Triterpenoids. Part XXXVI. Reactions of 18α-Olean-12-en-3β-ol Derivatives and Observations on the Stereochemistry of α-Amyrin.*

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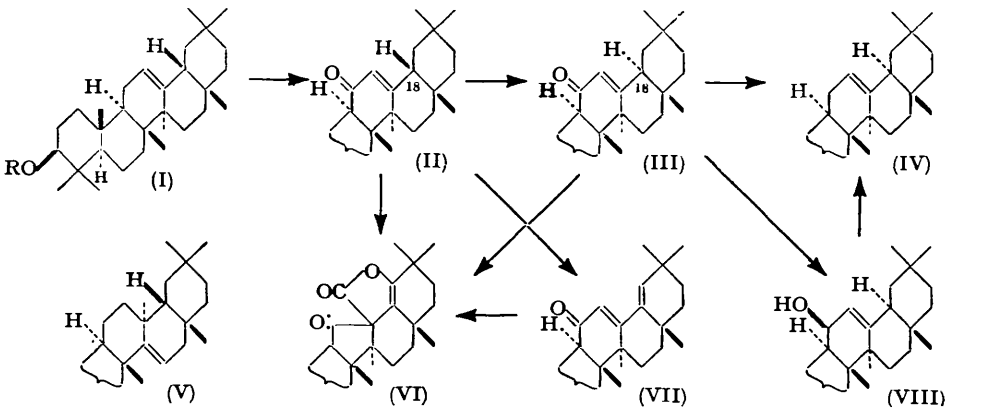
The reactions of 18α-olean-12-en-3β-ol (IV; R = H) are compared with those of its 18β-isomer, β-amyrin (I; R = H). A comparison of the properties of 12-oxo-18α-olean-9(11)-en-3β-yl acetate (XVI), 12-oxo-olean-9(11)-en-3β-yl acetate (XX), and 12-oxours-9(11)-en-3β-yl acetate leads to the view that the stereochemistry of the last compound is as shown in (XXIV), *i.e.*, that rings D and E in α-amyrin are *cis*-β-fused.

FOUR of the five oleanen-3β-ols containing the double bond in the 9 : 11 : 12 : 13 : 18 : 19 fragment are known Olean-18-en-3β-ol is the naturally occurring germanicol (Barton and Brooks, *J.*, 1951, 251); olean-13(18)-en-3β-ol has been prepared from β-amyrin (Jeger and Ruzicka, *Helv. Chim. Acta*, 1941, **24**, 1243; Ruzicka, Jeger, and Norymberski, *ibid.*, 1942, **25**, 457) and from lupeol (Ames, Halsall, and Jones, *J.*, 1951, 450) and it has been isolated from a natural source (Musgrave, Stark, and Spring, *J.*, 1952, 4393). Olean-9(11)-en-3β-ol has been prepared from β-amyrin (Jeger and Ruzicka, *Helv. Chim. Acta*, 1945, **28**,



209; Budziarek, Johnston, Manson, and Spring, *J.*, 1951, 3019) and olean-12-en-3β-ol (I; R = H)† is the naturally occurring β-amyrin.

One stereoisomer of the four unsaturated alcohols named above had been described when the present investigation was commenced. This is 18α-olean-12-en-3 β-ol (IV; R = H),

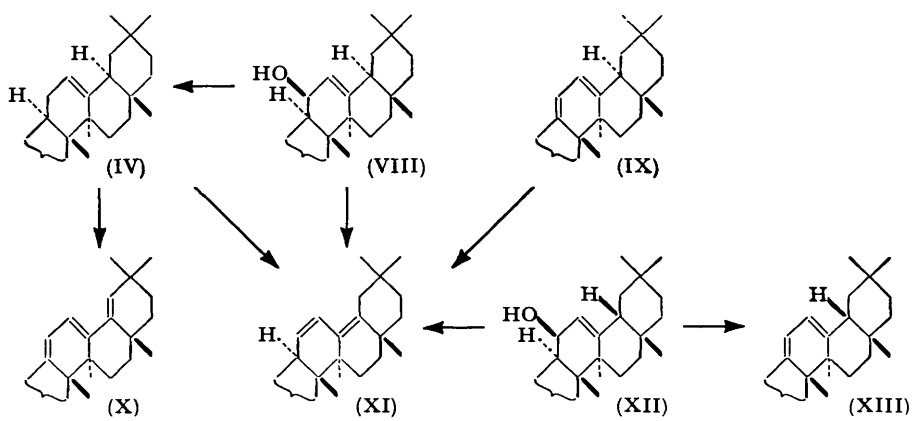
* Part XXXV, preceding paper. † Throughout this paper R = Ac unless otherwise stated.

