207. Studies on the Derivatives of Naphthoquinones. XII. The Pigments from the Sea-Urchins. VII

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The previous works¹⁾²⁾³⁾⁴⁾⁵⁾⁶⁾ by Kuroda and co-workers about the pigments Spinochrome Aka₁, Aka₂, M₁, M₂, B₁, B₂ and F, which were obtained from the spines of sea-urchins, are summarized as follows:

Source of material		Pigments
Japanese name		
Pseudocentrotus depressus	(Aka-uni) →	(Spinochrome Aka ₁ ,, Aka ₂)
Strongylocentrotus pulcherrimus	(Bahun-uni) →	(Spinochrome B ₁ ,, B ₂)
Heliocidaris crassispina	(Murasaki-uni) →	(Spinochrome M ₁ ,, M ₂)
Heterocentrotus mamillatus	(Futozawo-uni) →	(Spinochrome F)

Spinochrome Aka₁

Spinochrome B₁

Spinochrome M₁

Shikonin (Alkannin)

It was shown that Spinochrome M₂ is almost identical with Spinochrome B₁ and Spinochrome M₁ resembles Spinochrome B₂.

- 1) C. Kuroda and H. Ohshima: Proc. Imp. Acad., **16**, 214 (1940).
- 2) C. Kuroda and H. Iwakura: Proc. Imp. Acad., **18**, 74 (1942).
- 3) C. Kuroda and K. Koyasu: Proc. Imp. Acad., **20**, 23 (1943).
- 4) C. Kuroda and M. Okajima: Proc. Japan Acad., **26**, (6) 33 (1950).
- 5) C. Kuroda and M. Okajima: Proc. Japan Acad., **27**, 343 (1951).
- 6) C. Kuroda and M. Okajima: Proc. Japan Acad., **29**, 27 (1953).

However, the data have not been sufficient to determine the constitutions of Spinochrome Aka₂ and Spinochrome F. Spinochrome M₁ resembles Shikonin or Alkannin (pigments from plants), in their appearances, chemical behaviours and constitutions.

In the present paper, the results of spectroscopic investigation of some of the above-mentioned Spinochromes and some new experimental results of the Spinochromes and the related compounds with germanium oxide are reported. Some chemical experimental results of new derivatives from Spinochrome F, M₂ and of a new investi-

gation of the pigments from tests of sea-urchins are also described.

1) By the spectroscopic investigation it was decidedly proved that Spinochrome M₂ is identical with Spinochrome B₁ (Fig. 1). Spinochrome M₁ resembles Spinochrome B₂ closely, but does not coincide with each other (Fig. 2):

2) Behaviour of derivatives of the naphthoquinone towards germanium oxide. Recently several quinoid derivatives with hydroxy-groups (phenyl-fluorone, chinalizarin, quercetin, haematein, etc.) are used for the colorimetric determination of germanium oxide. Prof. K.

Kimura in the University of Tokyo, who wished to test with naphthoquinone derivatives for the same experiment, found that three synthetic naphthoquinones (2-hydroxy-, 5,8-dihydroxy-,

Fig. 1

Fig. 2

Fig. 3

2.5.8-trihydroxy-naphthoquinone (1,4)), when mixed with a solution of germanium oxide, showed no change in the colour nor any spectroscopic change. This is no doubt due to the absence of two hydroxy-groups in ortho-position. On the contrary, spinazarin (2.3.5.8-tetrahydroxy-naphthoquinone (1,4)), Spinochrome B₁, Spinochrome Aka₁, Spinochrome F, and Spinochrome M₁, when mixed with germanium oxide solution, exhibited, as the authors anticipated, a change of colour and displacement of absorption curve. This fact shows that Spinochrome M₁ and F, whose constitutions are yet unknown, must have two hydroxy-groups in ortho-position (Figs. 3-7).

Fig. 4

Fig. 5

3) Reductive

acetylation of Spinochrome F.⁴⁾ Spinochrome F which was obtained from *Heterocentrotus mammilatus* and purified with the previous method, was again carried out with benzene and purified as in the case of Spinochrome M₁.¹⁾ When the product thus obtained was treated with zinc dust, acetic anhydride and sodium acetate, a slightly

pale yellow crystalline compound (m.p. 219-219.5°) was obtained; Found C, 55.91, 55.65, H, 4.48, 4.62%.

This result along with that of spectroscopic investigation gives better data for study on Spinochrome F. More confirmative study on the pigment is in progress.

Fig. 6

4) Reductive acetylation of Spinochrome M₂. Spinochrome M₂⁴⁾ which was considered to be identical with Spinochrome B₁⁴⁾ obtained

from the spines of sea-urchins *Strongylocentrotus pulcherrimus*, was treated with zinc dust, acetic anhydride and sodium acetate. White crystalline compound was obtained. Found C, 55.30, H, 4.11%,

$C_{10}H_2O_6(Ac)_6$ requires C, 55.46, H, 4.20%.

No change of melting point was observed when mixed with an authentic sample of the reductive acetylation product from Spinochrome B₁.⁴⁾ Therefore this fact together with the result of the spectroscopic investigation gives more exact

Fig. 7

proof for identification of Spinochrome B₁ and Spinochrome M₂.

5) Isolation of Testachrome M₁ and M₂. Now, new results of further investigation for the pigments from the tests of sea-urchins above-mentioned will be reported here. Two kinds of pigments were isolated from the tests in the same manner as described in the previous report⁵⁾ and named them Testachrome M₁ and M₂ respectively. Testachrome M₁ (dark red needles, m.p. 192.5–193°) which was purified with acetic acid is soluble in benzene, whereas Testachrome M₂ (bright red needles) which was purified with methyl alcohol is insoluble in benzene.

Analytical values

Testachrome M₁ Found C, 50.70, H, 3.58%
 0.2g from
 3.262 kg of C₁₆H₁₄O₁₁ requires C, 50.24, H, 3.69%
 the tests

Testachrome M₂ Found C, 48.29, 48.13, H, 3.89, 3.89%
 0.1 g from the
 above

After all, it is interesting to notice that Testachrome M₁ resembles Spinochrome M₁, whereas Testachrome M₂ resembles with none of known pigments from any sea-urchin which was hitherto investigated by the present authors. However, more confirmative studies are wanted.

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