410. *The Resinols. Part III. α- and β-Amyrone Oxides and their Derivatives.*

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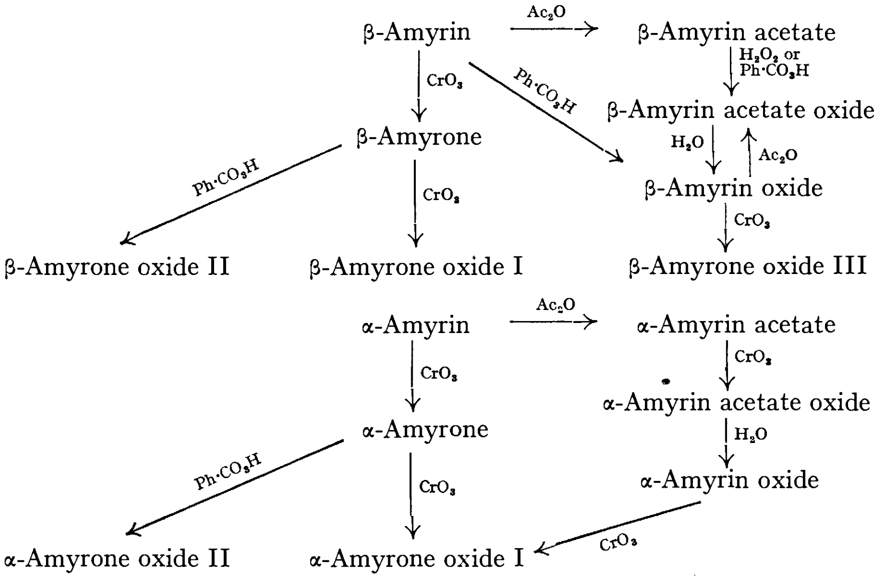
In an attempt to confirm the constitution suggested for α- and β-amyrone oxide (this vol., p. 650) α- and β-amyrone have been oxidised with perbenzoic acid; the two products, however, differ from the corresponding oxides obtained by chromic acid oxidation. The new perbenzoic acid oxides we designate as α- and β-*amyrone oxide* II, and the chromic anhydride products as α- and β-amyrone oxide I. Hitherto there has been little direct evidence that α-amyrin contains an ethenoid linkage apart from the fact that it gives a coloration with tetranitromethane, for Ruzicka, Silbermann, and Pieth (*Helv. Chim. Acta*, 1932, **15**, 482) found that α-amyrin was unaffected by perbenzoic acid. We also find that, in contradistinction to β-amyrin acetate, α-amyrin acetate is not oxidised to an acetate oxide on treatment with hydrogen peroxide in acetic acid solution. The ease of formation of α-amyrone oxide II leaves little doubt that α-amyrone contains a double bond; the possibility of a wandering of the double bond of α-amyrin during its conversion into α-amyrone has not, however, been excluded.

A β-amyrone oxide which does not correspond to either β-amyrone oxide I or II, and which we name β-*amyrone oxide* III, has been prepared by Rollett and Bratke (*Monatsh.*, 1922, **43**, 685) by the chromic acid oxidation of a β-amyrin oxide. The last oxide we now find to be identical with the β-amyrin oxide prepared by Spring (J., 1933, **1345**) by comparison of both the alcohol-oxides and the acetate-oxides prepared by the methods described by both of these authors. This β-amyrin oxide is formulated by Rollett and Bratke as $C_{30}H_{48}O_2$ and is apparently regarded by them as a substitution product and not as an addition product. This view we consider to be most improbable, for on oxidation of β-amyrin acetate with perbenzoic acid we obtained β-amyrin acetate oxide, identical with that of Rollett and Bratke and with that of Spring, and giving the same β-amyrin oxide on hydrolysis. β-Amyrone oxide III appears to be closely related to the product formed by the action of perbenzoic acid upon β-amyrin itself (cf. Ruzicka, Silbermann, and Pieth, *loc. cit.*). For instance, in one oxidation of β-amyrin with perbenzoic acid we obtained a product, m. p. 197° alone or when mixed with the β-amyrin oxide obtained by the hydrogen peroxide method. Furthermore, this product on acetylation gave the same acetate, and on oxidation the same ketone, as obtained from the hydrogen peroxide product. When the concentration of the perbenzoic acid solution was increased, however, an isomeric substance was obtained differing from the hydrogen peroxide product. It is evident that in addition to simple oxide formation the free alcohol is prone to oxidation at the secondary hydroxyl group when treated with perbenzoic acid.

An " oxy-α-amyrin," $C_{30}H_{48}O_2$, has been described by Vesterberg (*Ber.*, 1891, **24**, 3834); in this compound only one of the oxygen atoms has been characterised. Since oxy-α-amyrin was prepared by the chromic acid oxidation of α-amyrin acetate, it appeared probable that it was closely related to α-amyrone oxide I. This was found to be the case, for on mild oxidation of oxy-α-amyrin, α-amyrone oxide I was obtained identical with the product obtained by chromic acid oxidation of α-amyrin.

The oxide ring present in these various products is extraordinarily stable and has resisted all attempts at simple rupture.

In view of the complexity of the reactions of α- and β-amyrin, we append a table showing the various transformations described in this communication :



EXPERIMENTAL.

