*Triterpenoids. Part XLI.** 12-*Oxo*-13α-*ursan*-3β-*yl Acetate.*

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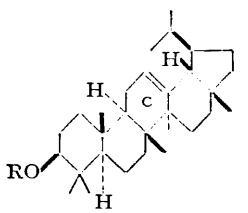
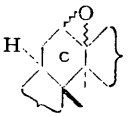
The products obtained by oxidation of α-amyrin esters with ozone or hydrogen peroxide, and hitherto considered to be esters of 12 : 13-epoxyursan-3β-ol (III; R = H), are now shown to be esters of an unstable ketone, 3β-hydroxy-13α-ursan-12-one (IV; R = H).

OXIDATION of α-amyrin benzoate (I; R = Bz) † with hydrogen peroxide in acetic acid gives a product $C_{37}H_{54}O_3$, $[\alpha]_D$ +132°, which was considered to be a saturated ketone (Seymour, Sharples, and Spring, *J.*, 1939, 1075). Later, however, the corresponding acetate, $C_{32}H_{52}O_3$, $[\alpha]_D$ +114°, was obtained by oxidation of α-amyrin acetate (I; R = Ac) with either ozone (Ruzicka, Jeger, Redel, and Volli, *Helv. Chim. Acta*, 1945, **28**, 199) or

* Part XL, *J.*, 1955, 2616.

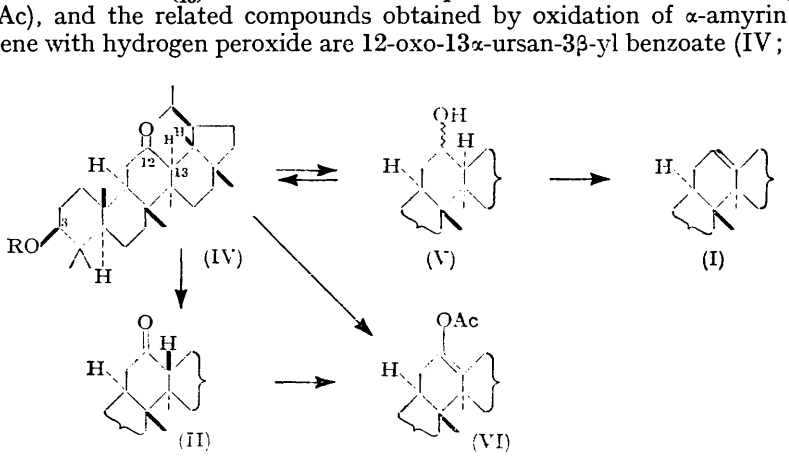
† The reasons for the assignment of the formula (I; R = H) to α-amyrin are given in Part XXXIX (*J.*, 1955, 2610) and the reason for the assignment of β-configuration to the 13-hydrogen in 12-oxoursan-3β-yl acetate (II) is to be found in Part XXXVI (*J.*, 1955, 2125).

hydrogen peroxide in acetic acid (McLean, Silverstone, and Spring, *J.*, 1951, 935) and, since this oxidation product is isomerised by mineral acid to 12-oxoursan-3β-yl acetate (II; R = Ac), $[\alpha]_D$ +11°, and carbonyl absorption was not observed in its ultraviolet absorption spectrum, it was considered to be 12 : 13-epoxyursan-3β-yl acetate (III; R = Ac). The structure of the related benzoate was revised to 12 : 13-epoxyursan-3β-yl benzoate (III; R = Bz), and a compound $C_{30}H_{50}O$, $[\alpha]_D$ +135°, obtained by oxidation of

(I)   (III)

urs-12-ene with hydrogen peroxide was described as 12 : 13-epoxyursane. Treatment of the benzoate, $C_{37}H_{54}O_3$, and the compound $C_{30}H_{50}O$ with hydrochloric acid gave 12-oxoursan-3β-yl benzoate (II; R = Bz), $[\alpha]_D$ +25°, and ursan-12-one, $[\alpha]_D$ ±0°, respectively. During an investigation of some derivatives of ursolic acid, to be described in a later paper, the structure assigned to the acetate, $C_{32}H_{52}O_3$, $[\alpha]_D$ +114°, became suspect, and a re-examination of this compound was undertaken.

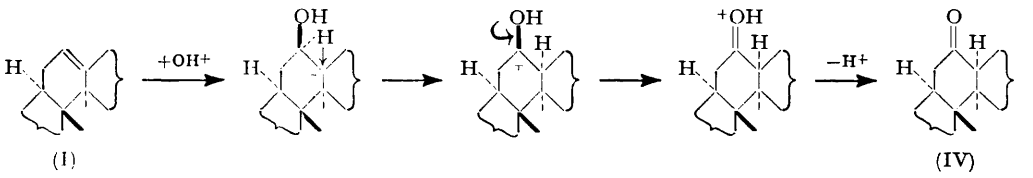
Treatment of the acetate $C_{32}H_{52}O_3$, $[\alpha]_D$ +114°, with lithium aluminium hydride yields a product, acetylation of which, at room temperature or at 100°, gives a diol monoacetate (V; R = Ac). Treatment of the diol monoacetate with phosphorus oxychloride in pyridine or with benzoyl chloride in pyridine yields α-amyrin acetate (I; R = Ac). Oxidation of the diol monoacetate with chromic acid at room temperature refurnishes the acetate $C_{32}H_{52}O_3$, $[\alpha]_D$ +114°, thus proving that the latter is a *ketone* and not an epoxide. This conclusion was confirmed by the infrared spectrum of the acetate which shows a well-defined carbonyl band at 1707 cm.$^{-1}$. The failure to detect low intensity ultraviolet carbonyl absorption in ethanol solution is probably due to the low concentrations employed (necessitated by sparing solubility); in high concentrations in chloroform solution, absorption at 2860° Å (ε 55) is apparent. The conversion of the acetate $C_{32}H_{52}O_3$, $[\alpha]_D$ +114°, into 12-oxoursan-3β-yl acetate (II; R = Ac) must therefore be represented as a simple inversion at $C_{(13)}$, *i.e.*, the former compound is 12-oxo-13α-ursan-3β-yl acetate (IV; R =Ac), and the related compounds obtained by oxidation of α-amyrin benzoate and urs-12-ene with hydrogen peroxide are 12-oxo-13α-ursan-3β-yl benzoate (IV; R = Bz)



