# Six New Triterpenoids and Other Triterpenoids and Steroids from Three *Quercus* Species of Hong Kong

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Six new triterpenoids have been isolated from three local *Quercus* species, and identified as taraxera-1,14-dien-3-one (1) and taraxer-14-ene-3β,16α-diol (7) (from *Q. bambusaefolia*), 21α*H*-hopane-3β,22-diol (14) (from *Q. championi*), and 24,25-dimethyl-lanosta-9(11),23-dien-3β-ol (30), its acetate (29), and the corresponding ketone (31) (from *Q. myrsinaefolia*). The isolation of two steroids and seventeen other triterpenoids, including olean-12-ene-3,16-dione (3), taraxer-14-ene-3,16-dione (6), hop-17(21)-en-3-one (13), 3β-hydroxylup-20(29)-en-30-al (23), and lup-20(29)-ene-3β,30-diol (24), is also reported.

THE leaves of *Quercus bambusaefolia* Hance, *Q. championi* Benth., and *Q. myrsinaefolia* Bl. have been examined for neutral triterpenoids and steroids in this laboratory.[1-3] We now report an investigation of both neutral and acidic constituents from the stems of the same plants.

The light petroleum extract of the stems of *Q. bambusaefolia* contained, besides the triterpenoids friedelin, taraxerone, friedelan-3β-ol, β-amyrin, taraxerol, and betulin and the steroids sitosterol and 6β-hydroxystigmast-4-en-3-one, four other triterpenoids, all of which gave positive results in the Liebermann–Burchardt reaction and tetranitromethane test. Subsequent extraction with ethanol yielded olean-12-ene-1,3-dione (isolated mainly as 3-methoxyoleana-2,12-dien-1-one as a result of partial methylation of the enol form), and betulinic and oleanolic acids.

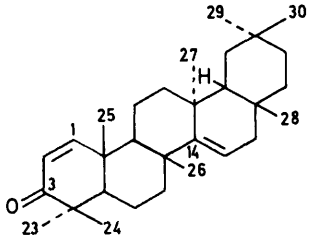
The least polar of the four new triterpenoids was a pentacyclic ketone (1), $C_{30}H_{46}O$, containing two double bonds, one of which was trisubstituted ($\nu_{max.}$ 3 090 and 827 $cm^{-1}$) and the other conjugated to the carbonyl function ($\nu_{max.}$ 3 050 and 1 670 $cm^{-1}$). The existence of the group $C-CH^{c}=CH-C=O$ was shown by the n.m.r. [δ 5.78 and 6.05 (1 H, each, d, *J* 11 Hz)] and u.v. [$\lambda_{max.}$ 229 nm (ε 9 800)] spectra. Such a system is only possible in ring A of common pentacyclic triterpenoids. The presence of eight tertiary methyl singlets and a well defined signal at δ 5.67 (1 H, q, *J* 4 and 7 Hz) for the olefinic proton of the trisubstituted double bond in the n.m.r. spectrum suggested the taraxer-14-ene skeleton.[4] This was supported by strong peaks at *m/e* 298, 283, 204, 203, and 189 in the mass spectrum,[5] which also confirmed

[1] H. R. Arthur, W. H. Hui, C. N. Lam, and S. K. Szeto, *Austral. J. Chem.*, 1964, **17**, 697.
[2] W. H. Hui, C. T. Ho, and C. W. Yee, *Austral. J. Chem.*, 1965, **18**, 2043.
[3] H. R. Arthur, K. F. Cheng, M. P. Lau, and K. J. Lie, *Phytochemistry*, 1965, **4**, 969.
[4] W. H. Hui and M.-M. Li, *J.C.S. Perkin I*, 1976, 23.
[5] H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 3688.

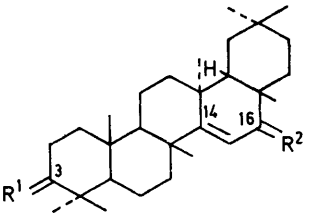
that the conjugated carbonyl function was in ring A. Thus compound (1) was either taraxera-1,14-dien-3-one or taraxera-2,14-dien-1-one. The latter was unlikely as an oxo-function at C-1 would give a prominent mass spectral peak at *m/e* 137 as a result of McLafferty rearrangement,[6] which was not observed. This was confirmed when hydrogenation under mild conditions gave taraxerone (2) as the sole product. Finally, the ketone (1) was identical with a sample of taraxera-1,14-dien-3-one prepared by dehydrogenation of taraxerone (2) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.[7]

The second compound (3), $C_{30}H_{46}O_2$, showed i.r. bands for two carbonyl groups ($\nu_{max.}$ 1 720 and 1 700) and a trisubstituted double bond ($\nu_{max.}$ 1 620 and 825 $cm^{-1}$). A one proton quartet at δ 5.63 (*J* 2 and 3 Hz) together with eight tertiary methyl singlets in its n.m.r. spectrum suggested an olean-12-ene skeleton.[8] A prominent peak in the mass spectrum at *m/e* 205 indicated one of the carbonyl groups to be in the usual 3-position, and other fragments at *m/e* 232, 217, and 147 showed the second to be in ring D at C-15 or -16.[5] The former was unlikely, since an oxo-function at C-15 would give a strong peak at *m/e* 233, which was absent.[5] Compound (3) was identical with a sample of olean-12-ene-3,16-dione (maniladione) prepared by oxidation of maniladiol (olean-12-ene-3β,16β-diol) (4)[9] obtained by hydrolysis of the diformate (5)[10] (kindly supplied by Professor C. Djerassi). The dione (3) has not formerly been reported as a natural product.

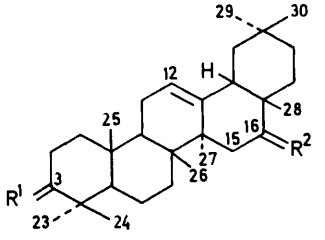
The second most polar compound (6), $C_{30}H_{46}O_2$, contained two carbonyl groups, one of which was conjugated [$\nu_{max.}$ 1 708 and 1 680 $cm^{-1}$, $\lambda_{max.}$ 241 nm (ε 9 870)]. A signal at δ 2.40 (2 H, m) in the n.m.r. spectrum suggested the $CH_2$·CO function; another at δ 5.84 (1 H, s) indicated that the conjugated carbonyl group was ββ-disubstituted, which agreed well with reported data for taraxer-14-en-16-one derivatives.[11,12] That compound (6) was taraxer-14-ene-3,16-dione was supported by peaks at *m/e* 314, 299, and 205 in its mass spectrum.[5] Treatment with concentrated hydrochloric acid–acetic acid yielded olean-12-ene-3,16-dione (3). Allylic oxidation of taraxerone (2) has been found to give (6).[12] We repeated the experiment under slightly different conditions, and obtained a mixture of (3) and (6); the former must have been formed by acid-catalysed isomerization of the latter.



