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STRUCTURE OF LITSOMENTOL, A NEW TETRACYCLIC TRITERPENE*

T. R. GOVINDACHARI, N. VISWANATHAN and P. A. MOHAMED
CIBA Research Centre, Goregaon East, Bombay 63, India

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Abstract—Litsomentol, a new tetracyclic triterpene, isolated from *Litsea tomentosa*. Heyne, has been shown to have structure Ia by degradation and correlation with agnosterol.

FROM THE BARK of *Litsea tomentosa* Heyne (Family: Lauraceae), besides the known compounds. caryophyllene oxide.[1] β-sitosterol and actinodaphnine. we have isolated a new triterpene alcohol. named litsomentol.[2] By degradation and direct correlation with agnosterol. litsomentol has been shown to have the cucurbitane-based structure (Ia). We present here details of this work.

Litsomentol. m.p. 218–219°. ν_{max}3260 cm^{-1} (OH). analyses for formula $C_{30}H_{52}O_2$. Its mass spectrum fails to show the molecular ion peak. the highest peak being at *m/e* 426. arising from facile dehydration of the compound. The presence of a secondary OH was shown by acetylation to give a monoacetate (Ib) and by oxidation to a ketone. litsomentone (Ic). The latter has ν_{max} 1700 cm^{-1} (six or higher-membered ring ketone) and gives a positive Zimmermann test indicative of a —$CO.CH_2$— group. Dehydration of acetyllitsomentol with potassium bisulphate gave the anhydroacetate (IIb) which was hydrolysed with alkali to anhydrolitsomentol (IIa).

The NMR spectrum ($CDCl_3$. 100 MHz) of acetyllitsomentol (Ib) shows the presence of one vinylic proton as a triplet at δ 5·1 (J = 6 cps). one C*H*–OAc proton as a narrow triplet at δ 4·80 (J = 1·5 cps). one OH at δ 3·10. one acetate Me as a singlet at δ 2·1. two vinylic C–Me groups at δ 1·69 and 1·61. five tertiary C–Me groups as singlets at δ 1·20. 1·04. 1·02. 0·94 and 0·83 and one secondary C–Me as a doublet at δ 0·88 (J = 7 cps).

The NMR spectrum ($CDCl_3$. 100 MHz) of anhydroacetyllitsomentol (IIb) shows the presence of two vinylic protons, at δ 5·47 (dd, J = 6, 1 cps) and 5·05 (t, J = 7 cps), the former arising from the newly formed trisubstituted double bond.

Reduction of litsomentone (Ic) with $NaBH_4$ or LAH gave a mixture of litsomentol (Ia) and 3-*epi*-litsomentol (Id). the latter being characterised as the acetate (Ie). Reduction using Na and n-propanol gave a larger proportion of Id. The multiplicity of the C*H*-OAc proton in acetylllitsomentol (Ib) (t. J = 1·5 cps) showed the hydrogen to be equatorial. In the epimer (Ie). this proton being axial. appears as a broad signal at δ 5·1 coinciding with the vinyl hydrogen. In keeping with this assignment 3-*epi*-litsomentol (eq. OH) is more easily acetylated than litsomentol (ax. OH).

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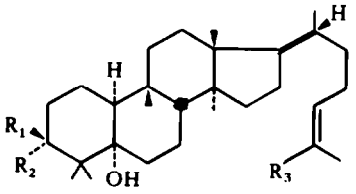
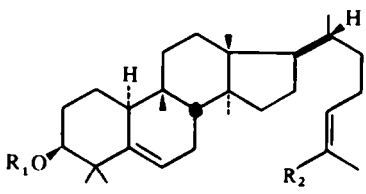


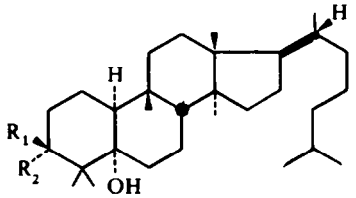
I

a: R_1=OH; R_2=H; R_3=Me
b: R_1=OAc; R_2=H; R_3 = Me
c: R_1R_2=O; R_3=Me
d: R_1=H; R_2=OH; R_3=Me
e: R_1=H; R_2=OAc; R_3=Me
f: R_1=O.C(=O)-C$_6$H$_4$-Br; R_2=H; R_3=Me
g: R_1=OMs; R_2=H; R_3=Me
h: R_1=OAc; R_2=H; R_3=CHO



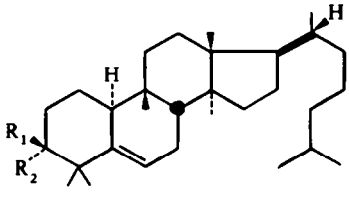
II

a: R_1=H; R_2=Me
b: R_1=Ac; R_2=Me
c: R_1=I.CH_2·CO; R_2=Me
d: R_1=Ac; R_2=CHO



III

a: R_1=OH; R_2=H
b: R_1=OAc; R_2=H
c: R_1=OMs; R_2=H
d: R_1=R_2=H

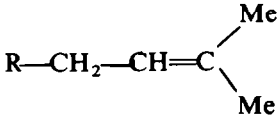


IV

a: R_1=OH; R_2=H
b: R_1=OAc; R_2=H
c: R_1=OMs; R_2=H
d: R_1R_2=O
e: R_1=R_2=H
f: R_1R_2=S·CH_2·CH_2·S
g: R_1=OEt; R_2=H

The presence of a double bond in litsomentol is indicated by the yellow colour it gives with tetranitromethane and by the NMR spectrum of its acetate which shows the presence of an isopropylidene group. This was proved by catalytic reduction to give dihydrolitsomentol (IIIa). The acetate (IIIb) of the latter was dehydrated smoothly with potassium bisulphate to give the anhydrodihydroacetate (IVb) which on aikaline hydrolysis gave anhydrodihydrolitsomentol (IVa).

Epoxidation of acetyllitsomentol (Ib) yielded epoxide V. The presence of an

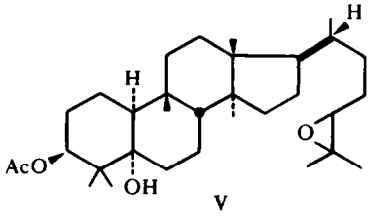


group in litsomentol was shown by ozonolysis of acetyllitso-

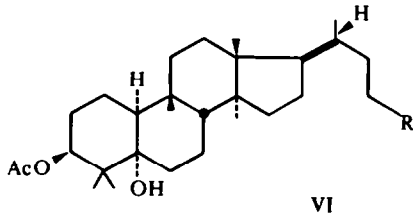
mentol which gave acetone and acetyltrisnorlitsomentic acid (VIa). The latter yielded a methyl ester (VIb) which could be dehydrated to the anhydroester (VIIb). Dehydration of acid VIa gave the anhydroacid (VIIa).

Hydroxylation of litsomentol and acetyllitsomentol with OsO_4 yielded the tetraol (VIIIa) and the triol (VIIIb) respectively. The latter was cleaved by $NaIO_4$ to give the aldehyde (VIc) whose NMR spectrum shows the aldehyde proton as a triplet at δ 9·8. SeO_2 oxidation of acetyllitsomentol yielded two $\alpha.\beta$-unsaturated aldehydes, separated by chromatography, the more polar compound (Ih) arising by oxidation of a vinylic Me to an aldehyde group and the less polar compound (IId) arising by oxidation of the Me and concomitant dehydration of the tertiary OH group.

Treatment of litsomentol with $MeSO_2Cl$ and pyridine gave isoanhydrolitsomentol (IX). Treatment of dihydrolitsomentol with the same reagents under milder conditions yielded a mixture of the mesylate (IIIc) and isoanhydrodihydrolitsomentol (X).

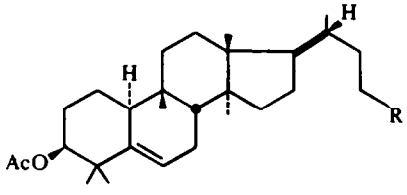


V



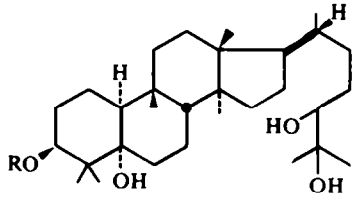
VI

a: R=COOH
b: R=COOMe
c: R=CHO



VII

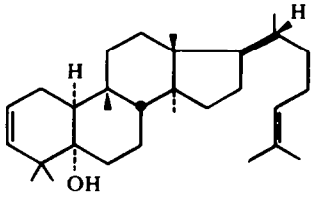
a: R=COOH
b: R=COOMe



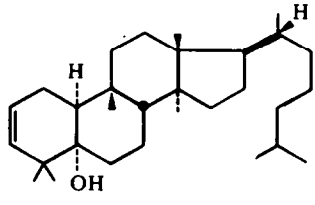
VIII

a: R=H
b: R=Ac

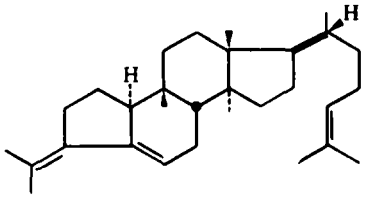
The NMR spectra of both IX and X show that the newly formed double bond is disubstituted, the vinylic protons of X appearing at δ 5·65 apd 5·25. Catalytic reduction of both IX and X yielded 3-desoxydihydrolitsomentol (IIId) which on dehydration with potassium bisulphate gave the hydrocarbon (IVe).



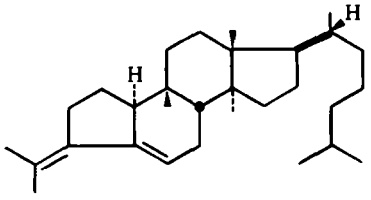
IX



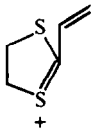
X



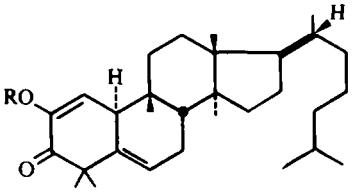
XI



XII



(a)
m/e 131



XIII
a: R = H
b: R = Me

The above data show that litsomentol is a tetracyclic triterpene having five tertiary C-Me, one secondary C—Me, one secondary axial OH, one tertiary OH and a side chain ending with the group $R—CH_2—CH=C\begin{matrix}Me\\Me\end{matrix}$. The secondary OH could be assigned to C_3 since all known tetracyclic triterpenes have an oxygen function at C_3.[3]

The tertiary OH was indicated to be at C_5 since treatment of litsomentol with PCl_5 or formic acid gave a heteroannular conjugated diene hydrocarbon (XI). λ_{max} 243 mμ (log ε 3·70). Anhydrodihydrolitsomentol (IVa) with PCl_5 similarly gave the diene (XII) which was also obtained by solvolysis of the mesylate (IVc). The formation of the diene supports the placement of the OH's in litsomentol at C_3 and C_5, the double bond in the dehydration products being at C_5–C_6.[4,5] This is further corroborated by the mass spectrum of the thioketal (IVf) of anhydrodihydrolitsomentone (IVd) which shows its base peak at *m/e* 131 due to the fragment (a) arising by fission of both the C_1–C_{10} and C_3–C_4 bonds which possess allylic activation.[6]

