1055. *The Chemistry of Triterpenes and Related Compounds. Part XLI.* The Bromination of Lupeol and its Esters.*

By S. R. Gupta, T. G. Halsall, and E. R. H. Jones.

The confused literature on the bromination of lupeol and its derivatives is reviewed. Bromination of lupenyl acetate gives the side-chain monobromo-compounds, 29- and 30-bromo-20(29)-en-3β-yl acetates (VII) and (X). The allylic bromide is isomerised to the vinyl bromide by hydrobromic acid. On further treatment with hydrogen bromide, addition is accompanied by the expected skeletal rearrangement yielding 19α,29(or 30)-dibromo-18α-oleanan-3β-yl acetate (IV).

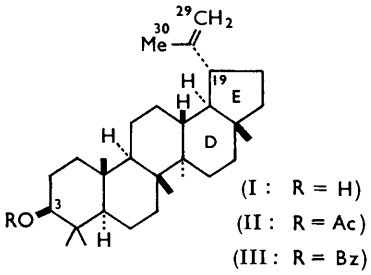
The bromination of lupeol (I) and its derivatives has been studied by a number of workers, but the structures of the products have not been elucidated. In the early 1900's Cohen [1,2] treated lupeol with one mol. of bromine in carbon disulphide and in chloroform; hydrogen bromide was evolved, and he obtained a monobromo-derivative, $C_{30}H_{49}BrO$, m. p. 185°, $[\alpha]_D$ +4°. No dibromide was isolated. When lupenyl benzoate was brominated in a mixture of carbon disulphide and acetic acid two monobromo-derivatives were obtained. Separation was effected by taking advantage of their different solubilities in acetone. Only the constants of the less soluble product, m. p. 243°, $[\alpha]_D$ +45°, were recorded. Goodson [3]

* Part XL, *J.*, 1961, 3891.

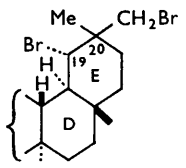
[1] Cohen, *Proc. k. Akad. Wetensch. Amsterdam*, 1906, **9**, 466.
[2] Cohen, *Rec. Trav. chim.*, 1909, **28**, 368.
[3] Goodson, *Biochem. J.*, 1921, **15**, 123.

later reported a monobromolupeol, m. p. 183°, and a monobromolupenyl acetate, m. p. 232°.

Subsequently the formation of a lupeol dibromide was reported. Dieterle [4] described such a product, m. p. 205—206° (decomp.), $[\alpha]_D$ +25°. Marker and Wittle [5] treated lupenyl acetate in ether with a slight excess of bromine in acetic acid and obtained a dibromide, m. p. 225° (decomp.). Similar treatment of lupeol yielded a dibromide, m. p. 186—190° (decomp.). Biedebach [6] also reported the isolation of lupenyl acetate dibromide, m. p. 225°, from the product of gradual addition of bromine in acetic acid to lupenyl



(I : R = H)
(II : R = Ac)
(III : R = Bz)



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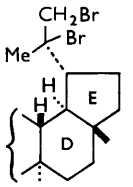

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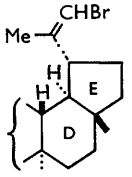
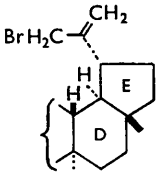
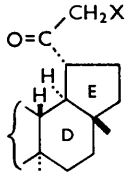


(VI ; 3-OH)
(VII ; 3-OAc)
(VIII ; 3-OBz)



(IX ; 3-OH)
(X ; 3-OAc)
(XI ; 3-OBz)



(XII ; X = H)
(XIII ; X = Br)

acetate in chloroform. When the dibromide was treated with silver nitrate in pyridine a product described as monobromolupenyl acetate, m. p. 205°, was isolated and hydrolysed to monobromolupeol, m. p. 196—197°.

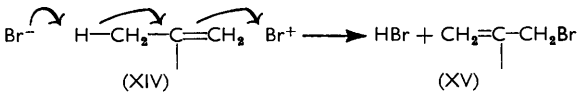
In view of these conflicting results a further investigation of the bromination of lupeol and its derivatives appeared desirable, more especially as, in the light of the known acid-catalysed rearrangements [7] of lupeol derivatives, it appeared possible that a dibromide might be formed by attack of Br^+ at $C_{(29)}$, rearrangement of the resulting carbonium ion, and attachment of Br^- at $C_{(19)}$ of the rearranged ion, compound (IV) being formed. The only structure which has been proposed [8] for lupeol dibromide is (V).