and 13α-ursan-12-one, respectively. Treatment of 12-oxo-13α-ursan-3β-yl acetate with acetic anhydride and sodium acetate gives an enol acetate (VI; R = Ac) identical with that obtained by similar treatment of 12-oxoursan-3β-yl acetate (II; R = Ac).

The conversion of α-amyrin acetate into 12-oxo-13α-ursan-3β-yl acetate can be visualised

as frontal (β) attack by the per-acid, followed by a hydride shift on the rear side and proton elimination :



(I) (IV)

Experimental

For general instructions see Part XXXVIII (*J.*, 1955, 2606).

12-Oxo-13α-ursan-3β-yl acetate (IV; R = Ac) was prepared by treating α-amyrin acetate with hydrogen peroxide in acetic acid; it has m. p. 210—211°, $[\alpha]_D$ +115° (*c*, 0·9). Infrared absorption in carbon tetrachloride solution: bands at 1732 (acetate) and 1707 cm.$^{-1}$ (6-ring ketone). McLean, Silverstone, and Spring (*loc. cit.*) give m. p. 207—209°, $[\alpha]_D$ +114° and Ruzicka, Jeger, Redel, and Volli (*loc. cit.*) give m. p. 204—205°, $[\alpha]_D$ +139° for the compound described as "α-amyrin acetate oxide."

12-Oxoursan-3β-yl acetate (II; R = Ac), m. p. 280—282°, $[\alpha]_D$ +12° (*c*, 1·0), was prepared by treatment of 12-oxo-13α-ursan-3β-yl acetate with hydrochloric acid in acetic acid–chloroform, as described by McLean, Silverstone, and Spring (*loc. cit.*) who give m. p. 280—282°, $[\alpha]_D$ +11·4°.

3β : 12-*Diacetoxyurs*-12-*ene* (VI; R = Ac).—A mixture of 12-oxo-13α-ursan-3β-yl acetate (1·0 g.), anhydrous sodium acetate (1 g.), and acetic anhydride (30 c.c.) was heated under reflux for 40 hr. The enol acetate (900 mg.), isolated in the usual way, crystallised from chloroform–methanol as needles, m. p. and mixed m. p. 257—259°, $[\alpha]_D$ +50° (*c*, 1·7). McLean, Silverstone, and Spring (*loc. cit.*) give m. p. 255—257°, $[\alpha]_D$ +49°, and Ruzicka, Jeger, Redel, and Volli (*loc. cit.*) give m. p. 256—257°, $[\alpha]_D$ +55°, for the enol acetate prepared from 12-oxoursan-3β-yl acetate.

12ξ-*Hydroxy*-13α-*ursan*-3β-*yl Acetate* (V; R = Ac).—Lithium aluminium hydride (1·5 g.) was added to a solution of 12-oxo-13α-ursan-3β-yl acetate (1·5 g.) in dry ether (750 c.c.), and the mixture kept overnight. The product, isolated in the usual way, was acetylated by pyridine and acetic anhydride at 100° for 15 min. Crystallisation of the product from chloroform–methanol yielded 12ξ-*hydroxy*-13α-*ursan*-3β-*yl acetate* (900 mg.) as plates, m. p. 234—235°, $[\alpha]_D$ +66° (*c*, 2·5) (Found: C, 78·7; H, 11·1. $C_{32}H_{54}O_3$ requires C, 79·0; H, 11·1%).

Oxidation of 12ξ-*Hydroxy*-13α-*ursan*-3β-*yl Acetate* (V; R = Ac) *with Chromic Acid.*—Chromium trioxide (75 mg.) in glacial acetic acid (15 c.c.) was added dropwise during 15 min. with stirring to a solution of 12ξ-hydroxy-13α-ursan-3β-yl acetate (500 mg.) in acetic acid (300 c.c.) at room temperature. After being kept overnight at room temperature the mixture was worked up in the usual way, to give 12-oxo-13α-ursan-3β-yl acetate (400 mg.) as plates, m. p. and mixed m. p. 209—211°, $[\alpha]_D$ +115° (*c*, 2·3), after crystallisation from chloroform–methanol.

Dehydration of 12ξ-*Hydroxy*-13α-*ursan*-3β-*yl Acetate* (V; R = Ac).—(*a*) A mixture of 12ξ-hydroxy-13α-ursan-3β-yl acetate (200 mg.), phosphorus oxychloride (5 c.c.), and pyridine (20 c.c.) was heated under reflux for 2 hr. The product, isolated with benzene, crystallised from chloroform–methanol, giving α-amyrin acetate (100 mg.) as plates, m. p. and mixed m. p. 225—227°, $[\alpha]_D$ +80° (*c*, 1·1).

(*b*) A solution of the diol monoacetate (500 mg.) in pyridine (15 c.c.) and benzoyl chloride (2 c.c.) was refluxed for 20 hr. The product, isolated in the usual way, was purified by chromatography on alumina and crystallisation from chloroform–methanol, to give α-amyrin acetate (160 mg.) as plates, m. p. and mixed m. p. 226—227°, $[\alpha]_D$ +80° (*c*, 0·9).

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