Structures of Eight New Triterpenoids and Isolation of Other Triterpenoids and Epi-ikshusterol from the Stems of *Lithocarpus cornea*

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Eight new triterpenoids from the light petroleum extract of the stems of *Lithocarpus cornea* (Lour.) Rhed. have been proved to be taraxer-14-ene-3β,29-diol (VIII) and its diacetate (VII), 29-hydroxytaraxer-14-en-3-one (X) and its acetate (IX), 14α-hydroxytaraxeran-3-one (XXIX), taraxerane-3β,14α-diol (XXX), 22-hydroxy-21α*H*-hopan-3-one (XXIII), and lup-20(29)-ene-3β,27-diol (XXXII). Other triterpenoids isolated from the same extract, besides those already reported [1] were lupeol, betulin, and myricadiol (I). The steroid epi-ikshusterol (stigmast-5-ene-3β,7β-diol) (XXXVII) was also obtained.

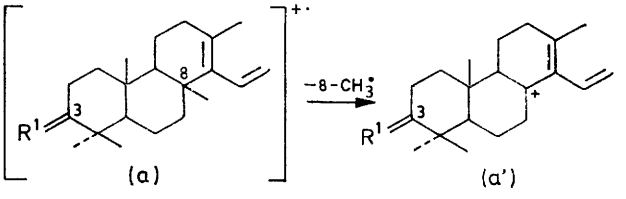
THE light petroleum extract from the stems of *Lithocarpus cornea* (Fagaceae) has been found to contain friedelin, taraxerone, friedelan-3β-ol, taraxerol, sitosterol, and three new pentacyclic triterpenoids designated A_1, A_2, and A_3.[1] On repeating the same investigation on a bigger scale, five more new triterpenoids and small quantities of lupeol, betulin, myricadiol (I),[2] and epi-ikshusterol (stigmas-5-ene-3β,7β-diol) (XXXVII) have been isolated. Compound (XXXVII) has been reported previously only once.[3] This paper describes the determination of the structures of the eight new triterpenoids. They all gave a positive Liebermann-Burchardt reaction.

The least polar of the eight new compounds isolated from column chromatography of the extract was the diacetate (VII), $C_{34}H_{54}O_4$. Its i.r. spectrum showed the presence of two OAc groups and a trisubstituted double bond, also indicated by n.m.r. signals at δ 2.05 (3H,s), 2.09 (3H,s), and 5.55 (1H, q). One of the OAc groups was shown to be primary by a signal at δ 3.80 (2H,s), also indicative of the CH_2OAc group being in a non-hindered equatorial [4] position attached to a tertiary carbon atom. The other was proved to be secondary, equatorial, and in the environment $CH_2{\cdot}CH{\cdot}OH$ by a signal at δ 4.47 (1H, q, $J_{ax,eq}$ 7 and $J_{ax,ax}$ 10 Hz). Compound (VII) was identical with the acetylation product of the diol A_3[1] (VIII), $C_{30}H_{50}O_2$.

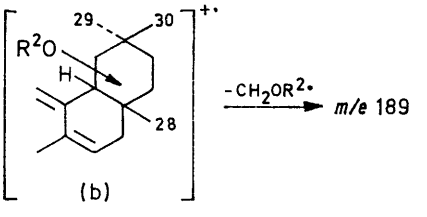
The next to least polar new compound (IX), $C_{32}H_{50}O_3$, showed in its i.r. spectrum the presence of one OAc group, one carbonyl function, and a trisubstituted double bond. Its n.m.r. spectrum indicated a non-hindered equatorial [4] $CH_2{\cdot}OAc$ group attached to a tertiary carbon atom [δ 3.78 (2H,s) and 2.06 (3H,s)], a CH_2–C=O function [δ 2.40 (2H, m)], and an olefinic proton (δ 5.62). Compound (IX) was identical with the acetate of the ketol A_2[1] (X), $C_{30}H_{48}O_2$. The n.m.r. spectrum of (X) revealed a CH_2C=O function [δ 2.40 (2H, m)], an olefinic proton (δ 5.57), and a non-hindered equatorial CH_2OH group attached to a tertiary carbon atom [δ 1.62 (1H, s, D_2O exchangeable) and 3.30 (2H, s)].[4]

Compounds (VII)—(X) each gave a yellow colour with tetranitromethane. Comparison of their molecular formulae and spectroscopic properties, indicated that they were all probably inter-related. Indeed reduction of compound (X) with borohydride gave the diol (VIII).

The presence of a $CH_2{\cdot}OH$ (or $CH_2{\cdot}OAc$) group together with seven tertiary Me groups as revealed in the n.m.r. spectrum of each of compounds (VII), (IX), and (X) suggested an oleanane or rearranged oleanane skeleton. The signal due to the olefinic proton in each of compounds (VII), (IX), and (X) [(VIII) was too insoluble in $CDCl_3$ for its n.m.r. spectrum to be determined] appeared as a well-defined quartet (J 4 and 7 Hz), which indicated two vicinal methylene but no allylic protons. This fitted well with a C-14 double bond, as in taraxer-14-ene derivatives. Taraxeryl acetate (II), taraxerone (III), epitaraxerol [5] (IV), and myricadiol diacetate (V) give similar quartets at δ 5.62, 5.62, 5.53, and 5.47, respectively. One of the oxygen functions was likely to be at the usual C-3 position, and this was proved by tosylation of the ketol (X) to give a keto-tosylate (XI), reduction



(IX),(X) R^1 = O *m/e* 300 *m/e* 285
(I),(VIII) R^1 = α-H, β-OH, *m/e* 302 *m/e* 287
(V),(VII) R^1 = α-H, β-OAc, *m/e* 344 *m/e* 329



(I), (VIII),(X) R^2 = H, *m/e* 220
(V), (VII),(IX) R^2 = Ac, *m/e* 262

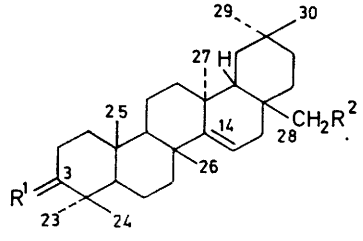
of which with lithium aluminium hydride yielded taraxerol (VI).

