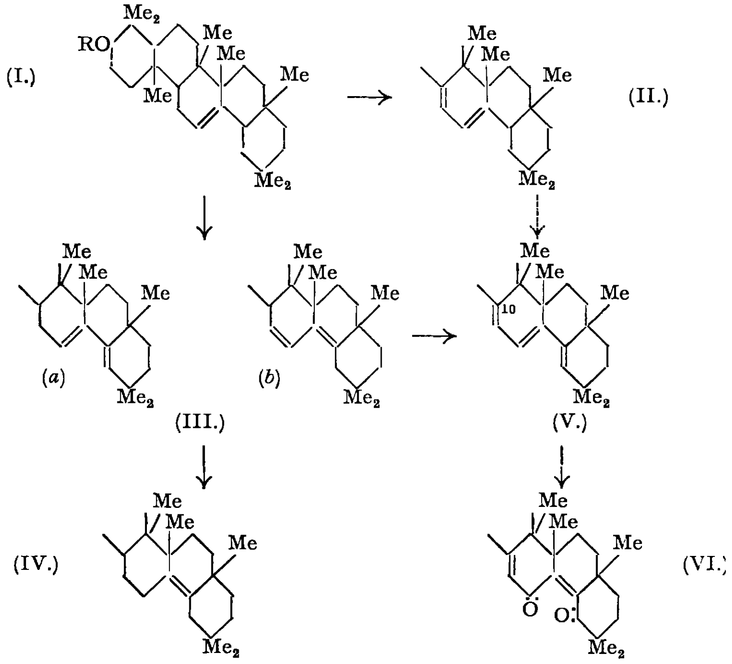
145. *Triterpene Resinols and Related Acids. Part XVIII. The Conversion of β-Amyratrienyl Acetate into β-Amyradiendionyl Acetate.*

By G. T. Newbold and F. S. Spring.

Treatment of β-amyrin benzoate (I, R = COPh) with *N*-bromosuccinimide gives *bromo-β-amyratrienyl benzoate* and *β-amyratrienyl benzoate* (V, R = COPh). Similar treatment of β-amyradienyl-II acetate (III*a* or III*b*, R = Ac) gives β-amyratrienyl acetate (V, R = Ac). Oxidation of β-amyratrienyl acetate with either chromic acid or selenium dioxide yields β-amyradiendionyl acetate (VI, R = Ac).

β-Amyradiendionyl acetate (VI, R = Ac) is obtained (*a*) by oxidation of either β-amyrin acetate (I, R = Ac) or δ-amyrin acetate (IV, R = Ac) with selenium dioxide (Ruzicka and Jeger, *Helv. Chim. Acta*, 1941, **24**, 1236; Ruzicka, Jeger, and Norymberski, *ibid.*, 1942, **25**, 457), (*b*) by oxidation of β-amyradienyl-I acetate (II, R = Ac) with selenium dioxide (Picard and Spring, J., 1941, 35), or (*c*) by oxidation of β-amyradienyl-II acetate (III*a* or III*b*, R = Ac) with selenium dioxide (Ruzicka, Jeger, and Norymberski, *loc. cit.*). Ruzicka, Jeger, and Redel (*Helv. Chim. Acta*, 1943, **26**, 1235) have found that treatment of β-amyrin acetate (I, R = Ac) with *N*-bromosuccinimide (Ziegler, Späth, Schaaf, Schumann, and Winkelmann, *Annalen*, 1942, **551**, 80) gives a β-amyratrienyl acetate which is formulated as (V, R = Ac) since it shows an intense absorption maximum at 3080 A. The appearance of this paper makes it desirable to record certain experiments which establish another link in the chain of reactions involved in the conversion of β-amyrin (I, R = H) into β-amyradiendionol (VI, R = H).



Treatment of β-amyrin benzoate (I, R = COPh) with *N*-bromosuccinimide in carbon tetrachloride gives a mixture from which was isolated *bromo-β-amyratrienyl benzoate*, m. p. 211—212°, $[\alpha]_D$ + 673°, which shows an intense absorption maximum at 3160 A. Hydrolysis of this benzoate gave *bromo-β-amyratrienol*, m. p. 160—170°, which also exhibits an absorption maximum at 3160 A. Concentration of the original mother-liquors of bromo-β-amyratrienyl benzoate gave *β-amyratrienyl benzoate* (V, R = COPh), m. p. 202—204°, $[\alpha]_D$ + 536°, hydrolysis of which yielded β-amyratrienol (V, R = H) identical with that described by Ruzicka, Jeger, and Redel (*loc. cit.*).