The presence of a hydrogen at C_{10} in litsomentol was shown by the Barton oxidation of anhydrodihydrolitsomentone (IVd) with t-BuOK and oxygen. The resultant diosphenol (XIIIa) had λ_{max} 273 mμ. shifted to 315 mμ on adding alkali. The NMR spectrum of the diosphenol showed the C_1–H as a doublet at δ 6·12 (J = 2·5 cps), C_6–H at δ 5·65 (multiplet) and C_{10}–H as a triplet (J = 2·5 cps) at δ 3·41. by vicinal coupling with C_1–H and allylic coupling with C_6–H. Methylation of the diosphenol yielded the methyl ether (XIIIb) whose NMR spectrum showed the C_1–H at δ 5·78 (d. J = 2·5 cps). C_6–H at δ 5·68 (m) and C_{10}–H at δ 3·41 (broad singlet), Irradication of the signal at δ 3·41 converted the signal at δ 5·78 into a sharp singlet and the signal at δ 5·68 into a neat quartet. This was strikingly similar to the reported NMR spectra of the diosphenols derived from cucurbitacins.[7]

The presence of a hydrogen at C_{10} and of a OH at C_5 indicated that litsomentol possessed the cucurbitane skeleton. This was supported by the ORD (Fig. 1) and CD

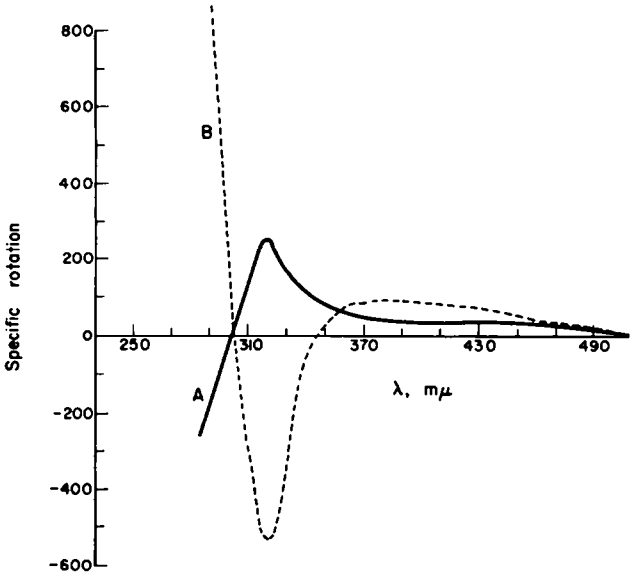


FIG 1. ORD curves: A, Litsomentone (Ic); B, Anhydrodihydrolitsomentone (Ivd)

(Fig. 2) of litsomentone (Ic) and anhydrodihydrolitsomentone (IVd). The CD of Ic is positive whereas that of IVd is negative. The sign and amplitude of the latter are those expected for a 3-ketocucurbitane having a C_5–C_6 double bond.[5,8]

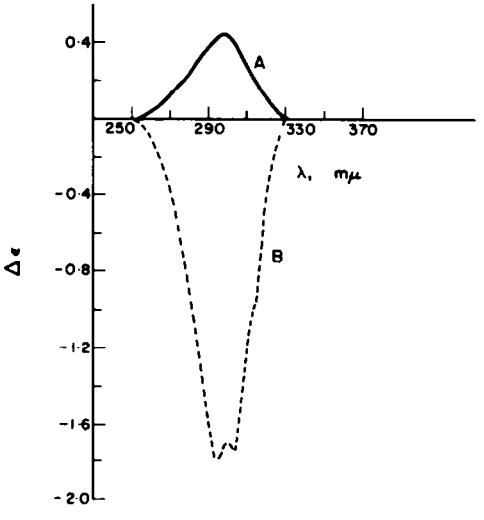
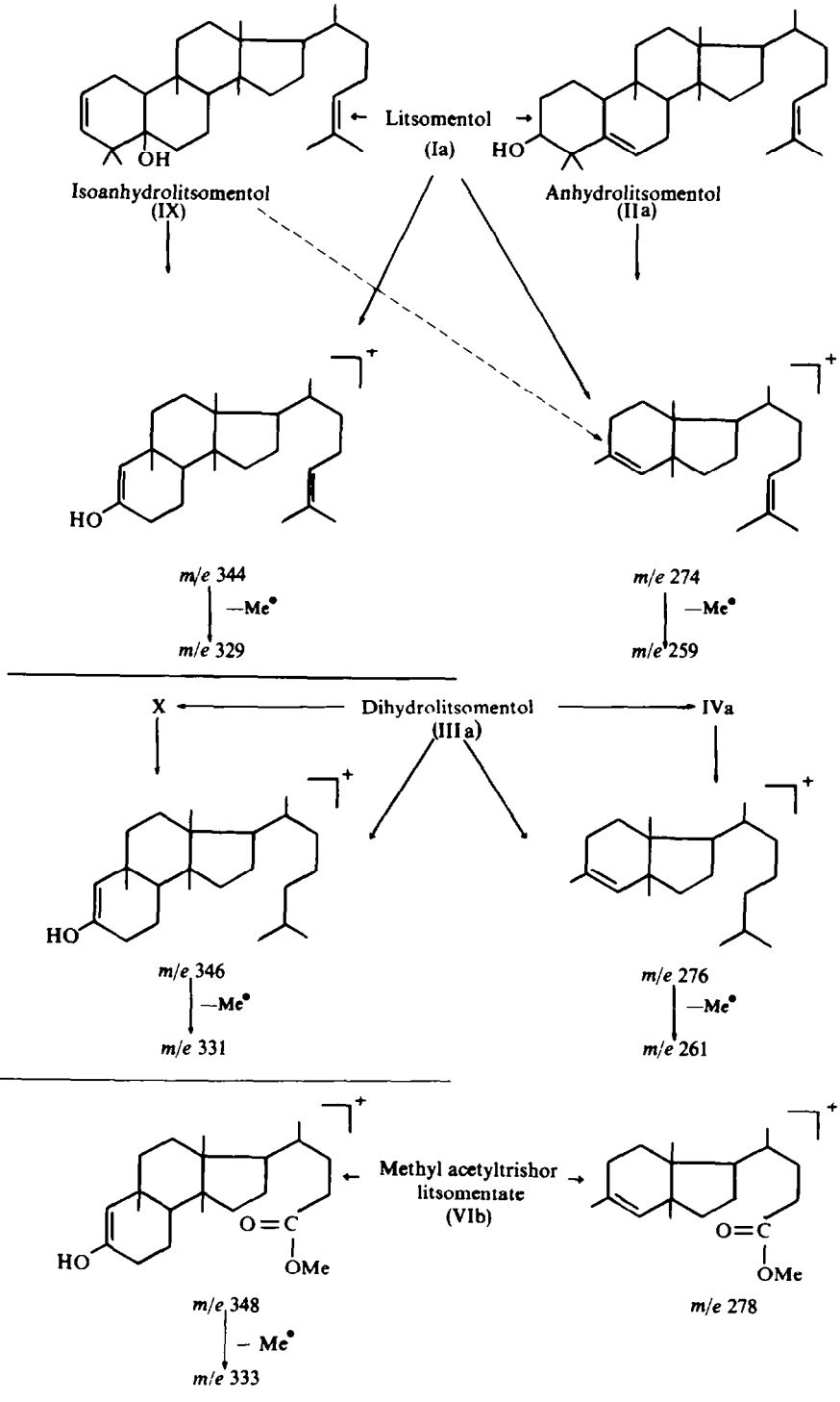
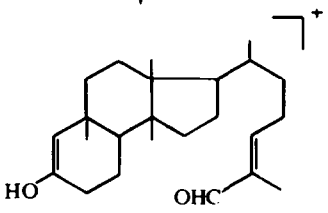


FIG 2. CD curves: A, Litsomentone (Ic); B, Anhydrodihydrolitsomentone (IVd)

The major mass spectral fragmentations of litsomentol and its derivatives can be rationalised as follows on the basis of structure (Ia).


Litsomentol
(Ia)
OH
HO
Isoanhydrolitsomentol
(IX)
Anhydrolitsomentol
(IIa)
HO
m/e 344
—Me•
m/e 329
m/e 274
—Me•
m/e 259
X
Dihydrolitsomentol
(IIIa)
IVa
HO
m/e 346
—Me•
m/e 331
m/e 276
—Me•
m/e 261
Methyl acetyltrishor
litsomentate
(VIb)
HO
O=C
OMe
m/e 348
— Me•
m/e 333
O=C
OMe
m/e 278

Aldehyde (Ih)

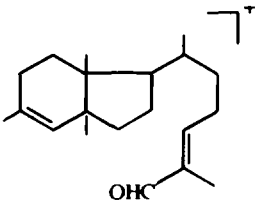


m/e 358

—Me•

m/e 343

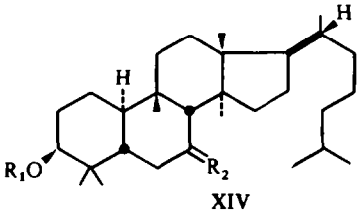
Aldehyde (IId)



m/e 288

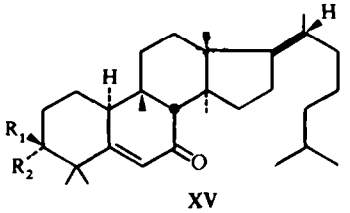
—Me•

m/e 275



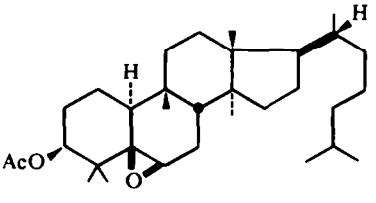
XIV

a: R_1=H; R_2=H_2
b: R_1=Ac; R_2=H_2
c: R_1=H; R_2=O

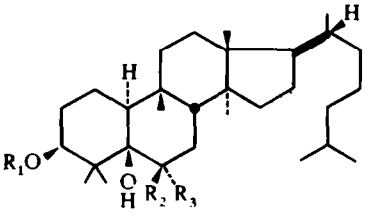


XV

a: R_1=OAc; R_2=H
b: R_1R_2=O

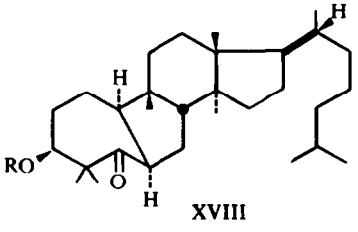


XVI



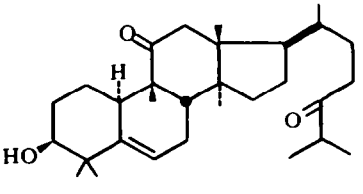
XVII

a: R_1=H; R_2=OH; R_3=H
b: R_1=Ac; R_2=OH; R_3=H
c: R_1=Ac; R_2=OMs; R_3=H
d: R_1=Ac; R_2R_3=O



XVIII

a: R=H
b: R=Ac



XIX

The double bond at C_5–C_6 in anhydrodihydroacetyllitsomentol (IVb) is inert as in the cucurbitacins. Catalytic reduction required very drastic conditions and yielded compound (XIVb) in poor yield. Attempted hydroboration of IVb left the double bond untouched and reduced the Ac group to give the ethyl ether (IV g). Such reductions of ester groups to ethers have previously been reported with diborane.[9] Ozone did not attack the double bond in IVb but oxidised the allylic methylene at C_7 to give the α.β-unsaturated ketone (XVa). This compound was more conveniently obtained by oxidation of IVb with chromic acid. The NMR spectrum of XVa showed the C_6–H at δ 6·1 as a doublet (J = 1·5 cps) due to allylic coupling with the C_{10}–H. C_{10}–H as a broad signal at δ 2·7. C_8–H as a singlet at δ 2·41 and the C*H*-OAc as a triplet (J = 1·5 cps) at δ 4·85. This is very reminiscent of the Δ^5-7-ketones obtained from cucurbitacins.[10] LAH reduction of XVa yielded the saturated ketone (XIVc). Oxidation of anhydrodihydrolitsomentol (IVa) with excess chromic acid also resulted in oxidation of the C_7-methylene to yield the diketone (XV b).

