Lichens and Fungi. Part VIII.[1] 18α-Oleanane

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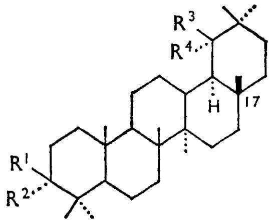
18α-Oleanane has been synthesized from lupeol. The methyl resonances in the ^{1}H n.m.r. spectrum of this compound and of its 3β-hydroxy- and 3-oxo-derivatives have been assigned.

ALTHOUGH derivatives of 18α-oleanane are known,[2] the parent hydrocarbon (5) has not been reported. Recently it became necessary to synthesize 18α-oleanane to compare its physical and spectral characteristics with those of a hydrocarbon obtained in the course of degradation experiments on certain lichen triterpenoids in progress in this department.

3β-Acetoxy-19α-chloro-18α-oleanane (1), which is readily available from lupeol,[3] was smoothly converted by the series of standard steps outlined in the Scheme into 18α-oleanane (5), m.p. 210°, $[\alpha]_D^{20}$ +40·3°.



(1) $R^2 = R^3 = H, R^1 = OAc, R^4 = Cl$
(2) $R^2 = R^3 = R^4 = H, R^1 = OAc$
(3) $R^2 = R^3 = R^4 = H, R^1 = OH$
(4) $R^3 = R^4 = H, R^1R^2 = O$
(5) $R^1 = R^2 = R^3 = R^4 = H$

SCHEME

$$(1) \xrightarrow{(i)} (2) \xrightarrow{(ii)} (3) \xrightarrow{(iii)} (4) \xrightarrow{(iv)} (5)$$

Reagents: (i) H_2–Raney Ni; (ii) $LiAlH_4$; (iii) CrO_3; (iv) Wolff-Kishner.

The methyl resonances in the ^{1}H n.m.r. spectrum of 18α-oleanane have been assigned in the following way. Since the configuration of rings A, B, C, and D of 18α-oleanane is the same as that of lupane, the chemical shifts of methyl groups associated with rings A, B, and C in the two classes of triterpenes should be almost identical and should be subject to similar substituent effects. Methyl-group assignments have been made for lupane by Lehn *et al.*[4] but the 4β-, 4α-, and 10β-methyl signals were not distinguished. More recently Cheung and Williamson,[5] from a study of methyl lupan-28-oate and its derivatives, have published a table of substituent increments which make the complete assignment of the methyl resonances in these compounds possible. No additional assignments of methyl signals of the parent lupane were made. The assignment of the 4β-, 4α-, and 10β-methyl resonances for lupane made in the table are based on the substituent effects of a 3β-hydroxy-group [5] while the 8β-, 14α-, and 17α-methyl assignments are those already proposed.

There is an almost exact correlation between the 4β-, 4α-, 10β-, and 8β-methyl signals of 18α-oleanane and its 3-substituted derivatives and the corresponding lupanes (Table). Signals at 0·94, 0·76, 0·92, and 0·88 p.p.m. remain to be assigned to the 14α-, 17β-, 20β-, and 20α-methyl groups. The 14α-methyl signal should resonate at a similar position in both 18α-oleanane and lupane, and should be little effected by substituents in rings A or E. It appears at 0·94 p.p.m. in lupane and derivatives and the signal at 0·94 p.p.m. in the spectra of 18α-oleanane and its derivatives is assigned to the 14α-methyl group. The signal at highest field in the spectra of lupane and its derivatives (*ca.* 0·76 p.p.m.) is assigned to the 17β-methyl group. This methyl group in lupane is most shielded, being at the *trans* junction of five- and six-membered rings. There is no such shielding of the 17β-methyl group in 18α-oleanane. In this molecule the 17β-methyl group is in a similar stereochemical environment to the 10β-methyl group in cholestane which resonates at 0·78 p.p.m.[6] A peak at 0·76 p.p.m., which is also present in the 3β-hydroxy-(3) and 3-oxo- (4) compounds is assigned to the 17β-methyl group. Of the two methyl signals remaining, that at higher field is attributed to the axial 20α-methyl group. The axial methyl group of the 4,4-dimethyl pair in a triterpene

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[1] Part VII, R. E. Corbett and Susan D. Cumming, *J. Chem. Soc. (C)*, 1971, 955.

