144. *Triterpene Resinols and Related Acids. Part XVII.* (A) *The Conversion of* β-*Amyradienonyl Acetate into* allo-β-*Amyrenonyl Acetate.* (B) *The Conversion of* β-*Amyrin into* iso-β-*Amyradienonol.*

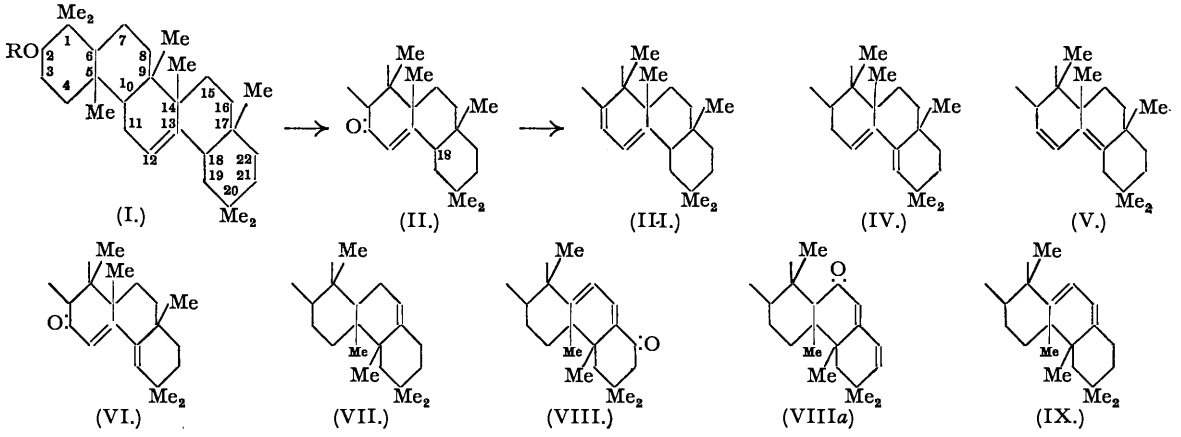
By James Green, (the late) Neville Mower, C. W. Picard, and F. S. Spring.

Reduction of β-amyradienonyl acetate (VI, R = Ac) with sodium ethoxide and hydrazine hydrate yields a mixture from which allo-β-*amyrenonyl acetate*, allo-β-*amyrin acetate*, and a mixed crystal containing β-amyradienyl-II acetate have been isolated. *allo*-β-Amyrenonyl acetate is an αβ-unsaturated ketone stereoisomeric with β-amyrenonyl acetate. In terms of the formula (I, R = H) for β-amyrin, *allo*-β-amyrenonyl acetate differs from β-amyrenonyl acetate (II, R = Ac) in the orientation around C_{18}. *allo*-β-Amyrin acetate is probably the corresponding stereoisomer of β-amyrin acetate.

Treatment of *iso*-β-amyrenonyl acetate (XV or XVI, R = Ac) with either selenium dioxide or bromine results in the introduction of a second ethylenic linkage, with the formation of iso-β-*amyradienonyl acetate* (XVII, R = Ac) which is formulated as a de-oxo-derivative of β-amyradiendionyl acetate (XVIII, R = Ac). However, *iso*-β-amyradienonyl acetate cannot be oxidised by means of selenium dioxide to β-amyradiendionyl acetate. The bearing of these results on the elucidation of the structure of the β-amyrin group of triterpenes is discussed.

(A) In previous Parts of this series it has been shown that reduction of β-amyrenonol (II, R = H) with sodium and ethyl or amyl alcohol yields the addition–reduction compounds, $C_{32}H_{56}O_3$ and $C_{35}H_{62}O_3$, respectively. These compounds are converted into β-amyradienyl-I acetate (III, R = Ac) by treatment with acetic anhydride (Beynon, Sharples, and Spring, J., 1938, 1233; Picard and Spring, J., 1940, 1198). Treatment of the addition reduction complex, $C_{35}H_{62}O_3$, with acetic anhydride also yields the isomeric β-amyradienyl-II acetate, as a minor product (Picard and Spring, J., 1941, 35). β-Amyradienyl-II acetate had previously been obtained by the oxidation of β-amyrin acetate with selenium dioxide (Ruzicka, Müller, and Schellenberg, *Helv. Chim. Acta*, 1939, **22**, 767; Ruzicka and Jeger, *ibid.*, 1941, **24**, 1236). The structure of β-amyradienol-I is securely established as (III, R = H) in terms of the hypothetical formula (I, R = H) for β-amyrin, since it exhibits the light absorption properties of a diene containing a conjugated system in a single six-membered ring, and when oxidised with chromic acid it gives β-amyrenedione (Picard and Spring, 1940, *loc. cit.*). β-Amyradienol-II is either (IV, R = H) or (V, R = H) (cf. Mower, Green, and Spring, J., 1944, 256).

