Triterpene Resinols and Related Acids. Part XXX. The Oxidation of 12-Oxo*isoo*leana-9(11) : 14-dienyl Acetate.*

By J. D. Johnston and F. S. Spring.

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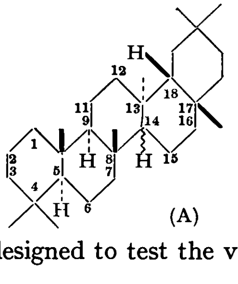
Oxidation of the pentacyclic 12-oxo*iso*oleana-9(11) : 14-dienyl acetate (I) with perbenzoic acid yields an oxide (II) which on treatment with hydrochloric acid is converted into a hexacyclic derivative with the formation of a new *cyclo*alkane ring. Related compounds are obtained when (I) is oxidised with hydrogen peroxide or when (II) is oxidised with chromic acid. Provisional structures are proposed. Treatment of the oxide (II) with hydrochloric acid gives a chloro-acetate $C_{32}H_{47}O_3Cl$, which on reductive removal of the halogen atom yields an acetate $C_{32}H_{48}O_3$. Wolff–Kishner reduction of the last compound gives an acetate $C_{32}H_{50}O_2$. The presence, in the acetate $C_{32}H_{50}O_2$, of a *cyclo*alkane ring sensitive to mineral acid is inferred, first, from its oxidation by perbenzoic acid to a monoxide $C_{32}H_{50}O_3$ which does not show ethylenic absorption at 2000—2200 Å and, secondly, from its conversion by mineral acid into the normal oleanane derivative, oleana-11 : 13(18)-dienyl acetate (X). A striking resemblance between the acetate $C_{32}H_{48}O_3$, provisionally formulated as (XIX), and "*iso*-α-amyradienonyl-II acetate" obtained from 12-oxo*iso*ursa-9(11) : 14-dienyl acetate (XXII) by treatment with hydrochloric acid is noted and it is suggested that the last reaction also involves the formation of a *cyclo*alkane bridge.

In Part XXIX * it was shown that the behaviour of oxo*iso*-β-amyradienyl acetate on reduction may be satisfactorily interpreted in terms of the expression (I). This compound is now named 12-oxo*iso*oleana-9(11) : 14-dien-3β-yl acetate.

The name *iso*oleanane will be used for the hydrocarbon (A) which is derived from oleanane by the transfer of an angular methyl group from $C_{(14)}$ to $C_{(13)}$. Oxo*iso*-β-amyradienyl acetate becomes 12-oxo*iso*oleana-9(11) : 14-dien-3β-yl acetate (I) and the non-conjugated dienyl acetates obtained from (I) by Wolff–Kishner reduction (Part XXIX) are *iso*oleana-9(11) : 14- (m. p. 231°) and -11 : 14-dien-3β-yl acetate (m. p. 203°) respectively. A similar nomenclature is adopted for oxo*iso*-α-amyradienyl acetate (XXI) which is now named 12-oxo*iso*ursa-9(11) : 14-dienyl acetate.



(A)

The experiments described in this paper were started at the same time as the reduction experiments and were also originally designed to test the validity of the expression (I).

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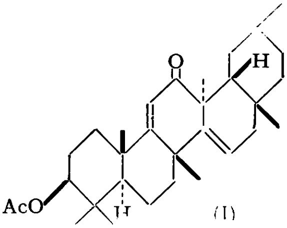
* Part XXIX, preceding paper.

Oxidation of 12-oxo*iso*oleana-9(11) : 14-dienyl acetate, $C_{32}H_{48}O_3$, with hydrogen peroxide in acetic acid gives as major product an acetate $C_{32}H_{48}O_4$ (diol monoacetate) which does not give a colour with tetranitromethane, shows selective absorption in the ultra-violet with an intense maximum at 2360 Å, and is hydrolysed by alkali to the diol, $C_{30}H_{46}O_3$. The oxygen atom introduced has been characterised as a hydroxyl group since the acetate, $C_{32}H_{48}O_4$, on acetylation, yields a diacetate, $C_{34}H_{50}O_5$, and on oxidation with chromic acid at room temperature yields a keto-acetate, $C_{32}H_{46}O_4$; this in turn was characterised by hydrolysis to the corresponding keto-alcohol, $C_{30}H_{44}O_3$, reacetylation of which yields the parent keto-acetate. The diol and the keto-acetate have been prepared by alternative methods from 12-oxo*iso*olean-9(11) : 14-dienyl acetate, as described below.

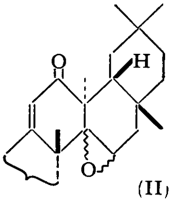
Oxidation of 12-oxo*iso*oleana-9(11) : 14-dienyl acetate (I) with perbenzoic acid, with potassium permanganate or, in sufficiently mild conditions, with chromic acid, gives 14 : 15-epoxy-12-oxo*iso*olean-9(11)-enyl acetate (II). This, in contrast to (I), does not give a colour with tetranitromethane, and shows the ultra-violet absorption spectrum characteristic of an αβ-unsaturated ketone, from which we conclude that it is formed from (I) by the saturation of the isolated ethylenic linkage. This conclusion is supported by the fact that both show the intense absorption band associated with an αβ-unsaturated ketone group but only (I) shows the absorption between 2050 and 2200 Å associated with the presence of an isolated ethylenic bond. The oxide is stable to cold alkali, but when heated therewith yields the alcohol-oxide, reactylation of which regenerates (II).

With hydrochloric acid 14 : 15-epoxy-12-oxo*iso*olean-9(11)-enyl acetate (II) yields a chloro-acetate, $C_{32}H_{47}O_3Cl$, which has been directly related to the diol monoacetate obtained by hydrogen peroxide oxidation of (I); alkaline hydrolysis of the chloro-compound gives the diol, $C_{30}H_{46}O_3$, obtained by similar hydrolysis of the diol monoacetate.

