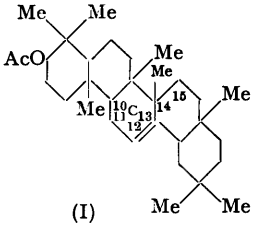
669. *Triterpene Resinols and Related Acids. Part XXII.** iso-β-*Amyrenonol and* iso-β-*Amyradienonol.*

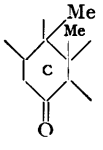
By Richard Budziarek, J. D. Johnston, William Manson, and F. S. Spring.

The reactions of the enol acetate of *iso*-β-amyrenonyl acetate show that the parent αβ-unsaturated ketone is correctly formulated as 2-acetoxyolean-10-en-12-one (VI). *iso*-β-Amyrin acetate, derived from *iso*-β-amyrenonyl acetate by catalytic or Clemmensen reduction, is shown to be 2-acetoxyolean-10-ene (IX) and it is concluded that the locking of rings B/C in β-amyrin corresponds to the more stable configuration. It is shown that Clemmensen reduction of *iso*-β-amyradienonyl acetate gives β-amyradienyl-II acetate (XVIII), and this and other reactions of *iso*-β-amyradienonyl acetate are discussed.

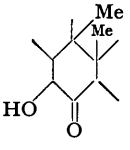
Oxidation of β-amyrin acetate (I) with hydrogen peroxide gives the saturated ketone β-amyranonyl acetate (II) (Spring, *J.*, 1933, 1345; Picard, Sharples, and Spring, *J.*, 1939, 1045). The amorphous solid obtained from the reaction mixture after the removal of β-amyranonyl acetate yielded an acetate $C_{32}H_{52}O_4$ which does not exhibit selective absorption of high intensity in the ultra-violet region and cannot be acetylated under normal conditions but is hydrolysed by alkali to the corresponding alcohol $C_{30}H_{50}O_3$. Of the structures (III) and (IV) which appear probable for this, the former was excluded since the acetate is stable to chromic anhydride at room temperature whereas (III) should give the enol of 2-acetoxy-oleanane-11 : 12-dione (Ruzicka and Jeger, *Helv. Chim. Acta*, 1941, **24**, 1178).



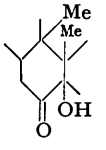
(I)



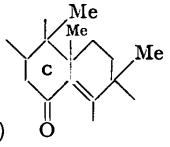
(II)



(III)



(IV)



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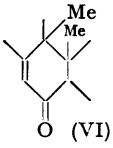
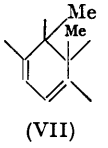
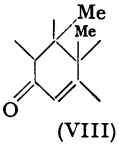


(VI)



(VII)

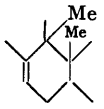


(VIII)

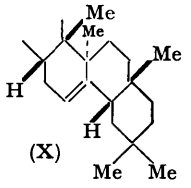
Treatment of the saturated ketone (II) with bromine gives bromo-β-amyranonyl acetate which readily loses hydrogen bromide to give *iso*-β-amyrenonyl acetate (Picard, Sharples, and Spring, *loc. cit.*; Seymour and Spring, *J.*, 1941, 319) for which the alternative structures (V) and (VI) have been considered (Green, Mower, Picard, and Spring, *J.*, 1944, 527; Spring, *Ann. Reports*, 1941, **38**, 198). A decision in favour of the latter has been made since reduction of *iso*-β-amyrenonyl acetate with sodium and alcohol, followed by treatment of the product with acetic anhydride, gives β-amyradienyl-I acetate (VII) containing a conjugated diene system in a single ring and identical with the product obtained by similar treatment of β-amyrenonyl acetate (VIII). Catalytic reduction of *iso*-β-amyrenonyl acetate gives an isomer of β-amyrin acetate which contains a >C:CH– linkage since it is oxidised by hydrogen peroxide to a saturated ketone isomeric with β-amyranonyl acetate. The isomeric β-amyrin acetate has been formulated as 2-acetoxyolean-10-ene (IX) (Jeger and Ruzicka, *Helv. Chim. Acta*, 1945, **28**, 209). This structure did not appear to us to be rigidly established, since hydrogenation of (VI) could proceed by reduction of the ethylenic linkage and simultaneous or consecutive reduction of the carbonyl group to a secondary alcohol, followed by dehydration to give an isomeric β-amyrin acetate (XI) differing from β-amyrin (X) solely in the orientation

* Part XXI, *J.*, 1951, 1093.

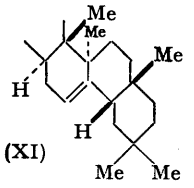
around $C_{(10)}$ * (cf. the catalytic reduction of β-amyranonol to β-amyrin described by Ruzicka and Jeger, *loc. cit.*, 1941). Of the alternative structures (IX) and (XI) for the isomeric β-amyrin acetate, the former has been established by Kishner–Wolff reduction of the derived isomeric β-amyranonyl acetate to a product which after acetylation gave β-amyranyl acetate (XII)



(IX)



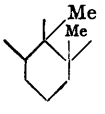
(X)

