141. Studies on the Derivatives of Naphthoquinones. XIV

The Pigments from Sea-urchins. IX

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In the previous papers by Kuroda and co-workers,1-7 the work on naphthoquinone derivatives concerning shikonin and the related synthetic compounds was reported. A systematic study on paper chromatographic adsorption of the above derivatives and compounds was also carried out for the first time and reported.8

In recent years, studies have been concentrated on spinochromes (sp.) from Japanese sea-urchins, and the authors have proposed structural formulas for sp. Aka1 (I) from Pseudocentrotus depressus (Japanese name: Aka-uni) and sp. M1 (II) and sp. M2 (III) from Heliocedaris crassispina (Japanese name: Murasaki-uni).

The present paper deals with new derivatives of sp. M1 and sp. M2 along with infrared absorption of the spinochromes and their derivatives.

The derivatives of spinochromes are generally difficult to prepare. The authors successfully obtained pentaacetyl, pentaacetyl-dihydro, monomethyl, trimethyl, and trimethyl-triaacetyl derivatives of sp. M1.

As for sp. M2 which was proved to be identical with sp. B1 obtained from Strongylocentrotus purcherrmus (Japanese name: Bafun-uni), tetraacetyl, dimethyl, trimethyl, monoaetyl-trimethyl, and hexaaetyl-dihydro derivatives of it were prepared.

As shown in the formulas, there are two hydrogen bondings in sp. Aka\textsubscript{1} (I) and sp. M\textsubscript{1} (II), and one in sp. M\textsubscript{2} (III), and this bonding makes the methylation of the hydroxyl group which attaches to 5 or 8 position difficult. Accordingly the preparation of the pentamethyl derivative of sp. Aka\textsubscript{1}, the hexamethyl derivative of sp. M\textsubscript{1} and the tetramethyl derivative of sp. M\textsubscript{2} is difficult. After several experiments, the authors were finally successful in obtaining the latter two derivatives by the treatment of a dried acetone solution of each pigment with dimethyl sulfate in the presence of unhydrous potassium carbonate. The hexamethyl derivative of sp. M\textsubscript{1} (IV) was obtained in crystalline state (yellow needles, m.p. 123–124.5°). The analytical result was as follows: found C, 60.05%; H, 5.53%. Hexamethyl sp. M\textsubscript{1}, C\textsubscript{20}H\textsubscript{21}O\textsubscript{9} requires C, 59.11%; H, 5.46%. The tetraacetyl derivative of sp. M\textsubscript{2} (V) was also obtained in crystalline state (yellow needles, m.p. 132–132.5°). The analytical result was as follows: found C, 60.89%; H, 5.22%. 2,3,6,8-Tetramethyl-naphthoquinone-(1,4), C\textsubscript{14}H\textsubscript{14}O\textsubscript{6} requires C, 60.43%; H, 5.07%. Methoxyl value: found 43.33%. (OCH\textsubscript{3})\textsubscript{4} requires 44.61%.

The above methyl ethers gave no color reactions with an aqueous ferric chloride solution and the infrared absorption spectra showed absence of the hydrogen bonding which existed in the original pigments. See Figs. 1 and 2.

The methyl ethers were respectively oxidized with a 30% aqueous solution of H\textsubscript{2}O\textsubscript{2} in acetic acid. A colorless solid substance was obtained in each case. The above product from the methyl ether of sp. M\textsubscript{1} was purified with methanol (plates, m.p. 183–184.5°). It was indicat-
ed to be 3, 4, 6-trimethoxy-phthalic acid since it agreed with the compound in melting point and physical and chemical behaviors.\textsuperscript{9) The oxidation product from the methyl ether of sp. M\textsubscript{2} was purified with methanol (plates, m.p. 158\textdegree) and believed to be 3, 5-dimethoxy-phthalic acid since it agreed with the compound in melting point and physical and chemical behaviors.\textsuperscript{10) Further studies are in progress.

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\textsuperscript{9) Bargellini: Gazzetta Chimica Italiana, 441, 188.
\textsuperscript{10) Fritsh: Ann., 296, 357.}