Triterpene Resinols and Related Acids. Part XXIX. The Structure of Oxo-*iso*-β-amyradienyl Acetate.*

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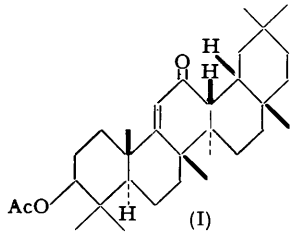
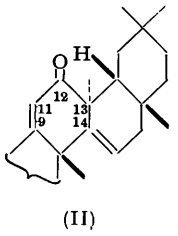
Wolff–Kishner reduction of oxo-*iso*-β-amyradienyl acetate (followed by acetylation of the product) yields a mixture of two isomeric non-conjugated dienyl acetates (VIII) and (XI), isomerised by hydrochloric–acetic acid to oleana-9(11) : 12-dienyl acetate (V) and oleana-11 : 13(18)-dienyl acetate (III) respectively. A mechanism for the conversion of oxo-*iso*-β-amyradienyl acetate into oleana-11 : 13(18)-dienyl acetate by Clemmensen reduction is based on the observation that oleana-9(11) : 12-dienyl acetate is converted into the 11 : 13(18)-isomer by prolonged refluxing with hydrochloric–acetic acid. Reduction of oxo-*iso*-β-amyradienyl acetate with lithium aluminium hydride (followed by acetylation) gives an *iso*-β-amyradienediol diacetate, which with mineral acid yields a trienyl acetate formulated as (XVII). Catalytic hydrogenation of (XVII) yields an isomer of β-amyrin acetate (*neo*-β-amyrin acetate). It is concluded that oxo-*iso*-β-amyradienyl acetate is correctly formulated as (II).

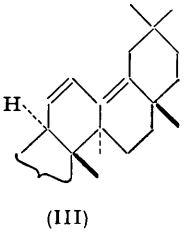
The discussion included in this paper is a continuation of that in Part XXII (Budziarek, Johnston, Manson, and Spring, *J.*, 1951, 3019) in which it was shown that Clemmensen reduction of oxo-*iso*-β-amyradienyl acetate, which is obtained from 12-oxo-olean-9(11)-enyl acetate (I) † by oxidation with either bromine or selenium dioxide and was formulated as (II) † by Jeger and Ruzicka (*Helv. Chim. Acta*, 1945, **28**, 209), yields oleana-11 : 13(18)-



(I)



(II)



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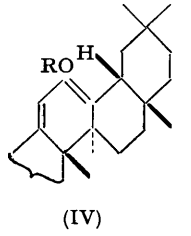


(IV)

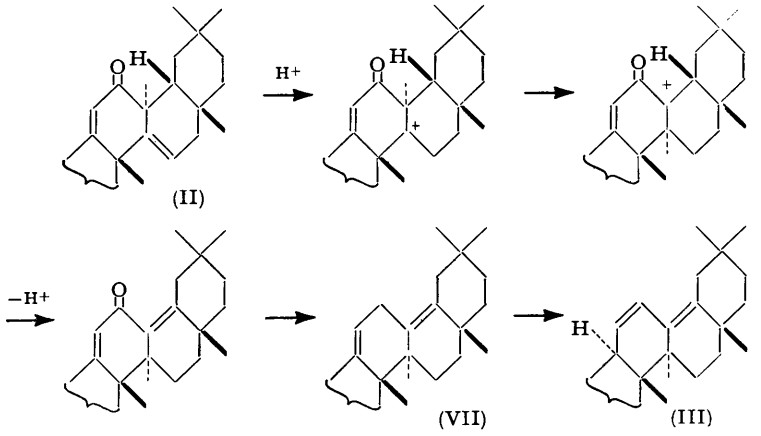
† The relative configurations shown in (I) are those established mainly by Barton and his collaborators (cf. Barton, *J.*, 1953, 1027). The configuration of the 13-methyl group in (II) is considered to be α since the transfer of this group from $C_{(14)}$ to $C_{(13)}$ during the conversion of (I) into (II) must involve its movement across the α-face.

dienyl acetate (III) in high yield. This result, it was contended, did not necessarily indicate that oxo-*iso*-β-amyradienyl acetate is incorrectly formulated by (II) since an alternative view is that the Clemmensen reaction medium induced a reverse methyl migration as shown in the series (II) ⟶ (VII) ⟶ (III). Such a series of changes was considered unlikely, however, since oxo-*iso*-β-amyradienyl acetate is stable to prolonged treatment with strong mineral acid. Arguments against the view that oxo-*iso*-β-amyradienyl acetate has a different carbon skeleton from that of β-amyrin acetate were adduced from the behaviour of the analogous oxo-*iso*-α-amyradienyl acetate and particularly from the observation that catalytic reduction of this compound yields a mixture of ursa-9(11) : 12-dienyl acetate and 12-oxours-9(11)-enyl acetate each of which is a normal ursane derivative (Ruzicka, Ruëgg, Volli, and Jeger, *Helv. Chim. Acta*, 1947, **30**, 140). The experiments described in this paper are limited to those directly bearing on the structure of oxo-*iso*-β-amyradienyl acetate; the chemistry of oxo-*iso*-α-amyradienyl acetate will form the subject of a later paper.

Our first objective was to obtain evidence for or against the presence of an angular methyl group attached to $C_{(13)}$ in oxo-*iso*-β-amyradienyl acetate. It has been shown

* Part XXVIII, *J.*, 1953, 3673.

