736. *Triterpene Resinols and Related Acids. Part XXIV.** 18-iso-β-*Amyranol.*

By Richard Budziarek, William Manson, and F. S. Spring.

Treatment of β-amyrenonyl benzoate (VIII; R = Bz, R′ = Me) with alkali is shown to give 18-*iso*-β-amyrenonol (XI; R = H). Catalytic hydrogenation of 18-*iso*-β-amyrenonyl acetate yields 18-*iso*-β-amyrin acetate (XII; R = Ac), oxidation of which with hydrogen peroxide yields a saturated ketone, 18-*iso*-β-amyranonyl acetate (XV; R = Ac). Reduction of the latter by the Kishner–Wolff procedure gives 18-*iso*-β-amyranol (XVI; R = H) which differs from the saturated pentacylic triterpenoid alcohols hitherto described.

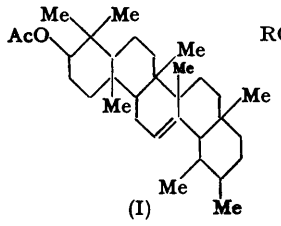
Oxidation of β-amyrin acetate with chromic anhydride in acetic acid gives an 8% yield of acetone, isolated as its 2 : 4-dinitrophenylhydrazone. Similar oxidation of α-amyrin acetate does not give acetone. The triterpenoid acetates employed were purified to constant optical rotation, and were rigorously dried; a common batch of purified acetic acid was employed and the oxidations were effected under as far as possible identical conditions. The structures ascribed to the α- (I) and the β- (II; R = Ac) acetate differ only in the nature of ring E, and there is evidence that they are sterically identical at $C_{(5)}$, $C_{(8)}$, $C_{(9)}$, $C_{(10)}$, and possibly at $C_{(14)}$.

Ames, Halsall, and Jones (*J.*, 1951, 450) have shown that lupenyl acetate (III; R = Ac), which contains an *iso*propenyl group attached to ring E, is isomerised by mineral acid to δ-amyrin acetate (IV), itself obtained from β-amyrin acetate by a two-stage process. It has been established (Davy, Halsall, and Jones, *Chem. and Ind.*, 1951, 233; Barton and Holness, *Chem. and Ind.*, 1951, 233) that rings D/E in lupeol (III; R = H) are *trans*-fused and that the rings D/E in β-amyrin (II; R = H) are *cis*-fused. Consequently, structural differences apart, lupanol (dihydrolupeol) (V) and β-amyranol (dihydro-β-amyrin) (VI) differ in orientation around $C_{(18)}$. Before attempting to assess the significance of the formation of acetone from β-amyrin acetate, we considered it essential to prepare 18-*iso*-β-amyranol (VII) in order to compare it with lupanol and other saturated pentacyclic triterpenoid alcohols.

A simple route to 18-*iso*-β-amyranol appeared to be available since indications existed in the literature that epimerisation at $C_{(18)}$ in β-amyrenonol could be achieved. Thus in a discussion

* Part XXIII, preceding paper.

