189. *Bromination of Triterpenoids of the Oleanane and Ursane Series.*

By O. P. Arya and R. C. Cookson.

Esters of β-amyrin and of oleanolic acid are brominated first at $C_{(12)}$ and then at $C_{(18)}$, while 18α-β-amyrin and α-amyrin are brominated at $C_{(12)}$ only. Transformations of the bromides are described.

Esters of α- and β-amyrin can be brominated.[1-5] We find that α-amyrin acetate or benzoate (Ia) takes up only one mol. of bromine in acetic acid–carbon tetrachloride, whereas β-amyrin acetate or benzoate (Ib) takes up one mol. rapidly and a second more slowly. The resulting bromo-α-amyrin and its acetate agreed in m. p. with Vesterberg's compounds,[1,3] and the benzoate roughly corresponded with Zinke, Friedrich, and Rollett's ester.[2] Our monobromo-β-amyrin acetate also had the m. p. reported by Vesterberg,[1,4]

[1] Vesterberg, *Ber.*, 1890, **23**, 3186.
[2] Zinke, Friedrich, and Rollett, *Monatsh.*, 1920, **41**, 253.
[3] Zinke, *ibid.*, 1921, **42**, 439.
[4] Rollett, *ibid.*, 1922, **43**, 413.
[5] *Idem, ibid.*, 1926, **47**, 437.

but the benzoate seems to be different from any of the monobromo-β-amyrin benzoates reported by Rollett [5] who may well have had mixtures.

Reduction of each monobromoamyrin with sodium and alcohol gave back the appropriate amyrin, proving that the bromination had not been attended with rearrangement of the carbon skeleton, and making it probable that the double bond in the bromides still occupied its original position. The great stability of the monobromides to base—for example, monobromo-α-amyrin was unchanged by long boiling with 10% potassium hydroxide in diethylene glycol (250°)—at once suggested that the bromine atom might be attached to a doubly bound carbon atom, probably $C_{(12)}$. This was verified by oxidation of monobromo-β-amyrin benzoate by chromic acid to an αβ-unsaturated ketone, with light absorption maxima at 1680 cm.$^{-1}$ and at 269 mμ. These are the spectral properties expected [6] of the bromo-ketone (IIIb), the ultraviolet maximum of the 12-en-11-one being shifted about 20 mμ to longer wavelengths by the 12-bromine atom. Reduction of monobromo-11-oxo-β-amyrin benzoate (IIIb) with lithium aluminium hydride, followed by acetylation, led to a bromo-diene, characterised as a 9(11) : 12-diene by its light absorption ($\lambda_{max.}$ 283 mμ) and high dextrorotation. Reduction of this diene with sodium and alcohol, and acetylation, indeed produced 3β-acetoxy-β-amyra-9(11) : 12-diene. Preparation of the bromo-ketone (IIIb) and bromo-diene (IVb) proves the absence of bromine at $C_{(9)}$ and $C_{(11)}$.

Monobromo-α-amyrin acetate and benzoate (IIa) were converted into the analogous compounds (IIIa) and (IVa) in the same way.

12-Bromo-α-amyrin benzoate did not react further with bromine in acetic acid, but 12-bromo-β-amyrin acetate or benzoate took up a second mol. of bromine in a few hours at room temperature, to form a mixture from which was isolated a dibromo-β-amyrin ester, the benzoate agreeing in m. p. with a dibromo-β-amyrin benzoate obtained by Zinke, Friedrich, and Rollett.[2]

Chromic acid in acetic acid oxidised dibromo-β-amyrin acetate or benzoate to the corresponding dibromo-11-ketone ($\lambda_{max.}$ 269 mμ), also produced by bromination of the appropriate ester of 12-bromo-11-oxo-β-amyrin (IIIb). The second atom of bromine can therefore be attached only to $C_{(9)}$ or $C_{(18)}$.