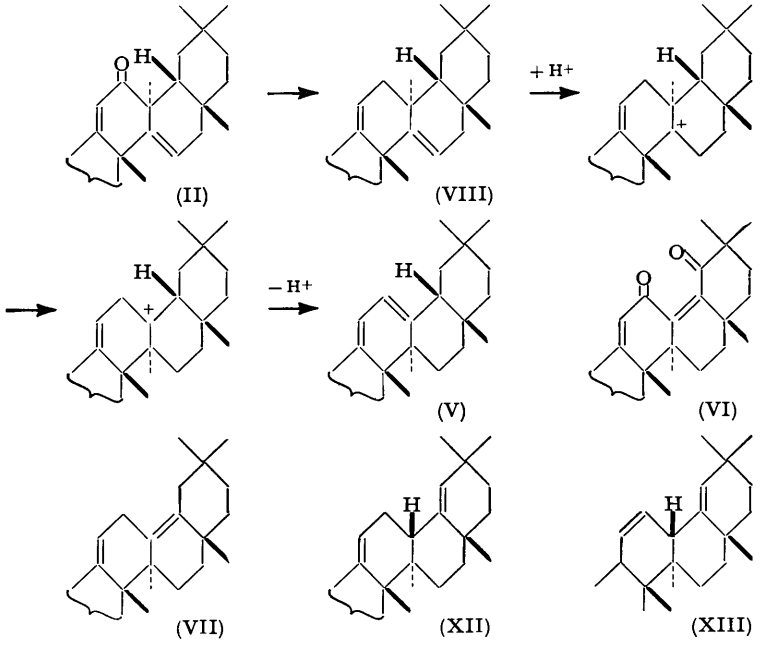
(Budziarek *et al.*, *loc. cit.*) that 12-oxo-olean-9(11)-enyl acetate (I) is readily converted into an enol acetate (IV; R = Ac) and into an enol benzoate (IV; R = Bz). In marked contrast, we find that oxo-*iso*-β-amyradienyl acetate is recovered unchanged after refluxing with acetic anhydride and anhydrous sodium acetate for 172 hr.; it is also recovered unchanged after being heated with the same reagents at 180—200° for 68 hr. and with benzoyl chloride–pyridine at 100° for 10 hr. This stability supports the view that oxo-*iso*-β-amyradienyl acetate carries a methyl substituent at $C_{(13)}$.



Our next objective was to prepare and examine the dienyl acetate corresponding to oxo-*iso*-β-amyradienyl acetate by reductive removal of the carbonyl group. Reduction of oxo-*iso*-β-amyradienyl acetate by the Wolff–Kishner procedure, followed by acetylation, gives a mixture from which two homogeneous products have been isolated. The major product (50%) is an acetate, $C_{32}H_{50}O_2$, m. p. 231°, which gives a yellow colour with tetranitromethane and shows an apparent absorption maximum in the 2000—2250 Å region only; it was recovered unchanged after being shaken in acetic acid solution with hydrogen and platinum at room temperature for 48 hr. It was characterised as homogeneous by alkaline hydrolysis to the corresponding alcohol and regeneration to a product with the same physical constants. Treatment of the acetate, m. p. 231°, with hydrochloric acid in acetic acid gives oleana-9(11) : 12-dienyl acetate (β-amyradienyl-I acetate) (V) in good yield.

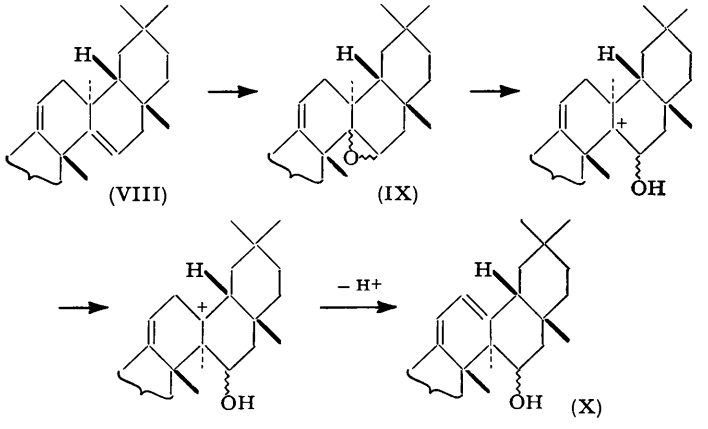
Oxidation of the acetate, m. p. 231°, with selenium dioxide yields 12 : 19-dioxo-β-amyra-9(11) : 13(18)-dienyl acetate (VI), presumably by initial isomerisation to oleana-9(11) : 12-dienyl acetate (V) which gives the dioxodienyl acetate on oxidation with selenium dioxide. We conclude that the acetate, m. p. 231°, is a non-conjugated dienyl acetate. The three possible non-conjugated oleanadienyl acetates, in which the double bonds are in the $C_{(9)}$–$C_{(19)}$ system, are oleana-9(11) : 13(18)- (VII), 9(11) : 18- (XII), and 11 : 18-dienyl acetate (XIII). The acetate, m. p. 231°, differs from oleana-9(11) : 13(18)- and -9(11) : 18-dienyl acetate, each of which has been prepared by unambiguous methods from β-amyrin (Beaton, Johnston, McKean, and Spring, *J.*, 1953, 3660) and each of which yields oleana-11 : 13(18)-dienyl acetate (III) when treated with mineral acid. Furthermore, the ready conversion of the acetate, m. p. 231°, into oleana-9(11) : 12-dienyl acetate (V) shows that it is not the unknown oleana-11 : 18-dienyl acetate since, in analogy with oleana-9(11) : 18-dienyl acetate, oleana-11 : 18-dienyl acetate would be expected to yield the stable oleana-11 : 13(18)-dienyl acetate (III) on treatment with mineral acid. These considerations support the view that the acetate, m. p. 231°, has a different carbon skeleton from that of β-amyrin, *i.e.*, that oxo-*iso*-β-amyradienyl acetate is formed from 12-oxo-olean-9(11)-enyl acetate (I) by a molecular rearrangement. The structure (II) proposed for oxo-*iso*-β-amyradienyl acetate by Ruzicka and Jeger affords a satisfactory explanation of the formation and properties of the dienyl acetate, m. p. 231°. The mechanism (II) ⟶

(VIII) ⟶ (V) for the isomerisation of the acetate, m. p. 231°, which is formulated as (VIII), is proposed.



Oxidation of the acetate, m. p. 231°, with perbenzoic acid gave a product, $C_{32}H_{50}O_3$, which showed the characteristic ultra-violet absorption spectrum of oleana-9(11) : 12-dienyl acetate (max. 2820 Å, ε 9100). The acetate, $C_{32}H_{50}O_3$, contains a secondary alcohol group since mild oxidation with chromic acid converts it into a keto-acetate, $C_{32}H_{48}O_3$, which also shows an intense ultra-violet absorption maximum at 2820 Å. The diol mono-acetate, $C_{32}H_{50}O_3$, and the keto-acetate, $C_{32}H_{48}O_3$, are, like oleana-9(11) : 12-dienyl acetate, strongly dextrorotatory.