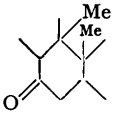


(XI)

identical with the compound obtained by similar treatment of β-amyranonyl acetate (Ruzicka and Jeger, *loc. cit.*, 1941). The isomeric β-amyranonyl acetate is therefore 2-acetoxyoleanan-11-one (XIII). An interesting point concerning the nature of the locking of rings B/C in the β-amyrin group of triterpenoids emerges from this series of changes. The conversion of β-amyrin into 2-acetoxyoleanan-11-one (XIII) and thence into β-amyranyl acetate (XII) proves that these rings are locked in the more stable configuration since the introduction of a carbonyl group at the 11-position and the subsequent treatment of this ketone would permit

(XII)

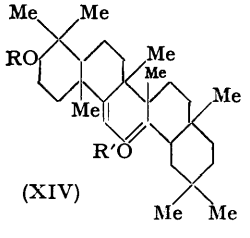




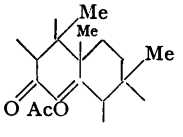
(XIII)

the change from a less to a more stable configuration at this junction. Since no such isomerisation occurs it is concluded that the more stable configuration exists in β-amyrin. Whether the more stable configuration is *cis* or *trans* remains to be established.

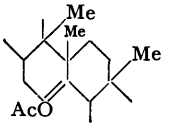
In an attempt further to characterise *iso*-β-amyrenonol by the formation of its benzoate, it was treated with benzoyl chloride and pyridine. The product proved to be an enol dibenzoate which gives a brown colour with tetranitromethane and exhibits selective absorption in the



(XIV)



(XV)

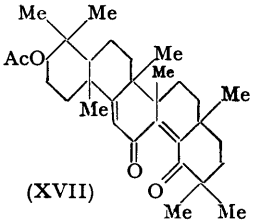


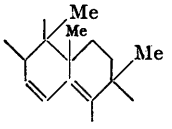
(XVI)

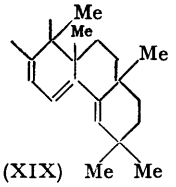
ultra-violet with maxima at 2300 Å (ε = 31,000) attributable to the two benzoyl groups and at 2750 Å (ε = 11,000) attributable to a diene system present in a single ring. The enol dibenzoate is therefore (XIV; R = R′ = COPh), and the structure of *iso*-β-amyrenonyl acetate as 2-acetoxyolean-10-en-12-one (VI) is confirmed. Treatment of *iso*-β-amyrenonyl acetate with acetic anhydride and sodium acetate gives an enol acetate (XIV; R = R′ = Ac) which exhibits an absorption maximum at 2780 Å characteristic of a conjugated diene system present in a single ring. The enol acetate grouping is easily hydrolysed with the re-formation of *iso*-β-amyrenonyl acetate. The structure (XIV; R = R′ = Ac) was supported by oxidation of the 10-ethylenic linkage of the enol acetate with hydrogen peroxide, with formation of 2-acetoxyoleanane-11 : 12-dione enol acetate (XV; R = Ac) previously obtained by Ruzicka and Jeger (*loc. cit.*, 1941) by chromic acid oxidation of the enol acetate of β-amyranonyl acetate (XVI; R = Ac). Two other oxidation products were obtained from the enol acetate (XIV; R = R′ = Ac) : selenium dioxide in acetic acid gave *iso*-β-amyradienonyl acetate, and *N*-bromosuccinimide in carbon tetrachloride gave, surprisingly, β-amyradienedionyl acetate (XVII).

* The configurations shown in (X) and (XI) are for the most part arbitrary and are used for comparative purposes only. The *cis*-locking of rings D/E, however, has been established by Barton and Holness (*Chem. and Ind.*, 1951, 233; Davy, Halsall, and Jones, *ibid.*, p. 233).

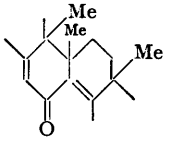
β-Amyradienedionyl acetate is obtained by the oxidation of β-amyrin acetate (I) (Jeger and Ruzicka, *Helv. Chim. Acta*, 1941, **24**, 1236), β-amyradienyl-I acetate (VII) (Picard and Spring, *J.*, 1941, 35), β-amyradienyl-II acetate (XVIII) (Ruzicka, Jeger, and Norymberski, *Helv. Chim. Acta*, 1942, **25**, 457; Barton and Brooks, *J.*, 1951, 257), and β-amyratrienyl acetate (XIX) (Newbold and Spring, *J.*, 1944, 532) with selenium dioxide; we find that

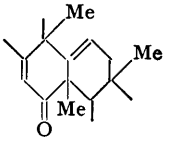

(XVII)

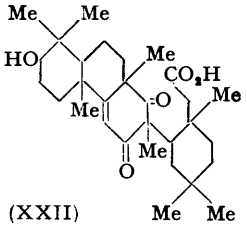

(XVIII)


(XIX)

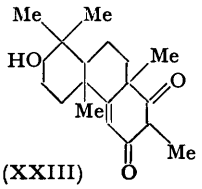
oxidation of *iso*-β-amyrin acetate (2-acetoxyolean-10-ene) (IX) with selenium dioxide also gives β-amyradienedionyl acetate. The interpretation of the complex reactions of β-amyradienedionyl acetate and of analogous compounds obtained from other members of the β-amyrin group of triterpenoids by Ruzicka and Jeger has provided weighty evidence in favour of part of the detail of the formula (I) for β-amyrin acetate. *iso*-β-Amyrenonyl acetate (VI) contains half of the chromophore of β-amyradienedionyl acetate (XVII) and accordingly