prepared by Budziarek, Manson, and Spring (*J.*, 1951, 3336) by treatment of 11-oxo-olean-12-en-3β-yl benzoate (II; R = Bz) with concentrated alkali, which furnished 11-oxo-18α-olean-12-en-3β-ol (III; R = H), the acetate of which was then hydrogenated. Taraxerol, formulated as 13α-olean-18-en-3β-ol by Brooks (*Chem. and Ind.*, 1953, 1178), has since been shown to be *iso*olean-14-en-3β-ol (V; R = H) (Beaton, Spring, Stevenson, and Stewart, *Chem. and Ind.*, 1954, 1454; 1955, 35).

The investigation of 18α-olean-12-en-3β-ol described in this paper was undertaken with the object of comparing it with α-amyrin in the hope that the comparison would disclose the stereochemistry of the D–E ring junction in the ursane group of triterpenoids. In our view, this objective has been achieved.

11-Oxo-18α-olean-12-en-3β-yl acetate (III) resembles its 18β-isomer (II) in that on oxidation with selenium dioxide it yields the "O_5-acetate" recently identified as the enol lactone (VI) (McKean and Spring, *J.*, 1954, 1989). It is probable that the formation of the enol lactone from (II) proceeds *via* 11-oxo-oleana-12:18-dien-3β-yl acetate (VII) which is readily obtained from (II) by treatment with bromine (Picard and Spring, *J.*, 1941, 35) and on oxidation with selenium dioxide gives the enol lactone (VI) (McKean and Spring, *loc. cit.*). The 18α-isomer (III), however, is recovered unchanged after treatment with bromine in conditions which lead to the formation of (VII) from (II).

Reduction of 11-oxo-18α-olean-12-en-3β-yl acetate (III) with lithium aluminium hydride, followed by acetylation of the product, yields 11β-hydroxy-18α-olean-12-en-3β-yl acetate (VIII); to the hydroxyl group in (VIII) is ascribed the β(axial)-configuration because of its hindered character. 11β-Hydroxyolean-12-en-3β-yl acetate (XII) [the 18β-isomer of (VIII); Allan, Johnston, and Spring *J.*, 1954, 1546] is smoothly dehydrated by treatment with acetic anhydride and sodium acetate, to oleana-9(11):12-dien-3β-yl acetate (XIII). Similar treatment of the 18α-compound (VIII), however, gives mixed crystals of 18α-oleana-9(11):12-dien-3β-yl acetate (IX) and oleana-11:13(18)-dien-3β-yl acetate (XI); the specific rotation and ultraviolet absorption spectrum of these show that they contain approximately 70% of the heteroannular and 30% of the homoannular dienyl acetate. Similar mixed crystals were obtained by refluxing 11β-hydroxy-18α-olean-12-en-3β-yl acetate with dimethylaniline; in neither case was it possible to separate the crystals into their components. Treatment with hydrochloric acid in acetic acid converted the mixture into the pure heteroannular dienyl acetate (XI) and this was obtained directly from (VIII) by treatment with the same acid mixture.