The keto-acetate, $C_{32}H_{46}O_4$, obtained by vigorous oxidation of 12-oxo*iso*oleana-9(11) : 14-dienyl acetate (I) with chromic acid, is similarly obtained from 14 : 15-epoxy-12-oxo*iso*olean-9(11)-enyl acetate (II).



(I)



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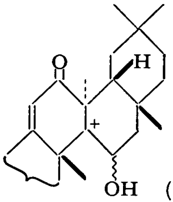
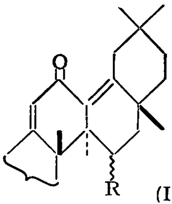


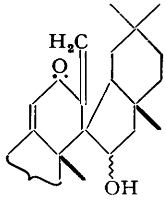
(III)

The conversions of (I) into the diol monoacetate and of the oxide (II) into the chloro-acetate, $C_{32}H_{47}O_3Cl$, can be represented as proceeding *via* the ion (III) which, although capable of rearrangement, must achieve stability by the ultimate loss of a proton with the consequent formation of an ethylenic bond or its equivalent; in the latter conversion, this change is probably followed by the replacement of the $C_{(15)}$-hydroxyl group by chlorine. The chloro-acetate, $C_{32}H_{47}O_3Cl$, the related diol monoacetate, $C_{32}H_{48}O_4$, and the keto-acetate, $C_{32}H_{46}O_4$, do not contain an isolated ethylenic linkage. Thus they do not give a colour with tetranitromethane and they are stable to per-acid. Furthermore, whilst their absorption spectra contain strong absorption bands at 2360 Å, they do not show the absorption in the region 2050—2200 Å characteristic of an isolated ethylene bond. Treatment of the chloro-acetate, $C_{32}H_{47}O_3Cl$, with collidine leads to the elimination of hydrogen chloride and the formation of an acetate, $C_{32}H_{46}O_3$, the absorption spectrum of which shows a band at 2320 Å (αβ-unsaturated ketone) and an apparent maximum at 2090 Å (ε 3000) attributed to an isolated ethylene bond; as expected, the acetate, $C_{32}H_{46}O_3$, gives a yellow colour with tetranitromethane. In our view an observation of considerable significance in the elucidation of the structure of the diol monoacetate and its congeners is that the double bond introduced by the removal of the elements of hydrogen chloride from the chloro-acetate is not conjugated with the original chromophore, and cannot be brought into conjugation with it, the acetate $C_{32}H_{46}O_3$ being recovered unchanged after treatment with hydrochloric acid.

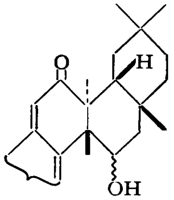
The possibility that the diol monoacetate and its related compounds contain a conjugated dienone group has been excluded by a number of considerations. Rearrangement of the ion (III) could give rise to one of the conjugated dienones (IV; R = OH), (V), and (VI); (VI) is excluded since this would show an intense absorption maximum at approximately 2900 Å (cf. 3α-hydroxy-12-oxochola-7 : 9(11)-dienoic acid, 2920 Å; Fieser, Rajagopalan, Wilson, and Tishler, *J. Amer. Chem. Soc.*, 1951, **73**, 4133) whereas the diol monoacetate exhibits an intense absorption maximum at 2360 Å. Structure (V) is excluded because the related chloro-acetate is recovered unchanged after treatment with ozone. Again, the stability of the related keto-acetate to chromic acid in boiling acetic acid makes such a structure extremely unlikely. Equally cogent reasons, in our opinion, lead to the view that the diol monoacetate cannot be (IV; R = OH). Treatment of the related chloro-acetate with activated zinc dust and acetic acid converts it into the diol diacetate, $C_{34}H_{50}O_5$, by replacement of the chlorine atom by an acetoxy-group; however, mild reduction with zinc in ether–ethanol gives a compound, $C_{32}H_{48}O_3$, by replacement of chlorine by hydrogen. Like the parent chloro-acetate, the compound, $C_{32}H_{48}O_3$, shows an intense absorption maximum at approximately 2340 Å. If (IV; R = Cl) correctly represented the chloro-acetate, the compound, $C_{32}H_{48}O_3$, would be 12-oxo-oleana-9(11) : 13(18)-dienyl acetate (IV; R = H), but this compound has been prepared by an unambiguous method (Beaton, Johnston, McKean, and Spring, *J.*, 1953, 3660) and differs markedly.



(IV)



(V)