The mass spectra of compounds (VII)—(X) confirmed the above by the presence of the species (a) and (a');

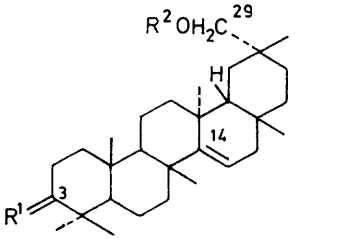
[1] W. H. Hui, P. D. S. Ko, Y. C. Lee, M. M. Li, and H. R. Arthur, *Phytochemistry*, 1975, **14**, 1063.
[2] A. A. Ryabinin and L. G. Matyukhina, *Doklady Akad. Nauk. S.S.S.R.*, 1959, **129**, 125.
[3] S. S. Deshmane and S. Dev, *Tetrahedron*, 1971, **27**, 1109.
[4] A. Gaudemer, M. J. Polonsky, and E. Wenkert, *Bull. Soc. chim. France*, 1964, 407.
[5] W. H. Hui and M. L. Sung, *Austral. J. Chem.*, 1968, **21**, 2137.

the second oxygen function appeared in species (b), which contained rings D and E. As the fragmentations of (VII) were similar to those of (V) with only slight differences in intensities,[6] but the two compounds were not identical, the second oxygen function must be at either C-29 or C-30. Since the n.m.r. spectra showed relatively high field methylene proton signals for the CH_2OR^2 group [R^2=Ac for (VII) and (IX), and H for (X)] the equatorial C-29 position was favoured.[4] Hence the structures of compounds (VII)—(X) were deduced.

The double bonds in taraxer-14-ene derivatives can be isomerized readily under mild acidic conditions to give the corresponding olean-12-enes. Thus, as expected, treatment of compound (VII) with hydrochloric acid–



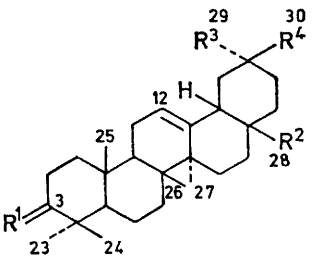
(I) R^1=α-H,β-OH,R^2= OH
(II) R^1=α-H,β-OAc,R^2=H
(III) R^1=O,R^2=H
(IV) R^1=α-OH,β-H, R^2=H
(V) R^1=α-H,β-OAc,R^2=OAc
(VI) R^1=α-H,β-OH, R^2=H



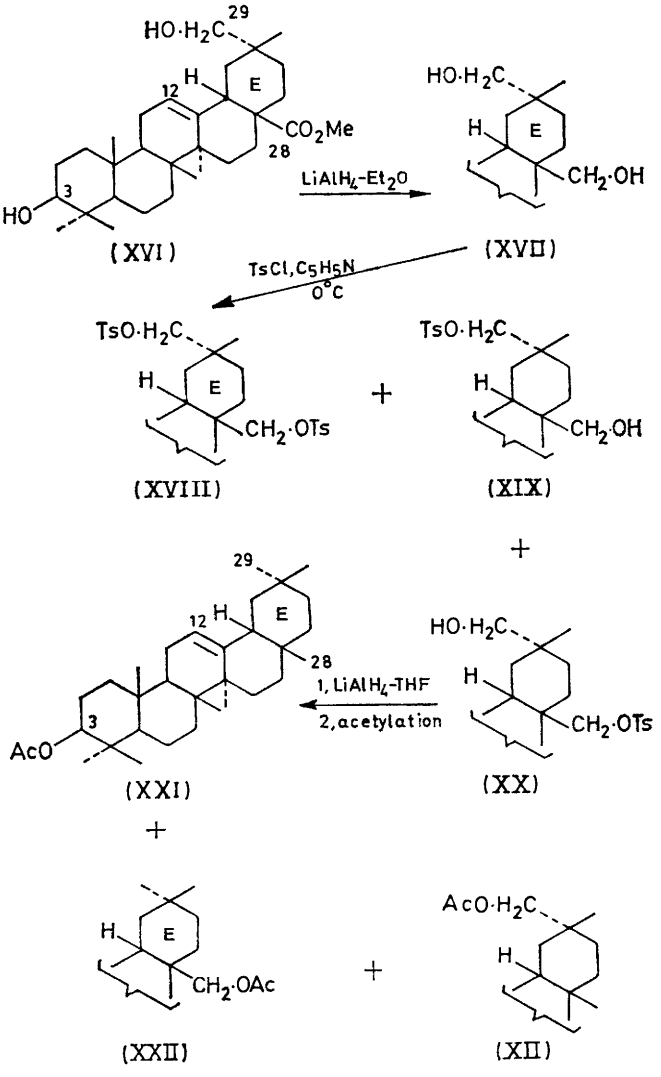
(VII) R^1=α-H,β-OAc,R^2=Ac
(VIII) R^1=α-H,β-OH, R^2=H
(IX) R^1=O,R^2=Ac
(X) R^1=O,R^2=H
(XI) R^1=O,R^2=Ts

acetic acid gave the diacetate (XII), $C_{34}H_{54}O_4$, δ 4.50 (1H, q, *J* 7 and 10 Hz, axial C*H*OAc), 3.73 (2H, s, equatorial CH_2OAc group [4]), and 5.22 (1H, q, *J* 3 and 4 Hz, olefinic proton of the olean-12-ene type [7]). Compound (XII) is not identical with olean-12-ene-3β,30-diol diacetate (XIII),[8] the n.m.r. spectrum of which showed a two-proton singlet at δ 4.02[9] (axial CH_2·OAc), although its mass spectrum [6] was very similar to that of (XII), with the base peak at *m/e* 276 and abundant fragments at *m/e* 249, 216, 203, and 189. Compound (XII) is thus the corresponding 3β,29-diol diacetate, which has not been reported previously.

Like compounds (VII), (IX), and (XII), methyl mesembryanthemoidigenate diacetate (methyl 3β,29-diacetoxyolean-12-en-28-oate) (XIV) gives a two-proton singlet at δ 3.80.[10] The structure of (XII) was finally confirmed by partial synthesis from methyl mesembryanthemoidigenate (XVI),[11] which was first reduced with



(XII) R^1=α-H,β-OAc, R^2=R^4=Me, R^3=CH_2·OAc
(XIII) R^1=α-H,β-OAc, R^2=R^3=Me, R^4=CH_2·OAc
(XIV) R^1=α-H,β-OAc, R^2=CO_2Me,R^3=CH_2·OAc,R^4=Me
(XV) R^1=O, R^2=R^3=R^4=Me



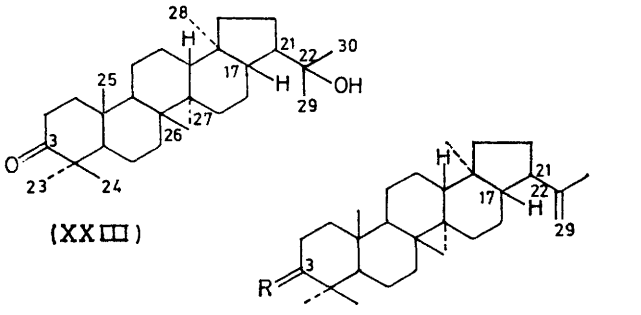
Scheme

lithium aluminium hydride to give the triol (XVII). Controlled tosylation of (XVII) gave a mixture of tosy-

[6] H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 3688.
[7] T. Kikuchi, M. Takayama, T. Toyoda, M. Arimoto, and M. Niwa, *Chem. and Pharm. Bull. (Japan)*, 1973, **21**, 2243.
[8] C. Djerassi, J. A. Henry, A. J. Lemin, and T. Rios, *Chem. and Ind.*, 1955, 1520.
[9] R. G. Wilson and D. H. Williams, *Tetrahedron*, 1969, **25**, 155.
[10] B. Tursch, J. Leclercq, and G. Chiurdogiu, *Tetrahedron Letters*, 1965, 4161.
[11] W. H. Hui and C. T. Ho, *Austral. J. Chem.*, 1968, **21**, 547.