Epoxidation of IVb gave the epoxide (XVI). This is assigned the β-epoxide structure since approach of the peracid from the α-side would be severely hindered by the C_{14}–Me in the most likely conformation of IVb—with ring C as chair to avoid the interaction between the C_9–Me and C_{13}–Me groups.

Hydroxylation of IVb with OsO_4 yielded the diol (XVIIb) which on hydrolysis yielded the triol (XVIIa). Oxidation of XVIIb with Jones reagent yielded the ketol acetate (XVIId), which had ν_{max} 1730 (OAc) and 1710 cm^{-1} (six-membered ring ketone), showing that the double bond in IVb was part of a six-membered ring.

Treatment of the diol (XVIIb) with $MeSO_2Cl$ and pyridine yielded the mesylate (XVIIc) and a ketone assigned formula (XVIIIb). The latter was also obtained by treatment of XVIIc with collidine. Hydrolysis of XVIIIb yielded the keto-alcohol (XVIIIa). Structure XVIIIb is assigned to the keto-acetate on the basis of its spectral properties and by analogy.[11]

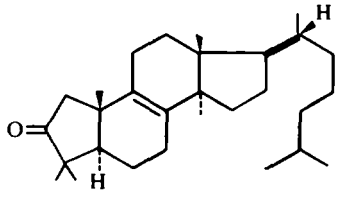
The foregoing evidence lend convincing support for structure (Ia) for litsomentol. In an initial unsuccessful attempt to correlate it with lanost-8.9-ene. the hydrocarbon, 3-desoxyanhydrodihydrolitsomentol (IVe) was subjected to the normal acid-catalysed backbone rearrangement conditions using trifluoroacetic acid, conc. HCl, H_2SO_4 and HCl in phenol. The products obtained were uncharacterisable gums. VPC examination showed them to consist of a mixture of several compounds including starting material.

Biglino *et al.*[5] had assigned structure XIX to bryogenin isolated from *Bryonia dioica* (Cucurbitaceae). An attempt to relate it to litsomentol failed since the C_{11}-carbonyl of bryogenin could not be reduced even under drastic Wolff-Kishner conditions.

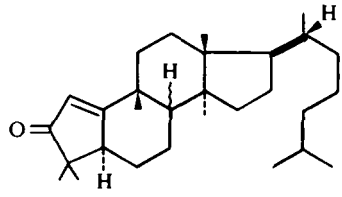
In an independent effort to correlate bryogenin with lanosterol. Ourisson and Ponsinet[12] carried out an acid-catalysed rearrangement of A-norlanostenone (XX) and obtained an α.β-unsaturated ketone assigned structure XXI. This was oxidised to a mixture of amorphous dienediones, the major product which was still non-crystalline being assigned structure XXIIa. The authors however pointed out that the evidence for this structure is not adequate.

With a view to confirm the nature of rings A and B of litsomentol and correlate it with the compound obtained by Ourisson and Ponsinet, the following sequence of reactions was carried out. The diosphenol (XIIIa) mentioned earlier was converted

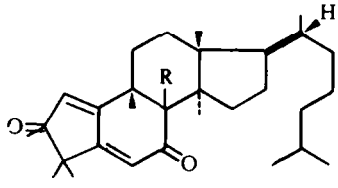
to the benzilic acid (XXIIIa). The derived ester (XXIIIb) was reduced with LAH to the diol (XXIIIc) which was cleaved by $NaIO_4$ to give the A-norketone (XXIVa). Oxidation of this with chromic acid yielded the α.β-unsaturated ketone (XXIVb) which was further oxidised with SeO_2 to yield the diene-dione (XXIIb). This diene-doine was not identical with the compound obtained by Ourisson and Ponsinet.



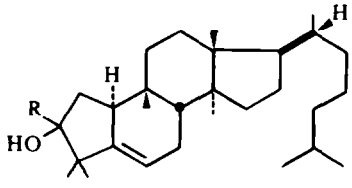
XX



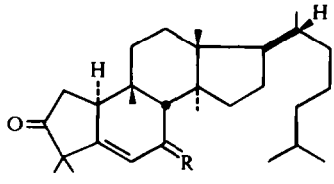
XXI



XXII
a: R=α—H
b: R=β—H



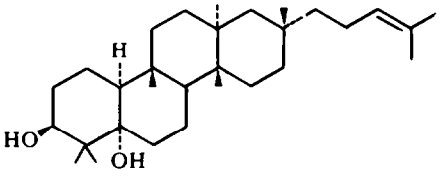
XXIII
a: R=COOH
b: R=COOMe
c: R=CH_2OH



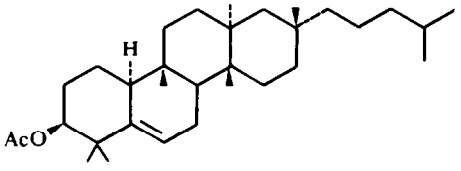
XXIV
a: R=H_2
b: R=O

Treatment of XXIIb with alkali failed to effect epimerisation at C_8. Since the structure of litsomentol has been independently confirmed, the diene-dione from it does have structure XXIIb and it is possible that the product from A-norlanostenone. arising by a drastic acid-catalysed reaction, is the result of a more deep-seated re-arrangement.

The degradation of litsomentol to the diene-dione (XXIIb) establishes the nature of rings A and B. A possible structure (XXV) for litsomentol. based on the shionane skeleton.[13,14] was discounted because of the absence of the diagnostic M-83 peaks in the mass spectrum of litsomentol and its derivatives (M-85 in the dihydro compounds) and by the non-identity of anhydrodihydroacetyllitsomentol (IVb) with the acetate (XXVI) prepared from shionone.[13] Such a shionane-based structure is also discounted by the unmistakable presence of a secondary C–Me in the NMR spectrum of acetyllitsomentol.

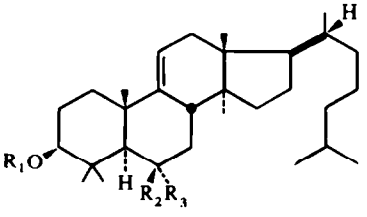


XXV



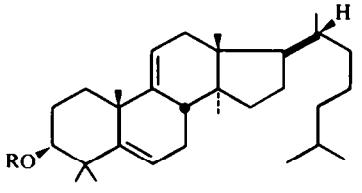
XXVI

A successful correlation of litsomentol with lanosterol was finally achieved as follows: The epoxide (XVI) of anhydrodihydroacetyllitsomentol. on treatment with $BF_3.Et_2O$ yielded a secondary alcohol (XXVIIb). possessing a trisubstituted double bond. Hydrolysis of XXVIIb yielded the diol (XXVIIa). the vinyl hydrogen of which appeared in the NMR spectrum as a quartet at δ 5·32. Oxidation of XXVIIb with chromic acid yielded the ketoacetate (XXVIIc). ν_{max} 1735 (OAc). 1710 cm^{-1} (ketone). Treatment of XXVIIb with $MeSO_2Cl$ and pyridine yielded the non-conjugated diene (XXVIIIb) whose vinylic hydrogens appeared in the NMR spectrum at δ 5·73 (t) and 5·38 (dd). Hydrolysis of XXVIIIb with alkali gave XXVIIIa without isomerising the double bonds. Treatment of XXVIIIb with N-lithioethylenediamine,[15] however, effected isomerisation as well as hydrolysis to yield a conjugated diene alcohol. m.p. 157°. whose physical and spectral properties agreed with the reported values for dihydroagnosterol (XXIXa).[3,16] a known constituent of sheep's wool fat. Acetylation of XXIXa gave the acetate (XXIXb). m.p. 167–168°. identical with an authentic sample of dihydroagnosterol acetate.



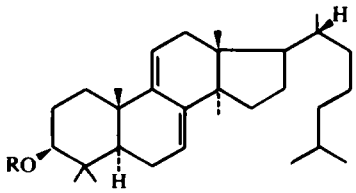
XXVII

a: R_1=R_3=H; R_2=OH
b: R_1=Ac; R_2=OH; R_3=H
c: R_1=Ac; R_2R_3=O



XXVIII

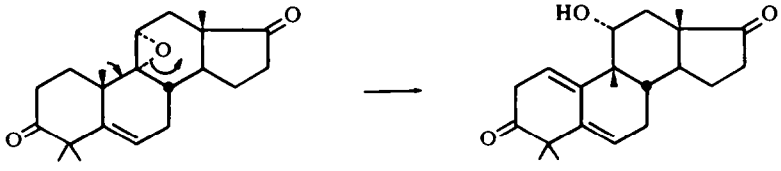
a: R=H
b: R=Ac



XXIX
a: R=H
b: R=Ac

This correlation confirms the gross structure of litsomentol as well as the stereochemistry at all the centres except that of the tertiary OH at C_5. Since the C_3-OH has been shown to be β (axial) and since litsomentol fails to form cyclic derivatives with reagents like phosgene, thiophosgene and benzaldehyde, the C_5-OH must be α (equatorial). This is also in keeping with the fact that dehydration of the tertiary OH proceeds to give a C_5–C_6 double bond and not a C_5–C_{10} double bond, indicating that the C_5-OH and C_{10}-H are *cis* to each other.

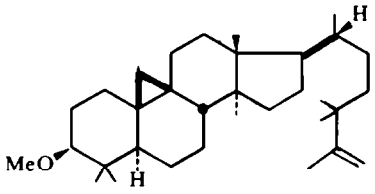
The conversion of litsomentol to dihydroagnosterol represents a simple correlation of the cucurbitanes and the lanostanes. The skeletal rearrangement observed in the opening of the epoxide (XVI) is a reversal of the recently reported rearrangement of XXX to XXXI.[17] The only other correlation between the cucurbitane and lanostane series has been reported by Barton *et al.*[18] who converted eburicoic acid and cucurbitacin A to a common intermediate by two extended series of reactions.



