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SOLDIER DEFENSE SECRETIONS OF THE SOUTH AMERICAN TERMITES *CORTARITERMES SILVESTRI, NASUTITERMES* SP N.D AND *NASUTITERMES KEMNERI*

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Abstract—The defense secretions of the soldiers of the South American termites *Cortaritermes silvestri, Nasutitermes* sp. n.D. and *Nasutitermes kemneri* have been investigated. The secretion of *C. silvestri* was shown to contain α-pinene, β-pinene, limonene and *cis*-pin-3-en-2-yl acetate. Three of the four diterpenes in this secretion were identified as the triacetate, diacetate propionate and acetate dipropionate of 3α, 9β, 12α-trihydroxy-11(12), 15(17-trinervitadiene. The soldier secretion of *Nasutitermes* sp. n.D and *Nasutitermes kemneri* were found to contain a mixture of monoterpene hydrocarbons and diterpenes. The major monoterpene in these two species was shown to be β-phellandrene and terpinolene, respectively. The major diterpene in *Nasutitermes* sp. n.D. was identified as 9β-hydroxy-1(15), 8(19)-trinervitadiene and, for *Nasutitermes kemneri*, 2α, 3β-dihydroxy-1(15), 8(9)- and 1(15), 8(19)-trinervitadiene were the major components.

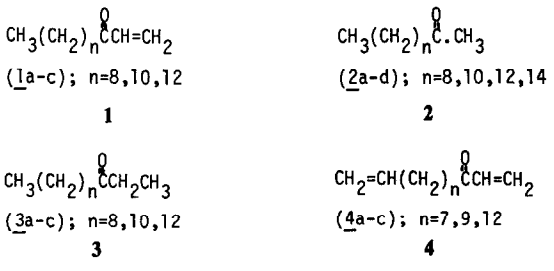
INTRODUCTION

The soldier caste of termites utilise both physical and chemical forms of defence which can be used separately or in combination. Physical defence involves the use of mandibles which have evolved into powerful weapons. Soldiers utilising this form of defence are large and their mandibles are designed for cutting and biting. The shape and precise action of the mandibles varies among the genera and their efficiency in defence has been related to their morphology. In three families, Mastotermitidae, Rhinotermitidae and Termitidae, the defence mechanisms in many species also include the use of a chemical secretion.[1] With species such as *Amitermes* and *Macrotermes*, the opponent is firmly grasped and a secretion is allowed to flow into the wound. The secretion can also be daubed onto the opponent using a labrial brush which involves physical contact but the mandibles do not cut the cuticle, e.g. *Rhinotermes*. The most highly evolved form of defence is used by the nasute soldiers who totally avoid any contact with the enemy. The head capsule has developed into an elongated rostrum called the nasus through which a gluey, viscous secretion is ejected. The nasus operates rather like a syringe and the secretion can cover a distance of several centimetres.

A great variety of different compounds have been identified as components of the defence secretion of termites. The soldiers of the sole member of the primitive family Mastotermitidae, *M. darweniensis* possess an elementary chemical defence system in addition to strong mandibles.[2] They produce a mixture of benzoquinone and toluquinone from the buccal cavity which are combined with proteins in the saliva producing a mixture which is initially mobile but sets to a dark rubber like material thus immobilising the enemy. In the Rhinotermitidae family certain species have evolved soldiers with highly developed frontal glands from which a chemical defence secretion is produced. The major component of the secretion of *Prorhinotermes simplex* has been identified as 1-nitro-*trans*-pentadecene.[3] Three normal ketones, 1-tetradecen-3-one (**1b**), 1-hexadecen-3-one (**1c**) and 2-tridecanone (**2b**) have been identified as major constituents of the secretion from the frontal gland of *Schedorhinotermes putorius*. Trace amounts of C_{14} and C_{15} saturated ketones were also present.[4] Similar types of ketones were found in the secretion of *S. lamanianus*. These were found to be C_{12}, C_{14} and C_{16} 3-alkanones (**3**), 1-alken-3-ones (**1**) and α, ω-alkadien-3-ones (**4**).[5] The major component for both major and minor soldiers being 1-tetradecen-3-one (**1b**) (>70%). Trace amounts of 3-tridecanone (**3b**) were found only in the minor soldiers. When alarmed the soldiers of *Coptotermes lacteus* emit a globule of a milk-like fluid from a large abdominal reservoir which subsequently hardens to a colourless-resilient film on the attacker.[2] No chemical reaction seems to be involved as the latex can be reconstituted with the addition of water. Analysis of the secretion showed it to be a suspension of lipids (largely saturated paraffins) in aqueous mucopolysaccharides based on glucosamine and glucose units.

The higher termites belong to the family Termitidae which consists of the sub-families macroterimitenae, Termitinae, Nasutitermitinae and Apicotermitinae.† The former three sub-families contain those soldiers with well developed frontal glands and chemical defence whereas the Apicotermitinae contains those species with regressed frontal glands and the soldierless genera, i.e. *Anoplotermes* and *Grigiotermes*.

In the sub-family Macrotermitinae the frontal gland is not generally well developed and secretions are often



†This is the new classification of Termitidae as proposed by W. Sands in 1972, where the old sub-family Amiternitinae has become part of the Termitinae and a new sub-family, Apicotermitinae has been created to include the soldierless termites (Anoplotermes branch) and the soldiers with regressed frontal glands (Apicotermes branch).

produced from the salivary glands. An aqueous solution of toluquinone with a small amount of benzoquinone is produced by the soldiers of *Macrotermes carbonarius*. These soldiers have sickle shaped mandibles with which they slab their foes and the secretion is pumped into the wounds from massive labial glands.[6] Soldiers of the termite *Odontotermes badius* and *O. stercorivrovs* emit an aqueous brown secretion from the labial gland which becomes sticky on exposure to the air. On analysis this secretion was found to be a mixture of benzoquinone and protein.[7] Similarly five other species of the oriental macrotermitine genera *Microtermes*, *Macrotermes*, *Hypotermes* and *Odontotermes* release non-proteinaceous quinone containing secretions when attacked. In two species, *Macrotermes gilvus* and *Odontotermes horm*, no quinones could be detected.[8] The frontal gland of the major soldiers of *Macrotermes goliath* were found to contain a large amount of normal and isoalkanes (C_{22}-C_{34}) in addition to free fatty acids, phospholipids and sterols.[9] Saturated straight chain and methyl branched and unsaturated alkanes were also found in the frontal gland secretion of *Macrotermes subhyalinus*.[10] (*Z*)-9-Heptacosene and (*Z*)-9-nonacosene were the major olefins and the paraffins were mainly n-tricosane n-pentacosane, 3- and 5- methylpentacosanes and 5-methylheptacosane.

