313. *The Resinols. Part I. β-Amyrin of* Manilla Elemi.

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A relatively simple and complete separation of α- from β-amyrin is effected by fractional solution of the anisates in chloroform.

By oxidation of β-amyrin acetate with hydrogen peroxide, oxy-β-amyrin acetate is produced. Neither this nor the oxy-β-amyrin obtained from it by hydrolysis gives a coloration with tetranitromethane in chloroform solution, or absorbs bromine in a variety of solvents. It follows that they are saturated oxides (acetate oxide $C_{32}H_{52}O_3$; alcohol oxide $C_{30}H_{50}O_2$) (compare Vesterberg, *Ber.*, 1891, **24**, 3836; Rollett and Bratke, *Monatsh.*, 1922, **43**, 685), from which it is clear that β-amyrin contains one double bond and is pentacyclic (compare Ruzicka, Huyser, Pfeiffer, and Seidel, *Annalen*, 1929, **471**, 21; Vesterberg, *Ber.*, 1890, **23**, 3186).

With a view to shifting this inert centre of unsaturation to a more reactive position, attempts have been made to isomerise β-amyrin. With concentrated formic acid, the alcohol gives a *formate*, which yields unchanged β-amyrin on hydrolysis. It was not found possible to prepare the γ-amyrin described by Dieterle (*Arch. Pharm.*, 1931, **269**, 78). Attempts to prepare an isomeride of β-amyrin by the reduction of β-amyrone with sodium and boiling ethyl alcohol were abortive, β-amyrin (isolated as the acetate) being the sole product of reaction.

Partial isomerisation of β-amyrin was achieved by treating the alcohol in glacial acetic acid with hydrogen chloride. The product was separated into β-amyrin acetate, identical with the ester obtained from β-amyrin by means of acetic anhydride, and β-*amyrin* iso-*acetate* differing considerably from the normal acetate in its physical characteristics. The new acetate resists all attempts at catalytic hydrogenation, although it still gives a coloration with tetranitromethane in chloroform solution. It is thus probable that its formation is not due to a wandering of the ethenoid linkage.

Attempts to prepare a fully saturated derivative of β-amyrin by the reduction of β-amyrilene with sodium and amyl alcohol gave β-amyrene ($C_{30}H_{50}$), a product still resistant to catalytic hydrogenation, although giving the colour reactions of an unsaturated hydrocarbon, and apparently identical with the hydrocarbon obtained by Ruzicka, Silbermann, and Furter (*Helv. Chim. Acta*, 1932, **15**, 482) by the catalytic hydrogenation of β-amyrilene. Catalytic reduction of β-amyrilene with palladium-black gave iso-β-*amyrene*, differing in physical characteristics from β-amyrene.

Experimental.

Separation of α- from β-Amyrin.—The amyrin mixture (170 g., isolated from *Manilla elemi* in the usual manner) in benzene (200 c.c.) was refluxed for 2 hours with pyridine (70 g.) and anisyl chloride (140 g.), the benzene then removed under reduced pressure, and the cooled solution treated with excess of dilute sulphuric acid. The solid was washed successively with dilute acid, water, and absolute alcohol, refluxed (170 g.) for 1 hour with ether (1000 c.c.), and then collected and thrice digested with cold chloroform (750 c.c.). From a solution of the residual solid in absolute alcohol, crystals of β-amyrin anisate separated on cooling, m.p. 251—252° as given by Dischendorfer (*Monatsh.*, 1925, **46**, 399). The three chloroform extracts, on concentration, gave decreasingly pure α-amyrin anisate, m. p. 191° after recrystallisation from ethyl acetate.

β-Amyrin anisate (30 g.), suspended in absolute alcohol (1500 c.c.), was refluxed with potassium hydroxide (40 g.) for 6 hours, water (300 c.c.) added, and the clear solution refluxed for 2 hours; β-amyrin was then precipitated by addition of water, and crystallised from ethyl acetate, forming long needles, m. p. 192°.

Oxy-β-amyrin.—A solution of β-amyrin acetate (4 g.) in glacial acetic acid (200 c.c.) was heated with perhydrol (10 c.c.) on the water-bath for 2 hours. The product precipitated by water was crystallised from absolute alcohol, oxy-β-amyrin acetate separating in plates, m. p. 291—292° (Found: C, 79·3; H, 10·4. Calc. for $C_{32}H_{52}O_3$: C, 79·3; H, 10·8%). Oxy-β-amyrin, obtained by hydrolysis of the acetate with 10% alcoholic potash, separated from dilute solutions in alcohol and acetone in plates, m. p. 201—202° (Found: C, 81·2; H, 11·3. Calc. for $C_{30}H_{50}O_2$: C, 81·4; H, 11·3%). Both the oxide and the acetate give a pink coloration with the Liebermann–Burchard reagent.

β-Amyrin Formate.—β-Amyrin (1 g.) was refluxed for 2 hours with formic acid (5 c.c., 99%). The red solution, on cooling, deposited plates, m. p. 238° after two recrystallisations from ethyl acetate (Found: C, 82·0; H, 11·1. $C_{31}H_{50}O_2$ requires C, 81·9; H, 11·1%).

β-Amyrin iso*Acetate.*—β-Amyrin (5 g.), in glacial acetic acid (200 c.c.) maintained at 5°, was treated with a rapid stream of hydrogen chloride for 6 hours and the solution was then concentrated under reduced pressure to 50 c.c. The crystals which separated on cooling were washed with acetic acid and with water and recrystallised from ethyl acetate, *β-amyrin* iso*acetate* forming large plates, m. p. 246° (Found: C, 82·3; H, 11·0. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%). The mother-liquor on concentration gave needles, m. p. 235° (after several recrystallisations), not depressed in admixture with authentic β-amyrin acetate. The *iso*acetate gives with tetranitromethane a less intense yellow coloration than that given by β-amyrin.

β-Amyrene.—(a) β-Amyrilene (Vesterberg, *Ber.*, 1887, **20**, 1242) (2 g.) in amyl alcohol (100 c.c.) was refluxed with sodium (20 g., added during 1 hour). Warm water was added to decompose the sodium amyloxide, the amyl alcohol removed under reduced pressure, and the residual oil distilled under reduced pressure. The main fraction, a yellow oil, b. p. 252°/12 mm., set on cooling to a resin, from which β-amyrene, m. p. 98°, was obtained in plates on repeated crystallisation from acetic acid (Found: C, 87·7; H, 12·2. Calc. for $C_{30}H_{50}$: C, 87·7; H, 12·3%).

(b) β-Amyrilene (1 g.) in glacial acetic acid (30 c.c.) was shaken with hydrogen in the presence of palladium-black (0·5 g.) at 70° for 4—5 hours, 1 mol. of hydrogen being absorbed. The solution was decanted from the catalyst, precipitated with water, and ether-extracted. Removal of the ether left a *solid*, which after several crystallisations from ethyl acetate gave plates, m. p. 82—83° (Found: C, 87·6; H, 12·2. $C_{30}H_{50}$ requires C, 87·7; H, 12·3%), depressed to 76° in admixture with the dihydro-derivative described above (a).

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