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In the subsequent experiments of the hydroxy naphthoquinones concerning Shikonin\(^1\) and Spinochrome\(^2\), the following interesting results were observed.

1. Method of methylation with diazomethane.

In this work the methylation with diazomethane is very important. However, sometimes the anticipated product was very poor in yield or nothing was formed owing to side reaction; and the result was indefinite. Similar experience with difficulty was recorded previously; the methylation of hydroxydroserone [IV] was carried out by A. K. Macbeth, J. R. Prince and F. L. Winzor\(^3\) with diazomethane in ethereal solution yielding only a crystalline product which was not the anticipated methyl ether (10\% N was found in analysis). As the result of the present author’s effort in several experiments, the most suitable conditions were found for obtaining the anticipated methyl ether in theoretical yields as shown in the following examples [I] [II] [III]* [IV]* and [V]*.

Note. The new compounds [I], [II] synthesized\(^4\) by the present author are related with the Spinochromes, therefore they are named spinazarin and 6-methyl-spinazarin respectively.

\[\text{Spinazarin} \quad \overset{[I]}{\longrightarrow} \quad \overset{[II]}{\longrightarrow} \quad \overset{[III]}{\longrightarrow} \quad \overset{[IV]}{\longrightarrow} \quad \overset{[V]}{\longrightarrow} \]

\[\text{6 methyl spinazarin} \quad \overset{[I]}{\longrightarrow} \quad \overset{[II]}{\longrightarrow} \quad \overset{[III]}{\longrightarrow} \quad \overset{[IV]}{\longrightarrow} \quad \overset{[V]}{\longrightarrow} \]

\[\text{Naphthopurpurin} \quad \overset{[I]}{\longrightarrow} \quad \overset{[II]}{\longrightarrow} \quad \overset{[III]}{\longrightarrow} \quad \overset{[IV]}{\longrightarrow} \quad \overset{[V]}{\longrightarrow} \]

\[\text{Hydroxydroserone} \quad \overset{[I]}{\longrightarrow} \quad \overset{[II]}{\longrightarrow} \quad \overset{[III]}{\longrightarrow} \quad \overset{[IV]}{\longrightarrow} \quad \overset{[V]}{\longrightarrow} \]

\[\text{Phthiocol} \quad \overset{[I]}{\longrightarrow} \quad \overset{[II]}{\longrightarrow} \quad \overset{[III]}{\longrightarrow} \quad \overset{[IV]}{\longrightarrow} \quad \overset{[V]}{\longrightarrow} \]

2) C. Kuroda and H. Ohshima, Proc. 16 (1940), 214.
4) C. Kuroda and H. Oshima, Proc. 16 (1940), 216.

* The compounds [III] [IV] and [V] are synthesized by C. Kuroda, Proc. 15 (1939), 227 and See Page 70 in this paper.
† The compounds [IV’] and [V’] are new, for mp. of [II’] See Page 70, 71.
In each case, the solid substance was spread out on a watch glass or a crystalline dish, and etherial solution of diazomethane was poured on the substance from a pipette, then after a vigorous reaction accompanied with sudden evaporation of N gas and ether, the anticipated ether separated out at once in crystalline state. Each product was recrystallized from a suitable solvent for analysis, although no insoluble matter in ether was found present. All the methyl ethers [I'] (brown crystals with dark greenish metallic lustre); [II'] (mp. 122°† brown needles with dark brownish metallic lustre); [III'] (mp. 178° reddish brown crystals); [IV'] (mp. 114° red needles) except [V'] (mp. 88° pale yellow needles) resemble naphthazarin in their appearances, and dissolve with blue colour in caustic alkali but give almost no reaction with bicarbonates of alkali or alkali earth metals, sod. acetate or phosphate. Applying the same method, methyl ethers of Spinochrome M. and F. for which hitherto attempts for methylation had given no effect were successfully obtained⁵.