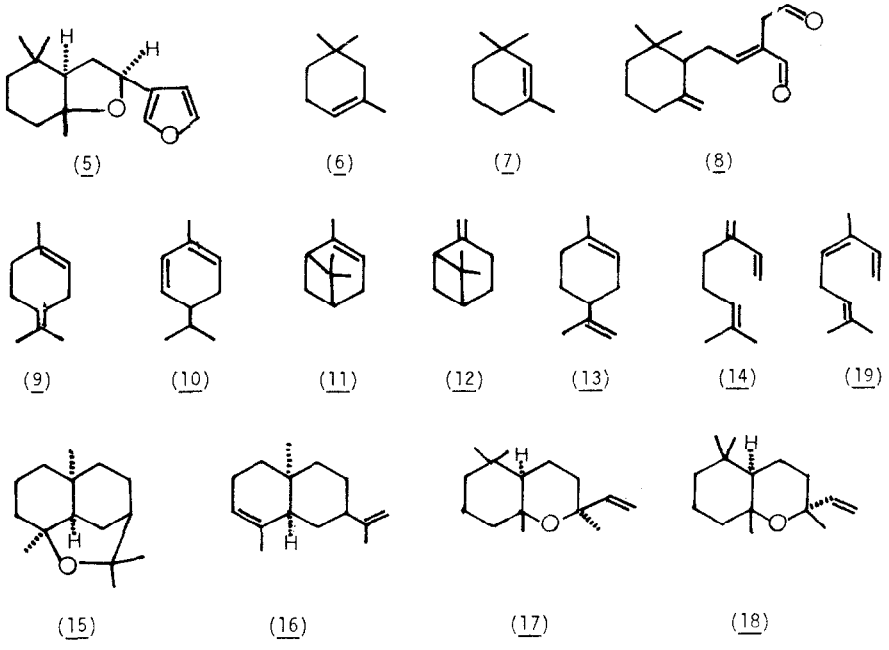
The soldiers of the macrotermitinae species *Ancistrotermes cavithorax* are dimorphic and it is interesting to note that the secretion is different in both castes.[11] The major soldiers produce a mixture of ancistrofuran (**5**) together with small amounts of α- and β-cyclogeraniolenes (**6** and **7**) and toluene. In contrast the minor soldiers produce ancistrodial (**8**) which constitutes *ca.* 90% of the volatile secretion.

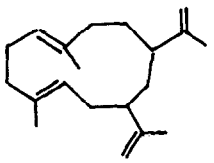
Several species of the sub-family Termitinae have soldiers which produce varied defence secretions. Monoterpene hydrocarbons have been found in a number of species. The soldiers of *Amitermes herbertensis* secrete a mixture of >98% terpinolene (**9**) with α-phellandrene (**10**). *A. laurensis* is a species in which soldiers are scarce, making up less than 0.1% of the total popualtion, but those that can be found produce a mixture of limonene (**13**), α-pinene (**11**) and **10** in small amounts.[2] A mixture of unknown resinous compounds in m ,ioterpene hydrocarbons are produced by *A. vitosus*, the latter being **10**, **13**, **11**, **9**, myrcene (**14**) and β-pinene (**12**) in order of abundance.[2]

The frontal gland of the soldiers of the West African termite *Amitermes evuncifer* contains a secretion which is composed of >90% of a sesquiterpene ether **4**, 11-epoxy-*cis*-eudesmane (**15**).[12] The minor components have been identified as the sesquiterpene hydrocarbon 10-epi-eudesma-3, 11-diene (**16**), 8-epi-cararrapi oxide (**17**), cararrapi oxide (**18**) and *cis*-β-ocimene (**19**).[13] The ether (**15**) has also been found in the soldiers of *Amitermes messinae* where it constitutes 90% of the secretion, however, in this case, the other 10% is linonene (**13**)[5,14] 11-, 13-, 15- and 17-Carbon methyl ketones (**2a-d**) are the major components of the secretion of *Amitermes unidentatus*.[15]

Diterpene hydrocarbons have been found in the frontal gland secretion of a number of *Cubitermes* species.[16-18] One of the four major constituents (*ca.* 18%) of the secretion of *C. umbratus* is cubitene (**20**) which possesses a novel skeleton arising from an irregular joining of isoprene units.[16] The other components of this secretion are biflora-4, 10, (19), 15-triene (**21**) which possesses a skeletal resemblance to the quinone antibiotic biflorins[17] and the similar compounds cembrene-A (**22**) and 3*Z*-cembrene A (**23**) found in 5% and 8% respectively.

The Nasutitermitinae sub-family contains those species which are the most highly evolved with respect to chemical defence. The soldiers of many species have vestigial mandibles and rely entirely on chemicals for defence. The soldiers of *Trinervitermes gratiosus* produce a secretion which contains the monoterpene hydrocarbons, (**11, 12, 13, 9**) and camphene (**24**) together with two unidentified monoterpene alcohols. Dissolved in this mixture were a number of oxygenated diterpenes which were identified as 9β-hydroxy-1(15), 8(19)-triner-





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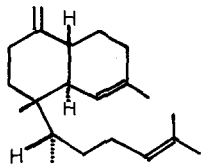

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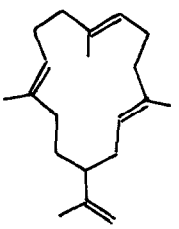

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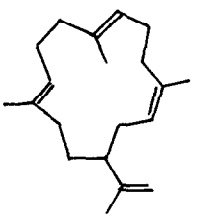
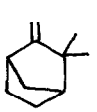


(23)

vitadiene (**25**), 2β, 3α-dihydroxy-1(15), 8(19)-trinervitadiene (**26**), 2β, 3α-dihydroxy-1(15), 8(9)-trinervitadiene (**27**) 2β, 3α, 9β-trihydroxy-1(15), 8(19)-trinervitadiene-9-acetate (**28**) and 2β, 3α, 9β-trihydroxy-1(15), 8(19)-trinervitadiene-2, 3-diacetate (**29**). Three other diterpenes were present in small amounts but were not identified.[19] Single crystal X-ray diffraction experiments on **28** gave the new trinervitane skeleton[20] and other spectroscopic techniques including ^{13}C, and ^{1}H NMR gave the structures of most of the remaining components.[21] Analysis of another population of *T. gratiosus* afforded a new structure, 2β-hydroxy-1(15)-8(9)-trinervitadiene (**30**).[22] The soldiers of *T. bettonianus* have been found to produce monoterpene hydrocarbons and the diterpenes (**25**, **26**, **27**, **28**) and 2β, 3α, 17 - trihydroxy - 1(15), 8(19) - trinervitadiene - 17 - acetate (**31**).[21,23]

The frontal gland secretion from the soldiers of the African termite *Nasutitermes costalis* have been shown



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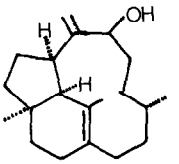

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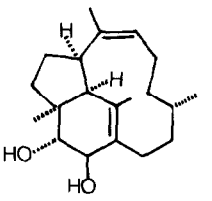

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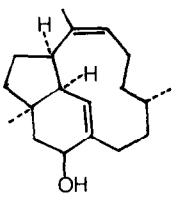

