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(1*S*)-1, 2-DIHYDRO-1-HYDROXYBROMOSPHAEROL, A MINOR BROMODITERPENE FROM THE RED ALGA *SPHAEROCOCCUS CORONOPIFOLIUS**

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Key Word Index—*Sphaerococcus coronopifolius*; Rhodophyta; diterpenes; (1*S*-1,2-dihydro-1-hydroxybromosphaerol.

Abstract—A new bromoditerpene, (1*S*)-1, 2-dihydro-1-hydroxybromosphaerol has been isolated from the marine alga *Sphaerococcus coronopifolius* and its structure determined on the basis of physical and chemical evidence.

Previous studies on the red alga *Sphaerococcus coronopifolius* have led to the isolation and characterization of several diterpenes based on new carbocyclic skeletons (**1–6**) [1–5]. In order to obtain useful information on their biogenesis, we have reinvestigated the minor lipids of this organism and here report the isolation and structure determination of a new bromoditerpene, (1*S*)-1,2-dihydro-1-hydroxybromosphaerol (**7**) which is structurally related to compounds **1–4**.

Conventional Si gel chromatography of the chloroform extract of the dried alga afforded **7** as colourless needles (from hexane), $[\alpha]_D^{20}$ +2.5°, mp 178–180°, $C_{20}H_{34}Br_2O_2$ (mass spectrum and elemental analysis).

The mass spectrum (Experimental) suggested that both oxygen atoms in **7** are present in hydroxyl groups. The ^{1}H NMR spectrum displayed signals at δ 3.99 (*dd*, $J = 3.5$ and 12.5 Hz) and 3.47 and 3.92 (1H each, AB doublets $J = 10.5$ Hz) that are indicative for CHBr and CH_2Br respectively, and a multiplet partially superimposed upon other signals at δ 3.96 attributable to a C$\underline{H}$OH group. Signals of four methyls at δ 1.35 and 1.30 (3H each, *s*, H-15 and H-16), 0.98 and 1.05 (3H each, *d*'s $J = 7.5$ Hz, H-19 and H-20) and of two methine groups [2.26 (*t*, $J = 11.5$ Hz, H-10) and 1.61 (*d*, $J = 11.5$ Hz, H-9)] were also observed.

The above data strongly suggested that **7** could be a hydroxy derivative of dihydrobromosphaerol. Information on the position of the secondary hydroxyl group was obtained from spin decoupling experiments: by irradiation at δ 3.96, the triplet at 2.26 collapsed to a doublet, while irradiation at 2.26 simplified the multiplet of the CHOH group and, at the same time, converted the doublet at 1.61 into a singlet. Finally irradiation at δ 1.61 caused the triplet at 2.26 to collapse into a doublet. These data are compatible only with the location of the secondary alcoholic function at C-1.

Definitive proof for the proposed structure was provided by comparison of its properties (IR, NMR, MS, mp, $[\alpha]_D$), with those of a synthetic sample obtained by hydroboration of **2** followed by oxidation with alkaline hydrogen peroxide. This result established the structure of **7** and at the same time determined its absolute configuration since the stereochemistry of **2** is known [3], apart from the configuration of C-1, which was established on the basis of the ^{1}H NMR spectrum of **7**. The *trans*-diaxial relationship between H-1 and H-10 was evidenced by the large coupling constant.

EXPERIMENTAL

^{1}H NMR spectra were run at 270 MHz with TMS as int. standard.

Isolation of **7**. The alga (15 kg fr. wt) collected in Autumn 1980 in the Bay of Salerno, Italy, was freeze-dried and ground to a fine powder with a blender. The dried alga (3.8 kg) was extracted with stirring for 12 hr with $CHCl_3$ (×3). The evaporation of the solvent *in vacuo* gave an oily residue (15 g) which was applied to a column (3.2 × 80 cm) of Si gel and eluted with a solvent gradient system from $CHCl_3$ to $CHCl_3$–Et_2O (8:2). Fractions of 200 ml were collected.

