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SPECIALIA

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Identification of an acyclic diterpene alcohol in the defense secretion of soldiers of *Reticulitermes lucifugus*[1]

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Summary. The defense secretion of soldiers of *Reticulitermes lucifugus* has been shown to contain, predominantly, (R)-(−)-(E,E)-geranyllinalool together with germacrene A and β-farnesene.

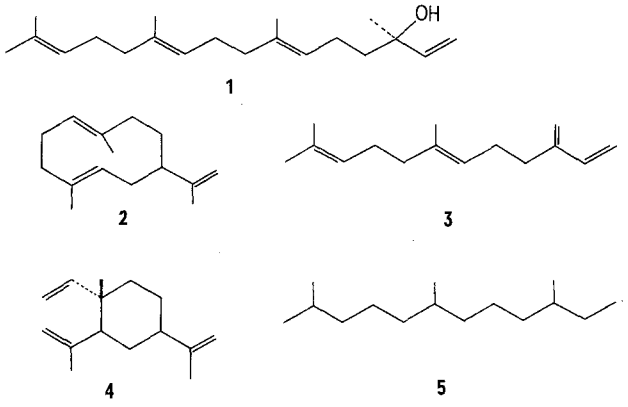
Soldiers of the termite *Reticulitermes lucifugus*, which is found in many areas of Southern Europe, produce a cephalic (frontal) gland secretion in response to provocation.

We wish to report results of chemical analysis of the secretion, including the identification of an acyclic diterpene alcohol, (R)-(-)-(E,E)-geranyllinalool (**1**) not previously found in termite defense secretions. Preliminary trials of biological activity using synthetic racemic (**1**) show that it is toxic to *Atta cephalotes*, *Camponotus vagus* and *Crematogaster scutellaris* on topical application. In feeding tests, quantities equivalent to those found in 10 soldiers were repellent to the 2 latter species[2]. Further tests are underway to determine the mechanisms of repellency and toxicity. Other components of the secretion are the sesquiterpene hydrocarbons germacrene A (**2**) and β-farnesene (**3**).

Soldiers of *Reticulitermes lucifugus* collected from South-West Spain (near Cadiz) were immersed in dichloromethane and the solution decanted and concentrated. Gas chromatography – mass spectrometry of the extract indicated the presence of sesquiterpene hydrocarbons (M^+ 204, approximately 10 µg/insect) and 1 diterpene alcohol (M^+290, approximately 40 µg/insect). Hydrocarbons of the type commonly found in insect cuticle were also recognized in the extract. A small sample of secretion collected from live soldiers, however, contained the terpene components only.

The diterpene was isolated by HPLC (reverse phase); 7 mg, prepared from approximately 200 soldiers, was used to obtain a 100 MHz ^{1}H-NMR-spectrum which confirmed the structure to be (E,E)-geranyllinalool by comparison with the previously published spectrum[3]. The chemical shifts of methyl groups on the double bonds (6H, 1.58δ; 3H, 1.60δ and 3H, 1.66δ, in CCl_4) enable the double bond geometry to be assigned E,E. Furthermore the optical rotation ($[\alpha]_D^{22} = -20° \pm 5°$) indicated that (**1**) was the enantiomer with R-(-)-configuration[3].

The major sesquiterpene component underwent rearrangement during gas chromatography and HPLC. When the



sesquiterpene fraction was separated by preparative GC, several isomeric products were obtained. The major product was shown by GC-MS, and after further separation, by ^{1}H-NMR[4] to be β-elemene (**4**). Some minor products were recognized by GC-MS as δ-elemene and selinenes. It is well known that β-elemene is formed efficiently by the thermal Cope rearrangement from germacrene A (**2**)[5], which is considered to be the major sesquiterpene component of the defensive secretion (approximately 10 µg/insect).

β-Farnesene (**3**) was also confirmed to be present in the secretion by GC-MS (base peak, m/e 69) in the sesquiterpene fraction, but it could not be isolated. Catalytic hydrogenation of the soldier extract (using palladium catalyst on calcium carbonate in methanol) produced a small amount of farnesane (**5**) (2,6,10-trimethyldodecane). The abundance of β-farnesene was estimated at 1 µg/insect.