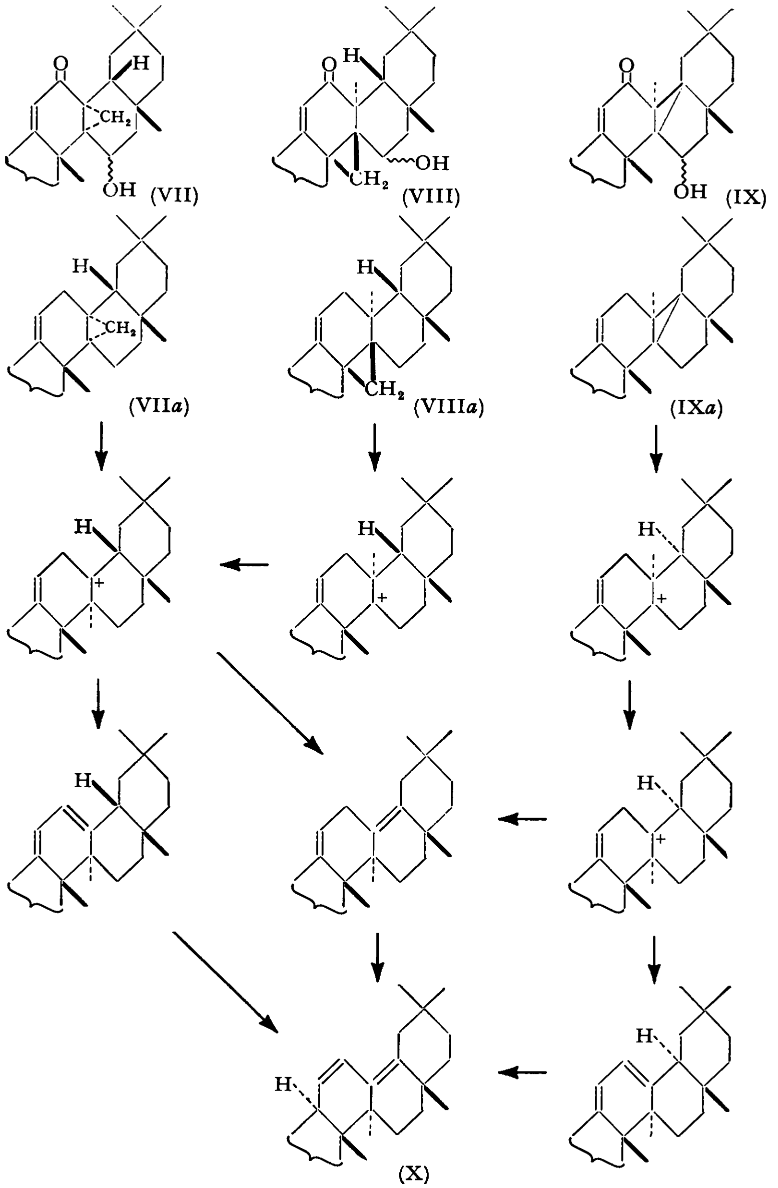


(VI)

In contrast to 12-oxo*iso*oleana-9(11) : 14-dienyl acetate and its oxide, the diol monoacetate and its relatives are all strongly dextrorotatory. Furthermore, the ultra-violet absorption maximum of each member of the last group is at a somewhat shorter wavelength than those of (I) and (II) (see Table). Further insight into the nature of this well-defined series of compounds was obtained from a study of their behaviour on reduction. As indicated above, reduction of the acetate, $C_{32}H_{47}O_3Cl$, with zinc in a neutral solvent, gives an αβ-unsaturated keto-acetate, $C_{32}H_{48}O_3$. Wolff–Kishner reduction of the last compound yields an acetate, $C_{32}H_{50}O_2$; unlike the parent acetate, $C_{32}H_{48}O_3$, this gives a yellow colour with tetranitromethane and its ultra-violet absorption spectrum is consistent with the presence of a >C:CH– linkage. The acetate, $C_{32}H_{50}O_2$, is also obtained as one product of the catalytic hydrogenolysis of the keto-acetate, $C_{32}H_{46}O_4$. Treatment of the acetate, $C_{32}H_{50}O_2$, with hydrochloric–acetic acid yields oleana-11 : 13(18)-dienyl acetate (X). The acetate, $C_{32}H_{50}O_2$, is not a non-conjugated dienyl acetate since, on oxidation with perbenzoic acid, it gives a product, $C_{32}H_{50}O_3$, which does not show any absorption in the ultra-violet between 2000 and 4000 Å and does not give a colour with tetranitromethane.

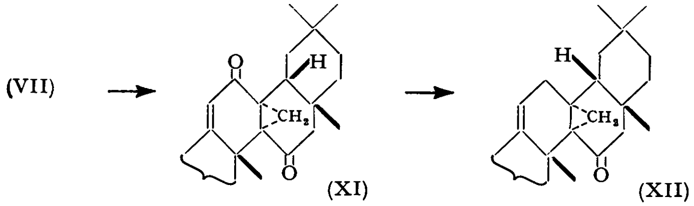
		$[\alpha]_D$ (in $CHCl_3$)	$\lambda_{max.}$ (Å) (in EtOH)	ε
12-Oxo*iso*oleana-9(11) : 14-dienyl acetate (I)	$C_{32}H_{48}O_3$	− 38°	2450	10,100
12-Oxo*iso*oleana-9(11) : 14-dienol	$C_{30}H_{46}O_2$	− 51	—	—
14 : 15-Epoxy-12-oxo*iso*olean-9(11)-enyl acetate (II)	$C_{32}H_{48}O_4$	− 12·5	2400	10,800
14 : 15-Epoxy-12-oxo*iso*olean-9(11)-enol	$C_{30}H_{46}O_3$	− 26	2420	14,000
Diol monoacetate	$C_{32}H_{48}O_4$	+155	2360	13,400
Diol diacetate	$C_{34}H_{50}O_5$	+141	2360	11,500
Diol	$C_{30}H_{46}O_3$	+167	2360	12,500
Chloro-acetate	$C_{32}H_{47}O_3Cl$	+117	2360	11,100
Keto-acetate	$C_{32}H_{46}O_4$	+ 94	2360	13,000
Keto-alcohol	$C_{30}H_{44}O_3$	+ 71	2360	13,000
Acetate	$C_{32}H_{48}O_3$	+130	2340	11,500
Acetate	$C_{32}H_{46}O_3$	+117	2320	12,500

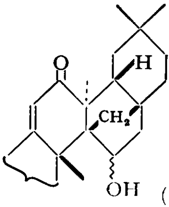
These facts lead to the conclusion that the diol monoacetate and its relatives are hexacyclic, and that notwithstanding an inherent difficulty in representing the mechanism of such a reaction, their formation from the pentacyclic *iso*oleanane derivative (I) includes the formation of a new *cyclo*alkane bridge. The transformations of the diol monoacetate and its derivatives appear at first sight to be best explained by the presence therein of a

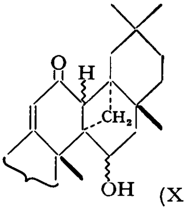


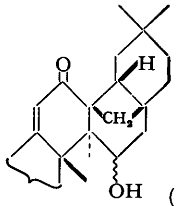
*cyclo*propane bridge. Thus the diol monoacetate may be represented by formulæ such as (VII), (VIII), and (IX), and the acetate, $C_{32}H_{50}O_2$, as (VII*a*), (VIII*a*), and (IX*a*) respectively; the acid-rearrangement of compounds of these structures to oleana-9(11) : 13(18)-dienyl acetate is adequately represented as in the annexed scheme.

