195. *Triterpene Resinols and Related Acids. Part XXVI.** *Ursa*-11 : 13(18)-*dienol.*

By J. D. EASTON, WILLIAM MANSON, and F. S. SPRING.

α-Amyrin acetate is oxidised by selenium dioxide to a dienyl acetate to which the structure ursa-11 : 13(18)-dienyl acetate is provisionally allocated.

IN contrast to the unsaturated centre in β-amyrin, that in α-amyrin is unreactive and in particular there is a lack of reactivity at the adjacent $C_{(18)}$-atom in α-amyrin. Whereas β-amyrin can be smoothly converted into oleana-10 : 12-dienol (Picard and Spring, *J.*, 1941, 35), oleana-10 : 12 : 18-trienol (Ruzicka, Jeger, and Redel, *Helv. Chim. Acta*, 1943, **26**, 1235), 11-keto-olean-12-enol (Picard and Spring, *J.*, 1940, 1198), and 11-keto-oleana-12 : 18-dienol (Picard and Spring, *J.*, 1941, 35), corresponding reactions with α-amyrin are limited to the formation of ursa-10 : 12-dienol and 11-keto-urs-12-enol (Spring and Vickerstaff, *J.*, 1937, 249). Again, β-amyrin acetate is readily oxidised by selenium dioxide to oleana-11 : 13(18)-dienyl acetate (Ruzicka, Muller, and Schellenberg, *Helv. Chim. Acta*, 1939, **22**, 767; Barton and Brooks, *J.*, 1951, 257) as initial product, further oxidation of which with the same reagent gives 12 : 19-diketo-oleana-10 : 13(18)-dienyl acetate (Ruzicka, Jeger, and Norymberski, *Helv. Chim. Acta*, 1942, **25**, 457). Hitherto attempts to duplicate the selenium dioxide reactions with α-amyrin have been unsuccessful. The present paper describes the preparation of what is believed to be ursa-11 : 13(18)-dienol from α-amyrin.

Treatment of α-amyrin acetate with selenium dioxide in dioxan at 200° or, better, in boiling benzyl acetate gives a mixture from which, in addition to much unchanged α-amyrin acetate, a dienyl acetate is isolated in 2—3% yield. That the dienyl acetate originates in α-amyrin acetate and not in a difficultly separable impurity follows from the observation that similar oxidation of α-amyrin acetate, recovered from a previous treatment with selenium dioxide, gives the same product in the same yield. A number of variations in the experimental conditions did not lead to an increase in the yield of the dienyl acetate; in one experiment using boiling diphenyl as solvent, ursa-10 : 12-dienyl acetate was isolated as sole product.

Analysis of the dienyl acetate indicates the formula $C_{32}H_{50}O_2$ or the lower homologue. The properties of the new dienyl acetate closely simulate those of oleana-11 : 13(18)-dienyl acetate, but a mixture of the two dienyl acetates shows a marked depression in melting point. The ultra-violet absorption spectra of the two dienyl acetates are very similar. Hydrogenation of the dienyl acetate from α-amyrin gives a dihydro-derivative which again closely resembles olean-13(18)-enyl acetate in optical properties.

We provisionally formulate the new compound as ursa-11 : 13(18)-dienyl acetate and its dihydro-derivative as urs-13(18)-enyl acetate. If the structure ascribed to α-amyrin by Meisels, Ruzicka, and Jeger (*Helv. Chim. Acta*, 1949, **32**, 1075) is true, these formulations are correct. However, satisfactory proof of the presence of a $C_{(18)}$-hydrogen atom in α-amyrin is lacking; we do not consider that the conversion of α-amyrin into an 11 : 13(18)-dienol supplies such a proof since it is possible that the formation of the dienyl acetate has involved elimination of a $C_{(18)}$-methyl group in α-amyrin in which case the dienyl acetate will be a norursa-11 : 13(18)-dienyl acetate.

EXPERIMENTAL

Specific rotations were measured in chloroform solution in a 1-dm. tube at approx. 16°. Ultra-violet absorption spectra were measured in ethanol solution. Grade II alumina was used for chromatography, and the light petroleum used had b. p. 60—80°.

