231. *Triterpene Resinols and Related Acids. Part VII.*

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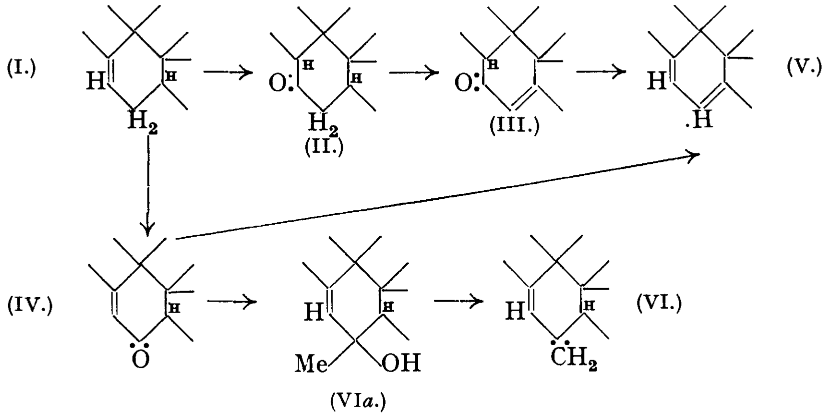
Oxidation of α-amyrenyl benzoate (I) with hydrogen peroxide is shown to give the saturated ketone *α-amyranonyl benzoate* (II), which, like β-amyranonyl acetate (Part VI, this vol., p. 1045), is partially dehydrogenated on treatment with bromine to yield the αβ-unsaturated ketone iso-*α-amyrenonyl benzoate* (III). The latter, on reduction with sodium and amyl alcohol, followed by treatment of the product with acetic anhydride, is converted into α-amyradienyl acetate (V), identical with that previously prepared from α-amyrenonol (IV) (Part IV, J., 1937, 249). This series of reactions emphasises the similarity in properties of the α- and β-amyrenols and points to a close structural resemblance of the unsaturated rings of these alcohols. Nevertheless, the unsaturated centre of the α-isomer is considerably less reactive than that of the β-isomer.

TREATMENT of β-amyrenyl acetate and of β-amyrenol with perbenzoic acid gives the saturated ketones β-amyranonyl acetate and β-amyranonol respectively (Spring and Vickerstaff, J., 1934, 1859; Picard, Sharples, and Spring, *J. Soc. Chem. Ind.*, 1939, **58**, 58; this vol., p. 1045). α-Amyrenol, on the other hand, is considerably more stable than the β-isomer; it is unaffected by perbenzoic acid (Ruzicka, Silbermann, and Furter, *Helv. Chim. Acta*, 1932, **15**, 482) and we find that its acetate is unchanged after prolonged treatment with the same reagent. In the same way, a marked difference in reactivity has been noted when α-amyrenyl acetate and β-amyrenyl acetate are treated with hydrogen peroxide, the latter being oxidised to β-amyranonyl acetate (Spring, J., **1933**, **1345**; Picard, Sharples, and Spring, *loc. cit.*), whereas the former is not changed under the same experimental conditions (Spring and Vickerstaff, *loc. cit.*; cf. Ruzicka, Müller, and Schellenberg, *Helv. Chim. Acta*, 1939, **22**, 760, footnote 6). By a change in the experimental conditions we have now enforced the oxidation of α-amyrenyl acetate with hydrogen peroxide; the yield of crystalline oxidation product is small and its nature will be reported upon later.

Oxidation of α-amyrenyl benzoate with hydrogen peroxide proceeds more smoothly than in the case of the acetate, giving a mixture of the saturated ketone *α-amyranonyl benzoate*, $C_{37}H_{54}O_3$ (II), m. p. 205—206°, and a much smaller amount of a compound, m. p.

