisation in the reductions described above. The first possibility considered was epimerisation of the secondary alcohol group at $C_{(16)}$ during the reduction whilst a free 3-oxo-group was still present. The epimerisation of secondary alcohols by alkali at elevated temperatures in the presence of a ketone is well known (cf. Aschner and Doering, *J. Amer. Chem. Soc.*, 1949, **71**, 838). "Ester B" was heated with alkali and a small amount of fluorenone in ethylene glycol. The product was methylated and found to

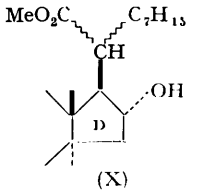
be a mixture of " ester A " and " ester B " in the approximate ratio 1 : 2 similar to that found in the reduction. However, oxidation of the two esters with chromic acid gave *two* keto-esters. Hence " ester A " and " ester B " must either differ in configuration at $C_{(16)}$ and also at least one other carbon atom or have the same configuration at $C_{(16)}$ but



(VIII)



(IX)



(X)

differ elsewhere. The almost identical molecular-rotation differences found when the two hydroxy-esters are acetylated indicate that the second alternative is correct (cf. Table 2). The differences further indicate that the hydroxyl groups in both esters have the α-configuration (cf. IX).

A difference in configuration at $C_{(17)}$ was considered. A mechanism which would bring it about involves equilibration of the hydroxy-esters with small amounts of keto-esters in

TABLE 2.

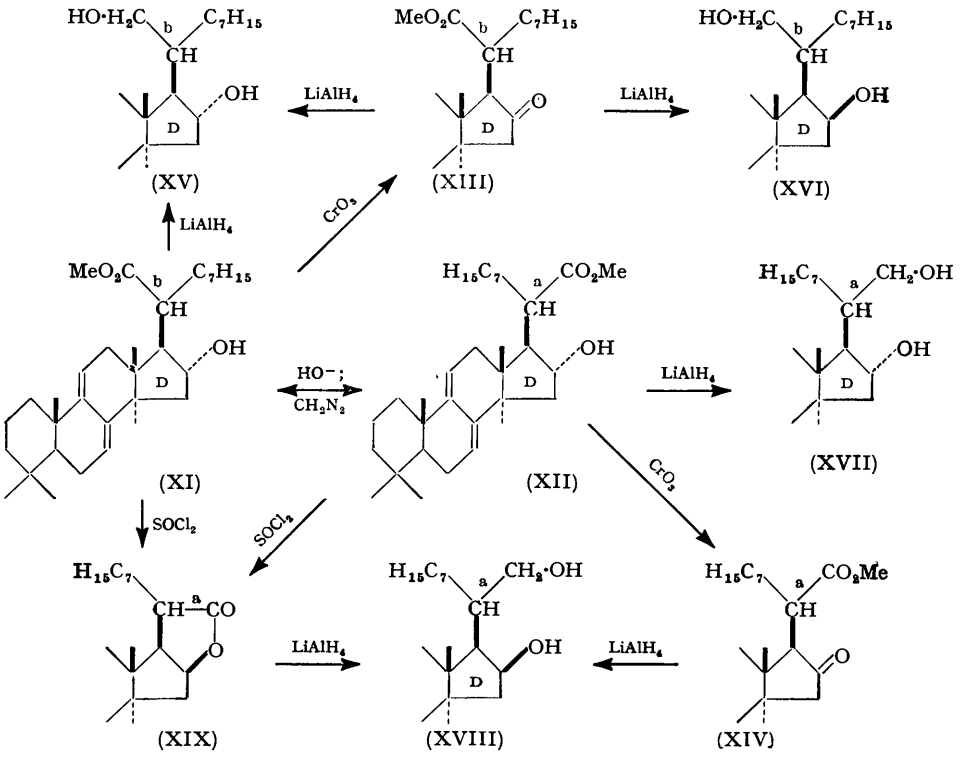
	$[M_D]$				
		Acetate	Ketone	ΔAc	ΔKet.
Methyl 16α-hydroxyeburico-7 : 9(11)-dien-21-oate (" ester A ")	+111°	−21°	−246°	−132°	−357°
Methyl 16α-hydroxy-20-*iso*eburico-7 : 9(11)-dien-21-oate (" ester B ")	+110	−37	−289	−147	−399

the reaction mixture. Isomerisation at a position α to a carbonyl group could then occur. In fact, as will become clear in the sequel, the side chains of both " ester A " and " ester B " must be *trans* to their respective 16-hydroxyl groups and hence both must have the β-configuration (cf. X). By exclusion therefore it is necessary to conclude that the esters differ at $C_{(20)}$.

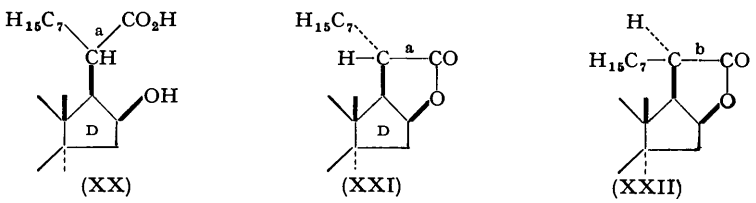
For simplification the chemistry of " ester A " and " ester B " is discussed in terms of their correct structures (XI; 20-normal series) and (XII; 20-*iso*-series) which follow from the arguments developed below. The ketone formed from " ester A " is (XIII; 20-normal series) and that from " ester B " is (XIV; 20-*iso*-series). Reduction of (XIII) with lithium aluminium hydride gave two diols (XV) and (XVI). One of these, (XV), was also obtained by direct reduction of " ester A " and must therefore be the 16α-hydroxy-derivative. (XVI) is then the 16β-hydroxy-derivative. Molecular rotations support these conclusions. The diol (XVI) has a higher molecular rotation ($[M_D]$ in pyridine = +470°) than the diol (XV) ($[M_D]$ in pyridine = +205°), in agreement with the results quoted earlier for 16-hydroxy-steroids. On acetylation of (XV) a diacetate is obtained with $[M_D]$ in chloroform equal to +32°, *i.e.*, a large negative change had occurred. Lahey and Strasser (*J.*, 1951, 873) have found that monoacetylation of 3β : 21-dihydroxyeburico-8 : 24(28)-diene to the 21-monoacetate is accompanied by a small positive change in molecular rotation ($\Delta[M_D]$ = +29°). Even allowing for a solvent effect it may be concluded that acetylation of the 16-hydroxyl group of (XV) is accompanied by a large negative change in molecular rotation, typical of that found with 16α-hydroxy-derivatives. Similar reduction of the ketone (XIV) from " ester B " gave only one diol (XVIII) which was different from that (XVII) obtained directly from " ester B." Thus (XVII) is the 16α-hydroxy- and (XVIII) the 16β-hydroxy-derivative. Again molecular rotations confirm this assignment. Diol (XVIII) has a higher positive rotation ($[M_D]$ in chloroform = +123°) than diol (XVII) ($[M_D]$ in chloroform = +45°), whilst acetylation of the 16α-diol (XVII) gives a diacetate with a negative rotation ($[M_D]$ in chloroform = −114°). The formation of two diols from the 16-oxo-derivative (XIII) of the 20-normal

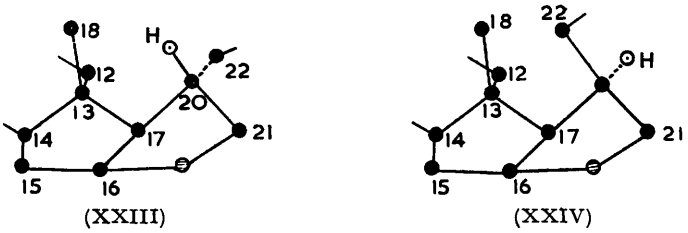
series corresponds to the formation of two triols from the corresponding 3β-hydroxy-16-oxo-derivative (II).

