

ISOLATION OF A NOVEL TRIACETOXYSECOTRINERVITANE FROM THE TERMITE
CONRICTOTERMES CYPHERGASTER (TERMITIDAE, SUB-FAMILY NASUTITERMITINAE)

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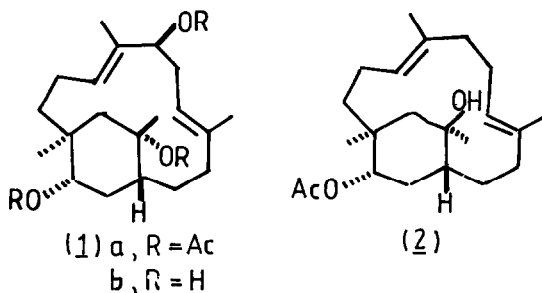
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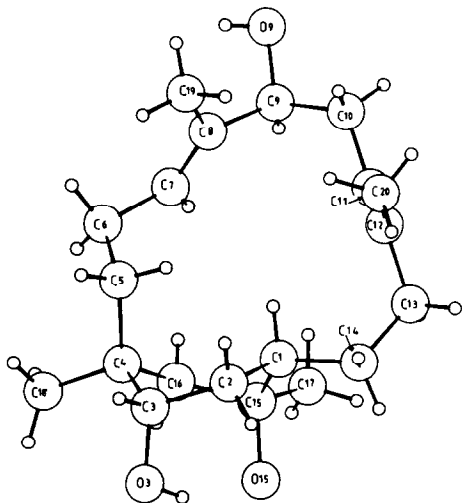
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A novel secotrinervitane, 3 α ,9 β ,15 α -triacetoxy-7,16-secotrinervita-7,11-diene has been isolated from the termite *Constrictotermes cyphergaster* and its structure assigned by X-ray crystallographic studies on the corresponding triol.

Soldiers of the highly evolved sub-family of termites, Nasutitermitinae, have been shown to have diverse defensive secretions. These consist of oxygenated diterpenes dissolved in a variety of monoterpenes.^{1,2} In nearly all cases the diterpenes possess the tricyclic trinervitane³ or tetracyclic kempene skeleton.⁴ In the present work a novel triacetoxy-trinervitane (1a) has been isolated from the defense secretion of the South American termite, *Constrictotermes cyphergaster* and its structure has been assigned by X-ray diffraction studies on the derived triol (1b).

A gc-ms of an extract of 200 termites revealed the presence of α -pinene and one diterpenoid derivative in a ratio of 1:3. The diterpene (15mg) was isolated by preparative hplc as an oil, ν_{\max} 1740cm⁻¹; ¹H nmr 100MHz (CDCl₃), δ 0.94(s, 3H, quaternary CH₃), 1.37(s, 3H, quaternary CH₃), 1.1-1.8(br. m, 11H), 1.58 and 1.62(2xbr. s, 2x3H, 2xvinyllic CH₃), 1.98, 2.05 and 2.16(3xs, 3x3H, 3xCH₃CO-), 2.25-2.7(m, 4H, allylic -CH₂-), 5.2(m, 2H, -CHO-), 5.5(m, 2H, vinyllic); m/z 388.211(1.11%, M-60⁺ calculated C₂₄H₃₆O₄, 388.161). It was evident that the molecular ion could not be obtained under EI conditions and the largest ion obtained resulted from loss of acetic acid. From this information the compound was considered to be a triacetoxy bicyclic diterpenoid with the molecular formula C₂₆H₄₀O₆. This triacetate was converted to the corresponding triol by reduction with lithium aluminium hydride (10 fold excess, THF, 25°C) to yield, after flash column chromatography, a crystalline triol in 60% yield, m.p. 193-5°C, ¹H nmr 360MHz (CDCl₃) δ 1.00(s, 3H, CH₃), 1.16(s, 3H, CH₃), 1.35-2.50(m, 18H),





Computer drawing
of (1b)

1.58(s,3H,CH₃), 1.59(s,3H,CH₃), 3.60(1H,dd,J=4.5,3Hz), 4.08(1H,dd,J=8,5Hz), 4.98(1H,dd,J=7.5,7.5Hz), 5.65(1H,dd,J=7.5,7.5Hz); m/z 322.223(M⁺,1.2%, calculated C₂₀H₃₄O₃ 322.196).

Crystals suitable for X-ray studies were grown by diffusion of hexane into a solution of the alcohol (1b) in CH₂Cl₂. Crystal data: C₂₀H₃₄O₃, M = 358.52, monoclinic, space group A2, a = 12.306(5), b = 8.880(2), c = 17.394(7)Å, β = 93.70(3), U = 1897Å³, Z = 4, D_c = 1.25g cm⁻³, F(000) = 784, μ(Cu-Kα) = 6.43 cm⁻¹. Data were measured (2θ_{max} = 140°) on an Enraf-Nonius CAD4 diffractometer using Cu-Kα radiation and ω-2θ scans. 1294 Independent reflections with I > 3σ(I) were used in the analysis. The structure was solved by direct methods⁶ and refined by least squares with the CRYSTALS package of crystallographic programs. Refinement converged to give final R values of 5.88 (R_w = 8.69).

Only one secotrinervitane, the hydroxy acetate (2), has been isolated previously from *Nasutitermes princeps*.⁷ The occurrence of a triacetoxysconervitane in the secretion of *Constrictotermes cyphergaster* is further evidence for the hypothesis that the biogenesis of tricyclic and tetracyclic diterpenes, found in other termites, proceeds via bicyclic intermediates from geranyl, geranyl pyrophosphate.¹ The triacetate, (1a), is the first example of a secotrinervitane where an oxygen functionality, namely the acetate at C-9, has arisen by the equivalent of an oxidative process at an allylic position.

References and Notes

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