Treatment of β-amyrenonyl acetate (II, R = Ac) with bromine yields β-amyradienonyl acetate which is represented by (VI, R = Ac), again in terms of the formula (I, R = H) for β-amyrin (Picard and Spring, 1941, *loc. cit.*). The hypothetical formula suggested by Bilham, Kon, and Ross (J., 1942, 532, 535, 540) for oleanolic acid leads to the expression (VII, R =H) for β-amyrin. This formulation, which has served the useful purpose of stimulating a more critical examination of the reactions of the β-amyrin group of triterpenes, leads to the expression (VIII, R = Ac) for β-amyradienonyl acetate and related dienones. Kon and Ross (J., 1942, 742) have observed that the alternative structure (VIII*a*) for these dienones is more in harmony with their properties.



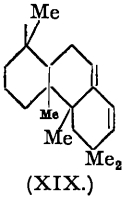
The present communication describes an examination of the reduction of β-amyradienonyl acetate with hydrazine hydrate and sodium ethoxide which was undertaken in order to examine the relationship of this dienone and the two β-amyradienols. A simple replacement of the carbonyl group of β-amyradienonol by methylene would, according to the β-amyrin formula (I, R = H), give the dienol (IV, R = H). A comparison of the product with β-amyradienol-II would allow a decision to be made in favour of one of the alternative formulæ (IV, R = H) and (V, R = H) for β-amyradienol-II. On the other hand, according to the formula (VIII, R = H) for β-amyradienonol, the product should be identical with β-amyradienol-I, which, according to Bilham, Kon, and Ross (*loc. cit.*, p. 538), is represented by (IX, R = H). The reaction product, however, proved to be complex. It was separated by a chromatographic method into three major fractions. The first fraction, obtained by washing the chromatogram with benzene, was acetylated to give allo-β-*amyrin*

acetate, $C_{32}H_{52}O_2$, m. p. 215—217°, $[\alpha]_D$ +147°. The second fraction from the chromatogram was obtained by continued washing with benzene, and on crystallisation gave an alcohol, $C_{30}H_{48}O$, m. p. 219—220°. This alcohol is very similar in its properties to β-amyradienol-II, m. p. 228—229°, and when mixed with the latter gives an intermediate m. p. The alcohol, m. p. 219—220°, shows the characteristic absorption spectrum of β-amyradienol-II, with maxima at 2430, 2510, and 2600 A., but the intensity of absorption (ε_{2510} = 21,000) is considerably less than that of β-amyradienol-II (ε_{2510} = 31,000). It was not possible appreciably to raise either the m. p. or the intensity of absorption by repeated crystallisation of the alcohol.

Acetylation of the alcohol, m. p. 219—220°, gave an acetate, m. p. 209—211°, a mixture of which with β-amyradienyl-II acetate (m. p. 228—229°) has m. p. 218—222°. In a second reduction of β-amyrenonyl acetate with hydrazine hydrate and sodium ethoxide, direct crystallisation of the reaction product gave the same alcohol, m. p. 217°, acetylation of which yielded an acetate, m. p. 206—208°, undepressed when mixed with the specimen of m. p. 209—211°; a mixture of this acetate with β-amyradienyl-II acetate shows an intermediate m. p., but a mixture with β-amyradienyl-I acetate shows a marked depression. The acetate, m. p. 206—208°, also exhibits the characteristic triplet absorption spectrum of β-amyradienyl-II acetate with maxima at 2430, 2510, and 2600 A., but the intensity (ε_{2510} = 21,600) was appreciably lower than that observed for the dienyl-II acetate ($\varepsilon_{2510} \approx$ 31,000). The specific rotation of the acetate, m. p. 206—208°, $[\alpha]_D$ +2°, is to be compared with $[\alpha]_D$ +62° for β-amyradienyl-II acetate. The acetate of m. p. 206—208° (and the corresponding alcohol) is almost certainly not homogeneous but a mixed crystal containing β-amyradienyl-II acetate together with a second component. The properties of the acetate, m. p. 206—208°, require that the second component should not exhibit selective absorption of appreciable intensity and that it should have a considerable dextrorotation. It is noteworthy that a 2 : 1 mixture of β-amyradienyl-II acetate and *allo*-β-amyrin acetate would be expected to show the characteristic absorption maxima of the former component with an intensity ε_{2510} = 20,000 and $[\alpha]_D$ +7°, values in fair agreement with those observed for the acetate, m. p. 206—208°.