concerning the physical constants of β-amyrenonol and its esters, Ruzicka, Müller, and Schellenberg (*Helv. Chim. Acta*, 1939, **22**, 758) reported that treatment of β-amyrenonol (m. p. 230—231°, $[\alpha]_D$ +102°) (VIII; R = H, R′ = Me) for a prolonged period with 10% alcoholic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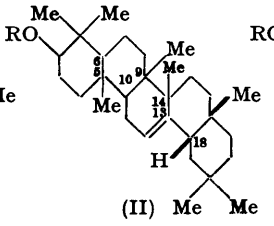
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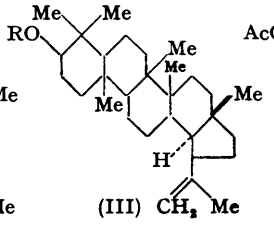
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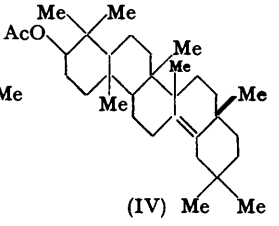
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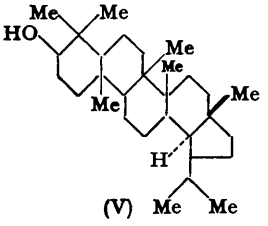
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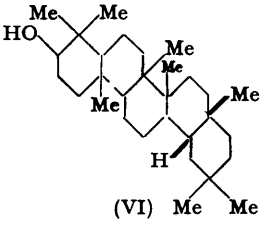
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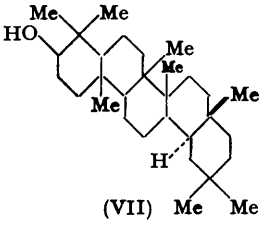
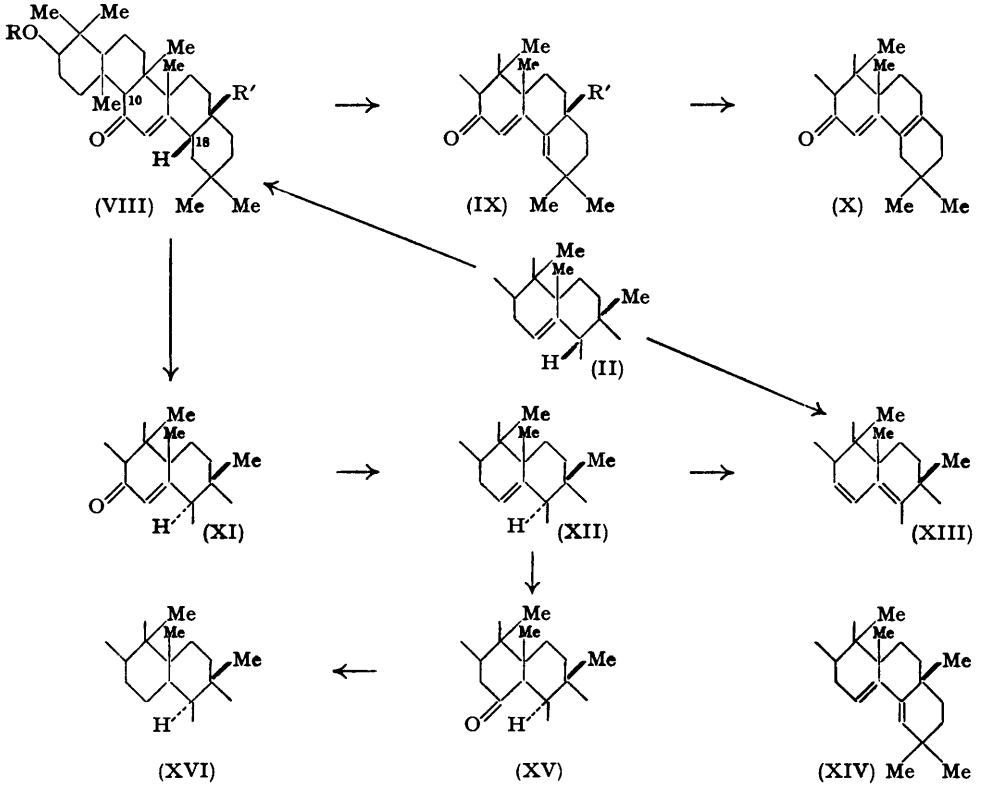

(VII)

alkali gave an isomer, m. p. 247—248°, $[\alpha]_D$ +81·5°. This isomerisation could involve either $C_{(10)}$ or $C_{(18)}$ or both centres simultaneously, but the fact that bromination of β-amyrenonyl acetate (VIII; R = Ac, R′ = Me) proceeds smoothly to give β-amyradienonyl acetate (Picard


(VIII) (IX) (X) (II) (XI) (XII) (XIII) (XVI) (XV) (XIV)

and Spring, *J.*, 1941, 35) (IX; R = Ac, R′ = Me) suggests that enolisation of β-amyrenonyl acetate involves $C_{(18)}$. Furthermore, reduction of β-amyradienonyl acetate by using sodium ethoxide and hydrazine gave a complex mixture from which an *allo*-β-amyrenonyl acetate was