Bromination of lupenyl acetate in the conditions used by Biedebach was first studied. His " dibromide," m. p. 225°, was not isolated. Instead two products were obtained. One was a monobromolupenyl acetate, m. p. 196—198°. The other was not homogeneous (see Experimental). The monobromo-derivative is 29-bromolupenyl acetate (VII), the structure being based on the following evidence. Reduction with sodium and isopropyl alcohol gave lupeol, and catalytic hydrogenation yielded lupanyl acetate. The carbon skeleton of lupeol is therefore present and ring enlargement has not occurred. On ozonolysis and treatment of the ozonide with boiling water the known norlupanonyl acetate [9] (XII) was isolated.

[4] Dieterle, *Arch. Pharm.*, 1923, **261**, 89, 97.
[5] Marker and Wittle, *J. Amer. Chem. Soc.*, 1939, **61**, 585.
[6] Biedebach, *Arch. Pharm.*, 1939, **277**, 163.
[7] Ames, Beton, Bowers, Halsall, and Jones, *J.*, 1954, 1905.
[8] Elsevier's " Encyclopaedia," Vol. XIV,S, p. 1122.
[9] Jones and Meakins, *J.*, 1940, 456.

When lupenyl acetate was brominated in ether at −78° two monobromolupenyl acetates were obtained. One was the 29-bromo-derivative (VII). The other, m. p. 235—236°, was shown to be the allylic bromo-compound, 30-bromolupenyl acetate (X). Reduction of the latter with sodium and isopropyl alcohol again gave lupeol, and hydrogenation lupanyl acetate. On ozonolysis formaldehyde was isolated as its dimethone. When the ozonide was reduced with zinc and acetic acid norlupanonyl acetate (XII), probably produced by reduction of an originally formed bromo-ketone, was again obtained. The ozonide was therefore decomposed in water at 100°, the bromoketo-acetate (XIII) being isolated.

The allylic bromide (X) was isomerised by hydrogen bromide in acetic acid–chloroform to the vinyl bromide (VII), but the reverse reaction did not occur (see below, however). The possibility therefore has to be considered that the allylic bromide is the first monobromo-product formed. It could arise from an initially formed, unstable dibromide, or be produced directly by the mechanism represented by (XIV ⟶ XV), this being akin to an S_N2' substitution. The vinyl bromide (VII) could then arise by isomerisation of the initially formed allylic bromide (X). However, bromination of lupenyl acetate in propylene oxide, which should act as a proton acceptor,[10] afforded only the vinyl bromide (VII). An alternative explanation of the results is that the two bromides are produced independently by distinct reactions.



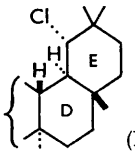
Similar results were obtained with lupenyl benzoate (III). When propylene oxide was used as solvent, only the vinyl bromide (VIII) was obtained. Its identity was established by comparison with the benzoate obtained from 29-bromolupeol (VI) which had been prepared from 29-bromolupenyl acetate. Bromination of lupenyl benzoate in ether gave a mixture of the vinyl (VIII) and allylic (XI) bromide. The latter was also prepared by benzoylation of 30-bromolupeol (IX).

The constants of 30-bromolupeol, m. p. 188—189°, $[\alpha]_D$ +2°, are very similar to those of Cohen's "monobromolupeol," [1,2] m. p. 185°, $[\alpha]_D$ +4°. The absence of specific rotations for most of the other earlier bromination products makes comparison impossible.

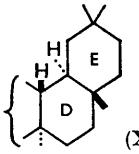
Biedebach [11] reported that "monobromolupeol" in boiling acetic anhydride was converted to a small extent into a compound which had the same melting point as γ-allolupenyl acetate (germanicyl acetate) [12] but with which he said it was not identical. In our work only starting material was recovered when 29-bromolupenyl acetate (VII) was heated under reflux in acetic anhydride. Silver acetate also failed to react with the acetate, thus confirming that the bromine atom attached to $C_{(29)}$ in the acetate (VII) is extremely unreactive.

