Tetrahedron Letters No. 15, pp 1463 - 1464, 1974. Pergamon Press. Printed in Great Britain.

1-NITRO-trans-1-PENTADECENE AS THE DEFENSIVE COMPOUND OF TERMITES

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(Received in UK 27 February 1974; accepted for publication 7 March 1974)

The frontal gland secretion of the soldier caste of some termite species has been recently subjected to chemical analysis. The secretion serving for the defence of the termite colony has been shown to contain compounds of the terpenoid nature, lipids, mucopolysaccharides, p-benzoquinone and aliphatic vinyl ketones with a longer chain[1]. In the frontal gland secretion of soldiers of the Cuban Prorhinotermes simplex (Hagen) (Rhinotermitidae, Isoptera), we have now found an aliphatic olefinic nitro compound. This finding is of interest also from the point of view that the number of naturally occurring nitro compounds is known to be very low[2].

The secretion, a colourless liquid, was withdrawn directly from the gland pore of about 500 soldiers by a capillary pipette or filter paper; the elution was performed with ether. As shown by gas chromatography (PYE 104; SE 30,OV 17, Carbowax 20 M, Apiezon L), the secretion contained one principal component along with a small amount of compounds (up to 5%) with a shorter elution time and a series of peaks with longer elution times. As inferred later on from comparison with the synthetically prepared 1-nitro-trans-1-pentadecene, the compounds with longer elution times are decomposition products formed during the gas chromatography. Measurement of the principal component by the GC-MS technique (PYE 104-A.E.I. MS 902) indicated that a nitro compound was involved. For the sake of identification, the nitro compound was preparatively isolated on a micro scale by means of an analytical GC column (OV 17,100°C); the amount of about 20 mg was isolated by TLC on silica gel with the use of 9:1 light petrol. benzene. The structure of 1-nitro-trans-1-pentadecene was ascribed on the basis of data obtained from mass, NMR, and IR spectra, and from ozonization experiments.

In the mass spectrum, the molecular peak is tiny in contrast to the peak of ions at m/e 238 ($C_{15}H_{28}NO$, as shown by high resolution (HR) measurement) corresponding to elimination of a hydroxyl from the molecular ion. Elimination of water leads to the m/e 220 ion (HR $C_{15}H_{26}N$) which probably exhibits the structure of a nitrile ion[3b]. Further peaks of the spectrum are not distinct and their analysis indicated the composition CH or CHN. The NO^+ ions were identified at the mass m/e 30. The present fragmentation is in accordance with the known spectra of aliphatic nitro compounds [3a,b].

The IR spectrum (KBr micropellets) exhibits bands at 1350 and 1522 cm^{-1}($-NO_2$); at 960, 1646, and 3095 cm^{-1}(disubst. trans-C=C-); and at 725 cm^{-1} ($-(CH_2)_n-$).

The NMR spectrum [CCl_4(TMS),delta(ppm),J(Hz)] is in full accordance with the structure proposed: 0.88 (t,CH_3,J=6.5); 1.15-1.70 (br s,$-(CH_2)_{11}-$); 2.25 (br q, $-CH_2-C=$); 6.87 (dt,$=CH-NO_2$,J_{vic}=13.4 (trans),J_{allyl}=1.0,0.9); 7.17 (dt,-C-CH=C-, J_{vic}=13.4(trans), 6.6,6.6).

Furthermore, the double bond position was supported by microozonization according to Beroza and Bierl[4]. The nitro compound (0.5 mg) was ozonized in CS_2, the product of ozonization reduced with triphenylphosphine, and the mixture analysed by GC-MS (SE 30,110°, program 2°/min). As the ozonization product, there was identified tetradecan-1-al (M^+ 212,M-18,M-28,M-44).

The structure of the nitro compound was proved by synthesis. Reaction of myristylaldehyde and nitromethane afforded a nitro alcohol [MS: M-17, M-(17+18), M-(17+18+18), M-(17+30), m/e 90, 213 + α-cleavages] which was dehydrated to a mixture of cis and trans isomers of 1-nitro-1-pentadecene (GC: SE 30, 70°, program 5°/min, separation at 25% valley). The pure 1-nitro-trans-1-pentadecene was prepared through the nitro alcohol acetate and its IR and mass spectra were identical with those of the native substance isolated from termites.

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