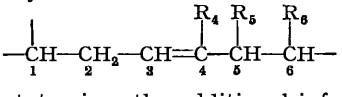
The final fraction was obtained from the chromatogram by washing with ether. Acetylation of this fraction readily gave allo-β-*amyrenonyl acetate*, $C_{32}H_{50}O_3$, m. p. 262—265°, $[\alpha]_D$ + 67°. It gives a negative unsaturation test with tetranitromethane, and its absorption spectrum shows a well-defined maximum at 2460 A., ε = 11,000; both of these properties indicate that *allo*-β-amyrenonyl acetate is an αβ-unsaturated ketone.

Although evidence for the formation of β-amyradienyl-II acetate from β-amyradienonyl acetate was obtained, but not for that of β-amyradienyl-I acetate, it cannot be claimed that this evidence alone eliminates formula (VIII, R = H) for β-amyradienonol. The complexity of the modified Kishner–Wolff reduction when applied to this conjugated dienone is such that reduction in the sense (VIII) → (XIX) is possible. In the same way it cannot be concluded that the formation of the dienol-II from β-amyradienonyl acetate means that this dienol must be represented by (IV, R = H), since the susceptibility of one of the ethylenic linkages of the dienonol to reduction means that the change (VI) → (V) is not excluded.

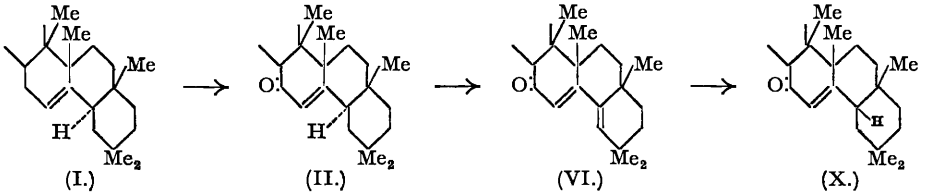


(XIX.)

allo-β-Amyrenonyl acetate differs markedly from the isomeric β-amyrenonyl acetate (Picard and Spring, J., 1940, 1200) and from the isomeric *iso*-β-amyrenonyl acetate (Picard, Sharples, and Spring, J., 1939, 1045). Furthermore, there is no reason to suppose that *allo*-β-amyrenonyl acetate differs from β-amyrenonyl acetate in the orientation around C_2, since it has been shown that β-amyrin is unchanged after prolonged heating with sodium ethoxide at 180—190° (Ruzicka and Wirz, *Helv. Chim. Acta*, 1941, **24**, 248). The formation of a new αβ-unsaturated ketone by reduction of β-amyradienonyl acetate is of considerable significance in the structural elucidation of the β-amyrin group of triterpenes. The absolute locations of both the carbonyl and the ethylenic linkage in *allo*-β-amyrenonyl acetate are the same as those in β-amyrenonyl acetate, since the latter is the parent of β-amyradienonyl acetate; the saturation of the terminal ethylenic linkage of β-amyradienonyl acetate has involved the formation of a new asymmetric centre. Our previous experiments in the β-amyrin field (see Picard and Spring, J., 1941, 37) have shown that the unsaturated centre is present in the system

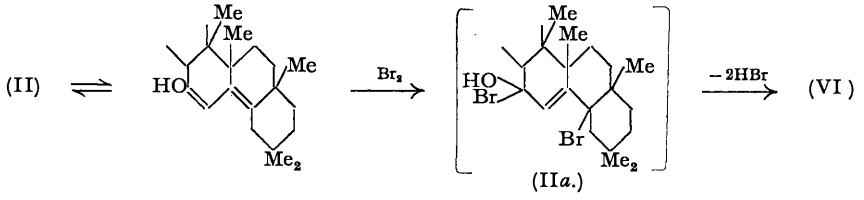


The formation of *allo*-β-amyrenonyl acetate gives the additional information that either C_5 or C_6 (or both) must be asymmetric in β-amyrin, *i.e.*, that R_4 and R_5 cannot both be hydrogens. The hypothetical β-amyrin structure (I) obeys this structural requirement, and represents β-amyrenonyl acetate (II, R = Ac) and *allo*-β-amyrenonyl acetate (X, R = Ac) as isomers differing solely in the orientation around C_{18}: *

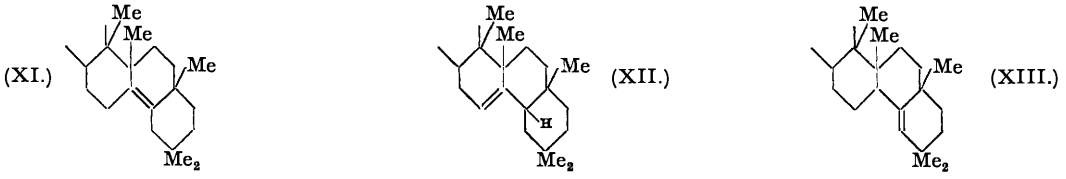


* The steric configurations around C_{18} shown in these formulæ are relative and not absolute.