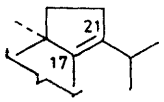
lates (XVIII)—(XX), which on reduction ($LiAlH_4$) followed by acetylation yielded a mixture of acetates. Chromatography of this mixture gave β-amyrenyl acetate (XXI), then erythrodiol diacetate (XXII), and finally olean-12-ene-3β,29-diol diacetate, $C_{34}H_{54}O_4$, identical with (XII) (see Scheme). The proposed structures of compounds (VII)—(X) are thus confirmed.

The fifth new compound (XXIII), $C_{30}H_{50}O_2$, which was more polar than sitosterol, gave a negative result in the tetranitromethane test. Its i.r. spectrum showed OH and C=O functions, but no C=C absorption. A CH_2·C=O function was indicated in its n.m.r. spectrum [δ 2.40 (2 H, m)]. There was no proton signal at $\delta > 3.0$, indicating the absence of olefinic protons and the tertiary nature of the OH group, which was also proved by the resistance of compound (XXIII) to oxidation with Jones reagent. Eight tertiary Me singlets, two of which occurred at δ 1.20, showed the presence of a pentacyclic molecule, probably belonging to the hopane series, containing a CMe_2OH group. This was also supported by strong peaks at *m/e* 384 ($M^+ - Me_2CO$), 207, 189, 149, and 59 in the mass spectrum, characteristic of 22-hydroxyhopane derivatives.[12] The spectra of (XXIII) and hydroxyhopanone (XXV) differ only in the intensities of the peaks.

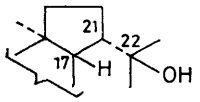


(XXIII)

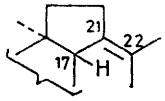
(XXVII) R = O
(XXVIII) R = α-H,β-OH



(XXIV)



(XXV)



(XXVI)

Attempted acetylation of compound (XXIII) with acetic anhydride–pyridine in the cold was unsuccessful; on boiling, a dehydration product, $C_{30}H_{48}O$, identical with hop-17(21)-en-3-one (XXIV)[13] was obtained. This is again characteristic of 22-hydroxyhopane derivatives.[14] Hence (XXIII) is 22-hydroxy-17ξ*H*,21ξ*H*-hopan-3-one. To determine the stereochemistry at C-17 and C-21, dehydration of (XXIII) was carried out under non-acidic conditions, with phosphoryl chloride in an excess of pyridine.[15] The product was a mixture, which on chromatography ($AgNO_3$–SiO_2) gave hopenone a [hop-21(22)-en-3-one] (XXVI)[15] and moretenone [21α*H*-hop-22(29)-en-3-one] (XXVII),[16] the latter being the more polar and minor product. Hence the configurations of (XXIII) at C-17 and C-21 must be the same as those of (XXVII), and (XXIII) is therefore 22-hydroxy-21α*H*-hopan-3-one.

Finally compound (XXIII) was partially synthesized from (XXVII) by oxymercuriation followed by reduction with sodium borohydride. The product (XXIII) was obtained in low yield, together with a large amount of unchanged (XXVII) and a small quantity of moretenol (XXVIII), formed from the latter during reduction of the intermediate.

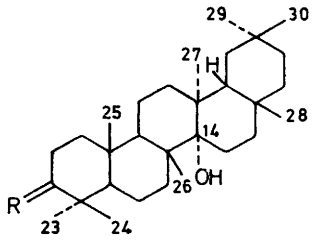
The sixth new compound isolated, A_1[1] (XXIX), $C_{30}H_{50}O_2$, was a ketol which gave no colour with tetranitromethane. Its n.m.r. spectrum indicated a CH_2CO function [δ 2.40 (2 H, m)]. The presence of a tertiary OH group and the absence of olefinic protons were shown by the absence of proton signals at $\delta > 3.0$. Reduction with borohydride, gave a diol, $C_{30}H_{52}O_2$, identical with the seventh new compound (XXX). The n.m.r. spectrum of (XXX) revealed a signal at δ 3.26 (1H, q, $J_{ax,eq}$ 7, $J_{ax,ax}$ 9 Hz) showing the presence of an equatorial OH group, in the environment CH_2·C*H*·OH. Both (XXIX) and (XXX) showed eight tertiary methyl proton absorptions, indicating an oleanane or rearranged oleanane skeleton.

Oxidation of compound (XXX) gave the ketol (XXIX); the latter (XXIX) was unchanged on similar treatment. The presence of a tertiary OH group in both compounds is thus confirmed. Attempted acetylation of (XXIX) at room temperature was unsuccessful; however at elevated temperature both (XXIX) and (XXX) gave mixtures of dehydration products. From the former, β-amyrenone (XV) and taraxerone (III), and from the latter β-amyrenyl acetate (XXI) and taraxeryl acetate (II) were obtained. Hence (XXIX) is either 13ξ-hydroxyoleanan-3-one or 14ξ-hydroxytaraxeran-3-one, and (XXX) is the corresponding 3β-hydroxy-compound. The presence of a taraxerane skeleton is more probable, as the olean-12-ene skeleton is more stable, and migration of the C-27 methyl group in the former from C-13 to C-14 to give the latter skeleton is well known. This was proved when compound (XXIX) was dehydrated under basic conditions with phosphoryl chloride in an excess of pyridine to give taraxerone (III) as the sole product.

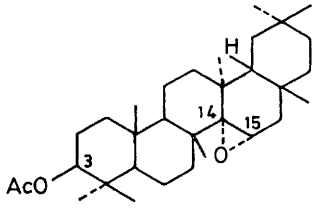
The configuration of the hydroxy-group at C-14 was finally shown to be α by partial synthesis of (XXX) from 14α,15α-epoxytaraxeran-3β-yl acetate (XXXI), first prepared by Beaton *et al.*[17] by action of perbenzoic acid

[12] R. E. Corbett and H. Young, *J. Chem. Soc.* (*C*), 1966, 1556.
[13] H. R. Arthur, W. H. Hui, C. N. Lam, and S. K. Szeto, *Austral. J. Chem.*, 1964, **17**, 697.
[14] J. Cerny, A. Vystrcil, and S. Huneck, *Chem. Ber.*, 1963, **96**, 3021.
[15] W. J. Dunstan, H. Fazakerley, T. G. Halsall, and E. R. H. Jones, *Croat. Chem. Acta*, 1957, **29**, 173.
[16] W. H. Hui and C. T. Ho, *Austral. J. Chem.*, 1968, **21**, 1675.
[17] J. M. Beaton, F. S. Spring, R. Stevenson, and J. L. Stewart, *J. Chem. Soc.*, 1955, 2131.

on taraxeryl acetate (II). We used freshly purified *m*-chloroperbenzoic acid for epoxidation since it is more stereospecific.[18] The epoxide (XXXI), $C_{32}H_{52}O_3$, showed an n.m.r. signal at δ 3.03 (1 H, m) for the C-15 methine proton. Treatment of (XXXI) with lithium aluminium hydride in tetrahydrofuran gave taraxerane-3β,14α-diol, identical with (XXX). Compound (XXIX) is therefore 14α-hydroxytaraxeran-3-one.