Fractions 15–19 were taken to dryness to afford 450 mg of an oil which was rechromatographed on a Si gel column (1 × 20 cm) which was eluted with a solvent gradient system of Et_2O–petrol from 7:3 to 9:1. Fractions of 12 ml were collected. Fractions 10–15 taken to dryness afforded 61 mg of crude product which was purified by repeated prep. TLC (Si gel) using Et_2O–petrol (7:3) as eluant to give 20 mg of **7**, mp 178–180°, $[\alpha]_D^{20}$ +2.5° ($CHCl_3$; *c* 0.80); EIMS 70 eV, *m*/*z*: 464, 466, 468 $[M]^+$; 446, 448, 450 $[M-H_2O]^+$; 431, 433, 435 $[M-H_2O-Me]^+$; 367, 369 $[M-H_2O-Br]^+$; 349, 351 $[M-2H_2O-Br]^+$; 353, 355 $[M-H_2O-CH_2Br]^+$; 323, 325 $[M-H_2O-HBr-C_3H_7]^+$; 287 $[M-H_2O-HBr-Br]^+$; 273 $[M-H_2O-HBr-$

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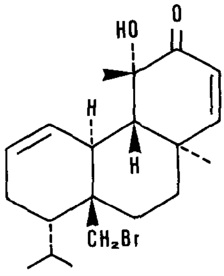

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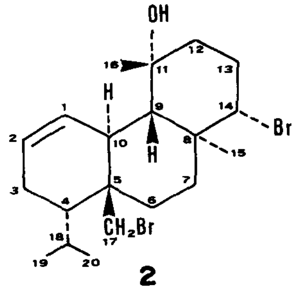

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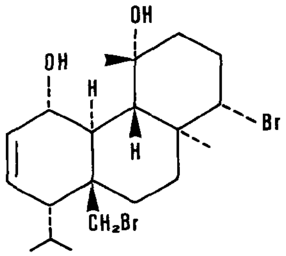

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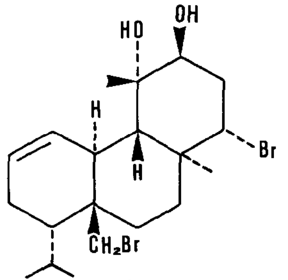

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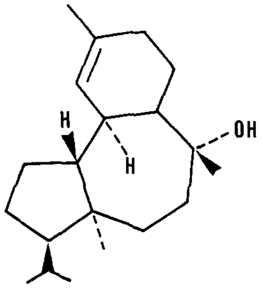

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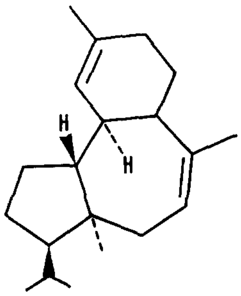

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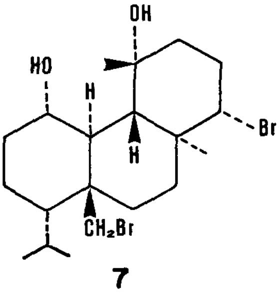

7

$CH_2Br]^+$; 255 $[M-2H_2O-HBr-CH_2Br]^+$. IR$\nu_{max}^{CHCl_3}$ cm^{-1}: 3600–3200. (Found: C, 51.37; H, 7.15; Br, 34.26. $C_{20}H_{34}Br_2O_2$ requires: C, 51.49; H, 7.35; Br, 34.29%.)

Hydroboration–oxidation of 2. Diborane (0.028 g, 1 mmol) in THF (1.5 ml) was added to bromosphaerol (2, 0.045 g, 0.1 mmol) in THF (2 ml) and the soln was stirred overnight at 20°. The resulting mixture was oxidized with 3 N NaOH (0.05 ml) and 30% H_2O_2 (0.06 ml) at 0° for 5 min and at 50° for 2 hr. After cooling, the mixture was concd and extracted with Et_2O. The organic phase was washed with brine, dried (Na_2SO_4) and taken to dryness. The residue was chromatographed on prep. TLC (Si gel) using $CHCl_3$–Et_2O (8:2) as eluant. The band R_f 0.4 when scraped and eluted with Et_2O afforded 0.019 g of 7.

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