Although a *cyclo*propane formulation gives a reasonable interpretation of the behaviour of the monoethenoid acetate, $C_{32}H_{50}O_2$, with mineral acid, some of the properties of this family of compounds cannot be thus accommodated. In the first place, the infra-red absorption spectra of compounds containing a *cyclo*propane ring include an intense band at approximately 1000 cm.$^{-1}$ (Derfer, Pickett, and Boord, *J. Amer. Chem. Soc.*, 1949, **71**, 2482; Barton, *J.*, 1951, 1444): the acetate, $C_{32}H_{50}O_2$, in carbon disulphide does not show such a band. In the second place, the optical effect associated with the hyperconjugation between a *cyclo*propane ring and a carbonyl group or an ethylenic linkage (Klotz, *J. Amer. Chem. Soc.*, 1944, **66**, 88) is not observed in this series of compounds: the keto-acetate, $C_{32}H_{46}O_4$, and the unsaturated acetate, $C_{32}H_{46}O_3$, show the same ultra-violet absorption characteristics as the diol monoacetate. A good illustration of this point is to be found in the following observations. Wolff–Kishner reduction of the keto-acetate, $C_{32}H_{46}O_4$, followed by acetylation, gives an acetate $C_{32}H_{48}O_3$, one of the two carbonyl groups being reduced to a methylene group; since the characteristic absorption spectrum of an αβ-unsaturated ketone has disappeared, the $C_{(12)}$-carbonyl group has been reduced. Consequently, if the diol monoacetate is correctly represented by one of these *cyclo*propanoid formulæ, *e.g.*, (VII), the keto-acetate will be (XI) and the Wolff–Kishner reduction product will be (XII) (or, possibly, the 11 : 12-unsaturated isomer). The ultra-violet


(VII) (XI) (XII)


(XIII)


(XIV)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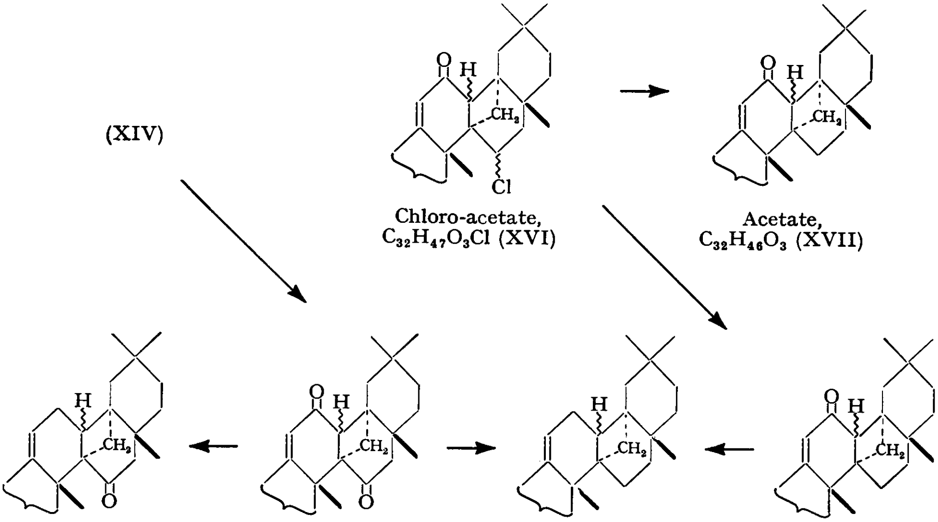

(XIV)

Chloro-acetate, $C_{32}H_{47}O_3Cl$ (XVI)

Acetate, $C_{32}H_{46}O_3$ (XVII)

Acetate, $C_{32}H_{48}O_3$ (XXI)

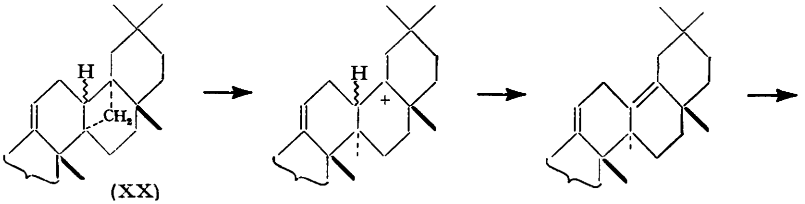
Keto-acetate, $C_{32}H_{46}O_4$ (XVIII)

Acetate, $C_{32}H_{50}O_2$ (XX)

Acetate, $C_{32}H_{48}O_3$ (XIX)

absorption spectrum of the Wolff–Kishner product does not show the pronounced shift towards longer wave-lengths expected for a compound containing a carbonyl group conjugated with a *cyclo*propane ring. In fact the spectrum of the Wolff–Kishner acetate, $C_{32}H_{48}O_3$, is very similar to that of the acetate, $C_{32}H_{50}O_2$, which in terms of (VII) is to be formulated as (VII*a*). For these reasons the presence of a *cyclo*propane ring in the diol monoacetate and its relatives is considered improbable and the alternative formulæ (XIII), (XIV), and (XV) are preferred for the time being. Each of these hypothetical formulæ reasonably accommodates the known reactions of the diol monoacetate. For purposes of illustration, only (XIV) will be used. Accordingly, the chloro-acetate is represented by (XVI), and the compounds derived from it are (XVII)—(XXI). The conversion of (XX) into oleana-11 : 13(18)-dienyl acetate (X) is represented as shown below. The last stage in this reaction sequence, the conversion of oleana-9(11) : 13(18)-dienyl acetate into (X) has been realised (Beaton, McKean, Johnston, and Spring, *loc. cit.*).

