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SECOTRINERVITANE, A NOVEL BICYCLIC DITERPENE SKELETON FROM A TERMITE SOLDIER (1).

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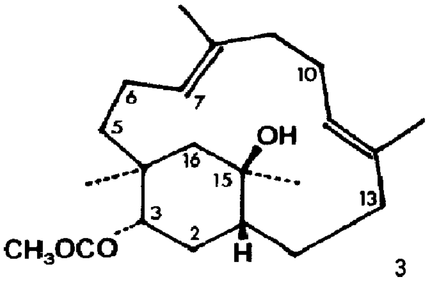
SUMMARY : The structure of 3α-acetoxy-15β-hydroxy-7,16-secotrinervita-7,11-diene, a diterpene possessing a novel bicyclic cembrane-derived carbon skeleton, has been determined by X-ray diffraction analysis.

When disturbed, soldiers of the nasute termites (Nasutitermitinae) eject from their frontal gland a viscous defensive secretion. It has been recently demonstrated that this secretion is a complex mixture of mono- and diterpenes (3,4). Until now, all the diterpenes isolated so far from *Nasutitermes* or *Trinervitermes* soldier secretions, belong to the kempane (1) or trinervitane (2) skeletons (4,5). In this communication we wish to present the structure elucidation of 3α-acetoxy-15β-hydroxy-7,16-secotrinervita-7,11-diene, a diterpene possessing a novel bicyclic cembrane-derived carbon skeleton.

Compound 3 (~10% of the diterpene fraction) was isolated together with six trinervitane diterpenes (6) from an hexane extract of *Nasutitermes princeps* soldiers collected in Papua-New Guinea (Nubia - Bogia subdistrict). The spectral properties of 3 ($C_{22}H_{36}O_3$ by HRMS ; $[\alpha]_{579}$ = 61°(CHCl$_3$, c = 0.52) ; m.p. 117° (pentane) ; IR (film) : $\nu_{C=O}$ at 1720 cm^{-1}, ν_{OH} at 3500 cm^{-1} ; ^{1}H NMR (CDCl$_3$/TMS -270 MHz - δppm) : 0.98 (3H,s), 1.22 (3H,s), 1.58 (3H,s), 1.61 (3H,s), 2.08 (3H,s), 5.20 (1H,bd, J=10 Hz), 5.39 (1H, bd, J=10 Hz), 5.56 (1H,dd, J=11 and 5 Hz)) suggest that it is a bicyclic diterpene possessing two methyl groups on trisubstituted double bonds, two tertiary methyl groups one of which is on a quaternary carbon atom bearing an hydroxyl group and a secondary acetoxyl group. These data together with the absence in the ^{1}H NMR spectrum of 3 of the characteristic HC-7 and HC-16 signals, observed for the 1(15),8-trinervitadiene (7) derivatives, suggest that this compound is a 7,16-secotrinervitane derivative. This hypothesis was confirmed by X-ray diffraction analysis.

The crystals of 3 belong to the space group $P2_12_12_1$, with a = 8.850 (4), b = 17.413 (7), c = 14.435 (7) Å and Z = 4 . Intensities of 1804 independent reflections were collected on a Syntex $P2_1$ diffractometer using MoKα radiation ($2\theta_{max}$ = 47°). The structure was solved using the MULTAN 78 programs (8) and the refinements were realized using the SHELX-76 program (9). R_{final} = 0.053. A computer generated drawing of 3, showing the relative configuration is depicted in figure 1 (10).



3

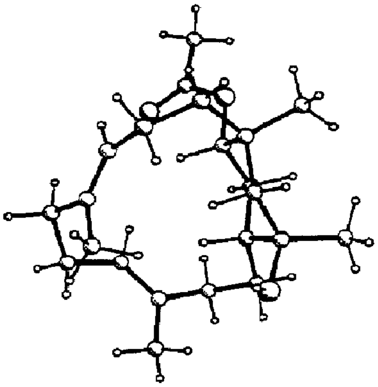
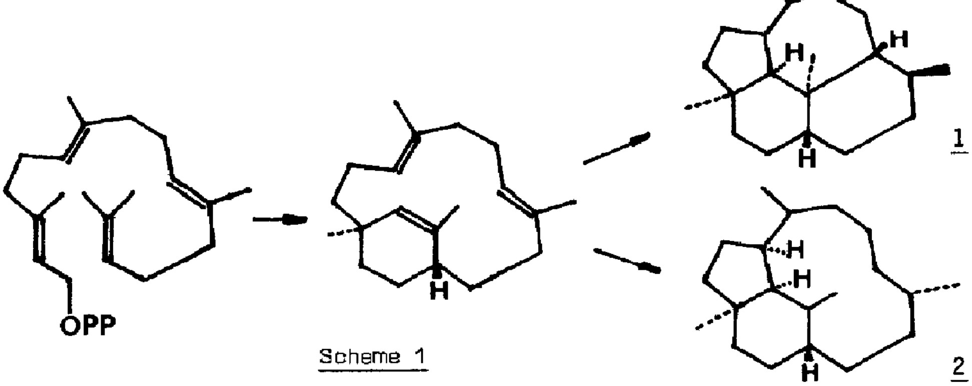


Figure 1 : Computer drawing of 3.

It has been postulated [4] that biogenetically, the kempane and the trinervitane skeletons result from the cyclization of farnesyl pyrophosphate following scheme 1. The coexistence in *N. princeps* of trinervitane and 7,16-secotrinervitane derivatives greatly supports this scheme and reinforces the view that the latter is a likely intermediate in the biosynthesis of the kempane and trinervitane diterpenes.



Scheme 1

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10. The atomic co-ordinates will be deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 IEW U.K.

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