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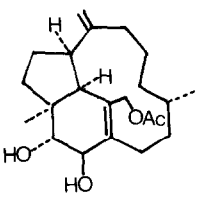

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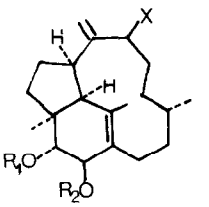


(26) $R_1 = R_2$, X = H

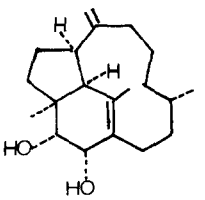
(28) $R_1 = R_2$ = H, X = OAc

(29) $R_1 = R_2$ = Ac, X = OH

(36) $R_1 = R_2$ = Ac, X = H

(37) R_1 = Ac, R_2 = X = H

(38) $R_1 = R_2$ = Ac, X = OAc



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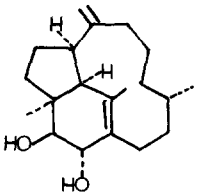

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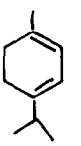

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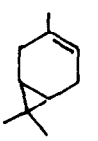

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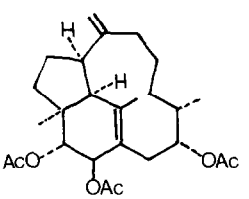

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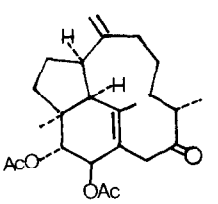

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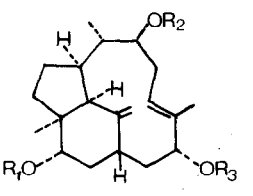


(41) $R_1 = R_2 = R_3 = C_2H_5CO$

(42) $R_1 = R_3 = C_2H_5CO$, $R_2 = CH_3CO$

to be similar to that produced by the two Trinervitermes species.[24] The major monoterpenes produced are **11, 12,** and **13** together with two diterpene diols (**32** and **33**) which have different configurations at the 2- and 3-positions to those found in *T. gratiosus*. Similarly the soldier secretion of *N. rippertii* contains **11**, **12**, **9**, α-terpinene (**34**) and Δ^3-carene (**35**) together with the diterpenes **25**, **26**, 2β, 3α-dihydroxy-1(15), 8(19)-trinervitadiene-2, 3-diacetate (**36**), 2α, 3β-dihydroxy-1(15), 8(19)-trinervitadiene-3-acetate (**37**), 2β, 3α, 9α-trihydroxy-1(15), 8(19)-trinervitadiene-2, 3, 9-triacetate (**38**), 2β, 3α, 13α-trihydroxy-1(15), 8(19)-trinervitadiene-2, 3, 13-triacetate (**39**) and 2β, 3α-dihydroxy-1(15), 8(19) trinervitadiene-13-one-2, 3-diacetate (**40**).[25] Two tricyclic propionate esters 3α, 9β, 13α-trihydroxy-11(12), 15(17)-trinervitadiene-tripropionate (**41**) and 3α, 9β, 13α-trihydroxy-11(12), 15(17)-trinervitadiene-9-acetate-3, 13-dipropionate (**42**) which have modified trinervitane skeletons have been found in the soldier secretion of a Malaysian *Nasutitermes* species.[26]

The soldiers on *Nasutitermes kempae* also produce a mixtures of mono- and diterpenes from the frontal gland. The latter includes two tetracyclic compounds with cembrene derived skeletons, 3α, 14β-dihydroxy-6(7), 8(9)-kempadiene-3, 14-diacetate (**43**) and 14α-hydroxy-6(7), 8(9)-kempadiene-3-one 14-acetate (**44**) which have been given the name kempenes after this termite.[27] These two diterpenes plus 3β, 14α-dihydroxy-6(7), 8(9)-kempadiene-3, 14-diacetate (**45**) are found in the secretion of another Malaysian termite *Bulbitermes singaporensis*.[28] The identities of two other kempenes (**46** and **47**) found in the secretion of the Guyanian termite *Nasutitermes octopilis* have also been established.[29] *Grallatotermes africanus* has soldiers which produce a secretion containing the monoterpene hydrocarbons **13, 9** and **14** together with the diterpenes (**25, 26, 27, 28 30** and 3α-hydroxy-15(16)-rippertene (**48**) which is a tetracyclic compound related to the kempenes but which has undergone a 1, 2-methyl shift.[30] A bicyclic cembrene-derived diterpene **49** has been isolated from the soldier secretion of *Nasutitermes princeps*, which has been identified by X-ray diffraction studies.[31]

In the current work we have examined the defensive secretions of the soldier caste of the termites *Cortaritermes silvestri, Nasutitermes* sp. n.D and *Nasutitermes kemneri.*

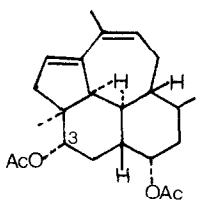
RESULTS

Defensive secretion of Cortaritermes silvestri

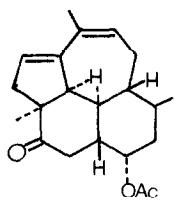
The soldiers of *Cortaritermes silvestri* possess an elongated nasus and vestigial mandibles and are therefore nasutes and rely entirely on chemical defence. When disturbed, the soldiers emerge at the ends of the opened galleries and stand with their heads raised pointing outwards. When further irritated, a clear sticky liquid is ejected from the nasus.[32]

A GLC trace of an extract of approximately 400 soldiers of *C. silvestri* is shown (Fig. 1). None of the compounds labelled (**A**)–(**H**) were found in similar extracts of the workers. Components (**A**)–(**C**) constituted 33.9% of the total secretion and were identified as the monoterpene hydrocarbons α-pinene (**11**), β-pinene (**12**) and limonene (**13**) respectively, by their mass spectra.[33] This assignment was confirmed by co-injection of these compounds with authentic material and obtaining coelution on a Carbowax 20M capillary glc column (100°). The fourth component (**D**) was present as 1.7% of the secretion and it was found to be a monoterpene acetate, *cis*-pin-3-en-2-yl acetate (**50**) by its mass and nmr spectra, *m/e* 166(3%, M^+), 119(100%), 91(76%), 44(64%), 36(51%), 117(44%), 132(39%), 134(38%), 115(23%) and δ($CDCl_3$, 100 MHz), 0.92 (3H, s, angular CH_3), 1.34(3 H, s, angular CH_3), 1.76(3 H, s, CH_3-C-OAc), 2.06(3 H, s, -OC-CH_3), 5.3-5.4(2 H, m, vinyl protons).[34] This is the first time that a monoterpene acetate has been identified from the soldier secretion of a termite.