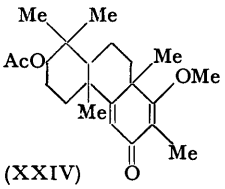

(XX)

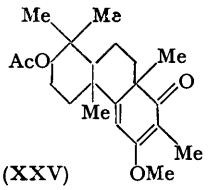

(XXI)


(XXII)

Green, Mower, Picard, and Spring (*loc. cit.*) attempted to correlate these two compounds by oxidation of the former with selenium dioxide in the expectation that β-amyradienedionyl acetate would result. Instead, the reaction gave *iso*-β-amyradienonyl acetate which shows an absorption maximum at 2450 Å (ε = 10,000) and unlike *iso*-β-amyrenonyl acetate gives a yellow colour with tetranitromethane. *iso*-β-Amyradienonyl acetate was also obtained by the action of bromine on *iso*-β-amyrenonyl acetate by the same workers and by Jeger and


(XXIII)

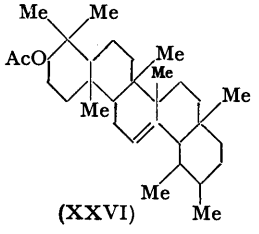

(XXIV)


(XXV)

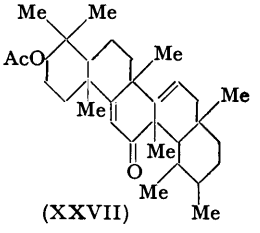
Ruzicka (*loc. cit.*, 1945); *iso*-β-amyradienonyl acetate can also be obtained directly from β-amyranonyl acetate by bromination. Green, Mower, Picard, and Spring (*loc. cit.*) suggested the structure (XX) for *iso*-β-amyradienonyl acetate, whereas Jeger and Ruzicka proposed the structure (XXI) in which it is represented as formed from *iso*-β-amyrenonyl acetate by the migration of the angular methyl group from $C_{(14)}$ to $C_{(13)}$ with simultaneous introduction of a 14 : 15-double bond. More recently Meisels, Jeger, and Ruzicka (*Helv. Chim. Acta*, 1950, **33**, 700) have oxidised *iso*-β-amyradienonyl acetate to a hydroxy-diketo-acid formulated as (XXII), the methyl ester of which on pyrolysis gave an acidic fraction represented as the hydroxy-diketone (XXIII). The hydroxy-diketone was characterised by methylation and acetylation which gave two isomeric compounds formulated as (XXIV) and (XXV) and identical with two compounds obtained by, in all essential features, the same route starting from α-amyrin. These reactions cannot be construed as *proof* of migration of the angular methyl group during conversion of *iso*-β-amyrenonyl acetate into *iso*-β-amyradienonyl acetate.

We find that Clemmensen reduction of *iso*-β-amyradienonyl acetate gives β-amyradienyl-II acetate (XVIII) which contains the same carbon skeleton as β-amyrin. In itself this reaction

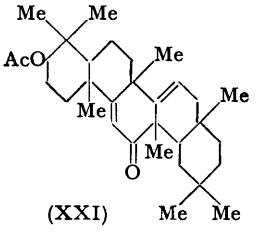
can be reconciled with the structure (XXI) for *iso*-β-amyradienonyl acetate by assuming that the strongly acid medium induces a second migration of the angular methyl group at $C_{(13)}$ to its original position at $C_{(14)}$, thus giving the dienone (XX), Clemmensen reduction of which would yield β-amyradienyl-II acetate. It was noted, however, that *iso*-β-amyradienonyl acetate was recovered unchanged after prolonged treatment with hydrochloric acid in acetic acid. On the other hand, the conversion of *iso*-β-amyradienonyl acetate into β-amyradienyl-II acetate could be considered to be proof that the carbon skeleton of both compounds is the same and that a methyl group has not changed its place during the conversion of the one into the other. In favour of such a view are the following very substantial facts: first, that *iso*-α-amyrenonyl acetate is oxidised by selenium dioxide to *iso*-α-amyradienonyl acetate which when oxidised and pyrolysed gives a product from which are isolated compounds (XXIV) and (XXV) identical with those obtained from *iso*-β-amyradienonyl acetate; and, secondly, that catalytic hydrogenation of *iso*-α-amyradienonyl acetate in acetic acid at room temperature gives *iso*-α-amyrenonyl acetate. The latter observation proves that *iso*-α-amyradienonyl acetate has the same carbon skeleton as α-amyrin and that *iso*-α-amyradienonyl acetate does not carry a methyl group at $C_{(13)}$ (McLean, Ruff, and Spring, *J.*, 1951, 1093). The conversion of both *iso*-α-amyradienonyl acetate and *iso*-β-amyradienonyl acetate into the compounds (XXIV) and (XXV) requires that *iso*-β-amyradienonyl acetate likewise does not carry such a methyl group. In marked contrast to the behaviour of *iso*-α-amyradienonyl acetate, *iso*-β-amyradienonyl acetate is reduced catalytically in acetic acid at room temperature with absorption of two molecular proportions of hydrogen and formation of *iso*-β-amyradienyl acetate which differs from each of the previously described isomers.