When the two hydroxy-esters (XI and XII) were treated with thionyl chloride in a



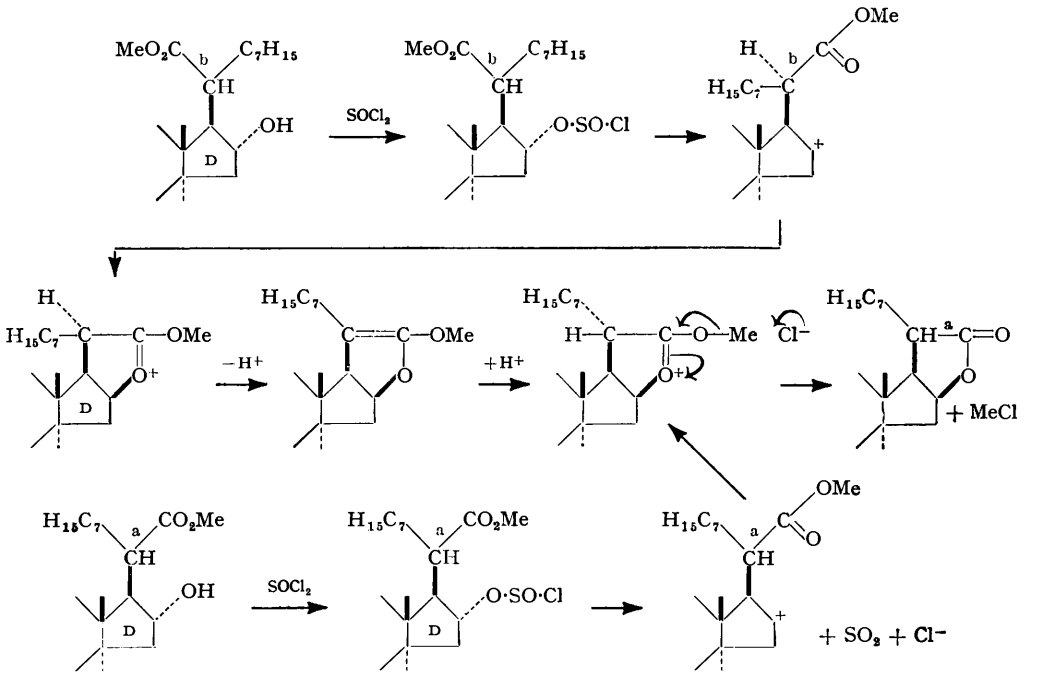
hydrocarbon solvent both yielded the *same* compound, $C_{31}H_{48}O_2$, the infra-red spectrum of which in carbon disulphide showed a band at 1771 cm.$^{-1}$ characteristic of a saturated γ-lactone. Reduction of the lactone with lithium aluminium hydride gave the diol (XVIII) obtained by similar reduction of the 16-oxo-derivative (XIV) from "ester B." The





lactone therefore must be derived from the hydroxy-acid (XX) which has the same configuration at $C_{(16)}$, $C_{(17)}$, and $C_{(20)}$ as the diol (XVIII). The 16-hydroxyl group of this diol has been shown above to have the β-configuration. On the

assumption that the lactone has a *cis*-structure the 17-side chain in both the lactone and the diol must also be β in configuration. There remains the problem of the configuration at $C_{(20)}$, the two possibilities in the case of the lactone being (XXI) and (XXII). Inspection of models indicates that the 20-*iso*-structure (XXI) (cf. XXIII *) should be much more stable than the 20-normal structure (XXII) (cf. XXIV *) since in the latter case there is very considerable compression between the 18-methyl group and the 22-methylene group. For this reason (XXI) is put forward for the lactone structure, with (XI) and (XII) following for " ester A " and " ester B " respectively. The suggested mechanisms for the formation of (XXI) from both esters are indicated below.

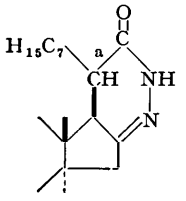


As indicated above, a number of Wolff–Kishner reductions have been carried out with eburicoic acid derivatives, *i.e.*, compounds without the 16-oxygen atom, without the formation of isomers. The reason for the formation of two products from the 16α-hydroxy-3-oxo-derivative (dihydro-V) is probably as follows. In the absence of a 16-hydroxyl group the normal configuration at $C_{(20)}$ is more stable than the *iso*-configuration. When a 16-hydroxyl group is present a 20-*iso*-ester may increase its stability by hydrogen-bond formation between the methoxycarbonyl and the hydroxyl group (cf. the formation of the 20-*iso*-lactone). The 20-normal ester is prevented from doing so, for hydrogen bonding can only occur in that conformation which leads to compression between the 22-methylene and 18-methyl groups (cf. XXIV). Hence it is possible for the energies of the 16α-hydroxy-ester of the 20-*normal* series, not stabilised by hydrogen bonding, and of the 16α-hydroxy-ester of the 20-*iso*-series, stabilised by hydrogen bonding, to become approximately equal. If this explanation is valid, the infra-red spectra of " ester A " and " ester B " should be significantly different. This is so. " Ester A " in Nujol shows only one band (at 3597 $cm.^{-1}$) due to the OH stretching frequency and one at 1713 $cm.^{-1}$ due to the carbonyl group of the ester grouping, whilst " ester B " in Nujol shows bands at 3356 (broad) and 3552 $cm.^{-1}$ (sharp) typical of a hydroxyl group involved in hydrogen bonding and a split band at 1724 and 1740 $cm.^{-1}$ due to a carbonyl group involved in hydrogen bonding.

To study further the effect of alkali on the 20-position the ketones (XIII) from "ester A " and (XIV) from " ester B " were subjected to Wolff–Kishner reduction.

* These two figures are based on a drawing by Klyne (*Chem. and Ind.*, 1951, 426).

From (XIII), after methylation of the reduction product, the expected methyl eburico-7 : 9(11)-dien-21-oate was obtained. From (XIV) the *same* ester was obtained in *ca.* 10% yield, but the main product was a nitrogenous compound, $C_{31}H_{48}ON_2$. This was identical with " compound Y," one of two nitrogenous products obtained along with the above ester on reduction of methyl 3 : 16-dioxoeburico-7 : 9(11)-dien-21-oate. " Compound Y " is believed to be the tetrahydro-oxopyridazine derivative (XXV) derived by cyclisation of a 16-hydrazone grouping with the methoxycarbonyl group when in the 20-*iso*-configuration. Just as only this configuration favours lactone formation, so only it



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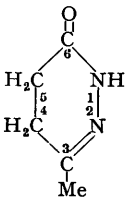
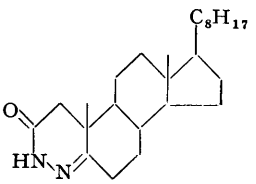


(XXVI)



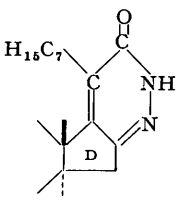
(XXVII)

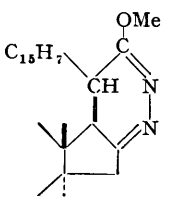
will favour the formation of a tetrahydro-oxopyridazine derivative. These results indicate that when no 16-substituent is present after completion of reduction the product will be of the 20-normal series whether the starting material is of the 20-normal or 20-*iso*-series, since under vigorous alkaline conditions the less stable 20-*iso*-structure will isomerise. If, however, the 20-*iso*-configuration can be stabilised, as in the case of " ester B " (XII), then products containing it may be obtained starting from eburicoic acid derivatives.