302—304°, which has not been examined. As in the case of β-amyranonyl acetate, the carbonyl group of α-amyranonyl benzoate is inert, failing to react with alcoholic solutions of semicarbazide acetate or hydroxylamine. α-Amyranonyl benzoate is unchanged after treatment with acetic anhydride and pyridine, but on reduction with sodium and amyl alcohol it gives *dihydroxy-α-amyrane*, m. p. 199—201°, characterised by the formation of its *diacetate*, m. p. 203—205°, neither of which gives a coloration with tetranitromethane in chloroform. We have previously shown that the ethenoid linkage of α-amyrenol is immediately adjacent to a methylene group, since oxidation of α-amyrenyl acetate (I) with chromic anhydride gives the αβ-unsaturated ketone, α-amyrenonyl acetate (IV) (Spring and Vickerstaff, J., 1937, 249). The formation of the saturated ketone α-amyranonyl benzoate by oxidation of α-amyrenyl benzoate with hydrogen peroxide may be interpreted to indicate that the ethenoid linkage of α-amyrenol is of the type $-\overset{|}{C}=C-CH_2-$ as in the case of β-amyrenol, in order to account for the facility with which the intermediate diol is dehydrated to the saturated ketone.

Treatment of α-amyranonyl benzoate with bromine gives the αβ-unsaturated ketone iso-*α-amyrenonyl benzoate* (III), m. p. 205—206°, a behaviour similar to that of β-amyranonyl acetate and of methyl ketoacetyldihydro-oleanolate (Picard, Sharples, and Spring, *loc. cit.*). It is worthy of comment that the melting points of α-amyranonyl benzoate and of *iso*-α-amyrenonyl benzoate are indistinguishable, as are those of β-amyranonyl acetate and *iso*-β-amyrenonyl acetate, although, in contrast to the latter pair, a marked depression is observed on admixture of the former pair; the analogously constituted compounds methyl ketoacetyldihydro-oleanolate (193—195°) and methyl *iso*ketoacetyloleanolate (203—204°) differ appreciably in melting point. Hydrolysis of *iso*-α-amyrenonyl benzoate gives iso-*α-amyrenonol*, m. p. 236—238°, further characterised by the formation of its *acetate*, m. p. 276·5°. *iso*-α-Amyrenonol exhibits the typical absorption spectrum of an αβ-unsaturated ketone.



Reduction of *iso*-α-amyrenonyl benzoate with sodium and amyl alcohol, followed by treatment of the product with acetic anhydride, gives α-amyradienyl acetate (dehydro-α-amyrenyl acetate) (V) identical with that prepared by reduction of α-amyrenonol (IV) (Spring and Vickerstaff, 1937, *loc. cit.*). α-Amyradienyl acetate was shown by Beynon, Sharples, and Spring (J., 1938, 1233) to contain a conjugated system of two ethylenic linkages situated in one ring and not distributed between two rings, since it exhibits intense absorption with a maximum at 2800 A., log $\epsilon = 4{\cdot}057$. It has recently been shown by Ruzicka, Müller, and Schellenberg (*Helv. Chim. Acta*, 1939, **22**, 767) that treatment of α- and β-amyrenonol (IV) with methylmagnesium iodide, followed by acetylation of the products, give " α- and β-methyl dehydro-acetates " respectively, which exhibit intense absorption at 2400 A., log $\epsilon = 4{\cdot}3$, from which the conclusion is drawn that the conjugated system of the " methyl dehydro-derivatives " is distributed between two adjacent rings. In the light of the established structures of the α- and β-amyrenonols and their conversion into the corresponding amyradienyl acetates (V) it appears to us highly probable that the "methyl dehydro-acetates" are in reality methylene-amyrenyl acetates of the structure (VI), dehydration of the intermediate tertiary alcohol (VI*a*) proceeding with formation of an exocyclic methylene group as in the case of 7-ketocholesteryl acetate, which on treatment with methylmagnesium iodide gives 7-methylenecholesterol (Bann, Heilbron, and Spring, J., 1936, 1274). The latter, like the dehydro-compounds described by Ruzicka, Müller, and Schellenberg, exhibits an absorption maximum at 2360 A., log $\epsilon = 4\cdot3$.

EXPERIMENTAL.

All melting points are uncorrected.