(XXVI)



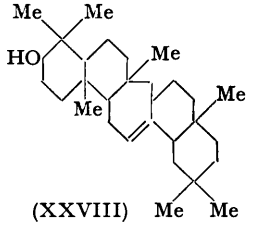
(XXVII)



(XXI)

iso-β-Amyradienyl acetate does not show selective absorption in the ultra-violet region, yet it gives an intense red colour with tetranitromethane in chloroform; within our experience this is the first example of a triterpene which does not contain a conjugated system of ethylenic bonds giving an intense red or brown colour with this reagent. This acetate is not isomerised by mineral acid. The carbonyl group of *iso*-β-amyradienonyl acetate is reduced by lithium aluminium hydride; the resulting diene-diol is characterised as its diacetate, catalytic reduction of which gives *iso*-β-amyradienyl acetate by hydrogenolysis of the acetoxy-group in ring C.

Our conclusions may be summarised as follows. A series of well-defined reactions of the α- and the β-amyrin group has been interpreted in terms of the formulations (I) for β-amyrin acetate and (XXVI) for α-amyrin acetate, by the assumption of migration of a methyl group in the changes *iso*amyrenonol ⟶ *iso*-amyradienonol. In the α-amyrin series the postulated migration is demonstrably incorrect since simple catalytic reduction of *iso*-α-amyradienonyl acetate yields the parent *iso*-α-amyrenonyl acetate. In the β-amyrin series, the postulated migration also appears unlikely (but not excluded) since *iso*-β-amyradienonol can be converted by Clemmensen reduction into a well-known derivative of β-amyrin which possesses the same carbon skeleton as the latter. The conversion of the *iso*-α- and the *iso*-β-amyradienonyl acetate into two common degradation products which apparently include the rings A—C of the triterpenes, suggests that in so far as these rings are concerned, the α- and β-amyradienonyl acetates have identical carbon skeletons; since (XXVII) is not an acceptable formulation for *iso*-α-amyradienonyl acetate, (XXI) for *iso*-β-amyradienonyl acetate is suspect. An attractive hypothesis to circumvent the anomalies described above is that neither α- nor β-amyrin carries a methyl group attachment at $C_{(14)}$ (cf. Jeger, Rüegg, and Ruzicka, *Helv. Chim. Acta*, 1947, **30**, 1294); in such an event the accommodation of the displaced carbon atom becomes a matter for speculation. The possibility that ring C is 7-membered (β-amyrin = XXVIII) (cf. Meyer, Jeger, Prelog, and Ruzicka, *Helv. Chim. Acta*, 1951, **34**, 747) has been considered by us for some



(XXVIII)

time, together with alternative methods for the accommodation of the carbon atom displaced from $C_{(14)}$. Such speculations are premature since the views expressed above are to a large measure dependent on the validity of the interpretation of the reactions leading from the *iso*-dienonyl acetates to the compounds (XXIV) and (XXV) and in particular on the validity of the structures ascribed to the last two compounds, which in our opinion require substantiation.

Experimental.

M. p. s are corrected; those taken on a Kofler block are marked (K). Specific rotations were measured at 15—20° in chloroform solutions in a 1-dm. tube.

β-Amyranonyl Acetate.—The following variation of the method described by Spring (*loc. cit.*) has been developed after many attempts to improve the yield of this intermediate. β-Amyrin acetate (m. p. 238—239°; 20 g.) in glacial acetic acid (1800 c.c.) was treated at 100° with a mixture of hydrogen peroxide (100-vol.; 150 c.c.) in glacial acetic acid (150 c.c.) added dropwise during 30 minutes with stirring. Stirring was continued for 2 hours at 100° and the solution again treated with hydrogen peroxide (100-vol.; 50 c.c.) in acetic acid (50 c.c.) during 15 minutes. The solution was kept at 100° for 1 hour and hot water was added until the mixture became faintly opalescent. The crystalline solid separating overnight was collected (m. p. 288—291°; 8·7 g.). The mother-liquor was heated to 100°, then treated with hot water until opalescent, and a second crop isolated (m. p. 286—287°; 2·0 g.). The two crops were combined, dissolved in light petroleum (b. p. 60—80°)–benzene (1 : 2; 300 c.c.), and purified by chromatography on an alumina column (Grade I/II, 46 × 3·5 cm.). Washing with the same solvent mixture (3450 c.c.) gave an eluate (7·05 g.) which when recrystallised from chloroform–methanol yielded β-amyranonyl acetate as plates, m. p. 300—301° (K) (299—300° in an open capillary), $[\alpha]_D$ −15° (*c*, 2·82), −15° (*c*, 5·83) (Found: C, 79·0; H, 10·7. Calc. for $C_{32}H_{52}O_3$: C, 79·3; H, 10·8%). Continued washing of the column successively with light petroleum (b. p. 60—80°)–benzene (1 : 4; 600 c.c.), benzene (600 c.c.), and benzene–ether (19 : 1) gave fractions (total, 1·3 g.), crystallisation of which from chloroform–methanol gave β-amyranonyl acetate, m. p. 299—300°, $[\alpha]_D$ −15°.

Hydrolysis of β-amyranonyl acetate by 3% alcoholic potassium hydroxide gave β-amyranonol as prisms (from aqueous acetone), m. p. 205—206°, $[\alpha]_D$ −26° (*c*, 2·77), acetylation of which gave β-amyranonyl acetate, m. p. 299—300°, $[\alpha]_D$ −15° (*c*, 2·50).