obtained; this probably differs from β-amyrenonyl acetate in the orientation around $C_{(18)}$ (Green, Mower, Picard, and Spring, *J.*, 1944, 527). Kitasato (*Acta Phytochim.*, 1934—1935, **8**, 1, 315) has shown that methyl acetylketo-oleanolate (VIII; R = Ac, R′ = CO_2Me) is isomerised by mineral acid to a ψ-isomer; that this isomerisation also involves $C_{(18)}$ is indicated by the fact that bromination of acetylketo-oleanolic acid (VIII; R = Ac, R′ = CO_2H) gives the conjugated acetylolean-12 : 18-dien-11-onolic acid (IX; R = Ac, R′ = CO_2H) (Ruzicka, Jeger, and Winter, *Helv. Chim. Acta*, 1943, **26**, 265). We have found that when melted, the dienone-acid loses carbon dioxide rapidly to give nor-β-amyradienonyl acetate (X; R = Ac) identical with the compound obtained originally by Ruzicka, Cohen, Furter, and Sluys-Veer (*Helv. Chim. Acta*, 1938, **21**, 1735) by prolonged treatment of acetylketo-oleanolic acid (VIII; R = Ac, R′ = CO_2H) with boiling quinoline. The ease of decarboxylation of the dienone-acid indicates that it is a βγ-unsaturated acid and that it is correctly formulated as (IX; R = Ac, R′ = CO_2H). Barton and Holness (*loc. cit.*) have recently reported that the alkali isomerisation of methyl acetylketo-oleanolate involves inversion at $C_{(18)}$.

We find that treatment of β-amyrenonyl benzoate with strong alcoholic alkali gives in high yield an isomeric β-amyrenonol which shows the characteristic light-absorption properties of an αβ-unsaturated ketone and was characterised by the formation of its acetate. The reactions described below establish that this αβ-unsaturated keto-acetate is 18-*iso*-β-amyrenonyl acetate (XI; R = Ac). 18-*iso*-β-Amyrenonyl acetate was recovered unchanged after treatment with bromine in acetic acid under conditions which led to the conversion of β-amyrenonyl acetate or acetylketo-oleanolic acid into the corresponding conjugated dienones (IX). Catalytic reduction of 18-*iso*-β-amyrenonyl acetate at room temperature gives in high yield an isomeric β-amyrin acetate, the relationship of which to β-amyrin acetate (II; R = Ac) was established by its easy oxidation with selenium dioxide to β-amyradienyl-II acetate. Of the two possible structures (XIII; R = Ac) and (XIV; R = Ac) previously considered for the last compound, first prepared by Ruzicka, Müller, and Schellenberg (*Helv. Chim. Acta*, 1939, **22**, 767) by the oxidation of β-amyrin acetate (II; R = Ac) with selenium dioxide, Barton and Brooks (*J.*, 1951, 257) have shown that the former is correct. The formation of β-amyradienyl-II acetate (XIII; R = Ac) by oxidation of both β-amyrin acetate and the isomeric β-amyrin acetate described above proves that the last compound is 18-*iso*-β-amyrin acetate (XII; R = Ac).

Oxidation of 18-*iso*-β-amyrin acetate with hydrogen peroxide gives a saturated ketone, 18-*iso*-β-amyranonyl acetate (XV; R = Ac), which is not isomerised by either mineral acid or strong alkali, and represents the sterically stable isomer in so far as the orientation at $C_{(13)}$ is concerned. Treatment of 18-*iso*-β-amyranonyl acetate with bromine gives bromo-18-*iso*-β-amyranonyl acetate. This is considerably more stable than the isomeric bromo-β-amyranonyl acetate, obtained by similar bromination of β-amyranonyl acetate, which readily loses hydrogen bromide when warmed with acetic acid, giving *iso*-β-amyrenonyl acetate (Seymour and Spring, *J.*, 1941, 319); bromo-18-*iso*-β-amyranonyl acetate is recovered unchanged after prolonged heating in glacial acetic acid.

Reduction of 18-*iso*-β-amyranonyl acetate by using the Kishner–Wolff method, followed by acetylation, gives 18-*iso*-β-amyranyl acetate (XVI; R = Ac), hydrolysis of which gives 18-*iso*-β-amyranol, which differs from previously described saturated pentacyclic triterpenoid alcohols. The constants of β-amyranol, lupanol, and taraxastanol (heterolupanol) are shown below, together with those of 18-*iso*-β-amyranol.

