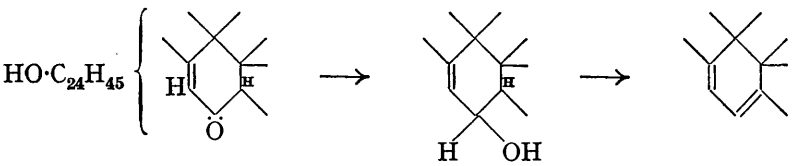
277. *The Triterpene Resinols and Related Acids. Part VIII.*

By E. S. Ewen, F. S. Spring, and T. Vickerstaff.

Reduction of α-amyrenonol (Part IV, J., 1937, 249) with sodium and ethyl alcohol gives a *compound* $C_{32}H_{56}O_3$, whilst with sodium and amyl alcohol, using specified conditions, a compound $C_{35}H_{62}O_3$ results. The formation of these two compounds has involved reduction of the carbonyl group of α-amyrenonol and simultaneous addition of ethyl or amyl alcohol to the ethenoid linkage, since on acetylation and benzoylation they each give α-amyradienyl acetate and benzoate respectively. If the concentration of sodium amyloxide be sufficiently great, reduction of α-amyrenonol with sodium and amyl alcohol leads to the direct formation of α-amyradienol, the intermediate compound $C_{35}H_{62}O_3$ spontaneously decomposing with loss of the elements of amyl alcohol and water. The compounds $C_{35}H_{62}O_3$ is unstable, suffering profound decomposition on crystallisation from acetic acid, and being converted into α-amyradienol on treatment with alcoholic potassium hydroxide.

In Part IV (Spring and Vickerstaff, J., 1937, 249) it was shown that reduction of the αβ-unsaturated ketone α-amyrenonol (I) with sodium and amyl alcohol gives α-amyradienol (dehydro-α-amyrenol) (III) identical with that prepared by Jacobs and Fleck (*J. Biol. Chem.*, 1930, **88**, 137) by the partial dehydrogenation of α-amyrenol with sulphur. It was postulated that an intermediate diol (II) is formed which spontaneously dehydrates to give α-amyradienol (III). The latter was later shown to contain a conjugated system of



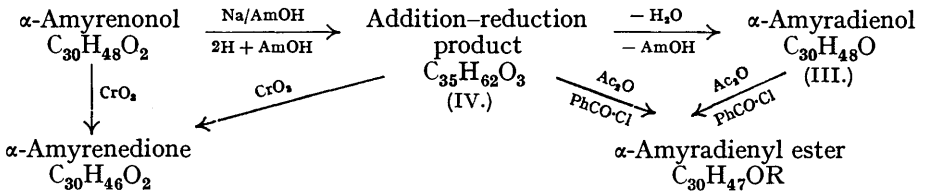
(I.) (II.) (III.)

ethylenic linkages situated in one ring since its acetate exhibits absorption in the ultraviolet region of the spectrum with a maximum at 2800 A, log ε = 4·06 (Beynon, Sharples, and Spring, J., 1938, 1233; Seymour, Sharples, and Spring, this vol., p. 1075). With the object of isolating the intermediate diol we have attempted to reduce α-amyrenonol using the Ponndorf–Meerwein method; the starting material was recovered unchanged. Reduction of α-amyrenonol with sodium and ethyl alcohol, however, gives a *compound*, $C_{32}H_{56}O_3$, m. p. 231°, the formation of which has involved reduction of the carbonyl group to give the diol (II) and simultaneous addition of ethyl alcohol to the ethylenic linkage.

That reduction of the carbonyl group has occurred follows from the observations that the compound, m. p. 231°, is converted into α-amyradienyl acetate on boiling with acetic anhydride and potassium acetate, and that on benzoylation it gives α-amyradienyl benzoate.

Ruzicka, Müller, and Schellenberg (*Helv. Chim. Acta*, 1939, **22**, 767) have reported that treatment of α-amyrenonol with sodium and amyl alcohol, using the conditions employed by Spring and Vickerstaff for the preparation of α-amyradienol, gives a compound $C_{35}H_{60}O_3$ (or $C_{35}H_{62}O_3$), m. p. 225—226°, $[\alpha]_D$ — 50·5°, exhibiting an absorption band at 2800 A, log ε = 1·5, which they conclude has been formed simply by the addition of amyl alcohol to the ethylenic linkage, the carbonyl group having been unaffected.* In the light of experience with the reduction of α-amyrenonol with sodium and ethyl alcohol, a much more attractive hypothesis appeared to us to be that the compound, m. p. 225—226°, is the amyl analogue of the compound, m. p. 231°.

