224. *The Triterpene Resinols and Related Acids. Part IX. The Oxidation of α-Amyradienyl Acetate.*

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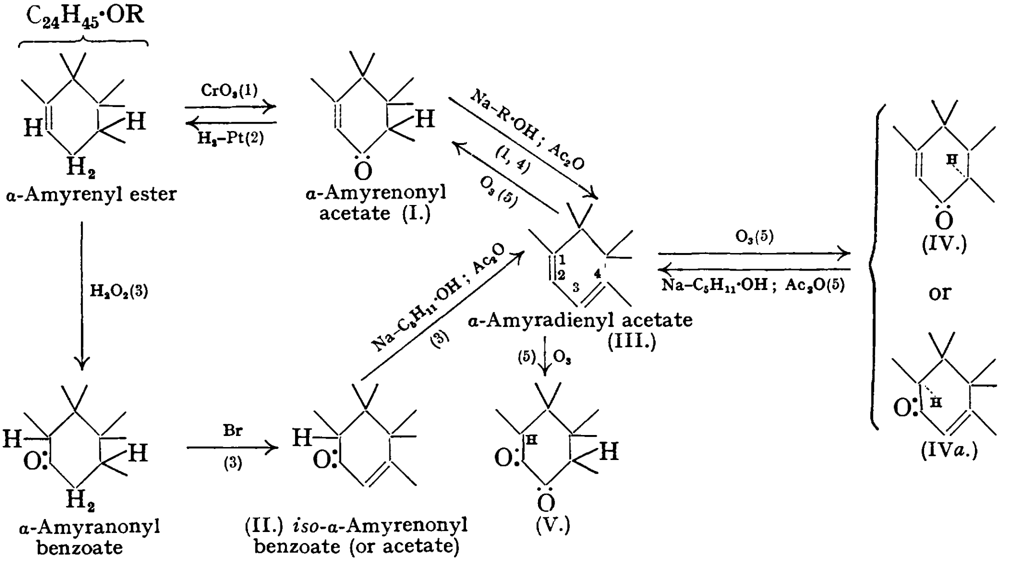
Ozonisation of α-amyradienyl acetate (III) gives α-amyrenonyl acetate (I), epi(iso)-*α-amyrenonyl acetate* (IV or IV*a*), and *α-amyradionyl acetate* (V), oxidation having occurred in each case without ring fission.

In continuation of our investigations into the location of the ethenoid linkage of α-amyrenol, we have undertaken a more detailed examination of α-amyradienyl acetate (III); the latter contains a conjugated system which we consider is located in a single ring, since it exhibits an absorption maximum at 2800 A., $\varepsilon_{max.} = 11,000$ (Spring and Vickerstaff, J., 1937, 239; Ewen, Spring, and Vickerstaff, J., 1939, 1303). The unsaturated ring in α-amyradienyl acetate must also include at least one angular methyl group attachment, since it does not show any tendency to oxidation to an aromatic ring. The dienyl acetate fails to react with bromine under conditions which successfully converted pyroquinovadiene acid into the corresponding partially aromatic pyroquinovatriene acid (Wieland and Schlenk, *Annalen*, 1939, **539**, 242).

Oxidation of the dienyl acetate with chromic anhydride gives an αβ-unsaturated hydroxy-ketone, $C_{32}H_{50}O_4$ (Beynon, Sharples, and Spring, J., 1938, 1233). In the hope of effecting oxidation of α-amyradienyl acetate (III) with extrusion of C_2 and C_3 we have examined its behaviour with ozone. Ozonisaton of the dienyl acetate at 0° gives a mixture of α-amyrenonyl acetate (I) (Spring and Vickerstaff, *loc. cit.*) and a more soluble acetate, m. p. 199—200°, $[\alpha]_D + 56°$. The latter, for which analysis indicates the formula $C_{32}H_{50}O_3$, exhibits the absorption spectrum of an αβ-unsaturated ketone and on reduction with sodium and amyl alcohol, followed by treatment with acetic anhydride, it is converted into α-amyradienyl acetate. This new αβ-unsaturated ketone must therefore be a stereoisomer of either α-amyrenonyl acetate (I) (Spring and Vickerstaff, *loc. cit.*) or *iso*-α-amyrenonyl acetate (II) (Seymour, Sharples, and Spring, J., 1939, 1075), each of which has been converted into α-amyradienyl acetate (III). The acetate, m. p. 199—200°, must differ from one of these αβ-unsaturated ketones in the orientation of the hydrogen attached to either C_4 or C_1 respectively and will be designated epi(iso)-*α-amyrenonyl acetate* (IV or IV*a*).