Other species in the family Rhinotermitidae produce secretions containing aliphatic ketones[6] and a nitro-alkene[7]. Studies on *Reticulitermes lucifugus* and its subspecies from other regions of Southern Europe have shown some diversity (mainly quantitative) in the nature of the frontal gland secretion which can be related to various morphological and genetic factors[8]. Terpenes have not previously been reported in defence secretions of lower termites. Germacrene A and its rearrangement product β-elemene have, however, recently been identified in the soldier defence secretion of several species of the primitive neotropical nasute genus *Syntermes*[9].

1 This report covers part of a collaborative study with J.-L. Clément, Lab. d'Evolution, Université P. et M. Curie, Paris, to whom we are grateful for supplies of material and discussions. We also thank Dr O.T. Jones for collections of *Reticulitermes lucifugus*.

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12S-Hydroxybromosphaerol, a new bromoditerpene from the red alga *Sphaerococcus coronopifolius*[1]

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Summary. A minor bromoditerpene, 12S-hydroxybromosphaerol has been isolated from the red alga *Sphaerococcus coronopifolius*, and its structure has been established on the basis of chemical and spectroscopic evidence.

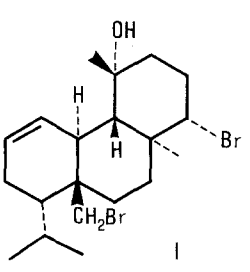
The red alga *Sphaerococcus coronopifolius* elaborates 3 bromoditerpenes with a rearranged tricyclic skeleton[2-4] **I, II, III.** From a further investigation of the lipid extract of this alga we have now isolated a new dibromocompound, 12S-hydroxybromosphaerol (**IV**), closely related to **I–III.**

Material and methods. Fresh material (5 kg), collected in the bay of Salerno during the autumn of 1980, was freeze-dried, pulverized and extracted with $CHCl_3$. Repeated silica-gel chromatography of the extract resulted in the isolation of 54 mg of **IV**, a colourless oil, $[\alpha]_D$ −2.2° (c 1 in chloroform).

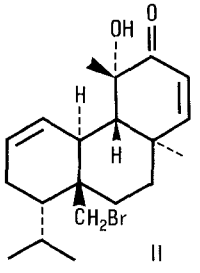
Acetylation of **IV** was performed with an excess of Ac_2O/Py at room temperature for 1 h. After chromatographic purification on PLC (SiO_2) pure **V** was obtained in 90% yield.

IV (30 mg) was oxidized with pyridinium-chlorochromate in CH_2Cl_2 in the presence of sodium acetate[5] at room temperature for 12 h. The crude product was purified by PLC (SiO_2) giving **II** (12 mg).

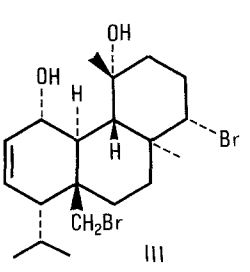
Results and discussion. Compound **IV** has the molecular formula $C_{20}H_{32}O_2Br_2$ (M^+ 462, 464, 466; high resolution m/e 462.0775, calculated for $C_{20}H_{32}O_2Br_2^{79}$ 462.0770), ν_{max} 3600–3400 cm^{-1} (OH). The NMR-spectrum [δ 0.91 and 0.97 (d's, 3H each, J 7.5Hz, H_3C-19 and H_3C-20), 1.29 (s, 3H, H_3C-15), 1.46 (s, 3H, H_3C-16), 3.62 and 3.95 (1H each, AB system, J 10Hz, CH_2Br), 4.48 (dd, 1H, J 3 and 13Hz, HC-14)] of **IV** is strongly reminiscent of that of **I**[2], the only remarkable difference being the presence of a C*H*OH signal at δ 3.47 (t, J 3.5Hz) and the downfield shifts of the signals of H_3C-16 and of HC-14.



I



II



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