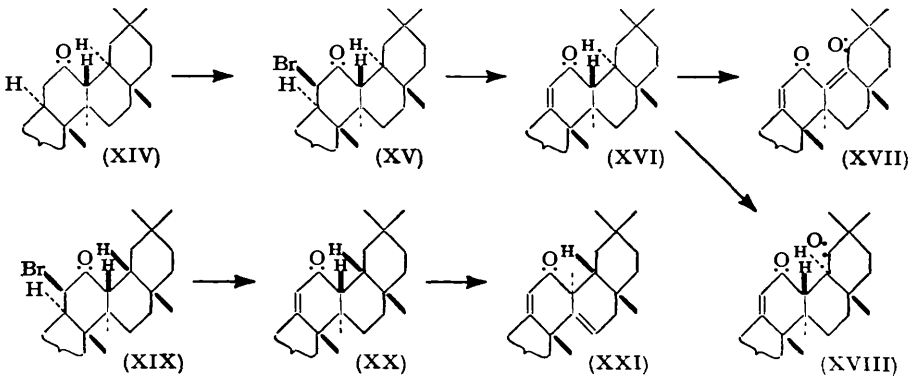


18α-Olean-12-en-3β-yl acetate (IV) was obtained by the method of Budziarek, Manson, and Spring (*loc. cit.*) and by hydrogenolysis of 11β-hydroxy-18α-olean-12-en-3β-yl acetate (VIII); it was characterised by hydrolysis to 18α-olean-12-en-3β-ol and by the preparation of esters. Oxidation of 18α-olean-12-en-3β-yl acetate (IV) with selenium dioxide or with *N*-bromosuccinimide proceeds in the same way as that of the 18β-isomer, β-amyrin acetate, giving (in similar conditions) oleana-11:13(18)-dien-3β-yl acetate (XI) (Budziarek,

Manson, and Spring, *loc. cit.*) and oleana-9(11) : 12 : 18-trien-3β-yl acetate (X) (Ruzicka, Jeger and Redel, *Helv. Chim. Acta*, 1943, **26**, 1235) respectively.

12-Oxo-18α-oleanan-3β-yl acetate (XIV) and its 11-bromo-derivative (XV) were prepared by improved methods (cf. Budziarek, Manson, and Spring, *loc. cit.*). An examination of the infrared absorption spectrum of the bromo-ketone, kindly made by Dr. G. Eglinton, shows that the bromine atom is axial (β). In spite of the fact that the geometry of (XV) favours easy elimination of hydrogen bromide, the bromo-ketone proved to be very stable. This behaviour is to be contrasted with the ease of dehydrobromination of the 18β-relative, (XIX; R = Bz), which is converted into 12-oxo-olean-9(11)-en-3β-yl benzoate (XX; R = Bz) by hydrogen bromide in warm acetic acid (Seymour and Spring, *J.*, 1941, 319); under these conditions the bromide (XV) is unchanged (Budziarek, Manson, and Spring, *loc. cit.*). Dehydrobromination of (XV), by prolonged refluxing with pyridine, gave 12-oxo-18α-olean-9(11)-en-3β-yl acetate (XVI) which shows the ultraviolet absorption of an αβ-unsaturated ketone and was characterised by the preparation of the related alcohol and benzoate.

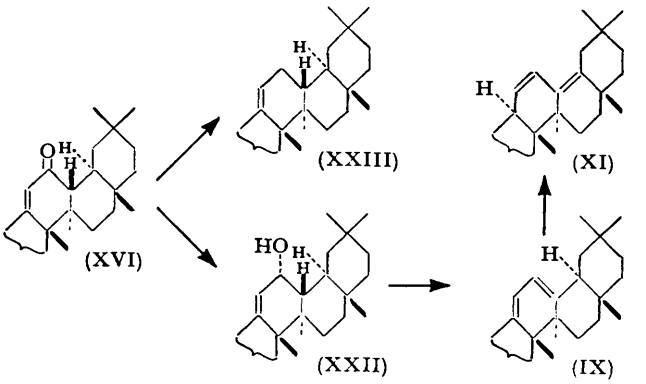
Reduction of 12-oxo-18α-olean-9(11)-en-3β-yl acetate (XVI) with lithium aluminium hydride followed by acetylation of the product gives 12α-hydroxy-18α-olean-9(11)-en-3β-yl acetate (XXII), the α-configuration being ascribed to the hydroxyl group because of its inertness and its relatively simple elimination on treatment of the diol monoacetate with



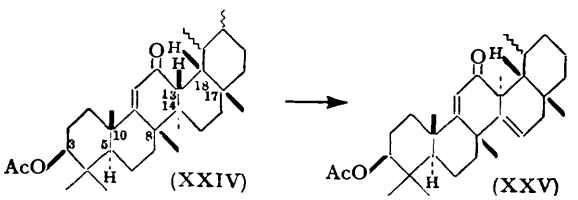
acetic anhydride and sodium acetate. The latter reaction yields 18α-oleana-9(11) : 12-dien-3β-yl acetate (IX) which shows an absorption maximum at 2780 Å (ε 9400) and is strongly dextrorotatory. It was characterised by conversion into the parent alcohol and into the corresponding benzoate. Treatment of the homoannular dienyl acetate (IX) with hydrochloric–acetic acid yields the heteroannular dienyl acetate (XI). 18α-Olean-9(11)-en-3β-yl acetate (XXIII) was obtained by hydrogenation of the αβ-unsaturated ketone (XVI).