(XXIX) R = O
(XXX) R = α-H,β-OH

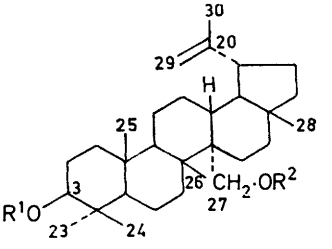


(XXXI)

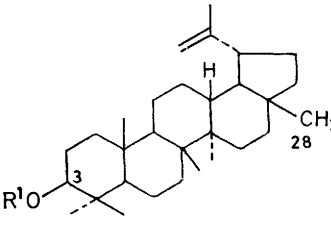
The structures of compounds (XXIX) and (XXX) were further confirmed by strong peaks at *m/e* 424 (base peak, $M^+ - H_2O$), 300, 285, and 205 for (XXIX) and 426 (base peak, $M^+ - H_2O$), 302, 287, 284, 269, 207, and 189 for (XXX) in their mass spectra, identical with those given by taraxerone (III) and taraxerol (VI), respectively.[6]

The eighth new compound (XXXII), $C_{30}H_{50}O_2$, was a diol which gave a yellow colour with tetranitromethane. On acetylation under mild conditions it gave a mixture of mono- and di-acetates, $C_{32}H_{52}O_3$ (XXXIII) and $C_{34}H_{54}O_4$ (XXXIV), respectively, separable by repeated recrystallization from chloroform–methanol, the former being less soluble. The n.m.r. spectrum of (XXXII) showed one equatorial hydroxy-group in the environment $CH_2{\cdot}CH{\cdot}OH$ [δ 3.20 (1 H, q, $J_{ax,eq}$ 7, $J_{ax,ax}$ 9 Hz)] and that the other hydroxy-group was primary and probably axially orientated [δ 3.32 (1 H, d J 11 Hz) and 3.77 (1 H, d, J 11 Hz)[4]]. The latter observation was confirmed by the mass spectra of (XXXII)—(XXXIV) which showed strong peaks at *m/e* 411, ($M^+ - CH_2OH$), 453 ($M^+ - CH_2OH$) and 453 ($M^+ - CH_2OAc$), respectively. These also indicated that monoacetylation had occurred at the secondary hydroxy-group.

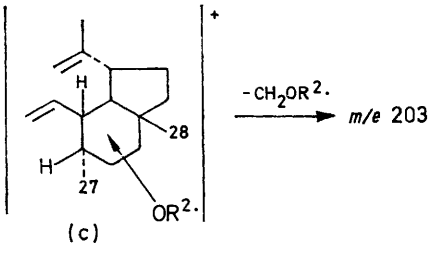
The n.m.r. spectrum of compound (XXXII) revealed the presence of five tertiary methyl groups and an isopropenyl group [δ 1.68 (3 H, s), 4.57 (1 H, d), and 4.68 (1 H, d)]. The two olefinic proton signals indicated that the isopropenyl group belonged to the lup-20(29)-ene and not to the hop-22(29)-ene skeleton, which would give a broadened singlet.[19] This supposition was confirmed by tosylation of (XXXIII) at high temperature in pyridine (tosylation at 0 °C or room temperature was unsuccessful) followed by reduction ($LiAlH_4$) to give lupeol (XXXV) as the final product. Compound (XXXII) is thus lup-20(29)-ene-3β,*x*-diol. The mass spectra of compounds (XXXII)—(XXXIV) indicated that the CH_2OR^2 function was at either C-27 or C-28 by fragments at *m/e* 234 for (XXXII) and (XXXIII) and *m/e* 276 for (XXXIV) comprising rings D and E and part of ring C [species (C)],[6] and base peaks at *m/e* 203 for all three compounds representing loss of CH_2OR^2 from the above fragments. The 28-position is ruled out as (XXXII) is not identical with betulin (XXXVI). Hence (XXXII) is lup-20(29)-ene-3β,27-diol.



(XXXII) $R^1 = R^2 = H$
(XXXIII) R^1 = Ac, R^2 = H
(XXXIV) $R^1 = R^2$ = Ac



(XXXV) $R^1 = R^2 = H$
(XXXVI) R^1 = H, R^2 = OH



(c)

(XXXII) R^2 = H, *m/e* 234
(XXXIII) R^2 = H, *m/e* 234
(XXXIV) R^2 = Ac, *m/e* 276

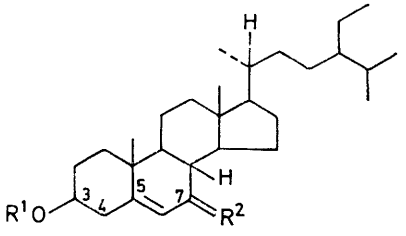
The 27-position in lupane derivatives is highly hindered;[20] this explains the difficulty in acetylation and tosylation of the $CH_2{\cdot}OH$ group. The location of this group was further supported by a comparison of the

[18] N. N. Schwartz and J. H. Blumbergs, *J. Org. Chem.*, 1964, **29**, 1976.
[19] W. J. Chin, R. E. Corbett, C. K. Heng, and A. L. Wilkins, *J.C.S. Perkin I*, 1973, 1437.
[20] C. S. Chopra, A. R. H. Cole, K. J. L. Theiberg, D. E. White, and H. R. Arthur, *Tetrahedron*, 1965, **21**, 1529.

methyl n.m.r. signals of (XXXII) with those of (XXXV) and (XXXVI) (see Experimental section).

After the isolation of compound (XXXII), betulin (XXXVI), myricadiol (I), and taraxer-14-ene-3β,29-diol (VIII) were obtained successively, followed by another compound (XXXVII), $C_{29}H_{50}O_2$, which was probably a steroid diol with one double bond. The n.m.r. spectrum revealed a pair of one-proton multiplets at δ 2.20 and 2.30 [21] for the C-4 protons and a one-proton multiplet at δ 3.55 for the C-3 (C*H*OH) proton, characteristic of a 5-en-3β-ol system. It also showed a low field C*H*OH signal at δ 3.80 together with an olefinic proton signal at δ 5.57 (1 H, d) suggesting the C=CH–CHOH grouping. Hence the second hydroxy-group was probably at C-7. The mass spectrum showed prominent peaks at *m/e* 289 ($M^+ - C_{10}H_{21}$), 271 (289 — H_2O), 253 (289 — $2H_2O$), 247 ($M^+ - C_{10}H_{21}$ — 42), 229 (247 — H_2O), and 211 (247 — $2H_2O$), characteristic of the stigmastane skeleton with a saturated side chain, and the two OH functions in the fragment containing rings A, B, and C. Compound (XXXVII) was thus stigmast-5-ene-3β,7ξ, diol, and was proved to be the 7β-isomer by the following reactions.

