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.

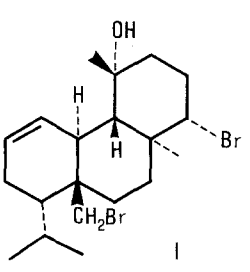
The red alga *Sphaerococcus coronopifolius* elaborates 3 bromoditerpenes with a rearranged tricyclic skeleton[2-4] **I, II, III.** From a further investigation of the lipid extract of this alga we have now isolated a new dibromocompound, 12S-hydroxybromosphaerol (**IV**), closely related to **I–III.**

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).

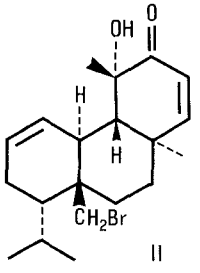
Acetylation of **IV** was performed with an excess of Ac_2O/Py at room temperature for 1 h. After chromatographic purification on PLC (SiO_2) pure **V** was obtained in 90% yield.

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).

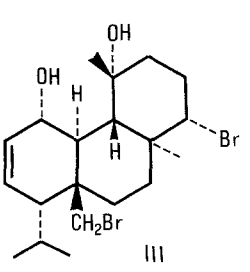
Results and discussion. Compound **IV** has the molecular formula $C_{20}H_{32}O_2Br_2$ (M^+ 462, 464, 466; high resolution m/e 462.0775, calculated for $C_{20}H_{32}O_2Br_2^{79}$ 462.0770), ν_{max} 3600–3400 cm^{-1} (OH). The NMR-spectrum [δ 0.91 and 0.97 (d's, 3H each, J 7.5Hz, H_3C-19 and H_3C-20), 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.



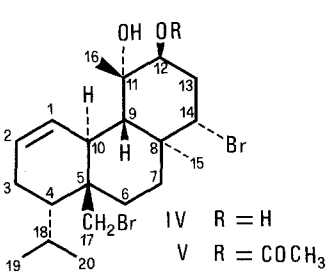
I



II



III



The presence of a secondary OH group was confirmed by acetylation of **IV** which afforded **V**, ν_{max} 1740 cm^{-1}; $\delta(CDCl_3)$ 2.12 (3H, s, CH_3CO), 4.69 (t, 1H, J 3.5Hz, HC-12).

Treatment of **IV** with pyridinium-chlorochromate in the presence of sodium acetate caused the oxidation of the secondary alcoholic group and the elimination of HBr to give the α,β-unsaturated ketone **II** (50%) identified by comparison ($[\alpha]_D$, m.m.p., IR, NMR, MS) with an authentic sample. This allowed the location of OH and Br at C-12 and C-14 respectively, taking into account the multiplicity of the signals of C*H*OH and C*H*Br groups in the NMR-spectrum of **IV**.

As a consequence, the stereostructure **IV** was assigned to the compound under investigation apart from the chiralities of C-12 and C-14. These were deduced from the NMR spectra of **IV** and **V** which indicated that HC-12 (t, J 3.5Hz) and HC-14 (dd, J 3 and 13Hz) must be equatorial and axial respectively.

The co-occurrence of the compounds **I** and **IV** in *Sphaerococcus coronopifolius* could be of biogenetic interest. We can now suppose that **IV** represents an intermediate in the transformation of bromosphaerol (**I**) into sphaerococcenol A (**II**).

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Deuterium isotope effects in the ninhydrin reaction of primary amines

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Summary. The rate of development of Ruhemann's purple in the ninhydrin reaction of two deuterated primary amines, $\alpha\alpha$-d_2-p-tyramine and $\alpha\alpha$-d_2-β-phenylethylamine, is significantly reduced. It appears to be a primary isotope effect and indicates that the cleavage of the carbon-hydrogen bond at the α-position is involved in the rate-determining step of the color reaction.

Ninhydrin, 2,2-dihydroxy-1,3-indandione, has been widely used for the quantitative determination of amino acids and amines for many years. Several reaction mechanisms have been proposed for the color development[2,3]. Recently during our study on the kinetic isotope effect on the enzymatic deamination of trace amines [4], the ninhydrin reaction was observed to be unsuitable for measurement of the deuterated amines, and it is now clear that this is due to a deuterium isotope effect.

The estimation of the rate of ninhydrin reaction was adopted according to Moore's method[5]. The reagent was prepared by dissolving ninhydrin (0.11 M) and hydrindantin (2,2-dihydroxy (2,2-biindan)-1,1',3,3'-tetrone) (0.002 M) in dimethylsulfoxide buffered with lithium acetate (0.5 M) at pH 5.2. The different deuterated amine analogs were synthesized as previously described[4]. Both the chemical and isotopic purities of these compounds were over 95% in all cases[4]. An aqueous solution (0.5 ml) of the deuterated amines or the non-deuterated amines (25 µg) was mixed with an equal volume of ninhydrin reagent and incubated at 55 °C. The optical density at a wavelength of 525 nm was measured at different time intervals. As can be

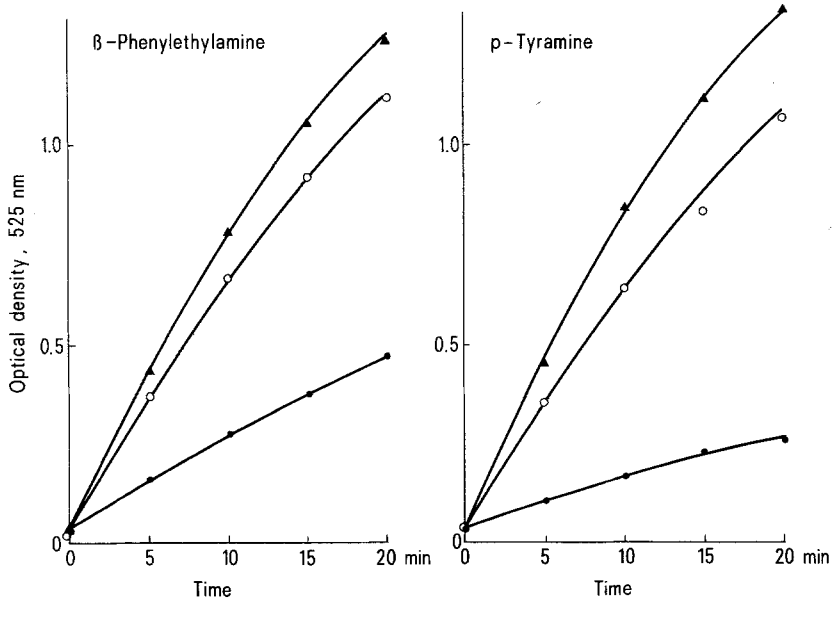

Figure 1. Relative rates of color development of primary amines in ninhydrin reaction. Protonated (○——○) phenylethylamine (25 µg) (left) and p-tyramine (25 µg) (right) and their α,α-deuterated (●——●) and β,β-deuterated (▲——▲) analogs were incubated with ninhydrin reagent at 55 °C. OD at 525 nm wavelength are plotted against time. Values are average of 4 experiments.