U. D. C. *547.673.6 : 545.821*

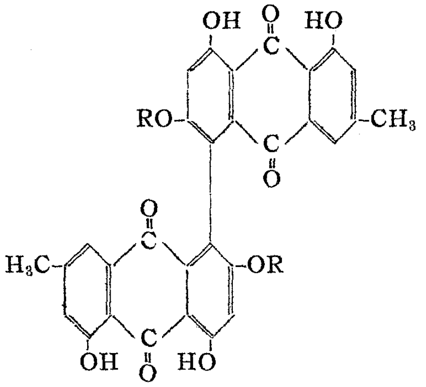
The Infrared Spectrum of Skyrin

Previously we confirmed the structure of skyrin, an orange red coloring matter produced by ***Penicillium islandicum*** Sopp, ***Endothia parasitica*** (Murr.) Anderson et Anderson, and ***E. fluens*** Shear et Stevens as being di-emodin(8,8′) (I) by the synthesis of β,β′-dimethylskyrin (di-physcion(8,8′)) (II).[1,2,3]

At that time, we stated that skyrin did not exhibit >C=O stretching absorption band in the 5.8~6.0 μ region of its infrared spectrum but a shifted >C=O band at 6.2 μ and a broad OH-stretching absorption band at 3.18 μ. We explained this as the results of hydroxyls in the 2- and 2′-positions forming intramolecular hydrogen bonds with the quinoid carbonyls of each emodin moiety.

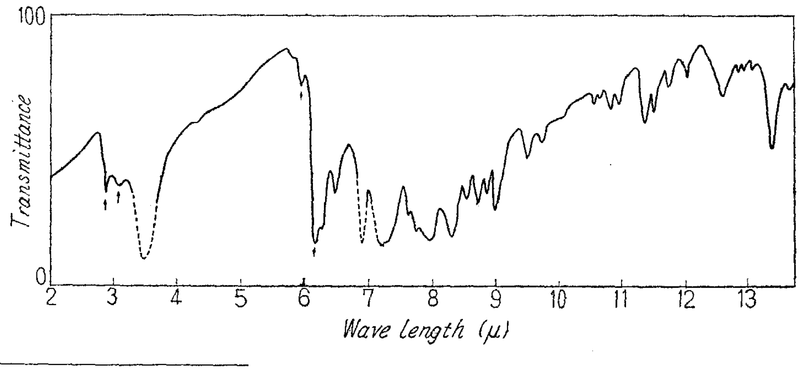
However, on repeated examination of the infrared spectrum of skyrin using a sufficient amount of sample and employing an instrument of higher sensibility, we observed that skyrin shows its OH-absorption which is divided into a sharp band at 2.86 μ and a broad one at 3.10 μ, and a band, though weak, at 5.95 μ indicative of non-chelated >C=O of anthraquinone.

The earlier interpretation of the infrared spectrum of skyrin must therefore be revised, though it does not result in any ammending of the final structure of skyrin itself.



(I) R : H
(II) R : CH_3

Brockmann *et al.*[4] asserted without reference to our earlier papers[1,2,3] that skyrin cannot be di-emodin(8,8′), since the recorded melting point of hexaacetyl-



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[1] S. Shibata, T. Murakami, O. Tanaka, G. Chihara, M. Sumimoto : This Bulletin, **3**, 274(1955).
[2] S. Shibata, O. Tanaka, I. Kitagawa : *Ibid.*, **3**, 278(1955).
[3] O. Tanaka, C. Kaneko : *Ibid.*, **3**, 284(1955).
[4] H. Brockmann, H. Eggers : Angew. Chem., **67**, 706(1955).

skyrin⁵⁾ shows a discrepancy with the observed melting point of hexaacetyl-di-emodin(8,8′) derived from penicilliopsin, which was proposed as being represented by di-emodinanthrone(8,8′).

As we pointed out,¹⁾ the melting point of hexaacetylskyrin is variable and is not suitable for identification.

The possibility of a hydrogen-bond formation between hydroxyls in the 2,2′-positions and quinoid ketones in 1,1′-bianthraquinone derivatives is now being reëxamined by the infrared spectra employing some additional model compounds.

The detail of this work will be reported in the future.

The infrared spectra were measured by Mr. H. Sindo, Sankyo Co. Ltd., Tokyo, using the double-beam Perkin-Elmer Type 21, and our thanks are due him.

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5) B. H. Howard, H. Raistrick : Biochem. J. (London), **56**,(1954).