XXX XXXI

The cucurbitacins have been encountered mainly in plants belonging to the Cucurbitaceae family. Exceptions to this are the isolation of some cucurbitacins from plants of the Cruciferae.[19] Scrophulariaceae[20,21] and Begoniaceae.[22] Litsomentol is the only member of the cucurbitacin group to be isolated from a plant belonging to the Lauraceae family. It represents the simplest member of the group and is unique in lacking an oxygen function at C_{11}.

It is interesting to note that the plant *Neolitsea dealbata* R.Br. Merr. (Lauraceae) which is closely related to *Litsea tomentosa* Heyne contains cycloneolitsin (XXXII)[23,24] which has a cycloartenol skeleton. The isolation of litsomentol and cycloneolitsin from two closely related species supports the intermediacy of cycloartenol in the biosynthesis[25] of the cucurbitacins.



XXXII

EXPERIMENTAL

M.ps are uncorrected. UV spectra were measured in EtOH on a Beckman DK 2A spectrophotometer and IR spectra on a Perkin-Elmer Model 421. Optical rotations were determined in 2–3% soln in $CHCl_3$ at 25° NMR spectra. unless otherwise stated. were recorded on a Varian A-60 instrument in $CDCl_3$. Figures given in parenthesis in the mass spectral fragmentations refer to the relative intensities of the ions concerned.

Isolation. The air-dried powdered bark (10 kg) of *Litsea tomentosa* Heyne. collected in Mysore State. was extracted repeatedly with hot hexane, the combined extracts concentrated and left on ice for a week. The solid that separated was filtered. washed with hexane and crystallised from $CHCl_3$-MeOH to yield litsomentol (Ia) (6 g). m.p. 218–219°. $[\alpha]_D \pm 0°$. ν_{max}(Nujol) 3260 cm^{-1} (Found: C. 80·61; H. 11·71; active H. 0·36. $C_{30}H_{52}O_2$ requires: C. 81·02; H. 11·79; active H. 0·45%). Mass spectrum: *m/e* 426 ($M-H_2O$) (41). 411 (20). 408 (6). 344 (65). 329 (100). 274 (45). 259 (28). 231 (33). 205 (16). 163 (32). 149 (55). 135 (22). 123 (32). 121 (35). 119 (38). 109 (46). 107 (41). 105 (63). 95 (44). 69 (57). Litsomentol gives a yellow colour with tetranitromethane. NMR (CF_3CO_2H): δ5·37 (1H. br). 3·55 (1H. br). 1·62 (6H. s).

The oil. after removal of litsomentol. was chromatographed over silica gel in hexane and eluted successively with hexane. C_6H_6-hexane. C_6H_6 and $CHCl_3$. The fractions eluted by hexane and C_6H_6-hexane were combined and rechromatographed to give caryophyllene oxide.[1] m.p. 62–63° (from MeOH). $[\alpha]_D$ 69·3°. ν_{max}(CH_2Cl_2) 1610 cm^{-1}. identical (m.m.p., TLC. IR. NMR) with an authentic sample. (Found: C. 81·72; H. 10·77. Calc. for $C_{15}H_{24}O$: C. 81·76; H. 10·98%). Mass spectrum: *m/e* 220 (M^+). NMR: δ 4·91 (1H. d. J = 1·5 cps). 4·8 (1H. d. J = 1·5 cps). 1·12 (3H. s). 1·0 (3H. s). 0·97 (3H. s). The fractions eluted by $CHCl_3$ yielded β-sitosterol. identical with an authentic sample.

The defatted bark was extracted with MeOH. the extract concentrated and treated with 0·5N HCl. The acid soln was filtered. basified with NH_4OH and extracted with CH_2Cl_2 to yield the crude alkaloid (7 g). Chromatography over silica in $CHCl_3$ yielded actinodaphnine (2·5 g). m.p. 210° (from MeOH-ether). $[\alpha]_D$ + 40·5°. M^+ at *m/e* 311, identical (m.m.p., TLC. UV. IR. NMR) with an authentic sample.

Acetyllitsomentol (Ib). Litsomentol (2 g) was refluxed with Ac_2O (15 ml) and Py (10 ml) for 5 hr. cooled and poured on ice. The solid that separated was filtered and crystallised from $CHCl_3$-MeOH to yield Ib (1·8 g). m.p. 166–168 . $[\alpha]_D$ + 26·7°. ν_{max}(Nujol) 3560. 1740 cm^{-1} (Found: C. 79·10; H. 10·94. $C_{32}H_{54}O_3$ requires: C. 78·96; H. 11·18%). Mass spectrum: *m/e* 486 (M^+) (1). 468 (2). 453 (1). 426 (15). 344 (48). 329 (100). 274 (5). 259 (8). 231 (22). Hydrolysis of acetyllitsomentol with 7% KOH in MeOH gave back litsomentol.

Anyhydrocetyllitsomentol (IIb). Acetyllitsomentol (1 g) was mixed with fused $KHSO_4$ (2 g) and heated at 160° for 1 hr. The mixture was cooled. extracted with ether and the product chromatographed over Al_2O_3 in C_6H_6 to yield IIb (0·7 g). m.p. 114–115° (from MeOH). $[\alpha]_D$ + 62·7°. ν_{max}(Nujol) 1740 cm^{-1} (Found: C. 81·72; H. 11·46. $C_{32}H_{52}O_2$ requires: C. 81·99; H. 11·18%). Mass spectrum: *m/e* 468 (M^+) (48). 453 (4). 408 (37). 393 (8). 274 (100). 259 (48). 231 (6). 205 (12). 189 (14). 173 (12). 163 (30). 150 (24). 134 (66), 123 (44). NMR ($CDCl_3$, 100 MHz δ 5·47 (1H, dd. J = 6, 1 cps). 5·05 (1H. t. J = 7 cps). 4·65 (1H. t. J = 2 cps). 1·96 (3H. s). 1·64 (3H. s). 1·56 (3H. s). 1·21 (3H. d. J = 6 cps). 1·02 (6H. s). 0·88 (3H. s). 0·83 (3H. s). 0·79 (3H. s).

Anhydrolitsomentol (IIa): The acetate (IIb) (1 g) was refluxed for 4 hr with methanolic KOH (7%; 40 ml) to yield IIa (0·9 g). m.p. 90–92° (from MeOH). $[\alpha]_D$ + 39·4°. ν_{max}(Nujol) 3360 cm^{-1}. (Found: C. 84·26; H. 12·03. $C_{30}H_{50}O$ requires: C. 84 44; H. 11 81%). Mass spectrum: *m/e* 426 (M^+) (100). 411 (32). 408 (40). 393 (12). 275 (80). 274 (90). 259 (80). 231 (19). 205 (40). 163 (57). 149 (40). 134 (62). 123 (53). 109 (47).

(b): Dehydration of litsomentol (2 g) with fused $KHSO_4$ (3·6 g) at 160° for 45 min and chromatography of the product over Al_2O_3 in C_6H_6-hexane yielded IIa (0·7 g). identical with the above product.

Litsomentone (Ic). A soln of Ia (1 g) in Py (10 ml) was added to Py–CrO_3 complex (prepared from 1 g

CrO_3 and 10 ml Py) and the mixture stirred overnight at 25°. C_6H_6 (100 ml) was added, the soln filtered, washed with dil HCl and H_2O, dried and evaporated. The residue crystallised from MeOH as needles (0·8 g), m.p. 170–172°, $[\alpha]_D$ + 16·3°, ν_{max} (CH_2Cl_2) 1700 cm^{-1}. (Found: C, 81·29; H, 11·34. $C_{30}H_{50}O_2$ requires: C, 81·39; H, 11·38%). Mass spectrum: *m/e* 442 (M^+) (66), 427 (100), 424 (11), 409 (8), 399 (9), 357 (11), 329 (13), 311 (7), 305 (4), 286 (16), 271 (4), 245 (5), 235 (8), 219 (9), 205 (21), 191 (7), 173 (9). NMR: δ 5·15 (1H, br), 1·7 (3H, d, J = 1·5 cps), 1·6 (3H, d, J = 1·5 cps), 1·17 (6H, s), 1·12 (3H, s), 1·03 (3H, s), 0·92 (3H, d, J = 6 cps), 0·86 (3H, s). ORD (dioxane, 2%): $[\alpha]_{590}$ + 16°, $[\alpha]_{315}$ + 190°, $[\alpha]_{285}$ − 260°. CD (dioxane): λ_{max} 298 mμ ($\Delta\varepsilon$ + 0·44).

Reduction of litsomentone. (a) *With* $NaBH_4$. $NaBH_4$ (1 g) was added to a soln of Ic (0·8 g) in MeOH (60 ml), kept at 40–50° for 12 hr and concentrated to 30 ml. The solid (0·4 g) that separated was identical (m.m.p., TLC) with litsomentol. The filtrate was evaporated, diluted with H_2O and extracted with $CHCl_3$. TLC showed the product to be a mixture of litsomentol and a slightly more polar compound which could not be separated satisfactorily by chromatography. Acetylation of the mixture with Ac_2O (2 ml) and Py (1 ml) at 30° and chromatography over silica in C_6H_6 yielded 3-*epi*-acetyllitsomentol (Ie) (0·2 g), m.p. 167–169° (from $CHCl_3$–MeOH), which was depressed on admixture with acetyllitsomentol. $[\alpha]_D$ − 31·6°, ν_{max} ($CHCl_3$) 3600, 1725 cm^{-1} (Found: C, 78·66; H, 11·33. $C_{32}H_{54}O_3$ requires: C, 78·96; H, 11·18%). Mass spectrum: *m/e* 486 (M^+) (1), 471 (1), 468 (1), 426 (3), 411 (6), 393 (2), 357 (3), 344 (20), 329 (100), 259 (7), 231 (30). NMR: δ 5·1 (2H, m), 1·7 (3H, d, J = 1 cps), 1·6 (3H, d, J = 1 cps), 1·21 (3H, s).

(b) *With* LAH. Ic (0·5 g) in dry THF (35 ml) was reduced with LAH (1 g) in the usual manner to yield Ia (0·3 g) and Id (70 mg), the latter being characterised as the acetate (Ie).

(c) *With* Na *and* n-PrOH. A soln of Ic (0·8 g) in boiling n-PrOH (140 ml) was treated with Na (9 g). After refluxing for 1 hr, the soln was evaporated, diluted with H_2O and extracted with CH_2Cl_2 to yield Ia (0·2 g) and Id (0·4 g), the latter being characterised as the acetate (Ie).

Dihydroacetyllitsomentol (IIIb). A soln of acetyllitsomentol (Ib) (2 g) in a mixture of AcOH (50 ml) and EtOAc (50 ml) was shaken for 6 hr with H_2 (40 lbs/in^2) in presence of PtO_2 (0·3 g). The soln was filtered, evaporated and the product crystallised from $CHCl_3$–MeOH to yield IIIb (1·9 g), m.p. 170°, $[\alpha]_D$ + 26·5°, ν_{max} (CH_2Cl_2) 1740 cm^{-1} (Found: C, 78·68; H, 11·60. $C_{32}H_{56}O_3$ requires: C, 78·63; H, 11·55%). Mass spectrum: *m/e* 488 (M^+) (1), 428 (10), 413 (11), 346 (80), 331 (100), 276 (6), 233 (7), 163 (5), 137 (5), 123 (7), 107 (10), 95 (20). NMR ($CDCl_3$, 100 MHz): δ 4·78 (1H, t, J = 1·5 cps), 3·05 (1H, s, OH), 2·04 (3H, s), 1·18 (3H, s), 1·02 (3H, s), 0·99 (3H, s), 0·93 (3H, s), 0·86 (6H, s), 0·82 (6H, s).