(1)



(2) $R^1$ = O, $R^2$ = $H_2$
(6) $R^1$ = $R^2$ = O
(7) $R^1$ = α-H, β-OH, $R^2$ = α-OH, β-H
(8) $R^1$ = α-H, β-OAc, $R^2$ = α-OAc, β-H
(9) $R^1$ = α-H, β-OAc, $R^2$ = α-H, β-OH



(3) $R^1$ = $R^2$ = O
(4) $R^1$ = $R^2$ = α-H, β-OH
(5) $R^1$ = $R^2$ = α-H, β-$O_2$CH
(10) $R^1$ = α-H, β-OAc, $R^2$ = α-OAc, β-H
(11) $R^1$ = α-H, β-OH, $R^2$ = α-OH, β-H

The most polar compound (7), $C_{30}H_{50}O_2$, was a diol ($\nu_{max.}$ 3 300) with a trisubstituted double bond ($\nu_{max.}$ 1 640 and 840 $cm^{-1}$). It formed a diacetate (8). One of the hydroxy-groups was probably at the usual 3β-position, as shown in its n.m.r. spectrum by a signal at δ 3.20 (1 H, q, $J_{ax,eq}$ 7, $J_{ax,ax}$ 9 Hz), shifted to δ 4.47 in that of the diacetate (8). The presence of the group C–C=C*H*–C*H*OH was indicated by peaks at δ 4.13 and 5.37 (1 H each, d, *J* 2 Hz) shifted to δ 5.23 (2 H, approx. s) in that of (8) (caused by deshielding of the former and slight shielding of the latter). This, together with mass spectral fragments at *m/e* 318, 303, 300, 285, and 207 for (7) and 402, 387, 342, 327, and 249 for (8), indicated the

[6] W. H. Hui and M.-M. Li, *Phytochemistry*, 1975, **14**, 785.
[7] B. Talapatra, S. Dutta, B. C. Maiti, D. K. Pradhan, and S. K. Talapatra, *Austral. J. Chem.*, 1974, **27**, 2711.
[8] T. Kikuchi, M. Takayama, T. Toyoda, M. Arimoto, and M. Niwa, *Chem. and Pharm. Bull. (Japan)*, 1973, **21**, 2243.
[9] I. M. Morice and J. C. E. Simpson, *J. Chem. Soc.*, 1942, 198.
[10] C. Djerassi, A. Bowers, S. Burstein, H. Estrada, J. Grossman, J. Herran, A. J. Lemin, A. Manjarrez, and S. C. Pakrashi, *J. Amer. Chem. Soc.*, 1956, **78**, 2312.
[11] B. W. Finucane and J. B. Thomson, *J.C.S. Perkin I*, 1972, 1856.
[12] R. E. Corbett, S. D. Cumming, and E. V. Whitehead, *J.C.S. Perkin I*, 1972, 2827.

taraxer-14-ene skeleton, with the second oxy-function at C-16.[5] Oxidation of (7) with Jones reagent gave taraxer-14-ene-3,16-dione (6). Thus compound (7) was taraxer-14-ene-3β,16ξ-diol. Reduction of (6) with sodium borohydride under vigorous conditions yielded (7). Since the β-face of taraxer-14-ene derivatives is less hindered,[11] reduction of (6) should give the 16α-hydroxy-compound. Also the 16α-proton in 16β-hydroxytaraxeryl acetate (9) gave an n.m.r. signal at δ 4.15 (1 H, d, *J* 4 Hz) [11] which was different from that of the second C*H*·OH group in (7). Therefore the 16-OH group in (7) must be α-oriented. Further, acid-catalysed isomerization of the diacetate (8) gave another diacetate (10), hydrolysis of which yielded a diol (11). Oxidation of the diol (11) then afforded olean-12-ene-3,16-dione (3). Compound (11), which gave an n.m.r. signal at δ 3.71 (1 H, t, *J* 2 and 3 Hz), shifted to δ 4.82 in the spectrum of the diacetate (10), for the 16β-proton was not identical, with maniladiol (4), and was therefore olean-12-ene-3β,-16α-diol; it was indeed identical with the reduction product of the dione (3). It was thus confirmed that compound (7) was taraxer-14-ene-3β,16α-diol. Compounds (6) and (7) are the first examples of naturally occurring C-16 oxygenated taraxerene derivatives.

The stems of *Q. championi* yielded, besides the known compounds friedelin, friedelan-3β-ol, hop-17(21)-en-3β-ol (12), lupeol, β-amyrin, sitosterol, betulin, betulinic acid, oleanolic acid, and hop-17(21)-en-3-one (13) (which has not been isolated previously from natural sources), three other triterpenoids, all of which gave a positive Liebermann–Burchardt reaction.

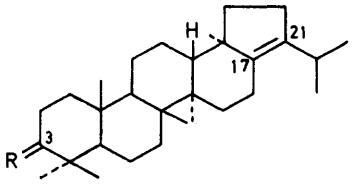
The second most polar compound (14), $C_{30}H_{52}O_2$, of the three was saturated; it gave a negative response to a tetranitromethane test and no C=C absorption in its i.r. spectrum, which showed OH function(s) ($\nu_{max.}$ 3 470 $cm^{-1}$). Acetylation of (14) at room temperature yielded a monoacetate (15), $C_{32}H_{54}O_3$, which still contained an OH group ($\nu_{max.}$ 3 500, 1 720, and 1 270 $cm^{-1}$). The OH function in (14) which was acetylated was proabably at the usual 3β-position, as shown by a signal at δ 3.20 [1 H (*eq*), q, $J_{ax,eq}$ 7, $J_{ax,ax}$ 9 Hz] in its n.m.r. spectrum, shifted to δ 4.47 in that of (15). The absence of other signals at $\delta > 3.0$ indicated the absence of olefinic protons, and the tertiary nature of the second OH group. Both (14) and (15) revealed singlets corresponding to eight tertiary methyl groups, two of which were almost equivalent (at δ 1.20 and 1.22, respectively), showing the presence of a $CMe_2$·OH group, probably belonging to the hopane or isohopane series.[4] This was supported by intense mass spectral peaks at *m/e* 386, 207, 189, 149, and 59, characteristic of 22-hydroxyhopanes.[13] Attempted acetylation with boiling acetic anhydride and pyridine led to a dehydration product, $C_{32}H_{52}O_2$, identical with hop-17(21)-en-3β-yl acetate (16). Oxidation of (14) gave a ketol identical with 22-hydroxy-21α*H*-hopan-3-one (17),[4] which on reduction with lithium aluminium hydride gave back (14). Hence (14) is 21α*H*-hopane-3β,22-diol; this was confirmed by partial synthesis from moretenone [21α*H*-hop-22(29)-en-3-one] (18), by treatment with *m*-chloroperbenzoic acid to give the epoxide (19), which on reduction with lithium aluminium hydride afforded the diol (14). The tertiary methyl resonances of compounds (14), (15), and (17) are almost identical with those of the corresponding compounds (20)—(22) in the 21β*H*-series (see Experimental section), with the exception of the C-28 methyl signals.

