225. *The Triterpene Resinols and Related Acids. Part X. β-Amyradienol.*

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Prolonged treatment of β-amyrenonyl benzoate with alkali gives a low-melting β-amyrenonol, probably contaminated with an isomeric αβ-unsaturated ketone. Purification cannot be achieved by crystallisation but is effected by acetylation, pure β-amyrenonyl acetate then being readily isolated.

Reduction of β-amyrenonol with sodium and ethyl and amyl alcohol gives the addition-reduction *compounds* $C_{32}H_{56}O_3$ and $C_{35}H_{62}O_3$ respectively. Treatment of either of these compounds with acetic anhydride yields β-amyradienyl acetate (Beynon, Sharples, and Spring, J., 1938, 1233), which has been further characterised by the preparation of *β-amyradienol*, *β-amyradienyl benzoate*, and *β-amyradienone*. The derivatives of β-amyradienyl acetate described by Simpson (this vol., p. 230) are not homogeneous; they are derived from a mixed crystal containing β-amyradienyl acetate and β-amyrenyl acetate; the β-amyradienone described by Simpson is impure β-amyrenone.

It was shown by Beynon, Sharples, and Spring (J., 1938, 1233), that oxidation of β-amyrenyl benzoate with chromic anhydride gives β-amyrenonyl benzoate, m. p. 265°, which was characterised as an αβ-unsaturated keto-ester. Hydrolysis gave β-amyrenonol, m. p. 175°, acetylation of which yielded β-amyrenonyl acetate, m. p. 260—261°. The oxidation of β-amyrenyl benzoate has been repeated by Ruzicka, Müller, and Schellenberg (*Helv. Chim. Acta*, 1939, **22**, 758), who obtained the αβ-unsaturated keto-benzoate, m. p.

262—263°, and the corresponding acetate, m. p. 264—265°, but in one respect their results differed appreciably from those of Beynon, Sharples, and Spring in that the β-amyrenonol obtained by hydrolysis of the corresponding benzoate (using different reaction conditions) had m. p. 230—231° and not 175°. In view of this discrepancy we have repeated the hydrolysis of β-amyrenonyl benzoate. Hydrolysis, by the method of Beynon, Sharples, and Spring (20 hours) gave a product which was extremely soluble in the common organic solvents and could only be crystallised with relatively large losses of material. After a single crystallisation the hydrolysis product melted to an opaque liquid at 172—174°, which is approximately the melting point recorded by Beynon, Sharples, and Spring for β-amyrenonol. After five further crystallisations a small proportion of the hydrolysis product was obtained, m. p. 222—225°, which was not appreciably altered by further crystallisation. Acetylation of either the material of m. p. 172—174° or that of m. p. 222—225° readily gave β-amyrenonyl acetate, m. p. 261·5—262·5°, in good yield. Hydrolysis of β-amyrenonyl benzoate by the method of Ruzicka, Müller, and Schellenberg (2 hours) gave an alcohol which before crystallisation had m. p. 230° and after two crystallisations attained the constant m. p. 231—233°; acetylation readily gave β-amyrenonyl acetate, m. p. 262—262·5°, identical with that first described by Beynon, Sharples, and Spring (*loc. cit.*). It is probable that the prolonged alkali treatment of β-amyrenonol in part isomerises it, so giving a mixture which is extremely difficult to separate, the corresponding acetylated product, however, being readily purified. Ruzicka, Müller, and Schellenberg (*loc. cit.*) obtained an oily product when β-amyrenonyl benzoate was hydrolysed for 50 hours with 10% alcoholic alkali, from which an isomeric amyrenonol, m. p. 247—248°, was isolated by slow crystallisation. In this experiment the isomerisation has apparently proceeded further than in the 20-hour hydrolysis.