Lupenyl acetate with hydrogen chloride gives [13] the "hydrochloride" (XVI) (19α-chloro-18α-oleanan-3β-yl acetate) which can be converted back into lupenyl acetate with silver acetate. When 29-bromolupenyl acetate (VII) was treated with hydrogen bromide a similar rearrangement accompanied addition of the hydrogen bromide and 19α,29(or 30)-dibromo-18α-oleananyl acetate (IV) was obtained. The structure, apart from the configuration at position 20, follows from the reduction of the dibromo-compound with sodium and isopropyl alcohol to the known 18α-oleanan-3β-ol [isolated as its acetate [14] (XVII)] and by its conversion back into 29-bromolupenyl acetate by silver acetate.

[10] Kirk, Patel, and Petrow, *J.*, 1956, 627.
[11] Biedebach, *Arch. Pharm.*, 1943, **281**, 49.
[12] Halsall, Jones, and Swayne, *J.*, 1954, 1902.
[13] Halsall, Jones, and Meakins, *J.*, 1952, 2862.
[14] Budziarek, Manson, and Spring, *J.*, 1951, 741.



(XVI)



(XVII)

The constants of the earlier bromination products and of the bromo-derivatives now prepared are given in the Table in the Experimental section.

Experimental

Rotations refer to solutions in chloroform at room temperature. M. p.s were determined on a Kofler block and are corrected. The alumina used for chromatography (unless otherwise stated) was alumina of activity I—II which had been deactivated with 5% of 10% aqueous acetic acid. Light petroleum refers to the fraction with b. p. 60—80°. Unless otherwise stated, ultraviolet spectra were determined for n-hexane solutions.

Bromination of Lupenyl Acetate (II).—(*a*) Bromine (0·36 g., 1·05 mol.) in acetic acid (5 c.c.) was added in 15 min. to lupenyl acetate (1·0 g.) in chloroform (6 c.c.) at 0°. After acetic acid (10 c.c.) had been added the mixture was kept in the dark at 20° overnight. The mixture was concentrated under reduced pressure and cooled, a product (0·85 g.) separating. This was filtered off, washed with acetic acid, dried, and adsorbed from light petroleum (75 c.c.) on alumina (50 g.). Elution with the solvents indicated gave the following fractions: (1—3) light petroleum (L.P.) (350 c.c.), 235 mg., m. p. 190—195°; (4) L.P. (50 c.c.), 89 mg., m. p. 190—202°; (5) L.P.–benzene (B.) (9 : 1) (50 c.c.), 89 mg., m. p. 195—210°; (6—7) L.P.–B. (9 : 1) (250 c.c.), 165 mg., m. p. 200—220°; (8) L.P.–B. (9 : 1) (50 c.c.), 64 mg., m. p. 214—230°; (9) L.P.–B. (1 : 1) (50 c.c.), 45 mg., m. p. 225—240°; (10) L.P.–B. (1 : 1) (50 c.c.), 33 mg., m. p. 234—243°; (11) L.P.–B. (1 : 1) (50 c.c.), 8 mg., m. p. 242—245°.

Fractions (1—3) were recrystallised from chloroform–methanol to give 29-*bromolup*-20(29)-*en*-3β-*yl acetate* (VII) as needles, m. p. 196—198°, $[\alpha]_D$ +30° (*c* 1·32) (Found: C, 70·0; H, 9·0; Br, 14·9. $C_{32}H_{51}BrO_2$ requires C, 70·2; H, 9·3; Br, 14·6%).

Fractions (9—11) were combined and adsorbed from light petroleum (50 c.c.) on alumina (30 g.). The product obtained by elution with light petroleum–benzene (1 : 1) crystallised from chloroform–methanol as plates (48 mg.), m. p. 250—252°, $[\alpha]_D$ −46° (*c* 1·23) (Found: C, 54·7; H, 7·2; Br, 32·0. Calc. for $C_{32}H_{51}Br_3O_2$: C, 54·3; H, 7·2; Br, 33·9%). This material was shown to be inhomogeneous (see later).