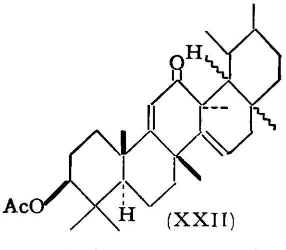
The *cyclo*alkane bridge in the chloro-acetate (XVI), (XVII), and (XVIII) is unaffected by hydrochloric acid. This relative stability appears to be associated with the presence of a carbonyl-oxygen atom at $C_{(12)}$ and/or $C_{(15)}$: thus, the acetates (XIX) and (XX) are stable to hydrochloric–acetic acid in conditions which readily rupture the *cyclo*alkane ring of (XX).



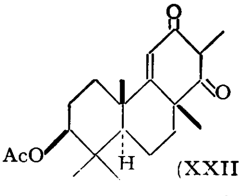
(XX)

(X)

We believe that the stability of (XIX) to mineral acid finds a counterpart in a reaction in the α-amyrin series. 12-Oxo*iso*ursa-9(11) : 14-dienyl acetate (XXII) is the α-amyrin analogue of the β-amyrin derivative, 12-oxo*iso*oleana-9(11) : 14-dienyl acetate (I); the two acetates (XXII) and (I) are formed by parallel routes from α- and β-amyrin respectively, and each has been converted by an oxidation and pyrolytic process into the diketone (XXIII). The two acetates (XXII) and (I) differ, however, in one important



(XXII)



(XXIII)

respect; whereas (I) is stable to vigorous and prolonged treatment with mineral acid, (XXII) is thereby converted into an isomer (" *iso*-α-amyradienonyl-II acetate ") (Ruzicka, Ruegg, Volli, and Jeger, *Helv. Chim. Acta*, 1947, **30**, 140) which no longer contains an isolated ethylenic linkage since, in contrast to 12-oxo*iso*ursa-9(11) : 14-dienyl acetate it does not give a colour with tetranitromethane or show the absorption at 2000—2200 Å. " *iso*-α-Amyradienonyl-II acetate " bears a very close resemblance in these and other respects to the isomeric acetate (XIX). The large change (+168°) in optical rotation associated with the conversion of 12-oxo*iso*oleana-9(11) : 14-dienyl acetate (I) into the acetate (XIX) is similar to that (+153°) accompanying the conversion of 12-oxo*iso*ursa-9(11) : 14-dienyl acetate into " *iso*-α-amyradienonyl-II acetate " {the $[\alpha]_D$ values from which this calculation was made were measured by Mr. J. D. Easton (Thesis, Glasgow University, 1953)}. We suggest that the acetate (XIX) and " *iso*-α-amyradienonyl-II acetate " have analogous structures. It is probable that the difference in behaviour of (I) and (XXII) towards mineral acid is to be ascribed to a difference in configuration at $C_{(18)}$ and/or $C_{(17)}$ in α- and β-amyrin.

EXPERIMENTAL

Rotations were measured in $CHCl_3$ solution at approx. 15°. Absorption spectra were measured in alcohol solution with a Unicam SP. 500 spectrophotometer. For chromatography a grade II alumina and a light petroleum fraction, b. p. 60—80°, were used unless otherwise specified.

14 : 15-*Epoxy*-12-*oxo*iso*olean*-9(11)-*enyl Acetate*.—(*a*) A solution of 12-oxo*iso*oleana-9(11) : 14-dienyl acetate (1 g.) in dry chloroform (10 c.c.) was treated at 0° with a solution of perbenzoic acid (1·2 mols.) in chloroform (9 c.c.) and then kept at 0° for 8 days. The product crystallised from chloroform–methanol, to yield 14 : 15-*epoxy*-12-*oxo*iso*olean*-9(11)-*enyl acetate* as plates, m. p. 280—281°, $[\alpha]_D$ −12° (*c*, 4·9) (Found: C, 77·3; H, 9·9. $C_{32}H_{48}O_4$ requires C, 77·4; H, 9·7%). The oxide does not give a colour with tetranitromethane. (The light absorption characteristics of this and other compounds are shown in the Table.)

(*b*) A stirred solution of 12-oxo*iso*oleana-9(11) : 14-dienyl acetate (1 g.) in acetic acid (150 c.c.) was treated dropwise with potassium permanganate (0·75 g.) in water (75 c.c.), during 30 min. After 2 hr.' stirring, the mixture was treated with 10% aqueous sodium metabisulphite, and the acetate-oxide isolated by means of ether and crystallised from methanol as rhombic plates (0·9 g.), m. p. and mixed m. p. 281—282°, $[\alpha]_D$ −12·5° (*c*, 2·1).

(*c*) 12-Oxo*iso*oleana-9(11) : 14-dienyl acetate (1·0 g.) in glacial acetic acid (80 c.c.) was treated dropwise at 60° with chromic oxide in glacial acetic acid (16 c.c., 1·5 atoms of O) during 1 hr. After 30 min.' stirring at 60°, the neutral product was isolated in the usual manner and crystallised from chloroform–methanol, to yield the acetate-oxide (0·5 g.), m. p. and mixed m. p. 280—281°, $[\alpha]_D$ −12° (*c*, 1·0).

14 : 15-*Epoxy*-12-*oxo*iso*olean*-9(11)-*enol*.—The acetate (100 mg.) was heated under reflux with 3% aqueous-ethanolic potassium hydroxide for 3 hr. Crystallisation of the product from methanol yielded 14 : 15-*epoxy*-12-*oxo*iso*olean*-9(11)-*enol* as prismatic needles, m. p. 249·5—250°, $[\alpha]_D$ −26° (*c*, 1·4) (Found: C, 79·15; H, 10·1. $C_{30}H_{46}O_3$ requires C, 79·2; H, 10·2%).

