135. *The Resinols. Part II. The Oxidation of α- and β-Amyrins with Chromic Anhydride.*

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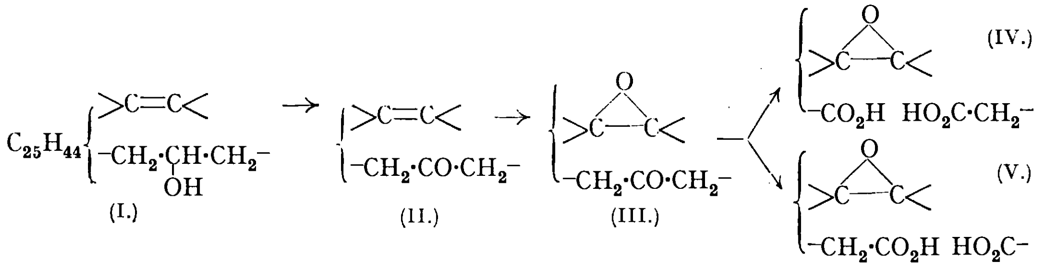
Oxidation of β-amyrin with chromic anhydride has been shown to give the ketone β-amyrone (Vesterberg, *Ber.*, 1891, **24**, 3834; Hormann, *Arch. Pharm.*, 1930, **268**, 64). Using 2—3 mols. of chromic anhydride, we now find that β-amyrin gives a neutral substance, $C_{30}H_{48}O_2$, together with acidic products. The former is a monoketone characterised by its *semicarbazone*, m. p. 232°. It is improbable that the second oxygen atom is present as a hydroxyl group, as the original substance is recovered unchanged after treatment with acetic anhydride and no methane is evolved on treating the substance with methylmagnesium iodide. In contradistinction to β-amyrin and β-amyrone, the substance $C_{30}H_{48}O_2$ is saturated in that it gives no coloration with tetranitromethane in chloroform solution. That β-amyrone is an intermediate in the oxidation of β-amyrin to the substance $C_{30}H_{48}O_2$ is shown by the formation of the latter by the further oxidation of β-amyrone with chromic anhydride. It follows that the substance $C_{30}H_{48}O_2$, *β-amyrone oxide* (III), is formed by addition of an oxygen atom to the ethenoid linkage of β-amyrone (II).

From the acid products of the oxidation of β-amyrin a crystalline acid, m. p. 252°, was separated which gave analytical data in agreement with the formula $C_{30}H_{48}O_5$. This acid is a saturated *oxide-dicarboxylic* acid (IV or V), from which it is clear that its formation is due to fission of the group $-CO-CH_2-$ in β-amyrone oxide (III). The main bulk of the acid mixture is non-crystalline, but readily yields a crystalline *dimethyl* ester, m. p. 268°, analysis of which indicates the formula $C_{30}H_{48}O_5$ for the parent acid. Hydrolysis of the ester gave a non-crystalline resinous acid. The formation of two isomeric oxide-dicarboxylic acids, $C_{30}H_{48}O_5$, indicates the existence of the cyclic group $-CH_2-CO-CH_2$ in β-amyrone. The mechanism of the oxidation of β-amyrin (I) is indicated in the following scheme:



α-Amyrin behaves in a similar manner to β-amyrin when oxidised with excess of chromic anhydride, giving *α-amyrone oxide* together with a non-crystalline acid. The former is also prepared by the further oxidation of α-amyrone; it gives a well-crystallised *mono-semicarbazone* and behaves in exactly the same way as its β-isomeride towards tetranitromethane and the Grignard reagent.

The non-crystalline acid is characterised by its *dimethyl* ester, analysis of which indicates the formula $C_{30}H_{48}O_5$ for the parent acid. The dimethyl ester does not react with semicarbazide acetate, hydroxylamine, or acetic anhydride; it is consequently an oxide-dicarboxylic acid of the type (IV) or (V).

From the close parallelism between the behaviour of α- and β-amyrin on oxidation, it is probable that, in so far as the hydroxyl group and the ethenoid linkage are concerned, the two resinols have similar constitutions (I) and that the structural differences occur in the $C_{25}H_{44}$ residue.

Experimental.

