The Pigments from Sea-urchins. XI

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The authors previously isolated spine pigments (spinochrome) from the sea-urchins of four varieties; namely, sp. Aka₁ and sp. Aka₂ from Pseudocentrotus depressus (Ag.) (Aka-uni**'); sp. M₁ and sp. M₂ from Anthocidaris crassispina (Ag.) (Murasaki-uni**'); sp. B₁ and sp. B₂ from Hemicentrotus pulcherrimus (Ag.) (Bafun-uni**'), and sp. F₁ from Heterocentrotus mammilatus (Linn.) (Futozao-uni**').

The authors proposed constitutional formulas for sp. Aka₁, sp. M₁, sp. B₁ to other spinochromes is shown as follows.

![Chemical structures of spinochromes Aka₁, M₁, and B₁](image_url)

The constitutional formula for spinochrome B₁ was synthetically confirmed by J. Smith and R. H. Thomson.

From the spines of Hemicentrotus pulcherrimus (Ag.) (Bafun-uni), another spinochrome has been obtained, and the authors have named it spinochrome B₂.

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**Abbreviation for “spinochrome”.

**' Japanese name.


It is proved that sp. $B_3$ is identical with sp. $M_1$ from the results of the examinations of the color reactions, analytical values, and absorption curves of the spinochrome and its acetyl derivative.

The results are shown as follows.

1. Isolation. The pigment was extracted from the spines by aid of hydrochloric acid and benzene; yield, 250mg from 1kg of the spines.

2. Analytical results. Sp. $B_3$ (m.p. 196.5–197°), dark red needles (from methanol), found C, 51.91; H, 3.60%. $C_{14}H_{10}O_9$ requires C, 52.18; H, 3.13%. No depression of the melting-point was observed when mixed with an authentic specimen of sp. $M_1$.

Acetyl derivative (m.p. 166–167.5° (decomp.), yellow needles (from methanol), found C, 54.14, H, 3.79%. $C_{14}H_5O_4\cdot (OAc)_5$ requires C, 54.56; H, 3.86%.

Admixture with an authentic pentaacetyl spinochrome $M_1$ showed no depression of the melting-point.

3. Color reactions.

- NaOH deep red
- NaHCO$_3$ purple
- FeCl$_3$ dark green (in methanol)
- Pb(CH$_3$CO$_2$)$_2$ blue (in methanol)

4. Absorption spectra. The ultraviolet and visible absorption curves of spinochrome $B_3$ are identical with those of spinochrome $M_1$. The infrared absorption curves of spinochrome $B_3$ (Fig. 3) and its acetyl derivative (Fig. 4) are identical with those of spinochrome $M_1$ and pentaacetyl spinochrome $M_1$, respectively. They are shown below.

Consequently, spinochrome $B_3$ is quite identical with spinochrome $M_1$, and it has become clear that the spines of Japanese sea-urchins of the three varieties (Aka-uni, Murasaki-uni, and Bafun-uni) all contain spinochrome $M$.

![Ultraviolet absorption curves of Sp. $B_3$ and Sp. $M_1$ in methanol.](image)
More exact confirmative experiments for spinochrome Aka₁, spinochrome M₁, and spinochrome B₂ are in progress.

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