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PRESPHAEROL, A NEW REARRANGED DITERPENE FROM THE RED ALGA SPHAEROCOCCUS CORONOPIFOLIUS

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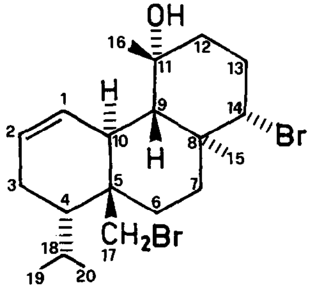
Three congener bromoditerpenes with a rearranged carbon skeleton, bromosphaerol[1] (1), sphaerococcenol A[2] (2) and bromosphaerodiol[3] (3), have been isolated recently from the red seaweed Sphaerococcus coronopifolius (Good. et Woodw.) C. Ag., family Sphaerococcaceae. A study of the minor diterpene constituents of this plant, undertaken in an attempt to trace the biosynthesis of the bromocompounds, has now allowed the isolation of a new diterpene alcohol, for which we propose the name presphaerol. Presphaerol (4) has been obtained in minute amounts (0.000008% fresh weight) from the chloroform extract of the alga (collected



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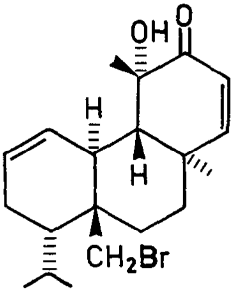

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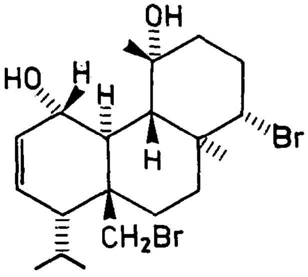

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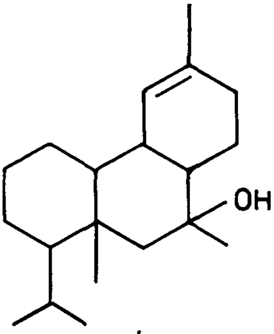
near Syracuse, Sicily, Italy, during the spring 1978) by careful chromatography on standard silica gel (chloroform as the eluent) followed by argentation chromatography of the appropriate fractions. Presphaerol was eluted with 5% ether in benzene as a colourless, viscous liquid, $[\alpha]_D$ = +26° (c 1 in $CHCl_3$). It had the molecular formula $C_{20}H_{34}O$; m/e M^+ = 290; high resolution m/e 290.2604 (calcd for $C_{20}H_{34}O$ 290.2609). Further intense peaks were found at m/e 275 (M^+-CH_3), 272 (M^+-H_2O), 257 (M^+-CH_3-H_2O) and 247 (M^+-C_3H_7). The infrared spectrum (CCl_4) contained absorptions at 3600 (OH), 1600 (C = C), 1385 and 1380 (isopropyl group) $cm.^{-1}$ The c.m.r. spectrum (25.18 MHz) contained 5 quartets (30.659, 23.550, 23.422, 22.791 and 14.676 p.p.m.), 6 triplets (38.066, 37.032, 30.472, 27.864, 26.894 and 22.369 p.p.m.), 6 doublets (125.967, 59.274, 50.348, 47.827, 35.840 and 28.830 p.p.m.) and 3 singlets (132.498, 75.317 and 45.199 p.p.m.). Thus, the four degrees of unsaturation implied by the formula of 4 are due to a trisubstituted double bond and three cycles, and the hydroxyl group is tertiary.
The p.m.r. spectrum (270 MHz, $CDCl_3$, δ-scale) displayed two three-proton doublets at 0.83 (J 7 Hz) and 0.92 (J 7 Hz) which are assigned to the non-equivalent methyls of an isopropyl group linked to a chiral centre; irradiation at 1.53 (tentatively the frequency of the isopropyl methine) caused both doublets to collapse into singlets. Two three-proton singlets at 1.21 and 1.62 were assigned to a methyl on oxygen-bearing carbon and a vinyl methyl, respectively. A fifth methyl was seen as a singlet at 0.84, while a single olefinic proton appeared at 5.27.