Structure (XXV) is assigned to " compound Y " on spectral evidence. After allowance for absorption due to the conjugated eburico-7 : 9(11)-diene system, " compound Y " exhibits maximum absorption at 2430 Å (ε *ca.* 8000) which is characteristic of the grouping (XXVI). For instance, Overend, Turton, and Wiggins (*J.*, 1950, 3500) report $\lambda_{max.}$ 2430 Å (ε 6000) for 1 : 4 : 5 : 6-tetrahydro-3-methyl-6-oxopyridazine while (XXVII) (Weisenborn, Remy, and Jacobs, *J. Amer. Chem. Soc.*, 1954, **76**, 552) absorbs in methanol at 2440 Å (ε 8300). " Compound Y " in carbon disulphide exhibits bands at 1660(s), 1692(s), 3245(m), and 3441(m) cm.$^{-1}$. The last two probably represent N–H stretching frequencies and the band at 1660 cm.$^{-1}$ a N–H bending frequency, whilst that at 1692 cm.$^{-1}$ will be due to the amide-type carbonyl group.

When " compound Y " was treated with alkali a new compound (" compound Z ") was obtained. Its ultra-violet spectrum had a band at 2840 Å (ε 3600). A similar band is found with pyridazones (Overend *et al.*, *loc. cit.*) and it is likely that " compound Z " is the pyridazone (XXVIII), being formed by atmospheric oxidation during the alkaline treatment.

(XXVIII)





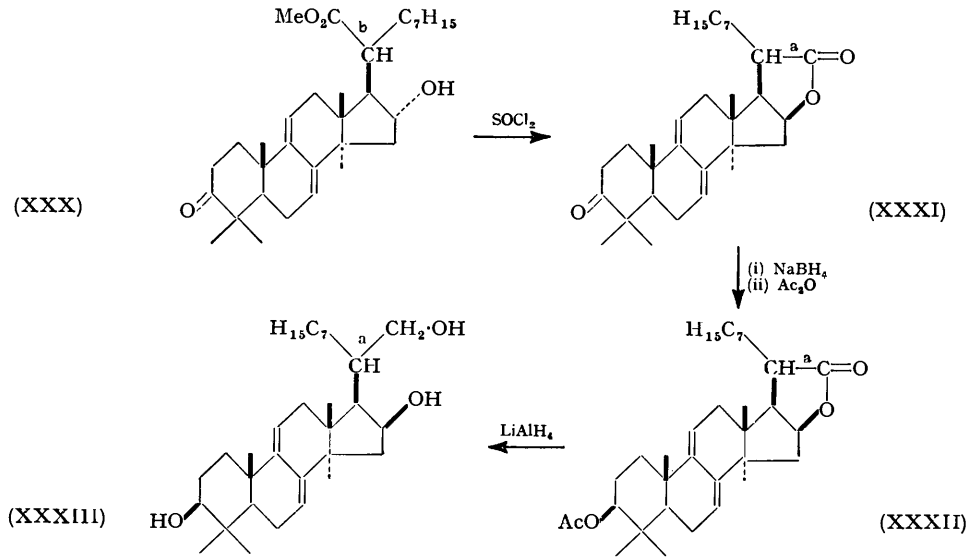
(XXIX)

Besides " compound Y " a second nitrogenous product (" compound X ") was obtained in small yield from methyl 3 : 16-dioxoeburico-7 : 9(11)-dien-21-oate. The main features of its infra-red spectrum determined in carbon disulphide [bands at 1618(s) and 3246(m) cm.$^{-1}$; shoulder at 1657 cm.$^{-1}$] are the presence of a band indicating either an OH or a >NH group, and the absence of a band corresponding to C=O stretching frequency. Its ultra-violet spectrum, in addition to showing very intense absorption in the region (2360—2520 Å) associated with the normal absorption of the eburico-7 : 9(11)-diene system, had an intense band at 3230—3300 Å (ε 19,300). At present it is not possible to put forward a satisfactory structure for " compound X." One possibility to be considered,

although it involves difficulties in the interpretation of the infra-red spectrum, is that it is a methylated product (*e.g.*, XXIX) formed during the diazomethane treatment after the completion of the reduction.

The results described above show that the isolation of deoxyeburicoic acid derivatives from Wolff–Kishner reductions does not necessarily prove that the carboxyl group in the starting material has the 20-normal configuration unless it is shown by other means that the configuration at $C_{(20)}$ in the reduction product is the same as in the starting material. In the inter-relation of eburicoic acid with lanosterol (Holker, Powell, Robertson, Simes, Wright, and Gascoigne (*loc. cit.*) specifically refer to this problem and provide the necessary additional evidence. In the conversion of polyporenic acid C into an eburicoic acid derivative (cf. Bowers, Halsall, Jones, and Lemin, *loc. cit.*) such evidence is not available. However, apart from that based on biogenetic arguments, it is possible to adduce chemical evidence to prove that in polyporenic acid C the configuration at $C_{(20)}$ is of the 20-normal and not of the 20-*iso*-eburicoic acid series.

The reduction of the 3β-hydroxy-16-oxo-derivative of polyporenic acid C (II) to the



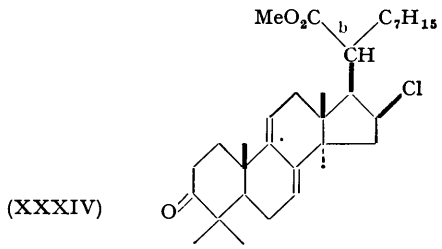
two triols, (III) and (IV), is analogous to the reduction of the ketone (XIII) from " ester A " by which two diols, (XV) and (XVI) are obtained, but not to that of the ketone (XIV) from " ester B " by which only one diol is obtained. This suggests that polyporenic acid C has the same configuration at $C_{(20)}$ as the ketone (XIII) from " ester A " of the 20-normal series.

If the 20-*iso*-structure were present in polyporenic acid C hydrogen bonding would occur in methyl polyporenate C between the methoxycarbonyl and the 16-hydroxyl group, as in the case of the analogous 20-*iso*-compound " ester B " (XII). The infra-red spectrum of methyl polyporenate C, however, indicates that no such hydrogen bonding occurs.

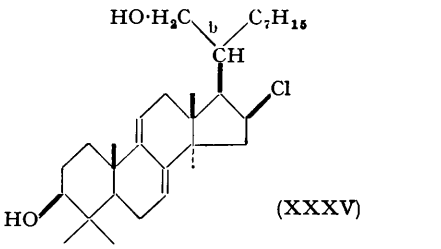
Treatment of methyl dihydropolyporenate C (XXX) with thionyl chloride in *iso*octane gave a lactone which, by analogy with the lactone (XXI) formed from both " ester A " and " ester B," must be the lactone (XXXI) of 16β-hydroxy-3-oxo-20-*iso*eburico-7 : 9(11)-dien-21-oic acid. Reduction of this lactone with sodium borohydride, followed by acetylation, gave the corresponding 3β-acetoxy-lactone (XXXII). This was in turn reduced with lithium aluminium hydride to a triol which must be 3β : 16β : 21-trihydroxy-20-*iso*-eburico-7 : 9(11)-diene (XXXIII). This triol was *not* identical with either of the triols, (III) and (IV), obtained by the lithium aluminium hydride reduction of the 3β-hydroxy-16-oxo-derivative (II) of methyl dihydropolyporenate C. One of these triols must have both its 3- and its 16-hydroxyl group in the β-configuration and hence must differ at $C_{(20)}$ from the triol from the lactone. Since the latter has the 20-*iso*-configuration the triol from

methyl dihydropolyporenate C, and hence polyporenic acid C, must have the 20-normal configuration and belong to the eburicoic acid series.

