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A PYRANONAPHTHAZARIN PIGMENT FROM THE SEA URCHIN ECHINOTHRIX DIADEMA

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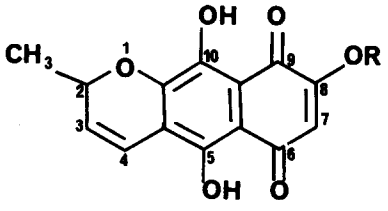
The spines of sea urchins (echinoids) of the genus Echinothrix, viz. E. diadema Linn. and E. calamaris Pallis from Kaneohe Bay, Oahu, elaborate no fewer than some 30 pigments. Sixteen of these spinochromes have been identified (1). The pigments are predominantly polyhydroxynaphthoquinones, the hydroxy groups of which are generally not methylated and which frequently bear a single two carbon side chain, but no one carbon side chain (2). We now wish to report the isolation and structure determination of the first pigment, 2-methyl-8-hydroxy-2H-pyrano [3,2-g]naphthazarin (1), possessing a four carbon unit attached to the naphthoquinone system.



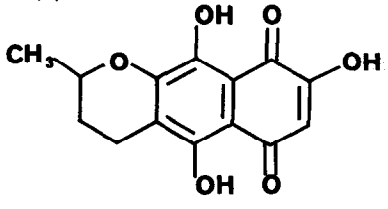
1, R = H

2, R = CH_3

Compound 1 is the sole pigment in fraction 3 obtained by partial separation of the Echinothrix pigments by column chromatography on deactivated silica gel (1) which after thin layer chromatography crystallizes from petroleum ether, mp 165-172° (dec), in 5 x 10^{-5}% yield. The exact molecular weight of 1 was 274.04765 by high resolution mass spectrometry, which corresponds to the empirical formula $C_{14}H_{10}O_6$ (calcd mol wt 274.04773). The facile loss of 15 mass units from the molecular ion (accompanied by a metastable ion at m/e 244.8) indicates the presence of a methyl substituent. The ultraviolet spectrum of 1 ($\lambda_{max}^{CHCl_3}$ 564 sh, 488, 340, and 292 mμ) is typical of a naphthazarin, but is unusual in that two peaks are displayed at 292 and 340 mμ while naphthazarins generally exhibit only one peak in this region (3). The mean (316 mμ), however, suggests that two β-oxygens are attached to the naphthazarin system (3). One of the β-oxygens is in a hydroxyl group as 1 is soluble in aqueous sodium bicarbonate and readily forms a monomethyl derivative 2 with diazomethane (4) (mol wt 288 by mass spectrometry).

The 100 Mc nmr spectrum* of 1 showed singlets at δ13.28 and 11.87 for the two peri hydroxyls at C-5 and C-10, a singlet at δ6.36 for the C-7 proton, a doublet of doublets at δ6.75 (J = 10 and 1.8 cps) for the C-4 proton, a doublet of doublets at δ5.84 (J = 10 and 4 cps) for the C-3 proton, a multiplet centered at ca. δ5.25 for the C-2 proton, and a doublet at δ1.54 for the methyl protons. The chemical shift of the C-7 proton indicates that the hydroxyl group is attached to a quinoidal ring (5). Irradiation of the C-2 proton produced a collapse of the methyl resonance to a singlet and removed the smaller couplings from the signals of the C-3 and C-4 protons.

Catalytic hydrogenation of 1, followed by oxidative regeneration of the naphthazarin system during workup, afforded 3 (mol wt 276 by mass spectrometry). The electronic spectrum of 3 ($\lambda_{max}^{CHCl_3}$ 560 sh, 516, 490 sh, and 450 sh mμ) had a shape almost identical with that of 2,7-dihydroxy-3-ethylnaphthazarin (6).



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* The nmr spectrum was determined on a Varian HA-100 instrument in deuteriochloroform and chemical shifts are reported as δ units relative to TMS (δ = 0).

One of the recurring hydroxylation patterns in echinoid pigments is based on 2,7-dihydroxynaphthazarin. Our new pigment clearly falls into this group. Its novelty consists of a four carbon side chain at C-6 which has cyclized with the oxygen function at C-7. The proposed structure is in accord with Lederer's recent finding (7) that the biosynthesis of echinochrome A (3,6,7-trihydroxy-2-ethylnaphthazarin) proceeds with incorporation of acetic acid in the naphthoquinone nucleus and in the side chain and without incorporation of propionic acid or methionine in the side chain.

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