Dihydrolitsomentol (IIIa). (a): Litsomentol (1 g) in EtOAc (70 ml) was reduced with H_2 at 50–60° at 40 lbs/in^2 using PtO_2 (0·2 g) to yield IIIa (1 g), m.p. 218–220° (from $CHCl_3$–MeOH). $[\alpha]_D$ + 1·6°, ν_{max} (Nujol) 3340, 3260 cm^{-1} (Found: C, 80·87; H, 12·15. $C_{30}H_{54}O_2$ requires: C, 80·65; H, 12·18%). This gave no colour with tetranitromethane. Mass spectrum: *m/e* 446 (M^+) (< 1), 428 (18), 413 (20), 346 (60), 331 (100), 276 (54), 261 (30), 233 (11), 163 (48), 152 (18), 150 (20), 134 (45), 123 (45), 107 (40), 95 (66).

(b): A soln of IIIb (2 g) in dioxane (60 ml) was refluxed with KOH (6 g) for 4 hr, concentrated *in vacuo* and diluted with H_2O to yield IIIa (1·8 g), m.p. 218–220°, identical with the above sample.

Acetylation of IIIa (Py, Ac_2O) gave IIIb.

Anhydrodihydroacetyllitsomentol (IVb). (a): Dehydration of IIIb (2 g) with fused $KHSO_4$ (4 g) and chromatography of the product over Al_2O_3 in hexane yielded IVb (1·3 g), m.p. 116–117° (from ether–MeOH), $[\alpha]_D$ + 58·8°, ν_{max} (KBr) 1735 cm^{-1} (Found: C, 81·86; H, 11·76. $C_{32}H_{54}O_2$ requires: C, 81·64; H, 11·56%). Mass spectrum: *m/e* 470 (M^+) (4), 455 (4), 410 (10), 395 (10), 331 (6), 276 (100), 261 (75), 163 (90), 150 (45), 134 (59), 123 (60), 107 (30), 95 (45). NMR: δ 5·56 (1H, dd, J= 6, 2 cps), 4·75 (1H, t, J = 2 cps), 2·0 (3H, s), 1·05 (6H, s), 0·91 (9H, s), 0·87 (3H, s), 0·83 (3H, s).

(b): A soln of IIIb (0·2 g) in AcOH (5 ml) was heated with 2N H_2SO_4 (0·2 ml) at 110° for 1 hr. Dilution with H_2O and extraction with ether gave IVb (50 mg), identical with the above product.

Anhydrodihydrolitsomentol (IVa). A soln of IVb (2 g) in dioxan (20 ml) was refluxed with methanolic KOH (10%; 100 ml) for 4 hr to yield IVa (1·8 g), m.p. 98–100° (from $CHCl_3$–MeOH) $[\alpha]_D$ + 47·8°, ν_{max} (CH_2Cl_2) 3600, 3450 cm^{-1} (Found: C, 84·11; H, 12·33. $C_{30}H_{52}O$ requires: C, 84·04; H, 12·23%). Mass spectrum: *m/e* 428 (M^+) (7), 413 (12), 410 (4), 395 (8), 276 (67), 261 (80), 163 (100), 150 (61), 137 (43), 134 (70), 123 (67), 107 (33), 95 (50).

Epoxyacetyllitsomentol (V). Acetyllitsomentol (Ib) (0·5 g) was added to a $CHCl_3$ soln (15 ml) of perbenzoic acid containing 30 mg of peracid per ml. After 48 hr at 5°, the soln was washed with Na_2CO_3 aq, H_2O, dried, evaporated and the product chromatographed over Al_2O_3 in C_6H_6 to yield V (0·4 g), m.p. 182–184° (from $CHCl_3$–MeOH). (Found: C, 76·73; H, 11·05. $C_{32}H_{54}O_4$ requires: C, 76·44; H, 10·83%). NMR: δ 4·82 (1H, t, J = 3 cps), 3·03 (1H, br s, OH), 2·65 (1H, br), 2·09 (3H, s).

Ozonolysis of acetyllitsomentol. (a) *Acetone.* A soln of Ib (1 g) in $CHCl_3$ (40 ml) was ozonised at 0° and the product steam-distilled after addition of Zn dust (0·4 g). the exit tube dipping into a soln of 2,4-dinitrophenylhydrazine in MeOH. The product was chromatographed over Al_2O_3 in C_6H_6 to yield acetone 2,4-DNP. m.p. 120–122° (from MeOH). identical (m.m.p., TLC, IR) with an authentic sample.

(b) *Acetyltrisnorlitsomentic acid* (VIa). A soln of Ib (1 g) in EtOAc (50 ml) was ozonised at 0°. The soln was shaken for 1 hr with H_2 at 1 atm in presence of Pd–C catalyst (5%; 0·2 g), filtered and evaporated. The residue was crystallised from $CHCl_3$–MeOH to yield VIa (0·8 g), m.p. 263–265°. $[\alpha]_D$ + 15·8°. ν_{max} (Nujol) 1740 cm^{-1}. (Found: C, 73·21; H, 10·23. $C_{29}H_{48}O_5$ requires: C, 73·07; H, 10·15%). Mass spectrum: *m/e* 458 ($M-H_2O$) (26). 398 (80). 383 (48). 354 (28). 319 (37). 290 (41). 275 (72). 264 (46). 249 (22). 220 (56). 205 (40). 163 (100). NMR: δ 4·82 (1H, t, J = 1·5 cps). 2·1 (3H, s). 1·22 (3H, s). 1·03 (6H, s). 0·95 (3H, s). 0·83 (3H, s).

Methyl acetyltrisnorlitsomentate (VIb). The above acid (VIa) (0·2 g) in ether (20 ml) was treated with excess CH_2N_2 to yield VIb (0·2 g), m.p. 190–191° (from $CHCl_3$–MeOH). $[\alpha]_D$ + 17·6°. ν_{max}(Nujol) 1745, 1735 cm^{-1}. (Found: C, 73·72; H, 10·45. $C_{30}H_{50}O_5$ requires: 73·43; H, 10·27%). Mass spectrum: *m/e* 490 (M^+) (<1). 472 (2). 430 (14). 415 (10). 348 (75). 333 (100). 330 (11). 278 (37). 233 (26). 215 (98). 209 (22). 206 (20). NMR: δ 4·81 (1H, t, J = 1·5 cps). 3·66 (3H, s). 2·1 (3H, s). 1·2 (3H, s). 1·02 (6H, s). 0·93 (3H, s). 0·8 (3H, s).

Methyl anhydroacetyltrisnorlitsomentate (VIIb). The ester VIb (0·8 g) was heated at 180–200° for 45 min with fused $KHSO_4$ (1·6 g) and the product chromatographed over silica gel in hexane to yield VIIb (0·25 g), m.p. 156–158° (from hexane). $[\alpha]_D$ + 55·8°. ν_{max}(KBr) 1735 cm^{-1} (Found: C, 76·38; H, 10·45. $C_{30}H_{48}O_4$ requires: C, 76·22; H, 10·24%). NMR: δ 5·53 (1H, dd, J = 6, 2 cps). 4·72 (1H, t, J = 2 cps). 3·66 (3H, s). 2·0 (3H, s). 1·05 (2H, s). 0·91 (3H, s). 0·87 (3H, s). 0·83 (3H, s).

Acetylanhydrotrisnorlitsomentic acid (VIIa). Dehydration of VIa (0·4 g) with fused $KHSO_4$ (0·8 g) as above yielded VIIa (80 mg), m.p. 228–231° (from MeOH) Found: C, 75·55; H, 10·21. $C_{29}H_{46}O_4$ requires: C, 75·94; H, 10·11%).

Osmylation of litsomentol. A soln of Ia (0·5 g) in dioxane (20 ml) was treated with OsO_4 (0·5 g) and Py (0·5 ml). After 3 days at 25°, the soln was saturated with H_2S and filtered. The filtrate was evaporated and the residue chromatographed over silica gel in $CHCl_3$. Elution with $CHCl_3$–MeOH (9:1) yielded the tetraol (VIIIa) (0·3 g), m.p. 190–193° (from C_6H_6-hexane). ν_{max}(Nujol) 3350 cm^{-1} (broad) (Found: C, 75·59; H, 11·22. $C_{30}H_{54}O_4$ requires: C, 75·26; H, 11·37%).

Osymlation of Ib as above yielded the triol (VIIIb), m.p. 230–232° (from C_6H_6-hexane). ν_{max}(Nujol) 3580, 3520, 3400, 1730 cm^{-1}. (Found: C, 74·03; H, 10·97. $C_{32}H_{56}O_5$ requires: C, 73·80; H, 10·84%). NMR: δ 4·82 (1H, t, J = 2 cps). 2·56 (3H, br. s, OH). 2·1 (3H, s).

Trisnoraldehyde (VIc). A soln of VIIIb (0·3 g) in MeOH (50 ml) was treated with a soln of $NaIO_4$ (0·5 g) in H_2O (40 ml) and allowed to stand at 25° for 24 hr. Extraction with CH_2Cl_2 gave VIc (0·1 g), m.p. 210–213° (from aq MeOH). ν_{max}(KBr) 3580, 1740, 1725 cm^{-1} (Found: C, 75·20; H, 10·43. $C_{29}H_{48}O_4$ requires: C, 75·60; H, 10·50%). NMR: δ 9·8 (1H, t, J = 1·5 cps). 4·82 (1H, t, J = 1·5 cps). 2·1 (3H, s). 1·2 (3H, s). 1·05 (3H, s). 1·03 (3H, s). 0·95 (3H, s). 0·81 (3H, s).