Selenium aromatization of 4 (48 hr at 350°) afforded 1-isopropyl-6,9-dimethylphenanthrene λ_{max} (log ε) 259 (4.76), 280 (4.13), 291 (4.09) and 303 (4.16); m/e 248 (M^+), 233 (M^+-CH_3), 218 (M^+-CH_3) and 203 (M^+-C_3H_7) identified by comparison with an authentic specimen[4]. In milder condition (36 hr at 270°), selenium treatment gave the octahydrophenanthrene 5, $C_{20}H_{30}$ (high resolution mass spectrometry), $[\alpha]_D$ = -52° (c 1 in $CHCl_3$), λ_{max} (log ε) 271 (2.8), 278 (2.9).

The p.m.r. spectrum showed three aromatic protons at 6.94 (d, J 5.7 Hz), 7.06 (d, J 5.7 Hz) and 7.02. Thus, the single aromatic nucleus must be 1,2,4-trisubstituted; two of the substituents are methines [3.26 (1H, dd, J 7 and 11 Hz) and 2.92 (1H, m)] and the remaining one is a methyl (2.32, 3H, s). The spectrum also contained a methyl bonded to a benzyl methine [doublet at 1.30 (J 6.8 Hz) which collapsed to a singlet by irradiation at 2.92], a methyl on quaternary carbon at 1.22 and the methyls of the isopropyl group at 0.88 (J 7 Hz) and 0.94 (J 7 Hz). These spectral data and the aromatization of the 1-isopropyl-6,9-dimethylphenanthrene led to assign unambiguosly structure 5 to the product obtained by milder selenium treatment. This established the carbon skeleton in 4.



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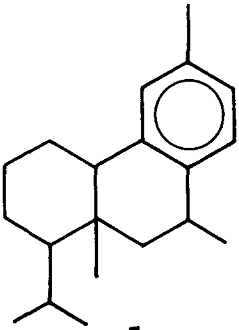

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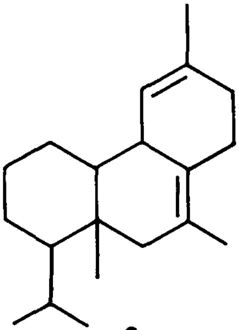

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The location of the double bond and the hydroxyl group in presphaerol was inferred by the dehydration reaction with acetyl chloride in hot xylene (4 hr) which gave the unconjugated diene 6, $C_{20}H_{32}$ (precise mass measurement), $[\alpha]_D$ +28° (c 1 in $CHCl_3$). The p.m.r. spectrum of 6 showed a single olefinic proton at 5.24 and two vinyl methyls at 1.65 and 1.63. From this, taking into account the spectral properties of 4, it can be deduced that the newly-generated double bond is tetrasubstituted and that one of the substituents is a methyl. Hence, this double bond is located between C_7 and C_8 and consequently the hydroxyl group in 4 must be linked to C_7. A one-proton signal at 2.82 present in the spectrum of 6 was assigned to the diallylic proton at C_9, since it was simplified by irradiation at the frequency of the olefinic proton (5.23). The above data allowed to assign structures 4 and 6 to presphaerol and its dehydration product.

Finally, we wish to recall here that sphaerococcenol A (2) according to Fenical could derive from tail to tail condensation of a farnesyl-precursor with an isoprene unit, followed by 1,2-shift of a methyl group from position 10 to position 5. Since presphaerol appears to derive from geranylgeranyl-precursor *via* cyclization followed by 1,3-shift of a methyl from position 1 to position 5 (possibly through the intermediacy of a cyclobutane-ring compound), the more plausible hypothesis can be put forward that sphaerococcenol A, and likely bromosphaerol and bromosphaerodiol, are synthesized from an intermediate possessing the carbon skeleton of presphaerol through 1,2-shifts of methyls.

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