Reduction of β-amyrenonol with sodium and amyl alcohol, followed by treatment of the product with acetic anhydride, gives β-amyradienyl acetate, m. p. 208—209°, $[\alpha]_D$ + 331°, in which the chromophoric system is located in a single ring, since it exhibits an absorption maximum at 2820 A., $\varepsilon_{max.} \simeq 9500$ (Beynon, Sharples, and Spring, *loc. cit.*). In the meantime Ewen, Spring, and Vickerstaff (J., 1939, 1303) have shown that reduction of the analogous α-amyrenonol with sodium and amyl alcohol or with sodium and ethyl alcohol gives unstable addition-reduction products, $C_{35}H_{62}O_3$ and $C_{32}H_{56}O_3$ respectively. In the same way we find that reduction of β-amyrenonol with sodium and amyl alcohol gives a *compound*, $C_{35}H_{62}O_3$, m. p. 238—239°, the formation of which has involved reduction of the carbonyl to a secondary alcohol group and simultaneous addition of amyl alcohol to the ethenoid linkage; reduction of β-amyrenonol with sodium and ethyl alcohol gives the corresponding addition-reduction *compound*, $C_{32}H_{56}O_3$, m. p. 236·5—239·5°. On treatment with acetic anhydride and sodium acetate both of these reduction-addition compounds give one and the same β-amyradienyl acetate, the melting point of which has now been raised to 216—217°, $[\alpha]_D$ + 342°. Hydrolysis of β-amyradienyl acetate gives *β-amyradienol*, m. p. 213·5—214·5°, $[\alpha]_D$ + 320°, further characterised by the preparation of *β-amyradienyl benzoate*, m. p. 250°, $[\alpha]_D$ + 317°.

Oxidation of β-amyradienol gives *β-amyradienone*, m. p. 206—208° (oxime, m. p. 230°), more drastic oxidation giving β-amyrenedione identical with that prepared by the oxidation of either β-amyrenonol (Beynon, Sharples, and Spring, *loc. cit.*) or β-amyrenol (Spring and Vickerstaff, J., 1934, 650). β-Amyradienyl acetate, β-amyradienol, and β-amyradienone all exhibit an absorption maximum at 2820 A., $\varepsilon_{max.} \simeq 10{,}000$.

If the product obtained by reduction of β-amyrenonyl benzoate with sodium and amyl alcohol is treated with acetic anhydride without purification of the intermediate addition-reduction compound, $C_{35}H_{62}O_3$, a mixed crystal, m. p. 223—224°, is obtained which cannot be separated into its components by crystallisation. The mixed crystal exhibits an absorption maximum of 2820 A., of approximately half the intensity ($\varepsilon_{max.} \simeq 5000$) of that of authentic β-amyradienyl acetate. The physical constants of the acetate, m. p. 223—224°, are very similar to those of " dehydro-β-amyrenyl acetate b " of Simpson (this vol., p. 230), which was prepared by the method of Beynon, Sharples, and Spring (*loc. cit.*) except that the intermediate addition reduction product was not purified. The derivatives of dehydro-β-amyrenyl acetate described by Simpson were prepared from this

mixed crystal and differ markedly from the corresponding derivatives of authentic dehydro-β-amyrenyl acetate (β-amyradienyl acetate). In particular the " β-amyradienone " described by Simpson, which exhibits two weak absorption maxima ($\varepsilon_{max.}$ in both cases < 2000), cannot be the ketone corresponding to β-amyradienol, as this would be expected to exhibit approximately the same light absorption properties as the parent alcohol, since both contain the same major chromophore. We have repeated the oxidation of the alcohol obtained by hydrolysis of " dehydro-β-amyrenyl acetate b " and obtained, in small yield, β-amyrenone (Rollett, *Monatsh.*, 1922, **43**, 417), thus proving the presence of β-amyrenyl acetate in the acetate, m. p. 223—224°. The constants recorded by Simpson for " β-amyradienone " show that it is impure β-amyrenone :

"β-Amyradienone" (Simpson) (a) M. p. 170—171°: (b) m. p. 176·5—178°. Oxime, m. p. 268·5—270°	*β-Amyrenone* (Rollett). M. p. 177—179°. Oxime m. p. 267°.

The analyses recorded by Simpson are in better agreement with the theoretical values for β-amyrenone ($C_{30}H_{48}O$) than with those for β-amyradienone ($C_{30}H_{46}O$).

The formation of a similar mixed crystal has been observed in the reduction of α-amyrenonyl esters (Ewen and Spring, preceding paper); this likewise has a higher melting point and a considerably lower intensity of absorption at 2800 A., than α-amyradienyl acetate.

Experimental.