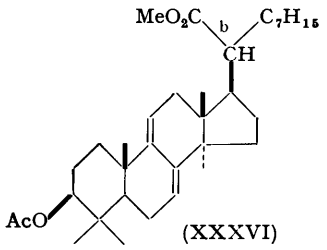
The tentative assignment of the β-configuration to the 16-hydroxyl group of polyporenic acid C by Bowers, Halsall, Jones, and Lemin (*loc. cit.*) was based on the interpretation of a most unexpected reaction of lithium aluminium hydride with the chloro-compound obtained by the action of phosphorus pentachloride on methyl dihydropolyporenate C. From this reduction, besides the expected chloro-diol, there was isolated the triol (III) obtained by the direct reduction of methyl dihydropolyporenate C with lithium aluminium hydride. On the assumption that the phosphorus pentachloride reaction brings about a S_N2 replacement of the 16-hydroxyl group by chlorine the chloro-ester obtained must be (XXXIV) and the chloro-diol (XXXV). Evidence that no drastic rearrangement had



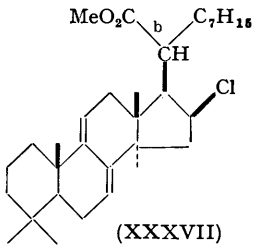
(XXXIV)



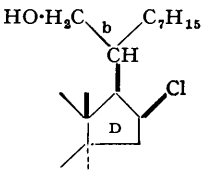
(XXXV)



(XXXVI)

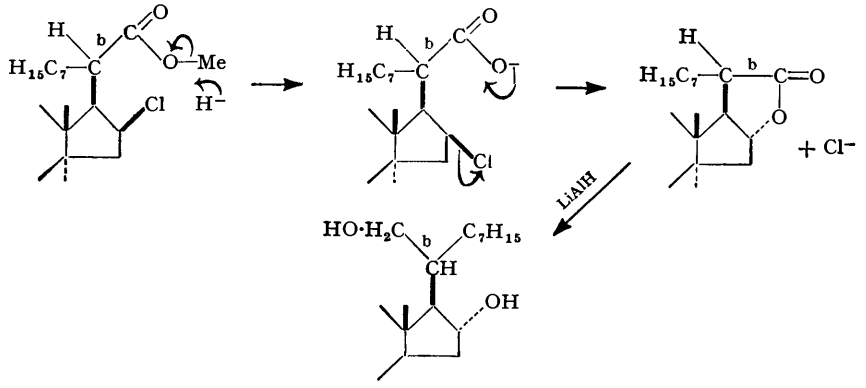


(XXXVII)



(XXXVIII)

been brought about by the phosphorus pentachloride was obtained when reduction of the chloro-ester (XXXIV) with sodium and *iso*propanol followed by acetylation gave methyl 3β-acetoxyeburico-7 : 9(11)-dien-21-oate (XXXVI). Structure (XXXIV) for the chloro-ester implies that during the reduction to the triol (III) the chlorine atom is replaced by a



hydroxyl group with *inversion* of configuration. A further example of this unusual reaction has also been provided in the 3-deoxy-series. Phosphorus pentachloride converted methyl 16α-hydroxyeburico-7 : 9(11)-dien-21-oate into a chloro-ester (XXXVII), reduction of which with lithium aluminium hydride led to a mixture of the chloro-alcohol (XXXVIII)

and the 16α : 21-dihydroxy-derivative (as XV). Again a chlorine atom has been replaced by a hydroxyl group with inversion of configuration.

The mechanism for this reaction which seems least unlikely is indicated below. The first step is O–alkyl fission of the ester grouping by hydride ion or its equivalent with the formation of the carboxylate anion. This then attacks $C_{(16)}$ from the rear-side, bringing about S_N2 displacement of chloride ion and the formation of a *trans*-γ-lactone. Inspection of models indicates that this is geometrically possible although the γ-lactone ring is strained. The lactone ring need only have transitory existence as it can be immediately attacked by lithium aluminium hydride with resultant fission to the 16α : 21-dihydroxy-derivative of the correct configuration. No evidence in support of this reaction mechanism has as yet been obtained. In its favour are that methyl polyporenate C is not easily hydrolysed and that alkaline hydrolysis of sterically hindered methyl esters may involve a S_N2-type displacement on the alkyl-carbon atom of the ester grouping accompanied by alkyl–oxygen fission rather than nucleophilic attack at the carbonyl-carbon atom (cf., for example, Goering, Rubin, and Newman, *J. Amer. Chem. Soc.*, 1954, **76**, 787).

Experimental

Rotations were determined in chloroform at room temperature unless otherwise stated. M. p.s were determined on a Kofler block and are corrected. The alumina used for chromatography had an activity I—II unless otherwise stated. Light petroleum refers to the fraction with b. p. 60—80°. Ultra-violet light absorption was determined in ethanol.

Note: The 16α- and 16β-indices used in the experimental section of Part XVIII (Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2548) should be reversed in view of the proof given in this paper that the hydroxyl group of polyporenic acid C has the 16α- and not the 16β-configuration.

Reduction of Methyl 3β-Hydroxy-16-oxoeburico-7 : 9(11)-dien-21-oate (II) *with Lithium Aluminium Hydride.*—Methyl 3β-hydroxy-16-oxoeburico-7 : 9(11)-dien-21-oate (II) (535 mg.) in ether (150 c.c.) was treated with lithium aluminium hydride (500 mg.) at 20° for 24 hr. After destruction of the excess of reagent with ethyl acetate and decomposition of the complex with hydrochloric acid (2N; 100 c.c.) isolation with ether gave a product which was adsorbed from benzene (150 c.c.) on alumina (60 g.) which had been deactivated by being shaken in benzene with water (3 c.c.). Elution with benzene–ether (7 : 3; 500 c.c.) gave *eburico-7 : 9(11)-diene-3β : 16β : 21-triol* (IV) (300 mg.) as needles, m. p. 238—240° (after purification by chromatography and several crystallisations from methanol) depressed on admixture with 3β : 16α : 21-triol, $[\alpha]_D$ +91° (*c*, 0·88 in pyridine) (Found: C, 75·9; H, 11·05. $C_{31}H_{52}O_3,CH_3{\cdot}OH$ requires C, 76·1; H, 11·2%). Light absorption: Max., 2370, 2440, and 2520 Å, ε = 15,300, 18,000, and 11,900. Further elution with benzene–ether (1 : 1; 400 c.c.) gave eburico-7 : 9(11)-diene-3β : 16α : 21-triol (III) (200 mg.) as plates (from ethyl acetate), m. p. 234—235°, raised by several crystallisations from ethanol to 240—242°, undepressed on admixture with a specimen prepared from methyl dihydropolyporenate C, $[\alpha]_D$ +38° (*c*, 0·84 in pyridine).

Methyl 3-Oxoburico-7 : 9(11)-dien-21-oate (VII).—Methyl 3β-acetoxyeburico-7 : 9(11)-dien-21-oate (Part XVIII, *loc. cit.*) (500 mg.) was hydrolysed with methanolic potassium hydroxide (200 c.c.; 0·5%) for 24 hr. at 20°. After addition of water, extraction with ether yielded a product which was dissolved in acetone (75 c.c.) and oxidised with chromic acid in the usual manner (cf. Bowers *et al.*, *loc. cit.*). Isolation with ether gave a product which was adsorbed from light petroleum (50 c.c.) on alumina (30 g.). Elution with light petroleum–benzene (1 : 1; 600 c.c.) afforded methyl 3-oxoeburico-7 : 9(11)-dien-21-oate as needles, m. p. 156—158° (after several crystallisations from methanol), $[\alpha]_D$ +24° (*c*, 1·1) (Found: C, 79·85; H, 10·5. Calc. for $C_{32}H_{50}O_3$: C, 79·6; H, 10·45%) [Gascoigne, Robertson, and Simes (*J.*, 1953, 1835) give m. p. 155—155·5°, $[\alpha]_D$ +24°, for methyl 3-oxoeburico-7 : 9(11)-dien-21-oate]. Light absorption: Max., 2360, 2430, and 2510 Å, ε = 16,200, 18,600, and 8750.