allo-β-Amyrenonyl acetate is recovered unchanged after treatment with bromine under conditions which convert β-amyrenonyl acetate into β-amyradienonyl acetate (Picard and Spring, 1941, *loc. cit.*). The introduction of a second ethylenic linkage into β-amyrenonyl acetate by means of bromine can be represented as 1 : 4-addition to the enolic form (II*a*) of β-amyrenonyl acetate followed by loss of hydrogen bromide (see below). The stability of *allo*-β-amyrenonyl acetate is to be attributed to its inability to enolise in the same direction.



The determination of the structure of *allo*-β-amyrin acetate in terms of that of β-amyrin acetate offers more difficulty. Its formation from β-amyradienonyl acetate has involved the replacement of the carbonyl group of the latter by methylene, and the simultaneous reduction of one ethylenic linkage. *allo*-β-Amyrin acetate differs markedly from β-amyrin acetate, and when mixed with this, it gives a large depression in m. p. *allo*-β-Amyrin acetate also differs from the isomeric *epi*-β-amyrin acetate (Ruzicka and Wirz, *Helv. Chim. Acta*, 1941, **24**, 248), which, in its turn, differs from β-amyrin solely in the orientation around C_2. δ-Amyrin acetate (XI, R = Ac) (Ruzicka and Jeger, *Helv. Chim. Acta*, 1941, **24**, 1237; Ruzicka, Jeger, and Norymberski, *ibid.*, 1942, **25**, 457), which is obtained by the catalytic reduction of β-amyradienyl-II acetate (IV or V, R = Ac), is also markedly different from *allo*-β-amyrin acetate. The most probable formulæ for *allo*-β-amyrin acetate are (XII, R = Ac) and (XIII, R = Ac). In (XII, R = Ac) it is represented as derived from *allo*-β-amyrenonyl acetate by simple replacement of the carbonyl by a methylene group, and accordingly differs from β-amyrin acetate solely in the orientation around C_{18}. In (XIII, R = Ac), *allo*-β-amyrin acetate is represented as derived from β-amyradienonyl acetate by the replacement of the carbonyl by methylene and the simultaneous saturation of the Δ^{12}-ethylenic linkage. An attempt to convert *allo*-β-amyrenonyl acetate into *allo*-β-amyrin acetate will be made when the opportunity occurs.

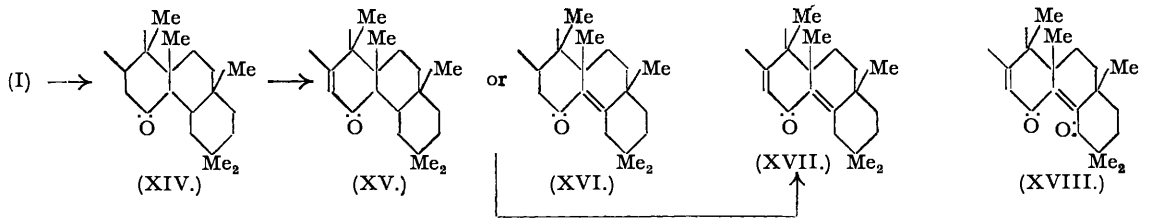


(B) β-Amyradienyl-II acetate is an intermediate in the oxidation of β-amyrin acetate to β-amyradiendionyl acetate, a substance which, together with analogous compounds from the related oleanolic and glycyrrhetic acids, has proved to be of considerable importance in the determination of the nature of the immediate environment of the ethylenic linkage in the β-amyrin group of triterpenes. β-Amyradiendionyl acetate is represented as (XVIII, R = Ac) (Ruzicka and Jeger, *Helv. Chim. Acta*, 1941, **24**, 1236; 1942, **25**, 775, 1409; Ruzicka, Jeger, and Winter, *ibid.*, 1943, **26**, 265; Ruzicka, Jeger, and Ingold, *ibid.*, p. 2278; Kon and Ross, J., 1942, 741; Simpson and Morton, J., 1943, 477). The nature of the chromophore system present in this diendionol has been established by Ruzicka and his collaborators * but there is no direct proof of the exact location of this chromophore in the triterpenoid nucleus. More precisely, it still remains to be established that the carbonyl group of β-amyranonol (J., 1939, 1045) is present in β-amyradiendionol. Our attack on this problem started from the observation that oxidation of β-amyradienyl-I acetate (III, R = Ac) with selenium dioxide gives a mixture of β-amyrenonyl acetate (II, R = Ac) and β-amyradiendionyl acetate (Picard and Spring, J., 1941, 35), which suggested that one of the carbonyl groups of β-amyradiendionyl acetate is either at C_{11} (as in β-amyrenonyl acetate) or at C_{12} (as in *iso*-β-amyrenonyl acetate). An investigation of the action of selenium dioxide on β-amyrenonyl acetate showed that it is oxidised by this reagent to give an acetate,