We have reinvestigated the reduction of α-amyrenonol with sodium and amyl alcohol, and find that the nature and yield of the product are very sensitive to changes in the concentration of accumulated sodium amyloxide. In the preparation quoted by Ruzicka, Müller, and Schellenberg, twice the volume of amyl alcohol used by Spring and Vickerstaff was employed (other quantities being the same); using the former conditions, we obtain a nearly quantitative yield of a product, m. p. 225—226°, analysis of which is in agreement with the formula $C_{35}H_{62}O_3$. This compound (IV) has been formed by the addition of amyl alcohol to the unsaturated linkage *and* reduction of the carbonyl to a secondary alcohol group since, as in the case of the analogous compound $C_{32}H_{56}O_3$, it is acetylated or benzoylated to the corresponding α-amyradienyl ester. These reactions have entailed elimination of the attached molecule of amyl alcohol, elimination of a molecule of water between the hydroxyl group derived from the carbonyl group of α-amyrenonol and a neighbouring hydrogen atom (with consequent appearance of a conjugated diene system), and acylation of the hydroxyl group corresponding to that of α-amyrenonol. Under different conditions, acylation of the compound $C_{35}H_{62}O_3$ yields products which are probably di-esters of the diol (II); an examination of these esters will be reported upon later. The instability of the compound $C_{35}H_{62}O_3$ is further exemplified by its conversion into α-amyradienol by heating with alcoholic potassium hydroxide and by its oxidation by means of chromic anhydride to α-amyrenedione, identical with the diketone obtained by oxidation of either α-amyrenol or of α-amyrenonol (Spring and Vickerstaff, J., 1934, 650, 1859).



When a more concentrated solution of α-amyrenonol in amyl alcohol is reduced by the addition of sodium, the compound, m. p. 225—226°, becomes a minor product, the major product being a syrup from which α-amyradienol, identical with the specimen prepared by Spring and Vickerstaff (1937, *loc. cit.*), is readily obtained. The proportion of the two products (IV) and (III) thus depends upon the concentration of sodium amyloxide during the reaction; if this is sufficiently high, the intermediate product (IV) spontaneously decomposes to give α-amyradienol.

Experimental.

All melting points are uncorrected.

Reduction of α-Amyrenonol with Sodium and Ethyl Alcohol.—α-Amyrenonol (Spring and Vickerstaff, *loc. cit.*) (10 g.) in boiling absolute alcohol (250 c.c.) was treated with sodium (10 g.), added as rapidly as the effervescence would permit, and the solution boiled under reflux for 30 mins. Sodium (7 g.) was again added, followed immediately by alcohol (150 c.c.), and the mixture boiled for 30 mins. A further addition of sodium (10 g.) and alcohol (100

* According to this mechanism the formula of the compound will be $C_{35}H_{60}O_3$ and not $C_{35}H_{62}O_3$.

c.c.) was made, and the mixture boiled for 1 hour. The mixture was diluted with water (500 c.c.), the precipitated solid collected, washed with water, and repeatedly crystallised from acetone, from which the *compound* separated in plates of the constant m. p. 231°, $[\alpha]_D^{19°}$ + 48·1° (l = 1, c = 0·64 in chloroform) (Found: C, 78·6, 78·6; H, 11·6, 11·5. $C_{32}H_{56}O_3$ requires C, 78·6; H, 11·5%).

α-Amyradienyl Acetate.—The compound, m. p. 231° (1 g.), was heated under reflux for 1 hour with acetic anhydride (50 c.c.) and anhydrous potassium acetate (0·1 g.). On standing the solution deposited long needles, which after crystallisation from glacial acetic acid melted indefinitely at 165—170°. Repeated crystallisation from methyl alcohol gave α-amyradienyl acetate in fine needles, m. p. 165—166°, $[\alpha]_D^{20°}$ + 325° (l = 1, c = 0·4 in chloroform) (Found: C, 82·1; H, 10·8. Calc. for $C_{32}H_{50}O_2$: C, 82·3; H, 10·8%). *Light absorption in alcohol:* Maximum at 2800 A, log ε = 4·06.

α-Amyradienyl Benzoate.—The compound, m. p. 231° (0·4 g.), was heated under reflux with benzene (1 c.c.), benzoyl chloride (3 c.c.), and pyridine (3 c.c.) for 2 hours. The solution was cooled, diluted with ether, and washed successively with dilute sodium hydroxide solution, dilute hydrochloric acid, and water. The solid obtained after removal of the solvent from the dried (sodium sulphate) solution was crystallised thrice from alcohol, from which α-amyradienyl benzoate separated in large plates, m. p. 173—174° (Found: C, 84·1; H, 9·9. Calc. for $C_{37}H_{52}O_2$: C, 84·0; H, 9·9%).

The Compound, $C_{35}H_{62}O_3$.—α-Amyrenonol (3·5 g.) in boiling technical amyl alcohol (200 c.c.) was treated with sodium (8 g.). The mixture was heated under reflux for 1½ hours, the sodium amyloxide decomposed by shaking with hot water, the solution washed repeatedly with water, and the amyl alcohol removed in steam. The solid was collected, dried by pressing on porous plate, and thrice crystallised from ethyl acetate; the compound was obtained in plates, m. p. 228—229°, which gave a very faint yellow coloration with tetranitromethane in chloroform. After drying for 4 hours in a high vacuum over phosphoric oxide at 80°, the m. p. fell to 225—226°; $[\alpha]_D^{20°}$ + 45·6° (m. p. 228—229°), + 41·5° (m. p. 225—226°) (l = 1, c = 0·44, c = 0·78 in chloroform) [Found (m. p. 225—226°): C, 79·0; H, 11·4. Calc. for $C_{35}H_{62}O_3$: C, 79·2; H, 11·7%].