Oxidation of the allylic OH group in (XXXVII) by manganese dioxide followed by acetylation gave a compound identical with 7-oxostigmast-5-en-3β-yl-acetate



(XXXVII) R^1=H, R^2=α-H, β-OH
(XXXVIII) R^1=Ac, R^2=O

(XXXVIII) prepared from sitosteryl acetate.[22] Reduction of (XXXVIII) ($LiAlH_4$) yielded stigmast-5-ene-3β,7β-diol (*epi*-ikshusterol) as the major product, identical with (XXXVII).

The total number of triterpenoids isolated from the stems of *L. cornea* in this and our former investigation amounts to fifteen. Of these, nine belong to the taraxerane, three to the lupane, two to the friedelane, and one to the hopane series. All four types have been found to be common to the other nine Hong Kong *Lithocarpus* species,[1] from all of which sitosterol has also been obtained. However, epi-ikshusterol has not been detected in any other species.

EXPERIMENTAL

Mass spectra were recorded with a Hitachi–Perkin-Elmer RMU-6E spectrometer, n.m.r. spectra (solvent $CDCl_3$) with a Hitachi R-20 (60 MHz) instrument, i.r. spectra (KBr discs) with a Perkin-Elmer 337 spectrophotometer, u.v. spectrum (solvent 95% ethanol) with a Unicam SP 8000 spectrophotometer, and optical rotations (solvent $CHCl_3$) with a Bellingham and Stanley Pepol 60 spectropolarimeter. Alumina (B.D.H. activity II) was used for column and silica gel G (Merck) for thin-layer chromatography. Light petroleum had b.p. 60—80°. Where compounds are stated to be identical, they were shown to be so by mixed m.p., i.r., n.m.r., and mass spectral comparisons with authentic samples.

Extraction and Isolation of Compounds.—Milled air-dried stems (43.5 kg) of *Lithocarpus cornea* were extracted twice with light petroleum at room temperature for 10 days, and the combined concentrated extracts were chromatographed on alumina (3 kg). Light petroleum eluted in succession friedelin (3.0 g), m.p. 261—263°, taraxerone (III) (0.02 g), m.p. 249—251°, compound (VII), plates (from light petroleum) (5 mg), friedelan-3β-ol (0.20 g), m.p. 285—287°, and lupeol (XXXV) (0.02 g), m.p. 209—211°. Light petroleum–benzene (1 : 1) eluted taraxerol (VI) (2.0 g), m.p. 287—289°, then a semi-crystalline mass, which after repeated recrystallization from chloroform–methanol afforded needles of compound (IX) (0.02 g), followed by sitosterol (0.80 g), m.p. 139—140°, and finally a gummy material, which after washing with light petroleum and recrystallization from methanol yielded prisms of compound (XXIII) (0.08 g). Benzene eluted compound A_1[1] (XXIX) (0.20 g) as prisms (from benzene), compound A_2[1] (X) (0.10 g) as prisms (from methanol), compound (XXX) (0.08 g) as plates (from chloroform–methanol), compound (XXXII) (0.04 g) as needles (from methanol), and betulin (XXXVI) (0.07 g), m.p. 253—256°. Benzene–chloroform (1 : 1) eluted myricadiol (I) (0.02 g), m.p. 271–273° (from methanol), $[\alpha]_D$ + 8.0° (*c* 0.8), M^+ 442, $\nu_{max.}$ 3 370 (OH), 3 060, 1 645, and 818 cm^{-1} (C=CH) [diacetate, m.p. 256—257°, M^+ 526, $\nu_{max.}$ 1 748, 1 260 (OAc), 3 070, 1 640, and 820 cm^{-1} (C=CH)], and compound A_3[1] (VIII) (0.04 g) as fine needles (from chloroform–methanol). Chloroform eluted epi-ikshusterol (XXXVII) as plates (0.028 g), m.p. 221—223°, $[\alpha]_D$ −20.8° (*c* 0.7) (lit.,[3] 211—214°, $[\alpha]_D$ −20.5°),[3] M^+ 430, $\nu_{max.}$ 3 410 (OH), 1 670, and 840 cm^{-1} (C=CH).

Compound (VII).—*Taraxer-14-ene-3β,29-diol diacetate* had m.p. 271—272°, $[\alpha]_D$ +39.0° (*c* 0.40) [Found: M^+ 526. $C_{34}H_{54}O_4$ requires *M*, 526), $\nu_{max.}$ 1 740, 1 730, 1 250 (2 × OAc), $C_{34}H_{54}O_4$ requires *M*, 526], $\nu_{max.}$ 1 740, 1 730, 1 250 (2 × OAc) 3 055, 1 650, and 820 cm^{-1} (C=CH).

Compound (VIII).—*Taraxer-14-ene-3β,29-diol* had m.p. 298—299° (formerly reported [1] as 295—297°), $[\alpha]_D$ +23.5° (*c* 0.10) (Found: M^+ 442. $C_{30}H_{50}O_2$ requires *M*, 442), $\nu_{max.}$ 3 380 (OH), 3 056, 1 650, and 818 cm^{-1} (C=CH); diacetate, m.p. 271—272° (Found: C, 77.4; H, 10.3%; *M*, 526. Calc. for $C_{34}H_{54}O_4$: C, 77.5; H, 10.3%; *M*, 526), identical with compound (VII).

Compound (IX).—*3-Oxotaraxer-14-en-29-yl acetate* had m.p. 198—200°, $[\alpha]_D$ +11.3° (*c* 1.2) (Found: M^+, 482. $C_{32}H_{50}O_3$ requires *M*, 482), $\nu_{max.}$ 1 745, 1 250 (OAc), 1 715 (C=O), 3 055, 1 648, and 820 cm^{-1} (C=CH).

Compound (X).—*29-Hydroxytaraxer-14-en-3-one* had m.p. 263—264° (formerly reported [1] as 238—242°), $[\alpha]_D$ +38.0° (*c* 0.8) (Found: M^+, 440. $C_{30}H_{48}O_2$ requires *M*, 440), $\nu_{max.}$ 3 550 (OH), 1 700 (C=O), 3 050, 1 645, and 810 cm^{-1} (C=CH); acetate, m.p. 197—199° (Found: C, 79.4; H, 10.4%; *M*,

[21] W. J. S. Lockley, D. P. Roberts, H. H. Rees, and T. W. Goodwin, *Tetrahedron Letters*, 1974, 3773.

[22] R. A. Abramovitch and R. G. Micetich, *Canad. J. Chem.*, 1962, **40**, 2017.

