Communication to the Editor

The Respective Identities of Endothianin and Radicalisin with Skyrin and Rugulosin; and the Structure of Skyrin.

We reported previously¹⁾ the isolation of two coloring matters, endothianin and radicalisin, from the mycelium of laboratory cultivated *Endothia fluens* Shear et Stevens (syn. *Endothia radicalis* Fr.) and *Endothia parasitica* (Murr.) Anderson et Anderson, the latter being known as the plant pathogenic fungus causing chestnut blight.

Endothianin has recently been proved by us to be identical with skyrin which was isolated from *Penicillium islandicum* Sopp. by Howard and Raistrick.²⁾ Since endothianin or skyrin does not melt below 360°, the identity of both pigments was established by the comparison of their infrared absorption spectra and a mixed fusion of their ethoxycarbonyl ethers (m.p. 171~173°), which showed no melting point depression.

Radicalisin has also been shown to be identical with rugulosin, a bright yellow pigment of *Penicillum rugulosum* Thom studied by Dacré and Raistrick,³⁾ by the comparison of their infrared spectra and a mixed fusion of their benzoates (m.ps. and mixed m.p. 224~226°).

Howard and Raistrick²⁾ proposed a molecular formula, $C_{30}H_{18}O_{10}$, for skyrin and suggested that it consists of two molecules of emodin joined together at one of the free positions, 1, 3, 6, or 8 in each of the moiety (methyl in the 2 position) since it was decomposed almost quantitatively into two moles of emodin by the action of alkaline sodium dithionite. So far as we are aware, there is no adequate example in the literature for the reductive cleavage of the carbon-carbon linkage in bianthraquinone with sodium dithionite.

We, therefore, studied the action of sodium dithionite on some model compounds, such as 2,2′-dihydroxy-, 4,4′-dihydroxy- and 2,2′-dimethoxy-4,4′-dihydroxy-bianthraquinones(1,1′). The result obtained showed us that the bianthraquinone having a hydroxyl or a methoxyl group in the *ortho*-position of the carbon-carbon linkage can readily be cleaved with sodium dithionite.

All the evidences have led us to draw the conclusion that skyrin should have the structure (VIII), which has finally been established by the synthesis of β,β′-dimethyl ether (VI) of skyrin. The synthesis was accomplished by the Ullmann condensation of the monobromo derivative of emodin trimethyl ether followed by partial demethylation with HBr. The identity of the synthesized di-physcion (di-emodin β,β′-dimethyl ether) with skyrin β,β′-dimethyl ether was confirmed by a mixed fusion of their ethoxycarbonyl ethers (VII) (m.ps. and mixed m.p. 247~249°).

The position of bromine in the monobromo emodin trimethyl ether, which was used as the starting material of the synthesis, was proved as shown in the formula (II). By the action of methanolic potash in the presence of manganese dioxide, bromine was substituted with methoxyl which gave hydroxyl on boiling with 48% hydrobromic acid. The final product, hydroxyphyscion (m.p. 244~246°) differs apparently with erythroglaucin (1,4,5-trihydroxy-7-methoxy-2-methylanthraquinone) (m.p. 205~206°)⁴⁾ while it exhibits a fluorescence in acetic acid solution showing the presence of hydroxyls in the *para*-

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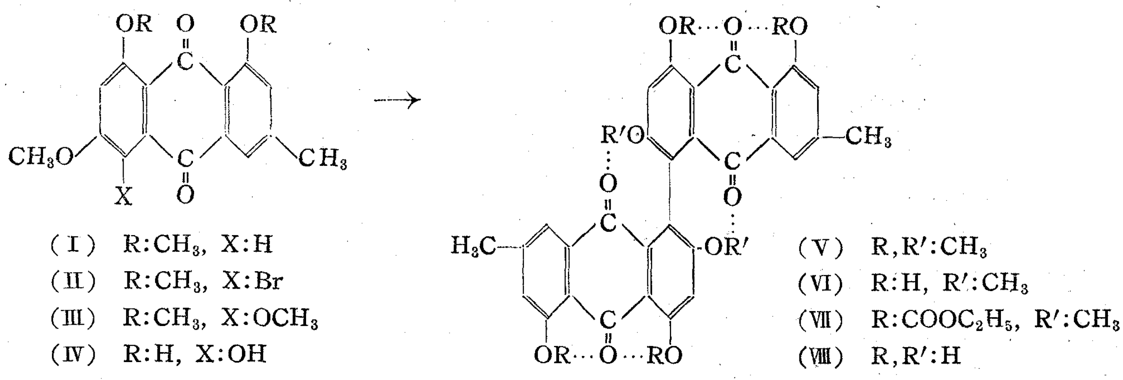
1) S. Shibata, O. Tanaka, G. Chihara, H. Mitsuhashi: This Bulletin, **1**, 302(1953).
2) B. H. Howard, H. Raistrick: Biochem. J., **56**, 56(1954).
3) H. Raistrick: Proc. Roy. Soc., A **199**, 141(1949); Private communications from Prof. Raistrick (1953~1955).
4) J. N. Ashley, H. Raistrick, T. Richard: Biochem. J., **33**. 1291(1939); W. K. Anslow, H. Raistrick: *Ibid.*, **34**, 790(1940), **35**, 1006(1941).

position, and consequently it was confirmed that bromine was substituted in the 8-position of the emodin ring.

Thus, the structure of the synthesized skyrin β,β'-dimethyl ether has unequivocally been established as 2,2′-dimethoxy-4,5,4′,5′-tetrahydroxy-7,7′-dimethylbianthraquinone-(1,1′) (VI).



(I) R:CH_3, X:H
(II) R:CH_3, X:Br
(III) R:CH_3, X:OCH_3
(IV) R:H, X:OH

(V) R,R′:CH_3
(VI) R:H, R′:CH_3
(VII) R:$COOC_2H_5$, R′:CH_3
(VIII) R,R′:H

The details will be published in the near fufure.

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