SeO_2 *oxidation of acetyllitsomentol.* A soln of Ib (1 g) in AcOH (50 ml) was heated at 90° for 2 hr with SeO_2 (1 g). The soln was filtered evaporated *in vacuo* and the residue chromatographed over silica gel in C_6H_6. The column was eluted with C_6H_6 and then with C_6H_6–$CHCl_3$ (3:1). 10 ml fractions, monitored by TLC. The less polar product crystallised from MeOH to yield IId (60 mg), m.p. 138–141°. λ_{max} 230 mμ (log ε 4·20). ν_{max}(KBr) 1740, 1690, 1635 cm^{-1}. (Found: C, 79·76; H, 10·62. $C_{32}H_{50}O_3$ requires: C, 79·62; H, 10·44%). Mass spectrum: *m/e* 482 (M^+) (21). 422 (48). 407 (16). 290 (26). 288 (32). 279 (45). 275 (32). 167 (24). 149 (100). NMR: δ 9·43 (1H, s). 6·5 (1H, t, J = 8 cps). 5·55 (1H, q, J = 6, 1·5 cps). 4·75 (1H, t, J = 2 1·75 (3H, d, J = 1·5 cps). 1·27 (3H, s). 1·05 (6H, s). 0·93 (3H, s). 0·87 (3H, s). The more polar product crystallised from MeOH to give Ih (90 mg), m.p. 165–167°. λ_{max} 230 mμ (log ε 4·23). ν_{max} (KBr) 3580, 1735, 1685, 1640 cm^{-1} (Found: C, 76·38; H, 10·50. $C_{32}H_{52}O_4$ requires: 76·75; H, 10·47%). Mass spectrum: *m/e* 482 ($M-H_2O$) (1). 440 (5). 358 (60). 343 (90). 279 (15). 149 (100). 134 (55). 121 (57). 113 (64). 109 (65). 95 (63). NMR: δ 9·43 (1H, s). 6·5 (1H, t, J = 7 cps). 4·82 (1H, t, J = 1 cps). 3·1 (1H, br s, OH). 2·1 (3H, 1·75 (3H, d, J = 1 cps). 1·22 (3H, s). 1·05 (3H, s). 1·03 (3H, s). 0·95 (3H, s). 0·83 (3H, s).

p-*Bromobenzoyllitsomentol* (If). A soln of Ia (0·5 g) in C_6H_6 (10 ml) and Py (10 ml) was refluxed for 5 hr with *p*-bromobenzoyl chloride (1 g), cooled and poured on ice. Extraction with ether and chromatography of the product over silica gel in C_6H_6 yielded If (0·3 g), m.p. 205–207° (from $CHCl_3$–MeOH). ν_{max}(CH_2Cl_2) 3610, 1735 cm^{-1}. (Found: C, 71·04; H, 8·87. $C_{37}H_{55}O_3Br$ requires:. H, 8·77%). NMR: δ 7·88 (2H, d, J = 9 cps). 7·6 (2H, d, J = 9 cps). 5·1 (1H, br). 5·02 (1H, t, J = 1·5 cps). 4·6 (1H, s, OH). 1·7 (3H, d, J = 1 cps). 1·6 (3H, d, J = 1 cps). 1·23 (3H, s). 1·1 (3H, s). 1·07 (3H, s). 1·05 (3H, s). 0·83 3H, s).

Iodoacetylanhydrolitsomentol (IIc). A soln of Ia (0·5 g) in dry dioxane (10 ml) was treated with chloroacetyl chloride (1 ml). After 48 hr at 30°. H_2O was added and the solid obtained chromatographed over silica gel in C_6H_6-hexane to give chloroacetylanhydrolitsomentol (0·3 g). m.p. 93–96° (from MeOH). This was refluxed for 3 hr in acetone (20 ml) with KI (0·8 g). filtered and evaporated. Extraction with $CHCl_3$ and chromatography of the product over silica gel in C_6H_6-hexane yielded IIc (0·2 g). m.p. 100–102° (from MeOH). ν_{max} (Nujol) 1735 cm^{-1}. (Found: C. 64·54; H. 8·45. $C_{32}H_{51}O_2I$ requires: C. 64·65; H. 8·62%). NMR: δ 5·55 (1H. dd. J = 6, 1 cps). 5·1 (1H. br). 4·73 (1H. t. J = 1·5 cps). 3·66 (2H. s). 1·6 (6H. br s). 1·07 (6H. s). 0·93 (3H. s). 0·87 (3H. s). 0·83 (3H. s).

Isoachydrolitsomentol (IX). Ia (2 g) was heated at 70–80° for 2 hr with $MeSO_2Cl$ (3 ml) and Py (5 ml). Addition of H_2O and extraction with CH_2Cl_2 yielded a brownish gum. chromatographed over silica gel in C_6H_6. Elution with C_6H_6–$CHCl_3$ (3:1) yielded IX (0·4 g). m.p. 131–132° (from MeOH). $[\alpha]_D$ − 40·6°. ν_{max}(CH_2Cl_2) 3580 cm^{-1} (Found: C. 84·25; H. 11·83. $C_{30}H_{50}O$ requires: C. 84·44; H. 11·81%). Mass spectrum: *m/e* 426 (M^+) (6). 408 (40). 393 (28). 344 (34). 329 (96). 274 (100). 259 (37). 231 (20). 205 (11). 163 (24). 150 (22). 134 (52). 123 (50). 119 (49). 109 (39). 95 (47). 81 (37). 69 (60). NMR: δ 5·7 (1H. m). 5·3 (1H. d. J = 9 cps). 5·15 (1H. br). 1·7 (3H. s). 1·6 (3H. s). 1·25 (6H. s). 1·03 (9H. s). 0·97 (3H. s). 0·87 (3H. s).

Isoanhydrodihydrolitsomentol (X). IIIa (3·3 g) was heated at 50–60° for 2 hr with $MeSO_2Cl$ (8 ml) and Py (15 ml) and worked up as above. Chromatography over silica gel in C_6H_6 gave. in the earlier fractions. X (0·8 g). m.p. 130–132° (from ether–MeOH). $[\alpha]_D$ − 5·6°. ν_{max}(CH_2Cl_2) 3580 cm^{-1}. (Found: C. 84·29: H. 12·34. $C_{30}H_{52}O$ requires: C. 84·04; H. 12·23%). Mass spectrum: *m/e* 428 (M^+) (1). 413 (3). 395 (2). 346 (33). 331 (100). 313 (4). 233 (15). 207 (7). 206 (7). 191 (5). 163 (6). 151 (6). 137 (9). 123 (14). 109 (20). 95 (40). NMR: δ 5·65 (1H. m). 5·25 (1H. dd. J = 9·1 cps). 1·25 (6H. s). 1·03 (9H. s). 0·97 (3H. s). 0·91 (3H. s). 0·87 (3H. s). 0·8 (3H. s). The later fractions in the chromatography eluted by C_6H_6-$CHCl_3$ (1:1) yielded the mesylate (IIIc) (1·5 g). m.p. 185° (d) (from ether–MeOH). ν_{max} (CH_2Cl_2) 3580 cm^{-1} (Found: C. 68·70; H. 10·45. $C_{31}H_{56}O_5S$ requires: C. 68·85; H. 10·44%). Use of more Py and higher temp resulted in more of X and less of IIIc.

3-*Desoxydihydrolitsomentol* (IIId). A soln of X (1·6 g) in EtOAc (60 ml) was reduced with H_2 in an Ente apparatus at 40° for 12 hr in presence of Pd–C (10%; 0·5 g). Chromatography of the product over silica gel in C_6H_6 yielded IIId (1·1 g). m.p. 114° (from CH_2Cl_2–MeOH). $[\alpha]_D$ − 8·8°. (Found: C. 83·37; H. 12·69. $C_{30}H_{54}O$ requires: C. 83·65; H. 12·64%). Mass spectrum: *m/e* 430 (M^+) (7). 415 (100). 397 (6). 345 (4). 331 (16). 276 (10). 261 (10). 207 (8). 193 (7). 181 (5). 177 (10). 163 (19). 150 (7). 136 (16). 123 (22). 121 (21). 109 (30). 107 (25). 95 (60). The compound could also be obtained by hydrogenation of IX as above.

3-*Desoxyanhydrodihydrolitsomentol* (IVe). A mixture of IIId (0·5 g) and fused $KHSO_4$ (1·5 g) was heated at 120° for 1 hr. Extraction with CH_2Cl_2 and chromatography over Al_2O_3 in hexane yielded IVe (0·2 g). m.p. 60–62° (from ether–MeOH). $[\alpha]_D$ + 47·2°. ν_{max}(KBr) 1650 cm^{-1}. (Found: C. 87·35; H. 12·90. $C_{30}H_{52}$ requires: C. 87·30; H. 12·70%). Mass spectrum: *m/e* 412 (M^+) (10). 397 (22). 276 (90). 261 (80). 257 (10). 207 (7). 205 (7). 191 (11). 189 (11). 177 (33). 163 (100). 150 (68). 136 (80). 123 (62). 121 (54). 109 (40). 107 (42). 105 (40). 95 (67). NMR; δ 5·5 (1H. d. J = 6 cps).

Diene (XI). (a) Ia (1 g) was added to a stirred suspension of PCl_5 (0·7 g) in dry hexane (25 ml). After 2 hr. the soln was washed with aq $NaHCO_3$. H_2O. dried. evaporated and the product chromatographed over Al_2O_3 in pentane to yield XI (0·5 g). as a gum homogeneous by TLC. λ_{max} 243 mμ (log ε 3·70). The later fractions gave IX (0·1 g). identical with the compound mentioned earlier.

(b) Ia (0·5 g) was refluxed with HCOOH (98%; 5 ml) for 45 min and worked up as above to yield XI (0·2 g). identical (TLC. UV. IR. NMR) with the above sample.

Diene (XII). (a) A soln of IVa (0·4 g) in $CHCl_3$ (25 ml) was stirred for 16 hr at 25° with PCl_5 (0·8 g) and worked up as above to yield XII (0·2 g) as a gum homogeneous by TLC. λ_{max} 245 mμ (log ε 3·67). NMR: δ 5·75 (1H. br). 1·72 (6H. s). 0·9 (6H. s). 0·87 (6H. s). 0·8 (6H. s).

(b) IVa (1 g) was heated at 70° for 3 hr with $MeSO_2Cl$ (4 ml) and Py (5 ml) to yield the mesylate (IVc) (0·5 g). m.p. 115–117° (d) (from ether–MeOH). (Found: C. 73·09; H. 10·85. $C_{31}H_{54}O_3S$ requires: C. 73·47: H. 10·74%). NMR: δ 5·58 (1H. dd. J = 6, 1 cps). 4·58 (1H. t. J = 1·5 cps). 2·97 (3H. s). A soln of IVc (0·7 g) and NaOAc (0·5 g) in AcOH (30 ml) was heated at 95° for 2 hr and the solvent removed *in vacuo*. Addition of H_2O. extraction with ether and chromatography of the product over silica in hexane yielded XII (0·2 g). identical (TLC. UV. IR. NMR) with the above sample.

Anhydrodihydrolitsomentone (IVd). A soln of IVa (2 g) in Py (15 ml) was added to Py–CrO_3 complex (from 2 g CrO_3 and 20 ml Py) at 5–10°. The mixture was stirred for 16 hr at 25° and worked up as usual. Chromatography over silica gel in C_6H_6 yielded IVd (1 g). m.p. 72–74 (from EtOH). $[\alpha]_D$ + 45·4 . λ_{max} 290 mμ (log ε 1·95). ν_{max}(KBr) 1710 cm^{-1}. (Found: C. 84·64; H. 11·87. $C_{30}H_{50}O$ requires: C. 84·44; H. 11·81%). Mass spectrum: *m/e* 426 (M^+) (10). 411 (10). 393 (3). 331 (8). 276 (100). 261 (68). 163 (96). 150 (53). 137 (44).