	Alcohol		Acetate	
	m. p.	$[\alpha]_D$	m. p.	$[\alpha]_D$
β-Amyranol [1]	186—186·5°	+18·5°	284·5—285°	+21°
Lupanol [2]	201—202	−17·8	245—246	−1·8
Taraxastanol (Heterolupanol) [3]	218—220	+11	262—263	+23
18-*iso*-β-Amyranol [4]	229—230	+36	280—282	+44

[1] Ruzicka and Jeger, *Helv. Chim. Acta*, 1941, **24**, 1178. [2] Heilbron, Kennedy, and Spring, *J.*, 1938, 329. [3] Lardelli and Jeger, *Helv. Chim. Acta*, 1948, **31**, 813; Lardelli, Jeger, Krüsi, and Ruzicka, *ibid.*, p. 1159. [4] This paper.

The orientation at $C_{(13)}$ in the two isomers, β-amyranol and 18-*iso*-β-amyranol, in each case represents the sterically stable configuration since neither β-amyranonol nor 18-*iso*-β-amyranonol is isomerised at $C_{(13)}$ under strongly acid or alkaline conditions. There is furthermore a strong *prima facie* case for a common $C_{(13)}$-configuration in β-amyranol, 18-*iso*-β-amyranol, germanicol [cf. the conversion of siaresinolic acid into morolic acid (Barton, Brooks, and Holness,

J., 1951, 278)], and lupeol [cf. the conversion of betulin into moradiol diacetate (Davy, Halsall, and Jones, *Chem. and Ind.*, 1950, 732)].

The non-identity of 18-*iso*-β-amyranol and lupanol leads us to the conclusion that the acetone obtained by oxidation of β-amyrin acetate originates in the *gem*-dimethyl group in ring E.

Experimental.

M. p.s are corrected; rotations (1-dm. tube) are for chloroform solutions at room temperatures and are approximated to the nearest degree.

Oxidation of β-Amyrin Acetate.—A solution of β-amyrin acetate [m. p. 240—241°, $[\alpha]_D$ +83° (*c*, 1·67)] (10 g.) in purified glacial acetic acid (600 c.c.) was gently boiled to effect slow distillation of the solvent. A solution of chromic anhydride (30 g.) in 80% acetic acid (100 c.c.) was added dropwise. The distillate was collected in fractions of approximately 40 c.c. Each of the fractions was neutralised with sodium hydroxide solution and redistilled. The first 2—3 c.c. of distillate from each fraction was treated with a solution of 2 : 4-dinitrophenylhydrazine in hydrochloric acid, and the yellow solid collected. After nine such fractions had been collected (134 mg. of dinitrophenylhydrazone), the reaction mixture was diluted with purified acetic acid (100 c.c.), and the distillation continued. Since treatment of fractions 9 and 10 gave only a trace of 2 : 4-dinitrophenylhydrazone, the reaction mixture was treated with a solution of chromic anhydride (10 g.) in water (10 c.c.) and purified acetic acid (50 c.c.), and the distillation continued, giving fractions 12—17, each of which, on treatment as described above, gave a 2 : 4-dinitrophenylhydrazone. The reaction mixture was diluted with purified acetic acid, and the distillation continued until the distillate gave a negative carbonyl reaction (fraction 20). The mixture was again treated with chromic anhydride (10 g.) in water (10 c.c.) and glacial acetic acid (100 c.c.), and the distillation continued to give fractions 21—26, the reaction mixture being diluted with acetic acid after the collection of fraction 23. Treatment of fractions 11—26 as described above gave a 2 : 4-dinitrophenylhydrazone (270 mg.). Further treatment of the reaction mixture with chromic acid gave distillates free from carbonyl component. The combined crops of 2 : 4-dinitrophenylhydrazone (404 mg.; 7·9%) were crystallised from ethanol, yielding acetone 2 : 4-dinitrophenylhydrazone as orange needles, m. p. 125—127° undepressed when mixed with an authentic specimen (Found : C, 45·5; H, 4·3; N, 24·0. Calc. for $C_9H_{10}O_4N_4$: C, 45·4; H, 4·2; N, 23·5%).

Acetone was not detected in the distillates obtained from an exactly similar oxidation of α-amyrin acetate in which the same batch of purified acetic acid was employed or in the distillates obtained from a blank experiment.