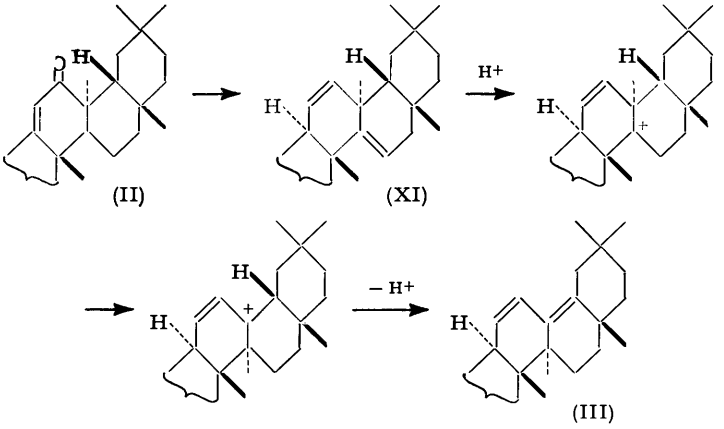
	$[\alpha]_D$	$\lambda_{max.}$	ε
Oleana-9(11) : 12-dienyl acetate	+337°	2820	9000
Oleana-9(11) : 12-diene-3 : 15-diol 3-acetate	+293	2820	9000
15-Oxo-oleana-9(11) : 12-dienyl acetate	+253	2820	9000



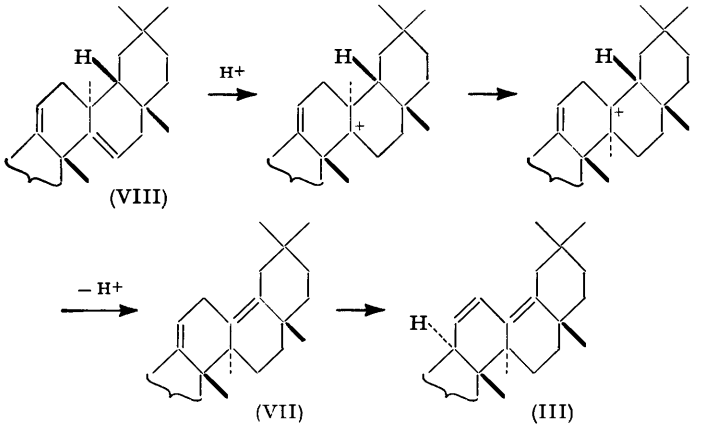
It is probable that treatment of the dienyl acetate (VIII) with perbenzoic acid results in attack of the 14 : 15-double bond to give an unstable oxide (IX), which either spontaneously, or during the isolation procedure, rearranges as shown. The alcohol-

acetate is accordingly considered to be oleana-9(11) : 12-diene-3 : 15-diol 3-acetate (X) and its oxidation product is 15-oxo-oleana-9(11) : 12-dienyl acetate.

The minor reaction product, m. p. 203°, from the Wolff–Kishner reduction of oxo-*iso*-β-amyradienyl acetate is also a non-conjugated dienyl acetate, $C_{32}H_{50}O_2$, which shows ethylenic absorption in the region 2000—2250 Å and gives a positive tetranitromethane test; it differs from oleana-9(11) : 13(18)- (VII) and -9(11) : 18-dienyl acetate. Treatment of the non-conjugated dienyl acetate, m. p. 203°, with hydrochloric acid in acetic acid yields oleana-11 : 13(18)-dienyl acetate (III). The acetate, m. p. 203°, is formulated as (XI) and a mechanism for its conversion into oleana-11 : 13(18)-dienyl acetate (III) is as depicted.

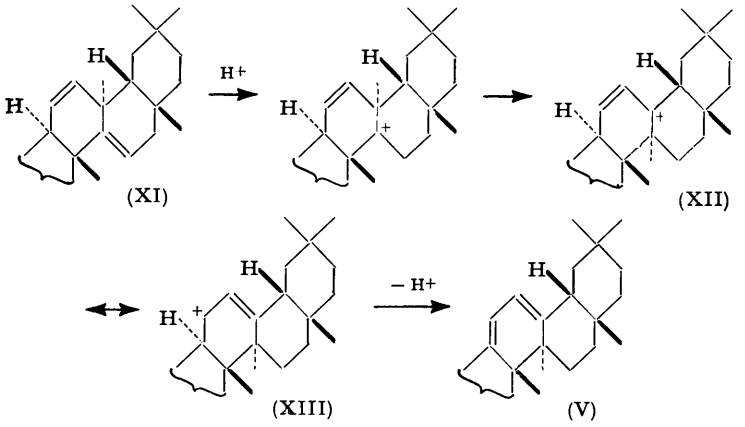


The two non-conjugated dienyl acetates, m. p.s 231° and 203°, obtained by Wolff–Kishner reduction of oxo-*iso*-β-amyradienyl acetate are assigned the structures (VIII) and (XI) respectively, the formation of (VIII) involving simple reduction of the carbonyl group of oxo-*iso*-β-amyradienyl acetate to a methylene group. The genesis of (XI) from oxo-*iso*-β-amyradienyl acetate involves reduction of the carbonyl group with double-bond migration; similar double-bond movements during Wolff–Kishner reductions are well

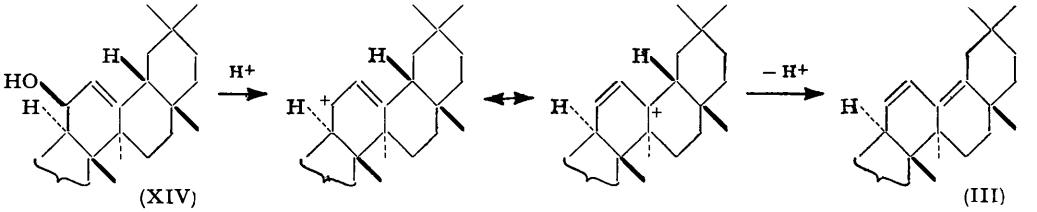


known. The mechanisms suggested above for the acid rearrangements of (VIII) and (XI) require support since an alternative mechanism for the acid rearrangement of (VIII), sketched in (VIII) ⇢ (VII) ⟶ (III), leads to oleana-11 : 13(18)-dienyl acetate (III); the last stage in this sequence has been realised (Beaton *et al.*, *loc. cit.*). The specific allocation of structure (VIII) rather than (XI) to the acetate, m. p. 231°, and consequently of (XI) rather than (VIII) to the acetate, m. p. 203°, rests on considerations which we believe to be compelling. If (VIII) is converted by acid into oleana-11 : 13(18)-dienyl

acetate as shown above, it follows that (VIII) represents the acetate, m. p. 203°, and consequently that the acetate, m. p. 231°, is (XI). In such a case, the conversion of the last acetate into (V) would proceed by the steps (XI) ⇢ (XII) ⟶ (XIII) ⟶ (V).



