further separated by repeated TLC (Si gel). Known compounds were identified by high field ^{1}H NMR spectroscopy. Finally, 50 mg **1**, 6 mg **2**, 80 mg **3**, 150 mg **4**, 3 mg **5** and 10 mg **7** were obtained.

2α-Acetoxyhelenium lactone (**2**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1740 (OAc); MS *m/z* (rel. int.): 246.126 $[M - HOAc]^+$ (9) ($C_{15}H_{18}O_3$), 55 $[C_4H_7]^+$ (100). CD (MeCN) Δ_{256} +0.3.

4-O-Tigloyl-6-epi-picrohelenin (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1725 ($C=CCO_2R$); MS *m/z* (rel. int.): 346.178 $[M - HOAc]^+$ (6), 306 $[M - HOTigl]^+$ (1), 246 $[306 - HOAc]^+$ (6), 228 $[246 - H_2O]^+$ (1.5), 218 $[246 - CO]^+$ (6.5), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (84). CD (MeCN) Δ_{260} negative.

4-O-Tigloyl-6-epi-autumnolide (**7**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1770 (γ-lactone), 1730 ($C=CCO_2R$); MS *m/z* (rel. int.): 362.173 $[M]^+$ (2) ($C_{20}H_{26}O_6$), 262 $[M - HOTigl]^+$ (2), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (73).

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THREE DITERPENES FROM THE RED ALGA *SPHAEROCOCCUS CORONOPIFOLIUS**

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Key Word Index—*Sphaerococcus coronopifolius*; Rodophyta; diterpenes; presphaerene; bromosphaerenes A and B.

Abstract—Three new diterpenes, presphaerene and bromosphaerenes A and B, have been isolated from the chloroform extract of the red alga *Sphaerococcus coronopifolius* and their structures determined.

Seven diterpenes have been isolated previously from the red alga *Sphaerococcus coronopifolius* [1–7]. In connection with our investigation of this alga, we have now isolated three further tricyclic diterpenes which we have named presphaerene (**1**) and bromosphaerenes A (**2**) and B (**3**).

Compounds **2** and **3** are closely related to bromosphaerol (**4**) [2], while **1** possesses the same carbocyclic skeleton as presphaerol (**5**) [4, 5]. The chloroform extract of *S. coronopifolius* was chromatographed on a Si gel column. Selected fractions were further purified by rechromatography on prep. TLC (Si gel) to obtain three diterpenes. In order of polarity these were **1** (0.01 %), **2** (0.04 %) and **3** (0.02 %). The structure of **1** was assigned by comparison of its properties [$[\alpha]_D^{20}$ −46°; EIMS 70 eV, *m/z*: 270 $[M]^+$; UV λ_{max} nm: 271 and 279, ^{1}H NMR: δ6.94 (1H, *d*, $J = 5.7$ Hz), 7.06 (1H, *d*, $J = 5.7$ Hz), 7.02 (1H, *br s*), 3.26 (1H, *dd*, $J = 7$ and 11 Hz), 2.92 (1H, *m*), 2.32 (3H, *s*), 1.30 (3H, *d*, $J = 6.8$ Hz), 0.94 and 0.88 (3H each, *d*, $J = 7$ Hz) and 0.48 (3H, *s*)] with those of a sample prepared from presphaerol by selenium treatment at 270° for 36 hr as previously described [4, 5].

Structure **2** was assigned to bromosphaerene A on the basis of its physical and spectral properties [$[\alpha]_D^{20}$ − 143°; EIMS 70 eV, *m/z*: 428, 430, 432 $[M]^+$; mp 101 − 103°; ^{1}H NMR: δ0.88 and 0.97 (3H each, *d*'s, $J = 7.5$ Hz), 1.31 and 1.66 (3H each, *s*), 3.46 (1H, *m*), 3.65 (2H, AB system, $J = 10.5$ Hz), 4.11 (1H, *dd*, $J = 3.5$ and 12 Hz), 5.57 (2H, AB system, $J = 10$ Hz)], which were identical to those of a

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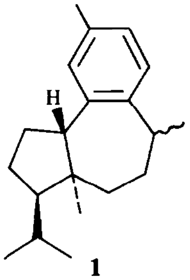

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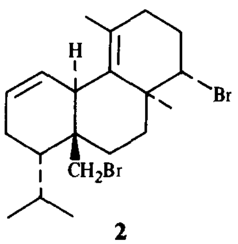