β-Amyrenonyl Benzoate.—A solution of β-amyrin benzoate (40 g.) in boiling purified glacial acetic acid (2 l.) was treated with a solution of chromic anhydride (40 g.) in water (10 c.c.) and glacial acetic acid (800 c.c.) added dropwise during 1 hour. The solution was boiled for 1·5 hours, after which time it was treated with boiling water (1200 c.c.) with vigorous stirring. Next morning the crystalline solid was collected, washed with aqueous methanol, and dried (21 g.; m. p. 261—263°). Crystallisation from chloroform–methanol gave β-amyrenonyl benzoate as prismatic needles, m. p. 269—270·5°, $[\alpha]_D$ +112° (*c*, 1·85) (Found : C, 81·1; H, 9·7. Calc. for $C_{37}H_{52}O_3$: C, 81·6; H, 9·6%). β-Amyrenonyl benzoate does not give a coloration with tetranitromethane in chloroform. Light absorption in ethanol : Maximum at 2300 Å (ε = 21,500) and an inflection at 2520 Å (ε = 13,800).

18-iso-*β-Amyrenonol* (XI; R = H).—A solution of β-amyrenonyl benzoate (14·7 g.) in 15% ethanolic potassium hydroxide (1200 c.c.) was heated under reflux for 52 hours. The pale yellow solution was concentrated to half-bulk and diluted with water. The solid was collected, washed with water until the washings were neutral (litmus), and dried (11·8 g.). Crystallisation from methanol gave 18-iso-*β-amyrenonol* as long plates, m. p. 254—255°, $[\alpha]_D$ +84° (*c*, 0·74) (Found : C, 81·3; H, 11·0. $C_{30}H_{48}O_2$ requires C, 81·8; H, 11·0%). Light absorption in ethanol : Maximum at 2440 Å (ε = 12,300). The alcohol, m. p. 247—248°, $[\alpha]_D$ +81·5°, obtained by Ruzicka, Müller, and Schellenberg (*Helv. Chim. Acta*, 1939, **22**, 758) by the action of alkali on β-amyrenonol is probably 18-*iso*-β-amyrenonol.

18-iso-*β-Amyrenonyl Acetate* (XI; R = Ac).—Acetylation of 18-*iso*-β-amyrenonol by heating it with pyridine (4 parts) and acetic anhydride (6 parts) on the steam-bath for 2·5 hours gave 18-iso-*β-amyrenonyl acetate* which separated from chloroform–methanol as hard, square, squat prisms, m. p. 277·5—279°, $[\alpha]_D$ +75° (*c*, 1·8) (Found : C, 79·8; H, 10·8. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%). Light absorption in ethanol : Maximum at 2450 Å (ε = 10,100). A mixture of 18-*iso*-β-amyrenonyl acetate and β-amyrenonyl acetate (m. p. 265—266°) had m. p. 254—256°, and a mixture of 18-*iso*-β-amyrenonyl acetate and α-amyrenonyl acetate (m. p. 275°) had m. p. 228—230°. The *allo*-β-amyrenonyl acetate [m. p. 262—265°, $[\alpha]_D$ +67° (pyridine), $\lambda_{max.}$ 2460 Å (ε = 11,000)] described by Green, Mower, Picard, and Spring (*loc. cit.*) is almost certainly a somewhat impure specimen of 18-*iso*-β-amyrenonyl acetate; like the latter, it was recovered unchanged after treatment with bromine in acetic acid.

18-iso-*β-Amyrin Acetate* (XII; R = Ac).—A solution of 18-*iso*-β-amyrenonyl acetate (1·0 g.) in glacial acetic acid (180 c.c.) was added to a suspension of freshly reduced platinum (from 300 mg. of platinic oxide) in acetic acid (15 c.c.), and the mixture shaken with hydrogen at room temperature. After 24 hours the reaction product separated as plates, and after 40 hours the absorption of hydrogen was complete (approximately 2 mols.). The mixture was heated to dissolve the product and filtered to remove platinum. The filtrate was concentrated under reduced pressure to approximately 60 c.c., and, after cooling, the separated solid was collected, washed with cold methanol, and dried. Recrystallisation from methanol–chloroform gave 18-iso-*β-amyrin acetate* as plates (740 mg.), m. p. 245—246·5°, $[\alpha]_D$ +53° (*c*, 0·96) (Found : C, 82·25; H, 11·2. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%). 18-*iso*-β-Amyrin acetate gives a bright yellow colour with the tetranitromethane reagent and does not exhibit selective absorption in the ultra-violet. A mixture of 18-*iso*-β-amyrin acetate with β-amyrin acetate

(m. p. 241—242°) had m. p. 218—222°, and a mixture of 18-*iso*-β-amyrin acetate with *iso*-β-amyrin acetate (2-acetoxyolean-10-ene) (m. p. 250—251°) had m. p. 212—220°.