* Discussing the nature of this compound, Picard and Spring (J., 1941, 35) say that " an examination of its reactions led this author (Simpson, J., 1938, 1313) to the view that it contains an isolated benzenoid ring." Simpson and Morton (J., 1943, 477) comment that " such a view was not expressed in the paper to which they refer and the phrase ' isolated benzenoid ring ' or its equivalent does not occur in it." This surprising declamation must be challenged. The substance of the paper by Simpson (*loc. cit.*) is that the compound now known to be β-amyradiendionol contains a benzenoid ring. The burden of positive proof of this conclusion lay in the observation that the compound exhibits an absorption maximum at 2780 A., which is similar in position to (though greater in intensity than) those exhibited by *neo*ergosterol, dihydrotrianhydrostrophanthidin, and dehydro-abietic acid. Each of these compounds contains an *isolated* benzene ring. If a benzene ring conjugated with another unsaturated system was envisaged, the analogies quoted are irrelevant. Again, Simpson and Morton say that Ruzicka, Müller, and Schellenberg (*Helv. Chim. Acta*, 1939, **22**, 767) " have rightly pointed out the inadequacy of an isolated aromatic ring to account for the intensity of absorption." It must, however, be added that Ruzicka and his collaborators also observed that the formal expression used by Simpson (*loc. cit.*) to represent β-amyradiendionol does not allow of conjugation of the postulated benzene ring with any other unsaturated system.

$C_{32}H_{46}O_5$ (" O_5-acetate ") in very high yield, and not β-amyradiendionyl acetate (Mower, Green, and Spring, *loc. cit.*). The " O_5-acetate " is also obtained in very high yield by the oxidation of β-amyradienonyl acetate either with selenium dioxide or, as we now find, with chromic anhydride. Once a carbonyl group has been introduced at C_{11}, it is impossible to oxidise the resulting compound to the β-diendionyl acetate, a conclusion in harmony with the postulated formula (XVIII, R = Ac) for the latter. According to the formulation (XVIII), the conjugated system of β-amyradiendionol includes the αβ-unsaturated ketone grouping of *iso*-β-amyrenonol. *iso*-β-Amyrenonyl acetate (XV or XVI, R = Ac) (J., 1939, 1045; J., 1941, 319; Spring, *Ann. Reports*, 1941, **38**, 198) is obtained by the action of bromine on the saturated ketone β-amyranonyl acetate (XIV, R = Ac). The carbonyl group in the saturated ketone, and hence that in *iso*-β-amyrenonyl acetate, is a label marking the position of the double bond of β-amyrin; a conversion of *iso*-β-amyrenonyl acetate into β-amyradiendionyl acetate should be possible if (I) and (XVIII) correctly represent the relationship of β-amyrin and the diendionol.

Picard and Spring (1941, *loc. cit.*) and Ruzicka, Jeger, and Norymberski (*loc. cit.*) have reported unsuccessful attempts to oxidise *iso*-β-amyrenonyl acetate with selenium dioxide. We now find that prolonged treatment of the αβ-unsaturated ketone with selenium dioxide in acetic acid under anhydrous conditions yields iso-β-*amyradienonyl acetate*, $C_{32}H_{48}O_3$, m. p. 208°, which gives a bright yellow coloration with the tetranitromethane reagent whereas the parent *iso*-β-amyrenonyl acetate gives a negative reaction. It exhibits a well-defined absorption maximum at 2450 A., ε = 10,000, and on hydrolysis it is converted into iso-β-*amyradienonol*, $C_{30}H_{46}O_2$, m. p. 239°, which also exhibits the characteristic absorption spectrum with a maximum at 2470 A. and gives a bright yellow colour with the tetranitromethane reagent. *iso*-β-Amyradienonyl acetate is also obtained by treatment of *iso*-β-amyrenonyl acetate with bromine in acetic acid. The most probable structure for *iso*-β-amyradienonyl acetate in terms of that of *iso*-β-amyrenonyl acetate is (XVII, R = Ac).