Compounds (**E**)–(**H**) were identified as diterpenoids by their mass spectra and account for the remaining 64.3% of the secretion. Further purification of these compounds was required before any additional information could be obtained. The solvent was removed from the whole extract *in vacuo* to give an oil (60 mg) which was dissolved in acetonitrile and the components separated by hplc on an ODS-2 magnum (A) using



(43) 3α-OAc, 14β-OAc
(45) 3β-OAc, 14α-OAc



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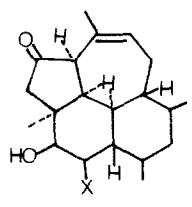
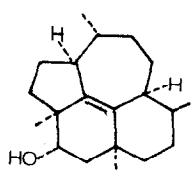


(46) X = H
(47) X = OAc



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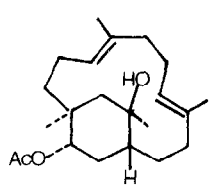

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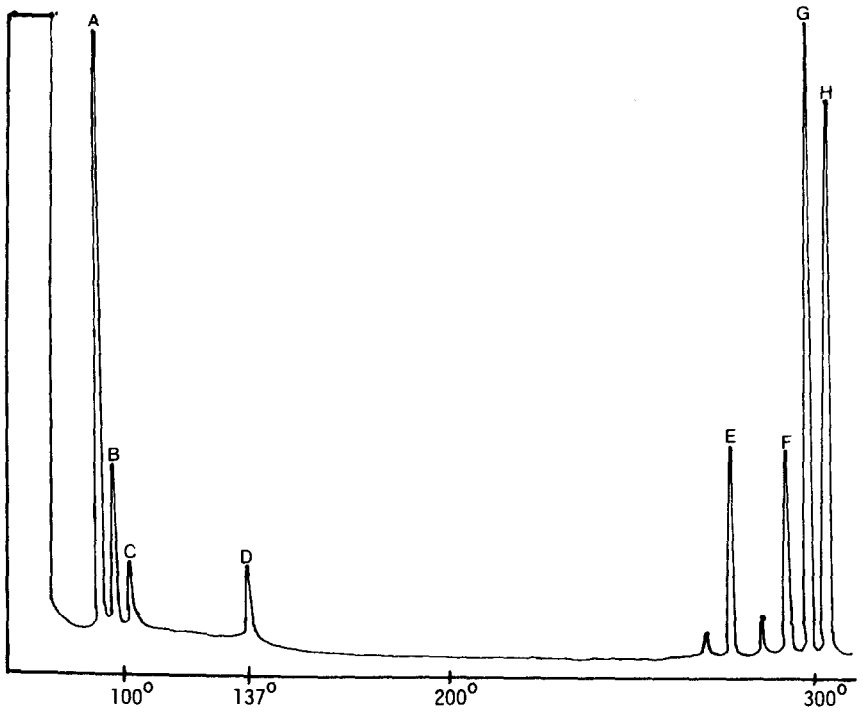


Fig. 1. Chromatogram of an extract of the soldier caste of *Cortaritermes silvestri* (5% OV 101, 70°–300°C at 5°C min^{-1}).

acetonitrile containing water (10%) elutant. Four major fractions were collected containing compounds **(E)–(H)** respectively, the remaining material being collected together as it was impossible to separate individual minor components. Further purification of these four compounds was carried out on hplc using a Lichrosorb 10 RP 18 column (B) and acetonitrile–water (10%) as elutant. The solvent was removed, *in vacuo*, additional acetonitrile being added to remove all the water as an azeotrope.

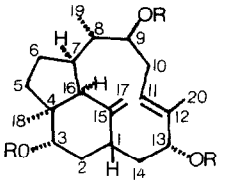
The analysis of **G** was carried out initially since a relatively large amount of material (approximately 20 mg) was available. The mass spectrum of **G** gave a molecular ion of *m/e* 460 (0.8%) indicating a molecular formula of $C_{27}H_{40}O_6$. This ion underwent fragmentation to give *m/e* 400 (M-acetate, 4.4%), 386 (M-propionate, 1.7%), 340 (M-acetatex 2, 56%), 326 (M-acetate and propionate, 31%) and 266 (M-acetatex 2 and propionate, 100%). This indicated that **G** was diterpene diacetate propionate with five degrees of unsaturation. The IR spectrum showed the presence of ester carbonyls at 1740 cm^{-1}. The ^{13}C NMR spectrum gave further information on the basic structure of the molecule. Four olefinic resonances were observed which were compatible with an exocyclic methylene (147.2, s, C-15 and 114.1, t, C-17) and a trisubstituted double bond (135.7, s, C-12 and 124.3, d, C-11). As these two double bonds would take up two of the five remaining degrees of unsaturation, the molecule was considered to be tricyclic. The resonances of the carbonyl groups of the esters could be seen at 173.4 (s, propionate), 169.9 and 169.1 (s, acetates). All three esters are secondary as the resonance for the supporting C atoms were doublets (79.5, 74.3 and 73.4). The presence of six Me groups could be seen from the ^1H 360 MHz NMR spectrum of **G**. Two acetate Me singlets appeared at 2.03 and 2.04 ppm, a Me triplet of a propionate at 1.12 ppm (t, J = 7.5 Hz), an olefinic Me at 1.66 ppm (H-20), a quaternary Me at 0.91 ppm (H-18) and a secondary Me doublet at 0.85 ppm (d, J = 6 Hz, H-19). The methylene group of the propionate occurred as a quartet at 2.30 ppm (q, J = 7.5 Hz). The protons of the exocyclic methylene were present at 5.04 and 5.07 ppm (2xbs, 2H, H-17) and a vinylic proton at 5.39 ppm (1 H, bt, H-11). The protons on the C atoms bearing the ester groups were all seen as doublets of doublets at 5.15 ppm (1 H, dd, J = 12.4 Hz, H-9), 5.07 ppm (1 H, dd, J = 12.4 Hz, H-3) and 4.90 ppm (1H, dd, J = 12.4 Hz, H-13).

It was not possible to identify the skeleton of **G** from this information and it was apparent that X-ray crystallography was required. Crystallisation of this compound from several different solvents was not, however, successful. The hydrolysis of **G** with formation of a triol, was successfully achieved by stirring overnight in 2% potassium hydroxide in methanol. The product was purified by hplc (B) but, due to the small amount of material (*ca.* 6 mg) no crystals could be formed.

The triol was, however, shown to be identical to **51** whose structure has been recently confirmed by X-ray crystallography.[26] This triol was obtained by hydrolysis of 3α, 9β, 13α,-trihydroxy-11(12), 15(17)-trinervitadiene-3, 9, 13-tripropionate (**41**) and 3α, 9β, 13α-trihydroxy-11(12), 15(17)-trinervitadiene-9-acetate-3, 13-dipropionate. From this information, component **G** was identified as 3α, 9β, 13α-11(12), 15(17)-trinervitadiene diacetate propionate (**52**).