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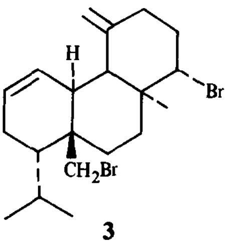

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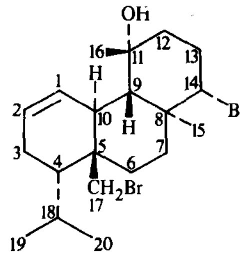

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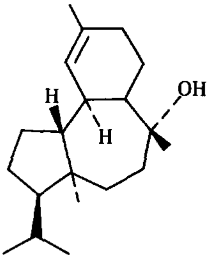

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compound previously obtained from bromosphaerol by dehydration with phosphorus oxychloride [2].

The crystalline compound **3** has the molecular formula $C_{20}H_{30}Br_2$. The ^1H NMR spectrum contained three methyl signals [doublets at $\delta 0.91$ and 0.98 (3H each, $J = 7.5$ Hz, H-19 and H-20) and a singlet at 0.92 (3H, H-15)], an AB system ($\delta 3.78$ and 3.62, 2H, $J = 12.5$ Hz) attributable to a $-CH_2Br$ group and signal at $\delta 4.13$ (*dd*, $J = 3.5$ and 10.5 Hz) due to a bromomethine group.

The low-field region of the ^1H NMR spectrum contained two 1H broad singlets at $\delta 4.40$ and 5.01 which suggested the presence of an exomethylene group, which was confirmed by its IR spectrum (IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3050, 1645, 895). A signal is also present as a further coupled AB system at 5.59 (2H, $J_{AB} = 11$ Hz, H-1 and H-2). These spectral data indicated the close relationship between **2** and **3** and suggested that **3** differs from **2** in the position of the double bond in ring C.

Structure **3** was definitively confirmed by accurate chromatographic analysis of the products obtained from bromosphaerol by treatment with phosphorus oxychloride–pyridine which revealed the presence, in addition to **2**, of small quantities of **3**. This evidence also established the stereochemistry of **3**.

EXPERIMENTAL

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

Isolation of **1**–**3**. The alga (24 kg fr. wt.) collected in the spring, 1982 in the Bay of Salerno, Italy, was freeze-dried and ground to a fine powder with a blender. The dried alga (6.2 kg) was extracted with stirring for 12 hr with $CHCl_3$ ($\times 3$). The combined solns were taken to dryness and the oily residue (20.4 g) was chromatographed on a Si gel column (2 kg) which was eluted with *n*-hexane. Fractions 7–10, taken to dryness, afforded 10 mg of an oily product which was rechromatographed on TLC (Si gel) using as eluant *n*-hexane. The band at R_f 0.7 when scraped and eluted with Et_2O gave 2 mg of **1**.

Fractions 13–18 were taken to dryness to afford 20 mg of a white solid which was recrystallized from EtOH; 8 mg of pure **2** was obtained.

Fractions 21–26, on evaporation, gave 10 mg of a crude product which was purified by prep. TLC (Si gel), using as eluant *n*-hexane. The band at R_f 0.4 when scraped and eluted with Et_2O afforded 4 mg of **3**, mp 96–98°, $[\alpha]_D^{20}$ $-95°$ ($CHCl_3$; *c* 1). EIMS 70 eV, *m/z*: 428, 430, 432 $[M]^+$; 413, 415, 417 $[M-Me]^+$; 385, 387, 389 $[M-C_3H_7]^+$; 349, 351 $[M-Br]^+$; 335, 337 $[M-CH_2Br]^+$; 269 $[M-Br-HBr]^+$; 255 $[M-HBr-CH_2Br]^+$. (Found: C, 55.71; H, 6.95. $C_{20}H_{30}Br_2$ requires: C, 55.80; H, 7.03%.)

Dehydration of bromosphaerol. Bromosphaerol (**4**) (300 mg) in pyridine (5 ml) was treated with $POCl_3$ (3 ml) for 30 min at 100°. Following the usual work-up crude **2** and **3** were obtained and purified by prep. TLC (Si gel) using as eluant *n*-hexane. The bands R_f 0.55 and 0.4 were eluted with Et_2O to give 170 mg and 11 mg of **2** and **3**, respectively.

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