123 (51). 107 (35). 95 (47). NMR: δ 5·7 (1H. d. J = 6 cps). 1·23 (3H. s. C_4-Me). 1·22 (3H. s. C_4-Me). ORD (dioxane. 2%): $[\alpha]_{590}$ + 30°. $[\alpha]_{420}$ + 120°. $[\alpha]_{390}$ + 70°. $[\alpha]_{370}$ + 90°. $[\alpha]_{320}$ − 530°. $[\alpha]_{265}$ + 2100°. CD (dioxane): λ_{infl} 312 mμ ($\Delta\varepsilon$ − 1·03). λ_{max}304 mμ ($\Delta\varepsilon$ − 1·73). λ_{max}295 mμ ($\Delta\varepsilon$ − 1·79). The later fractions in the chromatography yielded the diketone (XVb) (0·3 g). m.p. 149–151° (from CH_2Cl_2–MeOH). λ_{max}248 mμ (log ε 4·03). $[\alpha]_D$ ± 0°. ν_{max}(CH_2Cl_2) 1700. 1635. 1600 cm^{-1}. (Found: C. 81·79; H. 11·01. $C_{30}H_{48}O_2$ requires: C. 81·76; H. 10·98%). NMR: δ 6·18 (1H. d. J = 1·5 cps).

Thioketal (IVf). A soln of IVd (1·2 g) in ethanedithiol (3 ml) was cooled to 5° and treated with BF_3. Et_2O (3 ml). After 48 hr at 25°. H_2O was added and the product extracted with ether to yield IVf (1·1 g). m.p. 140–142° (from CH_2Cl_2-MeOH. (Found: C. 76·79; H. 10·80. $C_{32}H_{54}S_2$ requires: C. 76·44; H. 10·83%). Mass spectrum: *m/e* 502 (M^+) (1). 409 (1). 371 (1). 151 (2). 147 (2). 133 (10). 132 (8). 131 (100). 123 (3). 121 (4). 119 (5). 109 (4). 107 (4). 105 (4). 95 (9). 93 (5). 91 (4).

Diosphenol (XIIIa). IVd (0·6 g) was added to a soln of t-BuOK (prepared from 0·3 g K in 20 ml t-BuOH). stirred in O_2 for 3 hr. poured on ice. acidified with conc HCl and extracted with ether. Chromatography of the product over silica gel in C_6H_6 yielded XIIIa as an uncrystallisable gum. homogeneous by TLC which gave a positive $FeCl_3$ test. λ_{max}273 mμ. shifted to λ_{max}315 mμ on addition of KOH. ν_{max}(CH_2Cl_2) 3680. 3580. 1705. 1675 cm^{-1}. NMR: δ 6·12 (1H. d. J = 2·5 cps). 5·65 (1H. m). 5·35 (1H. br. OH). 3·41 (1H. t. J = 2·5 cps).

Diosphenol methyl ether (XIIIb). A soln of XIIIa (0·7 g) in acetone (30 ml) was refluxed for 5 hr with anhydrous K_2CO_3 (5 g) and MeI (5 ml). filtered and evaporated. Chromatography of the residue over silica gel in C_6H_6-$CHCl_3$ (1:1) yielded XIIIb (0·25 g). m.p. 115–117° (from MeOH). λ_{max} 265 mμ (log ε 3·86). ν_{max}(CH_2Cl_2) 1690. 1670. 1635 cm^{-1} (Found: C. 82·15: H. 11·35. $C_{31}H_{50}O_2$ requires: C. 81·88: H. 11·08%) NMR ($CDCl_3$. 100 MHz): δ 5·78 (1H. d. J = 2·5 cps). 5·68 (1H. t. J = 2·5 cps). 3·41 (1H, br s. width at half height 8 cps). 1·24 (3H. s). 1·2 (3H. s). 0·89 (12H. s). 0·83 (6H. s). Irradiation of the signal at δ 3·41 gives a sharp singlet at δ 5·78 and a neat quartet at δ 5·68 (J = 2·5 cps).

Catalytic reduction of IVb. A soln of IVb (1 g) in AcOH (150 ml) was shaken with H_2 at 700–900 lbs/in^2 at 100° for 16 hr in presence of PtO_2 (1 g). filtered and evaporated. Repeated crystallisation of the residue from ether–MeOH gave XIVb (0·1 g). m.p. 168–170°. which gave no colour with tetranitromethane. NMR: δ 4·64 (1H. t. J = 1·5 cps). 2·05 (3H. s). 1·03 (3H. s). 1·0 (3H. s). 0·9 (6H. s). 0·88 (3H. s). 0·87 (3H. s). 0·8 (6H. s).

The acetate (XIVb) (55 mg) in dioxane (15 ml) was refluxed with KOH (0·3 g in 1 ml H_2O) for 3 hr to yield XIVa. m.p. 153–155° (from MeOH). Mass spectrum: *m/e* 430 (M^+) (20). 412 (20). 397 (7). 290 (50). 276 (25). 275 (25). 272 (21). 259 (30). 189 (60). 175 (100). 163 (36).

Ethyl ether (IVg). A soln of IVb (1 g) and $LiBH_4$ (0·7 g) in dry ether (25 ml) was treated with a soln of BF_3. Et_2O (0·3 ml) in ether (2 ml). After stirring at 25° for 4 hr. H_2O (0·5 ml) was added followed by a soln of conc H_2SO_4 (0·4 ml) in H_2O (3 ml). The soln was stirred for 16 hr at 25° and then refluxed for ½ hr. Extraction with ether and chromatography of the product over silica gel in C_6H_6 yielded IVg (0·3 g). m.p. 76–77° (from ether–MeOH) which gave a yellow colour with tetranitromethane (Found: C. 83·66; H. 12·50. $C_{32}H_{56}O$ requires: C. 84·14: H. 12·36%). Mass spectrum: *m/e* 456 (M^+) (32). 441 (7). 410 (11). 395 (6). 276 (100). 261 (33). 180 (62). 163 (60). NMR: δ 5·5 (1H. d. J = 6 cps). 3·42 (2H. m). 3·02 (1H. t. J = 1·5 cps).

7-Oxoanhydrodihydroacetyllitsomentol (XVa). (a) *With* O_3. A soln of IVb (0·5 g) in EtOAc (30 ml) was ozonised at 0°. shaken with H_2 at 1 atm in presence of Pd–C (5%; 0·1 g) for 2 hr. filtered and evaporated. The residue was chromatographed over silica gel in C_6H_6. The initial fractions yielded a gum. Further elution with C_6H_6–$CHCl_3$ (1:1) gave XVa (0·2 g). m.p. 204–205° (from MeOH). $[\alpha]_D$ + 117·6°. λ_{max}247 mμ (log ε 4·06). ν_{max}(CH_2Cl_2) 1730. 1655. 1620 cm^{-1}. (Found: C. 78·87: H. 10·70. $C_{32}H_{52}O_3$ requires: C. 79·28; H. 10·81%). NMR: δ 6·1 (1H. d. J = 1·5 cps). 4·85 (1H. t. J = 1·5 cps). 2·7 (1H. br). 2·41 (1H. s). 2·0 (3H. s).

(b) *With* CrO_3. A soln of IVb (0·4 g) in AcOH (20 ml) was heated with CrO_3 (0·4 g) at 65–70° for 2 hr and left at 25° for 16 hr. Addition of H_2O and extraction with ether gave XVa (0·3 g). identical with the above sample.

LAH reduction of XVa. A soln of XVa (1·2 g) in ether (60 ml) was refluxed for 6 hr with LAH (2 g) and worked up as usual. Chromatography of the product over silica gel in C_6H_6–$CHCl_3$ (1:1) yielded XIVc (0·5 g). m.p. 161–163° (from MeOH). λ_{max} 295 mμ (log ε 1·85). ν_{max}(CH_2Cl_2) 3620. 1690 cm^{-1}. (Found: C. 80·75: H. 11·85. $C_{30}H_{52}O_2$ requires: C. 81·02; H. 11·79%). NMR: δ 3·46 (1H. t. J = 2 cps).

5.6-β-Epoxyanhydrodihydroacetyllitsomentol (XVI). A soln of IVb (2·3 g) in $CHCl_3$ (60 ml) was treated with *m*-chloroperbenzoic acid (2·5 g) and allowed to stand at 5° for 48 hr. The soln was washed with aq Na_2CO_3 and H_2O. dried and evaporated. Chromatography of the residue over Al_2O_3 in C_6H_6-hexane (1:1) yielded the epoxide (2 g). m.p. 98–99° (from EtOAc–MeOH). (Found: C. 78·87; H. 11·19. $C_{32}H_{54}O_3$ requires: C. 78·96; H. 11·18%). NMR: δ 4·82 (1H. t. J = 3 cps). 3·13 (1H. d. J = 5 cps). 2·09 (3H. s).

Diol (XVIIb). A soln of IVb (1·5 g) in dioxane (40 ml) containing Py (1 ml) was treated with OsO_4 (1

g) and allowed to stand at 25° for 5 days. The soln was saturated with H_2S. filtered. evaporated and chromatographed over silica gel in C_6H_6. Elution with C_6H_6 gave some unreacted IVb. Further elution with $CHCl_3$–5% MeOH yielded XVIIb (1 g). m.p. 130–132° (from MeOH). (Found: C. 76·46; H. 11·34. $C_{32}H_{56}O_4$ requires: C. 76·14: H. 11·18%).

Ketol (XVIId). A soln of XVIIb (0·4 g) in acetone (15 ml) was treated at 5–10 with Jones reagent (0·6 ml). After 5 min. acetone saturated with SO_2 was added. followed by aq K_2CO_3. Extraction with ether and chromatography of the product over silica gel in C_6H_6 yielded XVIId (0·15 g). m.p. 162–163° (from EtOAc–MeOH). ν_{max}(CH_2Cl_2) 3560. 1730. 1710 cm^{-1}. (Found: C. 76·08; H. 11·06. $C_{32}H_{54}O_4$ requires: C. 76·44; H. 10·83%).

Triol (XVIIa). A soln of XVIIb (0·4 g) in dioxane (20 ml) was refluxed with methanolic KOH (7%; 30 ml) for 5 hr. concentrated *in vacuo* and diluted with H_2O. The solid that separated was crystallised from MeOH to yield XVIIa (0·3 g). m.p. 165–166°. (Found: C. 78·11; H. 11·85. $C_{30}H_{54}O_3$ requires: C. 77·86; H. 11·76%).

Ketoacetate (XVIIIb). XVIIb (0·3 g) was heated at 55° for 3 hr with $MeSO_2Cl$ (0·6 ml) and Py (3 ml). cooled. poured on H_2O and extracted with ether. Chromatography over silica gel in C_6H_6 gave in the initial fractions XVIIIb (50 mg) as an uncrystalline gum. ν_{max}(CH_2Cl_2) 1735. 1705 cm^{-1}. NMR: δ 5·48 (1H. t. J = 9 cps). 3·3 (1H. br). 2·07 (3H. s). 1·12 (3H. s). 0·97 (3H. s). 0·92 (6H. s). 0·89 (3H. s). 0·83 (3H. s). 0·8 (3H. s). The later fractions in the chromatography gave the mesylate (XVIIc) (0·2 g). m.p. 135–136° (d) (from ether–MeOH). ν_{max}(CH_2Cl_2) 3580. 1740 cm^{-1}. (Found: C. 68·08; H. 10·15. $C_{33}H_{58}O_6S$ requires: C. 68·01; H. 10·03%). The mesylate (100 mg) on refluxing with γ-collidine (3 ml) for 2 hr and working up as above yielded XVIIIb (50 mg). identical (TLC. IR. NMR) with the above sample.

