

DITERPENES FROM THE RED ALGA *Sphaerococcus coronopifolius*. STRUCTURE OF  
SPHAERODIENE AND REASSIGNMENT OF STRUCTURE FOR PRESphaEROL.

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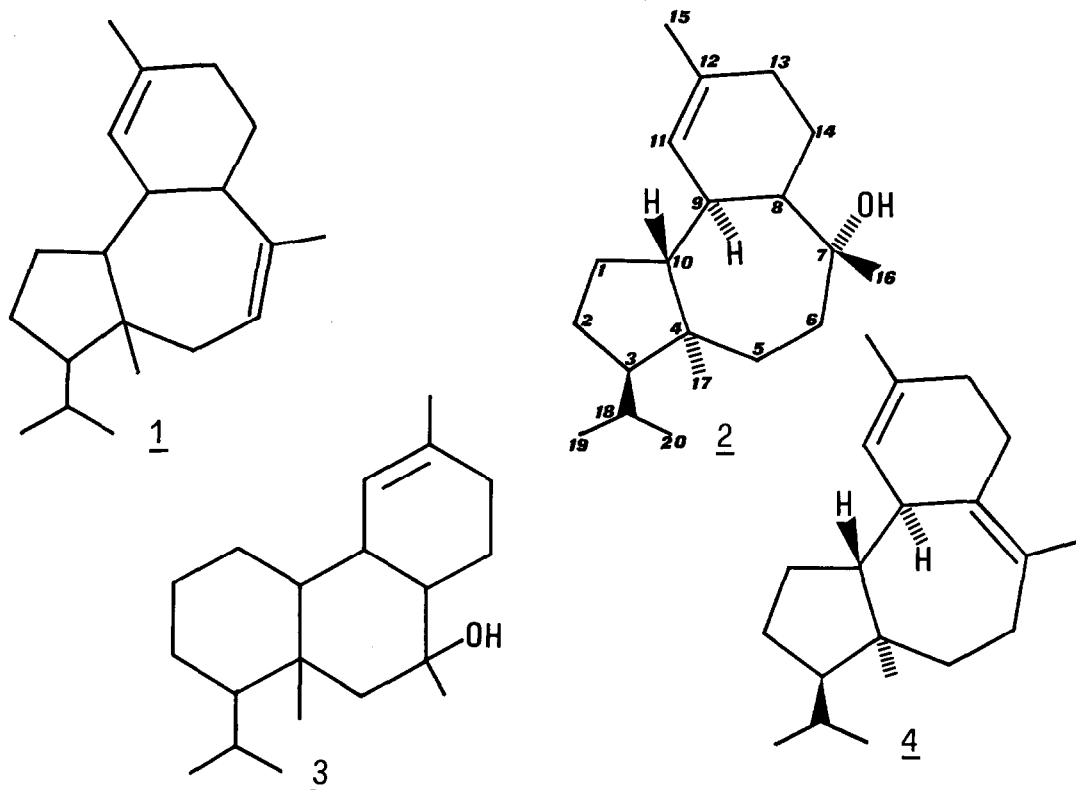
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Summary: On the basis of chemical and spectroscopic evidence and X-ray diffraction studies, structure 1 has been assigned to Sphaerodiene and structure 2 is reassigned to Presphaerol.

Several recent reports<sup>1-5</sup> have shown that the red marine alga *Sphaerococcus coronopifolius* constitutes an interesting source of diterpenes. Further examination of the less polar fraction of the chloroform extract of this organism led to the isolation of a new diterpene hydrocarbon, Sphaerodiene (1), whose structure determination is discussed here. We have also reinvestigated the structure of Presphaerol and have reassigned this compound as (2) rather than the previously proposed (3)<sup>4</sup>.

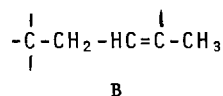
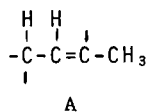
Sphaerodiene (1) was isolated as an oil from the CHCl<sub>3</sub> extract of the alga using conventional silica-gel chromatography (elution C<sub>6</sub>H<sub>6</sub>) followed by SiO<sub>2</sub>-AgNO<sub>3</sub> chromatography (light petroleum),  $[\alpha]_D + 44.93^\circ$  (c 1 in CHCl<sub>3</sub>). High resolution mass spectrum analysis of (1) indicated an elemental composition of C<sub>20</sub>H<sub>32</sub> for the molecular ion at  $m/e$  272. The <sup>1</sup>H-n.m.r. signals at  $\delta$  0.85 (3H, d,  $J$  6Hz) and  $\delta$  0.95 (3H, d,  $J$  6Hz) and spin decoupling experiments (irradiation at  $\delta$  1.58 collapses the two doublets into two singlets) are indicative of an isopropyl group, whose presence was confirmed by MS (intense peak at  $m/e$  229, M<sup>+</sup> - 43). In the <sup>1</sup>H-n.m.r. spectrum three further methyl signals appeared as singlets at  $\delta$  0.67, 1.61 and 1.74 and two vinyl hydrogens were observed at  $\delta$  5.40 (d,  $J$  5Hz) and  $\delta$  5.28 (bm), allylically coupled with the methyls at  $\delta$  1.61 and  $\delta$  1.74 re-

spectively. Decoupling revealed that the vinyl proton at  $\delta$  5.28 is adjacent to a methylene group (one H resonates at  $\delta$  2.34 as a dd ( $J$  9 and 15Hz), while the second H atom at  $\delta$  1.78 is superimposed to others signals) which in turn is adja-



cent to a fully substituted carbon atom. Irradiation at  $\delta$  5.28 collapses the dd at  $\delta$  2.34 into a doublet ( $J$  15Hz, geminal coupling constant) while irradiation at  $\delta$  1.78 simplifies the signal at  $\delta$  2.34 into a doublet ( $J$  9Hz) and the signal at  $\delta$  5.28 into a doublet ( $J$  9Hz) broadened by long range coupling.