As a test of the latter possibility, the acetate of the dibromide was heated with collidine at 300°. Instead of the expected elimination, reduction occurred, yielding an isomer of 12-bromo-11-oxo-β-amyrin acetate. Similarly, collidine or zinc and acetic acid reduced dibromo-β-amyrin acetate to an isomer of 12-bromo-β-amyrin acetate, identified as 12-bromo-18α-β-amyrin acetate (V) when the identical substance was produced by brominating 18α-β-amyrin acetate. 12-Bromo-18α-β-amyrin acetate was oxidised to 12-bromo-11-oxo-18α-β-amyrin acetate identical with the monobromo-ketone formed on reduction of dibromo-11-oxo-β-amyrin acetate. Since normal 12-bromo-β-amyrin acetate and its 11-oxo-derivative were stable to collidine under conditions that reduced the dibromo-compounds to the 18α-isomers, the isomerisation is produced by reduction and the second atom of bromine in the dibromide is thus located at $C_{(18)}$ (VI; R = Me).

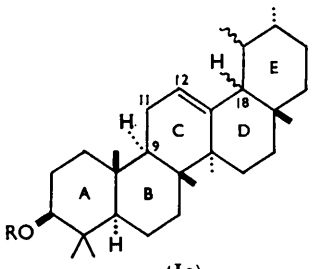
Like β-amyrin acetate, methyl *O*-acetyloleanolate absorbed one mol. of bromine in acetic acid to give the 12-bromo-derivative,* which more slowly took up a second mol. to give the 12 : 18-dibromide (VI; R = CO_2Me). Chromic acid oxidised the two bromides to the respective 11-ketones. Treatment of the dibromo-ketone (VII) with collidine resulted here in elimination of the elements of methyl bromide, producing in good yield a neutral, high-melting, methoxyl-free substance, the behaviour of which with alkali showed it to be a lactone. The band at 1890 cm.$^{-1}$ in the infrared spectrum indicated a γ-lactone, while the band at 1688 cm.$^{-1}$ and the maximum at 264 mμ in the ultraviolet

* In the less polar methylene chloride solution methyl *O*-acetyloleanolate reacts with bromine with participation of the methoxycarbonyl group to give the bromo-lactone.[7]

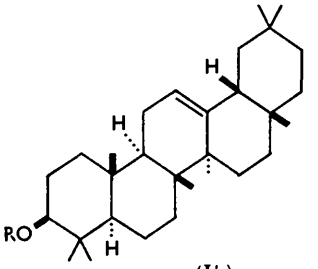
[6] Nussbaum, Mancera, Daniels, Rosenkranz, and Djerassi, *J. Amer. Chem. Soc.*, 1951, **73**, 3263.
[7] Corey and Ursprung, *ibid.*, 1956, **78**, 183; *Chem. and Ind.*, 1954, 1387.

spectrum showed that the 12-bromo-12-en-11-one chromophore was probably still intact. These structural features are most simply accommodated by the tentative constitution (VIII).

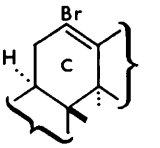
The configuration of the 18-bromine atom in the dibromides is uncertain, but the nearly identical ultraviolet spectra of the mono- and di-bromides in both the long and the



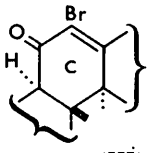
(Ia)



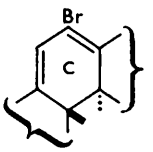
(Ib)



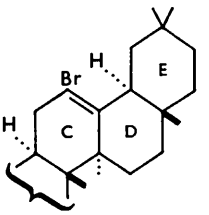
(II)



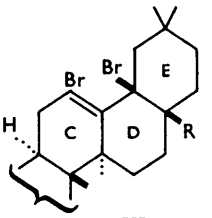
(III)



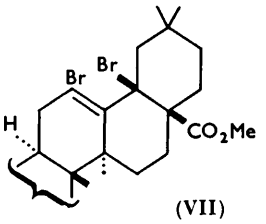
(IV)



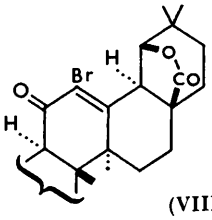
(V)



(VI)



(VII)



(VIII)

short wavelength bands suggests very strongly that the 18-bromine is equatorial [8] to ring D (18β), rather than axial as might have been expected from the operation of purely electronic effects.[9]

Experimental

Optical rotations were measured in $CHCl_3$ (*c* 1—2%), and ultraviolet spectra in EtOH. Infrared spectra (in CS_2) were very kindly determined by Glaxo Laboratories Ltd.