β-*Amyrone Oxide* II.—β-Amyrone (1 g.) in a chloroform solution of perbenzoic acid (130 c.c.; 0·4*N*) was set aside for 4 days at 0°. The solution was extracted with aqueous sodium carbonate and dried over sodium sulphate, the chloroform removed, and the residual oil repeatedly crystallised from methyl alcohol, β-*amyrone oxide* II being obtained as well-formed needles, m. p. 234° (Found : C, 7·90; H, 10·5. $C_{30}H_{48}O_3$ requires C, 78·9; H, 10·6%), and 210° in admixture with β-amyrone oxide I of m. p. 237°.

β-*Amyrin Acetate Oxide.*—(a) β-Amyrin acetate (4·8 g.), dissolved in a chloroform solution of perbenzoic acid (50 c.c.; 0·55*N*), was kept at 0° for 18 days. The neutral product, isolated in the usual manner, formed a resinous mass, which was dissolved in the least possible quantity of hot benzene, and ethyl acetate added until the solution became opalescent. On cooling, the oxide separated in transparent hexagonal laminæ, m. p. 293° after two recrystallisations. (b) β-Amyrin oxide (0·15 g.) prepared by method (b) (see below) was refluxed with acetic anhydride (4 c.c.) and potassium acetate (0·01 g.) for 30 minutes. The solution was poured into water, and the solid collected and recrystallised from benzene–ethyl acetate, ultimately giving laminæ, m. p. 292°. (c) β-Amyrin acetate oxide, prepared by the method of Rollett and Bratke (*loc. cit.*), separated from alcohol as ill-defined plates, but after crystallisation from benzene–ethyl acetate it formed hexagonal laminæ, m. p. 292°. The products obtained by methods (a), (b), and (c) were identical, no depression in melting point being observed on intermixing the three specimens. Furthermore, this acetate oxide is identical with the oxy-β-amyrin acetate prepared by Spring (*loc. cit.*), which showed no depression in melting point on admixture with each of the products prepared by methods (a), (b), and (c).

β-*Amyrin Oxide.*—(a) β-Amyrin acetate oxide (1 g.) in a mixture of benzene (10 c.c.) and absolute alcohol (20 c.c.) was refluxed for 3 hours with caustic potash (2 g.). The solution was diluted with water and extracted with ether, and the extract washed with dilute sulphuric acid and dried over sodium sulphate. Removal of the ether left a yellow resin, which crystallised from acetone when the solution was cooled very slowly. If the solution is cooled quickly, the oxide separates as a gelatinous mass. The oxide forms colourless prisms, m. p. 203—204°. (b) β-Amyrin (5 g.) was dissolved in a chloroform solution of perbenzoic acid (50 c.c.; 0·55*N*) and kept at 0° for 18 days. The neutral product was obtained in the usual manner, and the resulting yellow resin dissolved in a little ethyl acetate and kept at 0° for several days; solid then separated, and after two crystallisations from alcohol the oxide formed prisms, m. p. 197°. (c) β-Amyrin oxide (" oxy-β-amyrin ") prepared by the method of Rollett and Bratke (*loc. cit.*) formed prisms, m. p. 202°. (d) The method of Spring (*loc. cit.*) gave the same β-amyrin oxide as prisms, m. p. 203—204°. The oxides obtained by methods (a), (b), (c), and (d) gave no depressions in melting point on intermixing.

β-*Amyrone Oxide* III.—β-Amyrin oxide was oxidised by chromic anhydride in the manner described by Rollett and Bratke (*loc. cit.*). β-Amyrone oxide III was obtained as needles from alcohol, m. p. 217° (Rollett and Bratke give m. p. 217°). When mixed with β-amyrone oxide I, the m. p. was depressed to 198°, and with β-amyrone oxide II to 204°.

α-*Amyrone Oxide* I—Oxy-α-amyrin (0·9 g.) (Vesterberg, *loc. cit.*) in glacial acetic acid (20 c.c.) was treated with a solution of chromic anhydride (1 g.) in acetic acid (30 c.c.), added during 1 hour, the temperature being maintained at 70° throughout. The solid was precipitated with water, taken up in ether, and washed with sodium carbonate solution. The product separated from methyl alcohol in needles, m. p. 193° either alone or in admixture with α-amyrone oxide I prepared by the direct chromic acid oxidation of α-amyrin. Furthermore, the semicarbazone had m. p. 223° either alone or in admixture with the semicarbazone of α-amyrone oxide I (Spring and Vickerstaff, *loc. cit.*).

α-*Amyrone Oxide* II.—α-Amyrone (2 g.) in chloroform (20 c.c.) was treated with a solution of perbenzoic acid in chloroform (100 c.c.; 0·4*N*). After standing for 4 days at 0°, the neutral product was isolated and crystallised from methyl alcohol–acetone, *α-amyrone oxide* II separating in needles, m. p. 183° (Found: C, 81·6; H, 11·1. $C_{30}H_{48}O_2$ requires C, 81·7; H, 11·0%). $[\alpha]_D^{19°}$ + 125° (c = 4·7 in chloroform). The melting point is depressed to 165° on admixture with α-amyrone oxide I.

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