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BISINDOXYL-DERIVED BLUE MARINE PIGMENTS†

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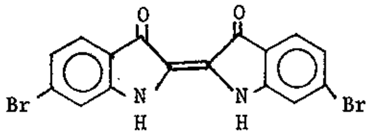
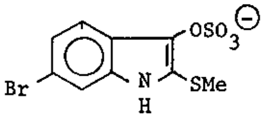
From the marine invertebrate *Ptychodera flava laysanica* we have isolated three blue pigments, the known 6,6'-dibromoindigotin (I) as well as the previously unreported 5,7,5',7'-tetrabromo-6,6'-dimethoxyindigotin (III) and 5,7,6'-tribromo-6-methoxyindigotin (IV) in addition to a colorless companion, 5,7-dibromo-6-methoxyindole (V).

In sharp contrast to the infinite variety of brilliant colors displayed by tropical reef fauna is the apparently small number of organic structural types that give rise to these colors. Most of the fully characterized pigments are derivatives of carotene or porphyrin.[1] Notable exceptions are the quinones of the echinoderms[2] and the apparently unique 6,6'-dibromoindigotin (Tyrian purple) (I) of the molluscan family Muricidae, which however has been shown to



(I)



(II)

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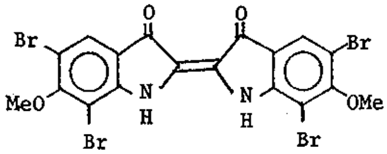
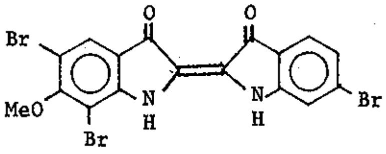
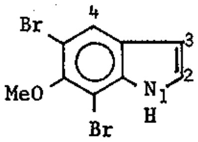
† Dedicated to Professor Tsunematsu Takemoto on the occasion of his retirement.



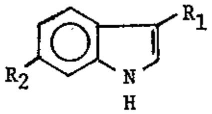
(III)



(IV)



(V)



(VI)

a R_1 = Cl, R_2 = H
b R_1 = Br, R_2 = H
c R_1 = Cl, R_2 = Br

be an artefact derived from the natural precursor tyrindoxyl sulfate (6-bromo-2-methylthioindoxyl-3-O-sulfate, II).[3] We now report the isolation of three natural blue pigments (I), (III), (IV) and of a colorless companion, 5,7-dibromo-6-methoxyindole (V) from the hemichordate Ptychodera flava laysanica Spengel.

We have recently shown that the compounds responsible for the reputedly iodoform-like odor of P. flava are 3-chloroindole (VIa) and trace amounts of 3-bromoindole (VIb) and 6-bromo-3-chloroindole (VIc).[4] As the name P. flava indicates, these animals are normally yellow in color. During a collection at Paiko lagoon, Oahu, we noted that the animals in that locale were distinctly green and had only a faint odor. In fact, we could not isolate the odor constituents from the Paiko animals. We were however able to extract the green color from the original acetone concentrate of the animals (2.4 kg) into petroleum ether. The residue (about 5 g) furnished a number of green fractions by chromatography on Bio-Sil A and elution with petroleum ether containing increasing amounts of ether. Thin layer chromatography (silica gel, chloroform) of the green fractions effected separation into yellow and blue zones. The blue zones furnished 3 pigments, all brilliantly blue in chloroform solution, all high melting (> 300°C) purple-blue powders after solvent removal: 5,7,6'-tribromo-6-methoxyindigotin (IV), 4 mg (1.7×10^{-4}%), 6,6'-dibromoindigotin (I), 0.8 mg (3.3×10^{-5}%), and 5,7,5',7'-tetrabromo-6,6'-dimethoxyindigotin (III), 0.6 mg (2.5×10^{-5}%).

The electronic spectrum of the major pigment (IV) (280, 346, 605 nm) paralleled that of indigotin (285, 320 sh, 600 nm). Mass spectral data, including exact mass measurements, of all these pigments led to the proposed structures (IV), (I), and (III).

We were unable to record pmr spectra of the trace pigments (I) and (III) since during attempted overnight accumulation of data on a Varian XLFT-100 instrument the compounds precipitated. This failure led us to suspect that our presumed pmr spectrum of major pigment (IV), though measured rapidly, might not be the spectrum of (IV) but of a soluble companion, since a precipitate was also observed in the nmr tube containing (IV). We confirmed this suspicion by measuring mass spectra of (IV) at two temperatures. At 250°C we recorded a spectrum, including composition (calc. for $C_{17}H_9{}^{79}Br_2{}^{81}BrN_2O_3$, 527.8143; found, 527.8142), compatible with (IV). Below 100°C, however, we obtained data for $C_9H_7Br_2NO$ (calc. for $C_9H_7{}^{79}Br_2NO$, 302.8893; found 302.8902), apparently a volatile companion that was completely chloroform-soluble and gave rise to a pmr spectrum compatible with (V): δ 6.53 (H-3, dd, J_{13} 2.2, J_{23} 3.3 Hz), 7.23 (H-2, dd, J_{12} 2.5, J_{23} 3.3 Hz), 7.74 (H-4, d, J_{14} 0.7 Hz), 8.38 (H-1, br). These values agree with published pmr data for indole.[5] In compound (V), the chemical shift of the proton at C-4 (δ 7.74) necessitates that C-5 bears a bromine rather than a methoxy group since in (VIc) the corresponding proton resonates at δ 7.43. A neighboring methoxy group would have a shielding effect on the proton at C-4, as seen in 5,6-dimethoxyindole, where the C-4 proton resonates at δ 7.11.[6] Finally, we can exclude a possible 5,6-dibromo-7-methoxyindole structure by comparing the NH resonance of (V) (δ 8.38 br) with that of 3,5,7,-tribromoindole (δ 8.37 br), which we isolated from *P. flava* collected elsewhere and which possesses an unambiguous pmr spectrum, including an H-4 signal at δ 7.60.[7]

ACKNOWLEDGEMENT We thank the National Science Foundation for financial support.

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7 Accompanying communication.

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