Ozonisation of α-amyradienyl acetate at 22° gives a mixture of acid and neutral products. The acid fraction is an amorphous powder, and gives a resinous methyl ester. The neutral fraction is a mixture of *epi*(*iso*)-α-amyrenonyl acetate (IV or IV*a*) and a less soluble acetate, m. p. 257—258°. Analysis of the latter indicates the formula $C_{32}H_{50}O_4$ and it has been characterised as an α-diketone or an enolic modification of an α-diketone by the following reactions: It gives an intense green coloration with ferric chloride solution, a pale yellow coloration with tetranitromethane, and when treated with methylmagnesium iodide it evolves one mole of methane. It exhibits an absorption maximum at 2900 A. ($\varepsilon_{max.} = 5400$); the intensity of absorption of the diketone (*α-amyradionyl acetate*, V) is considerably less than that of 6 : 7-diketocholestanyl acetate ($\varepsilon_{max.} = 10,000$) (Heilbron, Jones, and Spring, J., 1937, 801) but is of the same order as that of form A of cholestane-2 : 3-dione ($\varepsilon_{max.} = 5000$) (Stiller and Rosenheim, J., 1938, 353). The formation of α-amyradionyl acetate (V) from α-amyradienyl acetate (III) has involved simultaneous oxidation of both ethenoid linkages of the latter. Attempts to prepare a quinoxaline derivative of α-amyradionyl acetate either from an alcoholic solution of the diketone and *o*-phenylenediamine or by heating the two components to 150° were unsuccessful; this result is not surprising in view of the extremely inert nature of the carbonyl group both in α-amyranonyl benzoate (II) (Seymour, Sharples, and Spring, *loc. cit.*) and in α-amyrenonyl acetate (Spring and Vickerstaff, *loc. cit.*).



(1) Part IV, J., 1937, 249. (2) Ruzicka, Leuenberger, and Schellenberg, *Helv. Chim. Acta*, 1937, **20**, 1271. (3) Part VII, J., 1939, 1075. (4) Part VIII, J., 1939, 1303. (5) This paper.

EXPERIMENTAL.

In an attempt to facilitate the preparation of α-amyradienol, we have investigated the reduction of α-amyrenonyl benzoate with sodium and amyl alcohol. Crystallisation of the product gave the addition-reduction product, $C_{35}H_{62}O_3$, m. p. 228—229°, identical with that previously obtained by similar reduction of α-amyrenonol (Ewen, Spring, and Vickerstaff, J., 1939, 1303) and which on treatment with acetic anhydride and sodium acetate gave α-amyradienyl acetate, m. p. 165—166°. When, however, the gross reduction product (without crystallisation) was heated with acetic anhydride and sodium acetate, a mixture was obtained giving a less soluble fraction, m. p. 180—182°, and only a very small amount of α-amyradienyl acetate, m. p. 165—166°. The acetate, m. p. 180—182°, is less dextrorotatory than α-amyradienyl acetate, and although it exhibits an absorption maximum at 2810 A., the intensity of absorption ($\varepsilon_{max.} = 6000$) is considerably less than that of α-amyradienyl acetate ($\varepsilon_{max.} = 11,000$). It is in all probability a mixed crystal of α-amyradienyl acetate and a component which does not exhibit selective absorption in the ultra-violet; attempts to resolve the acetate, m. p. 180—182°, by crystallisation or by chromatography were unsuccessful.