Treatment of β-amyradienyl-II acetate (III*a* or III*b*, R = Ac) with *N*-bromosuccinimide gave β-amyratrienyl acetate (V, R = Ac), whereas reaction of the bromo-imide with β-amyradienyl-I acetate (II, R = Ac) did not proceed smoothly: the product, m. p. 170—178°, which was not obtained pure, showed no depression of m. p. when mixed with a specimen of β-amyratrienyl acetate and had the characteristic absorption spectrum of the latter (max. 3080 A., ε = 9000).

According to the provisional formula (I, R = H) for β-amyrin, the conjugated system in β-amyratrienyl acetate (V, R = Ac) is spread over the same part of the triterpenoid nucleus as that in β-amyradiendionyl acetate (VI, R = Ac). That these relative formulations are correct was established by an examination of the oxidation of the trienyl acetate. Oxidation of β-amyratrienyl acetate with chromic acid gives β-amyradiendionyl acetate. Again, with acetic acid as solvent, β-amyratrienyl acetate is smoothly oxidised by selenium dioxide to give β-amyradiendionyl acetate. The conditions employed for the chromic acid oxidation of the trienyl acetate did not give the oxide of β-amyradiendionyl acetate (Ruzicka and Jeger, *Helv. Chim. Acta*, 1942, **25**, 1409), which is known to result from the further chromic acid oxidation of β-amyradiendionyl acetate (Simpson, J., 1938, 1313). It is noteworthy that, had the oxidation of β-amyratrienyl acetate primarily involved the Δ^{10}-linkage, β-amyradienonyl acetate (Picard and Spring, *loc. cit.*) would be expected as an intermediate, and it is known that oxidation of β-amyradienonyl acetate with chromic acid gives the acetate $C_{32}H_{46}O_5$ ("O_5-acetate") and not β-amyradiendionyl acetate (Green, Mower, Picard, and Spring, preceding paper). Neither β-amyradienonyl acetate nor the "O_5-acetate" was detected as a product of the oxidation of β-amyratrienyl acetate.

EXPERIMENTAL.

Bromo-β-amyratrienyl Benzoate.—β-Amyrin benzoate (5 g.) in carbon tetrachloride (200 c.c.) was refluxed with *N*-bromosuccinimide (96%; 5 g.) for 3 hours. Hydrogen bromide was evolved throughout, and the solution gradually became red. The cold solution was filtered, and the filtrate washed successively with dilute sodium hydroxide solution, hydrochloric acid, and water. Removal of the solvent from the dried solution gave a resin which crystallised from acetone. Seven recrystallisations from the same solvent gave *bromo-β-amyratrienyl benzoate* as heavy plates, m. p. 211—212° (0·5 g.). It gives a deep brown coloration with tetranitromethane in chloroform, and a strong positive Beilstein test; $[\alpha]_D^{18^\circ}$ + 673° (l = 1, c = 2·2 in chloroform) (Found: C, 73·7; H, 8·2. $C_{37}H_{49}O_2Br$ requires C, 73·4; H, 8·2%). *Light absorption in alcohol*: Maximum at 3160 A., ε = 11,300.

Hydrolysis of the benzoate with 10% alcoholic potassium hydroxide gave *bromo-β-amyratrienol*, m. p. 160—170°, separating as plates from aqueous alcohol, and giving a strong positive Beilstein test (Found: C, 71·5; H, 9·0. $C_{30}H_{45}OBr$ requires C, 71·8; H, 9·0%). *Light absorption in alcohol*: Maximum at 3160 A., ε = 10,400.

β-Amyratrienyl Benzoate.—The mother-liquors remaining after the isolation of bromo-β-amyratrienyl benzoate were combined and evaporated, and the residue dissolved in methanol. A crop of ill-defined needles, m. p. 161—166°, separated which on recrystallisation from methanol gave a top crop, m. p. 182—188°, containing halogen; when mixed with bromo-β-amyratrienyl benzoate this gave an intermediate m. p. The second crop formed needles, m. p. 185—193°, raised by recrystallisation from acetone to 193—199°; when mixed with bromo-β-amyratrienyl benzoate, the m. p. was depressed to 170—182°. After four crystallisations from aqueous acetone, this gave *β-amyratrienyl benzoate*, m. p. 202—204°, $[\alpha]_D^{16.5^\circ}$ + 536° (l = 1, c = 0·3 in chloroform) (yield, 100 mg.), as fine needles which gave a negative Beilstein test (Found: C, 84·05; H, 9·3. $C_{37}H_{50}O_2$ requires C, 84·35; H, 9·6%). Hydrolysis of β-amyratrienyl benzoate with alcoholic potassium hydroxide (10%) gave β-amyratrienol as fine needles from aqueous acetone, m. p. 185—187° undepressed when mixed with a specimen of the trienol (m. p. 183—184°) prepared by hydrolysis of β-amyratrienyl acetate (Ruzicka, Jeger, and Redel, *loc. cit.*); $[\alpha]_D^{18^\circ}$ + 563° (l = 1, c = 0·36 in chloroform). *Light absorption in alcohol*: Maximum at 3120 A., ε = 12,000.

