

1,13-TETRADECADIEN-3-ONE AND HOMOLOGS:
 NEW NATURAL PRODUCTS ISOLATED FROM SCHEDORHINOTERMES SOLDIERS

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Chemical warfare is well-known among the soldier castes of many termite genera¹. We wish to report the results of our study of the defensive compounds produced by the soldier caste of the East African termite Schedorhinotermes lamanianus Sjostedt (Isoptera:Rhinotermitidae). The secretions collected from the frontal glands^{2a} of major and minor soldiers were analyzed by glc (FID) and by gc-ms^{2b, 3}. The secretion obtained from the major soldiers was found to contain nine volatile components (A1, A2, A3, C1,

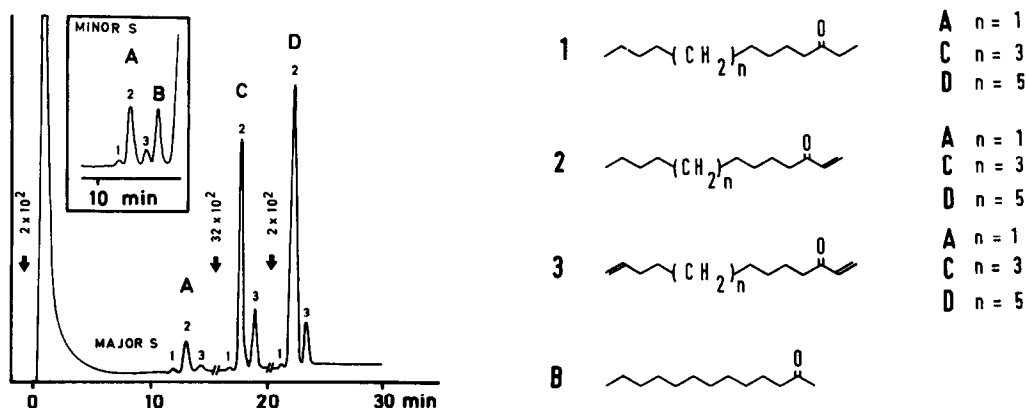


Fig. 1. Glc traces of the frontal gland secretions of S. lamanianus soldiers and the structures of the ten components. Glc conditions: 20% Carbowax 20M on 80/100 Gas Chrom Q, temperature programmed from 100° to 250° at 5°/min.

C2, C3, D1, D2, D3) as shown in Fig. 1. Secretions from the minor soldiers showed a similar composition but with a higher dienone/enone ratio and with the presence of a tenth compound, 2-tridecanone (B). Major soldiers contain about 1.0 mg of the ketonic mixture per termite (13% of body weight), of which 680 μg is 1-tetradecen-3-one (C2). Minor soldiers contain 0.2 mg of the secretion (10% of body weight). The secretion is applied to attacking ants by the soldiers by the use of an enlarged brush-like labrum.

Most of these compounds (A3 and D3 excepted) were identified by comparison of mass spectral and glc retention time data with those of authentic materials. Ketones B, C1, C2, and D2 (cf. Ref. 4) have been previously found in the West African termite Schedorhinotermes putorius⁵.

Enone A2 was synthesized via addition of vinylolithium to nonanal in ether at -70° followed by Jones oxidation of the resulting allylic alcohol. The mass spectrum of synthetic A2 was identical to that of the natural material, exhibiting a parent ion at m/e 182 and the characteristic vinyl ketone fragments at m/e 55 ($\text{CH}_2=\text{CHC}=\text{O}^+$) and m/e 70 ($\text{CH}_2=\text{CHC}(\text{OH})\text{CH}_2^+$) seen also in the enones C2 and D2.