The other two compounds, (23), $C_{30}H_{48}O_2$, and (24), $C_{30}H_{50}O_2$, were interrelated. Both contained a C-3 equatorial OH group [δ 3.20 (1 H, q, $J_{ax,eq}$ 7, $J_{ax,ax}$ 9 Hz)]. The former possessed a $CH_2$=C–CHO [δ 5.90 and 6.28 (1 H each, approx. s) and 9.63 (1 H, s)],[14] and the latter a $CH_2$=C–$CH_2$·OH [δ 4.12 (2 H, s) and 4.89 (2 H, broad s)] [14] side chain. Compound (23) formed a monoacetate (25) and compound (24) a diacetate (26). Reduction of (23) with lithium aluminium hydride gave (24), and oxidation of (24) with manganese dioxide in chloroform yielded (23). Treatment of (24) with concentrated hydrochloric acid and glacial acetic acid gave a saturated acetoxy-aldehyde (27), identical with the hydrogenation product of (25), Wolff–Kishner reduction of which followed by acetylation yielded lupenyl acetate (28). Hence (23) was 3β-hydroxylup-20(29)-en-30-al, and (24) lup-20(29)-ene-3β,30-diol. Neither compound has been isolated previously as a natural product, but they have been prepared from lupenyl acetate (28) by oxidation with selenium dioxide [15] and lead tetra-acetate,[16] respectively. These experiments have been repeated, and the products were identical with the naturally occurring compounds.

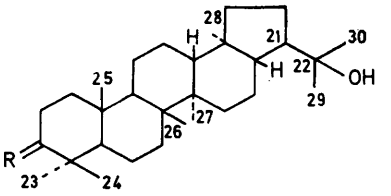
From the stems of *Q. myrsinaefolia*, in addition to friedelin, friedelan-3β-ol, lupeol, β-amyrin, sitosterol, 6β-hydroxystigmast-4-en-3-one, betulin, betulinic, and ursolic and oleanolic acids, three new $C_{32}$ tetracyclic triterpenoids were isolated. They all showed positive results in the Liebermann–Burchardt reaction and the tetranitromethane test.

The least polar compound (29), $C_{34}H_{56}O_2$, contained an acetoxy-group [$\nu_{max.}$ 1 740 and 1 240 $cm^{-1}$, δ 2.02 (3 H, s)], and on hydrolysis yielded an alcohol, $C_{32}H_{54}O$, identical with the most polar of the three compounds (30), in which the OH group was probably at the 3β-position [δ 3.27 (1 H, q, $J_{ax,eq}$ 7, $J_{ax,ax}$ 9 Hz), shifted to 4.50 for (29)]. Compound (30) on oxidation with Jones reagent gave a ketone, $C_{32}H_{52}O$, identical with the second most polar compound (31), which on reduction with lithium aluminium hydride gave back (30). All three compounds contained two trisubstituted double bonds as indicated in each of their n.m.r. spectra by two overlapping signals at δ 5.10 and 5.25 (1 H each, m), a vinyl $CH_3$ group [δ 1.59 (3 H, broad s)], eight tertiary methyl groups (see Experimental section), and a secondary methyl group [δ 8.50 (3 H, d, *J* 7 Hz)]. These compounds were thought

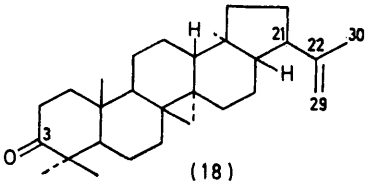
[13] R. E. Corbett and H. Young, *J. Chem. Soc.* (*C*), 1966, 1556.
[14] W. H. Hui and M.-M. Li, *Phytochemistry*, 1976, **15**, in the press.
[15] L. Ruzicka and G. Rosenkranz, *Helv. Chim. Acta*, 1939, **22**, 778.
[16] L. R. Row, C. S. Rao, and T. S. Ramaiah, *Indian J. Chem.*, 1968, **6**, 16.



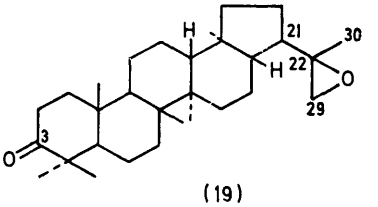
(12) R = α-H, β-OH
(13) R = O
(16) R = α-H, β-OAc



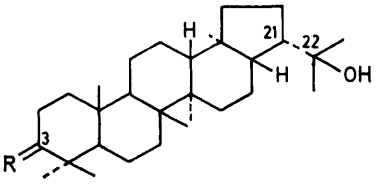
(14) R = α-H, β-OH
(15) R = α-H, β-OAc
(17) R = O



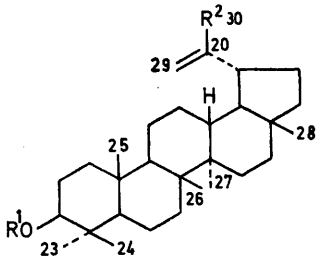
(18)



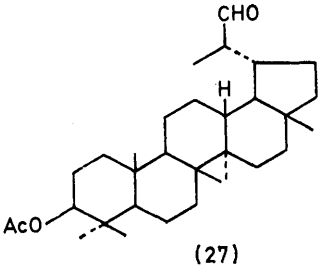
(19)