Acetate, $C_{32}H_{52}O_4$. After removal of the two crystalline crops from the "perhydrol" oxidation mixture, further dilution with water gave an amorphous solid. The liquor was poured into water and the solid collected. Attempted crystallisation of this solid was not successful. A solution of the dry amorphous solid (20 g.; obtained from the oxidation of 50 g. of β-amyrin acetate) in light petroleum (b. p. 60—80°)–benzene (3 : 1; 500 c.c.) was filtered through a column of activated alumina (Grade II/III, 40 × 3·5 cm.), and the column eluted with light petroleum–benzene (3 : 1). Fraction 1 (from 400 c.c.) was discarded. Fraction 2 (from 250 c.c.), thrice recrystallised from ethanol, gave β-amyranonyl acetate, m. p. and mixed m. p. 289—291° (0·7 g.). Fraction 3 (from 700 c.c.), recrystallised from ethanol to m. p. <280° and then from methanol, gave an *acetate* as prismatic needles, m. p. 288—289°, $[\alpha]_D$ +28·6° (*c*, 0·56) (Found: C, 76·5, 76·4; H, 10·5, 10·4. $C_{32}H_{52}O_4$ requires C, 76·75; H, 10·5%). A mixture with β-amyranonyl acetate had m. p. 263—273°. This acetate does not give a colour with tetranitromethane in chloroform or with aqueous alcoholic ferric chloride. The acetate was recovered unchanged after treatment (*a*) with acetic acid–hydrogen bromide at room temperature for 3 days, *b*) in benzene–acetic acid (1 : 9) with chromic anhydride (1·5 atoms of O) in acetic acid for 20 hours at room temperature, or (*c*) with bromine in acetic acid at 80°.

Attempted purification of other fractions from the chromatogram did not give homogeneous material.

Alcohol, $C_{30}H_{50}O_3$. A solution of the acetate (100 mg.) in alcoholic potassium hydroxide (3%; 5 c.c.) was refluxed for 3 hours. Isolation of the product by means of ether, followed by three crystallisations from methanol, gave the *alcohol* (60 mg.) as prisms, m. p. 249—250°, $[\alpha]_D$ +19·6° (±1·5°) (*c*, 1·33) (Found: C, 77·7; H, 11·2. $C_{30}H_{50}O_3$ requires C, 78·4; H, 11·0%). The alcohol separates from methanol with solvent of crystallisation which it retains tenaciously. When heated in a vacuum the substance disintegrates with loss of solvent which is complete only after three sublimations at 10^{-2} mm. and 180—210°, 210—230°, and 220—240° respectively. After this treatment the m. p. is unaltered.

The alcohol with pyridine–acetic anhydride gave the acetate $C_{32}H_{52}O_4$ as needles (from methanol), m. p. 292—293°, $[\alpha]_D$ +28·4° (*c*, 1·48), undepressed in m. p. when mixed with the acetate described above.

iso-*β-Amyrenonyl Acetate.*—This was prepared essentially as described by Picard, Sharples, and Spring (*loc. cit.*) except that the reaction was carried out at higher dilution (*e.g.*, 2·2 g. of β-amyranonyl acetate in 220 c.c. of acetic acid) and the bromine was reduced to 1·1—1·3 mols. After the bromination was complete, the solution was kept at room temperature for approx. 20 hours. To ensure that the dehydrohalogenation of the intermediate bromo-ketone (Seymour and Spring, *loc. cit.*) is complete, it is advisable to precipitate the reaction mixture with water, collect, wash, and dry the crude reaction product, and reflux a solution of this in acetic acid for 1 hour. Addition of boiling water to this solution gave *iso*-β-amyrenonyl acetate as hexagonal plates, m. p. 289—290°, $[\alpha]_D$ +62° (*c*, 1·33). Other preparations had m. p. 289—290°, $[\alpha]_D$ +61° (*c*, 1·15), m. p. 287—289°, $[\alpha]_D$ +60° (*c*, 2·2), and chromatography on alumina (Grade II) gave a specimen, m. p. 289—290°, $[\alpha]_D$ +60° (*c*, 2·3) (Found: C, 79·6; H, 10·4. Calc. for $C_{32}H_{50}O_3$: C, 79·6; H, 10·45%).

Hydrolysis of the acetate (purified by chromatography) gave *iso*-β-amyrenonol as prisms (from methanol), m. p. 249—250°, $[\alpha]_D$ +57·5° (*c*, 1·55). Acetylation by acetic anhydride–pyridine gave the acetate as plates (from acetone), m. p. 290—291·5°, $[\alpha]_D$ +61·5° (*c*, 1·40).

Enol Benzoate of iso-*β-Amyrenonyl Benzoate.*—A solution of *iso*-β-amyrenonol (90 mg.) in pyridine (1 c.c.) was treated with 3 drops of benzoyl chloride, and the mixture heated at 100° for 4 hours. The product, isolated by means of ether in the usual manner, crystallised from acetone–methanol (1 : 1) as plates (65 mg.), m. p. 225·5—227°. After four recrystallisations from methanol the *enol benzoate* was obtained as plates, m. p. 235—235·5°, $[\alpha]_D$ +246° (*c*, 1·22) (Found: C, 81·1; H, 8·4. $C_{44}H_{56}O_4$ requires C, 81·4; H, 8·6%). Light absorption in ethanol: Max. at 2300 (ε = 31,000) and 2750 Å (ε = 11,000). The enol benzoate gives a red-brown colour with chloroformic tetranitromethane.

