

A GUAIANOLIDE PIGMENT FROM A DEEP SEA GORGONIAN

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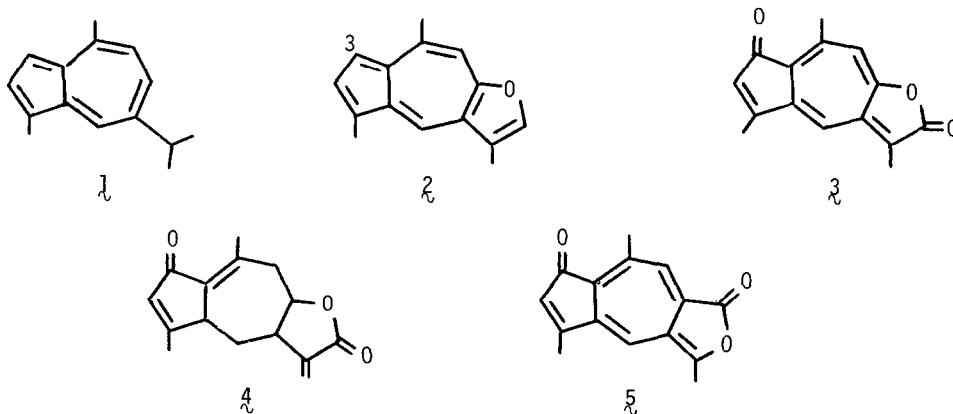
Abstract -- Yellow pigment **3** is one of the minor constituents of a deep sea gorgonian, *Placogorgia* sp.

Guaiazulene (**1**) and linderazulene (**2**) are the principal blue and purple pigments, which we have encountered in deep sea (-350 m) gorgonians that we collected with the aid of the minisub *Makali'i*.¹ Typically, the animals are frozen in Dry Ice as soon as the sub surfaces and remain frozen until work-up. Chromatography invariably has revealed complex mixtures of minor pigments, as e.g. halogenated guaiazulenes from a blue gorgonian, Family Paramuriceidae.²

A recent communication by Thomson and coworkers,³ in which keto-lactone **3** was described as a photo artefact of linderazulene prompts us to report our work, which strongly indicates that at least in our case keto-lactone **3** is a natural product.

An olive-colored gorgonian (95 g), *Placogorgia* sp.,⁴ was thawed and extracted by overnight immersion in hexane. The residue (300 mg) from the dried extract was separated on BioBeads SX-8 (BioRad Labs, Richmond, CA) with benzene/hexane (1:1) into a purple fraction (10 mg), which proved to be pure linderazulene (**2**), and a yellow fraction which required further purification. Linderazulene, mp 103-104°C, was identified by comparison of its spectral properties (ms, uv, ir, ¹H NMR) with the data reported by Thomson and coworkers,⁵ who had earlier isolated the pigment from a Sea of Marmara gorgonian, *Paramuricea chamaeleon*.

The yellow fraction was chromatographed on neutral alumina and eluted with hexane/EtOAc (3:1). The yellow residue of fraction 2 was triturated with hexane/EtOAc (4:1) and yielded a yellow ppt which was recrystallized from the same mixed solvents, furnishing yellow needles (2 mg), mp 190-191°C. The supernatant contained a second yellow pigment and a crystalline colorless compound, not yet identified.



Interpretation of spectral data⁶ suggested a guaiane skeleton with keto and lactone functions reminiscent of virginolide (4),⁷ since an alternate lactone ring closure as in matricarin,⁸ achillin,⁸ or malaphyllidin⁹ would have displayed two mutually coupled aromatic proton signals in the NMR spectrum, which are absent in the spectrum of 3. The spectral data, however, did not rigorously exclude a rearranged sesquiterpene skeleton as in 5.

We proved structure 3 by MCPBA oxidation of 2, a reaction which could not have led to 5. Peracid oxidation of furans to γ -lactones has been described.¹⁰ Hopefully, concomitant oxidation at C-3 might take place in view of the known high electron density at that carbon.¹¹ This proved to be the case.¹² To linderazulene (20 mg) dissolved in 10 mL of benzene was added 2 equiv. MCPBA at R.T. The mixture was cooled to 5°C and the reaction was monitored by TLC. After 8 h, the reaction mixture was extracted with 5% NaHCO₃, the aqueous phase backwashed with benzene, and the organic layers combined. Chromatography on BioBeads SX-8 (benzene) yielded 2 fractions. The yellow fraction was rechromatographed on neutral alumina (CH₂Cl₂) yielding keto-lactone 3 (4 mg), identical with the natural product in all respects (mp, mmp, uv, IR, MS, ¹H NMR).¹³

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References and Notes

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- Identified by Dr. K. Muzik.
- Imre, S.; Thomson, R. H.; Yalhi, B. Experientia **1981**, *37*, 442. -- Previously unreported ¹³C NMR (CD₂Cl₂): δ 143.6, 139.7, 139.4, 136.0, 133.0, 131.8, 127.4, 125.4, 121.4, 120.1, 116.4, 111.3, 24.6, 13.2, 8.2.
- Keto-lactone 3: IR: ν_{\max} 1754, 1687 cm⁻¹; UV (CHCl₃): λ_{\max} 239(9310), 270(18660), 280(18950), 290 sh, 412(9640), 433(10610), 460 nm (6660); HREIMS: M^+/Z 240.078647 (calcd for C₁₅H₁₂O₃ 240.07866); ¹H NMR (CDCl₃): δ 6.83 (1H, s), 6.52 (1H, s), 6.21 (1H, m), 2.67 (3H, s), 2.28 (3H, d, $J = 1.2$ Hz), 2.08 (3H, s).
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- In retrospect, this is not surprising as Thomson³ was able to achieve this transformation by slow photooxidation.
- Thomson (Ref. 3) reports mp 107-110°C (MeOH). From the same solvent we observe a mp of 207-212°C. We thank Professor Thomson for checking his mp data, which are compatible with ours (210-220°; 228-231; 238-241°C) and are in error in Ref. 3.
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