Ursa-11 : 13(18)-*dienyl Acetate.*—A mixture of α-amyrin acetate (18 g.; m. p. 227—228°, $[\alpha]_D$ +78·5°), dioxan (750 c.c.), and selenium dioxide (21·6 g.) was heated in an autoclave for 10 hours at 200°. The cold mixture was filtered, and the filtrate diluted with water and

---

* Part XXV, *J.*, 1952, 432.

extracted with ether. The ethereal solution was washed with aqueous potassium cyanide (5%), and the dried solution treated with charcoal. After removal of the ether, the red product was crystallised from chloroform–methanol, from which two crops of α-amyrin acetate (8·5 g.; m. p. and mixed m. p. 218—221°) were removed. The mother liquor on evaporation gave a partly crystalline residue (2·9 g.), a solution of which in benzene–light petroleum (1 : 10; 250 c.c.) was chromatographed on alumina (15 × 3·5 cm.). Washing the column with the same solvent mixture (500 c.c.) gave a fraction (352 mg.) which could not be crystallised. Continued washing with the same solvent mixture (625 c.c.) gave a crystalline eluate (550 mg.), recrystallisation of which from methanol–chloroform gave α-amyrin acetate, m. p. 220—221°, undepressed in m. p. when mixed with an authentic specimen. A third fraction (511 mg.) obtained by continued washing with the same solvent mixture (1125 c.c.), crystallised from methanol–chloroform as needles, m. p. 202—204°, and gave a red-brown colour with tetranitromethane in chloroform. Several recrystallisations of this fraction from methanol–chloroform gave *ursa*-11 : 13(18)-*dienyl acetate* as needles, m. p. 206—207°, $[\alpha]_D$ −77°, −79° (*c*, 1·2, 0·35) (Found: C, 82·3; H, 10·9. $C_{32}H_{50}O_2$ requires C, 82·3; H, 10·8%). Light absorption: Max. at 2440 (ε = 29,000), 2520 (ε = 31,200), and 2600 Å (ε = 21,400). A mixture with oleana-11 : 13(18)-dienyl acetate (m. p. 230—231°) had m. p. 183—190°.

Ursa-11 : 13(18)-dienyl acetate was also obtained in low yield (approx. 1%) by refluxing a solution of α-amyrin acetate in glacial acetic acid with selenium dioxide for 1 hour, and in better yield (2·5%) by refluxing a solution of α-amyrin acetate (40 g.) in benzyl acetate (500 c.c.) with selenium dioxide (48 g.) for 24 hours.

Ursa-10 : 12-*dienyl Acetate.*—A solution of α-amyrin acetate (2·0 g.) in molten diphenyl (15 g.) was treated with selenium dioxide (2·4 g.) and refluxed for 40 hours. The solvent was removed by steam-distillation and the residue extracted with ether (Soxhlet). The ether solution was washed with aqueous potassium cyanide (3%), and the product crystallised repeatedly from chloroform–methanol from which ursa-10 : 12-dienyl acetate (200 mg.) separated as needles, m. p. 166—167°, $[\alpha]_D$ +311° (*c*, 0·9), undepressed in m. p. when mixed with an authentic specimen. Light absorption: Max. at 2800 Å (ε = 11,700).

Ursa-11 : 13(18)-*dienol* was obtained from the acetate by hydrolysis with 5% ethanolic potassium hydroxide. It separates as needles, m. p. 194—195° (from aqueous methanol), $[\alpha]_D$ −83°, −86° (*c*, 1·2, 1·0) (Found: C, 84·65; H, 11·5. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4%). Acetylation of the alcohol, with pyridine and acetic anhydride, gave ursa-11 : 13(18)-dienyl acetate, m. p. 205—206°, $[\alpha]_D$ −76° (*c*, 0·44), undepressed in m. p. when mixed with the specimen described above.

Urs-13(18)-*enol.*—A solution of ursa-11 : 13(18)-dienyl acetate (300 mg.) in ethyl acetate (70 c.c.) and glacial acetic acid (80 c.c.) was shaken with hydrogen over platinum (150 mg.) for 21 hours. The filtered solution was evaporated and the residue hydrolysed by refluxing it for 2 hours with ethanolic potassium hydroxide (3%; 25 c.c.). The product was isolated in the usual manner and crystallised from methanol, giving *urs*-13(18)-*enol* as plates, m. p. 204—205°, $[\alpha]_D$ −35°, −36·5° (*c*, 1·2, 0·6) (Found: C, 84·1; H, 12·0. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8%). It gives a yellow colour with tetranitromethane in chloroform.

Urs-13(18)-*enyl acetate*, obtained from the alcohol, with pyridine and acetic anhydride, separated from chloroform–methanol as needles, m. p. 214—216°, $[\alpha]_D$ −23°, −22° (*c*, 1·4, 0·4) (Found: C, 82·3; H, 11·4. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%). It gave a yellow colour with tetranitromethane in chloroform. A mixture with olean-13(18)-enyl acetate (m. p. 209—210°) had m. p. 190—195°. Light absorption: $\varepsilon_{2100} = 4000$, $\varepsilon_{2150} = 5100$, $\varepsilon_{2200} = 2800$, and $\varepsilon_{2230} = 1100$.

Grateful acknowledgment is made to the Department of Scientific and Industrial Research for a maintenance grant (to J. D. E.).

THE ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, November 7th*, 1952.]