Enol Acetate of iso-*β-Amyrenonyl Acetate.*—A solution of *iso*-β-amyrenonyl acetate (1·0 g.) in acetic anhydride (60 c.c.) containing freshly fused sodium acetate (0·5 g.) was heated under reflux for 80 hours. The reaction mixture was treated with water and extracted with ether. The extract was washed with water, shaken with charcoal, and dried (Na_2SO_4). After removal of the ether the residue crystallised from chloroform–methanol, to give the *enol acetate* (0·85 g.) as prismatic needles, m. p. 216·5—217°, $[\alpha]_D$ +201° (*c*, 1·60) (Found: C, 77·5; H, 9·9. $C_{34}H_{52}O_4$ requires C, 77·8; H, 9·9%). Light absorption in ethanol: Max. at 2780 Å (ε = 8500). The enol acetate gives a brown colour with tetranitromethane in chloroform. The enol ester group is easily hydrolysed, attempted purification by chromatography on alumina giving *iso*-β-amyrenonyl acetate in quantitative yield. The enol acetate was recovered unchanged after treatment with bromine in glacial acetic acid at 60°.

Enol Acetate of 2-*Acetoxyoleanane*-11 : 12-*dione.*—A solution of the enol acetate of *iso*-β-amyrenonyl acetate (0·3 g.) in acetic acid (20 c.c.) was treated with vigorous stirring at 100° with 10 c.c. of a solution of hydrogen peroxide (30%; 25 c.c.) in acetic acid (25 c.c.). After 1 hour a second addition of the peroxide–acetic acid mixture (20 c.c.) was made, stirring continued for 2 hours, and the remainder of the peroxide solution added. After a further hour the solution was diluted with water, and the solid collected and crystallised from chloroform–methanol, giving the enol acetate of 2-acetoxyoleanan-11 : 12-dione as flat needles, m. p. 228—229°, $[\alpha]_D$ +80° (*c*, 1·50). The compound does not give a colour with tetranitromethane in chloroform and exhibits an absorption maximum at 2550 Å (ε = 10,900). A specimen prepared by oxidation of the enol acetate of β-amyranonyl acetate as described by Ruzicka and Jeger (*loc. cit.*, 1941) separated from chloroform–methanol as flat prismatic needles, m. p. 233—234° (K), $[\alpha]_D$ +78° (*c*, 1·2), exhibited an absorption maximum (in alcohol) at 2550 Å (ε = 11,200), and was undepressed in m. p. when mixed with the specimen obtained by the oxidation of the enol acetate of *iso*-β-amyrenonyl acetate.

β-Amyradienedionyl Acetate.—A solution of the enol acetate of *iso*-β-amyrenonyl acetate (0·4 g.) and *N*-bromosuccinimide (0·5 g.), in dry carbon tetrachloride was heated under reflux for 8 hours, during which the solution developed a deep yellow colour and hydrogen bromide was evolved. The filtered solution was evaporated to dryness, and the residue triturated with warm water. The solid was collected, dried, and twice crystallised from aqueous methanol, yielding β-amyradienedionyl acetate as square plates, m. p. 237—238° (K), $[\alpha]_D$ −95° (*c*, 0·25), giving a negative reaction with tetranitromethane and showing an absorption maximum (in alcohol) at 2780 Å (ε = 10,000). When mixed with a specimen obtained by the oxidation of β-amyrin acetate with selenium dioxide {m. p. 236—237°, $[\alpha]_D$ −94° (*c*, 1·73)} there was no depression in m. p.

2-*Acetoxyolean*-10-*ene.*—*iso*-β-Amyrenonyl acetate (0·30 g.) in acetic acid (80 c.c.) containing concentrated hydrochloric acid (15 c.c.) was treated with amalgamated zinc (9 g.) and kept at 100° for 6 hours during which additions of concentrated hydrochloric acid (5 c.c.) were made at two-hourly intervals. The hot solution was decanted into water, and the solid collected, washed, dried, and crystallised from methanol–chloroform, to yield a crystalline solid (155 mg.), m. p. 240—255°. The solid was readily separated by chromatography of a light petroleum–benzene solution (4 : 1; 50 c.c.) on activated alumina (Grade II, 14 × 1·5 cm.) into a fraction I (94 mg.) eluted by light petroleum–benzene (4 : 1; 200 c.c.) and a fraction II (53 mg.) eluted by benzene (150 c.c.). Crystallisation of fraction I from chloroform–methanol gave 2-acetoxyolean-10-ene as plates, m. p. 250—251°, $[\alpha]_D$ +77° (*c*, 0·3) (Found: C, 82·1; H, 11·4. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·2%). A mixture with a specimen of the isomeric β-amyrin acetate {plates from methanol–chloroform; m. p. 250—251°, $[\alpha]_D$ +77° (*c*, 1·64)} prepared by the catalytic hydrogenation of *iso*-β-amyrenonyl acetate (Jeger and Ruzicka, *loc. cit.*, 1945) showed no depression in m. p. Crystallisation of fraction II from chloroform–methanol gave *iso*-β-amyrenonyl acetate as plates, m. p. 285—286° undepressed when mixed with a specimen of the starting material.

