Deoxyemmolactone, a new A(1), 28-Bisnor-lupane Triterpene

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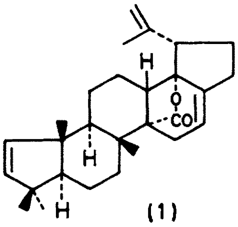
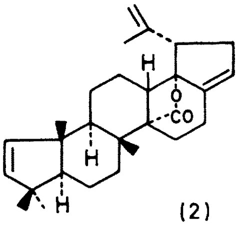
Summary A new member of the A-nor-lupane group of triterpenes has been isolated from *Alangium villosum* (Bl.) Wang. var. *vitiense* (A. Gray) Bloemb. and *Emmenospermum alphitonioides* F. Muell. and shown to be either 22-deoxyemmolactone (1) or its $\Delta^{17(22)}$-isomer (2).

A-NOR-TRITERPENES of the lupane class of triterpenes occur in a number of Rhamnaceae species,[1] and one example of an A(1),28-bisnor-lupane, *viz.* emmolactone,[2] is known. We report the isolation of emmolactone (3) and a new triterpenoid lactone, $C_{28}H_{38}O_2$ (elemental analyses and mass spectrum), m.p. 226—228° (capillary), $[\alpha]_D(CHCl_3) + 106°$ (yield 0·0016%), from the bark of *A. villosum* (fam. Alangiaceae). The same lactone, for which we suggest the 22-deoxyemmolactone structure (1) or the isomeric structure (2) [A(1),28-bisnorlupa-2,17(22),20(29)-trien-27→18α-olide] has also been isolated from *E.alphitonioides* (the best yielding specimen of which gave 80 mg from 5 kg of bark).


(1)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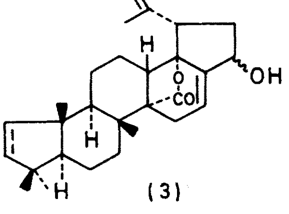
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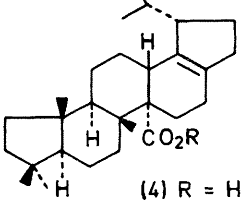
(4) R = H
(5) R = Me

The new triterpene showed strong end-absorption in the u.v. spectrum, and its i.r. spectrum indicated the presence of a γ-lactone, a vinylidene ($C=CH_2$) group and a *cis*-disubstituted double bond (ν_{max} 1762, 1645, 899, and 757 cm^{-1}). The n.m.r. spectrum indicated the presence of a *cis*-disubstituted double bond flanked by quaternary carbon atoms and located in a five-membered ring (δ 5·92 and δ 5·45, pair of doublets, 2H,J 5·4 Hz), an isopropenyl group (δ 4·77 and δ 4·48, 2H, pair of multiplets; δ 1·78, 3H, broadened singlet), a trisubstituted double bond (δ5·58, 1H, multiplet), and four tertiary methyl groups (δ 1·11—0·92 12H, four singlets). Lack of any signal near δ 4·0 indicated that the γ-lactone terminated at a tertiary centre.

The analytical and spectral evidence, together with the co-occurrence of emmolactone, suggested that the new triterpene might be the deoxyemmolactone (1). Catalytic hydrogenation (Pd/C, ethanol) afforded the acid (4) which was characterised as its methyl ester (5); the latter was identical with the methyl ester prepared from emmolactone by similar hydrogenation and subsequent methylation. This interconversion together with the spectral data resolved all features of the structure of the new triterpene, including the α-orientation of the isopropenyl group,[3] with the exception of the position of the trisubstituted double bond. This double bond may be situated either between C-16 and C-17 or between C-17 and C-22, since its location at either position (but only at these two positions) could give hydrogenolysis leading to the unsaturated acid (4). Hence the triterpene may have either structure (1) or (2).

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[1] R. A. Eade, J. Ellis, P. Harper, and J. J. H. Simes, *Chem. Comm.*, **1969**, 579 and references cited therein.
[2] R. A. Eade, J. Ellis, and J. J. H. Simes, *Austral. J. Chem.*, 1967, **20**, 2737.
[3] S. N. Bose and H. N. Khastgir, *J. Indian Chem. Soc.*, 1969, **46**, 860.