2. Demethylation with hot dil. caustic alkali.

The interesting phenomena of the above methyl ethers with aqueous caustic alkali was observed; it was attempted at first to synthesize Spinochrome Aka, [VIII] (the formula proposed by Kuroda and Ohshima) 6 methyl 7 hydroxy Spinazarin from 2.3 dimethyl ether of 6 methyl Spinazarin [II'] as follows. In the previous work by Kuroda⁷, hydroxydroserone [IV] and Phthiocol [V] were synthesized from β methylnaphthazarin [VI] (2 methyl 5.8 dihydroxy naphthoquinone 1:4) and 2 methyl naphthoquinone 1:4, [VII] respectively, by treating with hot aqueous caustic alkali solution. From the above fact it was shown that, when naphthoquinone 1:4 in which a methyl group exist in the position 2 is heated with aqueous dil. caustic alkali, the formation of a new OH group in position 3 is possible.

6) Kuroda and Ohshima, Proc. 16 (1940), 296 and See Kuroda and Iwakura, Proc. 18 (1942), 74.
Generally, the derivatives of 5,8 dihydroxy naphthoquinone 1:4 are considered to exist in the tautomeric forms as in the following examples [VI], [III] and [IV]; therefore, it was likewise considered that [II] and [II'] might exist in the following tautomeric forms. It was then anticipated that if the above alkali method is applied to [II'] the methyl ether of Spinochrome Aka, namely 2:3 dimethyl ether of 6 methyl 7 hydroxy Spinazarin may be synthesized. On the contrary, another reaction was observed; namely by heating it with 1% NaOH aq. on water bath, the liquid slowly changed in colour from blue to purple red. After one hour when the product was acidified and purified, a reddish crystalline compound mp. (188°) was obtained. The compound proved to be [IX] by 1) the result of analysis, 2) chemical behaviours, 3) the relation of its derivatives as below.
Then it was shown that in this case the CH₃ group from one of OCH₃ in the quinone ring was split off. To confirm this reaction, the method was applied to the following examples, [I'] [III'] [IV'] [V'] and the demethylation was observed.

The demethylation was slow taking about over one hour in the cases of [I'] [III'] [IV'] and [V'] as in the case of [II'] whereas the reactions were instantaneous in the cases of 2:3 dimethoxynaphthoquinone⁸ and 2 methoxy naphthoquine prepared by Kuroda.

All the demethylated products thus obtained dissolve in aqueous caustic alkali with reddish purple as in the case of naphthopurpurin, and also are soluble in aq. sol. of bicarbonates of alkali or alkaline earth metals, and sod. acetate or phosphate with purple colour.

The relation are also proved as shown below.

Analytical results [I'] found C, 57.74, 57.72; H, 4.27, 4.19% C₁₂H₁₀O₆ requires C, 57.60; H, 4.19%; [III'] found C, 60.13; H, 3.75% C₁₁H₈O₅ requires C, 60.00; H, 3.60%; [IV'] found C, 61.66; H, 4.50% C₁₂H₁₅O₅ requires C, 61.54; H, 4.27%; [IX] found C, 57.77; H, 4.24%; C₁₂H₁₀O₆ requires C, 57.60; H, 4.00%; [X] found C, 57.52; H, 4.27%; C₁₈H₁₆O₉ requires C, 57.45; H, 4.26%. [XI] tetra acetyl derivative of [II] (6-methyl-spinazarine tetra acetate) found C, 56.24; H, 4.00%; C₁₈H₁₆O₁₀ requires C, 56.42; H, 3.99%. [XII] found C, 58.53; H, 4.77%; C₁₇H₁₆O₈ requires, C, 58.62; H, 4.60%. [III''] found C, 58.23; H, 3.12%; C₁₀H₁₆O₅ requires C, 58.25; H, 2.91%.

Note. For the two compounds [I'] and [XI] which were previously⁹ mentioned, the analytical values are given here, mp. of [II'] is higher

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   " " " " 50 (1928), 461.

* This method was found by C. Kuroda previously, see, Proc. 15 (1938), 227.

9) C. Kuroda and H. Ohshima, Proc. 16 (1940), 216.
than that of previous specimen (mp. 117°C) obtained by Kuroda¹⁰).

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¹⁰) Proc. 16 (1940), 216.