β-Amyratrienyl Acetate from β-Amyradienyl-II Acetate.—The dienyl-II acetate (1 g.) in absolute carbon tetrachloride (50 c.c.) was heated under reflux for 3 hours with *N*-bromosuccinimide (0·6 g.; 99%). Hydrogen bromide was evolved. The product, isolated in the usual manner, was crystallised five times from acetone to give β-amyratrienyl acetate as blades, m. p. 184—185°, showing no depression with an authentic specimen; $[\alpha]_D^{18^\circ}$ + 560° (l = 1, c = 0·61 in chloroform).

Treatment of β-Amyradienyl-I Acetate with N-*Bromosuccinimide.*—The dienyl-I acetate (0·2 g.) in carbon tetrachloride (15 c.c.) was refluxed with *N*-bromosuccinimide (0·2 g.; 80%) for 2 hours. The mixture was filtered, and the filtrate washed successively with dilute sodium hydroxide solution, dilute acid, and water. The solvent was removed from the dried solution, and the residue heated on the water-bath in a high vacuum. A solution of the resinous residue in light petroleum (b. p. 40—60°)-benzene (1 : 1; 50 c.c.) was filtered through a column of activated alumina (Brockmann, 25 g.), and the column washed with the same solvent mixture to give the following fractions:

	Vol. of solvent, c.c.	Wt. of fraction, mg.	M. p.
1	50	50	160—172°
2	100	55	161—172
3	200	20	(Oil)

Fractions 1 and 2, which showed no depression in m. p. when mixed, were combined and crystallised twice from aqueous acetone, from which the impure β-amyratrienyl acetate separated as blades, m. p. 170—178°; mixed m. p. with β-amyratrienyl acetate, 175—181°. The acetate, m. p. 170—178°, gave a negative Beilstein test for halogen. *Light absorption in alcohol*: Maximum at 3080 A., ε = 9000.

β-Amyradiendionyl Acetate.—(*a*) β-Amyratrienyl acetate (0·5 g.) in glacial acetic acid (30 c.c.) was heated under reflux with selenium dioxide (0·5 g.) for 16 hours. The hot solution was filtered from red selenium, and the filtrate evaporated under reduced pressure. After the addition of water, the product was extracted with ether, the extract washed with water, dried (sodium sulphate), and the solvent removed. After four crystallisations of the residue from aqueous methanol, β-amyradiendionyl acetate (150 mg.) was obtained as colourless plates, m. p. 235—237°, undepressed when mixed with a specimen prepared from β-amyrin acetate. It gave a negative reaction with the tetranitromethane reagent (Found: C, 77·4; H, 9·45. Calc. for $C_{32}H_{46}O_4$: C, 77·7; H, 9·4%). *Light absorption in alcohol:* Maximum at 2785 A., ε = 11,800.

(*b*) β-Amyratrienyl acetate (0·4 g.) in boiling stabilised glacial acetic acid (35 c.c.) was treated with a solution of chromic anhydride (320 mg.) in water (0·5 c.c.) and acetic acid (15 c.c.) added over ½ hour. The solution was refluxed for a further hour. After the addition of a little methanol, the solvent was removed under reduced pressure, and the residue shaken with ether and dilute sulphuric acid. The ethereal extract was washed with dilute sodium hydroxide solution, then with water, and dried (sodium sulphate). Removal of the ether and crystallisation of the residue from aqueous methanol (seven times) gave β-amyradiendionyl acetate (100 mg.) as heavy plates, m. p. 235—237°, either alone or mixed with an authentic specimen; it gives a negative reaction with the tetranitromethane reagent (Found: C, 77·4; H, 9·4%). *Light absorption in alcohol:* Maximum at 2790 A., ε = 12,000.

THE UNIVERSITY, MANCHESTER.

[*Received, July* 13*th*, 1944.]