12-Bromo-β-amyrin Benzoate.—β-Amyrin benzoate (3·52 g.), dissolved in dry carbon tetrachloride (70 ml.), was treated with bromine (10·2 ml. of 10·4% solution in acetic acid). The mixture was diluted with acetic acid (120 ml.) and then left in the dark for 5 hr. After filtration in benzene through alumina and three crystallisations from acetone the 12-bromo-derivative, isolated normally, melted constantly at 140—145° and then at 216—217° after resolidifying, and had $[\alpha]_D$ +44°, $\lambda_{max.}$ 229 mμ (ε 17,100) (Found: C, 72·6; H, 8·7; Br, 12·9. Calc. for $C_{37}H_{53}O_2Br$: C, 72·9; H, 8·8; Br, 13·0%). It gave a yellow colour with tetranitromethane in chloroform.

[8] Bird, Cookson, and Dandegaonker, *J.*, 1956, 3675.
[9] Corey, *J. Amer. Chem. Soc.*, 1954, **76**, 175.

12-*Bromo*-β-*amyrin Acetate* —Bromine in acetic acid (6 ml. of 3% solution) was added to β-amyrin acetate (487 mg.) in carbon tetrachloride (20 ml.) and acetic acid (10 ml.). After 45 min. titration showed that one mol. of bromine had been taken up. The resulting bromo-derivative, filtered through alumina in benzene and recrystallised six times from chloroform–methanol, had m. p. 237—238°, $[\alpha]_D$ +44° (Found: C, 70·1; H, 9·3; Br, 14·8. Calc. for $C_{32}H_{51}O_2Br$: C, 70·2; H, 9·4; Br, 14·6%).

12 : 18-*Dibromo*-β-*amyrin Benzoate*.—Solutions of β-amyrin benzoate (3·0 g.) in carbon tetrachloride (20 ml.) and acetic acid (150 ml.) and of bromine in acetic acid (100 ml. of 3%) were mixed. After three days in the dark, reaction had ceased with the consumption of 2 mols. of bromine. The dibromide was filtered through alumina in benzene and recrystallised five times from chloroform–methanol to m. p. 214—215° (decomp.), $[\alpha]_D$ +50°, $\lambda_{max.}$ 230 mμ (ε 17,000), giving a yellow colour with tetranitromethane (Found: C, 64·2; H, 7·5; Br, 23·1. Calc. for $C_{37}H_{52}O_2Br_2$: C, 64·5; H, 7·6; Br, 23·2%).

12 : 18-*Dibromo*-β-*amyrin Acetate*.—Absorption of 2 mols. from an excess of bromine by β-amyrin under similar conditions gave the dibromo-acetate, m. p. 234—235° (decomp.), $[\alpha]_D$ +39°, after filtration through alumina in benzene and six recrystallisations from chloroform–methanol (Found: C, 61·6; H, 8·0; Br, 25·0. Calc. for $C_{32}H_{50}O_2Br_2$: C, 61·3; H, 8·0; Br, 25·5%).

12-*Bromo*-18α-β-*amyrin Acetate*.—18α-β-Amyrin acetate took up bromine much more slowly than the 18β-epimer. One mol. was absorbed in a few hours, and no more even in several weeks. The resulting 12-*bromide*, after chromatography and several recrystallisations from chloroform–methanol, had m. p. 218—219° (decomp.), $[\alpha]_D$ +47° (Found: C, 70·2; H, 8·9; Br, 14·8. $C_{32}H_{51}O_2Br$ requires C, 70·2; H, 9·4; Br, 14·6%).

Reduction of 12 : 18-*Dibromo*-β-*amyrin Acetate*.—The dibromide (1 g.) was treated with a large excess of zinc in boiling acetic acid for 3 hr. The product (820 mg.), recrystallised four times from chloroform–methanol, had m. p. 215—216° (decomp.), depressed by 12-bromo-β-amyrin acetate but not by 12-bromo-18α-β-amyrin acetate. The identity of the two compounds was confirmed by oxidation of each (see below) to the same 11-ketone (mixed m. p., identical rotations and spectra).

Dibromo-β-amyrin acetate was not affected by 24 hours' boiling in collidine, but when it was heated in collidine at 300° overnight the product yielded 12-bromo-18α-β-amyrin acetate (25%), m. p. and mixed m. p. 215—216° (decomp.) after chromatography and several recrystallisations.

