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LONGIPENOL, A NOVEL TETRACYCLIC DITERPENE FROM THE TERMITE SOLDIER LONGIPEDITERMES LONGIPES

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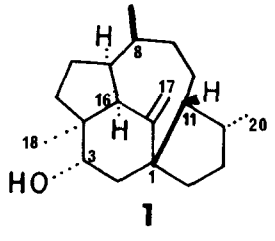
SUMMARY. Longipenol, a tetracyclic diterpenoid from soldiers of the nasute termite Longipeditermes longipes, has been shown by detailed carbon and proton NMR studies (COSY, NOSY) to have the novel spiro-fused structure (1).

Chemical defense by soldier termites reaches its zenith in the glue-squirting genera of the Nasutitermitinae (Isoptera, Termitidae).[1-3] The Oriental genus Longipeditermes is among the most primitive of this advanced diterpene-manufacturing subfamily, and its secretion chemistry is highly variable even within small populations.[4,5] Indeed, major and minor soldiers of Longipeditermes longipes from Malaysian rainforests produce bicyclic secotrinervitanes (2), tricyclic trinervitanes (3), tetracyclic rippertanes, and the new spiro-fused tetracyclic longipane 1. We now describe the results of 2D-NMR experiments which allow the assignment of stereochemistry and resonances for this unusual cage-like molecule.



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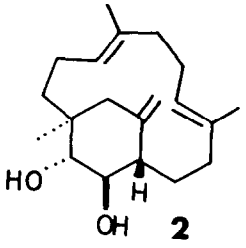

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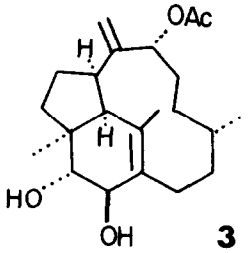

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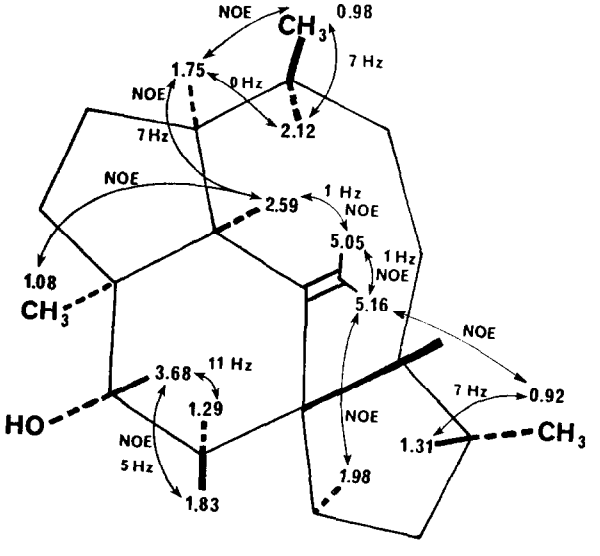
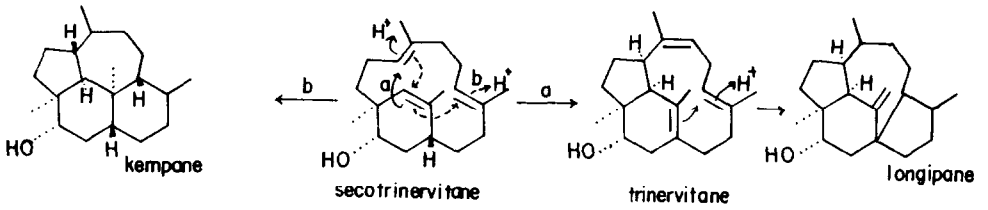


Longip-15(17)en-3α-ol, $C_{20}H_{32}O$ (m/z 288.246; calc. 288.245), oil, has bands in its i.r. [$\nu_{max}^{CHCl_3}$ 3320 cm^{-1}] spectrum consistent with the presence of a hydroxyl group. The ^1H and ^{13}C n.m.r. ($CDCl_3$) spectra[5] show the hydroxyl group as secondary [δ_H 3.68 (dd, J = 5, 11 Hz); δ_C74.2 (d, C-3)], as well as the presence of a tertiary methyl [δ_H 1.08, δ_C 26.6(C-18)], two secondary methyls [δ_H 0.98 and 0.92 (both d, J = 7 Hz, H-19 and H-20), δ_C 21.1 and 19.5 (C-19 and C-20)]; and a 1,1'-disubstituted ene [δ_H 5.05, 5.16 (both d, J = 1 Hz) δ_C 111.9 (t) and 152.9 (s)], indicating that (1) is tetracyclic. The spirocyclic junction at C-1 was originally deduced from the presence of a second quarternary carbon and the isolated dd pattern for H-2 of the C-3 ketone (δ_H 2.97, dd, ^2J = 14.0 Hz, ^4J = 0.9 Hz).

The results from the two-dimensional n.m.r. experiments (COSY, NOSY)[6,7] are tabulated in the Figure. This allowed most proton assignments to be made and revealed their relative stereochemistry confirming the structure as shown. The absolute stereochemistry depicted in (1) is based on biogenetic analogy with related termite diterpenoids.[1,5] It is fascinating that this new tetracycle, which represents a deviation from the pathway leading to the more common 5,6,6,7 kempane skeleton, occurs in this ancestral type nasute soldier. Moreover, its occurrence is highly idiosyncratic to specific nests within a given population.[5]



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References and Notes:

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