Additional quantities of 29-bromolup-20(29)-en-3β-yl acetate (250 mg.), m. p. 194—198°, and the tribromo-product (11 mg.), m. p. 250—252°, were obtained by further chromatography of the middle fractions.

(*b*) Lupenyl acetate (1·0 g.) in ether (50 c.c.) at −78° was treated with bromine (0·375 g., 1·1 mol.) in ether (50 c.c.) during 45 min. The light yellow mixture was then kept overnight at 20°. The solvent was removed and the residue was thrice crystallised from chloroform–methanol, to give 30-*bromolup*-20(29)-*en*-3β-*yl acetate* (X) as prisms (510 mg.), m. p. 235—236°, $[\alpha]_D$ +11° (*c* 1·34) (Found: C, 70·6; H, 9·2; Br, 14·35. $C_{32}H_{51}BrO_2$ requires C, 70·2; H, 9·3; Br, 14·6%).

The material (400 mg.) recovered from the mother liquors was adsorbed from light petroleum (75 c.c.) on alumina (50 g.). The fractions (128 mg.) obtained by elution with light petroleum (450 c.c.) had m. p. 192—195°. They crystallised from chloroform–methanol to give 29-bromolup-20(29)-en-3β-yl acetate (VII) as needles, m. p. and mixed m. p. 196—198°, $[\alpha]_D$ +30° (*c* 1·23).

(*c*) Lupenyl acetate (0·5 g.) in propylene oxide (100 c.c.) at −30° was treated with bromine (0·18 g., 1·05 mol.) in acetic acid (5 c.c.) during 30 min. The mixture was kept in the dark at 20° overnight, then diluted with water, and the precipitated solid was extracted with ether. The extract afforded 29-bromolup-20(29)-en-3β-yl acetate (VII) as needles (from chloroform–methanol) (280 mg.), m. p. and mixed m. p. 195—196°, $[\alpha]_D$ +30° (*c* 1·2).

Attempted Isomerisation of 29-*Bromolup*-20(29)-*en*-3β-*yl Acetate* (VII).—The acetate (0·5 g.), m. p. 196—198°, in chloroform (2 c.c.) was treated with hydrobromic acid (0·3 c.c.; 50% w/v in acetic acid) in acetic acid (5 c.c.) at 20° for 24 hr. The product (0·46 g.) was isolated in the usual manner. After two crystallisations from chloroform–methanol it afforded starting material, m. p. and mixed m. p. 193—195°, $[\alpha]_D$ +31° (*c* 1·2).

Reduction of 29-*Bromolup*-20(29)-*en*-3β-*yl Acetate* (VII) *with Sodium and Isopropyl Alcohol.*—Sodium (7 g.) was added in small pieces during 3 hr. to a boiling solution of the acetate (0·25 g.) in isopropyl alcohol (50 c.c.). After destruction of the excess of sodium with ethanol and dilution with water, extraction with chloroform afforded a product which was crystallised from chloroform–methanol to give lupeol (I) as needles, m. p. and mixed m. p. 211—213°, $[\alpha]_D$ +29° (*c* 1·1).

Hydrogenation of 29-*Bromolup*-20(29)-*en*-3β-*yl Acetate* (VII).—The acetate (0·29 g.) in ethanol (75 c.c.) was hydrogenated in the presence of Adams catalyst (110 mg.) for 11 hr. After removal of the catalyst, concentration of the solution afforded lupanyl acetate (0·21 g.), m. p. and mixed m. p. 241—242°, $[\alpha]_D$ +1° (*c* 1·8).

Ozonolysis of 29-*Bromolup*-20(29)-*en*-3β-*yl Acetate* (VII).—The acetate (130 mg.) in ethyl acetate (50 c.c.) at −78° was treated with ozonised oxygen (6%) until the solution became faintly blue (25 min.). Nitrogen was then bubbled through the solution and the mixture then washed twice with water. The solvent was removed and the residue was heated with water (150 c.c.) for 1·5 hr. The product (83 mg.) was adsorbed from light petroleum on alumina (20 g.). Elution with light petroleum afforded 3β-acetoxy-30-norlupan-20-one (XII) as plates (49 mg.) (from chloroform–methanol), m. p. and mixed m. p. 260—262°.

