Chemical Defence in the Termite *Ancistrotermes cavithorax:* Ancistrodial and Ancistrofuran

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Summary Soldiers of the termite *Ancistrotermes cavithorax* produce terpenoid defence secretions, but whereas the minor soldiers produce ancistrodial (**1**) exclusively, the major soldiers secrete ancistrofuran (**6**), together with (**4**) and (**5**).

The West African termite *Ancistrotermes cavithorax* is a small subterranean fungus-growing species characterised by a diffuse nest system. Major and minor soldier castes are responsible for colony defence, the major predators being ants. Field studies indicate that predation upon *A. cavithorax* is markedly lower than that observed for other common termite species, and this is almost certainly due in part to the chemical defence system of *A. cavithorax* soldiers. Indeed, the defence secretion has been shown to be repellent to the ant *Megaponera foetens*, a major predator of this species.[1]

A solvent extract (CH_2Cl_2) of the minor soldiers (*ca.* 50 individuals) was found to consist largely of one sesquiterpene component, ancistrodial (100 μg), for which we now propose structure (**1**).† Mass spectrometry indicated a molecular formula $C_{15}H_{22}O_2$, which together with microscale chemical reactions (2,4-dinitrophenylhydrazine, bromine in CCl_4, $NaBH_4$–MeOH) suggested the presence of one or more

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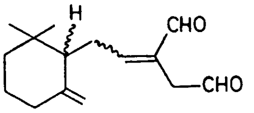
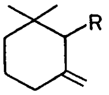
† The limited amount of material available has precluded investigations of absolute configuration and alkene geometry.

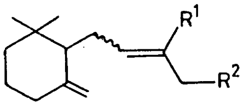
carbonyl groups and double bonds. N.m.r. spectroscopy (100 MHz, $CDCl_3$) showed the presence of two aldehyde groups [δ 9·45 (1H, s) and 9·64 (1H, t, J 2 Hz)]. Signals at δ 6·75 (1H, t, J 7 Hz) and 3·41 (2H, br s) support the presence of an unsaturated aldehyde entity $-CH_2-CH=C-CH_2-CHO$. Signals attributed to two methyl groups [δ 0·88 (3H, s) and 0·98 (3H, s)] and signals at δ 4·55 (1H) and 4·85 (1H) suggested the presence of a γ-cyclogeranyl ring system, and this assignment was corroborated by comparison with synthetic models [*e.g.* (**2a**) and (**2b**)].



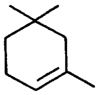
(1)



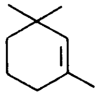
(2) a; R = CH_2OH
b; R = CH_2CHO



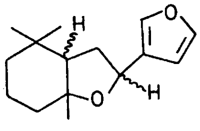
(3) a; $R^1 = CO_2Et, R^2 = CO_2H$
b; $R^1 = R^2 = CH_2OH$



(4)



(5)



(6)

Proof of structure was provided by synthesis of racemic (**1**). γ-Cyclohomocitral (**2b**) was synthesised from 2,2-dimethylcyclohexanone.[2] Stobbe condensation between (**2b**) and diethyl succinate in the presence of potassium t-butoxide afforded the half-ester (**3a**) in 68% yield which was reduced to the diol (**3b**)‡ with lithium aluminium hydride in diethyl ether. Mild oxidation (CrO_3–pyridine complex, CH_2Cl_2) gave the racemic dialdehyde (**1**) [50% yield from (**3a**)] as a 6 : 1 mixture of geometric isomers as determined from n.m.r. integration values. The major isomer and the natural compound were shown to be identical by comparison of mass spectral and n.m.r. data, and by comparative g.l.c. on 8 columns.

The major soldiers of *A. cavithorax* produce a defensive secretion which has been examined both by solvent extraction of whole insects, and by direct analysis of 'milked' secretion. In both cases, the presence of equal trace amounts of α- and β-cyclogeraniolene [(**4**) and (**5**), respectively] has been established by comparison with authentic samples.[3] The major component is a sesquiterpene furanoid ether (*ca.* 3 μg per soldier) which we have named ancistrofuran, and for which we propose structure (**6**). High resolution mass spectrometry indicated a molecular formula $C_{15}H_{22}O_2$ (calc. 234·1620; found 234·1616) and the n.m.r. spectrum was indicative of a 3-substituted furan attached to a bicyclic ring system [δ 0·89 (3H, s), 1·02 (3H, s), 1·14 (3H, s, CH_3-C-O), 2·10 (2H, m, CH_2-C-O), 4·84 (1H, m, $-CH-O$), 6·27 (1H, sharp m, β-furan H), and 7·29 (2H, sharp m, α-furan H)]. The relative and absolute stereochemical configuration of (**6**) and synthetic studies upon which these results are based will be published elsewhere.

It is interesting to note that the chemical constituents of the defence secretions of the major and minor soldiers of *A. cavithorax* are completely different. Nevertheless the major constituents in each case are isomeric sesquiterpenes and can be related to each other by unexceptional chemical transformation, pointing to a common biosynthetic origin.

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‡ The structures of all reported compounds are in accord with spectroscopic data and, where relevant, comparison with authentic samples.

[1] C. Longhurst, R. A. Johnson, and T. G. Wood, *Oecologia*, 1977, **32**, 101; C. Longhurst, Ph.D. Thesis, Southampton University, 1978.

[2] P. Seifert and H. Schinz, *Helv. Chim. Acta*, 1951, **34**, 727; S. Julia, M. Julia, H. Linarès, and J-C. Blondel, *Bull. Soc. chim. France*, 1962, 1952.

[3] Y-Henk Suen and H. B. Kagan, *Bull. Soc. chim. France*, 1970, 3552.