482. Calc. for $C_{32}H_{50}O_3$: C, 79.6; H, 10.4%; *M*, 482), identical with compound (IX).

Reduction of Compound (X).—Compound (X) (0.025 g) was refluxed with sodium borohydride (0.05 g) in propan-2-ol (30 ml) for 2 h. The product was recrystallized from methanol to give fine needles (0.02 g), m.p. 297—299°, identical with compound (VIII) [diacetate, m.p. 270–272°, identical with compound (VII)].

Tosylation of Compound (X).—Compound (X) (0.03 g) in pyridine (10 ml) was treated with toluene-*p*-sulphonyl chloride (0.5 g) at 0 °C for 24 h. The product was recrystallized from chloroform–methanol to give plates of the tosylate (XI) (0.04 g), m.p. 201—203°, $\nu_{max.}$ 1 720 (C=O), 1 605, 1 480, 1 460, 1 370, 1 170, 840, 820 (tosylate), 3 070, 1 650, and 820 cm^{-1} (C=CH); δ 7.80 (2 H, d, *J* 9 Hz), 7.33 (2 H, d, *J* 9 Hz), 3.67 (2 H, s), and 2.42 (3 H, s).

Reduction of the Tosylate (XI).—Compound (XI) (0.035 g) in dry tetrahydrofuran (35 ml) was refluxed with lithium aluminium hydride for 3 days. The product (0.02 g), m.p. 283—286° (from chloroform), $[\alpha]_D$ ±0.0° (*c* 0.80), M^+ 426, $\nu_{max.}$ 3 500 (OH), 3 070, 1 650, and 820 cm^{-1} (C=CH), was identical with taraxerol (VI); acetate, m.p. 301—302°, $\nu_{max.}$ 3 070, 1 735, 1 650, 1 250, and 820 cm^{-1}, identical with taraxeryl acetate (II).

Isomerization of Compound (VII) *in Acid.*—Compound (VII) (0.025 g) was suspended in glacial acetic acid (10 ml) at 90 °C and concentrated hydrochloric acid (0.5 ml) was added dropwise. The mixture was heated on a steam-bath for 15 min. The solid gradually dissolved, and M-sodium hydroxide was immediately added. The precipitate formed was recrystallized from light petroleum to give fine needles of *olean-12-ene-3β,29-diol diacetate* (XII) (0.02 g), m.p. 207—209°, $[\alpha]_D$ +51.0° (*c* 0.63) (Found: C, 77.65; H, 10.0%; M^+, 526. $C_{34}H_{54}O_4$ requires C, 77.5; H, 10.3%; *M*, 526), $\nu_{max.}$ 1 750, 1 745, 1 250 (2 × OAc), 3 050, 1 650, and 812 cm^{-1} (C=CH).

Reduction of Methyl Mesembryanthemoidigenate (XVI).—Compound (XVI) (0.10 g) was treated with lithium aluminium hydride in ether. The product was recrystallized from methanol to give plates of olean-12-ene-3β,28,29-triol (XVII) (0.08 g), (Found: M^+, 458. Calc. for $C_{30}H_{50}O_3$: *M*, 458), m.p. 288—289°, $[\alpha]_D$ +43.1° (*c*. 0.62), (lit.,[23] m.p. 287—289°, $[\alpha]_D$ +47.6°), $\nu_{max.}$ 3 350 (OH), 1 655, and 820 cm^{-1} (C=CH).

Partial Synthesis of the Diol Diacetate (XII) *from the Triol* (XVII).—Compound (XVII) (0.07 g) in pyridine (20 ml) was treated with toluene-*p*-sulphonyl chloride (0.50 g) at 0 °C for 30 min. The dried oily product (0.12 g) in tetrahydrofuran (30 ml) was refluxed with lithium aluminium hydride (0.10 g) for 3 days to give a mixture of hydroxy-compounds

Tertiary methyl resonances (δ values) *

Compound	C-23	C-24	C-25	C-26	C-27	C-28	C-29	C-30
(II)	0.89	0.89	0.91	1.10	0.96	0.83	0.91	0.96
(V)	0.87	0.87	0.92	1.06	0.92		0.91	0.92
(VII)	0.88	0.88	0.91	1.10	0.97	0.88		0.97
(IX)	1.13	0.92	1.07	1.07	1.07	0.85		0.96
(X)	1.13	0.93	1.07	1.07	1.07	0.85		0.93
(XI)	1.10	0.91	1.04	1.06	1.06	0.83		0.81
(XII)	0.85	0.85	0.93	0.96	1.11	0.85		0.96

* Interpretation according to Corbett *et al.*[24] and Tursch *et al.*[25]

(0.055 g), $\nu_{max.}$ 3 300 cm^{-1}, which showed 3 spots on t.l.c. This was acetylated, and the product mixture was chromatographed on silica gel (8 g) in light petroleum to give first β-amyrenyl acetate (XXI) (0.025 g), m.p. 241—242°, M^+ 468, $\nu_{max.}$ 1 745, 1 655, 1 250, and 812 cm^{-1}, followed by erythrodiol diacetate (XXII) (0.012 g), m.p. 185—186°, M^+ 526, $\nu_{max.}$ 1 750, 1 650, 1 250, and 830 cm^{-1}, and finally olean-12-ene-3β,29-diol diacetate as needles (8 mg), m.p. 206—208°, M^+ 526, $\nu_{max.}$ 1 750, 1 745, 1 650, 1 250, and 812 cm^{-1}, identical with compound (XII).

Compound (XXIII).—*22-Hydroxy-21αH-hopan-3-one* (XXIII) had m.p. 214—215°, $[\alpha]_D$ +50.0° (*c* 1.1) (Found: C, 81.3; H, 11.3%; M^+, 442. $C_{30}H_{50}O_2$ requires C, 81.4; H, 11.4%; *M*, 442), $\nu_{max.}$ 3 470 (OH) and 1 700 cm^{-1} (C=O).

Attempted Oxidation of the Hopanone (XXIII).—Compound (XXIII) (0.015 g) was treated with Jones reagent at room temperature. Unchanged (XXIII) (0.013 g), m.p. 214—215°, M^+ 442, $\nu_{max.}$ 3 470 and 1 700 cm^{-1}, was isolated.

Attempted Acetylation of the Hopanone (XXIII).—(*a*) Compound (XXIII) (0.01 g) was kept in cold acetic anhydride and pyridine for 3 days. The product (8 mg), m.p. 214—215°, was unchanged (XXIII).