α-Amyradienyl Acetate.—The compound, m. p. 225—226° (0·1 g.), was heated under reflux for 2 hours with acetic anhydride (3 c.c.) and a trace of potassium acetate. The white granular solid separating on cooling was collected, washed with water, and crystallised twice from aqueous acetone, from which α-amyradienyl acetate separated in fine needles, m. p. 165—166°, $[\alpha]_D^{20°}$ + 333° (l = 1, c = 0·2 in chloroform). It gives a deep brown coloration with tetranitromethane in chloroform, and the m. p. is not depressed on admixture with the specimen described above (Found: C, 82·05; H, 10·9. Calc. for $C_{32}H_{50}O_2$: C, 82·3; H, 10·8%). Hydrolysis of this acetate (0·1 g.) was effected by heating under reflux with alcoholic potassium hydroxide solution (3 c.c.; 10%) for 4 hours. The mixture was diluted with water, and the product isolated by means of ether. After two crystallisations from methyl alcohol, α-amyradienol was obtained as feathery needles, m. p. 157—159°, undepressed on admixture with the specimen prepared as described below.

α-Amyradienyl Benzoate.—The compound, $C_{35}H_{62}O_3$ (0·5 g.), was heated under reflux with benzene (3 c.c.), pyridine (2·5 c.c.), and benzoyl chloride (2·5 c.c.) for 1 hour. The product was isolated by means of ether and crystallised twice from alcohol, giving α-amyradienyl benzoate in plates, m. p. 173—174°, undepressed on admixture with the specimen described by Spring and Vickerstaff (1937, *loc. cit.*) or with that described above. It gives a deep brown coloration with tetranitromethane in chloroform, $[\alpha]_D^{18°}$ + 303° (l = 1, c = 0·76 in chloroform). Jacobs and Fleck (*loc. cit.*) give $[\alpha]_D$ + 305° (in pyridine).

Hydrolysis of the Compound, $C_{35}H_{62}O_3$.—This compound (0·5 g.) in benzene (1 c.c.) was heated under reflux for 6 hours with alcoholic potassium hydroxide (10 c.c.; 10%), and the solution largely diluted with water. The product was isolated by means of ether, and crystallised once from ethyl acetate and then from aqueous acetone, from which α-amyradienol separated as feathery needles, m. p. 159—160°, showing no depression on admixture with the specimens described above (Found: C, 84·8; H, 11·2. Calc. for $C_{30}H_{48}O$: C, 84·8; H, 11·4%).

α-Amyrenedione.—The compound $C_{35}H_{62}O_3$ (0·2 g.) in glacial acetic acid (5 c.c.) was treated with a solution of chromic anhydride (0·08 g.) in acetic acid (2 c.c.; 85%) added during 30 mins. at 70°. The temperature was maintained at 90° for a further 30 mins., the solution largely diluted with water, and the product isolated by means of ether. After two crystallisations from methyl alcohol, α-amyrenedione separated in needles, m. p. 192—193°, undepressed on admixture with the specimen prepared by Spring and Vickerstaff (1934, *loc. cit.*).

Formation of α-Amyradienol by Direct Reduction of α-Amyrenonol.—A solution of α-amyrenonol (5 g.) in boiling technical amyl alcohol (100 c.c.) was treated with sodium (5 g.) added during 2 minutes. When the vigorous reaction had subsided, sodium (5 g.) was again added, and the mixture boiled under reflux for 40 minutes. After the addition of amyl alcohol (50 c.c.), the mixture was boiled under reflux for 1 hour, cooled, shaken with warm water, and the amyl alcohol removed in steam; the resinous solid was collected and taken up in ether. The solution was washed with water, dried (sodium sulphate), and the ether removed. The residue was dissolved in boiling benzene (100 c.c.); the solution on standing deposited a solid, m. p. 222—225° (1·5 g.). Concentration of the mother-liquor failed to yield any solid material. Removal of the benzene gave a golden syrup which was freely soluble in cold ethyl acetate; crystallisation was readily achieved from aqueous acetone, giving fans of feathery needles which, after a single crystallisation from aqueous methanol, yielded α-amyradienol in fine needles, m. p. 157—158°, showing no depression on admixture with the specimens described earlier, $[\alpha]_D^{20\cdot5°}$ + 360° ($l = 1$, $c = 0{\cdot}4$ in chloroform) (Found: C, 84·8; H, 11·3. Calc. for $C_{30}H_{48}O$: C, 84·8; H, 11·4%). Benzoylation of this specimen and crystallisation of the product from alcohol gave α-amyradienyl benzoate as plates, m. p. 167—169°, not depressed on admixture with the two specimens described above.

Grateful acknowledgment is made to the Carnegie Trust for a scholarship which enabled one of us (E. S. E.) to participate in this investigation, and to the Chemical Society for a grant.

THE UNIVERSITY, MANCHESTER. (*Received, June 29th*, 1939.]