Oxidation of 12-*Oxo*iso*oleana*-9(11) : 14-*dienyl Acetate with Hydrogen Peroxide: Diol Monoacetate*, $C_{32}H_{48}O_4$.—Hydrogen peroxide (100-vol.) in acetic acid (1 : 1; 200 c.c.) was added during 2 hr. to 12-oxo*iso*oleana-9(11) : 14-dienyl acetate (1 g.) in acetic acid (150 c.c.) at 95°. The solution was stirred for 3 hr. at 95° and the neutral product isolated in the usual manner and chromatographed in light petroleum–benzene (7 : 3; 100 c.c.) on a column (14 × 1·75 cm.) of alumina. The fractions (690 mg.) eluted with light petroleum–benzene mixtures (7 : 3, 100 c.c.; 3 : 2, 200 c.c.), benzene (300 c.c.), and benzene–ether (9 : 1; 100 c.c.) were combined and re-chromatographed in light petroleum–benzene (4 : 5; 135 c.c.) on neutral activated alumina (18 × 2 cm.). Light petroleum–benzene (4 : 5, 300 c.c.; 2 : 3, 300 c.c.; 1 : 2, 200 c.c.) eluted a crystalline solid (134 mg.), repeated crystallisation of which from chloroform–methanol yielded an *acetate* (80 mg.), m. p. 225—226°, $[\alpha]_D$ +78° (*c*, 0·7) (Found: C, 74·4, 74·7; H, 10·2, 9·5%). The acetate does not give a colour with tetranitromethane or show selective absorption of high intensity between 2200 and 4000 Å. Continued washing of the column with light petroleum–benzene (1 : 3, 100 c.c.; 1 : 4, 100 c.c.) and with benzene (250 c.c.) gave only a trace of eluate, whereafter washing with benzene–ether (9 : 1, 600 c.c.) gave a fraction (238 mg.), crystallisation of which from methanol yielded the *diol monoacetate* as plates, m. p. 318—319°, $[\alpha]_D$ +155° (*c*, 1·3) (Found: C, 77·7, 77·6; H, 9·9, 9·8. $C_{32}H_{48}O_4$ requires C, 77·4; H, 9·7%).

Diol, $C_{30}H_{46}O_3$.—Hydrolysis of the diol monoacetate in boiling 3% aqueous-ethanolic potassium hydroxide for 4 hr. yielded the *diol* as prisms (from aqueous methanol), m. p. 290—291°, $[\alpha]_D$ +167° (*c*, 1·0) (Found: C, 79·4; H, 10·4. $C_{30}H_{46}O_3$ requires C, 79·2; H, 10·2%). It does not give a colour with tetranitromethane.

Diol Diacetate, $C_{34}H_{50}O_5$.—With acetic anhydride and pyridine the diol monoacetate gave the *diol diacetate*, needles from aqueous methanol, m. p. 194—194·5°, $[\alpha]_D$ +141° (*c*, 0·6) (Found: C, 75·7; H, 9·6. $C_{34}H_{50}O_5$ requires C, 75·8; H, 9·4%).

Keto-acetate, $C_{32}H_{46}O_4$.—(*a*) The diol monoacetate (120 mg.) in acetic acid (40 c.c.) was treated dropwise with chromic oxide in aqueous acetic acid (10 c.c., 1·3 atoms of O) at room temperature during 30 min. Next morning the mixture was heated on the steam-bath for 15 min., and the neutral product then isolated in the usual manner and crystallised from chloroform–methanol, to yield the *keto-acetate* as needles (80 mg.), m. p. 314—315°, $[\alpha]_D$ +94° (*c*, 1·0) (Found: C, 78·0, 77·4; H, 9·6, 9·2. $C_{32}H_{46}O_4$ requires C, 77·7; H, 9·4%).

(*b*) (i) A gently refluxing solution of 12-oxo*iso*oleana-9(11) : 14-dienyl acetate (5 g.) in glacial acetic acid (400 c.c.) was treated with chromic oxide (5 g.) in acetic acid (150 c.c.) during 1 hr. Refluxing was continued for 2 hr. and the neutral fraction isolated in the usual manner. Repeated crystallisation of this from chloroform–methanol yielded the product (1·5 g.) as needles, m. p. 315—316°, $[\alpha]_D$ +57° (*c*, 2·0). The m. p. of a mixture with the keto-acetate described under (*a*) was undepressed. A second experiment in which the crude neutral reaction product was purified by chromatography on alumina followed by crystallisation from chloroform–methanol yielded the product as needles, m. p. 313—314°, $[\alpha]_D$ +56°, +57° (*c*, 0·8, 0·3) (Found : C, 77·5, 77·4; H, 9·5, 9·2%), with an absorption maximum at 2340 Å (ε 13,000).

(ii) 14 : 15-Epoxy-12-oxo*iso*oleana-9(11)-enyl acetate (0·5 g.) in acetic acid (100 c.c.) was treated at 80° with chromic oxide (0·17 g.) in 95% acetic acid (22 c.c.), with stirring, during 4 hr. After 1 hr.' stirring the neutral product was isolated in the usual manner and crystallised from chloroform–methanol, to yield the product as needles (0·35 g.), m. p. 313—316°, $[\alpha]_D$ +58° (*c*, 1·0).

Repeated recrystallisation and careful chromatography of the neutral reaction products prepared by the two methods described under (*b*) failed to raise their rotation to that of the specimen prepared by method (*a*). It may be that the lower rotation is due to the presence of a small quantity of the acetate-oxide ($[\alpha]_D$ −12°).

Hydrolysis of the specimens of keto-acetate of low rotation for 3 hr. with boiling 3% aqueous ethanolic potassium hydroxide gave the *keto-alcohol* which, after several crystallisations from chloroform–methanol and then from methanol, separates as needles, m. p. 298—299°, $[\alpha]_D$ +71° (*c*, 0·5) (Found : C, 79·8; H, 9·9. $C_{30}H_{44}O_3$ requires C, 79·6; H, 9·8%).

The keto-alcohol was also prepared by refluxing the keto-acetate of $[\alpha]_D$ +58° (0·25 g.) in ethanol (60 c.c.) and concentrated hydrochloric acid (8 c.c.) for 3 hr. The neutral product was crystallised four times from chloroform–methanol, to yield the keto-alcohol as needles, m. p. 298—299°, $[\alpha]_D$ +71° (*c*, 0·7). A mixture with the specimen prepared by alkaline hydrolysis was undepressed in m. p. Acetylation of the keto-alcohol (pyridine–acetic anhydride) yielded the keto-acetate as needles, m. p. 313—314°, $[\alpha]_D$ +90° (*c*, 0·1), from chloroform–methanol. A mixture of this acetate with the specimen prepared by method (*a*) was undepressed in m. p.