epi(iso)-α-*Amyrenonyl Acetate.*—A solution of α-amyradienyl acetate (m. p. 165—166°, $[\alpha]_D^{20°}$ + 330°) (5 g.) in dry chloroform (80 c.c.) was treated with a slow stream of ozonised oxygen (4% ozone) for 15 hours, the temperature being maintained at 0°. The chloroform was removed under reduced pressure, and the residual resin heated under reflux with 2% acetic acid (200 c.c.) for 1 hour. The cooled solution was extracted with ether, and the extract washed with water and then with sodium carbonate solution. Acidification of the alkaline washings did not give a precipitate. Removal of the solvent from the dry ethereal solution yielded a golden resin, a solution of which in alcohol (25 c.c.) deposited a crystalline solid (4 g.). Recrystallisation of this solid gave a less soluble fraction, m. p. 240—250°, which after eight crystallisations from alcohol gave α-amyrenonyl acetate (200 mg.), m. p. 275—276° (constant), not depressed by an authentic specimen, and exhibiting the same characteristic absorption spectrum. The mother-liquor of the crop, m. p. 240—250°, slowly deposited the major product in plates. After several crystallisations from alcohol epi(iso)-α-*amyrenonyl acetate* separated in hexagonal plates or prismatic needles (the form depending upon the concentration of the solution), m. p. 199—200°, $[\alpha]_D^{20°}$ + 56° (l = 0·5, c = 0·5 in chloroform) (Found : C, 79·4; H, 10·6. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%). *Light absorption in alcohol*: Maximum at 2510 A., $\varepsilon_{max.}$ = 11,000.

α-Amyradienyl Acetate.—*epi*(*iso*)-α-Amyrenonyl acetate (1·0 g.) in boiling amyl alcohol (100 c.c.) was treated with sodium (5 g.), added during 30 minutes. The mixture was refluxed for 1 hour, and the amyl alcohol removed in steam. The residue was dried and refluxed with acetic anhydride (35 c.c.) and sodium acetate (0·2 g.) for 2 hours. The product, isolated in the usual manner, after four crystallisations from methyl alcohol gave α-amyradienyl acetate, m. p. 165—166°, $[\alpha]_D^{22°}$ + 329° (l = 1, c = 0·8 in chloroform); on admixture with an authentic specimen the m. p. was 165—166°.

α-Amyradionyl Acetate (V).—A solution of α-amyradienyl acetate (4 g.) in chloroform (50 c.c.) was treated with a slow stream of ozonised oxygen for 8 hours. The reaction mixture was worked up as described above. The acid fraction formed a white amorphous powder, m. p. 150—175°, extremely soluble in the common organic solvents. It was not improved by redissolution in sodium carbonate, extraction of the solution with ether, and reprecipitation with mineral acid. Methylation with methyl sulphate and sodium hydroxide gave a resinous neutral methyl ester. The neutral fraction (2·5 g.) formed a pale yellow resin, a solution of which in alcohol deposited plates, which after five recrystallisations from this solvent yielded *α-amyradionyl acetate*, m. p. 257—258° (constant), $[\alpha]_D^{21°}$ + 120° (l = 0·5, c = 0·5 in chloroform). It gave a pale straw coloration with tetranitromethane in chloroform, and in alcoholic solution an intense dark green coloration with aqueous ferric chloride (Found : C, 76·6; H, 10·3. $C_{32}H_{50}O_4$ requires C, 77·1; H, 10·1%). *Active hydrogen determination* (Zerewitinoff) : 5·52 mg. gave 0·29 c.c. of methane at 18·8° and 758 mm., corresponding to 1·1 atoms of active hydrogen per mole. *Light absorption in alcohol*: Maximum at 2900 A., $\varepsilon_{max.}$ = 5390. After continued scratching, the original mother-liquor of the diketone deposited a second crop (1·5 g.), which on repeated crystallisation from alcohol gave *epi*(*iso*)-α-amyrenonyl acetate in hexagonal plates, m. p. 197—199°, $[\alpha]_D^{20°}$ + 51° (l = 0·5, c = 0·67 in chloroform), showing no depression on admixture with the specimen prepared as described above.

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