Decoupling experiments on the proton spectrum of **52** led to further assignment of certain resonances. The single proton at position 8 must be at 2.10 ppm as irradiation at this position causes the signal for the methyl group at 0.86 ppm (H-19) to change from a doublet to a singlet. H-13 is assigned to the resonance at 4.9 ppm due to its allylic position, and it occurs as a broad doublet of doublets. This signal collapses to a broad doublet by irradiation at 1.7 ppm, thus one of the protons at C-14

(50)



(51) R = H
(52) R = C_2H_5CO, CH_3CO x 2
(53) R = CH_3CO
(54) R = CH_3CO, C_2H_5CO x 2

must resonate at 1.7 ppm. The signal for H-7 occurs at 2.0 ppm as irradiation here causes the signal for H-16 at 2.60 ppm to change from a doublet to a singlet.

The resonance at 2.3 ppm must be assigned to one of the C-10 protons as irradiation at this frequency causes the signal for the vinyl proton at 5.39 ppm to change from a broad triplet to a broad doublet. However, irradiation at 2.3 ppm has no effect on the signal at 5.09 ppm but causes the signal at 5.15 ppm, to collapse from a doublet of doublets to a doublet. It is therefore evident that the signals at 5.15 ppm and 5.09 ppm should be assigned to the H-9 and H-3 protons. This result differs slightly from the conclusion reached by Prestwich *et al.*,[26] based on partial hydrolysis studies, that these two assignments should be exchanged. The other C-10 protons occurs at 2.0 ppm as irridiation here has the same effect on the vinyl proton. Thus both a C-10 proton and the C-8 proton resonate at *ca.* 2.0 ppm, but only one of them is coupled to H-9 as it occurs as a doublet of doublets. Obviously irradiation at 2.0 ppm also collapses the H-9 signal to a doublet.

Due to the small amount of **52** and because hydrolysis gave the triol (**51**) and no partially hydrolysed compounds, it is not possible, at this stage, to ascertain the precise positions of the two acetate and one propionate groups in this compound.

†This is a new species of *Nasutitermes* identified by H. R. Coles and has not yet been named.

Components **F** and **H** from *Cortariterme silvestri* were found to be identical to **52** in all respects except that the former was a triacetate and the latter a dipropionate acetate. The ^{1}H 360MHz NMR spectrum of **F** is identical to that of **52** with the following exceptions, 2.02, 2.03 and 2.05 ppm (s, acetate Me's) and its ^{13}C NMR spectrum in the resonances at 169.8, 169.8 and 169.1 (s, acetate CO's). Similarly the ^{1}H 360MHz NMR spectrum of **H** is different from that of **52** by the following resonances, 2.30 ppm (q, J = 7.5 Hz, propionate methylenes x2), 2.03 ppm (s, acetate Me) and 1.12 ppm (t, J = 7.5 Hz, propionate Me's x2). The ^{13}C NMR spectrum shows resonances at 173.3 and 172.5 ppm (s, propionate CO's) and 169.9 (s, acetate CO). This identified **F** as 3α, 9β, 13α-trihydroxy 11(12), 15(17)-trinervitadiene-3, 9, 13-triacetate **53** and **H** as 3α, 9β, 13α-11(12), 15(17)-trinervitadiene acetate dipropionate (**54**). This later derivative would appear to the same compound as that previously identified by Prestwich *et al.*[26] As for compound **52** the exact position of the ester groups in **54** has not been established. The fourth diterpene (**E**) could only be isolated in very small quantities (*ca.* 7 mg) and no final indentification of this compound has been made. The identities of the components A–H from *Cortaritermes silvestri* are summarised together with their relative percentages (Table 1).

Defensive secretion of Nasutitermes sp. n.D.

Nasutitermes sp. n.D.† emerge in large numbers when their mounds are opened. In each case a clear liquid is sprayed from the nasus which has a strong terpenoid odour.

The glc trace obtained from approximately 1000 soldiers of *Nasutitermes* sp. n.D is shown (Fig. 2). None of the compounds were present in a similar extract of the workers. Each soldier contains approximately 130 μg of material. The first seven compounds, labelled **A** to **G** were found to be monoterpene hydrocarbons which were identified by their mass spectra[33] and by coelution with standard monoterpenes when co-injected on several GLC columns, including 5% OV 101, 5% FFAP, 5% XE 60, 10% PPGA and 5% Carbowax 20 M. Thus the monoterpenes were identified as α-thujene **55** (trace), α-pinene

Table 1. Relative proportions (%) of the compounds identified from the soldiers secretion of *Cortaritermes silvestri*

Component	Compound	% of total secretion	% of mono- and diterpene fractions
(A)	α-Pinene (11)	30.3	
(B)	β-Pinene (12)	3.0	35.7
(C)	Limonene (13)	0.6	
(D)	*Cis*-pin-3-en-2-yl acetate (50)	1.8	
(E)	Unknown diterpene	4.8	
(F)	3α,9β,13α-trihydroxy trinervitadiene triacetate (53)	4.8	64.3
(G)	3α,9β,13α-trihydroxy trinervitadiene diacetate propionate (52)	31.5	
(H)	3α,9β,13α-trihydroxy trinervitadiene acetate dipropionate (54)	23.5	

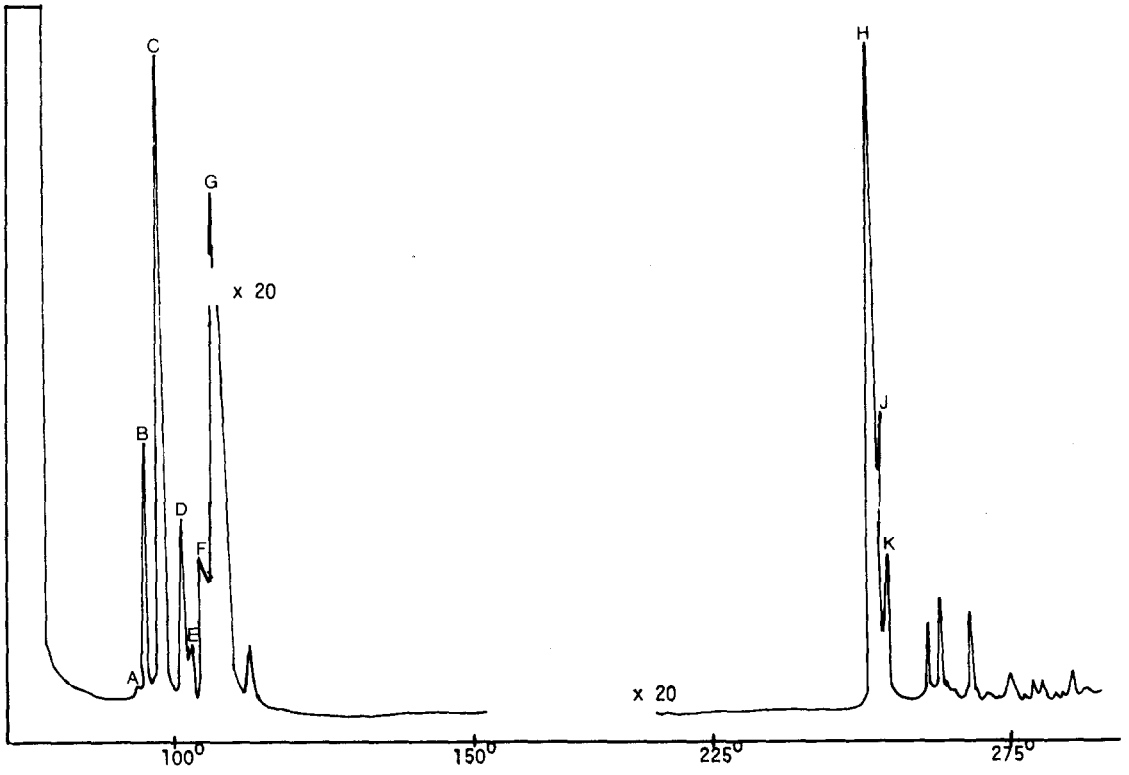


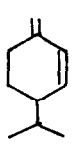
Fig. 2. Chromatogram of an extract of the soldier caste of *Nautitermes* sp. n.D. (5% OV 101, 70°–300°C at 5°C min^{-1}).