β-Amyradienyl-II *Acetate* (XIII; R = Ac).—A solution of 18-*iso*-β-amyrin acetate (220 mg.) in boiling acetic acid (20 c.c.) was treated with a solution of selenium dioxide (200 mg.) in water (0·5 c.c.) and glacial acetic acid (10 c.c.) added dropwise during 20 minutes, and the mixture refluxed for 1 hour. Freshly fused sodium acetate (1 g.) was added and the refluxing continued for 20 minutes. The hot mixture was filtered through sintered glass, the filtrate diluted with water, and the precipitated solid collected, washed with water, and dried. A solution of the solid in ether was washed with 3% aqueous potassium cyanide and with water, and dried. The residue obtained after removal of the solvent was twice crystallised from methanol–chloroform, giving β-amyradienyl-II acetate (150 mg.) as plates, m. p. 225·5—227°, $[\alpha]_D$ −63° (*c*, 1·01); the m. p. was not depressed when the acetate was mixed with a specimen (m. p. 228°) obtained by the same method starting from β-amyrin acetate. Light absorption in ethanol: Maxima at 2510 (ε = 29,100), 2430 (ε = 27,300), and 2600 Å (ε = 19,500). Ruzicka, Müller, and Schellenberg (*Helv. Chim. Acta*, 1939, **22**, 767) give m. p. 228—229°, $[\alpha]_D$ −62°, for β-amyradienyl-II acetate.

18-iso-*β-Amyranonyl Acetate* (XV; R = Ac).—A solution of 18-*iso*-β-amyrin acetate (0·7 g.) in glacial acetic acid (200 c.c.), heated on a boiling-water bath with stirring, was treated with a solution of hydrogen peroxide (30%; 20 c.c.) in glacial acetic acid (20 c.c.) added dropwise during 15 minutes. The solution was maintained at the same temperature for 2 hours and again treated with a solution of hydrogen peroxide (30%; 15 c.c.) in acetic acid (15 c.c.) added during 15 minutes. After being stirred for 1 hour on the boiling-water bath, the solution was treated dropwise with boiling water with vigorous stirring until crystallisation commenced. Next morning the solid was collected, washed with aqueous methanol, and dried (m. p. 276—283°, 250 mg.). A solution of the solid in benzene (20 c.c.) was filtered through a column of alumina (Brockmann Grade I/II; 1·5 × 5 cm.) and the column washed with benzene (60 c.c.). The benzene filtrate was evaporated to dryness and the solid residue (180 mg.), after crystallisation from methanol–chloroform and then from methanol, gave 18-iso-*β-amyranonyl acetate* as plates, m. p. 286—287°, $[\alpha]_D$ +77° (*c*, 1·22) (Found: C, 79·5; H, 10·8. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%). In four different oxidations of 18-*iso*-β-amyrin acetate the yield of pure 18-*iso*-β-amyranonyl acetate varied between 22% and 26%. A mixture of 18-*iso*-β-amyranonyl acetate (m. p. 286—287°) with β-amyranonyl acetate (m. p. 300°) did not show a marked depression in m. p. (284—290°). Light absorption in ethanol: Inflection at 3000 Å (ε = 126).

A solution of 18-*iso*-β-amyranonyl acetate (90 mg.) in chloroform (0·5 c.c.)–glacial acetic acid (10 c.c.) was treated with 3 drops of concentrated hydrochloric acid and kept at 35—45° for 1 hour. The reaction mixture gave 18-*iso*-β-amyranonyl acetate (80 mg.) as plates, m. p. 286—287°, $[\alpha]_D$ +77° (*c*, 1·15), after one crystallisation from methanol.