This mechanism includes an assumption which has been shown to be unwarranted. Reduction of 11-oxo-olean-12-enyl acetate with lithium aluminium hydride yields olean-12-ene-3β : 11β-diol, characterised as its 3-acetate (XIV). The β-configuration is ascribed to the 11-hydroxyl group because it is not acylatable and because on treatment with sodium acetate–acetic anhydride the diol monoacetate is readily dehydrated (*trans*-elimination) to oleana-9(11) : 12-dienyl acetate (V). Relatively mild treatment of (XIV) with mineral acid yields oleana-11 : 13(18)-dienyl acetate (III) and not oleana-9(11) : 12-dienyl acetate (V). It follows that the mechanism shown immediately above is incorrect. These considerations support the view that the non-conjugated dienyl acetate, m. p. 203°, is (XI) and that the non-conjugated dienyl acetate, m. p. 231°, is (VIII).

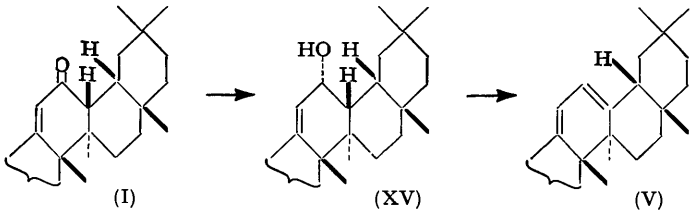


A consideration of the intensity of ultra-violet absorption in the region 2000—2250 Å does not allow differentiation between the two formulæ (VIII) and (XI) for the two non-conjugated dienyl acetates. Since (VIII) contains two triply substituted ethylene bonds, whereas (XI) has one triply substituted and one doubly substituted ethylene bond, it was expected that the former would show more intense absorption in the ethylenic region. The differences in this region are in fact trivial, probably because of vicinal optical effects, particularly in the case of (XI). However, molecular-rotation differences support the choice of (VIII) for the acetate, m. p. 231°; thus the conversion of 12-oxo-olean-9(11) enyl acetate into oxo*iso*-β-amyradienyl acetate is accompanied by a change in $[M]_D$ of approximately −480° and the comparable change from olean-9(11)-enyl acetate to the acetate, m. p. 231°, is accompanied by a $[M]_D$ change of −410°.

The behaviour of the two non-conjugated dienyl acetates with mineral acid raises the question of the mechanism of the conversion of oxo-*iso*-β-amyradienyl acetate into oleana-11 : 13(18)-dienyl acetate by Clemmensen reduction. It is known that simple Clemmensen reduction of 12-oxo-olean-9(11)-enyl acetate (I) proceeds without bond migration (Budziarek *et al., loc. cit.*). If this is the case with oxo-*iso*-β-amyradienyl acetate (II), the non-conjugated dienyl acetate (VIII) would be expected as an intermediate, and this, in the presence of mineral acid, is known to give oleana-9(11) : 12-dienyl acetate (V).

Since the reaction in fact leads to oleana-11 : 13(18)-dienyl acetate (III), either the mechanism of the Clemmensen reduction of (II) does not follow the simple course suggested, or the intermediate oleana-9(11) : 12-dienyl acetate (V) isomerises to the 11 : 13(18)-dienyl acetate (III). Although it is known that the 9(11) : 12-dienyl acetate is stable to relatively vigorous treatment with mineral acid, as shown by its formation from the acetate, m. p. 231°, with hydrochloric–acetic acid, we now find that prolonged treatment of the 9(11) : 12-dienyl acetate (V) with refluxing hydrochloric–acetic acid converts it into oleana-11 : 13(18)-dienyl acetate (III). This satisfactorily accounts for the formation of oleana-11 : 13(18)-dienyl acetate rather than oleana-9(11) : 12-dienyl acetate by the Clemmensen reduction of oxo-*iso*-β-amyradienyl acetate; it does not conflict with our views on either the structure of the dienyl acetate, m. p. 203°, or the mechanism of the conversion of this compound into oleana-11 : 13(18)-dienyl acetate since the acid conditions which complete this change do not isomerise oleana-9(11) : 12-dienyl acetate. In addition, the reaction conditions which convert olean-12-ene-3β : 11β-diol 3-acetate into oleana-11 : 13(18)-dienyl acetate are without effect on oleana-9(11) : 12-dienyl acetate. The reactions of oxo-*iso*-β-amyradienyl acetate described above are uniformly consistent with the view that it is correctly formulated as (II).

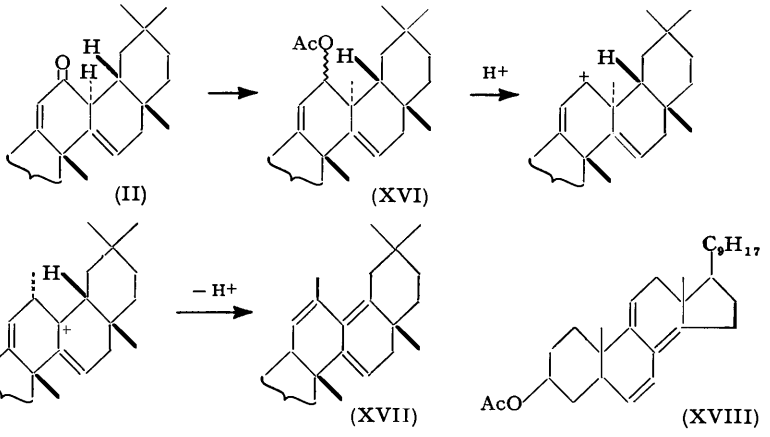
A related reaction leading to the formation of oleana-9(11) : 12-dienyl acetate in acid conditions is worthy of mention. Reduction of 12-oxo-olean-9(11)-enyl acetate (I) with lithium aluminium hydride followed by acetylation gives olean-9(11)-ene-3β : 12α-diol 3-acetate (XV). The configuration of the 12-hydroxyl group is considered to be α because the monoacetate undergoes simple dehydration (*trans*-elimination) when heated with pyridine– or sodium acetate–acetic anhydride, yielding oleana-9(11) : 12-dienyl acetate. When (XV) is treated with acetic–hydrochloric acid in conditions which convert olean-12-ene-3β : 11β-diol 3-acetate into oleana-11 : 13(18)-dienyl acetate, it is converted into oleana-9(11) : 12-dienyl acetate (V).