12-*Bromo*-α-*amyrin Benzoate*.—α-Amyrin benzoate (2·46 g.) in carbon tetrachloride (30 ml.) and acetic acid (45 ml.) was treated with bromine in acetic acid (7·7 ml. of 10·4% solution). The mixture was worked up after 2 days, to give the bromo-ester as needles, m. p. 237—238°, $[\alpha]_D$ +65°, $\lambda_{max.}$ 229 mμ (ε 17,000), after filtration in benzene through alumina and four recrystallisations from chloroform–methanol (Found: C, 72·6; H, 8·5; Br, 13·4. Calc. for $C_{37}H_{53}O_2Br$: C, 72·9; H, 8·8; Br, 13·0%). It gave a yellow colour with tetranitromethane.

12-*Bromo*-α-*amyrin Acetate*.—α-Amyrin acetate (900 mg.) in carbon tetrachloride (20 ml.) and acetic acid (30 ml.), mixed with bromine in acetic acid (10 ml. of 3% solution), was left for one day. After filtration through alumina and three recrystallisations from chloroform–methanol the resulting bromo-derivative had m. p. 272—273°, $[\alpha]_D$ +66° (Found: C, 70·3; H, 9·2; Br, 14·5. Calc. for $C_{32}H_{51}O_2Br$: C, 70·2; H, 9·4; Br, 14·6%).

Hydrolysis of 12-bromo-α-amyrin benzoate by 10 hours' treatment with a 10% solution of potassium hydroxide in boiling diethylene glycol gave 12-bromo-α-amyrin, m. p. 177—178°, which gave the original acetate (mixed m. p.) on acetylation.

Debromination of 12-*Bromo*-β-*amyrin*.—Small pieces of sodium were added gradually to a solution of 12-bromo-β-amyrin benzoate (470 mg.) in boiling pentyl alcohol (20 ml.) until the solution became saturated (*ca.* 1½ hr.). The resulting β-amyrin had m. p. and mixed m. p. 195—196°, $[\alpha]_D$ +87°, after recrystallisation. The identity was confirmed by conversion of the alcohol into the acetate, m. p. 240—241°, not depressed by β-amyrin acetate.

Debromination of 12-*Bromo*-α-*amyrin*.—12-Bromo-α-amyrin benzoate, treated in the same way, gave α-amyrin, m. p. and mixed m. p. 184—185°, $[\alpha]_D$ +82°. Comparison of the corresponding acetate and benzoate with authentic α-amyrin esters confirmed the identity.

12-*Bromo*-11-*oxo*-β-*amyrin Benzoate*.—Solutions of 12-bromo-β-amyrin benzoate (700 mg.) in warm acetic acid (80 ml.) and of chromic oxide (350 mg.) in wet acetic acid (10 ml.) (*i.e.*, chromic oxide dissolved in the minimum of water, and the solution made up to 10 ml. with

dry acetic acid) were mixed and kept at 82—85° for 40 min. The resulting 11-*ketone*, recrystallised thrice from chloroform–methanol, had m. p. 246—247°, $[\alpha]_D$ +54°, $\lambda_{max.}$ 230 (ε 15,000) and 269 mμ (ε 9500), $\nu_{max.}$ 1714 and 1678 cm.$^{-1}$; no colour with tetranitromethane (Found: C, 71·3; H, 8·0; Br, 12·65. $C_{37}H_{51}O_3Br$ requires C, 71·2; H, 8·2; Br, 12·8%).

12-*Bromo*-11-*oxo*-β-*amyrin Acetate*.—Chromic acid oxidised 12-bromo-β-amyrin acetate under the above conditions to the corresponding 11-*ketone*, m. p. 276—277°, $[\alpha]_D$ +51°, $\lambda_{max.}$ 269 (ε 10,000), 317 (ε 51), and 323—324 mμ (ε 54), $\nu_{max.}$ 1735 and 1680 cm.$^{-1}$, after three recrystallisations from chloroform–methanol (Found: C, 68·5; H, 8·8; Br, 14·25. $C_{32}H_{49}O_3Br$ requires C, 68·4; H, 8·8; Br, 14·25%). This acetate could also be made by hydrolysis of the benzoate with potassium hydroxide in methanol–benzene, followed by acetylation.