No data are available for the optical properties of conjugated dienones in which the chromophore is distributed over two rings as in (XVII) but the analogously constituted 3-keto-$\Delta^{1:4}$-cholestadiene (Inhoffen and Huang-Minlon, *Ber.*, 1938, **71**, 1721) and santonin (Ruzicka, Cohen, Furter, and Sluys-Veer, *Helv. Chim. Acta*, 1938, **21**, 1735) each exhibit an absorption maximum at approximately 2400 A. In spite of the close relationship of *iso*-β-amyradienonyl acetate and β-amyradiendionyl acetate according to the hypothetical formulæ (XVII, R = Ac) and (XVIII, R = Ac), *iso*-β-amyradienonyl acetate is recovered unchanged after prolonged treatment with selenium dioxide; under conditions which convert both β-amyrin acetate (I, R = Ac) and δ-amyrin acetate (XI, R = Ac) into the diendionyl acetate. The stability of *iso*-β-amyradienonyl acetate may mean that the diendionyl acetate does not contain a carbonyl group in the same position as that in β-amyranonyl acetate, *i.e.*, that (I, R = H) is an inadequate expression of the structure of β-amyrin. An alternative, but less convincing, conclusion is that oxidation of β-amyrin acetate and its derivatives to β-amyradiendionyl acetate requires in all cases the intermediate formation of β-amyratrienyl acetate (see Newbold and Spring, following paper).

In a further attempt to obtain an intermediate product in the oxidation of β-amyradienyl-II acetate to β-amyradiendionyl acetate, the action of hydrogen peroxide upon the former has been investigated. As minor reaction product an *acetate*, $C_{32}H_{50}O_4$, m. p. 310—313°, was obtained. It is an αβ-unsaturated ketone exhibiting an absorption maximum at 2530 A., ε = 11,000, and it gives a negative test wth the tetranitromethane reagent. The acetate is recovered unchanged after prolonged boiling with acetic anhydride and does not give an oxime under normal reaction conditions. This acetate is not directly related to β-amyradiendionol, since on oxidation with selenium dioxide it gives the " O_5-acetate " identical with that prepared by similar oxidation of β-amyrenonyl acetate. The major product of the oxidation of β-amyradienyl-II acetate with hydrogen peroxide proved to be of little interest in the present study. It is a *diacetate*, $C_{34}H_{50}O_6$ or $C_{34}H_{48}O_6$, m. p. 238°, which gave a negative tetranitromethane test and showed no selective absorption of appreciable intensity above 2200 A.

Experimental.

Reduction of β-Amyradienonyl Acetate.—(*a*) The dienonyl acetate {Picard and Spring, J., 1941, 35; m. p. 248—249°; $[\alpha]_D^{15°}$ +342° (*l* = 1, *c* = 1·1 in pyridine), 1·3 g.} was heated in a sealed tube at 200° for 12 hours with a solution of sodium ethoxide in alcohol (1·2 g. of sodium in 30 c.c. of alcohol) and hydrazine hydrate (99·5%; 3·4 c.c.). The cold solution was poured into water, and the neutral product isolated by means of ether. The ethereal solution was washed with hydrochloric acid, then with water, and dried (sodium sulphate). The residue (1·0 g.) obtained after removal of the ether was dried in a vacuum at 100°, dissolved in a mixture of light petroleum (b. p. 40—60°) (50 c.c.) and benzene (20 c.c.), and filtered through a column (21 × 3 cm.) of activated alumina (Brockmann). The column was washed

successively with light petroleum (b. p. 40—60°), light petroleum–benzene, benzene, and ether to give the following fractions :

	Solvent, c.c.	Wt. of fraction, g.		Solvent, c.c.	Wt. of fraction, g.
1	Light petroleum, 300	nil	6	Benzene 250	0·3
2	,, ,, 250	,,	7	,, ,,	0·2
3	Light petroleum–benzene (1 : 1), 250	,,	8	,, ,,	0·02
4	,, ,, ,, ,, ,,	trace	9	Ether, 250	0·32
5	Benzene, 250	0·05	10	,, ,,	nil

Fraction 6 was difficult to crystallise. It separated in a crystalline condition on careful cooling of a solution in methanol, but it showed a great tendency to separate in a gelatinous form. The fraction was reconstituted by removal of solvent, dried, and acetylated by heating on the steam-bath for 1 hour with pyridine (6 c.c.) and acetic anhydride (4 c.c.). The product was crystallised thrice from methanol–acetone, from which allo-*β-amyrin acetate* separated in plates, m. p. 215—217°, $[\alpha]_D^{20°}$ +147° (*l* = 0·5, *c* = 1·3 in pyridine); it gives a pale yellow colour with tetranitromethane in chloroform. When mixed with *β*-amyradienyl-II acetate the m. p. was depressed to 203—207° (Found : C, 81·9; H, 10·9. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%).