(I) (XV) (V)

The reduction of oxo-*iso*-β-amyradienyl acetate with lithium aluminium hydride has been described by Budziarek, Johnston, Manson, and Spring, and the product characterised as a diacetate, $C_{34}H_{52}O_4$, now formulated as (XVI); it shows strong ethylenic absorption between 2000 and 2250 Å. This diacetate is also obtained from oxo-*iso*-β-amyradienyl acetate by treatment with alcoholic sodium methoxide at 200°, followed by acetylation. Treatment of the diacetate (XVI) with hydrochloric–acetic acid leads to loss of acetic acid and formation of an acetate, $C_{32}H_{48}O_2$, which shows absorption maxima (in alcohol) at 2280 (ε 18,500), 2820 (ε 16,000), and 2940 Å (ε 12,500), from which we conclude that it is a conjugated trienyl acetate; it is different, however, from oleana-9(11) : 12 : 18-trienyl acetate, the only conjugated trienyl acetate in the oleanane series. The new trienyl acetate is provisionally formulated as (XVII) and contains a crossed chromophore similar to that in ergosta-6 : 8(14) : 9(11) : 22-tetraenyl acetate (XVIII) (Laubach, Schreiber, Agnello, Lightfoot, and Brunings, *J. Amer. Chem. Soc.*, 1953, **75**, 1514) which shows absorption maxima (in ether) at 2325 (log ε 4·25) and 2875 Å (log ε 3·82). The new trienyl acetate in presence of platinum in acetic acid very rapidly absorbs two mols. of hydrogen, to yield an isomer of β-amyrin acetate which we name *neo*-β-amyrin acetate. This is identical with the compound described as *iso*-β-amyradienyl acetate by Budziarek *et al.* (*loc. cit.*) who obtained it by catalytic reduction of either oxo-*iso*-β-amyradienyl acetate or the diacetate $C_{34}H_{52}O_4$. We find that the last two reactions proceed extremely slowly in highly purified acetic acid, rapidly in the presence of a trace of mineral acid. It is our view that a trace of mineral acid is essential for the success of these

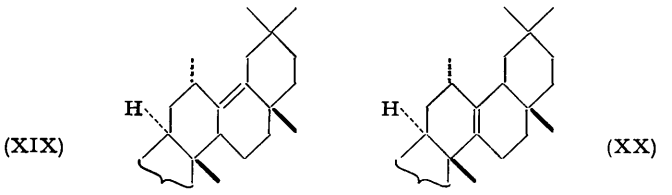
hydrogenolyses and that they proceed *via* the intermediate trienyl acetate. *neo*-β-Amyrin acetate gives an intense orange-red colour with tetranitromethane, and shows absorption



between 2000 and 2250 Å which is very similar to that of olean-13(18)-enyl acetate (δ-amyrin acetate) (see Table: as far as possible the measurements were made under comparable conditions):

	$\lambda_{max.}$	$\varepsilon_{max.}$	ε_{2100}	ε_{2150}	ε_{2200}	ε_{2250}
Olean-12-enyl acetate	2080	3200	3000	1550	520	190
Olean-9(11)-enyl acetate	2070	3100	2200	850	260	185
Olean-13(18)-enyl acetate	2110	5900	—	5100	3500	1800
neo-β-Amyrin acetate	2110	5000	—	4450	3100	1800

That *neo*-β-amyrin acetate is mono- and not di-ethenoid (as assumed by Budziarek *et al.*) was established by oxidation with chromic anhydride, potassium permanganate, or perbenzoic acid to an oxide, $C_{32}H_{52}O_3$, which does not give a colour with tetranitromethane and shows no absorption between 2000 and 3500 Å. When treated with hydrochloric acid the oxide gives a conjugated dienyl acetate which is different from the three known conjugated oleanadienyl acetates. The properties of *neo*-β-amyrin acetate show that it contains a fully substituted double bond; the most probable structures for it are (XIX) and (XX).



(XIX) (XX)

Experimental

Rotations were measured in $CHCl_3$ solutions at approx. 15°, and ultra-violet absorption spectra in EtOH with a Unicam SP. 500 spectrophotometer. A light petroleum fraction, b. p. 60—80°, was used for chromatography.

Wolff–Kishner Reduction of Oxo-iso-β-*amyradienyl Acetate.*—A mixture of oxo-*iso*-β-amyradienyl acetate (m. p. 220—221°; 2 g.), methanolic sodium methoxide (from 2 g. of sodium and 25 c.c. of methanol), and hydrazine hydrate (100%; 10 c.c.) was kept at 200° in an autoclave for 13 hr. The crude product was isolated in the usual manner and acetylated on the steam-bath for 2 hr. with pyridine (20 c.c.) and acetic anhydride (20 c.c.). The acetylated product crystallised from methanol–chloroform as plates (1·0 g.), m. p. 228—231° which, after four recrystallisations from the same solvent, yielded the *dienyl acetate*, m. p. 230—231°, $[\alpha]_D$ −9° (*c*, 2·0) (Found: C, 82·2; H, 10·9. $C_{32}H_{50}O_2$ requires C, 82·3; H, 10·8%). Light absorption: ε_{2120} 5000, ε_{2150} 4180, ε_{2200} 1700, ε_{2250} 320.

Concentration of the original methanol–chloroform mother-liquor yielded a second crop of

plates (0·5 g.), m. p. 175—195°, two recrystallisations of which from chloroform–methanol gave the same dienyl acetate, m. p. and mixed m. p. 230—231° (0·16 g.). Concentration of the mother-liquor from the second crop gave a third crop of plates (0·27 g.), m. p. 180—186°, five recrystallisations of which from chloroform–methanol yielded the isomeric *dienyl acetate*, m. p. 202—203°, $[\alpha]_D$ −95°, −93° (*c*, 1·0, 0·75) (Found: C, 82·6; H, 10·8%). It was recovered unchanged after being shaken in acetic acid with hydrogen and platinum at room temperature for 48 hr. Light absorption: ε_{2100} 5900, ε_{2150} 3700, ε_{2200} 1460, ε_{2250} 430.