Ketoalcohol (XVIIIa). XVIIIb (0·3 g) was refluxed with methanolic KOH (10%; 10 ml) for 3 hr to give XVIIIa (0·2 g). m.p. 224–226° (from $CHCl_3$–MeOH). ν_{max} (CH_2Cl_2) 3610. 1705 cm^{-1} (Found: C. 80·75; H. 11·79. $C_{30}H_{52}O_2$ requires: C. 81·02: H. 11·79%). Acetylation (Py. Ac_2O) of XVIIIa gave XVIIIb. identical (TLC. IR. NMR) with the above sample.

Benzilic ester (XXIIIb). The diosphenol (XIIIa) (1·6 g) was refluxed in N_2 for 7 hr with a soln of KOH (2·4 g) in H_2O (6 ml) and EtOH (70 ml). The soln was evaporated. diluted with H_2O. acidified with HCl and extracted with ether to yield the benzilic acid (XXIIIa) as an uncrystallisable gum. The acid (1 g) in ether (20 ml) was treated with excess ethereal CH_2N_2 and the product chromatographed in C_6H_6 over silica gel to yield XXIIIb as an uncrystallisable gum (0·9 g) homogeneous by TLC. ν_{max}(CH_2Cl_2) 3560. 1718 cm^{-1}. NMR: δ 5·33 (1H. dd. J = 3 cps). 3·72 (3H. s). 2·9 (1H. br s. OH).

Diol (XXIIIc). A soln of XXIIIb (1 g) in dry ether (50 ml) was refluxed with LAH (0·8 g) for 3 hr with stirring and worked up as usual to yield XXIIIc (0·9 g). m.p. 177–179° (from ether–hexane). (Found: C. 80·70; H. 11·87. $C_{30}H_{52}O_2$ requires: C. 81·02; H. 11·79%).

Anhydrodihydronorlitsomentone (XXIVa). A soln of $NaIO_4$ (1·3 g) in H_2O (60 ml) was added to a soln of the diol (0·9 g) in dioxane (150 ml). After 24 hr at 25°. the soln was concentrated *in vacuo* to 50 ml. diluted with H_2O and extracted with CH_2Cl_2. Chromatography of the product over silica gel in CH_2Cl_2 gave XXIVa (0·5 g). m.p. 100–101° (from CH_2Cl_2–MeOH). ν_{max} (CH_2Cl_2) 1740 cm^{-1}. (Found: C. 80·57; H. 11·43. $C_{29}H_{48}O$.MeOH requires: C. 81·02 H. 11·79%). NMR: δ 5·53 (1H. d. J = 6, 3 cps). 1·1 (3H. s). 1·05 (3H. s). 0·9 (6H. s). 0·87 (9H. s). 0·85 (3H. d. J = 6 cps).

Ene-dione (XXIVb). A soln of XXIVa (0·5 g) in AcOH (10 ml) was heated at 70° for 2 hr with CrO_3 (0·6 g). diluted with H_2O and extracted with CH_2Cl_2. Chromatography over silica gel in CH_2Cl_2 yielded XXIVb (0·2 g). m.p. 210–212° (from CH_2Cl_2–hexane). λ_{max}245 mμ (log ε 4·02). ν_{max}(KBr) 1745. 1645 cm^{-1}. (Found: C. 81·95; H. 11·06. $C_{29}H_{46}O_2$ requires: C. 81·63; H. 10·87%). NMR: δ 6·06 (1H. d. J = 3 cps). 3·6 (1H. m). 2·5 (2H. m). 2·5 (1H. s).

Diene-dione (XXIIb). A mixture of XXIVb (50 mg) and SeO_2 (0·15 g) in t-BuOH (4 ml) containing AcOH (0·1 ml) was refluxed in N_2 for 4 hr. evaporated *in vacuo* and extracted with CH_2Cl_2. Chromatography of the product in CH_2Cl_2 over silica gel impregnated with 2% Ag NO_3 yielded the diene-dione (30 mg). m.p. 160–162° (from CH_2Cl_2–MeOH) λ_{max}286 mμ (log ε 4·33). ν_{max}(KBr) 1705. 1655. 1575 cm^{-1}. (Found: C. 82·77; H. 10·73. $C_{29}H_{44}O_2$ requires: C. 82·02; H. 10·44%). Mass spectrum: m/e 424 (M^+) (30). 409 (18). 396 (55). 311 (11). 269 (30). 256 (20). 241 (72). 234 (72). 213 (30). 207 (33). 202 (72). 190 (98). 189 (100). 161 (62). 149 (23). 121 (70). NMR: δ 6·23 (1H. d. J = 1·5 cps). 6·09 (1H. d. J = 1·5 cps). 2·75 (1H. s). 1·27 (3H. s). 1·21 (9H. s). 0·95 (3H. s). 0·9 (3H. s). 0·8 (3H. s). 0·71 (3H. s). CD (dioxane): λ_{max}346 ($\Delta\varepsilon$ − 2·10). 284 (+5·56). 252 mμ (+4·74).

BF_3-catalysed rearrangement of the epoxide (XVI). A soln of XVI (2 g) in dry ether (150 ml) was treated with $BF_3.Et_2O$ (3 ml) and allowed to stand at 25° for 48 hr. The soln was washed with aq Na_2CO_3 and

H_2O. dried and evaporated. Chromatography of the residue over silica gel in C_6H_6 yielded the acetate XXVIIb (1·3 g) as an amorphous solid. $[\alpha]_D$ + 48·2°. ν_{max}(KBr) 3500. 1720. 1630 cm^{-1}. Hydrolysis of the acetate (0·3 g) with methanolic KOH (7%; 25 ml) yielded the diol (XXVIIa). m.p. 179–180° (from MeOH). $[\alpha]_D$ + 34·71°. ν_{max}(CH_2Cl_2) 3610. 1610 cm^{-1}. (Found: C. 80·85; H. 11·94. $C_{30}H_{52}O_2$ requires: C. 81·02; H. 11·79%). Mass spectrum: *m/e* 444 (M^+) (4). 429 (6). 426 (100). 411 (30). 408 (4). 393 (22). 340 (10). 313 (12). 271 (11). 253 (5). NMR: δ 5·32 (1H. m). 4·54 (1H. t. J = 3 cps). 3·15 (1H. br).

Ketoacetate (XXVIIc). The hydroxyacetate (XXVIIb) (0·5 g) was oxidised with Py–CrO_3 complex (from 0·5 g CrO_3 and 5 ml Py) and worked up as usual to yield XXVIIc (0·25 g). m.p. 145° (from CH_2Cl_2–MeOH). $[\alpha]_D$ + 70·2°. ν_{max}(KBr) 1735. 1710 cm^{-1} (Found: C. 79·35; H. 10·74. $C_{32}H_{52}O_3$ requires: C. 79·28; H. 10·81%). Mass spectrum: *m/e* 484 (M^+) (100). 469 (53). 424 (2). 409 (17). 391 (7). 315 (13). 303 (24). 274 (80). 269 (40). 260 (53). 259 (68). 255 (37). 243 (18). 207 (16). 189 (17). 169 (45). 161 (25). NMR: δ 5·51 (1H. dd. J = 6, 3 cps). 4·4 (1H. br). 2·05 (3H. s). 1·35 (6H. s). 1·1 (3H. s). 0·97 (3H. s). 0·92 (6H. s).

Diene (XXVIIIb). The hydroxyacetate (XXVIIb) (0·7 g) was heated at 60° for 2 hr with $MeSO_2Cl$ (1·5 ml) and Py (5 ml) and the soln left for 16 hr at 30°. Extraction with CH_2Cl_2 and chromatography of the product over silica gel in C_6H_6-hexane (1:1) yielded the unconjugated diene (XXVIIIb) (0·25 g). m.p. 132–133° (from EtOAc–MeOH). $[\alpha]_D$ + 41·8°. ν_{max}(CH_2Cl_2) 1730 cm^{-1}. (Found: C. 82·28: H. 11·13. $C_{32}H_{52}O_2$ requires: C. 81·99; H. 11·18%). Mass spectrum: *m/e* 468 (M^+) (95). 453 (61). 408 (40). 393 (100). 340 (7). 171 (19). NMR: δ 5·73 (1H. t. J = 3 cps). 5·38 (1H. dd. J = 6, 2 cps). 4·53 (1H. t. J = 6 cps). 2·03 (3H. s).

Hydrolysis of XXVIIIb (0·4 g) with methanolic KOH (10%; 20 ml) yielded XXVIIIa (0·3 g). m.p. 110° (from CH_2Cl_2–MeOH). $[\alpha]_D$ + 8·4°. (Found: C. 84·59; H. 11·63. $C_{30}H_{50}O$ requires: C. 84·44; H. 11·81%). NMR: δ 5·72 (1H. t. J = 3 cps). 5·37 (1H. dd. J = 5, 3 cps). 3·27 (1H. t. J = 6 cps).

Dihydroagnosterol (XXIXa). Freshly distilled ethylenediamine (15 ml) was treated at 100° in N_2 with stirring with Li (0·4 g) and the soln heated at 100° for 1 hr till the blue colour faded completely. To this was added the diene (XXVIIIb) (0·5 g) and the soln heated at 100° for 5 hr. After 15 hr more at 30°. H_2O was added followed by conc HCl and the mixture extracted with $CHCl_3$. The $CHCl_3$ extract was washed with HCl and H_2O. dried and evaporated. Chromatography of the product over silica gel in C_6H_6–CH_2Cl_2 (1:1) yielded the conjugated diene. dihydroagnosterol (XXIXa) (0·3 g). m.p. 157° (from CH_2Cl_2–MeOH). $[\alpha]_D$ + 65·3°. λ_{max} 236. 244. 252 mμ (log ε 4·07. 4·13. 3·96). ν_{max}(CH_2Cl_2) 3600 cm^{-1}. (Found: C. 82·74. 82·67: H. 11·85. 11·82. Calc for $C_{30}H_{50}O$. 0·5 MeOH: C. 82·75; H. 11·84%). Mass spectrum: *m/e* 426 (M^+) (100). 411 (75). 408 (6). 393 (53). 313 (24). 271 (100). 258 (29). 253 (58). 240 (44). 185 (29). 171 (55). 157 (50). 145 (57). NMR: δ 5·4 (2H. m). 3·25 (1H. t. J = 7 cps).

Acetylation of the product (0·5 g) with Ac_2O (4 ml) and Py (5 ml) at 80° for 4 hr yielded the acetate (XXIXb) (0·4 g). m.p. 167–168° (from CH_2Cl_2–MeOH). $[\alpha]_D$ + 79·6°. λ_{max} 235. 243. 252 mμ (log ε 4·31. 4·37. 4·18). ν_{max}(KBr) 1725 cm^{-1}. (Found: C. 82·38; H. 11·51. Calc for $C_{32}H_{52}O_2$: C. 81·99; H. 11·18%). NMR: δ 5·4 (2H. br). 4·52 (1H. br). 2·05 (3H. s). The sample was identical (m.m.p., TLC. UV. IR) with an authentic sample of acetyldihydroagnosterol.

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