11 (1.7%), β-pinene **12** (5.3%), α-phellandrene **10** (1.6%), myrcene **14** (0.5%), limonene **13** (1.1%) and β-phellandrene **56** (89.8%) respectively. The whole monoterpene fraction constitutes 35.1% of the volatile components of the total secretion.

The remaining compounds in this extract were found to be diterpenoids by their mass spectra and constitute 64.9% of the secretion. Additional purification of the extract (130 mg) was carried out by hplc using a Lichrosorb 10 RP 18 column and 15% water in acetonitrile as elutant. The three major components **H**, **J** and **K** were successfully separated using this method but all of the other components were present in too small an amount for any further analytical work to be carried out.

A molecular formula of $C_{10}H_{32}O$ was assigned to the major diterpene **H** from a consideration of the mass spectrum and a molecular ion *m/e* 288(37%); the base peak of the spectrum was found at *m/e* 136(100%). The IR spectrum indicated the presence of an alcohol with an O-H stretching absorption at 3600 cm^{-1}. On the basis of the 360 MHz ^1H and ^{13}C NMR the structure of spectra compound **H** was assigned as 9β-hydroxy-1(15), 8(19)-trinervitadiene (**25**) which has been found in several termite species including *Trinervitermes gratiosus*,[19]

(55)



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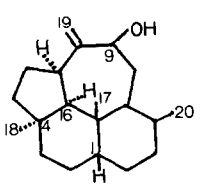


(57)

Grallatotermes africanus[30] and *Nasutitermes rippertii*.[25] The resonances of the ^1H NMR spectrum can be assigned as follows: the three Me groups can be seen at 0.89 ppm (d, J = 6 Hz, H-20), 0.94 ppm (s, H-18) and 1.70 ppm (s, *H*-17). The exocyclic methylene protons resonate at 4.81 and 4.39 ppm (2H, 2xbs, H-19). The proton on the C bearing the alcohol group is at 4.09 ppm (1 H, dd, J = 10.3, 6 Hz, H-9). This is a high chemical shift for the C-9 proton when compared to 2β, 3α, 9α-trihydroxy-1(15), 8(19)-trinervitadiene-9-acetate (**28**). The structure of this compound was identified by X-ray crystallography and the protons on the same carbon atom as the α-acetate group occurred at 5.56 ppm.[20] In a corresponding compound with an alcohol function α at C-9, the proton on this carbon occurs at 4.9 ppm. Thus in compound **H** the alcohol is β as the resonance of this proton occurs at 4.09 ppm. The alcohol is situated inside the 11-membered ring structure in the shielding cone of the 8(19) double bond. In this position the alcohol is sterically prevented from H-bonding which is confirmed by the IR absorption at 3600 cm^{-1}. The anomalously low chemical shift (3.20 ppm) of the C-7 proton can be explained by the fact that it lies in the deshielding cone of the exocyclic methylene. H-16 occurs as a broad doublet at 2.41 ppm due to coupling with the C-7 proton. The significant ^{13}C NMR signals can be assigned as follows: 151.7 (s, C-8)M 128.7, ł27.2 (C-1, C-15), 112.5 (t, C-19), 67.8 (d, C-9), 39.3 (d, C-16), 52.3 (d, C-7), 45.8 (s, C-4) and 28.8 ppm (s, C-12). A pure sample of 9β-hydroxy-1(15), 8(19)-trinervitadiene (**25**) supplied by G. D. Prestwich coeluted with the major diterpene **H** from *Nasutitermes* sp. n.D on a 5% OV 101 glc column.

Compounds **J** and **K** also have mass spectra with a molecular ion of *m/e* 288 (31% and 71%) giving the molecular formula of $C_{20}H_{32}O$. The fragmentation pat-

tern in both cases showed *m/e* 270 (M-water, 40% and 28%) indicating the presence of an alcohol group. This was confirmed by the IR spectra which showed absorptions at 3500 cm^{-1} in each case. The NMR spectrum of **J** indicated the presence of three Me groups, a secondary Me at 0.88 ppm (d, C-20) and two quarternary Me's at 0.92 and 0.97 ppm (s,x2, C-17, C-18). The protons of an exocyclic methylene can be seen at 5.15 and 5.01 ppm (C-19) and a doublet of doublets at 4.05 ppm (1 H, dd, J = 10, 6 Hz, C-9) is due to the proton at H-16 which is coupled to the one at C-7. There is no vinyl Me group or any other vinyl protons so this compound must be tetracyclic as only one of its five degrees of unsaturation is taken up by the exocyclic double bond. The skeleton of this compound is likely to be that of a kempene and a possible structure for this compound **J** could be the kempene version of **25** with the 8(19) double bond and the C-9 alcohol, 9β-hydroxy-8(19)-kempene (**57**). It was not possible to obtain a ^{13}C NMR spectrum of **J** due to the small amount of material isolated, and the identity of this compound could not be investigated further. Insufficient amounts of **K** were obtained to allow positive structural elucidation.

The identities of components **A** to **H** isolated from *Nasutitermes* sp. D are listed (Table 2) together with their relative percentages

Analysis of the secretion of Nasutitermes kemneri

The glc trace of an extract of 400 soldiers of *Nasutitermes kemneri* is shown (Fig. 3). Approximately 130 μg of material was obtained per soldier. The two monoterpene components **A** and **B** were identified as limonene **13** (0.7%) and terpinolene **9** (36.5%) by their mass spectra[33] and by coelution studies on a capillary carbowax 20M glc column at 100°. The mass spectrum of terpinolene **9** is very similar to that of α-terpinene, the major difference being the size of the molecular ion *m/e* 136 which is 74% in the former case and 45% in the latter. The mass spectrum of the compound from *N. kemneri* has a molecular ion of 136(76%). This component was also purified by preparative gas chromatography and collected in carbon tetrachloride and an NMR spectrum of terpinolene was obtained. $\delta(CCl_4$, 1000 MHz), 1.6 – 1.72(3 × CH_3- =) and 5.31 (vinyl proton). The solvent was removed from the extract *in vacuo* leaving 50 mg of a viscous oil. Purification of the diterpene fraction which constituted 62.8% of the total extract was carried out using an hplc ODS2 magnum column and 10% water in methanol as the elutant for the preliminary purification. This was followed by further hplc on a Lichrosorb 10 RP 18 column with 15% water in acetonitrile as elutant. Four major fractions were collected which contained compounds **F** and **G**, **E**, **D** and **C** in that order.