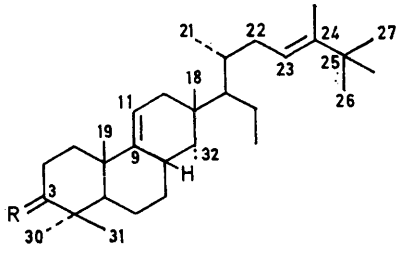
(20) R = α-H, β-OH
(21) R = α-OH, β-OAc
(22) R = O



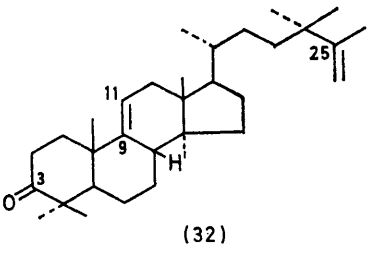
(23) $R^1$=H, $R^2$=CHO
(24) $R^1$=H, $R^2$=$CH_2$·OH
(25) $R^1$=Ac, $R^2$=CHO
(26) $R^1$=Ac, $R^2$=$CH_2$·OAc
(28) $R^1$=Ac, $R^2$=Me



(27)



(29) R = α-H, β-OAc
(30) R = α-H, β-OH
(31) R = O



(32)

to belong to the lanostane series, as do all known $C_{32}$ triterpenoids. One of the double bonds was likely to be at the 9(11)-position, since the mass spectrum of the acetate (29) showed intense peaks at *m/e* 315, 301, and 289, that of the alcohol (30) peaks at 273, 259, and 247, and that of the ketone (31) at 271, 257, and 245.[17,18] That the other double bond was in the side chain was indicated by the presence of the vinylic methyl group. Ozonolysis of (31) gave pinacolone, which indicated the presence of both a methyl and a t-butyl group on the double bond, and the presence of the latter was supported by a signal at δ 1.02 (9 H, s) in the n.m.r. spectra of compounds (29)—(31). Hence the double bond was at C-23, and the additional methyl groups at C-24 and -25; this was confirmed by treating 24,24-dimethyl-lanosta-9(11),25-dien-3-one (32) with perchloric–acetic acid in benzene [17-19] to give 24,25-dimethyl-lanosta-9(11),23-dien-3-one, identical with (31). Hence (30) was 24,25-dimethyl-lanosta-9(11),23-dien-3β-ol, and (29) the corresponding acetate.

The isolation of these three $C_{32}$ triterpenoids represents the second example of such compounds from *Quercus* species, the first being cyclobalanone [24,24-dimethyl-9(19)-cyclolanost-25-en-3-one] from *Q. glauca*.[20]

From the stems and leaves of the three species under examination, altogether two steroids and twenty-seven different triterpenoids have been isolated, five of which belong to each of the oleanane, taraxerane, and lupane, four to the hopane, three to each of the friedelane and lanostane, and one to each of the ursane and arborane series. With the exception of the arborane and hopane types, compounds belonging to all the other series have been found in other *Quercus* species;[21] *Q. championi* appears to be the only such species from which arborane and hopane derivatives have been isolated.

## EXPERIMENTAL

Mass spectra were recorded with a Hitachi–Perkin-Elmer RMU-6E spectrometer, n.m.r. spectra (solvent $CDCl_3$; $Me_4Si$ as internal standard) with a Hitachi R-20 (60 MHz) instrument, i.r. spectra (KBr discs) with a Perkin-Elmer 577 spectrophotometer, and u.v. spectra (solvent 95% ethanol) with a Unicam SP 8000 spectrophotometer. Optical rotations were taken for solutions in $CHCl_3$. 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 °C. 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 of each plant were extracted twice with light petroleum at room temperature for 10 days, and the combined concentrated extracts were chromatographed on alumina. The stems were then extracted twice with 95% ethanol at room temperature for 10 days. The combined extracts were distilled to give a dry residue, which was thoroughly extracted with ether. The combined ethereal solutions were repeatedly shaken with M-sodium hydroxide. The aqueous layers on acidification gave a solid acid mixture, which was then treated with an excess of diazomethane in ether, and the dried product was dissolved in light petroleum, and chromatographed on alumina.

Quercus bambusaefolia.—The crude light petroleum extract (74 g) from air-dried stems (13.5 kg) was chromatographed on alumina (1.5 kg). Light petroleum eluted in succession friedelin (7 g), m.p. 261—262°, $[\alpha]_D$ −28.3°, $\nu_{max.}$ 1 720 $cm^{-1}$ (C=O); taraxerone (2) (0.02 g), m.p. 249—251°, $[\alpha]_D$ +10.0°, $\nu_{max.}$ 1 720 (C=O), 3 050, 1 640, and 840 $cm^{-1}$ (C=CH); compound (1), prisms (from light petroleum) (0.05 g); and friedelan-3β-ol (0.5 g), m.p. 286—289°, $[\alpha]_D$ +23.9°, $\nu_{max.}$ 3 630 $cm^{-1}$ (OH). Light petroleum–benzene (1 : 1) eluted β-amyrin (0.02 g), m.p. 198—201°, $[\alpha]_D$ +86.5°, $\nu_{max.}$ 3 300 (OH), 1 640, and 840 $cm^{-1}$ (C=CH); taraxerol (0.1 g), m.p. 283—285°, $[\alpha]_D$ 0°, $\nu_{max.}$ 3 500 (OH), 3 060, 1 640, and 820 $cm^{-1}$ (C=CH), sitosterol (0.3 g), m.p. 139—140°, $[\alpha]_D$ −35.8°; and compound (3), needles (from light petroleum–chloroform) (0.03 g). Elution with benzene yielded compound (6) as needles (from light petroleum) (0.04 g); 6β-hydroxystigmast-4-en-3-one (0.01 g), m.p. 213—215°, $[\alpha]_D$ +27.5°, $\nu_{max.}$ 3 510 (OH), 1 695, and 1 620 $cm^{-1}$ (C=C–C=O), $\lambda_{max.}$ 246 nm (ε 12 900); and betulin (0.02 g), m.p. 252—254°, $[\alpha]_D$ +18.0°, $\nu_{max.}$ 3 385 (OH), 3 090, 1 650, and 882 $cm^{-1}$ ($C=CH_2$). Elution with benzene–chloroform (1 : 1) gave compound (7), needles (from methanol) (0.04 g).