Whereas oxidation of 12-oxo-olean-9(11)-en-3β-yl acetate (XX) with selenium dioxide in acetic acid yields 12-oxo*iso*oleana-9(11) : 14-dien-3β-yl acetate (XXI) (Green, Mower, Picard, and Spring, *J.*, 1944, 527; Allan, Johnston, and Spring, *J.*, 1954, 1546; Johnston and Spring, *ibid.*, p. 1556), the same treatment of the 18α-isomer (XVI) is without effect. Heating with selenium dioxide in dioxan at 200° has no effect on the ketone (XX) (Ruzicka, Jeger, and Norymberski, *loc. cit.*); similar oxidation of the 18α-isomer (XVI) gives a mixture of 12 : 19-dioxo-oleana-9(11) : 13(18)-dien-3β-yl acetate (XVII), as major product, and 12 : 19-dioxo-18α-olean-9(11)-en-3β-yl acetate (XVIII). The formation of the 18α-diketone (XVIII) by oxidation of (XVI) with selenium dioxide is remarkable; (XVIII) is not an intermediate in the oxidation of (XVI) to (XVII) since the 18α-diketone is recovered unchanged after treatment with selenium dioxide in dioxan at 200°. We attribute its formation to a reduction of the dioxo-dienyl acetate (XVII), the reducing agent being 12-oxo-18α-olean-9(11)-en-3β-yl acetate (XVI) which is thereby oxidised to 12-oxo-oleana-9(11) : 13(18)-dien-3β-yl acetate and then further oxidised to the dioxo-dienyl acetate (XVII) by selenium dioxide. The last stage in this reaction sequence has been described

(Beaton, Johnston, McKean, and Spring *J.*, 1953, 3660). The difference in behaviour between the isomers (XVI) and (XX) suggests that the formation of an *iso*oleanane derivative requires specific relative configurations at $C_{(13)}$, $C_{(14)}$, and $C_{(18)}$. The configurations at these centres in 12-oxo-olean-9(11)-en-3β-yl acetate (XX) permit a synchronous reaction, including the removal of the 13-hydrogen (β) and leading to a favourable conformation in the resulting 12-oxo*iso*oleana-9(11) : 14-dien-3β-yl acetate (XXI) in which the 13-methyl group (α) and the 18-hydrogen atom (β) are *anti*-related. This path is not open to 12-oxo-18α-olean-9(11)-en-3β-yl acetate (XVI) because of the unfavourable relative configurations at $C_{(14)}$ and $C_{(18)}$.



The views outlined above led us to a consideration of the configurations at $C_{(14)}$, $C_{(17)}$, and $C_{(18)}$ in α-amyrin. The α-amyrin analogue of 12-oxo-olean-9(11)-en-3β-yl acetate (XX) is 12-oxours-9(11)-en-3β-yl acetate, in which the configurations at $C_{(3)}$, $C_{(5)}$, $C_{(8)}$, and $C_{(10)}$ have been established (Jeger, Rüegg, and Ruzicka, *Helv. Chim. Acta*, 1947, **30**, 1294; Meisels, Jeger, and Ruzicka, *ibid.*, 1950, **33**, 700). When oxidised with selenium dioxide, 12-oxours-9(11)-en-3β-yl acetate gives 12-oxo*iso*ursa-9(11) : 14-dien-3β-yl acetate, in this respect resembling 12-oxo-olean-9(11)-en-3β-yl acetate (XX) and differing from 12-oxo-18α-olean-9(11)-en-3β-yl acetate (XVI). This similarity in behaviour between (XX) and



12-oxours-9(11)-en-3β-yl acetate and that between *iso*oleana-9(11) : 14-dien-3β-yl acetate and *iso*ursa-*x* : 14-dien-3β-yl acetate with mineral acid (see preceding paper) are best explained by assuming identical configurations at $C_{(13)}$, $C_{(14)}$, $C_{(17)}$, and $C_{(18)}$ in the two αβ-unsaturated ketones. We therefore represent the steric structure of 12-oxours-9(11)-en-3β-yl acetate as (XXIV) and that of 12-oxo*iso*ursa-9(11) : 14-dien-3β-yl acetate as (XXV). As a corollary rings D and E in α-amyrin are *cis*-β-fused, a conclusion also reached by Corey and Ursprung (*Chem. and Ind.* 1954, 1387; cf. Jeger, *Angew. Chem.*, 1951, **63**, 196; Ruzicka, *Experientia*, 1953, **9**, 357; Beton and Halsall, *Chem. and Ind.*, 1954, 1560; Zürcher, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1954, **37**, 2145).

