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DIOSPHENOL FROM THE ASCIDIAN *Diplosoma* SP.

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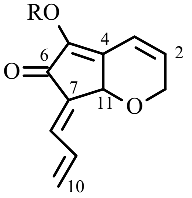
The tunicate family Didemnidae, including the genus *Diplosoma*, is a rich source of biologically active compounds [1-11]. We isolated **1** from the ascidian *Diplosoma* sp. collected during an expedition of the SRS Academic Oparin in the waters of Viet Nam in January 2005.



1, 2

1: R = H; **2:** R = Ac

The ascidian *Diplosoma* sp. (Didemnidae) (dry weight 176 g, Tai Island, Van-Fong Bay, South China Sea) was extracted three times with ethanol. The extract was concentrated in vacuo. The residue was distributed betweeen EtOH (90%) and hexane. The aqueous ethanol layer was treated with water (to obtain 50% EtOH) and extracted with CH_2Cl_2. The resulting extract was concentrated in vacuo to a dry oily residue (2.3 g) and chromatographed over a column of Sephadex LH-20 using $CHCl_3$:EtOH (1:1) to afford **1** (157.2 mg, 0.09% of dry weight).

The molecular formula of **1** $C_{11}H_{10}O_3$ was confirmed by EI MS and the NMR spectrum. The mass spectrum contained a peak for the molecular ion at m/z 190. The ^{13}C NMR spectrum had 11 resonances including those for carbonyl (δ_C 187.4), three quaternary C atoms (δ_C 148.4, 134.2, and 130.2), four methine C atoms of double bonds (δ_C 134.2, 132.8, 131.1, and 118.2), an exo-methylene conjugated to a double bond (δ_C 127.1), $-\underline{C}HO-$ (δ_C 70.4), and a $-\underline{C}H_2O$ group (δ_C 66.5). The PMR spectrum, in addition to resonances for methylene and methine protons bonded to oxygen (δ_H 4.57 ddd, 4.40 dd, and 5.02 s), olefin protons [δ_H 6.85 m (2H), 6.78 m, 6.23 ddd], and exo-methylene protons (δ_H 5.77 m and 5.63 m), exhibited a resonance for a hydroxyl (δ_H 10.39 s). The presence of an OH in the isolated compound was confirmed by absorption at 3261 cm^{-1} in the IR spectrum.

Acetylation of **1** by a mixture of acetic anhydride and pyridine gave acetate **2**, which was isolated in low yield (part of the starting material polymerized upon acetylation) by column chromatography over silica gel in ethylacetate.

The 1D NOESY spectrum [12] of **1** (D_2O) showed a response of H-11 (δ_H 5.08 d, J = 1.7 Hz) and no response of H-8 (δ_H 6.93 dd, J = 2.0, 11.5 Hz) upon irradiation of H-9 (δ_H 6.80 m) and no response of H-11 upon irradiation of H-8. This was consistent with the *E*-configuration of the 7,8-double bond. The structure of **1** as diosphenol was proved by 2D NMR spectroscopy (DEPT, HMQS, HMBC, COSY).

A search of the literature showed that this compound was isolated previously in a mixture with the *Z*-isomer of the 7,8-double bond from the sponge *Ulosa* sp. [13]. The observation of diosphenol in representatives of another large taxon, namely ascidians, was unexpected. It could be that diosphenol in sponges (species *Porifera*) and ascidians (subspecies *Tunicata*) is produced by microbial symbionts of these invertebrates. It was recently shown that several secondary metabolites that were

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earier considered metabolites of sponges or ascidians were in fact biosynthesized by symbiotic bacteria or microalgae colonizing these animals [14].

Compound 1. IR spectrum (KBr, ν, cm^{-1}): 3345, 3261, 1681, 1665, 1621. Mass spectrum (EI, 70 eV, m/z, I_{rel}, %): 190 (100) $[M]^+$.