These data suggested that (1) could be a rearranged tricyclic diterpene possessing the two partial structures A and B, but failed to define an unambiguous skeleton.



In an attempt to relate (1) to the several tricyclic diterpenes co-occurring in *S. coronopifolius* the compound under investigation proved to be identical to the minor compound obtained from Presphaerol on dehydration with acetyl chloride

in hot xylene. This result, in light of the accumulated spectral data on Sphaerodiene, indicated that very probably the proposed structure for Presphaerol was incorrect. To obtain unambiguous information on the structure of Presphaerol and, consequently, of Sphaerodiene, an X-ray diffraction analysis was performed on the major dehydration product (4) of Presphaerol [m.p. 58-59°;  $[\alpha]_D^{25} + 28^\circ$  (c 1 in  $\text{CHCl}_3$ )]<sup>4</sup> (other analogues were less satisfactory).

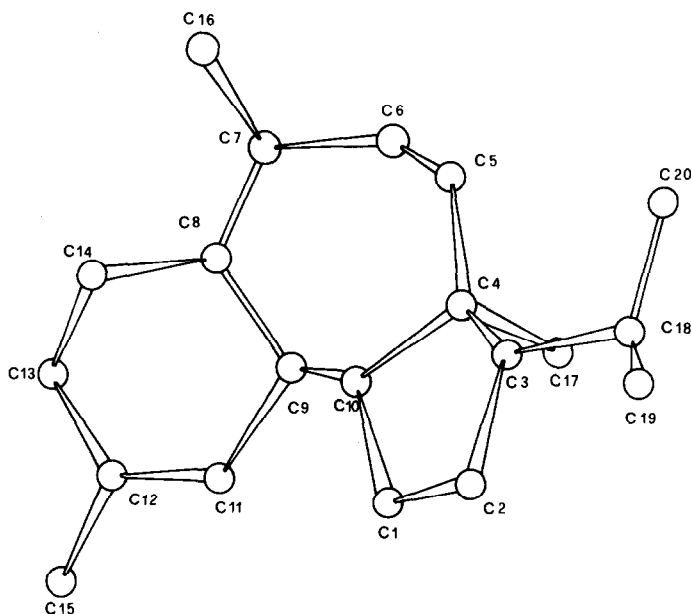
The crystallographic data determined rigorously the structure and the relative stereochemistry of (4), and showed that the structure of Presphaerol is represented by the formula (2) in which the configurations at C(3), C(4), C(9) and C(10) were deduced from those of (4); the others at C(7) and C(8) were established on the basis of spectroscopic evidence as follows. The trans relationship between H-C(8) and H-C(9) was evident from the large coupling constant (10Hz) in the n.m.r. spectrum of Presphaerol [H-C(9) resonates as a multiplet at  $\delta$  2.30 and is simplified to a triplet ( $J$  10Hz) by irradiation at  $\delta$  5.27 [H-C(11)]]<sup>5</sup>, while the chirality at C(7) was deduced by dehydration of Presphaerol to (4) with  $\text{CH}_2\text{COCl}$  assuming that under these conditions a strict trans elimination takes place<sup>6</sup>.

The error in the original assignment of structure (3) arose from the formation of 1-isopropyl-6,9-dimethylphenanthrene by aromatization of Presphaerol with  $\text{Se}^{\text{H}}$ , which gave rise to a skeletal rearrangement.

The determination of the structure (2) allowed us to assign structure (1) to Sphaerodiene, as this compound was shown to be identical to the minor dehydration product of Presphaerol.

Crystal data. Crystals of (4) in the form of colourless prisms were grown from ethanol by slow evaporation at room temperature, and used as such for X-ray investigation. Lattice constants, data collection, structure determination and refinement were carried out on a CAD4-Enraf Nonius diffractometer equipped with a PDP8 and a PDP11/34 digital computers. The SDP (structure determination programs) package of crystallographic programs was used for most of the calculations. Crystallographic data of (4):  $\text{C}_{20}\text{H}_{32}$ , Mw = 272.5, orthorhombic, space group  $\text{P}2_12_12_1$ ,  $Z = 4$ ,  $a = 7.211(1) \text{ \AA}$ ,  $b = 10.563(1) \text{ \AA}$ ,  $c = 22.757(2) \text{ \AA}$ ,  $V = 1733.4 \text{ \AA}^3$ ,

$\rho_{\text{floatation}} = 1.10 \text{ g cm}^{-3}$ ,  $\rho_c = 1.04 \text{ g cm}^{-3}$  [ $\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$ ]. The structure was determined by a straightforward application of direct methods using MULTAN in the form programmed by Germain et al.<sup>7</sup> and refined with the usual least squares procedure to an  $R$  and  $wR$  values of 0.055 and 0.053 respectively on 1762 no-zero reflections with  $F_o^2 > 3\sigma(F_o^2)$ .

Molecular model of 4

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