Dienone C3 was prepared as follows. Commercially available 10-undecen-1-ol was converted to the corresponding bromide with phosphorus tribromide in pyridine⁶. Addition of an ether solution of dry acrolein to an ether solution of the Grignard reagent prepared from 10-undecenyl bromide at 25° afforded an 85% yield of the crude 1,13-tetradecadien-3-ol. The crude dienol was then stirred with a twenty-fold excess of activated manganese dioxide⁷ (25° , 3 hr). The reaction mixture was filtered through Celite overlaid with Silica Gel, the precipitate was washed several times with chloroform, and the crude product (after concentration in vacuo) was chromatographed (Florisil, 5% ethyl acetate-hexane) to yield 35% of the dienone C3 as a clear oil: ir, $\lambda_{\text{max}}^{\text{film}}$ 3.24 (C=C-H), 5.92, 5.97 (C=O), 6.14 (C=C), 10.2, 10.4 (vinyl), and 11.15 μ (C=CH₂); uv, $\lambda_{\text{max}}^{\text{hexane}}$ 217 nm ($\epsilon = 545$); nmr (CDCl_3 , 60 MHz, relative to TMS = 0 δ), δ 1.1-1.8 (m, 14H, -CH₂-), 1.9-2.3 (m, 2H, -CH₂C=C), 2.57 (t, 2H, -CH₂CO-, J = 14 Hz), 4.80-5.15 (m, 2H, vinyl H), 5.5-6.4 (m, 4H, vinyl H). The mass spectra (Fig. 2) and glc retention times of synthetic and natural C3 were identical. The two most prominent peaks were again the vinyl ketone fragments (m/e 55 and 70) as seen in the corresponding enone.

The structures of dienones A3 (cf. Ref. 8) and D3 are proposed to be homologous to C3 on the basis of analogous glc, nmr, and mass spectral characteristics.

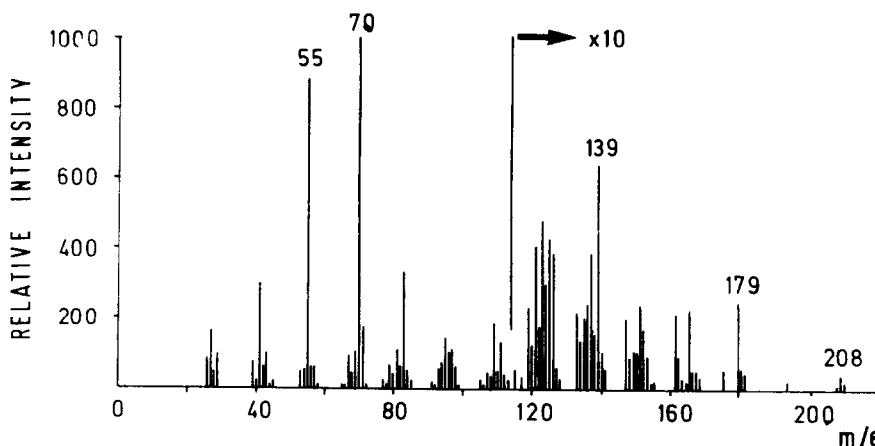


Fig. 2. EI mass spectrum of 1,13-tetradecadien-3-one².

The toxicity of the *S. putorius* secretion to several species of ants has already been demonstrated^{5,9}. Preliminary results from our laboratories indicate that the dienone C3 may have a significantly lower LD₅₀ for certain insect species than enone C2 (the major component in both East and West African species). Further investigation into the biological roles of these ketones in alarm behavior, defense, and inhibition of soldier development¹⁰ are currently in progress, and the results will be presented elsewhere.

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REFERENCES AND NOTES

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- 2.(a) The frontal glands of these termites extend into the abdomen, so that in bulk collections, whole soldiers were homogenized in

hexane and the crude extract was then chromatographed on Florisil with 1% ethyl acetate-hexane.

- (b) Gc-ms analyses were performed using a Finnigan 1015D quadrupole mass spectrometer interfaced with a column of 5% Carbowax 20M on 80/100 Gas Chrom Q.
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