Methyl Eburico-7 : 9(11)-dien-21-oate.—Methyl 3-oxoeburico-7 : 9(11)-dien-21-oate (VII) (80 mg.) in ethylene glycol (30 c.c.) was heated with hydrazine hydrate (1 c.c.; 60%) at 100° for 40 min. Potassium hydroxide (175 mg.) was then added and the solution heated under reflux for 5 hr. After acidication with acetic acid and dilution with water, extraction with ether yielded a product which was suspended in acetone (15 c.c.) and treated with ethereal diazomethane for 16 hr. at 20°. The methylated product was adsorbed from pentane (10 c.c.) on alumina (10 g.). Elution with light petroleum (300 c.c.) gave *methyl eburico-7 : 9(11)-dien-21-oate* (62 mg.) as plates, m. p. 137—139° (several crystallisations from methanol), $[\alpha]_D$ +36°

(*c*, 0·79) (Found: C, 81·5; H, 11·2. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%). Light absorption: Max., 2370, 2440, and 2520 Å, ε = 14,950, 17,550, and 11,350.

Wolff–Kishner Reduction of Methyl 16α-*Hydroxy*-3-*oxoeburico*-7 : 9(11)-*dien*-21-*oate*.—Methyl 16α-hydroxy-3-oxoeburico-7 : 9(11)-dien-21-oate (2·4 g.) in diethylene glycol (120 c.c.) was heated at 100° for 1 hr. with hydrazine hydrate (5 c.c.; 90%), after which the excess of hydrazine and water was removed by distillation. Potassium hydroxide (2·0 g.) was then added and the solution heated under reflux for 5 hr. After acidification with acetic acid and dilution with water, ether-extraction yielded a product which was suspended in acetone and treated with an excess of ethereal diazomethane at 20° for 16 hr. The resulting mixture of methyl esters was adsorbed from benzene on alumina (150 g.). Elution with benzene–ether (7 : 1; 2 l.) gave *methyl* 16α-*hydroxyeburico*-7 : 9(11)-*dien*-21-*oate* ("ester A") (XI) (0·80 g.) as needles, m. p. 184—185° (after several crystallisations from methanol), $[\alpha]_D$ +23° (*c*, 0·81 (Found: C, 79·3; H, 10·8. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%). Light absorption: Max 2370, 2440, and 2520 Å, ε = 15,500, 18,200, and 12,050. Infra-red absorption in Nujol: bands at 1713 and 3597 cm.$^{-1}$.

Further elution with benzene–ether (1 : 1; 2·5 l.) gave *methyl* 16α-*hydroxy*-20-iso-*eburico*-7 : 9(11)-*dien*-21-*oate* ("ester B") (XII) (1·5 g.) as needles, m. p. 146—148° (after purification by chromatography and several crystallisations from methanol), $[\alpha]_D$ +22° (*c*, 0·90) (Found: C, 78·0; H, 10·7. $C_{32}H_{52}O_3,\frac{1}{2}CH_3{\cdot}OH$ requires C, 77·95; H, 10·85%). Light absorption: Max., 2360, 2440, and 2520 Å; ε = 14,300, 16,700, and 11,000. Infra-red absorption in Nujol: bands at 1724, 1740, 3356 (broad), and 3552 (sharp) cm.$^{-1}$.

Partial Isomerisation of Methyl 16α-*Hydroxy*-20-iso-*eburico*-7 : 9(11)-*dien*-21-*oate to Metnyl* 16α-*Hydroxyeburico*-7 : 9(11)-*dien*-21-*oate with Alkali*.—Methyl 16α-hydroxy-20-*iso*eburico-7 : 9(11)-dien-21-oate (525 mg.) in diethylene glycol (50 c.c.) was heated under reflux. With potassium hydroxide (500 mg.) and fluorenone (15 mg.) for 3½ hr. After acidification with acetic acid and dilution with water the product was separated by filtration and dried. It was suspended in acetone (50 c.c.) and methylated with ethereal diazomethane at 20° for 16 hr. The methylated product was adsorbed from benzene (50 c.c.) on alumina (50 g.). Elution with benzene–ether (4 : 1; 400 c.c.) gave methyl 16α-hydroxyeburico-7 : 9(11)-dien-21-oate (135 mg.) as needles, m. p. 180—182° (after several crystallisations from methanol), undepressed on admixture with an authentic sample, $[\alpha]_D$ +25° (*c*, +0·94).

Elution with benzene–ether (1 : 1; 400 c.c.) gave methyl 16α-hydroxy-20-*iso*-eburico-7 : 9(11)-dien-21-oate (310 mg.) as needles (from methanol–nitromethane), m. p. 143—145° after several crystallisations from methanol–nitromethane), undepressed on admixture with an authentic sample, $[\alpha]_D$ +24°, (*c*, 1·16).

Methyl 16α-*Acetoxyeburico*-7 : 9(11)-*dien*-21-*oate*.—Methyl 16α-hydroxyeburico-7 : 9(11) dien-21-oate (200 mg.) in pyridine (10 c.c.), treated with acetic anhydride (1 c.c.) at 20° for 24 hr., gave a product which was adsorbed from light petroleum (100 c.c.) on alumina (30 g.). Elution with light petroleum–benzene (1 : 1; 250 c.c.) gave the 16α-*acetoxy-ester* as needles, (190 mg.), m. p. 123—125° (after several crystallisations from methanol), $[\alpha]_D$ −4° (*c*, 1·06) (Found: C, 76·9; H, 10·85. $C_{34}H_{54}O_4$ requires C, 77·5; H, 10·35%). Light absorption: Max. 2360, 2430, and 2510 Å, ε = 13,350, 16,900, and 10,000.

Methyl 16α-*Acetoxy*-20-iso-*eburico*-7 : 9(11)-*dien*-21-*oate*.—Methyl 16α-hydroxy-20-*iso*-eburico-7 : 9(11)-dien-21-oate (500 mg.) in pyridine (20 c.c.), treated with acetic anhydride (2·5 c.c.) at 20° for 24 hr., gave the 16α-*acetoxy-ester* as a white solid (480 mg.) wh ch was crystallised several times from methanol–ethyl acetate, giving needles, m. p. 178—180°, $[\alpha]_D$ −7° (*c*, 1·0) (Found: C, 77·55; H, 10·45. $C_{34}H_{54}O_4$ requires C, 77·5; H, 10·35%) Light absorption: Max., 2360, 2430, and 2510 Å, ε = 14,050, 16,350, and 10,860.

Methyl 16-*Oxoeburico*-7 : 9(11)-*dien*-21-*oate* (XIII).—Methyl 16α-hydroxyeburico-7 : 9(11)-dien-21-oate (110 mg.) in acetone (25 c.c.) was oxidised with chromic acid in the usual manner (cf. Bowers *et al.*, *loc. cit.*). Isolation with ether gave a product which was adsorbed from benzene (5 c.c.) on alumina (6 g.). Elution with benzene (150 c.c.) gave *methyl* 16-*oxoeburico*-7 : 9(11)-*dien*-21-*oate* (85 mg.) as plates, m. p. 159·5—161° (after several crystallisations from methanol), $[\alpha]_D$ −51° (*c*, 0·98) (Found: C, 79·85; H, 10·5. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%). Light absorption: Max., 2430 Å; ε = 17,600; inflexions, 2360 and 2510 Å, ε = 15,600 and 11,900.

Methyl 16-*Oxo*-20-iso*eburico*-7 : 9(11)-*dien*-21-*oate* (XIV).—Methyl 16α-hydroxy-20-*iso*eburico-7 : 9(11)-dien-21-oate (290 mg.) in acetone (25 c.c.) was oxidised with chromic acid in the usual manner. Isolation with ether gave a product which was absorbed from light petroleum on alumina (25 g.). Elution with benzene gave *methyl* 16-*oxo*-20-iso*eburico*-7 : 9(11)-*dien*-

21-*oate* (220 mg.) as needles, m. p. 120—121° (after several crystallisations from methanol), $[\alpha]_D$ −60° (*c*, 1·07) (Found: C, 79·75; H, 10·45. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%). Light absorption: Max., 2430 Å, ε = 18,400; inflexions, 2370 and 2510 Å, ε = 16,300 and 12,200.