(*b*) Compound (XXIII) (0.018 g) was refluxed with acetic anhydride and pyridine for 4 h. The product afforded prisms (0.015 g), m.p. 197—199° (from methanol), $[\alpha]_D$ +83.0° (*c* 0.50), M^+ 424, $\nu_{max.}$ 1 720 (C=O) and 1 675 cm^{-1} (C=C), identical with hop-17(21)-en-3-one (XXIV).[13]

Dehydration of the Hopanone (XXIII).—A solution of compound (XXIII) (0.04 g) in pyridine (10 ml) was treated with phosphoryl chloride (1 ml) at room temperature for 24 h. The product (0.035 g) showed two spots on t.l.c. ($AgNO_3$–SiO_2; $CHCl_3$). The mixture was chromatographed on an $AgNO_3$–SiO_2 column. Elution with light petroleum–benzene (4 : 1) gave needles (0.025 g), m.p. 189–190° (from light petroleum), $[\alpha]_D$ +63.5° (*c* 0.82), M^+ 424. $\nu_{max.}$ 1 700 (C=O) and 1 650 cm^{-1} (C=C), identified as hopenone-a (0.025 g) (XXVI) (lit.,[15] m.p. 189—193°, $[\alpha]_D$ +67.0°). Elution with light petroleum–benzene (2 : 3) yielded plates (0.012 g), m.p. 204–205° (from methanol), $[\alpha]_D$ +59.3° (*c* 0.30), M^+ 424, $\nu_{max.}$ 1 710 (C=O), 3 080, 1 645, and 880 cm^{-1} ($C=CH_2$) identical with moretenone (XXVII).

Hydration of Moretenone (XXVII); *Partial Synthesis of the Hopanone* (XXIII).—A solution of compound (XXVII) (0.20 g) in tetrahydrofuran (40 ml) was added with stirring to a solution of mercury(II) acetate (0.20 g) in aqueous tetrahydrofuran (1 : 1) (80 ml). The mixture was stirred at 0 °C for 5 h, then at room temperature for 16 h. A solution of sodium borohydride (0.04 g) in 3M-sodium hydroxide (40 ml) was then added with stirring. The precipitated mercury was filtered off and the mother liquor was saturated with sodium chloride. The tetrahydrofuran layer was evaporated to dryness to yield a solid (0.18 g), which was chromatographed on alumina (10 g) in light petroleum to give unchanged (XXVII) (0.15 g). Elution with light petroleum–benzene (1 : 1) gave first moretenol (XXVIII) (0.010 g), m.p. 234—236° (from methanol), $[\alpha]_D$ +30.5° (*c* 0.30), M^+ 426, $\nu_{max.}$ 3 400 (OH), 3 080, 1 645, and 892 cm^{-1} ($C=CH_2$), then prisms (0.012 g), m.p. 213—215° (from methanol), $[\alpha]_D$ +51.0° (*c* 0.40), M^+ 442, $\nu_{max.}$ 3 470 (OH) and 1 700 cm^{-1} (C=O), identical with compound (XXIII).

Methyl resonances (δ values)

Compound	C-23	C-24	C-25	C-26	C-27	C-28	C-29	C-30
(XXIII)	1.09	1.03	0.95	1.03	0.95	0.70	1.20	1.20
(XXV)	1.08	1.02	0.93	1.02	0.96	0.78	1.20	1.20
(XXIV)	1.06	1.01	0.93	1.01	0.93	0.83	1.01 *	1.01 *
(XXVII)	1.08	1.02	0.94	1.02	0.94	0.68		1.66 †

* Pri (d, *J* 6 Hz). † CH_2=CMe.

[23] S. Rangaswami and S. Sarangan, *Tetrahdron*, 1969, **25**, 3701.
[24] R. E. Corbett, S. D. Cumming, and E. V. Whitehead, *J.C.S. Perkin I*, 1972, 2827.
[25] B. Tursch, R. Savoi, R. Ottinger, and G. Chiurdoglu, *Tetrahedron Letters*, 1967, 539.

Compound (XXIX).—14α-*Hydroxytaraxeran*-3-*one* had m.p. 259—261° (formerly reported [1] as 254—256°), $[\alpha]_D$ −43.0° (*c* 1.1) (Found: C, 81.3; H, 11.55%; M^+, 442. $C_{30}H_{50}O_2$ requires C, 81.4; H, 11.4%; *M*, 442), $\nu_{max.}$ 3 480 (OH) and 1 700 cm^{-1} (C=O).

Compound (XXX).—*Taraxerane*-3β,14α-*diol* had m.p. 269—270°, $[\alpha]_D$ −58.0° (*c* 0.3) (Found: C, 78.0; H, 11.7%; M^+, 444. $C_{30}H_{52}O_2 \cdot H_2O$ requires C, 77.9; H, 11.8%; *M*, 444), $\nu_{max.}$ 3 450 cm^{-1} (OH).

Tertiary methyl resonances (δ values)

Compound	C-23	C-24	C-25	C-26	C-27	C-28	C-29	C-30
(XXIX)	1.08	1.08	1.08	1.18	1.18	0.83	0.94	1.02
(XXX)	0.96	0.76	0.83	1.17	1.17	0.83	0.94	1.04

Reduction of the Hydroxy-ketone (XXIX) *to the Diol* (XXX).—Compound (XXIX) (0.05 g) was stirred with a solution of sodium borohydride (0.05 g) in propan-2-ol (25 ml) for 4 h. The product (0.045 g) had m.p. 268—270° (from methanol), $[\alpha]_D$ −53.0° (*c* 0.3), $\nu_{max.}$ 3 450 cm^{-1}, and was identical with (XXX).

Attempted Oxidation of the Hydroxy-ketone (XXIX).—Compound (XXIX) (0.01 g) was treated with Jones reagent at room temperature. The product, m.p. 259—261°, $\nu_{max.}$ 3 480, 1 700 cm^{-1}, was unchanged (XXIX).

Oxidation of the Diol (XXX).—A solution of compound (XXX) (0.03 g) in pyridine (50 ml) was stirred with a suspension of chromium trioxide (0.10 g) in pyridine (2 ml) at 0 °C for 3 h, then at room temperature for 12 h. The product was extracted into benzene and recrystallized from chloroform–methanol to give prisms of the hydroxy-ketone (XXIX) (0.02 g), m.p. 258—260°, $[\alpha]_D$ −41.0° (*c* 1.0), $\nu_{max.}$ 3 480 and 1 700 cm^{-1}.

Attempted Acetylation of the Hydroxy-ketone (XXIX).—(*a*) Compound (XXIX) was kept at room temperature in acetic anhydride and pyridine for 2 days. The product, m.p. 258—260°, was unchanged (XXIX). (*b*) Compound (XXIX) (0.05 g) was refluxed with acetic anhydride and pyridine for 3 h. The product was separated by preparative t.l.c. [$AgNO_3$–SiO_2; C_6H_6–$CHCl_3$ (1 : 3)] into β-amyrenone (XV) (0.25 g), m.p. 179–181°, M^+ 424, $\nu_{max.}$ 1 720 (C=O), 1 660, and 818 cm^{-1} (C=CH), and taraxerone (III) (0.013 g), m.p. 248—250°, M^+ 424, $\nu_{max.}$ 1 720 (C=O), 3 055, 1 645, and 820 cm^{-1} (C=CH).