Experimental

Specific rotations were measured in chloroform solution at room temperature and ultraviolet absorption spectra in ethanol.

11-*Oxo*-18α-*olean*-12-*en*-3β-*yl Benzoate*.—11-Oxo-18α-olean-12-en-3β-ol (Budziarek, Manson, and Spring, *loc. cit.*; m. p. 254—255°, $[\alpha]_D$ + 84°) was treated with benzoyl chloride and pyridine and the product crystallised from chloroform–methanol to give 11-*oxo*-18α-*olean*-12-*en*-3β-*yl*

benzoate as plates, m. p. 263—264°, $[\alpha]_D$ +86° (*c*, 1·8) (Found: C, 81·2; H, 9·6. $C_{37}H_{52}O_2$ requires C, 81·6; H, 9·6%).

Oxidation of 11-*Oxo*-18α-*olean*-12-*en*-3β-*yl Acetate with Selenium Dioxide*.—A solution of the acetate (0·5 g.) in glacial acetic acid (20 c.c.) was refluxed with selenium dioxide (0·5 g.) for 20 hr. The product, isolated in the usual manner, crystallised from methanol to give the "$O_{(5)}$-acetate" as needles (300 mg.), m. p. 255—257°, $[\alpha]_D$ +33° (*c*, 1·1), undepressed in m. p. when mixed with an authentic specimen (Found: C, 75·1; H, 9·0. Calc. for $C_{32}H_{46}O_5$: C, 75·3; H, 9·1%).

11β-*Hydroxy*-18α-*olean*-12-*en*-3β-*yl Acetate*.—A solution of 11-oxo-18α-olean-12-en-3β-yl acetate (4 g.) in ether (500 c.c.) was heated under reflux with lithium aluminium hydride (2 g.) for 2 hr. The reaction product was treated with acetic anhydride and pyridine for 1 hr. on the water-bath. The acetylated product was isolated in the usual manner and crystallised from chloroform–methanol, to give 11β-*hydroxy*-18α-*olean*-12-*en*-3β-*yl acetate* (3·5 g.) as needles, m. p. 238—239°, $[\alpha]_D$ +46° (*c*, 1·3) (Found: C, 79·4; H, 11·0. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%). Light absorption: $\varepsilon_{2800} = 5600$.

Treatment of 11β-*Hydroxy*-18α-*olean*-12-*en*-3β-*yl Acetate with Hydrochloric Acid*.—A solution of the diol monoacetate (270 mg.) in glacial acetic acid (150 c.c.) was treated with concentrated hydrochloric acid (1 c.c.) and heated on the steam-bath for 72 hr. The product, crystallised from chloroform–methanol, yielded oleana-11 : 13(18)-dienyl acetate (150 mg.), m. p. and mixed m. p. 227—228°, $[\alpha]_D$ −63° (*c*, 1·1), $\lambda_{max.}$ 2420, 2500, and 2600 Å (ε 27,000, 29,000, and 20,000) (Found: C, 82·4; H, 10·9. Calc. for $C_{32}H_{50}O_2$: C, 82·3; H, 10·8%).