18-iso-*β-Amyranonol* (XV; R = H).—A solution of 18-*iso*-β-amyranonyl acetate (m. p. 284—285°; 300 mg.) in 15% ethanolic potassium hydroxide (60 c.c.) was refluxed for 50 hours. The prismatic needles separating on cooling were collected, washed with methanol, and dried (180 mg.; m. p. 308—310°). Recrystallisation from methanol containing a trace of acetic acid and then from methanol gave 18-iso-*β-amyranonol* (110 mg.) as prismatic rods, m. p. 309—310°, $[\alpha]_D$ +91° (*c*, 1·07) (Found: C, 81·3; H, 11·45. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%). Light absorption in ethanol: Inflection at 3000 Å (ε = 40). The alkaline mother-liquor was diluted with water and the precipitated solid collected, dried, and acetylated by using pyridine (2 c.c.) and acetic anhydride (1 c.c.). Crystallisation of the product from chloroform–methanol gave 18-*iso*-β-amyranonyl acetate (90 mg.) as elongated plates, m. p. 284—285°, $[\alpha]_D$ +77° (*c*, 0·70), undepressed in m. p. when mixed with the starting material.

Acetylation of 18-*iso*-β-amyranonol (m. p. 309—310°; 60 mg.), by using acetic anhydride and pyridine in the usual manner, gave 18-*iso*-β-amyranonyl acetate (50 mg.) as elongated plates, m. p. 287—288·5°, $[\alpha]_D$ +78° (*c*, 0·84), unchanged by a recrystallisation from the same solvent, and undepressed in m. p. when mixed with a specimen of the starting material. Light absorption in ethanol: Maximum at 3000 Å (ε = 140).

Bromo-18-iso-*β-amyranonyl Acetate*.—A solution of 18-*iso*-β-amyranonyl acetate (250 mg.; m. p. 284·5—286°) in glacial acetic acid (20 c.c.) was treated with a solution of bromine in glacial acetic acid (5%; 1·2 mol.) added during 1 hour at 65—80°. The solution was maintained at 80° for 3 hours and then diluted with water, and the solid collected, washed with water, dried, and crystallised from methanol–chloroform. The first crop (160 mg.) separated as plates, m. p. 245—246° (decomp.), $[\alpha]_D$ +17·5° (*c*, 1·15), which did not give a coloration with tetranitromethane in chloroform and gave a positive halogen test. From the mother-liquors a second crop (65 mg.) of flat needles, m. p. 260—265° (decomp.), separated. The first crop was heated on the steam-bath for 3½ hours with glacial acetic acid. On concentration and cooling of the solution, *bromo*-18-iso-*β-amyranonyl acetate*, separated as plates, m. p. 249—250° (decomp.) unchanged by two recrystallisations from methanol–chloroform, $[\alpha]_D$ +18° (*c*, 1·06) (Found: C, 68·4; H, 9·1. $C_{32}H_{51}O_3Br$ requires C, 68·2; H, 9·1%). Light absorption in ethanol: Maximum at 3100 Å (ε = 155). Similar treatment (heating with acetic acid) of the second crop gave elongated plates, m. p. 276—278° undepressed when mixed with 18-*iso*-β-amyranonyl acetate, $[\alpha]_D$ +73° (*c*, 0·93). Light absorption in ethanol: Maximum at 2900 Å (ε = 50). The physical properties of this fraction show that it is essentially 18-*iso*-β-amyranonyl acetate contaminated with the bromo-ketone described above.

18-iso-*β-Amyranyl Acetate* (XVI; R = Ac).—A mixture of 18-*iso*-β-amyranonyl acetate (m. p. 284—285·5°; 300 mg.), alcoholic sodium ethoxide (from 750 mg. of sodium and 10 c.c. of ethanol), and hydrazine hydrate (2 c.c.; 100%) was heated in an autoclave at 200° for 17 hours. The cooled mixture was diluted with water and extracted with ether. The extract was washed successively with hydrochloric acid (3%) and water and dried. After removal of the solvent, the solid residue was heated on the steam-bath for 2 hours with pyridine (3 c.c.) and acetic anhydride (2 c.c.). The crystalline solid separating on

cooling was collected, washed with methanol, and dried (155 mg.; m. p. 277—279°). A second crop (m. p. 263—266°; 25 mg.) was undepressed in m. p. when mixed with the first crop. The first crop was twice recrystallised from methanol–chloroform, giving 18-iso-*β-amyranyl acetate* as plates, m. p. 280—282°, $[\alpha]_D$ +43° (*c*, 0·88) (Found: C, 81·6; H, 11·7. $C_{32}H_{54}O_2$ requires C, 81·6; H, 11·6%). 18-*iso*-*β*-Amyranyl acetate does not give a colour with tetranitromethane in chloroform. A mixture of 18-*iso*-*β*-amyranyl acetate with *β*-amyranyl acetate (m. p. 284°) had m. p. 256—262°, and a mixture with lupanyl acetate (m. p. 246—248°) had m. p. 233—237°.