The methylated acid mixture (7.5 g) was chromatographed on alumina (150 g). Elution with light petroleum gave prisms of 3-methoxyoleana-2,12-dien-1-one (0.015 g), m.p. 234—246°, $[\alpha]_D$ +223.5°, $\nu_{max.}$ 1 675, 1 615 (C=C–C=O), 1 196 (vinyl ether), and 832 $cm^{-1}$ (C=CH–), $\lambda_{max.}$ 251 nm (ε 12 000); and needles of olean-12-ene-1,3-dione (enol form) (2 mg), m.p. 120—125°, resolidified with m.p. 205—208°, $\nu_{max.}$ 3 400 (OH), 1 660, and 1 575 $cm^{-1}$ (C=C–C=O). Elution with light petroleum–benzene (1 : 1) gave methyl betulinate (0.05 g), m.p. 228—230°, $[\alpha]_D$ +7.0°, $\nu_{max.}$ 3 550 (OH), 1 720, 1 174 ($CO_2Me$), 3 080, 1 650, and 880 $cm^{-1}$ ($C=CH_2$); and methyl oleanolate (0.03 g), m.p. 198—201°, $[\alpha]_D$ +70.1°, $\nu_{max.}$ 3 380 (OH), 1 730, 1 160 ($CO_2Me$), 3 030, 1 650, and 850 $cm^{-1}$ (C=CH).

Quercus championi.—The crude light petroleum extract (62 g) from the stems (15 kg) was chromatographed on alumina (1.2 kg). Elution with light petroleum gave friedelin (0.1 g); prisms of compound (13) (0.02 g), m.p. 197—199° (from methanol) $[\alpha]_D$ +83.0°, $M^+$ 424, $\nu_{max.}$ 1 720 (C=O) and 1 675 $cm^{-1}$ (C=C), identical with hop-17(21)-en-3-one; and friedelan-3β-ol (0.02 g). Elution with light petroleum–benzene (1 : 1) gave needles of hop-17(21)-en-3β-ol (12) (0.03 g), m.p. 228—230°, $[\alpha]_D$ +45.3°, $\nu_{max.}$ 3 670 (OH) and 1 675 $cm^{-1}$ (C=C); lupeol (0.5 g), m.p. 194—196°, $[\alpha]_D$ +28.1° $\nu_{max.}$ 3 350 (OH), 3 070, 1 650, and 880 $cm^{-1}$ ($C=CH_2$); β-amyrin (0.04 g); sitosterol (0.1 g); and compound (23), needles (from chloroform) (0.04 g). Benzene eluted compound (14) as needles (from methanol) (0.05 g); and betulin (0.1 g). Benzene–chloroform (1 : 1) eluted compound (24), needles (from methanol) (0.15 g).

The methylated acid mixture (5.7 g) was chromatographed on alumina (120 g). Elution with light petroleum–benzene

[17] W. H. Hui, K. Luk, H. R. Arthur, and S. N. Loo, *J. Chem. Soc.* (*C*), 1971, 2826.
[18] W. S. Chan and W. H. Hui, *J.C.S. Perkin I*, 1973, 490.
[19] R. Ritchie, R. G. Senior, and W. C. Taylor, *Austral. J. Chem.*, 1969, **22**, 2371.
[20] Y. Tachi, S. Taga, Y. Kamamo, and M. Komatsu, *Chem. and Pharm. Bull.* (*Japan*), 1971, **19**, 2193.
[21] H. R. Arthur, P. D. S. Ko, and H. T. Cheung, *Phytochemistry*, 1974, **13**, 2551.

(1 : 1) gave methyl betulinate (0.05 g) and methyl oleanolate (0.01 g).

Quercus myrsinaefolia.—The crude light petroleum extract (47 g) from the stems (18 kg) was chromatographed on alumina (1 kg). Elution with light petroleum gave compound (29), plates (0.025 g); friedelin (0.3 g); compound (31), prisms (from petroleum) (0.15 g); and friedelan-3β-ol (0.1 g). Light petroleum–benzene (1 : 1) eluted lupeol (0.2 g); β-amyrin (0.1 g); sitosterol (0.3 g); and compound (30) (0.02 g), needles (from chloroform–methanol). Benzene eluted 6β-hydroxystigmast-4-en-3-one (0.01 g); and betulin (0.01 g).

The methylated product (10.7 g) was chromatographed on alumina (250 g). Elution with light petroleum–benzene (1 : 1) gave methyl betulinate (0.02 g); methyl ursolate (0.02 g), m.p. 168—170°, $[\alpha]_D$ +63.0°, $\nu_{max.}$ 3 350 (OH), 1 740, 1 200 ($CO_2Me$), 1 640, and 820 $cm^{-1}$ (C=CH); and methyl oleanolate (0.01 g).

*Compound* (1).—*Taraxera-1,14-dien-3-one* (1) had m.p. 247—248°, $[\alpha]_D$ −10.0° (*c* 0.5) (Found: C, 85.3; H, 11.0%; $M^+$, 422. $C_{30}H_{46}O$ requires C, 85.2; H, 11.0%; *M*, 422).

*Hydrogenation of Compound* (1).—Compound (1) (0.03 g) in hexane–chloroform (1 : 1) (50 ml) was shaken with Adams catalyst (5 mg) in hydrogen at room temperature and atmospheric pressure for 1 h. The product was recrystallized from light petroleum–chloroform to give prisms (0.025 g), m.p. 249—250°, $[\alpha]_D$ ±0°, $\nu_{max.}$ 3 055, 1 720, 1 640, and 820 $cm^{-1}$, identical with taraxerone (2).

*Dehydrogenation of Taraxerone* (2).—Taraxerone (2) (0.3 g) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.3 g) in dried dioxan (freshly distilled over sodium) (100 ml) were refluxed for 3 days. On cooling, the precipitated solid was filtered off, and the filtrate was diluted with water and extracted with ether. The residue (0.15 g) from the dried ethereal extracts was dissolved in light petroleum and chromatographed on alumina (15 g). Elution with light petroleum gave prisms (0.08 g), m.p. 249—250°, $M^+$ 424, $\nu_{max.}$ 3 055, 1 720, 1 640, and 820 $cm^{-1}$, identified as unchanged taraxerone (2), then prisms of taraxera-1,14-dien-3-one (0.05 g), m.p. 247—248°, $[\alpha]_D$ −10.5°, $M^+$ 422, $\nu_{max.}$ 3 090, 3 050, 1 670, and 827 $cm^{-1}$, identical with compound (1).

*Compound* (3).—Olean-12-ene-3,16-dione (3) (maniladione) had m.p. 210—211°, $[\alpha]_D$ +49.5° (*c* 0.3) (lit.,[9] m.p. 209—210°, $[\alpha]_D$ +48°), $M^+$ 438.