Fission of 14 : 15-*Epoxy*-12-*oxo*isoo*lean*-9(11)-*enyl Acetate with Hydrochloric Acid*: *Chloro-acetate* $C_{32}H_{47}O_3Cl$.—A solution of the oxide (1·2 g.) in chloroform (20 c.c.) and acetic acid (50 c.c.) containing concentrated hydrochloric acid (5 c.c.) was kept at 60° for 2 hr. The neutral product was isolated by means of ether and crystallised from chloroform–methanol, to yield the *chloro-acetate* as needles, m. p. 227—228° (decomp. and evolution of acidic vapour), $[\alpha]_D$ +117°, +118° (*c*, 1·3, 0·7) (Found : C, 74·8; H, 9·3; Cl, 6·5. $C_{32}H_{47}O_3Cl$ requires C, 74·6; H, 9·2; Cl, 6·9%). The chloro-acetate does not give a colour with tetranitromethane.

The chloro-acetate (150 mg.) was refluxed with potassium hydroxide (1 g.) in water (5 c.c.) and ethanol (25 c.c.) for 4 hr. The diol, $C_{30}H_{46}O_3$, isolated by means of ether in the usual manner and crystallised from aqueous methanol, formed needles, m. p. 289·5—291°, $[\alpha]_D$ +167° (*c*, 0·7). Light absorption in EtOH : Max. at 2380 Å (ε 13,500). A mixture with the diol prepared by hydrogen peroxide oxidation of 12-oxo*iso*oleana-9(11) : 14-dienyl acetate (followed by hydrolysis) was undepressed in m. p.

Treatment of the Chloro-Acetate, $C_{32}H_{47}O_3Cl$, *with Zinc* : *Acetate* $C_{32}H_{48}O_3$.—(*a*) The chloro-acetate (1 g.) in glacial acetic acid was treated with zinc (6 g.; not activated) and the mixture refluxed for 5 hr. The product was isolated by means of ether and chromatographed in light petroleum–benzene (3 : 2; 50 c.c.) on alumina (14 × 2 cm.). The fractions eluted with light petroleum–benzene (3 : 2, 550 c.c.; 2 : 3, 100 c.c.) and benzene (300 c.c.) were combined (504 mg.) and repeatedly crystallised from aqueous acetone, to give the *acetate*, $C_{32}H_{48}O_3$, as prismatic needles, m. p. 274—275°, $[\alpha]_D$ +130° (*c*, 1·4) (Found : C, 79·6; H, 10·3. $C_{32}H_{48}O_3$ requires C, 79·95; H, 10·1%). This does not give a colour with tetranitromethane in chloroform.

(*b*) The chloro-acetate (0·5 g.) in ether (75 c.c.) and methanol (75 c.c.) was treated with freshly activated zinc (5 g.) and the mixture refluxed for 5 hr. The product was isolated by means of ether, and chromatographed in light petroleum–benzene (2 : 3, 50 c.c.) on alumina (grade I) (9 × 2 cm.). The fractions eluted with light petroleum–benzene (2 : 3, 450 c.c.; 1 : 2, 300 c.c.; 1 : 5, 150 c.c.) and benzene (1000 c.c.) were combined and crystallised from aqueous acetone, to yield the acetate $C_{32}H_{48}O_3$ (400 mg.; m. p. 268—271°) which after several crystallisations from the same solvent had m. p. and mixed m. p. 273—275°, $[\alpha]_D$ +139° (*c*, 1·1). Light absorption : Max. at 2350 Å (ε 11,900).

The chloro-acetate $C_{32}H_{47}O_3Cl$ (0·25 g.) in glacial acetic acid was treated with freshly activated zinc (1·5 g.), and the mixture refluxed for 5 hr. The diol diacetate, isolated by means of ether, crystallised from light petroleum (b. p. 40—60°) as prisms, m. p. and mixed m. p. 197—198°, $[\alpha]_D$ +134° (*c*, 0·5) (Found: C, 75·8; H, 9·7. Calc. for $C_{34}H_{50}O_5$: C, 75·8; H, 9·4%). Light absorption: Max. at 2360 Å (ε 13,000).

Treatment of the Chloro-Acetate, $C_{32}H_{47}O_3Cl$, *with Collidine: Acetate*, $C_{32}H_{46}O_3$.—A mixture of the chloro-acetate (250 mg.) and redistilled collidine (25 c.c.) was kept at 200° in an autoclave for 3 hr. The *product* was isolated by means of ether and crystallised from chloroform–methanol as plates (180 mg.), m. p. 286—287°, $[\alpha]_D$ +117° (Found: C, 80·3; H, 9·9. $C_{32}H_{46}O_3$ requires C, 80·3; H, 9·7%). This gives a yellow colour with tetranitromethane. Light absorption: Max. at 2090 (ε 3000) and 2320 Å (ε 12,500). A solution of the acetate (30 mg.) in benzene (3 c.c.) and glacial acetic acid (10 c.c.) was treated with concentrated hydrochloric acid (0·5 c.c.) and the solution kept at room temperature for 5 days and then at 60° for 3 hr. Unchanged acetate {25 mg., m. p. 283—285°, $[\alpha]_D$ +115° (*c*, 0·5)} was recovered from the solution.