18α-*Olean*-12-*en*-3β-*ol*.—A solution of 11β-hydroxy-18α-olean-12-en-3β-yl acetate (200 mg.) in glacial acetic acid (150 c.c.) was shaken with platinum (from 100 mg. of PtO_2) and hydrogen for 16 hr. The product, isolated in the usual manner, crystallised from chloroform–methanol from which 18α-olean-12-en-3β-yl acetate separated as plates (150 mg.), m. p. 243—244°, $[\alpha]_D$ +50° (*c*, 0·8); the m. p. was undepressed when mixed with a specimen (m. p. 246°, $[\alpha]_D$ +53°) prepared as described by Budziarek, Manson, and Spring (*loc. cit.*). 18α-*Olean*-12-*en*-3β-*ol* was prepared by heating the acetate with 5% ethanolic potassium hydroxide. It separates from chloroform–methanol as long needles, m. p. 213—214°, $[\alpha]_D$ +50° (*c*, 1·9) (Found: C, 84·3; H, 11·9. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8%). 18α-*Olean*-12-*en*-3β-*yl benzoate*, obtained from the alcohol in the usual manner, separates from chloroform–methanol as plates, m. p. 223—225°, $[\alpha]_D$ +64° (*c*, 3·5) (Found: C, 83·4; H, 10·4. $C_{37}H_{54}O_2$ requires C, 83·7; H, 10·3%). The benzoate was hydrolysed by boiling 10% ethanolic potassium hydroxide for 16 hr. to 18α-olean-12-en-3β-ol, m. p. and mixed m. p. 212—214°, $[\alpha]_D$ +49° (*c*, 1·2). 18α-*Olean*-12-*en*-3β-*yl hexahydrobenzoate* was obtained by shaking a solution of 11-oxo-18α-olean-12-en-3β-yl benzoate (0·8 g.) in glacial acetic acid (300 c.c.) with hydrogen and platinum (from 0·3 g. of PtO_2) for 48 hr. The product separated as plates after 30 hr.; it was isolated in the usual manner and crystallised from chloroform–methanol as plates (600 mg.), m. p. 210—211°, $[\alpha]_D$ +48° (*c*, 2·3) (Found: C, 82·4; H, 11·1. $C_{37}H_{60}O_2$ requires C, 82·8; H, 11·3%). Hydrolysis of the hexahydrobenzoate by 10% ethanolic potassium hydroxide, followed by crystallisation of the product from chloroform–methanol, gave 18α-olean-12-en-3β-ol as needles, m. p. and mixed m. p. 211—213°, $[\alpha]_D$ +48° (*c*, 0·8).

Treatment of 18α-*Olean*-12-*en*-3β-*yl Acetate with* N-*Bromosuccinimide*.—A solution of the acetate (0·5 g.) in carbon tetrachloride (50 c.c.) was refluxed with *N*-bromosuccinimide (0·4 g.) and anhydrous calcium carbonate (1 g.) for 3 hr. The filtered solution was washed with 10% sodium thiosulphate solution, and the product isolated in the usual way. Crystallisation from acetone gave oleana-9(11) : 12 : 18-trienyl acetate (300 mg.) as plates, m. p. and mixed m. p. 184—185°, $[\alpha]_D$ +525° (*c*, 0·7), $\lambda_{max.}$ 3100 Å (ε 12,000).

12-*Oxo*-18α-*oleanan*-3β-*yl Acetate*.—The following method is better than that described by Budziarek, Manson, and Spring (*loc. cit.*). A solution of 18α-olean-12-en-3β-yl acetate (7 g.) in ethyl acetate (500 c.c.) was treated at 50—60° with a solution of hydrogen peroxide (30%; 30 c.c.) in formic acid (98%; 100 c.c.) with stirring during 1 hr. The mixture was kept for 24 hr., and concentrated under reduced pressure. The crystalline solid A (m. p. 280°; 3 g.) was collected and the filtrate evaporated to dryness. The residue (4 g.) in benzene (100 c.c.) was chromatographed on a column of Grade II/III alumina (2 × 10 cm.), and the column washed with benzene (1000 c.c.) to give a crystalline solid (1 g.). This was combined with solid A and recrystallised from methanol to yield 12-oxo-18α-oleanan-3β-yl acetate (3 g.) as plates, m. p. and mixed m. p. 286—287°, $[\alpha]_D$ +77° (*c*, 1·5) (Found: C, 79·1; H, 10·8. Calc. for $C_{32}H_{52}O_3$: C, 79·3; H, 10·8%). Hydrolysis of the acetate by 5% ethanolic potassium hydroxide followed by crystallisation from methanol yielded 12-oxo-18α-oleanan-3β-ol as rods, m. p.