β-Amyranyl Acetate.—2-Acetoxyoleanan-11-one [plates from chloroform–methanol; m. p. 338—339° (evacuated tube)] was prepared as described by Jeger and Ruzicka (*loc. cit.*, 1945). A solution of the keto-acetate (250 mg.) and hydrazine (100%; 2 c.c.) in ethanolic sodium ethoxide (7·5%; 10 c.c.) was kept at 200—210° for 18 hours in an autoclave. The acetylated reaction product (85 mg.) was dissolved in light petroleum (b. p. 60—80°)–benzene (2 : 1; 50 c.c.) and filtered through a column of alumina (Grade II, 10 × 1·25 cm.). Washing with the same solvent mixture (50 c.c.) gave a fraction (30 mg.), crystallisation of which from chloroform–methanol yielded β-amyranyl acetate as plates, m. p. 282—284°, $[\alpha]_D$ +24° (*c*, 0·46), undepressed when mixed with a specimen prepared by reduction of β-amyranonyl acetate as described by Ruzicka and Jeger (*Helv. Chim. Acta*, 1941, **24**, 1178).

iso-*β-Amyradienonyl Acetate.*—(a) *Selenium dioxide method.* Oxidation of *iso*-β-amyrenonyl acetate ($[\alpha]_D$ +60°; 1 g.) was effected as described by Green, Mower, Picard, and Spring (*loc. cit.*) with the difference that the period of reflux was 48 hours. The hot mixture was filtered and the solution diluted with water. The solid was collected, washed, and dried. A solution of the solid in ether was washed with 5% aqueous potassium cyanide. After being washed with water and freed from ether, the solid crystallised from acetone as plates, m. p. 208—216°. Recrystallisation again gave plates, m. p. 212—213°, but a third crystallisation from the same solvent gave prisms (0·3 g.), m. p. 220—221°, not altered in crystalline form or in m. p. by further crystallisation. After sublimation at 180—190°/10^{-3} mm., *iso*-β-amyradienonyl acetate had m. p. 220—221·5°, $[\alpha]_D$ −38·3° (*c*, 1·07) (Found: C, 79·6; H, 9·9.

Calc. for $C_{32}H_{48}O_3$: C, 80·0; H, 10·1%). By combination and concentration of mother-liquors, a further crop (0·2 g.) of *iso*-β-amyradienonyl acetate was obtained having m. p. 217—218·5°.

In another experiment, the crude reaction product separated as plates, m. p. 202—204°, from aqueous alcohol. When this material was recrystallised from acetone, large plates separated which were kept overnight in contact with its mother-liquor. The plates had then changed into prisms, m. p. 215—217·5°. Recrystallisation from the same solvent gave *iso*-β-amyradienonyl acetate as prisms which when dried for a week in a vacuum over phosphoric oxide at 135° had m. p. 220—221°, $[\alpha]_D$ −39·8° (*c*, 1·32). Light absorption in ethanol: Max. at 2450 Å (ε = 10,100) with an inflection at 3400 Å.

(b) *Bromine method.* β-Amyranonyl acetate (1·9 g.; m. p. 292°) in glacial acetic acid (150 c.c.) was treated with a solution of bromine in glacial acetic acid (8%; 2·1 mols.) during 5 minutes at 90°. The solution was kept at 90° for 1 hour and then overnight at room temperature. The mixture was diluted with water, and the solid collected, washed, dried, and crystallised from acetone. The first crop (0·34 g.) separated as plates, m. p. 278—280°, which did not give a colour with tetranitromethane in chloroform and proved to be *iso*-β-amyrenonyl acetate. The second crop consisted of prisms contaminated with a small number of plates. The two forms were separated mechanically into plates (0·03 g.), m. p. 215—255°, giving no colour with tetranitromethane, and prisms (0·69 g.), m. p. 207—209°, $[\alpha]_D$ −25° (*c*, 2·1), which gave a yellow colour with tetranitromethane. Recrystallisation of the prisms from acetone gave prisms (0·56 g.), m. p. 214—217°. A solution of this solid (0·53 g.) in light petroleum (b. p. 60—80°)–benzene (5 : 1; 100 c.c.) was filtered through a column of activated alumina (Grade II, 15 × 2 cm.). Light petroleum (330 c.c.), followed by light petroleum–benzene (4 : 1; 220 c.c.), eluted *iso*-β-amyradienonyl acetate (400 mg.) which after crystallisation from acetone (prisms), followed by sublimation, had m. p. 218—219·5°, $[\alpha]_D$ −39·8° (*c*, 1·97) (Found: C, 80·0; H, 9·7. Calc. for $C_{32}H_{48}O_3$: C, 79·95; H, 10·1%).

(c) *From the enol acetate of* iso-β-*amyrenonyl acetate.* The enol acetate of *iso*-β-amyrenonyl acetate (0·45 g.; m. p. 216—217°) was refluxed in stabilised glacial acetic acid with selenium dioxide for 72 hours. Selenium was removed by filtration, the filtrate diluted with water, and the mixture extracted with ether. The extract was washed successively with water and 5% potassium cyanide solution. After drying ($MgSO_4$), the extract was evaporated to dryness and the residue (0·43 g.) fractionally crystallised from chloroform–methanol. The first two crops (0·34 g.) separated as needles, m. p. 215—216° undepressed when mixed with the enol acetate of *iso*-β-amyrenonyl acetate. The third crop (0·06 g.) separated as needles, m. p. 190—196°; it was thrice recrystallised from the same solvent, to give *iso*-β-amyradienonyl acetate as prisms, m. p. 218—219°, depressed to 180—195° when mixed with the enol acetate of *iso*-β-amyrenonyl acetate, and undepressed when mixed with a specimen of *iso*-β-amyradienonyl acetate prepared by method (a); it had $[\alpha]_D$ −39° (*c*, 0·70). Light absorption in ethanol: Max. at 2450 Å (ε = 11,200).