*Compound* (6).—Taraxer-14-ene-3,16-dione (6) had m.p. 263—264°, $[\alpha]_D$ +83.0° (*c* 0.3) (lit.,[12] m.p. 261°), $M^+$ 438.

*Oxidation of Olean-12-ene-3β,16β-diol (Maniladiol)* (4).—Compound (4) (0.011 g), m.p. 220—222°, obtained by hydrolysis of the diformate (5), was treated with Jones reagent to give needles of maniladione (5 mg), m.p. 209—211° (from chloroform), $\nu_{max.}$ 1 720, 1 700, 1 620, and 825 $cm^{-1}$, identical with compound (3).

*Isomerization of Compound* (6) *in Acid.*—Compound (6) (0.025 g) was suspended in glacial acetic acid (15 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 precipitate obtained on addition of M-sodium hydroxide was recrystallized from chloroform to give needles (0.02 g), m.p. 209—216°, identical with olean-12-ene-3,16-dione (3).

*Allylic Oxidation of Taraxerone* (2).—Taraxerone (2) (0.2 g) was treated with chromium trioxide (0.2 g) in glacial acetic acid (150 ml) at 80 °C for 6 h. The product (0.15 g) in light petroleum was chromatographed over alumina (100 g). Elution with light petroleum gave prisms of taraxerone (2) (0.07 g), m.p. 249—251°; elution with light petroleum–benzene (1 : 1) gave needles of olean-12-ene-3,16-dione (3) (0.02 g), m.p. 209—210°, $M^+$ 438; and elution with benzene, needles of taraxer-14-ene-3,16-dione (0.025 g), m.p. 261—263°, $[\alpha]_D$ +80.0°, $M^+$ 438, $\nu_{max.}$ 1 708, 1 680, and 1 620 $cm^{-1}$, identical with compound (6).

*Compound* (7).—*Taraxer-14-ene-3β,16α-diol* (7) had m.p. 231—234°, $[\alpha]_D$ −20.0° (*c* 0.1) (Found: C, 81.2; H, 10.95%; $M^+$, 442. $C_{30}H_{50}O_2$ requires C, 81.4; H, 11.35%; *M*, 442). Treatment with cold acetic anhydride–pyridine for 12 h gave the diacetate (8) (0.035 g), m.p. 196—198°, $[\alpha]_D$ +18.0° (*c* 0.2), $M^+$ 526, $\nu_{max.}$ 1 735, 1 250 (OAc), 1 640, and 840 $cm^{-1}$ (C=CH).

*Oxidation of Compound* (7).—Compound (7) (0.03 g) in pyridine (40 ml) was stirred with a suspension of chromium trioxide (0.10 g) in pyridine (3 ml) at 0 °C for 3 h, then at room temperature for 12 h. The product was extracted into benzene and recrystallized from chloroform to give needles (0.015 g), m.p. 261—263°, $\nu_{max.}$ 1 708, 1 680, and 1 620 $cm^{-1}$, identical with taraxer-14-ene-3,16-dione (6).

*Reduction of the Diketone* (6).—Compound (6) (0.035 g) was refluxed with sodium borohydride (0.1 g) in propan-2-ol (25 ml) for 3 h. The product (0.03 g), m.p. 230—231°, $\nu_{max.}$ 3 300, 1 640, and 840 $cm^{-1}$, was identical with compound (7).

*Acid-catalysed Isomerization of the Diacetate* (8).—Compound (8) (0.035 g) in glacial acetic acid was treated with concentrated hydrochloric acid (5 ml) at 90 °C for 15 min to give needles of compound (10) (0.03 g), m.p. 227—228°, $[\alpha]_D$ +12.0°, $M^+$ 526, $\nu_{max.}$ 1 730, 1 255 (OAc), 1 630, and 820 $cm^{-1}$ (C=CH).

*Hydrolysis of Compound* (10) *and Oxidation of the Product* (11).—Compound (10) (0.03 g) was refluxed with 5% potassium hydroxide in methanol for 4 h to give needles of compound (11) (0.025 g), m.p. 198—200°, $[\alpha]_D$ +56.5°, $M^+$ 442, $\nu_{max.}$ 3 380 (OH), 1 640, and 820 $cm^{-1}$ (C=CH). Compound (11) (0.02 g) on treatment with Jones reagent gave a diketone (0.013 g), identical with olean-12-ene-3,16-dione (3).

*Reduction of the Diketone* (3).—Compound (3) (0.04 g) was refluxed with sodium borohydride in propan-2-ol for 4 h. The product was recrystallized from methanol to give needles of olean-12-ene-3β,16α-diol (0.035 g), m.p. 199—200°, $[\alpha]_D$ +55.0° (lit.,[22] m.p. 197—198°, $[\alpha]_D$ +54.5°),

TABLE 1

Tertiary methyl resonances (δ values)

| Compound | C-23 | C-24 | C-25 | C-26 | C-27 | C-28 | C-29 | C-30 |
|---|---|---|---|---|---|---|---|---|
| (1) | 1.08 | 1.06 | 1.06 | 1.20 | 1.08 | 0.83 | 0.90 | 0.93 |
| (3) | 1.07 | 0.94 | 1.04 | 1.07 | 1.10 | 1.37 | 0.92 | 0.94 |
| (7) | 0.97 | 0.79 | 0.92 | 1.10 | 0.79 | 0.79 | 0.91 | 0.97 |
| (8) | 0.87 | 0.89 | 0.89 | 0.97 | 0.82 | 0.82 | 0.89 | 0.89 |
| (10) | 0.87 | 0.89 | 0.99 | 1.09 | 1.17 | 0.99 | 0.89 | 0.89 |
| (11) | 1.01 | 0.79 | 0.95 | 1.09 | 1.09 | 0.97 | 0.97 | 0.97 |

$M^+$ 442, $\nu_{max.}$ 3 380 (OH), 1 640, and 820 $cm^{-1}$ (C=CH), δ 3.22 (1 H, q, $J_{ax.eq}$ 7, $J_{ax.ax}$ 10 Hz, 3α-H), 3.71 (1 H, q, *J* 2 and 3 Hz, 16β-H), and 5.28 (1 H, q, *J* 3 and 4 Hz, 12-H), which yielded a diacetate, m.p. 229—230°, $[\alpha]_D$ +12.0° (lit.,[22] m.p. 227—228°, $[\alpha]_D$ +11.3°), $M^+$ 526, $\nu_{max.}$ 1 730, 1 255 (OAc), 1 630, and 820 $cm^{-1}$ (C=CH), δ 4.49 (1 H, q, $J_{ax.eq}$ 7, $J_{ax.ax}$ 10 Hz, 3α-H), 4.82 (1 H, q, *J* 2 and 3 Hz,

[22] O. Jeger, Cl. Nisoli, and L. Ruzicka, *Helv. Chim. Acta*, 1946, **29**, 1183.

