Isodeoxyemmolactone, a New A(1), 28-Bisnorlupane Triterpene

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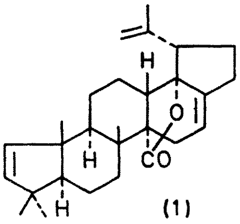
Summary Isodeoxyemmolactone has been isolated from *Alangium villosum* (Bl) Wang var *vitiense* (A Gray) Bloemb and *Emmenospermum alphitonioides* F Muell , and shown to be A(1), 28-bisnorlupa-2 17,20(29)-trien-27 → 16α-olide

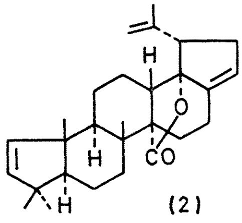
IN a recent communication we reported[1] the isolation of deoxyemmolactone from the barks of *Alangium villosum* and *Emmenospermum alphitonioides*, and showed that it was a member of the A(1), 28-bisnorlupane group of triterpenes of probable structure (1) or (2) We report now the isolation of isodeoxyemmolactone from the barks of *A villosum* (yield 0 005%) and *E alphitonioides* (the best yielding specimen of which gave 65 mg from 6 kg of bark), for which we suggest structure (3)

Isodeoxyemmolactone, $C_{28}H_{38}O_2$ (elemental analyses and mass spectrum), m p 189—190°, $[\alpha]_D$ ($CHCl_3$) $-$ 25°, 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} 1755, 1640, 881, and 754 cm^{-1}) The 100 MHz spectrum indicated the presence of a *cis*-disubstituted double bond flanked by quaternary carbon atoms and located in a five-membered ring (δ 5 98 and 5 46, pair of doublets 2H J 5 5 Hz), an isopropenyl group (δ 4 70, 2H, multiplet, δ 1 61, 3H, broadened singlet), and four tertiary methyl singlets (δ 1 08 to 0 90, 12H, four singlets) It differed from the n m r spectrum of deoxyemmolactone in having a one proton doublet at δ 4 55 (J 5 3 Hz) instead of the one-proton multiplet at δ 5 58 which has been attributed to the trisubstituted olefinic proton of deoxyemmolactone [1] Spin-decoupling experiments revealed that the doublet at δ 4 55 was part of an ABX system, it was coupled to a one-proton doublet of doublets at δ 2 50 (J 5 3 and 10 7 Hz), which in turn was coupled to a one-proton doublet at δ 1 88 (J 10 7 Hz)

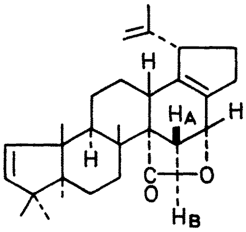
Since all possible trisubstituted olefinic protons in a bisnorlupane skeleton would resonate as triplets or multiplets in the n m r spectrum, then isodeoxyemmolactone must contain a tetrasubstituted double bond and a γ-lactone terminating at a secondary centre Examination of molecular models of the nine possible structures for isodeoxyemmolactone showed that only (3) had dihedral angles between H_A–C(15)–C(16)H_X, H_B–C(15)–C(16)–H_X, and H_A–C(15)–H_B of the right order of magnitude, *viz* approximately 78°, 33°, and 111°, respectively Application of the Karplus equation to these values afforded[2] coupling constants $J_{AX} <$ 0 2 Hz, J_{BX} 5 5 Hz, and J_{AB} 10 7 Hz consistent with experimentally determined values



(1)



(2)



(3)

Circular dichroism studies showed that the $n \rightarrow \pi^*$ transition of the lactone carbonyl group in the two compounds gave rise to a positive Cotton effect in deoxyemmolactone ($\Delta\epsilon$ + 0 975, 237 nm) and a negative Cotton effect in isodeoxyemmolactone ($\Delta\epsilon$ $-$ 1 38, 237 nm) These findings are in agreement with the results obtained by application of the lactone sector rule to structures (1) and (3) [3]

The analytical and spectroscopic evidence suggested that isodeoxyemmolactone was (3) This was confirmed by acid-catalysed rearrangement of deoxyemmolactone to isodeoxyemmolactone The ease with which this rearrangement occurred has suggested that isodeoxyemmolactone could be an artefact, although the methods used to isolate the compound would seem to preclude this

(*Received, December* 29*th*, 1970, *Com* 2221)

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[1] M B Burbage, K Jewers R A Eade, P Harper, and J J H Simes, *Chem Comm* , 1970, 814

[2] N S Bhacca and D H Williams, "Applications of N M R Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, 1964, p 49

[3] J P Jennings, W Klyne, and P M Scopes, *Tetrahedron*, 1965, **26**, 7229