Hydrolysis of the Dienyl Acetate, m. p. 230—231°.—The acetate, when refluxed with 3% ethanolic potassium hydroxide for 3 hr., gave a product which separated from methanol as needles, m. p. 193—195°. The *dienol* was obtained after four recrystallisations from methanol as needles, m. p. 195—196°, $[\alpha]_D$ −12° (*c*, 0·8), which gave a yellow colour with tetranitromethane in chloroform. Light absorption in EtOH: Max. at 2110 Å (ε 4500) (Found: C, 84·8; H, 11·4. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4%). Acetylation with acetic anhydride and pyridine followed by crystallisation of the product from methanol–chloroform gave the dienyl acetate as plates, m. p. 230·5—231°, $[\alpha]_D$ −8° (*c*, 2·5); the m. p. was undepressed when mixed with the parent dienyl acetate.

Conversion of the Dienyl Acetate, m. p. 230—231°, *into Oleana*-9(11) : 12-*dienyl Acetate.*—The dienyl acetate (150 mg.) in acetic acid (25 c.c.) was heated with concentrated hydrochloric acid (1 c.c.) on the steam-bath for 4 hr. The product was isolated by means of ether and warmed with acetic anhydride (5 c.c.) and pyridine (5 c.c.) for 1 hr. The acetylated product, isolated by means of ether and crystallised from chloroform–methanol, gave oleana-9(11) : 12-dienyl acetate as needles, m. p. and mixed m. p. 219·5—220°, $[\alpha]_D$ +337° (*c*, 1·5) (Found: C, 82·6; H, 11·1%). Light absorption: Max. at 2820 Å (ε 9000).

Conversion of the Dienyl Acetate, m. p. 202—203°, *into Oleana*-11 : 13(18)-*dienyl Acetate.*—A solution of the acetate (60 mg.) in acetic acid (50 c.c.) and concentrated hydrochloric acid (1 c.c.) was heated on the steam-bath for 7 hr. The product was isolated by means of ether and crystallised thrice from chloroform–methanol to yield oleana-11 : 13(18)-dienyl acetate (35 mg.) as plates, m. p. 227—228°, $[\alpha]_D$ −62° (*c*, 0·6), which gave a red-brown colour with tetranitromethane; a mixture with an authentic specimen prepared by oxidation of β-amyrin acetate with selenium dioxide was undepressed in m. p. Light absorption: Max. at 2420 (ε 22,000), 2510 (ε 27,200), and 2600 Å (ε 17,000). The same treatment of oleana-9(11) : 12-dienyl acetate gave, after two recrystallisations from aqueous acetone, a 70% return of the 9(11) : 12-dienyl acetate, m. p. 215—217°, $[\alpha]_D$ +336° (*c*, 0·7), absorption max. at 2820 Å (ε 9000).

Oxidation of the Dienyl Acetate, m. p. 230—231°, *with Selenium Dioxide.*—A solution of the acetate (0·5 g.) in glacial acetic acid (100 c.c.) was heated under reflux with selenium dioxide (0·5 g.) for 24 hr. The product was isolated by means of ether, and its solution in benzene filtered through a short column of alumina. The solvent was removed from the filtrate and the residue crystallised from chloroform–methanol, to give unchanged dienyl acetate (m. p. and mixed m. p. 230—231°; 50 mg.). The mother-liquor was evaporated to dryness and the residue crystallised from light petroleum (b. p. 60—80°), to yield 2 : 19-dioxo-β-amyra-9(11) : 13(18)-dienyl acetate (200 mg.) as prisms, m. p. 239—242°, which separated from aqueous methanol as square plates, m. p. 240—241°, $[\alpha]_D$ −91° (*c*, 1·5) undepressed in m. p. when mixed with an authentic specimen prepared by oxidation of β-amyrin acetate with selenium dioxide. Light absorption: Max. at 2780 Å (ε 11,700).

Oleana-9(11) : 12-*diene*-3 : 15-*diol* 3-*Acetate.*—A solution of the dienyl acetate, m. p. 230—231° (0·75 g.), in chloroform (35 c.c.) was treated with perbenzoic acid in chloroform (4·6 c.c., 1·3 mol.) at 0° and the solution kept at 0° for 4 days. A solution of the product, which was isolated by means of ether, in light petroleum (b. p. 60—80°)–benzene (3 : 1; 120 c.c.) was filtered through a column (14 × 2 cm.) of activated alumina (Grade I). The column was washed with light petroleum–benzene (3 : 1, 500 c.c.; then 9 : 4, 150 c.c.) which eluted a gum (197 mg.). Continued washing of the column with light petroleum–benzene (3 : 2, 150 c.c.; 9 : 7, 150 c.c.; 1 : 1, 550 c.c.; 2 : 3, 150 c.c.; 1 : 4, 100 c.c.) and with benzene (150 c.c.) eluted crystalline fractions which were combined (289 mg.) and recrystallised from light petroleum and then repeatedly from aqueous methanol, to yield *oleana*-9(11) : 12-*diene*-3 : 15-*diol* 3-*acetate* as plates, m. p. 270—270·5°, $[\alpha]_D$ +293° (*c*, 0·5) (Found: C, 79·6; H, 10·5. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%). It gives a brown colour with tetranitromethane.

15-*Oxo-oleana*-9(11) : 12-*dienyl Acetate.*—A solution of oleana-9(11) : 12-dien-3 : 15-diol 3-acetate (100 mg.) in glacial acetic acid (50 c.c.) was treated at room temperature with a solution of chromic anhydride (15·4 mg.) in acetic acid (12·5 c.c.), dropwise during 30 min. After 2 hr.

the green solution was diluted with water and the neutral product isolated by means of ether and crystallised from aqueous methanol, to yield 15-*oxo-oleana*-9(11) : 12-*dienyl acetate* (33 mg.) as prismatic needles, m. p. 249—250° $[\alpha]_D$ +252°, +253° (*c*, 0·5, 0·6) (Found: C, 79·9; H, 10·3. $C_{32}H_{48}O_3$ requires C, 79·95; H, 10·1%); it gives a red colour with tetranitromethane.

Rearrangement of Oleana-9(11) : 12-*dienyl Acetate to Oleana*-11 : 13(18)-*dienyl Acetate.*—A solution of oleana-9(11) : 12-dienyl acetate (200 mg.; m. p. 215—217°, $[\alpha]_D$ +338°) in acetic acid (100 ml.) was treated with a solution of concentrated hydrochloric acid (10 c.c.) in acetic acid (50 c.c.). The mixture was refluxed for 6 hr. with the addition of concentrated hydrochloric acid (5 c.c.) after 2, 4, and 6 hr. The mixture was set aside overnight and the product was isolated by means of ether and crystallised from chloroform–methanol, to yield oleana-11 : 13(18)-dienyl acetate (100 mg.) as plates, m. p. 224—225°, $[\alpha]_D$ −63° (*c*, 0·6). Light absorption: Max. at 2420 (ε 21,000), 2500 (ε 26,000), and 2600 Å (ε 16,000). A mixture with a specimen prepared by oxidation of β-amyrin acetate with selenium dioxide was undepressed in m. p.