Acetate, $C_{32}H_{50}O_2$.—(a) *Catalytic hydrogenolysis of the keto-acetate*, $C_{32}H_{46}O_4$. The keto-acetate ($[\alpha]_D$ +90°; 1·6 g.) in glacial acetic acid (250 c.c.) was added to a suspension of freshly reduced platinum (from 0·5 g. of PtO_2) in glacial acetic acid (20 c.c.), and the mixture shaken with hydrogen for 48 hr. The filtered solution was shaken with fresh platinum catalyst (from 0·25 g. of PtO_2) for 24 hr. and the product isolated in the usual manner. The product was chromatographed in light petroleum–benzene (2 : 1; 150 c.c.) on alumina (grade II/III; 14 × 2 cm.). Light petroleum–benzene (2 : 1, 400 c.c.) eluted a fraction (1·34 g.) which was repeatedly crystallised, first from methanol–ether and then from methanol–chloroform, to yield (with considerable loss) the *acetate*, $C_{32}H_{50}O_2$, as hexagonal plates, m. p. 231—232°, $[\alpha]_D$ +86°, +87° (*c*, 1·0, 1·5) (Found: C, 82·5; H, 10·8. $C_{32}H_{50}O_2$ requires C, 82·3; H, 10·8%). Light absorption: $\varepsilon_{2080} = 3000$, $\varepsilon_{2100} = 2800$, $\varepsilon_{2150} = 1800$, $\varepsilon_{2200} = 860$.

The earlier mother-liquors obtained from the crystallisation of the foregoing acetate were combined and concentrated, to give needles, m. p. 164—166° (0·6 g.). Four crystallisations of these from methanol yielded an *acetate*, $C_{32}H_{52}O_2$, as needles, m. p. 168—170°, $[\alpha]_D$ +12°, +13° (*c*, 1·3) (Found: C, 81·95; H, 11·4. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%). Light absorption: $\varepsilon_{2060} = 1520$, $\varepsilon_{2100} = 1000$, $\varepsilon_{2150} = 650$, $\varepsilon_{2250} = 280$.

(b) *Wolff–Kishner reduction of the acetate*, $C_{32}H_{48}O_3$. A mixture of the acetate, $C_{32}H_{48}O_3$ (obtained by reduction of the chloro-acetate, $C_{32}H_{47}O_3Cl$, with zinc) (0·5 g.), methanolic sodium methoxide (from 2 g. of sodium and 25 c.c. of methanol), and hydrazine hydrate (100%; 5 c.c.) was kept at 200° in an autoclave for 10 hr. The product was isolated in the usual manner and acetylated with pyridine and acetic anhydride. A solution of the acetylated product in light petroleum (50 c.c.) was chromatographed on alumina (14 × 2 cm.). The fractions eluted with light petroleum (500 c.c.) were combined (240 mg.) and crystallised from chloroform–methanol, to give the acetate, $C_{32}H_{50}O_2$, as plates, m. p. 226—228°, $[\alpha]_D$ +84° (*c*, 1·0), undepressed in m. p. when mixed with the specimen prepared by method (a). Light absorption: $\varepsilon_{2100} = 2600$, $\varepsilon_{2150} = 2000$, $\varepsilon_{2200} = 850$. A second experiment gave the same acetate as plates (from chloroform–methanol), m. p. 230—231°, $[\alpha]_D$ +86°.

Oleana-11 : 13(18)-*dienyl Acetate from the Acetate*, $C_{32}H_{50}O_2$.—The acetate, $C_{32}H_{52}O_2$ (65 mg.), in acetic acid (35 c.c.) was heated with concentrated hydrochloric acid (3 c.c.) on the steam-bath for 5 hr. and then kept overnight at room temperature. The product was isolated by means of ether, acetylated (warm pyridine–acetic anhydride), and crystallised from chloroform–methanol, to yield oleana-11 : 13(18)-dienyl acetate (38 mg.) as plates, m. p. and mixed m. p. 226—228°, $[\alpha]_D$ −61° (*c*, 0·7). Light absorption: Max. at 2430 (ε 26,000), 2510 (ε 28,000) and 2600 Å (ε 20,000).

Treatment of the Acetate, $C_{32}H_{50}O_2$, *with Perbenzoic Acid*.—The acetate, $C_{32}H_{50}O_2$ (340 mg.), in chloroform (25 c.c.) was treated at 0° with perbenzoic acid (210 mg.) in chloroform (2 c.c.) and then kept at 0° for 4 days. Crystallisation from chloroform–methanol gave, as first crop, unchanged acetate $C_{32}H_{50}O_2$ (100 mg.), m. p. 219—223°, m. p. and mixed m. p. 225—227°, $[\alpha]_D$ +81° (*c*, 1·5), on recrystallisation. The original chloroform–methanol mother-liquor was concentrated to give a second crop (110 mg.), recrystallisation of which from the same solvent mixture yielded the *oxide* as plates, m. p. 194—195°, $[\alpha]_D$ +23° (*c*, 1·0) (Found: C, 79·4; H, 10·7. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%). The oxide does not give a colour with tetranitromethane or show selective absorption between 2000 and 4000 Å.

Wolff–Kishner Reduction of the Keto-acetate, $C_{32}H_{46}O_4$.—The acetate $C_{32}H_{46}O_4$ (m. p. 313—314°, $[\alpha]_D$ +90°; 1 g.), methanolic sodium methoxide (from 30 c.c. of methanol and 2·5 g. of sodium), and hydrazine hydrate (100%; 10 c.c.) were heated at 200° in an autoclave for 16 hr. The product was isolated by means of ether, acetylated (acetic anhydride–pyridine at 80°), dried, and chromatographed in light petroleum (50 c.c.) on grade II—III alumina (14 × 2 cm.). Elution with light petroleum–benzene mixtures gave a solid (500 mg.), crystallisation of which from methanol yielded the *acetate* as plates, m. p. 227—229°, $[\alpha]_D$ −2·5°, −2° (*c*, 2·0, 2·8) (Found : C, 79·6; H, 10·1. $C_{32}H_{48}O_3$ requires C, 79·95; H, 10·1%). Light absorption : $\varepsilon_{2090} = 3400$, $\varepsilon_{2150} = 2000$, $\varepsilon_{2200} = 1100$. The acetate gives a yellow colour with tetranitromethane and was recovered unchanged after 3 hr.' warming of 50 mg. on the water-bath with glacial acetic acid (25 c.c.) and concentrated hydrochloric acid (3·5 c.c.).

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