29-*Bromolup*-20(29)-*en*-3β-*ol* (VI).—The corresponding acetate (1·0 g.) was dissolved in benzene (80 c.c.) and ether (80 c.c.). Powdered lithium aluminium hydride (500 mg.) was added with shaking and the mixture heated under reflux for 30 min. The product crystallised from light petroleum and then from methanol, affording 29-*bromolup*-20(29)-*en*-3β-*ol* (VI) as needles (820 mg.), m. p. 180—182°, $[\alpha]_D$ +18° (*c* 1·42) (Found: C, 71·6; H, 9·7. $C_{30}H_{49}BrO$ requires C, 71·3; H, 9·7%).

Hydrolysis of the acetate (1 g.) with boiling 3% ethanolic potassium hydroxide (60 c.c.) for 40 min. afforded the same alcohol, m. p. 180—182°, $[\alpha]_D$ +34° (*c* 0·9) (Found: C, 71·35; H, 9·8%).

The alcohol (230 mg.) was treated with benzoyl chloride (3 c.c.) and pyridine (5 c.c.) at 100° for 1 hr., to give 29-*bromo*-20(29)-*en*-3β-*yl benzoate* (VIII) as plates (from methanol–chloroform), m. p. 234—236°, $[\alpha]_D$ +54° (*c* 1·75) (Found: C, 73·0; H, 8·75; Br, 12·95. $C_{37}H_{53}BrO_2$ requires C, 72·75; H, 8·7; Br, 13·15%).

Isomerisation of 30-*Bromolup*-20(29)-*en*-3β-*yl Acetate* (X).—The acetate (200 mg.) in chloroform–acetic acid (1 : 1; 10 c.c.) was treated with hydrobromic acid (1 c.c.; 50% w/v in acetic acid) for 24 hr. The product (190 mg.) was adsorbed from light petroleum (25 c.c.) on alumina (20 g.) and eluted with light petroleum. The fraction (110 mg.) obtained with the first 50 c.c. of eluent had m. p. 187—192°. It crystallised from ethanol, to give 29-bromolup-20(29)-en-3β-yl acetate as needles, m. p. and mixed m. p. 196—198°, $[\alpha]_D$ +30° (*c* 1·2). More of the 29-bromo-derivative (40 mg.) was obtained from later fractions from the chromatogram.

Reduction of 30-*Bromolup*-20(29)-*en*-3β-*yl Acetate* (X) *with Sodium and Isopropyl Alcohol.*—To a boiling solution of the acetate (1 g.) in isopropyl alcohol (200 c.c.) were added small pieces of sodium (22—23 g.) in 4 hr. The excess of sodium was destroyed with ethanol, and the solution was diluted with water. Extraction with chloroform afforded a product which was purified by percolation through alumina (50 g.) in light petroleum to give lupeol (560 mg.) as needles, m. p. and mixed m. p. 208—212°. Acetylation afforded lupenyl acetate, m. p. and mixed m. p. 215—217°.

Hydrogenation of 30-*Bromolup*-20(29)-*en*-3β-*yl Acetate* (X).—The acetate (247 mg.) in ethanol (150 c.c.) was completely hydrogenated in 4 hr. in the presence of Adams catalyst (100 mg.). After the catalyst had been removed the solution was concentrated to afford lupanyl acetate (172 mg.), m. p. and mixed m. p. 239—241°, $[\alpha]_D$ +3° (*c* 1·40) (Found: C, 81·3; H, 11·2. Calc. for $C_{32}H_{52}O_2$: C, 81·7; H, 11·5%).

Ozonolysis of 30-*Bromolup*-20(29)-*en*-3β-*yl Acetate.*—The acetate (182 mg.) in ethyl acetate (75 c.c.) was treated with ozonised oxygen (6%) until the solution became slightly bluish (16 min.). The mixture was treated with zinc and acetic acid and then steam distilled until 350 c.c. of distillate had been collected. The distillate afforded formaldehyde dimethone (24 mg., 25%), m. p. and mixed m. p. 189°. The ketone remaining after distillation was isolated, purified by chromatography on alumina, and crystallised from chloroform–methanol, to give 3β-acetoxy-30-norlupan-20-one (XII) as plates, m. p. and mixed m. p. 260—262°.