Olean-12-*ene*-3β : 11β-*diol* 3-*Acetate.*—A solution of 11-oxo-olean-12-enyl benzoate (1 g.; m. p. 269—271°, $[\alpha]_D$ +112°) in dry ether (250 c.c.) was treated with lithium aluminium hydride (1 g.) and kept overnight. The product was isolated by means of ether and acetylated by acetic anhydride–pyridine on the steam-bath for 1 hr. The acetylated product separated from chloroform–methanol as needles (900 mg.), m. p. 200—205°, which gave a yellow colour with tetranitromethane. Four recrystallisations gave *olean*-12-*ene*-3β : 11β-*diol* 3-*acetate*, m. p. 209—210°, $[\alpha]_D$ +29° (*c*, 2·2) (Found: C, 79·1; H, 11·2. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%). Light absorption: Max. at 2100 Å (ε 5600).

Oleana-9(11) : 12-*dienyl Acetate from Olean*-12-*ene*-3β : 11β-*diol* 3-*Acetate.*—The diol monoacetate (250 mg.), anhydrous sodium acetate (400 mg.), and acetic anhydride (30 c.c.) were refluxed for 2 hr. The product was isolated by means of ether and crystallised from aqueous acetone, to give oleana-9(11) : 12-dienyl acetate (120 mg.) as fine needles, m. p. and mixed m. p. 214—217°, $[\alpha]_D$ +338° (*c*, 0·9). Light absorption: Max. at 2820 Å (ε 9000).

Oleana-11 : 13(18)-*dienyl Acetate from Olean*-12-*ene*-3β : 11β-*diol* 3-*Acetate.*—The diol monoacetate (200 mg.) in acetic acid (50 c.c.) was heated with concentrated hydrochloric acid (0·5 c.c.) on the steam-bath for 5 hr. The product was isolated by using ether and crystallised from chloroform–methanol, to give oleana-11 : 13(18)-dienyl acetate (120 mg.) as plates, m. p. and mixed m. p. 228—230°, $[\alpha]_D$ −62° (*c*, 0·8). Light absorption: Max. at 2500 (ε 29,000), 2420 (ε 24,000), and 2600 Å (ε 19,000).

Olean-9(11)-*ene*-3β : 12α-*diol* 3-*Acetate.*—12-Oxo-olean-9(11)-enyl acetate (1 g.) in dry ether (250 c.c.) was treated with lithium aluminium hydride (1 g.), and the mixture kept overnight. The product was isolated by means of ether (avoiding the use of mineral acid) and acetylated by acetic anhydride–pyridine at room temperature overnight. The acetylated product crystallised from aqueous acetone, to give *olean*-9(11)-*ene*-3β : 12α-*diol* 3-*acetate* (750 mg.) as needles, m. p. 177—178°, $[\alpha]_D$ +36° (*c*, 0·6) (Found: C, 79·51; H, 11·2. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%).

Oleana-9(11) : 12-*dienyl Acetate from Olean*-9(11)-*ene* 3β : 12α-*diol* 3-*Acetate.*—(*a*) The diol monoacetate (200 mg.), anhydrous sodium acetate (400 mg.), and acetic anhydride (30 c.c.) were refluxed for 2 hr. Crystallisation of the product from aqueous acetone gave oleana-9(11) : 12-dienyl acetate (100 mg.) as needles, m. p. 216—217°, $[\alpha]_D$ +335° (*c*, 0·7). Light absorption: Max. at 2820 Å (ε 9000). A mixture with an authentic specimen, m. p. 219—220°, was undepressed.

(*b*) A solution of the diol monoacetate (200 mg.) in acetic acid (50 c.c.) was heated with concentrated hydrochloric acid (0·5 c.c.) on the steam-bath for 3 hr. The product, isolated by means of ether and crystallised from aqueous acetone, gave oleana-9(11) : 12-dienyl acetate (110 mg.) as needles, m. p. and mixed m. p. 218—219°, $[\alpha]_D$ +338° (*c*, 0·6). Light absorption: Max. at 2820 Å (ε 9000). Oleana-9(11) : 12-dienyl acetate was isolated in similar yield when the solution in acetic acid containing hydrochloric acid was kept overnight at room temperature.

Reduction of Oxo-iso-β-*amyradienyl Acetate with Lithium Aluminium Hydride.*—A solution of oxo-*iso*-β-amyradienyl acetate (0·4 g.) in dry ether (100 c.c.) was refluxed with lithium aluminium hydride (0·3 g.) for 4 hr. The product isolated in the usual way (avoiding the use of mineral acid) was crystallised from aqueous methanol from which iso-β-*amyradienediol* separated as felted needles (0·3 g.), m. p. 202—204°, $[\alpha]_D$ −17° (*c*, 0·8) (Found: C, 81·8; H, 11·1. $C_{30}H_{48}O_2$ requires C, 81·8; H, 11·0%). The diol gives a yellow colour with tetranitromethane in chloroform.

Acetylation of the diol with pyridine and acetic anhydride gave the diacetate which separates as plates from methanol, m. p. 167—168°, $[\alpha]_D$ +25° (*c*, 1·0), undepressed in m. p. when mixed

with the specimen described by Budziarek *et al.* (*loc. cit.*). Benzoylation yielded iso-β-*amyradienediol dibenzoate*, fine needles (from chloroform–methanol), m. p. 233—234°, $[\alpha]_D$ +70° (*c*, 1·0) (Found: C, 81·6; H, 8·8. $C_{44}H_{56}O_4$ requires C, 81·4; H, 8·7%).

Reduction of Oxo-iso-β-*amyradienyl Acetate with Sodium Methoxide.*—A mixture of oxo-*iso*-β-amyradienyl acetate (1·0 g.) and methanolic sodium methoxide (from 1·25 g. of sodium and 15 c.c. of methanol) was kept at 200° in an autoclave for 6 hr. The product was isolated in the usual manner and acetylated by warm acetic anhydride–pyridine. A solution of the dry acetylated product in light petroleum (b. p. 60—80°; 50 c.c.) was filtered through activated alumina (Grade II) (18 × 2 cm.). Light petroleum (900 c.c.) eluted a fraction (500 mg.) which was crystallised from methanol, to yield *iso*-β-amyradienediol diacetate (400 mg.) as square plates, m. p. and mixed m. p. 165—167°, $[\alpha]_D$ +24° (*c*, 1·4) which gave a yellow colour with tetranitromethane.