Eburico-7 : 9(11)-*diene*-16α : 21-*diol* (XV).—Methyl 16α-hydroxyeburico-7 : 9(11)-dien-21-oate (XI) (600 mg.) in ether (150 c.c.) was heated under reflux with lithium aluminium hydride (400 mg.) for 45 min. The excess of reagent was destroyed with ethyl acetate, and the complex decomposed with hydrochloric acid (2N; 100 c.c.). Isolation with ether gave the 16α : 21-*diol* (XV) (530 mg.) as needles, m. p. 247—249° (after several crystallisations from ethanol), $[\alpha]_D$ +45° (*c*, 0·95 in pyridine) (Found: C, 81·4; H, 11·6. $C_{31}H_{52}O_2$ requires C, 81·5; H, 11·5%). Light absorption: Max., 2360 and 2440 Å, ε = 14,400, and 17,000; inflexion, 2510 Å, ε = 11,100.

This diol (170 mg.) in pyridine (15 c.c.), treated with acetic anhydride (2·5 c.c.) at 20° for 15 hr., gave a product which was adsorbed from benzene (15 c.c.), on alumina (15 g.). Elution with light petroleum–benzene (1 : 1; 600 c.c.) gave 16α : 21-*diacetoxyeburico*-7 : 9(11)-*diene* (120 mg.) as needles, m. p. 135—136° (after several crystallisations from methanol), $[\alpha]_D$ +6° (*c*, 0·98) (Found: C, 78·0; H, 10·3. $C_{35}H_{56}O_4$ requires C, 77·75; H, 10·45%). Light absorption: Max., 2360, 2430, and 2510 Å, ε = 15,700, 18,200, and 11,900.

Reduction of Methyl 16-*Oxoeburico*-7 : 9(11)-*dien*-21-*oate* (XIII) *with Lithium Aluminium Hydride*.—The ester (350 mg.) in ether (100 c.c.) was treated with lithium aluminium hydride (350 mg.) at 20° for 16 hr. Isolation as above yielded a product which was absorbed from benzene (30 c.c.) on alumina (40 g.). Elution with benzene–ether (4 : 1; 500 c.c.) gave *eburico*-7 : 9(11)-*diene*-16β : 21-*diol* (XVI) (150 mg.) as needles, m. p. 247—249° (after several crystallisations from ethanol) (depressed on admixture with the 16α : 21-diol), $[\alpha]_D$ +103° (*c*, 1·2 in pyridine) (Found: C, 81·15; H, 11·6%). Light absorption: Max. 2360, 2440, and 2520 Å, ε = 14,050, 16,700, and 11,500.

Elution with benzene–ether (7·3; 500 c.c.) gave the 16α : 21-diol (135 mg.), m. p. 246—248° (after several crystallisations from ethanol; undepressed on admixture with an authentic sample), $[\alpha]_D$ +43° (*c*, 0·91 in pyridine).

Reduction of Methyl 16α-*Hydroxy*-20-iso*eburico*-7 : 9(11)-*dien*-21-*oate with Lithium Aluminium Hydride*.—Methyl 16α-hydroxy-20-*iso*eburico-7 : 9(11)-dien-21-oate (XII) (230 mg.) in ether (75 c.c.) was heated under reflux with lithium aluminium hydride (200 mg.) for 1 hr. The product was isolated and chromatographed as above on alumina (20 g.). Elution with benzene–ether (7 : 3; 500 c.c.) gave 20-iso*eburico*-7 : 9(11)-*diene*-16α : 21-*diol* (XVII) (180 mg.) as needles, m. p. 189—191° (after several crystallisations from methanol), $[\alpha]_D$ +10° (*c*, 1·09) (Found: C, 81·7; H, 11·4%). Light absorption: Max., 2360, 2430, and 2520 Å, ε = 13,200, 15,300, and 10,300.

Acetylation, as above, of the diol (350 mg.) for 24 hr. gave a product which was adsorbed from light petroleum (30 c.c.) on alumina (45 g.). Elution with benzene (500 c.c.) gave 16α : 21-*diacetoxy*-20-iso*eburico*-7 : 9(11)-*diene* (310 mg.) as needles, m. p. 109—111° (after several crystallisations from methanol), $[\alpha]_D$ −21° (*c*, 0·93) (Found: C, 78·05; H, 10·5%). Light absorption in ethanol: Max., 2360, 2430, and 2510 Å, ε = 14,600, 16.900, and 11,300. Further elution with ether (300 c.c.) gave a small amount of unchanged starting material.

Reduction of Methyl 16-*Oxo*-20-iso*eburico*-7 : 9(11)-*dien*-21-*oate with Lithium Aluminium Hydride*.—The keto-ester (XIV) (205 mg.) in ether (100 c.c.) was treated with lithium aluminium hydride at 20° for 16 hr. Isolation as above gave a product which was adsorbed from benzene (20 c.c.) on alumina (20 g.). Elution with benzene–ether (1 : 1; 300 c.c.) gave 20-*iso*eburico-7 : 9(11)-diene-16β : 21-diol (175 mg.) as needles, m. p. 214—215° (after several crystallisations from ethanol–nitromethane), undepressed on admixture with a specimen prepared by the reductive fission of the lactone of 16β-hydroxy-20-*iso*eburico-7 : 9(11)-dien-21-oic acid (see below), $[\alpha]_D$ +27° (*c*, 0·93).

Reaction of Methyl 16α-*Hydroxyeburico*-7 : 9(11)-*dien*-21-*oate* (XI) *with Thionyl Chloride* — Methyl 16α-hydroxyeburico-7 : 9(11)-dien-21-oate (265 mg.) in light petroleum (b. p. 80—100°) was heated under reflux with thionyl chloride (0·25 c.c.) for 2 hr. After addition of water, isolation with light petroleum yielded a product which was adsorbed from light petroleum (30 c.c.) on alumina (30 g.). Elution with light petroleum–benzene (7 : 3; 400 c.c.) gave the *lactone* (XIX) (73 mg.) of 16β-hydroxy-20-*iso*eburico-7 : 9(11)-dien-21-oic acid as needles, m. p. 202—204° (after several crystallisations from methanol), $[\alpha]_D$ −13° (*c*, 1·12) (Found: C, 82·25; H, 10·9. $C_{31}H_{48}O_2$ requires C, 82·2; H, 10·7%). Light absorption: Max., 2430 Å, ε = 16,000; inflexions, 2360 and 2510 Å, ε = 13,800 and 10,500. Infra-red absorption in CS_2: band at 1771 cm.$^{-1}$.

Reaction of Methyl 16α-*Hydroxy*-20-iso*eburico*-7 : 9(11)-*dien*-21-*oate* (XII) *with Thionyl Chloride*.—Methyl 16α-hydroxy-20-*iso*eburico-7 : 9(11)-dien-21-oate (290 mg.) in benzene (20 c.c.) was heated under reflux with thionyl chloride (0·35 c.c.) for 1 hr. After addition of water, isolation with benzene gave the lactone of 16β-hydroxy-20-*iso*eburico-7 : 9(11)-dien-21-oic acid as needles (220 mg.), m. p. 202—204° [three crystallisations from methanol; undepressed on admixture with the lactone obtained by the action of thionyl chloride on methyl 16α-hydroxy-eburico-7 : 9(11)-dien-21-oate], $[\alpha]_D$ −13° (*c*, 1·11). The infra-red spectra of the lactones from the two esters were identical.