Oxidation of β-Amyrin.—β-Amyrin (10 g.), dissolved in glacial acetic acid (500 c.c.), was treated with a solution of chromic anhydride (8 g.) in glacial acetic acid (100 c.c.), added during

2 hours, the mixture being mechanically stirred and maintained at 70° throughout. After a further 2 hours, a solid was precipitated with water, collected, dissolved in ether, and extracted with 10% caustic soda solution. On evaporation the ethereal solution.of the neutral products yielded a thick yellow oil, which on treatment with acetone gave 3 g. of crude β-amyrone oxide, m. p. 220°.

β-Amyrone Oxide.—After repeated crystallisation from acetone, the *oxide* was obtained in colourless plates, m. p. 237°, $[\alpha]_D^{20°} + 143°$ ($c = 6{\cdot}3$ in chloroform) (Found : C, 82·2, 82·1; H, 10·6, 10·4; *M*, 423. $C_{30}H_{48}O_2$ requires C, 81·8; H, 10·9%; *M*, 440). The *semicarbazone* was obtained by mixing cold solutions of β-amyrone oxide and semicarbazide acetate in ethyl alcohol. After 2 days the solution was diluted with water, and the precipitate recrystallised from methyl alcohol; m. p. 232° (Found : N, 8·2. $C_{31}H_{51}O_2N_3$ requires N, 8·4%).

Acid Products from the Oxidation of β-Amyrin.—The caustic soda solution of the acids was acidified and extracted with ether. On evaporation a thick viscous yellow resin was obtained. This was dissolved in ethyl acetate and after several days a crystalline *acid* separated. The yield of this acid was very small, 0·15 g. being obtained by the oxidation of 20 g. of β-amyrin. It was sparingly soluble in ether, alcohol, chloroform, and ethyl acetate. After several crystallisations from methyl alcohol it separated in small cubes, m. p. 252° [Found : C, 73·9; H, 9·7; equiv., 251. $C_{30}H_{48}O_5$ (dibasic) requires C, 73·8; H, 9·8%; equiv., 244]. The acid (0·1 g.) was boiled with a solution of acetic anhydride in pyridine for 3 hours. After precipitation with water and recrystallisation the acid was recovered unchanged. The dimethyl ester formed by the action of diazomethane upon the acid could not be crystallised. Neither the acid nor the non-crystalline ester would give a semicarbazone or an oxime.

The resin remaining after removal of the crystalline acid was found to have a molecular weight of 500 by Rast's method. Titration with caustic soda indicated an equivalent weight of 270. The resin was dissolved in twice its weight of dry methyl alcohol, and hydrogen chloride passed in until the solution was saturated. After 24 hours a solid was precipitated with water, collected, dissolved in ether, and separated into neutral and acid fractions. The neutral fraction yielded a product which after two recrystallisations from alcohol formed colourless needles, m. p. 268°, $[\alpha]_D + 137°$ ($c = 6{\cdot}7$ in chloroform) (Found : C, 74·3; H, 10·2. $C_{32}H_{52}O_5$ requires C, 74·5; H, 10·1%).

Hydrolysis of this ester gave a non-crystalline acid, m. p. 286°. Neither the acid nor its ester gave any coloration with tetranitromethane in chloroform solution, thus indicating their saturated nature.

The Oxidation of α-Amyrin and α-Amyrone.—The methods used were exactly as described for the β-series. Both α-amyrin and α-amyrone yielded *α-amyrone oxide*, m. p. 193°, $[\alpha]_D^{20°} + 141°$ ($c = 9{\cdot}5$ in chloroform) (Found : C, 82·8, 82·6; H, 10·6, 10·4. $C_{30}H_{48}O_2$ requires C, 81·8; H, 10·9%). The semicarbazone had m. p. 223° (Found : N, 8·3. $C_{31}H_{51}O_2N_3$ requires N, 8·4%). The α-amyrone oxide yielded no methane when treated by the Zerewitinoff method.

From the acid products no crystalline free acid could be isolated, but on esterification with methyl alcohol and hydrogen chloride a *dimethyl* ester was obtained, separating from methyl alcohol in needles, m. p. 251°, $[\alpha]_D + 170°$ ($c = 8{\cdot}9$ in chloroform) (Found : C, 74·6; H, 9·3; *M*, 523. $C_{32}H_{52}O_5$ requires C, 74·5; H, 10·1%; *M*, 516).

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