12-*Bromo*-11-*oxo*-18α-β-*amyrin Acetate*.—Oxidation of 12-bromo-18α-β-amyrin acetate with chromic acid in acetic acid gave the 18α-11-*ketone*, m. p. 263—264°, $[\alpha]_D$ 49°, $\lambda_{max.}$ 267 mμ (ε 9050) (Found: C, 68·8; H, 8·7; Br, 14·25. $C_{32}H_{49}O_3Br$ requires C, 68·4; H, 8·8; Br, 14·25%).

Reduction of 12 : 18-*Dibromo*-11-*oxo*-β-*amyrin Acetate*.—The dibromo-ketone (200 mg.) in redistilled collidine (6 ml.) was heated at 300° for 24 hr. After chromatography and recrystallisation from chloroform–methanol the product (100 mg.) had m. p. 261—262°, alone and mixed with 12-bromo-18α-β-amyrin acetate, $[\alpha]_D$ 48°, $\lambda_{max.}$ 267 mμ (ε 9100).

12-*Bromo*-11-*oxo*-α-*amyrin Benzoate*.—This *compound*, recrystallised thrice from chloroform–methanol, had m. p. 252—253°, $[\alpha]_D$ +100°, $\lambda_{max.}$ 230 (ε 15,000) and 269—270 mμ (ε 9700), no colour with tetranitromethane (Found: C, 71·0; H, 7·9; Br, 12·8. $C_{37}H_{51}O_3Br$ requires C, 71·2; H, 8·2; Br, 12·8%).

12-*Bromo*-β-*amyra*-9(11) : 12-*dien*-3β-*yl Acetate*.—A solution of 12-bromo-11-oxo-β-amyrin benzoate (890 mg.) in dry benzene (5 ml.) and ether (30 ml.) was added to lithium aluminium hydride (450 mg.) in ether (110 ml.). The mixture was boiled for 45 min. and the crude isolated product was then boiled for 3 hr. with acetic anhydride (10 ml.) containing toluene-*p*-sulphonic acid (*ca.* 15 mg.). The resulting *bromo-diene*, after filtration in benzene through alumina and four recrystallisations from chloroform–methanol, had m. p. 213—214°, $[\alpha]_D$ +206°, $\lambda_{max.}$ 282—283 mμ (ε 9500) (Found: C, 70·2; H, 8·85; Br, 15·0. $C_{32}H_{49}O_2Br$ requires C, 70·4; H, 9·05; Br, 14·7%). It gave a deep brown colour with tetranitromethane in chloroform.

12-*Bromo*-α-*amyra*-9(11) : 12-*dien*-3β-*yl Acetate*.—Reduction, dehydration, and acetylation of 12-bromo-11-oxo-α-amyrin benzoate as for the β-amyrin derivative afforded the *bromo-diene*, which was recrystallised four times from chloroform–methanol. It then had m. p. 212—213°, $[\alpha]_D$ +229°, $\lambda_{max.}$ 282—283 mμ (ε 9200) (Found: C, 70·4; H, 8·8; Br, 14·9. $C_{32}H_{49}O_2Br$ requires C, 70·4; H, 9·05; Br, 14·7%). It gave a deep brown colour with tetranitromethane in chloroform. It was unchanged by bromine in acetic acid at 90°.

Debromination of 12-*Bromo*-9(11) : 12-*dienes*.—A solution of 12-bromo-β-amyra-9(11) : 12-dien-3β-yl acetate (400 mg.) in boiling *n*-pentyl alcohol (20 ml.) was saturated with small pieces of sodium during 1 hr. After acetylation, the crude product was filtered through alumina in benzene. Four recrystallisations produced crystals, m. p. 215—216°, $[\alpha]_D$ +335, $\lambda_{max.}$ 282 mμ (ε 9800), which had the same m. p. when mixed with β-amyra-9(11) : 12-dien-3β-yl acetate. The m. p.s of the derived alcohol, 211—212°, and benzoate, 248—249°, were also undepressed by genuine samples.

Reduction of 12-bromo-α-amyra-9(11) : 12-dien-3β-yl acetate in the same way led to α-amyra-9(11) : 12-3β-yl acetate, m. p. and mixed m. p. 166—167°, $[\alpha]_D$ +305°.