[2] O. Wintersteiner, G. Krakower, and M. Moore, *J. Org. Chem.*, 1965, **30**, 2847.

[3] T. G. Halsall and E. R. H. Jones, *J. Chem. Soc.*, 1952, 2862.

[4] J. M. Lehn and G. Ourisson, *Bull. Soc. Chem., France*, 1962, 1137.

[5] H. T. Cheung and D. G. Williamson, *Tetrahedron*, 1969, **25**, 119.

[6] N. S. Bhacca and D. H. Williams, 'Applications of N.M.R. Spectroscopy in Organic Chemistry,' Holden-Day, New York, 1964, p. 7.

normally resonates at higher field, and in this case the anisotropic effects of the C-18(19) and C-21(22) bonds should lead to a similar effect.

Chemical shifts (δ) of methyl groups expressed as p.p.m. from tetramethylsilane

Compound	4α	4β	10β	8β	14α	17β	20β	20α
Lupane	0·84	0·81	0·84	1·04	0·94	0·76		
18α-Oleanane	0·84	0·81	0·87	1·03	0·94	0·76	0·92	0·88
Lupan-3β-ol	0·97	0·77	0·84	1·05	0·94	0·79		
18α-Oleanan-3β-ol	0·98	0·77	0·84	1·08	0·97	0·76	0·93	0·87
Lupan-3-one	1·08	1·04	0·96	1·08	0·96	0·79		
18α-Oleanan-3-one	1·10	1·08	1·03	1·08	0·96	0·76	0·95	0·87

EXPERIMENTAL

Experimental procedures are as described in Part VI.[7]

18α-*Oleanan*-3-*one* (4).—18α-Oleanan-3β-ol[3] (0·21 g) in acetone (80 ml) was oxidised at room temperature with Jones reagent (2·5 ml), added dropwise from a microburette until a persistent orange colour was obtained. The reaction mixture was then worked up and the product was applied to a silica-gel plate (1·25 mm × 0·5 m × 20 cm) and subjected to the multiple-run procedure (×4) in hexane–ether (9 : 1). Elution of the product from the dissected plate with ether gave 18α-*oleanan*-3-*one* (0·15 g). It had m.p. 243° after crystallisation from chloroform–methanol; $[\alpha]_D^{20}$ +32·5° (*c* 0·3 in $CHCl_3$); $\nu_{max.}$ 1695 (C=O) cm^{-1} (Found: C, 84·3; H, 11·8. $C_{30}H_{50}O$ requires C, 84·5; H, 11·8%).

18α-*Oleanane* (5).—18α-Oleanan-3-one (85 mg) in freshly redistilled diethylene glycol (20 ml) was treated with 99—100% w/w hydrazine hydrate (1·5 ml) and concentrated hydrochloric acid (0·12 ml). The reaction mixture was heated under reflux for 3 h at 120°. Potassium hydroxide pellets (0·68 g) were then added and the mixture was heated under reflux for a further 1 h. The temperature was then raised to 210° by distilling off some of the hydrazine and the reaction mixture was heated under reflux for a further 12 h. The solution was cooled, neutralised with 2N-HCl, and worked up. The product (85 mg) was adsorbed from hexane on to alumina (15 g); elution with hexane gave 18α-*oleanane* (80 mg), which after crystallisation from hexane–ethanol had m.p. 208°, raised after sublimation at 10^{-3} mm/Hg to 210°; $[\alpha]_D^{20}$ +40·3 (*c* 0·5 in $CHCl_3$) (Found: C, 87·5; H, 12·3. $C_{30}H_{52}$ requires C, 87·4; H, 12·6%).

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