16β-H), and 5.30 (1 H, q, *J* 3 and 4 Hz, 12-H). These products were identical with compounds (11) and (10), respectively.

*Compound* (14).—21α*H-Hopane*-3β,22-*diol* (14) had m.p. 209—211°, $[\alpha]_D$ +35.0° (*c* 0.2) (Found: C, 77.9; H, 11.9%; $M^+$, 444. $C_{30}H_{52}O_2,H_2O$ requires C, 77.9; H, 11.8%; $C_{30}H_{52}O_2$ requires *M*, 444). Treatment with acetic anhydride–pyridine at room temperature for 10 h gave plates of the monoacetate (15) (0.025 g), m.p. 225—227°, $[\alpha]_D$ +21.0° (*c* 0.3), $M^+$ 486.

*Attempted Acetylation of the Monoacetate* (15).—Compound (15) (0.02 g) was refluxed with acetic anhydride and pyridine for 4 h. The product (0.02 g), m.p. 259—261°, $[\alpha]_D$ +54.0°, $M^+$ 468, $\nu_{max.}$ 1 740 and 1 250 $cm^{-1}$ (OAc), was identical with hop-17(21)-en-3β-yl acetate (16).

*Oxidation of the Diol* (14).—Compound (16) (0.03 g) was oxidized with Jones reagent. The product (0.022 g), m.p. 214—215°, $[\alpha]_D$ +53.0°, $\nu_{max.}$ 3 470 (OH) and 1 700 $cm^{-1}$ (C=O), was identical with 22-hydroxy-21α*H*-hopan-3-one (17).[4]

*Partial Synthesis of the Diol* (14) *from Moretenone* (18).—Compound (18) (0.05 g) was treated with *m*-chloroperbenzoic acid (0.05 g) in chloroform (50 ml), at 0 °C for 4 h to give needles of the epoxide (19) (0.04 g), m.p. 205—207°, $[\alpha]_D$ +17.0° (*c* 0.5), $M^+$ 440, $\nu_{max.}$ 1 720 (C=O) and 880 $cm^{-1}$ (epoxide). The epoxide (19) (0.03 g) was then refluxed with lithium aluminium hydride (0.03 g) in dry ether (25 ml) for 16 h. The product (0.02 g), m.p. 209—210°, $M^+$ 444, $\nu_{max.}$ 3 470 $cm^{-1}$, was identical with compound (14).

TABLE 2

Tertiary methyl resonances (δ values)

| Compound | C-23 | C-24 | C-25 | C-26 | C-27 | C-28 | C-29 | C-30 |
|---|---|---|---|---|---|---|---|---|
| (14) | 0.98 | 0.76 | 0.82 | 0.98 | 0.93 | 0.69 | 1.20 | 1.20 |
| (15) | 0.84 | 0.84 | 0.84 | 0.98 | 0.92 | 0.69 | 1.22 | 1.22 |
| (17) | 1.09 | 1.03 | 0.95 | 1.03 | 0.95 | 0.70 | 1.20 | 1.20 |
| (20) | 0.98 | 0.77 | 0.82 | 0.96 | 0.94 | 0.77 | 1.20 | 1.20 |
| (21) | 0.84 | 0.84 | 0.84 | 0.96 | 0.93 | 0.76 | 1.20 | 1.20 |
| (22) | 1.08 | 1.02 | 0.95 | 1.02 | 0.96 | 0.78 | 1.20 | 1.20 |
| (19) | 1.08 | 1.02 | 0.94 | 1.02 | 0.94 | 0.65 | | 1.20 |

*Compound* (23).—3β-Hydroxylup-20(29)-en-30-al (23) had m.p. 234—235°, $[\alpha]_D$ +3.0° (*c* 0.3) (lit.,[15] m.p. 232—233°, $[\alpha]_D$ +1.1°), $M^+$ 440, $\nu_{max.}$ 3 320 (OH), 2 845, 2 720, 1 690, and 1 630 $cm^{-1}$ (C=C–CHO), $\lambda_{max.}$ 228 nm (ε 9 800). The monoacetate (25) had m.p. 227—228°, $[\alpha]_D$ +20.0° (lit.,[15] m.p. 224—226°, $[\alpha]_D$ +17.0°), $M^+$ 482, $\nu_{max.}$ 1 740, 1 250 (OAc), 2 825, 2 720, 1 690, and 1 630 $cm^{-1}$ (C=C–CHO), δ 2.02 (3 H, s, OAc).

*Compound* (24).—Lup-20(29)-ene-3β,30-diol (24) had m.p. 235—236°, $[\alpha]_D$ −7.8° (lit.,[23] m.p. 231—233°, $[\alpha]_D$ −3.5°), $M^+$ 442, $\nu_{max.}$ 3 380 (OH), 1 650, and 915 $cm^{-1}$ ($CH_2$=C–$CH_2$-OH).[14] The diacetate (26) had m.p. 165—166°, $[\alpha]_D$ +11.0° (lit.,[23] m.p. 163—164°, $[\alpha]_D$ +9.7°), $M^+$ 526, $\nu_{max.}$ 1 745, 1 245 (OAc), 1 650, and 915 $cm^{-1}$ ($CH_2$=C–$CH_2$·OAc), δ 2.01 (3 H, s, OAc), and 2.08 (3 H, s, $H_2C$=C–$CH_2$·*Ac*).

*Reduction of the Aldehyde* (23).—Compound (23) (0.03 g) was refluxed with lithium aluminium hydride (0.1 g) in dry ether (25 ml) for 2 h to give needles (0.02 g), m.p. 233—234°, $\nu_{max.}$ 3 380, 1 650, and 915 $cm^{-1}$, identical with (24).

*Oxidation of the Diol* (24).—Compound (24) (0.02 g) was shaken with manganese dioxide (0.1 g) in chloroform (25 ml) for 3 days. The product was recrystallized from chloroform to give needles (0.015 g), m.p. 232—234°, $\nu_{max.}$ 3 320, 2 845, 2 720, 1 690, and 1 630 $cm^{-1}$, identical with (23).