Reduction of the Lactone (XIX) *with Lithium Aluminium Hydride*.—The lactone (185 mg.) in ether (100 c.c.) was heated under reflux with lithium aluminium hydride (200 mg.) for 1·5 hr. Isolation as usual yielded a product which was adsorbed from benzene on alumina (10 g.). Elution with benzene–ether (3 : 2; 300 c.c.) gave 20-iso*eburico*-7 : 9(11)-*diene*-16β : 21-*diol* (160 mg.) as needles, m. p. 214—215° (after several crystallisations from ethanol–nitromethane), $[\alpha]_D$ +27° (*c*, 1·15) (Found: C, 81·65; H, 11·6%). Light absorption: Max., 2360, 2440, and 2520 Å, ε = 13,300, 15,700, and 10,400. It gave on acetylation a gum, $[\alpha]_D$ +102° (*c*, 1·01).

Wolff–Kishner Reduction of Methyl 3 : 16-*Dioxoeburico*-7 : 9(11)-*dien*-21-*oate*.—Methyl 3 : 16-dioxoeburico-7 : 9(11)-dien-21-oate (1·3 g.) was reduced under the conditions described above for the reduction of methyl 3-oxoeburico-7 : 9(11)-dien-21-oate. The methylated reduction product was adsorbed from light petroleum–benzene (4 : 1; 200 c.c.) on alumina (75 g.). Elution with light petroleum–benzene (4 : 1; 500 c.c.) gave methyl eburico-7 : 9(11)-dien-21-oate (300 mg.) as plates, m. p. 139—141° [after several crystallisations from methanol; undepressed on admixture with a sample prepared from methyl 3-oxoeburico-7 : 9(11)-dien-21-oate], $[\alpha]_D$ +40° (*c*, 0·95).

Elution with light petroleum–benzene (1 : 1; 400 c.c.) gave "*compound X*" (168 mg.) as needles, m. p. 210—213° (after purification by chromatography and several crystallisations from ethyl acetate), $[\alpha]_D$ −200° (*c*, 0·87) (Found: C, 80·1; H, 9·9. $C_{31}H_{48}ON_2$ requires C, 80·1; H, 10·4. $C_{31}H_{46}ON_2$ requires C, 80·45; H, 10·0. $C_{32}H_{50}ON_2$ requires C, 80·3; H, 10·5%. Light absorption: Max., 2370, 2430, and 3230—3300 Å, ε = 22,400, 23,200, and 19,350; inflexion, 2510 Å, ε = 17,800. Infra-red absorption in CS_2: bands at 1618(s), 1657(sh)(m), and 3246(m) cm.$^{-1}$.

Elution with benzene–ether (1 : 1; 600 c.c.) gave "*compound Y*" (XXV) (585 mg.) as needles, m. p. 224—226° (several crystallisations from ethyl acetate), $[\alpha]_D$ −124° (*c*, 1·03) (Found: C, 80·25; H, 10·1; N, 6·3. $C_{31}H_{48}ON_2$ requires C, 80·1; H, 10·4; N, 6·05%). Light absorption: Max., 2430 Å, ε = 22,400; inflexions, 2360 and 2510 Å, ε = 19,150 and 16,900. Infra-red absorption in CS_2: bands at 1660(s), 1692(s), 1744(vw), 3245(m), and 3441(m).

Action of Alkali on Compound Y (XXV).—Compound Y (270 mg.) in diethylene glycol (50 c.c.) containing potassium hydroxide (200 mg.) was heated under reflux for 1¼ hr. After acidification with acetic acid the mixture was diluted with water. Isolation with ether yielded a product which was adsorbed on alumina (30 g.). Elution with benzene–ether (1 : 1; 300 c.c.) gave "compound Y" (165 mg.) as needles, m. p. 226—228° (from ethyl acetate; undepressed on admixture with starting material), $[\alpha]_D$ −128° (*c*, 0·92).

Elution with benzene–ether (3 : 7; 200 c.c.) gave "*compound Z*" (58 mg.) as needles, m. p. 281—284° (from ethyl acetate), $[\alpha]_D$ +50° (*c*, 0·78) (Found: C, 80·1; H, 10·1. $C_{31}H_{46}ON_2$ requires C, 80·45; H, 10·0%). Light absorption: Max., 2420 and 2840 Å, ε = 21,100, and 3600; inflexions, 2360 and 2510 Å, ε = 19,800 and 14,000. Infra-red absorption in CCl_4: bands at 1631(s), 1653(s), 1746(w), 3153(m), 3265(sh), and 3426(mw).

Wolff–Kishner Reduction of Methyl 16-*Oxoeburico*-7 : 9(11)-*dien*-21-*oate* (XIII).—Methyl 16-oxoeburico-7 : 9(11)-dien-21-oate (300 mg.) in diethylene glycol (50 c.c.) was heated at 100° 3 hr. with hydrazine hydrate (2 c.c.; 60%). Potassium hydroxide (0·3 g.) was added and the excess of water removed by distillation. The solution was then heated under reflux for 7 hr. After acidification with acetic acid and dilution with water, extraction with ether yielded a product which was suspended in acetone (70 c.c.) and treated with ethereal diazomethane at 20° for 24 hr. The methylated product was adsorbed from light petroleum on alumina (30 g.). Elution with light petroleum–benzene (9 : 1; 300 c.c.) gave methyl eburico-7 : 9(11)-dien-21-oate (70 mg.) as plates, m. p. and mixed m. p. 139—141° (after several crystallisations from methanol), $[\alpha]_D$ +42° (*c*, 0·99).

Wolff–Kishner Reduction of Methyl 16-*Oxo*-20-iso-*eburico*-7 : 9(11)-*dien*-21-*oate* (XIV).—The keto-ester (450 mg.) in diethylene glycol (50 c.c.) was heated at 100° for 2 hr. with hydrazine hydrate (3 c.c.; 60%). Potassium hydroxide (0·45 g.) was added and the excess of water

removed by distillation. The solution was heated under reflux for 5½ hr. After isolation and methylation as in the preceding case the product was adsorbed from light petroleum (200 c.c.) on alumina (45 g.). Elution with light petroleum–benzene (9 : 1; 200 c.c.) gave methyl eburico-7 : 9(11)-dien-21-oate (40 mg.) as needles, m. p. and mixed m. p. 137—139° (from methanol), $[\alpha]_D$ +42° (*c*, 0·96). Further elution with benzene–ether (1 : 1; 500 c.c.) afforded "compound Y" (XXV) (300 mg.) as needles, m. p. 222—224° (after several crystallisations from ethyl acetate), $[\alpha]_D$ −125° (*c*, 1·03). Its infra-red spectrum was identical with that of an authentic sample.

Reaction of Methyl 16α-*Hydroxy*-3-*oxoeburico*-7 : 9(11)-*dien*-21-*oate* (*Methyl Dihydropolyporenate C*) (XXX) *with Thionyl Chloride.*—Methyl dihydropolyporenate C (500 mg.) in *iso*-octane (50 c.c.) was heated with thionyl chloride (0·5 c.c.) at 100° for 2 hr. After addition of water, isolation with benzene gave a product which was adsorbed from light petroleum on alumina (50 g.). Elution with benzene (500 c.c.) gave the *lactone* (XXXI) (300 mg.) of 16β-hydroxy-3-oxo-20-*iso*-eburico-7 : 9(11)-dien-21-oic acid as needles, m. p. 247—249° (after several crystallisations from ethyl acetate and ethanol–chloroform), $[\alpha]_D$ −14° (*c*, 1·11) (Found: C, 79·5; H, 10·15. $C_{31}H_{46}O_3$ requires C, 79·8; H, 9·9%). Light absorption: Max., 2360, 2430, and 2500 Å, ε = 14,500, 16,600, and 10,950. Infra-red absorption in CCl_4: bands at 1713 and 1766 cm.$^{-1}$.