iso-β-*Amyradienonol.*—This was obtained by hydrolysis of the acetate (m. p. 219—220°; $[\alpha]_D$ −38°) with 3% alcoholic potassium hydroxide. It separates from methanol as large hard prisms, m. p. 241—242°, $[\alpha]_D$ −51° (*c*, 1·24). Reacetylation using pyridine and acetic anhydride gave *iso*-β-amyradienonyl acetate as prisms (from methanol), m. p. 220—221°, $[\alpha]_D$ −40° (*c*, 0·95).

A solution of *iso*-β-amyradienonol (80 mg.) in pyridine (1 c.c.) and benzoyl chloride (0·15 c.c.) was heated at 100° for 3 hours. The product, isolated in the usual manner, crystallised from methanol to give iso-β-*amyradienonyl benzoate*, m. p. 207—208°, $[\alpha]_D$ −23° (*c*, 0·80) (Found: C, 81·5; H, 9·0. $C_{37}H_{50}O_3$ requires C, 81·9; H, 9·3%).

Clemmensen Reduction of iso-β-*Amyradienonyl Acetate.*—A hot solution of *iso*-β-amyradienonyl acetate (prepared by the selenium dioxide method; 0·5 g.) in hot acetic acid (40 c.c.) was treated with concentrated hydrochloric acid (10 c.c.) and added to freshly amalgamated zinc (from 15 g. of zinc), and the mixture heated under reflux for 30 minutes. The product, isolated in the usual manner, separated from acetic acid as plates (220 mg.), m. p. 204—210°. It was recrystallised from acetone and then thrice from alcohol, to yield β-amyradienyl-II acetate as plates, m. p. 227—228°, $[\alpha]_D$ −61·8° (*c*, 2·08) (Found: C, 82·6; H, 10·6. Calc. for $C_{32}H_{50}O_2$: C, 82·3; H, 10·8%). It gives a red-brown colour with tetranitromethane in chloroform. Light absorption in alcohol: Max. at 2515 (ε = 28,200), 2435 (ε = 24,700), and 2600 Å (ε = 18,000). A mixture with a specimen (m. p. 227—228°) prepared by selenium dioxide oxidation of β-amyrin acetate had m. p. 227—228°.

iso-β-*Amyradienyl Acetate.*—(*a*) A solution of *iso*-β-amyradienonyl acetate (200 mg.; m. p. 220°) in glacial acetic acid (50 c.c.) was added to a suspension of freshly reduced platinum catalyst (from 100 mg. of platinum oxide) in glacial acetic acid (10 c.c.) and the mixture shaken with hydrogen at 16°. Absorption of hydrogen was at first rapid, and after 45 minutes approximated to 1 mol. After 44 hours the apparent absorption of hydrogen was between 2 and 3 mols. The product, isolated in the usual manner and crystallised repeatedly from methanol, gave iso-β-*amyradienyl acetate* as feather-like crystals, m. p. 225—226°, $[\alpha]_D$ +5·2° ±1° (*c*, 1·95) (Found: C, 82·0; H, 11·2. $C_{32}H_{50}O_2$ requires C, 82·3; H, 10·8%). *iso*-β-Amyradienyl acetate gives a red-brown colour with chloroformic tetranitromethane and does not exhibit selective absorption in the ultra-violet region.

(*b*) A solution of *iso*-β-amyradienonyl acetate (400 mg.) in ether (50 c.c.) was added dropwise to a suspension of lithium aluminium hydride (300 mg.) in ether (40 c.c.). The mixture was refluxed for 4 hours, treated with water, and acidified with dilute sulphuric acid. The ethereal solution was separated, washed, dried, and evaporated. The product was acetylated by warming it with acetic anhydride (0·5 c.c.) in pyridine (3 c.c.) for 3 hours; crystallisation from aqueous methanol then gave the *diacetate* (360 mg.) as square plates, m. p. 167—168°, $[\alpha]_D$ +25·4° (*c*, 1·0) (Found: C, 78·0; H, 10·05. $C_{34}H_{52}O_4$ requires C, 77·8; H, 10·0%). The diacetate gives a yellow colour with tetranitromethane in chloroform and does not exhibit selective absorption of appreciable intensity in the ultra-violet region.

A solution of the diacetate, m. p. 167—168° (100 mg.), in glacial acetic acid (20 c.c.) was added to a suspension of a freshly reduced platinum catalyst (from 100 mg. of platinum oxide) in glacial acetic acid (100 c.c.) and the mixture shaken with hydrogen for 20 hours. The product was isolated in the usual manner and crystallised from methanol, to give *iso*-β-amyradienyl acetate as needles, m. p. 223—224°, $[\alpha]_D$ +5·3° (*c*, 0·95), giving a red colour with tetranitromethane and showing no selective absorption in the ultra-violet region. A mixture with a specimen m. p. 225° prepared by method (*a*) had m. p. 224—225°.

Grateful acknowledgment is made to the Department of Scientific and Industrial Research for the award of a maintenance grant (to J. D. J.).

THE ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, June 25th*, 1951.]