*Acid-catalysed Isomerization of the Diol* (24).—Compound (24) (0.03 g) was treated with concentrated hydrochloric acid (5 ml) in glacial acetic acid (50 ml) at room temperature for 18 h. The product was recrystallized from light petroleum to give plates of compound (27) (0.02 g), m.p. 227—229°, $[\alpha]_D$ +10.8° (*c* 0.5), $M^+$ 484, $\nu_{max.}$ 1 730, 1 250 (OAc), 2 840, 2 720, and 1 730 $cm^{-1}$ (CHO).

*Hydrogenation of the Conjugated Aldehyde* (25).—Compound (25) (0.02 g) in chloroform (20 ml) was shaken with Adams catalyst (5 mg) in hydrogen at room temperature for 1 h. The product (0.15 g), m.p. 228—230°, $\nu_{max.}$ 2 840, 2 720, 1 730, and 1 250 $cm^{-1}$, was identical with compound (27).

*Wolff–Kishner Reduction of Compound* (25).—Compound (25) (0.04 g), sodium hydroxide (0.2 g), and hydrazine hydrate (0.2 ml) in diethylene glycol (30 ml) were heated at 120 °C for 1 h, then at 210 °C for 6 h. The product after acetylation was purified by preparative t.l.c. to give needles (0.015 g), m.p. 219—220°, $\nu_{max.}$ 1 735, 1 250 (OAc), 3 070, 1 650, and 880 $cm^{-1}$ (C=$CH_2$), identical with lupenyl acetate (28).

*Partial Synthesis of Compound* (23).—Lupenyl acetate (28) was oxidized with selenium dioxide in acetic acid.[15] Hydrolysis then gave needles of 3β-hydroxylup-20(29)-en-30-al (23).

*Partial Synthesis of Compound* (24).—Lupenyl acetate (28) was oxidized with lead tetra-acetate in acetic acid.[16] Hydrolysis then gave lup-20(29)-ene-3β,30-diol (24).

TABLE 3

Tertiary methyl resonances (δ values)

| Compound | C-23 | C-24 | C-25 | C-26 | C-27 | C-28 |
|---|---|---|---|---|---|---|
| (23) | 0.96 | 0.75 | 0.82 | 1.01 | 0.92 | 0.82 |
| (24) | 0.96 | 0.75 | 0.82 | 1.01 | 0.93 | 0.78 |
| (25) | 0.85 | 0.85 | 0.85 | 1.01 | 0.91 | 0.81 |
| (26) | 0.85 | 0.85 | 0.85 | 1.02 | 0.93 | 0.78 |

*Compound* (29).—24,25-Dimethyl-lanosta-9(11),23-dien-3β-yl acetate (29) had m.p. 209—210°, $[\alpha]_D$ +60.6° (*c* 0.5), $M^+$ 496, $\nu_{max.}$ 3 040, 1 630, and 812 $cm^{-1}$ (C=CH).

*Compound* (30).—24,25-*Dimethyl-lanosta*-9(11),23-*dien*-3β-*ol* (30) had m.p. 194—195°, $[\alpha]_D$ +44.0° (*c* 0.3) (Found: C, 82.8; H, 11.7%; $M^+$, 454. $C_{32}H_{54}O,\frac{1}{2}MeOH$ requires C, 82.9; H, 12.0%. $C_{32}H_{54}O$ requires *M*, 454), $\nu_{max.}$ 3 500, 3 350 (OH), 3 020, 1 630, and 812 $cm^{-1}$ (C=CH).

*Compound* (31).—24,25-*Dimethyl-lanosta*-9(11),23-*dien*-3-*one* had m.p. 146—147°, $[\alpha]_D$ +70.0° (*c* 0.7) (Found: C, 85.0; H, 11.6%; $M^+$, 452. $C_{32}H_{52}O$ requires C, 84.9; H, 11.7%; *M*, 452), $\nu_{max.}$ 1 710 (C=O), 3 020, 1 630, and 815 $cm^{-1}$ (C=CH).

*Hydrolysis of the Acetate* (29).—Compound (29) (0.025 g) was refluxed with 5% potassium hydroxide in methanol (25 ml) to give needles (0.02 g), m.p. 195—196°, $[\alpha]_D$ +45.0°, $M^+$, 454, $\nu_{max.}$ 3 500, 3 350, 3 020, 1 630, and 812 $cm^{-1}$, identical with compound (30).

*Oxidation of the Alcohol* (30).—Compound (30) (0.03 g) was treated with Jones reagent to give prisms (0.02 g), m.p. 145—147°, $[\alpha]_D$ +68.0°, $M^+$, 452, $\nu_{max.}$ 3 020, 1 710, 1 630. and 815 $cm^{-1}$, identical with compound (31).

*Reduction of the Ketone* (31).—Compound (31) (0.025 g) was stirred with lithium aluminium hydride (0.15 g) in dry ether (25 ml) for 3 h to give needles (0.02 g), m.p. 194—196°, identical with compound (30).

*Ozonolysis of* (31).—Compound (31) (0.05 g) in chloroform (50 ml) was treated with ozonized oxygen at 0 °C for 2½ h. The mixture was then steam distilled into a solution of

[23] E. R. H. Jones and R. J. Meakins, *J. Chem. Soc.*, 1941, 757.

2,4-dinitrophenylhydrazine in methanol–sulphuric acid to give yellow needles, m.p. 129—130°, identical with pinacolone 2,4-dinitrophenylhydrazone.

TABLE 4

Tertiary methyl resonances (δ values)

| Compound | C-18 | C-19 | C-26 | C-27 | C-30 | C-31 | C-32 | 25-Me |
|---|---|---|---|---|---|---|---|---|
| (29) | 0.75 | 1.08 | 1.02 | 1.02 | 0.88 | 0.88 | 0.66 | 1.02 |
| (30) | 0.75 | 1.02 | 1.02 | 1.02 | 0.80 | 1.00 | 0.66 | 1.02 |
| (31) | 0.76 | 1.22 | 1.02 | 1.02 | 1.08 | 1.08 | 0.69 | 10.2 |

*Partial Synthesis of* (31) *from* (32).—Compound (32) (0.1 g) in benzene (5 ml), acetic acid (25 ml), was treated with perchloric acid (0.5 ml) at 60 °C for 5 h. The product obtained on dilution with water was recrystallized from light petroleum–chloroform to give prisms of 24,25-dimethyllanosta-9(11),23-dien-3-one (31) (0.06 g), m.p. 145—146°, $[\alpha]_D$ +71.2° (*c* 0.3), $M^+$ 452, $\nu_{max.}$ 3 020, 1 720, 1 630, and 815 $cm^{-1}$

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