β-Amyrenonyl Benzoate (cf. Beynon, Sharples, and Spring, *loc. cit.*)—The oxidation was effected in the manner previously described. On dilution of the boiling solution with water until crystals separated, followed by cooling, the solution deposited scintillating plates (yield, 33%). When crystallised from acetic acid, β-amyrenonyl benzoate separated in long stout needles or scintillating plates, m. p. 265°, the form depending upon the concentration of the solution and the rate of cooling; the two forms were readily interconvertible; $[\alpha]_D^{20°}$ + 156° ($l = 1$, $c = 0{\cdot}9$ in chloroform).*

Hydrolysis of β-Amyrenonyl Benzoate.—(a) A solution of the benzoate (5 g.) in benzene (25 c.c.) was refluxed with alcoholic potassium hydroxide (10%; 250 c.c.) for 20 hours. The product, isolated in the usual manner, separated from slightly aqueous acetone in needles, m. p. 172—174° to an opaque liquid, which finally cleared at 216—218° After five crystallisations from aqueous acetone, the product was obtained in felted needles, m. p. 222—225° after sintering at 218°. A mixture of this with the alcohol, m. p. 231—233°, obtained by method (b) had m. p. 228—231°.

(b) The hydrolysis was carried out by the method of Ruzicka, Müller, and Schellenberg (*loc. cit.*). After two crystallisations from aqueous acetone the product had m. p. 231—233°. It did not give a coloration with tetranitromethane in chloroform solution (Found: C, 81·6; H, 11·0. Calc. for $C_{30}H_{48}O_2$: C, 81·8; H, 11·0%).

β-Amyrenonyl Acetate.—The alcohol (1·0 g.), obtained by method (b), in pyridine (5 c.c.) and acetic anhydride (5 c.c.) was heated on the steam-bath for 75 minutes. The product, isolated in the usual manner, after one crystallisation from alcohol gave β-amyrenonyl acetate in hard needles, m. p. 262—262·5°, $[\alpha]_D^{20°}$ + 116° ($l = 1$, $c = 0{\cdot}7$ in chloroform) (Found: C, 79·6; H, 10·6. Calc. for $C_{32}H_{50}O_3$: C, 79·6; H, 10·4%). The m. p. of the acetate was not depressed by the original specimen of Beynon, Sharples, and Spring (*loc. cit.*). Similar acetylation of the alcohols, m. p. 172—174° and m. p. 222—224°, prepared by method (a) gave β-amyrenonyl acetate, $[\alpha]_D^{20°}$ + 117° ($l = 0{\cdot}5$, $c = 0{\cdot}7$ in chloroform), m. p. 261—262·5°, undepressed by the specimen described above [Found (specimen from alcohol, m. p. 222—224°): C, 79·5; H, 10·3%].

β-Amyradienyl Acetate.—(a) A solution of β-amyrenonol (11 g., m. p. 230—231°) in boiling absolute alcohol (275 c.c.) was treated with sodium (11 g.), added during 20 minutes with vigorous stirring. After refluxing for a further 10 minutes, the solution was diluted with alcohol (175 c.c.) and further additions of sodium (11 g.) were made during 25 minutes. The mixture was refluxed for 1 hour and largely diluted with water, and the solid collected, washed with water, and dried. The solid was again taken up in alcohol and treated with sodium as described above. The product obtained by precipitation with water was crystallised thrice from ethyl alcohol, from which the addition-reduction *compound* separated in long needles, m. p. 236·5—239·5°.

* The rotations recorded for β-amyrenonyl benzoate and β-amyrenonyl acetate in Part V are to be interchanged; they were interplaced in error.

It gave a faint yellow coloration with tetranitromethane in chloroform (Found: C, 78·6; H, 11·5. $C_{32}H_{56}O_3$ requires C, 78·6; H, 11·5%).

The compound $C_{32}H_{56}O_3$ (2 g.) in acetic anhydride (50 c.c.) was refluxed for 2 hours with sodium acetate (0·25 g.). On cooling, the solution deposited prismatic needles, which after recrystallisation from acetone gave β-amyradienyl acetate in needles, m. p. 217°, $[\alpha]_D^{20°}$ + 342° (l = 1, c = 1·0 in chloroform). It gave a deep brown coloration with tetranitromethane in chloroform and a yellow coloration with antimony trichloride in chloroform (Found: C, 82·4; H, 10·9. Calc. for $C_{32}H_{50}O_2$: C, 82·3; H, 10·8%). Removal of the solvent from the alcoholic mother-liquors of the compound $C_{32}H_{56}O_3$ gave a resin, which after treatment with acetic anhydride and sodium acetate gave a further quantity of β-amyradienyl acetate; this after three crystallisations from acetone separated in needles, m. p. 216·5—217°, undepressed by the specimen described above. Experience has shown that the most direct way to prepare β-amyradienyl acetate is by a *single* reduction of β-amyrenonol with sodium and alcohol, followed by direct treatment of the product (without purification) with acetic anhydride; the dienyl acetate so obtained has m. p. 216—217°. *Light absorption in alcohol:* Maximum at 2820 A., $\varepsilon_{max.}$ = 10,750.