In a second experiment the acetate (320 mg.) in ethyl acetate (75 c.c.) was ozonised. The excess of ozone was then expelled with nitrogen. The solvent was removed and the residue

heated with water (150 c.c.) for 1·5 hr., giving a product (234 mg.) that was adsorbed from light petroleum on alumina (30 g.). The fractions obtained by elution with light petroleum–benzene (9 : 1) crystallised from ethanol, to give 3β-*acetoxy*-29-*bromo*-30-*norlupan*-20-*one* (XIII) as plates, m. p. 207—210° (Found: C, 67·5; H, 8·6. $C_{31}H_{49}BrO_3$ requires C, 67·75; H, 8·9%).

30-*Bromolup*-20(29)-*en*-3β-*yl Benzoate* (XI).—30-Bromolup-20(29)-en-3β-yl acetate (X) (1·30 g.) was dissolved in ether (700 c.c.); powdered lithium aluminium hydride (900 mg.) was added with shaking and then the mixture was boiled under reflux for 30 min. The product afforded 30-bromolup-20(29)-en-3β-ol (IX) as needles (from ethanol) (910 mg.), m. p. 188—189°, $[\alpha]_D$ +2° (*c* 1·2). The alcohol (280 mg.) was treated with benzoyl chloride (2 c.c.) and pyridine (3 c.c.) at 100° for 3 hr. to give 30-*bromolup*-20(29)-*en*-3β-*yl benzoate* as plates (from chloroform–methanol), m. p. 251—252°, $[\alpha]_D$ +56° (*c* 1·2) (Found: C, 72·3; H, 8·7; Br, 12·9. $C_{37}H_{53}BrO_2$ requires C, 72·75; H, 8·7; Br, 13·15%).

Bromination of Lupenyl Benzoate in Propylene Oxide.—Lupenyl benzoate (500 mg.) in propylene oxide (75 c.c.) was treated with bromine (0·18 g., 1·05 mol.) in acetic acid (5 c.c.) during 15 min. The mixture was kept for 15 min. and then diluted with water. The precipitate (400 mg.) was collected, washed, and dried. It was adsorbed from light petroleum (75 c.c.) on alumina (50 g.). Elution with light petroleum afforded 29-bromolup-20(29)-en-3β-yl benzoate (VIII) as plates (190 mg.) (from chloroform–methanol), m. p. and mixed m. p. 234—236°; $[\alpha]_D$ +54°.

Bromination of Lupenyl Benzoate in Ether.—The benzoate (590 mg.) in ether (150 c.c.) was treated with bromine (1·2 mol.) in ether (50 c.c.) during 25 min. The solution was kept for 8 hr. at 20°. Removal of the ether by distillation afforded a product which crystallised from chloroform–methanol to give 30-bromolup-20(29)-en-3β-yl benzoate (XI) as plates, m. p. and mixed m. p. 249—250°, $[\alpha]_D$ +54° (*c* 1·25).

Reduction of the Bromination Product, m. p. 250—252°.—Sodium (*ca.* 8 g.) in small pieces was added gradually during 2 hr. to a boiling solution of the bromination product, m. p. 250—252° (300 mg.), in isopropyl alcohol (60 c.c.). The reduction product (150 mg.), m. p. 165—190°, with pyridine and acetic anhydride at 100° gave a product (90 mg.), m. p. 244—246°, $[\alpha]_D$ +44° (*c* 0·8). This (70 mg.) was adsorbed from light petroleum (b. p. 38°) on alumina (70 g.) and eluted with light petroleum. The first fraction (23 mg.) had m. p. 275—278°. Recrystallisation from chloroform–methanol gave 18α-oleanan-3β-yl acetate (XVII) as plates, m. p. and mixed m. p. 280—282°. The last fraction (fourth) gave crystals (8 mg.), m. p. 229—232°, $[\alpha]_D$ +29° (*c* 0·9). The acetate (XVII) most likely arises from 19α,29,29(or 30,30)-tribromo-18α-oleanan-3β-yl acetate.