Compounds **C** and **D** were identified as diterpene alcohols by their IR spectra which showed absorptions at 3500 cm^{-1} in each case. The mass spectrum of the compound **D** was found to be identical to that of the major diterpene of *N.* sp. n.D. (**H**). The ^1H NMR spectrum of **D** was also identical to that of 9β-hydroxy-1(15), 8(19)-trinervitadiene (**25**). The mass spectrum of compound **C** showed it to have the molecular formula $C_{20}H_{30}O$ and indicated the presence of an alcohol group. A very weak Fourier transfer 1H NMR spectrum of **C** was obtained. This showed an exocyclic methylene at 4.96 and 4.82 ppm, the proton of a secondary alcohol at 3.71 (m), an olefinic Me at 1.6 ppm and two Me's at 0.88 ppm (probably a quarternary and a secondary Me). This compound probably has the same skeleton as **D** but with the alcohol group in a different position but no further assignment could be made.

Components **E**, **F** and **G** were identified as diterpene diols by their mass spectra which gave molecular ions of *m/e* 304 and therefore molecular formulae of $C_{20}H_{32}O_2$. The IR spectra showed bands for OH groups at 3400 cm^{-1}. Although compounds **F** and **G** could be separated by GLC, they could not be purified by this method due to decomposition at 270° and hplc, column chromatography and tlc all failed to separate these two compounds. However, it could be seen from the ^1H

Table 2. Relative proportions (%) of the compounds present in the secretion of the soldiers of *Nasutitermes* sp. n.D

Component	Compound	% of Total Secretion	% of Mono and Diterpene Factors
A	α-Thujene (55)	Trace	
B	α-Pinene (11)	0.6	
C	β-Pinene (12)	1.8	
D	α-Phellandrene (10)	0.5	35.1
E	Myrcene (14)	0.2	
F	Limonene (13)	0.4	
G	β-Phellandrene (56)	31.6	
H	9β-Hydroxy trinervita diene (25)	42.7	
J	9β-Hydroxy-8(19)-kempene (57)	7.9	64.9
K	$C_{20}H_{32}O$	3.2	
	Other unidentified components	11.1	

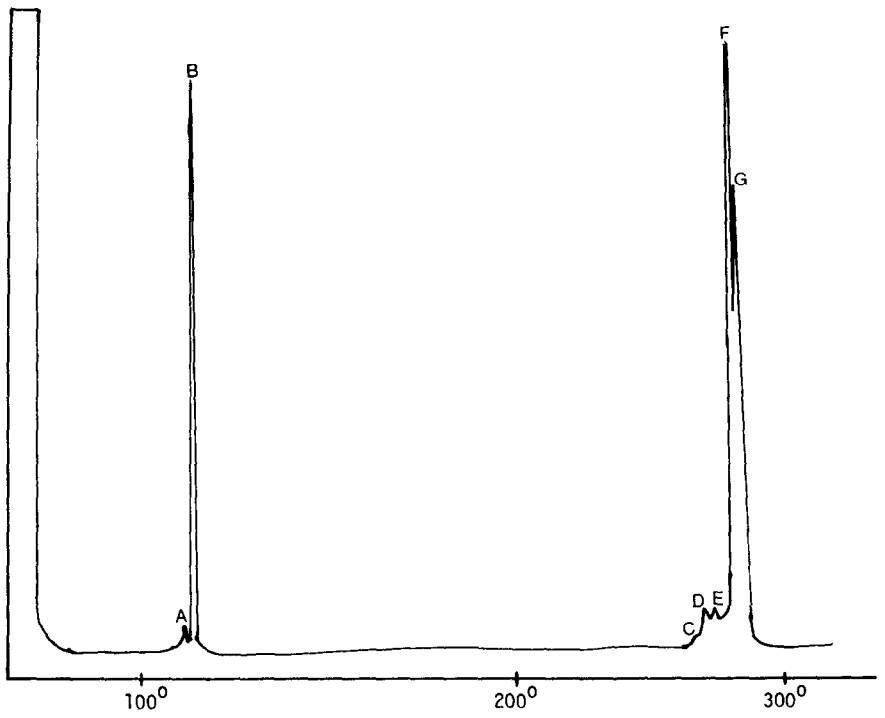
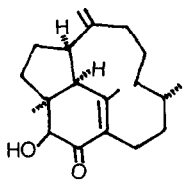


Fig. 3. Chromatogram of an extract of the soldier caste of *Nasutitermes kemneri* (5% OV 101, 70°–300° at 5° min^{-1}).

NMR spectra that all three compounds were trinervitine-2, 3-diols. These compounds were not sensitive to aerial oxidation over a couple of days, thus in all three cases, the 2-OH substituent is α. Vrkoc *et al.*[24] have shown that the 2β, 3α diol (**26**) is oxidised to the 3α-hydroxy-1(15), 8(19)-trinervitadiene-2-one (**58**) by air, but the 2α, 3α diol is not oxidised. From this data, component **E** was identified as 2α, 3α-dihydroxy-1(15), 8(19)-trinervitadiene (**32**) which has also been found in *Nasutitermes costalis*.[24] The ^1H NMR spectra shows three Me groups at 0.87 ppm (d, J = 6 Hz, H-20), 1.09 (s, H-18) and 1.77 (s, H-17). A broad doublet at 2.5 ppm (d, J = 12 Hz, H-16) can be assigned to H-16 and a doublet of triplets at 3.25 ppm (dt, J = 12, 10, 10 Hz, H-7) to H-7. The AB quartet at 3.89 ppm (d, J = 5 Hz, H-3) and 4.06 ppm (bd, J = 5 HZ, H-2) belong to the vicinal diol unit. As this coupling is small (5 Hz) the alcohol in the 3-position must be β as the 2-OH group has previously been assigned to the α position. Thus the two protons at 2 and 3 are in quasiequitorial and quasiaxial positions respectively and thus the observed coupling is small.

