

SYNTHESIS OF A DERIVATIVE OF SULOCHRIN (BIOCHEMISTRY OF FILAMENTOUS FUNGI. IX)

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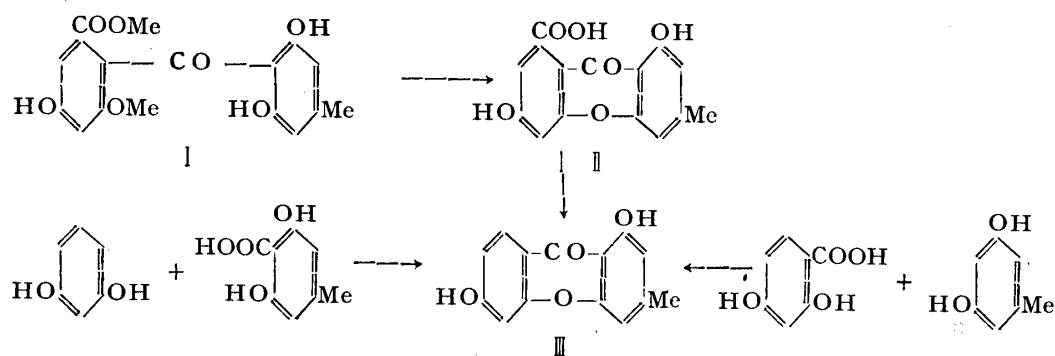
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In a previous paper (1) sulochrin, one of mycelial constituents of a fungus *Oospora sulphurea-ochracea* v. Beyma, was described with the conclusion that its molecular structure was 4-methyl-2:6:4'-trihydroxy-2'-methoxybenzophenone-6'-carboxylic acid methyl ester [I] based on its degradation reactions. As one of its derivatives, 1:6-dihydroxy-3-methylxanthone-8-carboxylic acid [II] was formed from sulochrin by boiling with 10 per cent methanolic potassium hydroxide. Decarboxylation of this substance has now been attained by means of sublimation, the product being 1:6-dihydroxy-3-methylxanthone [III]. It is presumed on the other hand that the compound [III] can be obtained synthetically if the condensation of either *p*-orsellinic acid with resorcinol or orcinol with β -resorcylic acid proceed respectively according to the alternative course indicated in the following scheme. The results of experiments confirmed that this is actually the case. This will provide a proof by way of synthesis of the constitution of sulochrin.



Experimental

1:6-Dihydroxy-3-methylxanthone.

1:6-Dihydroxy-3-methylxanthone-8-carboxylic acid was sublimed over

300° in a tube in quantities of 0.05 g. 0.15 G in all of pale yellow microcrystalline needles was obtained from 1.5 g of the initial substance. The product was digested with dilute bicarbonate solution to remove any unchanged material (practically *nil*) and re-sublimed under reduced pressure (20 mm), yield nearly quantitative. This compound does not show any definite melting point, partly subliming in the neighbourhood of 300°. It is sparingly soluble in acetone, ethanol, methanol, benzene, hardly soluble in ether, light petroleum, and insoluble in water. Unlike the original substance it does not dissolve in bicarbonate solution. (Found: C, 69.51, 69.14; H, 4.17, 3.93%. $C_{14}H_{10}O_4$ requires C, 69.42; H, 4.13%.)

1:6-Diacetoxy-3-methylxanthone.

0.1 G of the above substance was treated with 2 ml of acetic anhydride and a few drops of conc. sulphuric acid. The resulting yellow solution was poured into ice-water. Solids that separated were collected, dried and recrystallized from ethanol. Colourless needles, m. p. 168°. It is soluble in ethanol, methanol, acetone, benzene, sparingly soluble in ether and light petroleum, insoluble in water. (Found: C, 66.52; H, 4.37; Acetyl, 26.38, 26.89%. $C_{18}H_{14}O_6 = C_{14}H_8O_4 (CO.CH_3)_2$ requires C, 66.26; H, 4.29; $(CO.CH_3)_2$, 26.38%.)

Synthesis of 1:6-dihydroxy-3-methylxanthone.

(1) *p*-Orsellinic acid (0.5 g) and resorcinol (0.4 g) were intimately mixed with phosphorus pentoxide (0.3 g) and the mixture was heated in a metal bath up to 200° for 5 min. The resulting dark reddish-brown melt was then digested with water, filtered and dried (0.25 g). The amorphous product was purified by sublimation under reduced pressure (40 mm) at 300°. Pale yellow needles (0.23 g), having no definite melting point, partly subliming at about 300°, insoluble in $NaHCO_3$. Its acetyl derivative was prepared by treatment with acetic anhydride and conc. sulphuric acid in the usual way. After recrystallization from ethanol colourless needles were obtained which melted at 168° and showed no depression in admixture with the diacetate from the derivative of sulochrin.

(2) Orcinol (0.18g) and β -resorcylic acid (0.22g) were intimately mixed with phosphorus pentoxide (0.2 g), fused, digested with water, filtered, dried and sublimed as above. The sublimate (0.05 g) was acetylated and the product was recrystallized from ethanol. The product seems to be less pure than that from *p*-orsellinic acid and resorcinol, melting at 165~6° after several recrystallizations and showed 167° in admixture with an authentic specimen of m.p. 168°.

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Summary

1 : 6-Dihydroxy-3-methylxanthone was derived from sulochrin and compared with synthetic specimens.

Reference

- 1) Nishikawa, H. (1939). *Acta Phytochim.*, **11**, 179.