(b) A boiling solution of β-amyrenonol (m. p. 231—233°) (2·2 g.) in amyl alcohol (technical, 80 c.c) was treated during 5 minutes with sodium (4·4 g.), the mixture being stirred. Stirring was continued for 1 hour, the solution washed with hot water, and the amyl alcohol removed in steam. The separated solid was collected, dried, taken up in amyl alcohol (80 c.c.), and again treated with sodium as described above. The product was crystallised thrice from acetone, from which the addition-reduction *compound* separated in long needles, m. p. 238—239° [Found (Specimen dried in a vacuum over phosphoric oxide for 8 hours at 80°): C, 78·9; H, 11·4. $C_{35}H_{62}O_3$ requires C, 79·2; H, 11·7%]. As in the case of α-amyrenonol, this addition-reduction compound is not stable when crystallised from amyl alcohol, the melting point progressively sinking to 215° after three crystallisations.

The compound $C_{35}H_{62}O_3$ (m. p. 238—239°) (0·3 g.) was refluxed with acetic anhydride (25 c.c.) and sodium acetate (0·1 g.) for 2 hours. The product, isolated in the usual manner, was crystallised thrice from acetone, from which β-amyradienyl acetate separated in needles m. p. 216·5—217·5° (constant), undepressed by the specimen prepared by method (a). *Light absorption in alcohol:* Maximum at 2820 A., $\varepsilon_{max.}$ = 10,600.

β-Amyradienol.—β-Amyradienyl acetate (0·2 g.) was refluxed with alcoholic potassium hydroxide (1%; 26 c.c.) for 5 hours. The solution was concentrated to 7 c.c. and diluted with water, and the mixture extracted with ether. Removal of the solvent and crystallisation of the residue from methyl alcohol gave *β-amyradienol* in well-defined needles, m. p. 213·5—214·5°, $[\alpha]_D^{20°}$ + 319° (l = 0·5, c = 0·7 in chloroform). When it was mixed with β-amyradienyl acetate, the m. p. was depressed to 183—189°. β-Amyradienol gave a deep brown coloration with tetranitromethane in chloroform and a yellow solution with antimony trichloride in chloroform (Found: C, 84·4; H, 11·5. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4%). *Light absorption in alcohol:* Maximum at 2810 A., $\varepsilon_{max.}$ 9500.

β-Amyradienol (0·1 g.) was refluxed with acetic anhydride (5 c.c.) for 2 hours. On cooling, prismatic needles separated, which after a single crystallisation from acetone gave β-amyradienyl acetate, m. p. 216—217°, undepressed by the specimens described above, showing an absorption maximum at 2820 A., $\varepsilon_{max.}$ = 10,800.

β-Amyradienyl Benzoate.—β-Amyradienol (0·2 g.) in pyridine (3 c.c.) and benzoyl chloride (1 c.c.) was heated on the steam-bath for 80 minutes. After the addition of 3N-sodium carbonate (30 c.c.) the mixture was extracted with ether. Removal of the solvent and two crystallisations of the residue from methyl alcohol gave *β-amyradienyl benzoate* in scintillating plates, m. p. 250° (constant), $[\alpha]_D^{20°}$ + 317° (l = 0·5, c = 0·9 in chloroform). It gave a deep brown coloration with tetranitromethane in chloroform (Found: C, 84·0; H, 10·2. $C_{37}H_{52}O_2$ requires C, 84·05; H, 9·9%).

