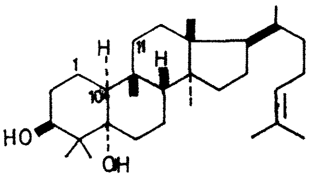
Litsomentol, A New Tetracyclic Triterpene†

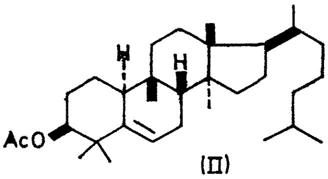
By T. R. GOVINDACHARI,* N. VISWANATHAN, and P. A. MOHAMED
(*CIBA Research Centre, Goregaon East, Bombay 63, India*)

Summary Litsomentol, a new tetracyclic triterpene, has been proved to have the cucurbitacin-type structure (I) by degradation and correlation with agnosterol.

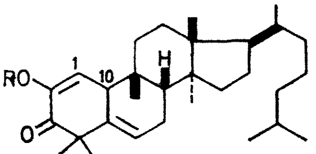
BESIDES β-sitosterol and actinodaphnine, we have isolated a triterpene alcohol, litsomentol,‡ from the bark of *Litsea tomentosa* Heyne (Family: Lauraceae), and established its structure as (I). This is the simplest member of the cucurbitacin[1] group and is unique in lacking an oxygen function at C-11 and in being the only member of the group as yet discovered in a plant belonging to the Lauraceae family. The proof of structure involves a rearrangement of the cucurbitacin to the lanosterol skeleton and comparison with the known agnosterol.



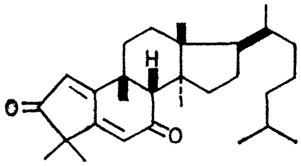
(I)



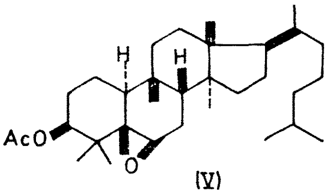
(II)



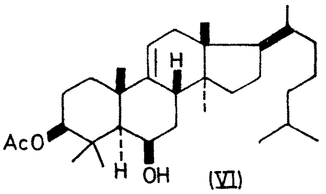
(III)
a; R = H
b; R = Me



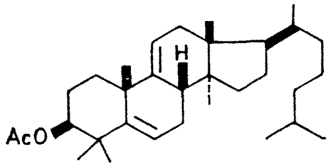
(IV)



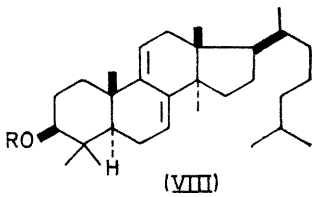
(V)



(VI)



(VII)



(VIII)
a; R = H
b; R = Ac

Litsomentol, m.p. 218—219°, $[\alpha]_D \pm 0°$, $C_{30}H_{52}O_2$, has one secondary hydroxy-group (formation of acetate and ketone), one tertiary hydroxy-group (dehydration with anhydrous potassium bisulphate to give the anhydro-derivative), and a trisubstituted double bond (reduction to dihydrolitsomentol and epoxidation to a monoepoxide). The double bond is situated on the side-chain since ozonolysis gives acetone and a trisnor-acid.

The presence of a hydrogen at C-10 is shown by the conversion of anhydrodihydroacetyl-litsomentol (II) by Barton oxidation of the 3-ketone into the diosphenol (IIIa) and the diosphenol methyl ether (IIIb) in both of which 1-H appears as a doublet: at δ 6·12 p.p.m. (*J* 2·5 Hz) in (IIIa) and at 5·78 (*J* 3 Hz) in (IIIb).

The circular dichroism of the ketone, litsomentone, obtained by oxidation of litsomentol is positive whereas that of anhydrodihydrolitsomentone is negative. The sign and amplitude of the latter are those expected for a 3-oxo-cucurbitacin.[2] The mass spectral fragmentations of litsomentol and its derivatives are well explained on the basis of structure (I). The location of the hydroxy-groups was confirmed by degradation of litsomentol to the dienedione (IV), m.p. 160—162°, λ_{max} (EtOH) 286 nm (log ε 4·33).

The structure and the stereochemistry depicted in formula (I) have been confirmed as follows. Anhydrodihydroacetyl-litsomentol (II) was epoxidised to give (V) which rearranged with boron trifluoride–ether to give the alcohol (VI). Treatment of this with methanesulphonyl chloride and pyridine gave the unconjugated diene (VII). The latter, when refluxed with *N*-lithioethylenediamine, underwent isomerisation and hydrolysis to yield dihydroagnosterol (VIIIa),[3] m.p. 157—158°. The acetate, m.p. 167—168°, (VIIIb), was identical with an authentic sample kindly supplied by Professor Jeger.

(*Received, March 15th, 1971; Com. 284.*)

---

† Part of this work was presented at the First Indo-Soviet Symposium on the Chemistry of Natural Products, Tashkent, September 1968.

‡ The compound was first isolated by Dr. A. K. Ganguly.

[1] D. H. R. Barton, C. F. Garbers, D. Giacopello, R. G. Harvey, J. Lessard, and D. R. Taylor, *J. Chem. Soc. (C)*, 1969, 1050.
[2] G. Biglino, J. M. Lehn, and G. Ourisson, *Tetrahedron Letters*, 1963, 1651.
[3] L. Ruzicka, R. Denss, and O. Jeger, *Helv. Chim. Acta.*, 1946, 29, 204.