Action of Hydrobromic Acid on 29-*Bromolup*-20(29)-*en*-3β-*yl Acetate* (VII).—The acetate (1 g.) in acetic acid (75 c.c.) was treated with hydrobromic acid (50% w/v in acetic acid) (20 c.c.) at 20° and the solution was kept in the dark for 48 hr. Dilution of the reaction mixture with water (500 c.c.) gave a precipitate (0·86 g.) which was collected and washed with water. Crystallisation from ethanol and from chloroform–ethanol gave 19α,29(or 30)-*dibromo*-18α-*oleanan*-3β-*yl acetate* (IV) as plates (100 mg.), m. p. 235—236°, $[\alpha]_D$ −4° (*c* 1·0) (Found: C, 60·9; H, 8·3; Br, 23·5. $C_{32}H_{52}Br_2O_2$ requires C, 61·15; H, 8·3; Br, 25·5%). The mother liquors yielded starting material (250 mg.).

Reduction of 19α,29(*or* 30)-*Dibromo*-18α-*oleanan*-3β-*yl Acetate* (IV) *with Sodium and Isopropyl Alcohol.*—Sodium (*ca.* 6 g.) was added in small pieces during 2 hr. to a boiling solution of the acetate (230 mg.) in isopropyl alcohol (30 c.c.). The product (150 mg.) was treated at 100° for 2 hr. with pyridine and acetic anhydride, and the acetate adsorbed from light petroleum on alumina (20 g.). Elution with light petroleum (500 c.c.) yielded 18α-oleanan-3β-yl acetate (XVII) as plates (30 mg.) (from chloroform–methanol), m. p. and mixed m. p. 278—282°, $[\alpha]_D$ +39° (Found: C, 81·5; H, 11·55. Calc. for $C_{32}H_{54}O_2$: C, 81·65; H, 11·6%).

Action of Acetic Anhydride on 29-*Bromolup*-20(29)-*en*-3β-*yl Acetate.*—The acetate (1·0 g.) in acetic anhydride (25 c.c.) was heated under reflux for 22 hr. The anhydride was distilled off and the residue macerated with ice to decompose any anhydride. The product (0·98 g.) was purified by percolation through alumina. The resulting solid crystallised from chloroform–methanol to give starting material as needles (0·81 g.), m. p. and mixed m. p. 193—195°, $[\alpha]_D$ +30° (*c* 1·2).

Action of Silver Acetate on 19α,29(*or* 30)-*Dibromo*-18α-*oleanan*-3β-*yl Acetate* (IV).—The acetate (450 mg.) in ethanol (50 c.c.) was heated under reflux with silver acetate (800 mg.) for 20 hr. During this period the suspended solid became dark and a silver mirror formed on the surface

of the flask. Dilution with water and extraction with ether afforded a product which was heated with acetic anhydride (10 c.c.) for 30 min. The solution was poured into water and extracted with ether. The product crystallised from chloroform–methanol to give 29-bromolup-20(29)-en-3β-yl acetate (VII) as needles (230 mg.), m. p. and mixed m. p. 195—196°, $[\alpha]_D$ +30° (*c* 1·2).

Constants of bromination products.

Product	M. p.	$[\alpha]_D$	Ref.
" Monobromolupeol "	185°	+4°	1, 2
" Monobromolupeol "	183	—	3
" Monobromolupeol "	196—197	—	6
29-Bromolup-20(29)-en-3β-ol (VI)	180—182	+18(24)	This paper
30-Bromolup-20(29)-en-3β-ol (IX)	188—189	+2	This paper
" Monobromolupenyl acetate "	232	—	3
" Monobromolupenyl acetate "	197—205	—	6
29-Bromolup-20(29)-en-3β-yl acetate (VII)	196—198	+30	This paper
30-Bromolup-20(29)-en-3β-yl acetate (X)	235—236	+11	This paper
" Monobromolupenyl benzoate "	243	+45	1, 2
" Monobromolupenyl benzoate "	—	—	1, 2
29-Bromolup-20(29)-en-3β-yl benzoate (VIII)	234—236	+54	This paper
30-Bromo-20(29)-en-3β-yl benzoate (XI)	251—252	+56	This paper
" Lupeol dibromide "	205—206	+25	4
" Lupeol dibromide "	186—189	—	5
" Lupenyl acetate dibromide "	225	—	5
" Lupenyl acetate dibromide "	225	—	6
19α,29(or 30)-Dibromo-18α-oleanan-3β-yl acetate	235—236	−4	This paper

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