α-Amyranonyl Benzoate.—α-Amyrenyl benzoate (m. p. 194°, 10 g.) in glacial acetic acid (300 c.c.) was treated with 80 c.c. of a solution of hydrogen peroxide (60 c.c.; 30%) in glacial acetic acid (60 c.c.), added uniformly during 15 minutes, after 2 hours the remainder of the hydrogen peroxide solution was added during 10 minutes, and after 1 hour the mixture was largely diluted with water. All these operations were done at the temperature of the steam-bath and stirring was continuous throughout. The solid was collected, washed with water, and extracted with boiling acetone. The insoluble residue was crystallised four times from chloroform–methyl alcohol (1 : 1), from which an unidentified compound separated in plates, m. p. 302—304° (yield, 5%) (Found : C, 77·3, 77·2, —; H, 8·5, 8·85, 8·4%). On standing, the acetone extract deposited *α-amyranonyl benzoate* in needles, m. p. 205—206° after six crystallisations from acetone, $[\alpha]_{\mathrm{D}}^{19\cdot5^\circ} + 113\cdot6^\circ$ ($l = 1$, $c = 0\cdot66$ in chloroform). It did not give a coloration with tetranitromethane in chloroform (Found: C, 81·2; H, 9·8. $C_{37}H_{54}O_3$ requires C, 81·3; H, 10·0%). Under as far as possible the same experimental conditions, the yield of α-amyranonyl benzoate varied considerably; in one experiment it was at least 70%, whereas in several others it was 20—30%. In one experiment, when the oxidation was complete, water was added to the hot solution until it became opalescent, and the solution cooled. The fine needles separating had m. p. 190—195° and after three crystallisations from acetone gave α-amyranonyl benzoate, m. p. 205—206° (Found : C, 81·2; H, 10·0%). The aqueous acetic acid mother-liquor was largely diluted with water, and the solid that separated was collected and taken up in hot acetone. The crystalline solid obtained was recrystallised from chloroform–methanol, from which the compound, m. p. 302—304°, separated in plates.

Dihydroxy-α-amyrane.—α-Amyranonyl benzoate (4 g.) in boiling amyl alcohol (technical, 50 c.c.) was treated with sodium (4 g.). After 30 minutes sodium (4 g.) was again added, and the mixture boiled for 1 hour, further additions of amyl alcohol being made from time to time. The sodium amyloxide was decomposed by the addition of water and the amyl alcohol, after being washed repeatedly with water, was removed in steam, leaving the crude diol as a brittle solid. After four crystallisations from methyl alcohol–acetone (1 : 1) *dihydroxy-α-amyrane* was obtained in compact rosettes of needles, m. p. 199—201°, unaltered by recrystallisation. After drying in a high vacuum over phosphoric oxide for 4 hours, it melted at 198—199° and had $[\alpha]_{\mathrm{D}}^{19\cdot5^\circ} + 70\cdot3^\circ$ ($l = 1$, $c = 0\cdot47$ in chloroform) (Found: C, 81·3; H,12·1. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%).

Diacetoxy-α-amyrane.—The crude diol (2 g.) was heated on the water-bath with pyridine (20 c.c.) and acetic anhydride (20 c.c.) for 2½ hours. The mixture was largely diluted with water and extracted with ether, and the extract washed with water and dried (sodium sulphate). Removal of the ether gave a resin, a solution of which in acetic anhydride deposited slender needles on cooling. After three crystallisations from methanol *diacetoxy-α-amyrane* was obtained in long needles, which, after drying in a high vacuum at 100° over phosphoric oxide for 4 hours, had m. p. 203—205°, $[\alpha]_{\mathrm{D}}^{19\cdot5^\circ} + 90\cdot0^\circ$ ($l = 1$, $c = 0\cdot17$ in chloroform) (Found : C, 77·3; H, 10·6. $C_{34}H_{56}O_4$ requires C, 77·2; H, 10·7%).