β-Amyrenedione from β-Amyradienol.—A solution of β-amyradienol (m. p. 214°) (2·0 g.) in glacial acetic acid (50 c.c.) was treated at 70° with a solution of chromic anhydride (0·7 g.) in water (1 c.c.) and acetic acid (40 c.c.), added during 30 minutes with stirring. The solution was concentrated under reduced pressure to one-quarter bulk and diluted with water, and the product extracted with ether. The extract was washed with sodium carbonate solution (10%) and dried, and the ether removed. The residue was crystallised thrice from methanol, yielding β-amyrenedione in plates, m. p. 235°, undepressed by the specimen described by Spring and Vickerstaff (J., 1934, 650; Beynon, Sharples, and Spring, *loc. cit.*). It did not give a coloration with tetranitromethane in chloroform; $[\alpha]_D^{24°}$ + 144° (l = 1, c = 0·1 in chloroform) (Found:

C, 81·5; H, 10·7. Calc. for $C_{30}H_{46}O_2$: C, 82·1; H, 10·6%). *Light absorption in alcohol:* Maximum at 2510 A., $\varepsilon_{max.}$ = 10,500.

β-*Amyradienone.*—A solution of β-amyradienol (0·6 g.) in glacial acetic acid (50 c.c.) was heated at 70° with a solution of chromic anhydride (0·11 g.) in acetic acid (95%; 20 c.c.), added during 80 minutes with mechanical stirring. The solution was maintained at 70° for a further hour and set aside overnight. The product obtained by precipitation with water contained unchanged β-amyradienol, which was best separated by heating the mixture with pyridine (4 c.c.) and acetic anhydride (4 c.c.) on the steam-bath for 1 hour. The product isolated by means of ether was taken up in alcohol, from which β-amyradienyl acetate separated; after one recrystallisation from methanol it had m. p. 212—214°, undepressed by an authentic specimen. The alcoholic mother-liquors were concentrated and cooled to 0°, giving a second crop which after three crystallisations from methanol–acetone gave β-*amyradienone* in long fine needles, m. p. 206—208°, depressed to 175—189° by β-amyradienyl acetate and to 170—190° by β-amyradienol. It gave a strong brown coloration with tetranitromethane in chloroform (Found: C, 85·1; H, 11·2. $C_{30}H_{46}O$ requires C, 85·2; H, 11·0%). *Light absorption in alcohol:* Maximum at 2820 A., $\varepsilon_{max.}$ = 9200. The oxime, prepared in the usual manner, separated from methanol–ethanol (1 : 1) in small hard prisms, m. p. 234—235° (decomp.).

Acetate, m. p. 223—224°.—A boiling solution of β-amyrenonyl benzoate (6 g.) in amyl alcohol (200 c.c.) was treated with sodium (12 g.), added in small quantities during 30 minutes. After boiling for 2 hours, the amyl alcohol was removed in steam, and the residual solid collected and refluxed with acetic anhydride (70 c.c.) and potassium acetate (5 g.) for 1 hour. The solution was decomposed with water, and the solid collected and crystallised thrice from acetone, giving the *acetate* in long thick needles, m. p. 223—224°; this gave a strong brown coloration with tetranitromethane in chloroform (Found: C, 82·3; H, 11·1. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%. $C_{32}H_{50}O_2$ requires C, 82·3; H, 10·8%). *Light absorption in alcohol:* Maximum at 2820 A., $\varepsilon_{max.}$ = 4740.

β-*Amyrenone.*—The acetate (m. p. 223—224°) (0·26 g.) was refluxed with alcoholic potassium hydroxide (4%; 50 c.c.) for 3 hours; the solution was then concentrated to half bulk and diluted with water, and the product isolated by means of ether. When crystallised from methyl alcohol, it had m. p. 209—211° (sintering at 198°). The m. p. gradually rose with repeated crystallisation. The crude hydrolysis product (0·24 g.) in glacial acetic acid (15 c.c.) was treated at 60° with a solution of chromic anhydride in 95% acetic acid (0·28N; 7 c.c.), added during 30 minutes. After standing overnight at room temperature, the solution was concentrated under reduced pressure to approximately one-third bulk and largely diluted with water, and the mixture extracted with ether. The extract was washed with 10% sodium carbonate solution, and the solvent removed after drying. Crystallisation of the residue from methanol gave small needles, which after two recrystallisations from this solvent attained the constant m. p. 176—178°. The product gave a yellow coloration with tetranitromethane, in contrast to the deep brown coloration produced by β-amyradienol and its derivatives. The m. p. of a mixture with β-amyrenone (m. p. 178—180°) was 179° (Found: C, 84·7; H, 11·5. Calc. for $C_{30}H_{48}O$: C, 84·8; H, 11·4%). The semicarbazone separated from alcohol–benzene in plates, m. p. 242—243°, undepressed by β-amyrenone semicarbazone (m. p. 243—244°).

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