Treatment of iso-β-*Amyradienediol Diacetate with Hydrochloric Acid.*—A solution of the diol diacetate (1·0 g.) in acetic acid (80 c.c.) was treated with concentrated hydrochloric acid (4 c.c.). After 1 hr., crystalline solid separated from the yellow mixture. Next morning the product was isolated by means of ether, and acetylated by pyridine–acetic anhydride. A solution of the acetylated product (900 mg.) in light petroleum (100 c.c.) was filtered through alumina (Grade I/II) (8·5 × 2 cm.), and the column washed with light petroleum (200 c.c.) and then with light petroleum–benzene (5 : 1; 750 c.c.) which eluted a crystalline solid (550 mg.; m. p. 163°). Crystallisation of this from methanol yielded the *trienyl acetate* as plates, m. p. 168—169°, $[\alpha]_D$ +58° (*c*, 1·0) (Found: C, 82·8; H, 10·2. $C_{32}H_{48}O_2$ requires C, 82·7; H, 10·4%). It gives a purple colour with tetranitromethane.

neo-β-*Amyrin Acetate.*—(*a*) A solution of the trienyl acetate (1·0 g.) in glacial acetic acid was shaken with hydrogen and platinum (from 0·5 g. of PtO_2). Hydrogen absorption was complete after 30 min. (approx. 110 c.c. at N.T.P.). The product, isolated in the usual manner, was crystallised from methanol–chloroform to give *neo*-β-amyrin acetate as needles, m. p. 225—227°, $[\alpha]_D$ +5·0° (*c*, 0·7), undepressed in m. p. when mixed with the specimen described as *iso*-β-amyradienyl acetate by Budziarek *et al.* *neo*-β-Amyrin acetate (m. p. 224—226°; $[\alpha]_D$ +6°) was also obtained by hydrogenation of the trienyl acetate in ethanol over palladised strontium carbonate.

(*b*) A solution of *iso*-β-amyradienediol diacetate (1·0 g.) in purified glacial acetic acid (75 c.c.) was shaken with platinum (from 0·7 g. of PtO_2) and hydrogen. Hydrogen uptake was extremely slow. After 18 hr. one drop of concentrated hydrochloric acid was added and shaking with hydrogen continued. Hydrogen uptake was then rapid. After 6 hr., the product was isolated in the usual manner and crystallised from chloroform–methanol, to yield *neo*-β-amyrin acetate (600 mg.) as needles, m. p. 226—227° undepressed when mixed with the specimen described above. A similar behaviour was observed with oxo-*iso*-β-amyradienyl acetate. When a platinum catalyst and glacial acetic acid were used, reduction of oxo-*iso*-β-amyradienyl acetate was extremely slow (complete after 4 days), the product being *neo*-β-amyrin acetate. Addition of one drop of concentrated hydrochloric acid to the acetic acid solution led to rapid absorption of hydrogen, the reaction being complete in 4 hr. The product was again identified as *neo*-β-amyrin acetate (m. p. and mixed m. p. 224—225°, $[\alpha]_D$ +5°). Hydrolysis of the acetate and benzoylation gave neo-β-*amyrin benzoate* as long needles, m. p. 186—187°, $[\alpha]_D$ +26° (*c*, 3·7) (Found: C, 83·3; H, 10·4. $C_{37}H_{54}O_2$ requires C, 83·7; H, 10·3%).

neo-β-*Amyrin Acetate Oxide.*—(*a*) *neo*-β-Amyrin acetate (0·55 g.) in acetic acid (50 c.c.) was treated at 100° with a solution of chromic oxide (0·25 g.) in water (5 c.c.) and acetic acid (80 c.c.), added dropwise during 30 min. The solution was kept at 100° for 90 min. and the neutral product isolated by means of ether. A solution of the product in light petroleum–benzene (5 : 2, 70 c.c.) was chromatographed on alumina (Grade II; 15 × 2 cm.). Elution with light petroleum–benzene (3 : 2, 200 c.c.) gave a fraction (175 mg.) which after crystallisation from methanol yielded neo-β-*amyrin acetate oxide* as prismatic needles, m. p. 203·5—204·5°, $[\alpha]_D$ −4° (*c*, 1·0) (Found: C, 79·4; H, 10·9. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%).

(*b*) A solution of *neo*-β-amyrin acetate (0·4 g.) in glacial acetic acid (150 c.c.) was treated with a solution of potassium permanganate (100 mg.) in acetic acid (25 c.c.) added dropwise at room temperature during 30 min. After 1 hr.' stirring the mixture was decolorised by the gradual addition of aqueous sodium hydrogen sulphite, and the product isolated by means of ether. Crystallisation from methanol yielded *neo*-β-amyrin acetate oxide (0·22 g.) as prisms, m. p. 207—208°, $[\alpha]_D$ −6° (*c*, 1·5) (Found: C, 79·3; H, 11·2%). A mixture with the specimen prepared by method (*a*) was undepressed in m. p. The oxide (m. p. 207—208°, $[\alpha]_D$ −5°) was obtained in 60% yield by oxidation of *neo*-β-amyrin acetate with perbenzoic acid in chloroform.

Treatment of neo-β-*Amyrin Acetate Oxide with Hydrochloric Acid* (with L. C. McKean).—A solution of *neo*-β-amyrin acetate oxide (150 mg.) in chloroform (3 c.c.) and glacial acetic acid (20 c.c.) was treated with concentrated hydrochloric acid (2 c.c.) and the mixture kept at room temperature for 18 hr. The neutral product, isolated by means of ether, was acetylated with pyridine–acetic anhydride. A solution of the acetylated product in light petroleum was decolorised by filtration through a short column of alumina. Evaporation of the filtrate followed by crystallisation (4 times) of the solid from aqueous acetic acid gave the *dienyl acetate* as plates, m. p. 192—194°, $[\alpha]_D$ −34° (*c*, 0·85) (Found: C, 82·3; H, 10·8. $C_{32}H_{48}O_2$ requires C, 82·7; H, 10·4%). Light absorption: Max. at 2580 Å (ε 20,000). The dienyl acetate gives a brown colour with tetranitromethane.

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