Fraction 7 separated from aqueous alcohol as plates, m. p. 216—217·5°. After two further crystallisations from acetone, this alcohol was obtained as plates, m. p. 219—220°. It gives a brown coloration with tetranitromethane in chloroform. When mixed with *β*-amyradienol-II it melted at 220·5—221° (Found : C, 85·2; H, 11·4. Calc. for $C_{30}H_{48}O$: C, 84·8; H, 11·4. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%). *Light absorption in alcohol :* Principal maximum at 2510 A., ε = 21,000, with subsidiary maxima at 2430 and 2600 A. Ruzicka, Müller, and Schellenberg (*loc. cit.*) give max. 2510, log ε = 4·5 for *β*-amyradienol-II. The alcohol (20 mg.) was acetylated by heating on the steam-bath with pyridine (1 c.c.) and acetic anhydride (1 c.c.) for 30 minutes. The product was precipitated by addition of water, filtered, dried, and crystallised twice from methanol–acetone, from which the acetate separated as plates, m. p. 209—211°.

Fraction 9 from the chromatogram separated from aqueous alcohol as prismatic needles. As the purification of the free alcohol was wasteful, the fractions were combined, the solvents removed, and the residue was acetylated by 14 hours' keeping with pyridine (1 c.c.) and acetic anhydride (1 c.c.). The mixture was then heated on the steam-bath for 10 minutes, and the acetate isolated in the usual way by means of ether. After three crystalllisations from methanol–acetone, allo-*β-amyrenonyl acetate* separated as iridescent plates, m. p. 262—265°—depressed to 248·5—250° when mixed with *β*-amyrenonyl acetate (m. p. 260—261°); $[\alpha]_D^{18°}$ +67° (*l* = 0·5, *c* = 0·5 in chloroform) (Found : C, 79·8; H, 10·6. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·45%). *Light absorption in alcohol :* Maximum at 2460 A., ε = 11,000.

(*b*) *β*-Amyradienonyl acetate (0·7 g.) was heated in an autoclave for 12 hours at 200° with an alcoholic solution of sodium ethoxide (0·6 g. of sodium in 12 c.c. of alcohol) and hydrazine hydrate (90%; 1·7 c.c.). The cold reaction mixture was poured into water, and the neutral product isolated by means of ether. The product was crystallised from acetone containing a small amount of methyl alcohol, giving needles, m. p. 208—211°, which after two further crystallisations from acetone had m. p. 217° (100 mg.); the m. p. could not be raised appreciably by repeated crystallisation. This alcohol gives an intense red-brown colour with tetranitromethane in chloroform, and when mixed with *β*-amyradienol-I (m. p. 215·5—216·5°) the m. p. was depressed to 175—180°. When mixed with *β*-amyradienol-II (m. p. 228·5°), the m. p. was 218·5—220°. The alcohol, m. p. 217°, was acetylated in the usual manner, and the product crystallised from alcohol to give needles, m. p. 199·5—200·5°, which after two recrystallisations from aqueous acetone formed plates, m. p. 201—202°; $[\alpha]_D^{23°}$ +2° (*l* = 1, *c* = 2 in chloroform); mixed with *β*-amyradienyl-II acetate (m. p. 226°) the m. p. was 210—212°. A solution of the acetate, m. p. 201—202° (25 mg.), in light petroleum (b. p. 40—60°; 35 c.c.) was filtered through a column of activated alumina (10 × 1·5 cm.) and the column washed to give the following fractions :

	Solvent, c.c.	Wt. of fraction.		Solvent, c.c.	Wt. of fraction.
1	Light petroleum (b. p. 40—60°), 110	traces	3	Benzene, 125	20 mg.
2	,, ,, ,, ,, 120	nil	4	,, ,,	nil

Fraction 3 separated from acetone as plates, m. p. 206—208°, $[\alpha]_D$ +2° (*l* = 0·5, *c* = 2·0 in chloroform); when mixed with the acetate of m. p. 209—211°, the m. p. was 208—209°. *Light absorption in alcohol :* Maxima at 2430, 2510, and 2600 A., ε_{2510} = 22,000.

Oxidation of β-Amyradienyl-II Acetate with Hydrogen Peroxide.—A solution of this acetate (4 g.) in glacial acetic acid (200 c.c.) was treated during 20 minutes with hydrogen peroxide (100-vol.; 10 c.c.) with stirring on the steam-bath. The mixture was heated for a further 2 hours on the steam-bath, and the cold solution precipitated with water. The solid was collected, dried, and fractionally crystallised from acetone. The least soluble crop (fraction A) separated as needles which melted at 283° after sintering at 224°. After three more crystallisations from acetone, the *compound*, $C_{32}H_{50}O_4$, was obtained as small prisms, m. p. 310—313° (sintering at 304°). By concentration of the mother-liquors obtained during the crystallisation of fraction A, further small crops of the same compound were obtained (total yield, *ca.* 35 mg.). It gives a negative reaction with the tetranitromethane reagent (Found : C, 76·6; H, 9·9. $C_{32}H_{50}O_4$ requires C, 77·0; H, 10·1%). *Light absorption in alcohol :* Maximum at 2533 A., ε = 11,000.