Lactone of 3β-*Acetoxy*-16β-*hydroxy*-20-iso*eburico*-7 : 9(11)-*dien*-21-*oic Acid* (XXXII).—The lactone of 16β-hydroxy-3-oxo-20-*iso*-eburico-7 : 9(11)-dien-21-oic acid (400 mg.) in dioxan (75 c.c.) was treated with sodium borohydride (100 mg.) in aqueous dioxan (1 : 1; 3 c.c.) at 20° for 1½ hr. After addition of water, isolation with ether yielded a product which was acetylated in pyridine (10 c.c.) with acetic anhydride (3 c.c.) at 100° for 1 hr. The acetylated product was isolated with ether and adsorbed from light petroleum (50 c.c.) on alumina (50 g.). Elution with benzene (400 c.c.) gave the *lactone* (310 mg.) of 3β-acetoxy-16β-hydroxy-20-*iso*-eburico-7 : 9(11)-dien-21-oic acid as needles (from methanol, m. p. 207—210°) (several crystallisations from light petroleum), $[\alpha]_D$ +29° (*c*, 1·3) (Found: C, 77·9; H, 10·15. $C_{33}H_{50}O_4$ requires C, 77·6; H, 9·9%). Light absorption: Max., 2360 and 2430 Å, ε = 15,600 and 18,100; inflexion, 2500 Å, ε = 11,750. Infra-red absorption in CCl_4: bands at 1733 and 1771 cm.$^{-1}$.

Reduction of the Lactone of 3β-*Acetoxy*-16β-*hydroxy*-20-iso-*eburico*-7 : 9(11)-*dien*-21-*oic Acid with Lithium Aluminium Hydride.*—The lactone (106 mg.) in ether (50 c.c.) was heated under reflux with lithium aluminium hydride (150 mg.) for 1·25 hr. Isolation as usual yielded a product (88 mg.) which was adsorbed from benzene (75 c.c.) on alumina (10 g.) which had been deactivated by shaking a suspension in benzene with water (0·5 c.c.). Elution with benzene–ether (3 : 1; 300 c.c.) gave 20-iso-*eburico*-7 : 9(11)-*diene*-3β : 16β : 21-*triol* (XXXIII) (71 mg.) as needles, m. p. 233—235° (after several crystallisations from ethyl acetate), depressed on admixture with the 3β : 16α : 21-trihydroxy-7 : 9(11)-diene, $[\alpha]_D$ +38° (*c*, 0·98) (Found: C, 78·4; H, 11·0. $C_{31}H_{52}O_3$ requires C, 78·75; H, 11·1%). Light absorption: Max., 2370, 2440, and 2520 Å, ε = 14,400, 16,800, and 11,550.

Reduction of Methyl 16β-*Chloro*-3-*oxoeburico*-7 : 9(11)-*dien*-21-*oate* (XXXIV) *with Sodium and* iso*Propyl Alcohol.*—Sodium (2·3 g.) was added to the chloro-ester (530 mg.) in *iso*propyl alcohol (50 c.c.), and the solution heated under reflux for 40 min. After dilution with water, isolation with ether gave a product which was acetylated in pyridine (10 c.c.) with acetic anhydride (5 c.c.) for 16 hr. at 20°. Isolation with ether yielded a product which was adsorbed from light petroleum (100 c.c.) on alumina (50 g.). Elution with benzene–ether (9 : 1; 400 c.c.) gave methyl 3β-acetoxyeburico-7 : 9(11)-dien-21-oate (440 mg.) as needles (from methanol), m. p. and mixed m. p. 172—174° (after several crystallisations from ethanol), $[\alpha]_D$ +70° (*c*, 1·33).

Methyl 16β-*Chloroeburico*-7 : 9(11)-*dien*-21-*oate* (XXXVII).—A suspension of methyl 16α-hydroxyeburico-7 : 9(11)-dien-21-oate (400 mg.) in light petroleum (40 c.c.) was shaken with phosphorus pentachloride (300 mg.) at 20° for 8 min., the ester dissolving completely. After addition of water, isolation with light petroleum yielded *methyl* 16β-*chloroeburico*-7 : 9(11)-*dien*-21-*oate* (330 mg.) as needles, m. p. 156—157° (after several crystallisations from ethanol), $[\alpha]_D$ +45° (*c*, 0·98) (Found: C, 71·3; H, 9·8; Cl, 7·25. $C_{32}H_{57}O_2Cl$ requires C, 76·35; H, 10·2; Cl, 7·05%). Light absorption: Max., 2360, 2440, and 2520 Å, ε = 13,200, 15,700, and 10,400.

Reduction of Methyl 16β-*Chloroeburico*-7 : 9(11)-*dien*-21-*oate with Lithium Aluminium Hydride.*—The ester (350 mg.) in ether (125 c.c.) was treated with lithium aluminium hydride (400 mg.) at 20° for 48 hr. Isolation as usual yielded a product (308 mg.) which was adsorbed from benzene (75 c.c.) on alumina (30 g.). Elution with benzene–ether (9 : 1; 400 c.c.) gave 16β-*chloroeburico*-7 : 9(11)-*dien*-21-*ol* (XXXVIII) (210 mg.) as needles (from methanol), m. p. 171—178°, raised by chromatographic purification and crystallisation from methanol to 177—

179°, $[\alpha]_D$ +83° (*c*, 1·08) (Found: C, 78·25; H, 10·95; Cl, 8·0. $C_{31}H_{51}OCl$ requires C, 78·3; H, 10·8; Cl, 7·5%). Light absorption: Max., 2360, 2440, and 2520 Å, ε = 13,000, 15,300, and 10,150.

Further elution with ether gave eburico-7 : 9(11)-diene-16α : 21-diol (86 mg.) as plates (from methanol), m. p. 240—244°, raised by crystallisation from ethanol to 244—247°, undepressed on admixture with an authentic sample, $[\alpha]_D$ +43° (*c*, 0·74 in pyridine). The infra-red spectrum was identical with that of an authentic sample.

Eburico-7 : 9(11) : 24(28)-*triene*-3β : 16α : 21-*triol*.—Methyl 3β : 16α-dihydroxyeburico-7 : 9(11) : 24(28)-trien-21-oate (460 mg.) in ether (100 c.c.) was heated under reflux with lithium aluminium hydride (500 mg.) for 1 hr. Isolation as usual gave *eburico*-7 : 9(11) : 24(28)-*triene*-3β : 16α : 21-*triol* as needles (375 mg.) (from methanol), m. p. 213—220°, raised by several crystallisations from methanol and ethyl acetate to 219—221°, $[\alpha]_D$ +36° (*c*, 0·99 in pyridine) (Found: C, 79·1; H, 10·4. $C_{31}H_{50}O_3$ requires C, 79·1; H, 10·7%). Light absorption: Max., 2370, 2440, and 2520 Å, ε = 13,200, 15,700, and 10,400.

Eburico-7 : 9(11)-*dien*-21-*ol*.—Methyl eburico-7 : 9(11)-dien-21-oate (240 mg.) in ether (30 c.c.) was treated with lithium aluminium hydride (200 mg.) at 20° for 16 hr. Isolation as usual, adsorption on alumina (20 g.), and elution with benzene–ether (9 : 1; 300 c.c.) gave *eburico*-7 : 9(11)-*dien*-21-*ol* (200 mg.) as needles (from methanol), m. p. 101—103°, raised by several crystallisations from aqueous acetone to 106—108° (after melting and resolidifying at 95—97°), $[\alpha]_D$ +62° (*c*, 1·26) (Found: C, 84·2; H, 12·0. $C_{31}H_{52}O$ requires C, 84·5; H, 11·9%). Light absorption: Max., 2360, 2430, and 2510 Å, ε = 15,000, 17,200, and 11,650.

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