305—307°, $[\alpha]_D$ +89° (*c*, 0·7) which, without further purification, was treated with benzoyl chloride and pyridine to give 12-*oxo*-18α-*oleanan*-3β-*yl benzoate* which separates from chloroform–methanol as plates, m. p. 294—295°, $[\alpha]_D$ +90° (*c*, 2·5) (Found: C, 80·9; H, 9·8. $C_{37}H_{54}O_3$ requires C, 81·3; H, 9·95%). Heating this for 16 hr. with 10% ethanolic potassium hydroxide gave 12-oxo-18α-oleanan-3β-ol, m. p. and mixed m. p. 307—309°, $[\alpha]_D$ +91° (*c*, 0·7).

11β-*Bromo*-12-*oxo*-18α-*oleanan*-3β-*yl Acetate*.—The following method is better than the one described by Budziarek, Manson, and Spring (*loc. cit.*). A solution of 12-oxo-18α-oleanan-3β-yl acetate (0·8 g.) in acetic acid (100 c.c.) containing hydrobromic acid (40%; 1 c.c.) was treated at 80° with bromine (320 mg.) in glacial acetic acid (10 c.c.) during 1 hr. with stirring. The mixture was exposed to ultraviolet light (quartz flask) during the addition and for a further 4 hr. Next morning the product was isolated in the usual manner and crystallised from chloroform–methanol to give the bromo-ketone (400 mg.) as plates, m. p. 246—247°, $[\alpha]_D$ +19° (*c*, 0·7). Its infrared spectrum (in $CHCl_3$) shows a strong band at 1076 cm.$^{-1}$, in addition to bands at 1720 and 1257 cm.$^{-1}$ (acetate).

12-*Oxo*-18α-*olean*-9(11)-*en*-3β-*yl-Acetate*.—A solution of 11β-bromo-12-oxo-18α-oleanan-3β-yl acetate (250 mg.) in pyridine (30 c.c.) was refluxed for 16 hr. The pyridine was removed under reduced pressure and the product crystallised from methanol to yield 12-*oxo*-18α-*olean*-9(11)-*en*-3β-*yl acetate* as plates (125 mg.), m. p. 261—263°, $[\alpha]_D$ +145° (*c*, 0·7), $\lambda_{max.}$ 2420 Å (ε 9500) (Found: C, 79·6; H, 10·7. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%). It does not give a colour with tetranitromethane. 12-*Oxo*-18α-*olean*-9(11)-*en*-3β-*ol*, obtained from the acetate by using 5% ethanolic potassium hydroxide, crystallises from methanol as blades, m. p. 318—320°, $[\alpha]_D$ +138° (*c*, 1·3) (Found: C, 81·6; H, 10·8. $C_{30}H_{48}O_2$ requires C, 81·8; H, 11·0%). 12-*Oxo*-18α-*olean*-9(11)-*en*-3β-*yl benzoate* separates from chloroform–methanol as needles, m. p. 254—256°, $[\alpha]_D$ +147° (*c*, 0·7) (Found: C, 81·4; H, 9·4. $C_{37}H_{52}O_3$ requires C, 81·6; H, 9·6%).

12-Oxo-18α-olean-9(11)-en-3β-yl acetate was recovered unchanged (*a*) after 52 hours' refluxing with 15% ethanolic potassium hydroxide, followed by reacetylation, and (*b*) after 24 hours' refluxing in acetic acid with selenium dioxide.

Oxidation of 12-*Oxo*-18α-*olean*-9(11)-*en*-3β-*yl Acetate with Selenium Dioxide in Dioxan*.—A mixture of 12-oxo-18α-olean-9(11)-en-3β-yl acetate (200 mg.), dioxan (100 c.c.), and selenium dioxide (400 mg.) was kept at 200° for 18 hr. The product was isolated in the usual manner and crystallised from methanol to yield a first crop, recrystallisation of which gave 12 : 19-dioxo-18α-olean-9(11)-en-3β-yl acetate (25 mg.) as needles, m. p. and mixed m. p. 279—281°, $[\alpha]_D$ +95° (*c*, 0·5), $\lambda_{max.}$ 2420 Å (ε 10,000). Dilution of the combined mother-liquors with water gave a second crop, recrystallisation of which from aqueous methanol yielded 12 : 19-dioxo-oleana-9(11) : 13(18)-dien-3β-yl acetate (100 mg.) as plates, m. p. and mixed m. p. 240—241°, $[\alpha]_D$ −83° (*c*, 0·3), $\lambda_{max.}$ 2780 Å (ε 11,200).