PMR spectrum (500 MHz, DMSO-d_6, δ, ppm, J/Hz): 4.40 (ddd, J = 18.7, 4.1, 1.5, H-1), 4.57 (dd, J = 18.7, 2.5, H-1), 5.02 (s, H-11), 5.63 (m, H-10), 5.77 (m, H-10), 6.23 (ddd, J = 9.9, 4.1, 2.5, H-2), 6.78 (m, H-3), 6.85 (m, H-8,9), 10.39 (s, OH).

^{13}C NMR spectrum (125 MHz, DMSO-d_6, δ, ppm): 66.5 (C-1), 70.4 (C-11), 118.2 (C-3), 127.1 (C-10), 130.2 (C-4), 131.1 (C-8), 132.8 (C-9), 134.2 (C-2,7), 148.4 (C-5), 187.4 (C-6).

HMBC(H/C): H-1/C-2,3,4,5,6,11; H-2/C-1,4; H-3/C-1,4,5,11; H-8/C-7,9,10,11; H-9/C-7,9,10,11; H-10/C-6,7,8,9,11; OH/C-4,5,6.

Compound 2. PMR spectrum (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 7.10 (dd, J = 2.0, 11.5, H-8), 6.89 (m, J = 9.8, 11.5, 16.5, H-9), 6.65 (m, J = 1.2, 2.2, 9.9, H-3), 6.36 (m, J = 2.2, 4.1, 9.9, H-2), 5.74 (dd, J = 1.9, 16.5, H-10), 5.66 (dd, J = 1.9, 9.8, H-10), 5.12 (d, J = 1.7, H-11), 4.63 (m, J = 2.2, 2.6, 18.7, H-1), 4.54 (m, J = 1.9, 4.1, 18.7, H-1), 2.31 (s, OAc).

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REFERENCES

1. A. R. Carroll, Y. J. Feng, B. F. Bowden, and J. C. Coll, *J. Org. Chem.*, **61**, 4059 (1996).
2. G. A. Charyulu, T. C. McKee, and C. M. Ireland, *Tetrahedron Lett.*, **30**, 4201 (1989).
3. H. Kobayashi, J. Ohashi, T. Fujita, T. Iwashita, Y. Nakao, S. Matsunaga, and N. Fusetani, *J. Org. Chem.*, **72**, 1218 (2007).
4. T. Teruya, K. Suenaga, S. Maruyama, M. Kurotaki, and H. Kigoshi, *Tetrahedron*, **61**, 6561 (2005).
5. T. Teruya, H. Shimogawa, K. Suenaga, and H. Kigoshi, *Chem. Lett.*, **33**, 1184 (2004).
6. H. Vervoort, W. Fenical, and R. D. Epifanio, *J. Org. Chem.*, **65**, 782 (2000).
7. B. Banaigs, E. A. Mansour, I. Bonnard, A. Boulanger, and C. Francisco, *Tetrahedron*, **55**, 9559 (1999).
8. E. A. Mansour, A. Boulanger, A. Badre, I. Bonnard, B. Banaigs, G. Combaut, and C. Francisco, *Tetrahedron*, **51**, 12591 (1995).
9. A. Boulanger, E. A. Mansour, A. Badre, B. Banaigs, G. Combaut, and C. Francisco, *Tetrahedron Lett.*, **35**, 4345 (1994).
10. A. Badre, A. Boulanger, E. A. Mansour, B. Banaigs, G. Combaut, and C. Francisco, *J. Nat. Prod.*, **57**, 528 (1994).
11. J. M. Aracil, A. Barde, M. Fadli, G. Jeanty, B. Banaigs, C. Francisco, F. Lafargue, A. Heitz, and A. Aumelas, *Tetrahedron Lett.*, **32**, 2609 (1991).
12. C. J. Bauer, R. Freeman, T. Frenkiel, J. Keeler, and A. J. Shaka, *J. Magn. Reson.*, **58**, 442 (1984).
13. S. J. Wratten and D. J. Faulkner, *Tetrahedron Lett.*, **19**, 961 (1978).
14. D. J. Newman and R. T. Hill, *J. Ind. Microbiol. Biotech.*, **33**, 539 (2006).