12 : 18-*Dibromo*-11-*oxo*-β-*amyrin Benzoate*.—(a) *From* 12 : 18-*dibromo*-β-*amyrin benzoate*. 12 : 18-Dibromo-β-amyrin benzoate (200 mg.) in acetic acid (50 ml.) was oxidised at 82—85° with chromic oxide (100 mg.) in wet acetic acid (5 ml.). After 30 min. the mixture was worked up. The *dibromo-ketone* melted at 253—254° (decomp.) after four recrystallisations from chloroform–methanol, and had $[\alpha]_D$ +59°, $\lambda_{max.}$ 230 (ε 17,000) and 269 mμ (ε 10,200) (Found: C, 63·2; H, 7·1; Br, 22·75. $C_{37}H_{50}O_3Br_2$ requires C, 63·2; H, 7·2; Br, 22·8%).

(b) *From* 12-*bromo*-11-*oxo*-β-*amyrin benzoate*. Bromine in acetic acid (3 ml. of 3% solution) was added drop by drop to a solution of 12-bromo-11-oxo-β-amyrin benzoate (234 mg.) in acetic acid (60 ml.) at *ca.* 90° during 30 min. Having been left for another hour at 90° the mixture was worked up. The product was filtered through alumina in benzene and recrystallised twice from chloroform–methanol, to give the dibromo-ketone, m. p. 252—253° (not depressed by the above sample), $[\alpha]_D$ +61°, $\lambda_{max.}$ 230 (ε 17,800) and 268 mμ (ε 10,500), $\nu_{max.}$ 1714 and 1682 cm.$^{-1}$.

12 : 18-Dibromo-11-oxo-β-amyrin benzoate was recovered unchanged after 3 hours' boiling with hydrogen bromide in acetic acid, or 1½ hours' boiling with collidine.

12 : 18-*Dibromo*-11-*oxo*-β-*amyrin Acetate*.—Oxidation of 12 : 18-dibromo-β-amyrin acetate as for the benzoate gave the 11-*oxo-acetate*, m. p. 247—248° (decomp.) (after six recrystallisations from chloroform–methanol), $[\alpha]_D$ +51°, $\lambda_{max.}$ 269 (ε 10,500) and 320—321 mμ (ε 58) (Found : C, 60·3; H, 7·6. $C_{32}H_{48}O_3Br_2$ requires C, 60·0; H, 7·55%).

An identical acetate (mixed m. p., ultraviolet spectrum, and rotation) was produced by hydrolysis of the corresponding benzoate and acetylation.

β-*Amyra*-9(11) : 12 : 18-*trien*-3β-*yl Acetate*.—A solution of 11-oxo-β-amyra-12 : 18-dien-3β-yl benzoate (270 mg.) in ether (200 ml.) was added to one of lithium aluminium hydride (500 mg.) in ether (100 ml.). After an hour's boiling the crude, isolated product was boiled for 3 hours in acetic anhydride (5 ml.). The resulting β-amyra-9(11) : 12 : 18-trien-3β-yl acetate was purified by filtration in benzene through alumina and six recrystallisations from chloroform–methanol. It then showed m. p. 180—181°, $[\alpha]_D$ +510°, $\lambda_{max.}$ 308 mμ (ε 13,500). A sample of the triene made by dehydrogenation of β-amyrin acetate with *N*-bromosuccinimide had almost identical physical properties and a mixture of the two samples had the same m. p.

Bromination of 11-*Oxo*-β-*amyrin Benzoate*.—The ketone (580 mg.), dissolved in chloroform (10 ml.), was treated with bromine in acetic acid (50 ml. of 4·2% solution) in the presence of hydrogen bromide (10 drops of 50% solution in acetic acid). A week later the mixture was worked up, to yield a *dibromo-ketone*, which after four recrystallisations from chloroform–methanol melted first at 215° and then at 234—235° (decomp.) and had $[\alpha]_D$ +455° and $\lambda_{max.}$ 230 (ε 22,000) and 272 mμ (ε 8200) (Found : C, 63·1; H, 6·85; Br, 21·3. $C_{37}H_{50}O_3Br_2$ requires C, 63·2; H, 7·2; Br, 22·8%).