iso-*α-Amyrenonyl Benzoate.*—A solution of α-amyranonyl benzoate (0·5 g.) in glacial acetic acid (25 c.c.) containing a trace of hydrobromic acid was treated at 55—60° with a solution of bromine in glacial acetic acid (8%; 4 c.c.), added during 5 minutes with vigorous shaking. A crystalline mass separated; when the mixture was heated for 1 hour at 70°, the solid redissolved. The solution was diluted with water, and the precipitated resinous solid collected and crystallised thrice from methyl alcohol–acetone (1 : 1) containing a little water, from which iso-*α-amyrenonyl benzoate* separated in highly refractive octahedra, m. p. 205—206°, unaltered by recrystallisation. In admixture with α-amyranonyl benzoate it melted at 183°. It did not give a coloration with tetranitromethane in chloroform. $[\alpha]_{\mathrm{D}}^{19\cdot5^\circ} + 81\cdot66^\circ$ ($l = 1$, $c = 0\cdot60$ in chloroform) (Found : C, 81·4; H, 9·6. $C_{37}H_{52}O_3$ requires C, 81·6; H 9·6%). *Light* *absorption in alcohol :* The absorption of the αβ-unsaturated ketone chromophore (maximum 2530 A., log ε = 4·042) is clearly present, but is to some extent masked by the high intensity end-absorption (log ε = 4·19, measured at 2415 A.) attributable to the benzoyl group.

α-*Amyradienyl Acetate.*—*iso*-α-Amyrenonyl benzoate (0·3 g.) in boiling amyl alcohol (technical; 12 c.c.) was treated with sodium (0·75 g.), and the mixture heated under reflux for 1 hour, an addition of amyl alcohol (2 c.c.) being made after 30 minutes. The cooled solution was washed with water, and the amyl alcohol removed by distillation in steam. The residual resinous solid was taken up in ether and dried (sodium sulphate). Removal of the ether yielded a solid, which was heated under reflux with acetic anhydride for 1 hour. The excess of acetic anhydride was decomposed with water, the mixture extracted with ether, and the extract washed with water and dried (sodium sulphate). The resin obtained after removal of the ether was taken up in methyl alcohol, and the solution refrigerated, giving α-amyradienyl acetate in fine needles which after three crystallisations from aqueous acetone had m. p. 165—166°, showing no depression on admixture with a specimen prepared from α-amyrenonol (Spring and Vickerstaff, 1937, *loc. cit.*, give m. p. 170°; the slight variation in m. p. of this derivative according to its method of preparation will be discussed in a later communication). It gave a deep yellow coloration with tetranitromethane in chloroform. $[\alpha]_D^{19.5°}$ + 319·2° (l = 1, c = 0·052 in chloroform). *Light absorption in alcohol :* Maximum at 2815 A., log ε = 4·063.

iso-α-*Amyrenonol.*—*iso*-α-Amyrenonyl benzoate (1 g.) was heated under reflux with alcoholic potassium hydroxide solution (12%, 75 c.c.) for 4 hours. The mixture was diluted with water, and the solid collected, washed with water, and taken up in slightly aqueous methyl alcohol–acetone (1 : 1), from which fine needles separated on cooling. After three further crystallisations (charcoal) from aqueous acetone iso-α-*amyrenonol* separated in long slender needles, m. p. 236—238°, $[\alpha]_D^{19.5°}$ + 72·11° (l = 1, c = 0·624 in chloroform). It was freely soluble in chloroform and moderately soluble in acetone and did not give a coloration with tetranitromethane in chloroform (Found : C, 81·8; H, 10·9. $C_{30}H_{48}O_2$ requires C, 81·7; H, 11·0%). *Light absorption in alcohol :* Maximum at 2500 A., log ε = 4·015.

iso-α-*Amyrenonyl Acetate.*—*iso*-α-Amyrenonol (0·25 g.) was heated on the steam-bath for 3 hours with pyridine (2 c.c.) and acetic anhydride (3 c.c.). After 2 days large plates separated, m. p. 276·5° after three crystallisations from ethyl acetate containing some methyl alcohol (Found : C, 79·5; H, 10·7. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·45%).

Grateful acknowledgment is made to the Chemical Society and Imperial Chemical Industries, Ltd., for grants and to Dr. A. E. Gillam for the absorption spectrum measurements.

THE UNIVERSITY, MANCHESTER. [*Received, June 7th,* 1939.]