Structure of Namakochrome. II*

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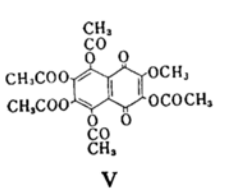
Previous paper[1] has reported that namakochrome which is a new pigment isolated from *polycheira rufescens*, should be either 2-hydroxymethyl-3, 6, 7-trihydroxy-naphthazarin (I or II) or 2-methoxy-3, 6, 7-trihydroxy-naphthazarin (III or IV). Thus, for the complete elucidation of the namakochrome structure there remains to be established the form of the functional group in 2-position of the naphthalene nucleus.

I II

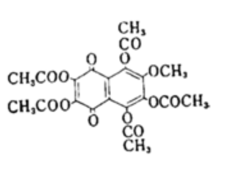
III IV

Although, in the preceding work[1], a qualitative detection of the quinone group in namakochrome by reductive acetylation has been also described, the isolation of crystalline products from the resulting solution was unsuccessful. Namakochrome-trimethyl ether was then acetylated in the presence of zinc dust, and a benzene solution of the reaction products was filtrated through an alumina column, and afforded a leuco-acetyl derivative, $C_{11}H_3O_5\cdot(OCH_3)_3(COCH_3)_4$, as colorless prisms, m. p. 226~227°C.

Now, in order to characterize the unascertained oxygen atom in 2-position of namakochrome, the 3, 5-dinitrobenzoate was prepared by the action of 3, 5-dinitrobenzoyl chloride on namakochrome-trimethyl ether. By carrying out this process in the presence of pyridine, there were obtained lemon yellow prisms, melting at 218~220°C. Its analytical composition is in agreement with a formula $C_{11}H_3O_3\cdot(OCH_3)_3[C_6H_3(NO_2)_2(COO)]_2$. The fact that namakochrome-trimethyl ether reacted with two molecular equivalents of 3, 5-dinitrobenzoyl chloride suggests, that the positions for the 3, 5-dinitrobenzoyl groups in the naphthalene nucleus should be at 5 and 8. The functional group at 2-position of the naphthalene nucleus might be a methoxyl group because of its resistance to both of the acetylation[1] and the 3, 5-dinitrobenzoylation. A qualitative detection of the methoxyl group in namakochrome was then made. In the alkoxyl microapparatus of Zeisel, namakochrome was treated with hydriodic acid as usual. The resulting vapor was passed through a bubbler which contained a mixed aqueous solution of sodium thiosulfate and cadmium sulfate, and then swept into a 10% alcoholic solution of dimethylaniline. Thus, it was possible to isolate trimethyl phenyl ammonium iodide, colorless plates, subliming at 216°C. This showed a methoxyl group to be present in namakochrome. The quantitative determination was then carried out by the same method, and namakochrome had shown an average value of 9.26% for the methoxyl group content (calcd. for III or IV: CH_3O, 11.6%). Similarly the determination was effected on a few derivatives of namakochrome described in the previous paper[1] and in this paper. A pentaacetyl-derivative[1] was found to show the methoxyl group content of 4.42% (calcd. for V and VI: CH_3O, 6.5%).

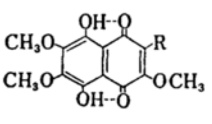


V



VI

The result for trimethyl ether of namakochrome was 37.38% of the methoxyl group content (calcd. for VII: $4CH_3O$, 40.0%, and for VIII: $3CH_3O$, 30.0%), and then for the leuco-acetyl derivative was found the methoxyl group content of 23.38% (calcd. for IX: $4CH_3O$, 25.81%, and for X: $3CH_3O$, 19.24%).



VII, R=$-OCH_3$,

VIII, R=$-CH_2OH$.

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* "Pigments of Marine Animals", X. IX of this series; This Bulletin, 33, 453 (1960).

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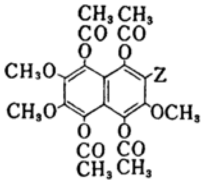
[1] This Bulletin, 33, 453 (1960).



IX, Z=$-OCH_3$,
X, Z=$-CH_2OH$.

From these experimental results, it is considered to be very likely that the structure of namakochrome is 2-methoxy-3, 6, 7-trihydroxynaphthazarin (beta-position in I or II: methoxyl group)***. Although many compounds which contain methoxyl groups have been known as plant components, the author has been unable to find in the literature any reports on the marine-animal pigments, especially on naphthoquinone-derivatives, which contain methoxyl groups. This must be, therefore, the first time, that the pigment containing a methoxyl group is isolated from the marine animal.

Experimental

Reductive Acetylation of Namakochrome-trimethyl Ether.—To a solution of 55 mg. of namakochrome-trimethyl ether in 1 g. of acetic anhydride and 1.5 g. of anhydrous pyridine was added 500 mg. of zinc dust, and shaken at room temperature until the solution becomes colorless. But the colorless solution soon acquired a yellow color and finally an orange yellow color. The colored reaction mixture, after setting overnight and removal of zinc dust, was poured into ice-water and extracted with several portions of benzene. The yellow benzene layer was washed with dilute hydrochloric acid solution and with water. The resulting colorless benzene solution was then dried with sodium sulfate. Removal of all solvent under the diminished pressure left 72 mg. of a pale yellow colored residue. It was purified by recrystallization from ethanol; colorless prisms, m. p. 226∼227°C.

Found: C, 55.26; H, 5.22; CH_3O-, 23.38; CH_3CO-, 35.27. Calcd. for $C_{22}H_{24}O_{12}$: C, 55.00; H, 5.01; CH_3O-, 25.81; CH_3CO-, 35.87%.

5, 8-Di-(3′, 5′-dinitrobenzoyl)-namakochrome-trimethyl Ether.—40 mg. of namakochrome was dissolved in 10 ml. of hot anhydrous pyridine. To the crimson-colored solution, about 55 mg. of finely pulverized 3, 5-dinitrobenzoyl chloride was added at room temperature, and the reaction mixture was gently shaken. The color changed through yellow to orange red. After an hour, the mixture was poured into ice-water and extracted with benzene. The orange red benzene layer was washed with dilute hydrochloric acid solution, followed by dilute sodium carbonate solution and water. The orange red benzene solution was dried with sodium sulfate, and concentrated to a small volume under reduced pressure. The concentrate was filtered through a calcium carbonate column (3×15 cm.). The orange eluate was evaporated to dryness under reduced pressure, and there was obtained an orange-yellow pasty product which was recrystallized (acetone-ethanol=2 : 1) to afford 66 mg. of the 3, 5-dinitrobenzoate, lemon yellow prisms, m. p. 218∼220°C.

Found: C, 48.41; H, 3.09; N, 7.70. Calcd. for $C_{28}H_{18}O_{18}N_4$: C, 48.15; H, 2.60; N, 8.02%.

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*** That tautomerisation of this type readily occurs had been synthetically demonstrated[2] in the case of methylnaphthazarin, which was prepared (a) by condensing maleic anhydride with toluquinol and (b) by condensing citraconic anhydride with quinol, and the two products were identical.

2) A. K. Macbeth et al., *J. Chem. Soc.*, **1935**, 333.