Although various changes were made in the reaction conditions in three different experiments, the yield of the compound $C_{32}H_{50}O_4$ could not be appreciably increased.

Concentration of the original acetone mother-liquor from fraction A gave a more soluble product which, after repeated crystallisation from methanol, gave the major oxidation product as fine needles, m. p. 238°, evidently a *diacetate* (Found : C, 73·4; H, 8·6. Ac, 15·5. $C_{34}H_{50}O_6$ requires C, 73·6; H, 9·1. 2Ac, 15·5. $C_{34}H_{48}O_6$ requires C, 73·9; H, 8·7. 2Ac, 15·6%). With tetranitromethane in chloroform, it gives only a very pale yellow coloration, and it does not give a coloration with aqueous ferric chloride solution. It is recovered unchanged after being heated with acetic anhydride, and does not contain any active hydrogen (Zerewitinoff).

" O_5-Acetate " from Compound $C_{32}H_{50}O_4$.—This compound (33 mg.) in glacial acetic acid (2 c.c.) was refluxed with selenium dioxide (70 mg.) for 6 hours. The solution was filtered from selenium, the filtrate precipitated with water, and the solid collected and dried. Two crystallisations from methyl alcohol gave the " O_5-acetate " as fine white needles, m. p. 251·5—252° undepressed when mixed with a specimen prepared by oxidation of *β*-amyrenonyl acetate with selenium dioxide (Mower, Green, and Spring, *loc. cit.*). *Light absorption in alcohol :* Maximum at 2260 A., ε = 3,600.

iso-*β-Amyradienonyl Acetate.*—(*a*) *iso*-*β*-Amyrenonyl acetate (m. p. 288°; 2·0 g.) in boiling glacial acetic acid (60 c.c.) was refluxed for 20 hours with powdered selenium dioxide (2·0 g.). The hot mixture was filtered from selenium, and the yellow-green filtrate treated with water. The solid was collected, washed with water, and dried in an air-oven (1·9 g.). Crystallisation of this solid from aqueous acetone yielded well-defined plates (1·2 g.), m. p. 204°, which after a second crystallisation from the same solvent had m. p. 206° (0·8 g.) and gave a bright yellow colour with the tetra-

nitromethane reagent. A solution of this solid (770 mg.) in benzene (30 c.c.) was filtered through a column of activated alumina (20 g.), and the column washed with benzene. After removal of the benzene, the residue was twice crystallised from aqueous acetone, giving iso-*β-amyradienonyl acetate* (0·4 g.) as plates, m. p. 208°; $[\alpha]_D^{18°}$ − 36·5° (l = 1, c = 0·7 in chloroform). It gives an intense yellow colour with tetranitromethane in chloroform (Found : C, 80·0; H, 10·1. $C_{32}H_{48}O_3$ requires C, 80·0; H, 10·1%).

iso-*β-Amyradienonol* was obtained by refluxing the acetate (200 mg.) for 3 hours with methanolic potassium hydroxide (5%; 20 c.c.). The product, isolated by means of ether, separated from methyl alcohol as hard prisms, m. p. 239° (Found : C, 81·9; H, 10·5. $C_{30}H_{46}O_2$ requires C, 82·1; H, 10·6%).

(*b*) A solution of *iso-β*-amyrenonyl acetate (600 mg.) in glacial acetic acid (25 c.c.) was treated at 75—80° with a solution of bromine in glacial acetic acid (3%; 7·5 c.c.) added dropwise over 15 minutes. Hydrogen bromide was evolved. The pale yellow solution was kept at 80° for another hour, and the product collected by addition of water and filtration. The pale yellow solid was dried in a desiccator, and fractionally crystallised from methanol. The first crop (270 mg., plates) after three recrystallisations from methylated spirit gave *iso-β*-amyrenonyl acetate as plates, m. p. 282—283° undepressed when mixed with a specimen of the starting material. The second crop (30 mg.; m. p. 267—273°) proved to be impure *iso-β*-amyrenonyl acetate. The third crop (100 mg.), obtained by further concentration of the methanolic mother-liquor from the second crop, separated as plates, m. p. 200—203°, which after two recrystallisations from aqueous acetone gave *iso-β*-amyradienonyl acetate as plates, m. p. 204—206° undepressed when mixed with the specimen prepared by method (*a*). It gives a bright yellow colour with the tetranitromethane reagent.

THE UNIVERSITY, MANCHESTER.

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