12α-*Hydroxy*-18α-*olean*-9(11)-*en*-3β-*yl Acetate*.—A solution of 12-oxo-18α-olean-9(11)-en-3β-yl acetate (1 g.) in ether (500 c.c.) was refluxed with lithium aluminium hydride (1 g.) for 3 hr. The product was isolated in the usual manner (avoiding the use of mineral acid) and kept with pyridine and acetic anhydride at room temperature overnight. The acetylated product was crystallised from aqueous acetone to yield 12α-*hydroxy*-18α-*olean*-9(11)*en*-3β-*yl acetate* as needles (660 mg.), m. p. 192—193°, $[\alpha]_D$ +140° (*c*, 1·4) (Found: C, 79·0; H, 10·9. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%). Light absorption: ε_{2060} 5,600. It gives a yellow colour with tetranitromethane.

18α-*Oleana*-9(11) : 12-*dien*-3β-*yl Acetate*.—A solution of 12α-hydroxy-18α-olean-9(11)-en-3β-yl acetate (400 mg.) in acetic anhydride (20 c.c.) containing freshly fused sodium acetate (400 mg.) was refluxed for 3 hr. The product was isolated in the usual manner and crystallised from aqueous acetone to yield 18α-*oleana*-9(11) : 12-*dien*-3β-*yl acetate* (150 mg.) as plates, m. p. 217—218°, $[\alpha]_D$ +255° (*c*, 1·5), $\lambda_{max.}$ 2780 Å (ε 9,400) (Found: C, 81·9; H, 10·7. $C_{32}H_{50}O_2$ requires C, 82·3; H, 10·8%). 18α-*Oleana*-9(11) : 12-*dien*-3β-*ol*, obtained from the acetate by using 5% ethanolic potassium hydroxide, separates from acetone as square plates, m. p. 203—204°, $[\alpha]_D$ +262° (*c*, 1·7) (Found: C, 84·5; H, 11·3. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4%). 18α-*Oleana*-9(11) : 12-*dien*-3β-*yl benzoate* separates from chloroform–methanol as needles, m. p. 238—239°, $[\alpha]_D$ +250° (*c*, 0·5) (Found: C, 83·7; H, 9·8. $C_{37}H_{52}O_2$ requires C, 84·0; H, 9·9%). Hydrolysis for 16 hr. by 10% ethanolic potassium hydroxide gave 18α-oleana-9(11) : 12-dien-3β-ol, m. p. 200—203°, $[\alpha]_D$ +259° (*c*, 0·5).

Treatment of 18α-*Oleana*-9(11) : 12-*dien*-3β-*yl Acetate with Hydrochloric Acid*.—The 18α-dienyl acetate (100 mg.) in acetic acid (50 c.c.) and concentrated hydrochloric acid (2 c.c.) was heated on the steam-bath for 20 hr. The product was isolated in the usual manner and crystallised from chloroform–methanol to yield oleana-11 : 13(18)-dien-3β-yl acetate (50 mg.) as plates, m. p.

and mixed m. p. 224—226°, $[\alpha]_D$ −59° (*c*, 0·5), $\lambda_{max.}$ 2420, 2500, and 2600 Å (ε 23,000, 25,200, and 17,000).

18α-*Olean*-9(11)-*en*-3β-*yl Acetate*.—A solution of 12-oxo-18α-olean-9(11)-en-3β-yl acetate (125 mg.) in glacial acetic acid was shaken with hydrogen and platinum (from 100 mg. of PtO_2) for 48 hr. The product was isolated in the usual manner and crystallised from chloroform–methanol to yield 18α-*olean*-9(11)-*en*-3β-*yl acetate* (110 mg.) as plates, m. p. 248—249°, $[\alpha]_D$ +120° (*c*, 1·2) (Found: C, 82·4; H, 11·5. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%). Light absorption: $\varepsilon_{2980} = 4550$. It gives a yellow colour with tetranitromethane. The acetate was refluxed with 5% methanolic potassium hydroxide for 3 hr. to give 18α-*olean*-9(11)-*en*-3β-*ol*. It separates from methanol as needles, m. p. 215—217°, $[\alpha]_D$ +128° (*c*, 1·1) (Found: C, 84·0; H, 12·0. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8%), and gives a yellow colour with tetranitromethane.

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