Compounds **F** and **G** are very closely related and the NMR of a mixture of these two compounds was obtained. It appears from this spectrum that the difference between these compounds is the position of the second double bond wihch is exocyclic in the 8(19) position in one case and internal in the 8(9) position in the second case. The hydroxyl groups of the vicinal diol moiety are in the 2α, 3β positions in both compounds. The 2-position alcohol is α due to the lack of oxidation as described previously and 3-position alcohol must be β to give a coupling constant of 9 Hz as the coupling for the 2α, 3α diol (**32**) has been shown to be 5 Hz.[24] One might expect that with the 2α, 3β configuration the two OH groups might take up the diaxial position but this would lead to a smaller coupling constant than observed. However, by examining models it has been shown that the hydroxyl groups take up quasiequatorial positions[24] thus forcing the two protons to be diaxial leading to the large observed coupling of 9 Hz. By studying the integration of the vinyl protons in the NMR spectrum it can be seen that the major component of these two diols has the internal double bond. Thus from this data, **F** is identified as 2α, 3β-dihydroxy-1(15), 8(9)-trinervitadiene (**59**) and **G** is 2α, 3β-dihydroxy-1(15), 8(19)-trinervitadiene (**33**). The resonances of the NMR spectrum can be assigned as follows: $\delta(CDCl_3$, 100 MHz), 0.94 (d, J = 6 Hz, H-20), 1.18 (s, H-18), 1.58 (s, H-19, (**59**)), 1.70 (s, H-17), 2.60 (bd, J = 11 Hz, H-16), 3.20 (d, J = 9 Hz, H-3), 4.02 (bd, H-2), 4.80 and 4.88 (bsx2, H-19, (**42**)), 5.11 (bt, H-9, (**59**)). The ^1H NMR of **G** compares favourably with a recently published NMR of this compound **33**.

The identities and relative proportions (%) of the compounds isolated from the soldier secretion of *N. kemneri* are summarized (Table 3).



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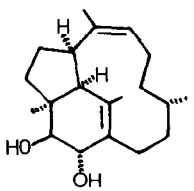

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DISCUSSION

The soldiers of each of the nasute termites discussed all eject a sticky secretion from a nozzle-like nasus. This secretion has been shown to contain a number of different oxygenated diterpenes dissolved in monoterpene hydrocarbons. In addition, soldiers of *Cortaritermes silvestri* also produce small amounts of *cis*-pin-3-en-3-yl acetate. Vrkoc *et al.*[35] have shown that secretion of *Nasutitermes rippertii* and *N. costalis* are not dietary in

Table 3. Relative proportions (%) of the compounds isolated from the soldiers of *Nasutitermes kemneri*

Component	Compound	% of the total secretion	% of the mono- and diterpene fractions
A	Limonene (13)	0.7	
B	Terpinolene (9)	36.5	37.2
C	$C_{20}H_{32}O$	0.7	
D	9β-Hydroxy-1(15),8(19)-trinervitadiene (25)	3.6	
E	2α,3α-Dihydroxy-1(15),8(19)-trinervitadiene (32)	1.8	62.8
F	2α,3β-Dihydroxy-1(15),8(9)-trinervitadiene (59)	32.9	
G	2α,3β-Dihydroxy-1(15),8(19)-trinervitadiene (33)	23.8	

origin. These two species do not attack coniferous trees, rich in monoterpenes but eat deciduous trees low in these compounds. No terpenoid compounds are found in an extract of the workers who are responsible for feeding the soldiers. It was further established that laboratory reared colonies of these two termites fed on a specially controlled diet produces similar secretions to field colonies.

There has been considerable discussion on the role of the components of these secretions. Monoterpene hydrocarbons have been shown to act as alarm pheromones for several species. Soldiers of *N. rippertii* and *N. costalis* exhibit alarm behaviour on exposure to certain monoterpenes.[36] The major component of the secretion of the former is α-pinene which evokes greatest response from soldiers of this species. For *N. costalis* the strongest alarm effect is elicted by Δ^3-carene which is the major monoterpene constituent of this species. The effect of limonene with a small amount of terpinolene and α-phellandrene on *Drepanotermes rubricepts* is to produce a short-lived snapping frenzy.[2] The secretion of the soldiers of *N. exitosus* serves as an alarm pheromone and attracts other soldiers from a distance of 30 m. The recruited soldiers do not eject their own secretion unless they are themselves attacked. This secretion does not appear to alarm the workers in any way. Three monoterpenes have also been shown to act as feeding deterrents to the giant anteater, *Myrmecophaga tridactyla*. Limonene was found to be the most effective deterrent followed by β-pinene and *cis*-β-ocimene.[32]

We have also shown that many monoterpene hydrocarbons are toxic to several species of indigenous camponotine ants. Limonene, β-pinene, α-phellandrene, α-pinene, α-thujene and *cis*-β-ocimene gave LT_{50} of between 6 and 37 minutes at 0.15 μl per ant, the toxicity decreasing from limonene to *cis*-β-ocimene.[32] Several monoterpenes have been shown to be toxic to the house fly, *Musca domestica*, and the diterpene 2β, 3α, 13β-trihydroxy-trinervitadiene-2, 3, 13-triacetate was found to show average toxicity in comparison with the monoterpenes.[37] However, tests using a 26% solution of 2β, 3α, 9α-trihydroxy-trinervitadiene-2, 3, 9-triacetate in α-pinene produced no additional toxicity over pure α-pinene on topical application to a formicine ant.[19] It has also been found that α- and β-pinene act as surface irritants to ants causing scratching and other cleaning reflexes which serve to spread the compound over the ant's body.[38]

On the basis of the present and previously published studies, the defense secretions of the nasute soldiers are more highly evolved. Together with the possible role of the components as alarm pheromones, feeding deterrents, topical poisons and irritants, the secretion might also be employed as a viscous entangling agent acting as a glue which could also block sensillae and spiracles. Monoterpene hydrocarbons are hydrophobic which could act to dissolve cuticular waxes. The evaporation of the monoterpenes would be reduced by the presence of diterpenes thus enhancing the stickiness and irritancy of the secretion. Prestwich[39] had suggested that the role of the diterpenes is to provide high viscosity required of a good glue. Given that there are specialised enzymatic systems to synthesise these terpenoids it would be optimal for the termites to produce several compounds with the same skeleton but different functionalities. This would cause the glue to be more viscous without spontaneous crystallisation of any single component.

EXPERIMENTAL

Collection procedures. Workers and soldier termites were collected from opened mounds in the Distrito Federal, Brazil. Termites were dropped into vials of methylene chloride which were then sealed and stored under refrigeration until dispatch by air to Southampton. This procedure was adopted since substantial loss of material would have taken place if collection had involved decapitation since some of the secretion seemed to be fairly volatile. An extract was prepared by crushing the insect under methylene chloride followed by filtration of the crude extract through a glass wool plug. In this way separate extracts were obtained from workers and soldiers which enabled the soldier specific components to be identified.

Instrumental methods. NMR spectra were obtained in solns of $CDCl_3$ containing 1% TMS using a Varian XL-100 spectrometer or a Bruker WH 360 NMR spectrometer. Microscale Fourier transform spectra were run with an internal deuterium lock. Samples were collected in $CDCl_3$ at room temp by preparative gas chromatography using the all glass splitter of Baker *et al.*[40] Mass spectra were obtained using an AEI-MS 12 spectrometer interfaced with a Pye Unicam 104 gas chromatograph via a Watson–Bieman glass separator. The gas chromatograph was equipped with a 2m × 2 mm ID glass column packed with 5% OV-101 on

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