Bulletin of the Agricultural Chemical Society of Japan.

TRANSACTIONS

Biochemistry of Filamentous Fungi. VI.

Mycelial Constituents of *Oospora sulphurea-ochracea*. Part III. Trimethylsulochrin and its Fission Products.

By Hidejiro NISHIKAWA.

(Tottori Agricultural College.)

Received May 11, 1940.

Of the crystalline constituents of the mycelium of *Oospora sulphurea-ochracea* described in the previous communication,⁽¹⁾ sulochrin (substance B) was proved by further experiments to be methyl ester of 2:6:4'-trihydroxy-4-methyl-6'-methoxy-benzophenone-2'-carboxylic acid, the structural discussion having been advanced in detail in a separate paper.⁽²⁾

Of the three hydroxyl groups which are present in the sulochrin molecule two could be readily methylated by means of diazomethane; one of the two hydroxyl groups in the *p*-orsellinic moiety situated at ortho-position to the central carbonyl resisted this means of methylation.

The fully methylated derivative has now been prepared by repeated application of dimethylsulphate on sulochrin. Trimethylsulochrin thus obtained can be split neatly into two halves by means of conc. sulphuric acid followed by the addition of water, just as in the case of sulochrin and dimethylsulochrin, resulting fragments being, as is anticipated, dimethyl-*p*-orsellinic acid and methyl dimethyl- α -resorcylate and thus giving an additional evidence of the structure of sulochrin. A more drastic measure of hydrolysis, however, is required in this case. While in the case of sulochrin and dimethylsulochrin extreme decomposition had to be controlled by ice-cooling the mixture, for the complete hydrolysis of trimethylsulochrin it was necessary to warm the sulphuric acid solution for some time on a water-bath.

Action of methyl alcoholic potash on trimethylsulochrin yields monomethyl-tetramethoxy-benzophenonecarboxylic acid which is isomeric with dimethylsulochrin, one methoxyl of ester-form having been lost.

EXPERIMENTAL.

Trimethylsulochrin (4-methyl-2 : 6 : 4' : 6'-tetramethoxy-2'-carbomethoxybenzophenone).

Five grams of sulochrin was dissolved in 12.5 cc of 10% NaOH and shaken vigorously on a machine, 15 cc of dimethyl sulphate and 77.5 cc of 10% NaOH being alternately dropped in during three hours. Amorphous solids separated and were collected, yield nearly quantitative. One gram of the crude material, which contained incompletely methylated impurities, was dissolved in acetone, 2 cc of dimethyl sulphate was added and, while shaking, 12 cc of 10% NaOH was added drop by drop. To the resulting clear solution much water was added till the precipitation of crystals occurred (yield nearly quantitative) which melted at 152°. On recrystallization from benzene the substance crystallized in platelets and melted at 157°, turning pink. The melting-point was quite similar to that of dimethylsulochrin and to make sure of their dissimilarity a mixed melting-point was taken which showed marked depression. (Found: C, 64.40; H, 5.94%. $C_{20}H_{22}O_7$ requires C, 64.17; H, 5.88%. Methoxyl. Found: 40.93%. $5(CH_3O)$ in $C_{20}H_{22}O_7$ requires 41.44%.)

Trimethylsulochrin dissolves readily in acetone, chloroform, methyl alcohol, ethyl acetate, moderately in ethyl alcohol and benzene, slightly in ether, but not in light petroleum and water. It does not give a $FeCl_3$ reaction.

Fission of trimethylsulochrin by means of conc. sulphuric acid.

To 2.4 g of trimethylsulochrin was added 24 cc of conc. sulphuric acid and the mixture was warmed on a water-bath until the initial dark brown colour of the solution changed into a deep reddish purple tint. The whole matter was then poured into a large amount of water, the resulting emulsion being thoroughly extracted with ether. The ether layer was shaken twice with 5% bicarbonate solution, this in turn was acidified and again extracted with ether. The ether solution was dried and distilled, 0.7 g substance being left behind. For purification it was dissolved in methyl alcohol and precipitated by the addition of water. It melted at about 165° and gave a green $FeCl_3$ reaction. The crystals were again dissolved in a small quantity of warm methyl alcohol and cooled with ice, when beautiful square platelets devoid of $FeCl_3$ reaction separated out. The melting point now rose to 182° and mixed melting point with a synthetic specimen of dimethyl-*p*-orsellinic acid showed no depression.

The fraction insoluble in bicarbonate, after distilling off the solvent, was left behind as a yellowish oil (0.7 g), in which was seeded a tiny fragment of methyl dimethyl- α -resorcyate. A magma of large needle crystals separated which melted at 44° alone or mixed with an authentic specimen of methyl- α -resorcyate.

4-Methyl-2 : 6 : 4' : 6'-tetramethoxy-2'-carboxybenzophenone.

Trimethylsulochrin (1 g) was boiled with methyl alcohol (30 cc) and KOH (1 g) under reflux for five hours. On cooling it was diluted with water and acidified with HCl, when the liquid became turbid and gradually separated prism crystals (0.75 g). It melts at 194° and gives neither FeCl_3 nor CaOCl_2 reaction. (Found: C, 63.04; H, 5.61%. $\text{C}_{19}\text{H}_{20}\text{O}_7$ requires C, 63.33; H, 5.56%. Methoxyl, Found: 34.11%. $4(\text{CH}_3\text{O})$ in $\text{C}_{19}\text{H}_{20}\text{O}_7$ requires 34.44%). It readily dissolves in acetone, methyl alcohol, chloroform, moderately in ethyl alcohol, less in ethyl acetate and benzene, sparingly or not in light petroleum, ether and water.

REFERENCES.

- (1) Nishikawa: Bull. Agr. Chem. Soc. Jap., **13**, 1 (1937).
- (2) Nishikawa: Acta Phytochim., **11**, 167 (1939).