The original mother-liquors from 18-*iso*-*β*-amyranyl acetate deposited on long storage a crop of large prisms (40 mg.), m. p. 179—180°, recrystallisation of which from methanol gave prismatic needles, m. p. 180—181°, $[\alpha]_D$ −5° (*c*, 1·11) (Found: C, 81·1; H, 11·6. $C_{32}H_{54}O_2$ requires C, 81·6; H, 11·6. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%). The *substance* gives a very faint yellow coloration with the tetranitromethane reagent, and it does not show selective absorption in the ultra-violet region of the spectrum.

18-iso-*β-Amyranol* (XVI; R = H).—Hydrolysis of 18-*iso*-*β*-amyranyl acetate (90 mg.) was effected by heating it under reflux with 3% alcoholic potassium hydroxide for 6 hours. The product, isolated in the usual manner, separated from ethanol as plates (50 mg.), m. p. 228—229°, which after two crystallisations from methanol–chloroform gave 18-iso-*β-amyranol* as flat prisms (thick plates), m. p. 229—230°, $[\alpha]_D$ +36° (*c*, 1·21) (Found: C, 83·85; H, 12·4. $C_{30}H_{52}O$ requires C, 84·0; H, 12·2%). Acetylation of 18-*iso*-*β*-amyranol (30 mg.) by warming it on the steam-bath for 3 hours with pyridine (1 c.c.) and acetic anhydride (1 c.c.) gave 18-*iso*-*β*-amyranyl acetate (25 mg.) as plates (from methanol), m. p. 280—282° undepressed when mixed with the specimen described above, $[\alpha]_D$ +44° (*c*, 1·11).

Decarboxylation of Acetylolean-12 : 18-dien-11-onolic Acid (IX; R = Ac, R′ = CO_2H). *Nor-β-amyradienonyl Acetate* (X) (With L. C. McKean).—Acetylolean-12 : 18-dien-11-onolic acid (250 mg.; m. p. 287—288°), prepared by Ruzicka, Jeger, and Winter's method (*loc. cit.*), was heated in an atmosphere of nitrogen at 285—295°. After 5 minutes, when evolution of carbon dioxide had ceased, the mixture was cooled and dissolved in ether. The solution was washed with 5% sodium hydroxide solution and then with water, and dried ($MgSO_4$). After removal of the ether, a solution of the residue (184 mg.) in light petroleum (b. p. 60—80°; 100 c.c.) was filtered through a column of activated alumina (Grade II). After the column had been washed with light petroleum (200 c.c.) and light petroleum–benzene (7 : 1; 100 c.c.), eluates were obtained by washing it with light petroleum–benzene (4 : 1; 100 c.c.), light petroleum–benzene (1 : 1; 500 c.c.), and ether (100 c.c.); these were combined (75 mg.) and thrice crystallised from methanol, giving nor-*β*-amyradienonyl acetate as prisms, m. p. 203—205°, $[\alpha]_D$ +144° (*c*, 1·23) (Found: C, 80·0; H, 10·1. Calc. for $C_{31}H_{46}O_3$: C, 79·8; H, 9·9%). Nor-*β*-amyradienonyl acetate gave a bright yellow coloration with tetranitromethane in chloroform, and showed a light-absorption maximum in ethanol at 2970 Å (ε = 22,000). Ruzicka, Jeger, and Winter (*loc. cit.*) report m. p. 202°, $[\alpha]_D$ +150°, and light-absorption maximum at 2970 Å (ε = 22,400), for nor-*β*-amyradienonyl acetate, obtained by treatment of acetylketo-oleanolic acid with boiling quinoline.

Acidification of the alkaline washings of the ethereal extract, followed by crystallisation of the product from methanol–chloroform, yielded unchanged acetylolean-12 : 18-dien-11-onolic acid (28 mg.), m. p. 283—285° undepressed when mixed with the starting material.

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