Methyl O-*Acetyl*-12-*bromo-oleanolate*.—Methyl *O*-acetyloleanolate (1·55 g.) in dry carbon tetrachloride (20 ml.) and acetic acid (100 ml.) was treated with bromine in acetic acid (16 ml. of 3% solution). After 1½ hr. one mol. of bromine had been consumed and the mixture was worked up normally. The 12-*bromo-derivative* was filtered through alumina in benzene and recrystallised twice from chloroform–methanol to m. p. 217—218°, $[\alpha]_D$ +32°, yellow with tetranitromethane (Found : C, 66·9; H, 8·6; Br, 13·4. $C_{33}H_{51}O_4Br$ requires C, 66·9; H, 8·7; Br, 13·5%).

Methyl O-*Acetyl*-12 : 18-*dibromo-oleanolate*.—Solutions of methyl *O*-acetyloleanolate (1·09 g.) in carbon tetrachloride (50 ml.) and acetic acid (125 ml.) and of bromine in acetic acid (50 ml. of 2% solution) were mixed. After three days two mols. of bromine had been absorbed. The *dibromo-derivative*, isolated as usual, was filtered in benzene through alumina and recrystallised four times from chloroform–methanol. It then had m. p. 210—212° (decomp.) and $[\alpha]_D$ +38°, and gave a yellow colour with tetranitromethane (Found : C, 59·0; H, 7·3; Br, 23·6. $C_{33}H_{50}O_4Br_2$ requires C, 59·0; H, 7·5; Br, 23·8%).

Methyl O-*Acetyl*-12-*bromo*-11-*oxo-oleanolate*.—Methyl *O*-acetyl-12-bromo-oleanolate (700 mg.) in acetic acid (50 ml.) was treated with chromic oxide (500 mg). in water (3 drops) and acetic acid (3 ml.). The mixture was heated on the steam-bath for 45 min. and the isolated product was filtered through alumina in benzene and recrystallised four times from chloroform–methanol. The *bromo-ketone* then had m. p. 276—277°, $[\alpha]_D$ +62°, $\lambda_{max.}$ 268—269 mμ (ε 10,500), no colour with tetranitromethane (Found : C, 65·15; H, 8·1; Br, 13·7. $C_{33}H_{49}O_5Br$ requires C, 65·4; H, 8·1; Br, 13·2%).

Methyl O-*Acetyl*-12 : 18-*dibromo*-11-*oxo-oleanolate*.—Oxidation of methyl *O*-acetyl-12 : 18-dibromo-oleanolate with chromic acid as above gave the *dibromo-ketone*. After filtration through alumina in benzene and four recrystallisations from chloroform–methanol it had m. p. 230° (decomp.) and then *ca.* 260° after re-solidifying, $[\alpha]_D$ +54°, $\lambda_{max.}$ 269 mμ (ε 11,000) (Found : C, 58·0; H, 6·9; Br, 23·0. $C_{33}H_{48}O_5Br_2$ requires C, 57·9; H, 7·1; Br, 23·3%).

Action of Collidine on Methyl O-*Acetyl*-12 : 18-*dibromo*-11-*oxo-oleanolate*.—The dibromo-ester (180 mg.) was heated with freshly distilled collidine (2 ml.) at 200° for 16 hr. The resulting *bromo-lactone* (140 mg.), crystallised twice from methanol, had m. p. 325—326° (decomp.), $[\alpha]_D$ −23°, $\lambda_{max.}$ 263—264 mμ (ε 10,000), $\nu_{max.}$ 1790, 1730, and 1688 cm.$^{-1}$ (Found : C, 65·3; H, 7·8; Br, 13·6. $C_{32}H_{45}O_5Br$ requires C, 65·2; H, 7·7; Br, 13·6%).

Methyl *O*-acetyl-12-bromo-11-oxo-oleanolate was unchanged by collidine under the same conditions.

Pyrolysis of Methyl O-*Acetyl*-12 : 18-*dibromo*-11-*oxo-oleanolate*.—The dibromo-ester was

heated at 230—235° and room pressure for 5 min. Two crystallisations of the product from methanol gave the bromo-lactone, m. p. 321—322° (decomp.), $[\alpha]_D$ −21·5°, $\lambda_{max.}$ 263—264 mμ (ε 10,000) : mixed with the sample made with collidine, it had m. p. 324—325° (decomp.).

We are most grateful to Professor D. H. R. Barton, F.R.S., for his continual encouragement and guidance.

BIRKBECK COLLEGE, MALET STREET,
LONDON, W.C.1.

[*Received, September 26th*, 1956.]