Attempted Acetylation of the Diol (XXX).—Compound (XXX) (0.03 g) was refluxed with acetic anhydride and pyridine for 3 h. The product was separated by preparative t.l.c. ($AgNO_3$–SiO_2; C_6H_6) into β-amyrenyl acetate (0.015 g), m.p. 240—241°, M^+ 468, $\nu_{max.}$ 1 740, 1255 (OAc), 1 660, and 820 cm^{-1} (C=CH), and taraxeryl acetate (II) (8 mg), m.p. 303—304°, M^+ 468, $\nu_{max.}$ 1 740, 1 255 (OAc) 3 060, 1 645, and 820 cm^{-1} (C=CH).

Dehydration of the Hydroxy-ketone (XXIX) *to Taraxerone* (III).—Compound (XXIX) (0.05 g) was refluxed with phosphoryl chloride (0.2 ml) and pyridine (25 ml) for 2 h. The product on recrystallization from light petroleum afforded prisms of taraxerone (III) (0.035 g), m.p. 248–249°, M^+ 424, $\nu_{max.}$ 3 055, 1 720, 1 646, and 820 cm^{-1}.

14α,15α-*Epoxytaraxeran*-3β-*yl Acetate* (XXXI).—Taraxeryl acetate (II) (0.08 g) in chloroform (30 ml) was treated with freshly purified *m*-chloroperbenzoic acid (0.11 g) at 0 °C for 18 h. The product on recrystallization from chloroform–methanol yielded needles of 14α,15α-epoxytaraxeran-3β-yl acetate (XXXI) (0.065 g), m.p. 254—257°, $[\alpha]_D$ +43.0 (*c* 0.92) (lit.,[17] m.p. 257—260°, $[\alpha]_D$ +47°), M^+ 484, $\nu_{max.}$ 1 740, 1 250 (OAc), 890, and 870 cm^{-1} (epoxide ring).

Reduction of the Epoxide (XXXI).—Compound (XXXI) (0.05 g) was refluxed with lithium aluminium hydride (0.03 g) in tetrahydrofuran (25 ml) for 3 days. The product on recrystallization from methanol gave prisms of taraxerane-3β,14α-diol (0.03 g), m.p. 268—269°, M^+ 444, $\nu_{max.}$ 3 450 cm^{-1} (OH), identical with (XXX).

Compound (XXXII).—*Lup*-20(29)-*ene*-3β,27-*diol* had m.p. 214—215°, $[\alpha]_D$ +67.0° (*c* 0.52) (Found: C, 78.5; H, 11.4%; M^+, 442. $C_{30}H_{50}O_2$, H_2O requires C, 78.2; H, 11.4%; *M*, 442), $\nu_{max.}$ 3 500 (OH), 3 075, 1 650, and 885 cm^{-1} ($C=CH_2$).

Tertiary methyl signals (δ values)

Compound	C-23	C-24	C-25	C-26	C-27	C-28	C-30
(XXXII)	0.97	0.77	0.85	1.05		0.80	1.68
(XXV)	0.97	0.77	0.84	1.05	0.97	0.80	1.68
(XXXVI)	0.98	0.77	0.83	1.02	0.98		1.68

Acetylation of the Diol (XXXII).—Compound (XXXII) (0.03 g) was treated with acetic anhydride and pyridine at room temperature for 7 days. The product on t.l.c. gave two spots. It was fractionally recrystallized from chloroform–methanol to give the major product in the less soluble fractions as plates of the 3-*monoacetate* (XXXIII) (0.019 g), m.p. 287–289°, $[\alpha]_D$ +93.0° (*c* 0.4) (Found: M^+, 484. $C_{32}H_{52}O_3$ requires *M*, 484), $\nu_{max.}$ 3 575 (OH), 1 740, 1 250 (OAc), 3 050, 1 660, and 890 cm^{-1} ($C=CH_2$). The filtrates on concentration deposited a solid which on repeated recrystallization from light petroleum afforded needles of the *diacetate* (XXXIV) (5 mg), m.p. 249—250°, $[\alpha]_D$ +73.0° (*c* 0.20) (Found: M^+, 526. $C_{34}H_{54}O_4$ requires *M*, 526), $\nu_{max.}$ 1 750, 1 745, 1 250 (2 × OAc), 3 080, 1 645, and 892 cm^{-1} ($C=CH_2$).

Lupeol (XXXV) *from the Monoacetate* (XXXIII).—Compound (XXXIII) (0.015 g) in pyridine (20 ml) was refluxed with toluene-*p*-sulphonyl chloride (0.02 g) for 24 h. The dried oily product (0.023 g) was then refluxed with lithium aluminium hydride (0.05 g) in tetrahydrofuran (20 ml) for 3 days. The purified product (0.01 g), m.p. 205—207°, M^+ 428, $\nu_{max.}$ 3 360 (OH), 3 080, 1 640, and 880 cm^{-1} ($C=CH_2$), was lupeol (XXXV); acetate, m.p. 219—220°, $\nu_{max.}$ 3 080, 1 740, 1 645, 1 250, and 880 cm^{-1}.

Oxidation of Stigmast-5-*ene*-3β,7β-*diol* (XXXVII) *with Manganese Dioxide followed by Acetylation.*—Compound (XXXVII) (0.02 g) was stirred at room temperature with a suspension of manganese dioxide (0.50 g) in chloroform (25 ml) for 2 days. The oily product was treated with acetic anhydride and pyridine at room temperature for 2 days to give needles of the ketone (XXXVIII) (0.013 g), m.p. 174—176°, $[\alpha]_D$ −10.6° (*c* 0.72), M^+ 470, $\nu_{max.}$ 1 680, 1 640 (C=C–C=O), 1 735, and 1 270 cm^{-1} (OAc), $\lambda_{max.}$ 240 nm (ε14 000).

7-*Oxostigmast*-5-*en*-3β-*yl Acetate* (XXXVIII) *from Sitosteryl Acetate.*—Sitosteryl acetate (0.2 g) in glacial acetic acid (10 ml) containing sodium acetate (0.2 g) was warmed to 60 °C, and chromium trioxide (0.2 g) in glacial acetic acid (10 ml) was added. The mixture was kept at 60 °C for 5 h. The product (0.2 g) was chromatographed on alumina (20 g) to give unchanged sitosteryl acetate (0.08 g), m.p. 126—128°, followed by 7-oxostigmast-5-en-3β-yl acetate (0.09 g), m.p. 175—176°, M^+ 470, $\nu_{max.}$ 1 680, 1 640 (C=C–C=O), 1 735, and 1 270 cm^{-1} (OAc), identical with (XXXVIII).

Reduction of the Ketone (XXXVIII).—Compound (XXXVIII) (0.05 g) was refluxed with lithium aluminium

hydride in ether for 3 h. The product was purified by preparative t.l.c. (SiO_2) to give the major product (0.025 g), m.p. 220—222° (from chloroform–methanol), $[\alpha]_D$ −20.8° (*c* 0.70) $\nu_{max.}$ 3 410, 1 670, and 840 cm^{-1}, identical with (XXXVII).

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