

Shoji Shibata, Isao Kitagawa,* and Hidejiro Nishikawa : Metabolic Products of Fungi. XIII.*** The Identification of Flavomycelin and Luteoskyrin.**

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A yellowish sterile mycelium grown on Koji-agar was found by Nishikawa¹⁾ to produce three coloring matters, which were respectively named rhodomycelin, flavomycelin, and purpurmycelin.

Rhodomycelin was proved by Nishikawa¹⁾ to be identical with islandicin (=1,4,5-trihydroxy-2-methylantraquinone) from *Penicillium islandicum* SOPP.²⁾

Flavomycelin, a yellow pigment, m.p. 277~278°(decomp.), for which a molecular formula, C₁₅H₁₂O₆, was proposed, was found to yield rhodomycelin (=islandicin) on dehydration reaction with conc. sulfuric acid, or by sublimation.

Purpurmycelin, which was obtained in a very minute amount as dark purple microcrystals, shows no melting point below 270°, being characterized by a blue coloration in caustic alkaline solution.

When studies on the coloring matters of *Penicillium islandicum* had been advanced, our attention was drawn to the close similarity between flavomycelin and luteoskyrin.³⁾

Luteoskyrin is a poisonous pigment of *P. islandicum* causing a severe damage in the liver when administered to animals. The chemical structure of luteoskyrin was studied by analogy to rugulosin⁴⁾ and a structural formula, 2,2',4,4',5,5',8,8'-octahydroxy-2,2',3,3'-tetrahydro-7,7'-dimethyl-bianthraquinone-(1,1') or its tautomeric form, was proposed.³⁾

The comparison of physical and chemical properties of flavomycelin and luteoskyrin has now been made and it was established that the two pigments are identical.

As being elucidated in our previous paper,³⁾ luteoskyrin is photo-sensitive and is converted readily into deep purple-colored crystals on exposing the acetonic solution to light. It has now been confirmed that purpurmycelin is identical with irradiated luteoskyrin, which is assumed to be formed from flavomycelin(=luteoskyrin) in the course of isolation by its high photo-sensitivity.

The paper chromatographical investigation of the extracts of the sterile mycelium showed that it gives only islandicin and luteoskyrin, and shows no evidence of existence of other structurally related coloring matters.

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Experimental

Purification of Flavomycelin and its Identification with Luteoskyrin—Flavomycelin isolated by Nishikawa from yellowish *Mycelia sterilia* growing on 2.5~3% Koji-agar was dissolved in acetone and was chromatographed on a column consisting of active charcoal and anhydrous Na₂SO₄(1 : 15).

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The eluant was recrystallized from a mixture of acetone and hexane to give yellow prisms, m.p. 274°(decomp., darkens from 260°); $[\alpha]_D^{25} - 880^{\circ}(0.1\%$ in acetone). The pigment is soluble in 5% NaHCO₃ and its alcoholic solution gives no obvious change of color on addition of Mg(OAc)₂. Flavomycelin gave islandicin and iridoskyrin on being allowed to stand overnight in conc. H₂SO₄ at room temperature. Islandicin and catenarin were formed by the thermal decomposition of flavomycelin (0.5 mm. Hg, 250~260°). On exposing the acetonic solution to light, flavomycelin was converted into dark purple crystals (purpurmycelin). The above properties of flavomycelin agree well with that of luteoskyrin isolated from *Penicillium islandicum* Sopp, N. R. R. L. 1036. Flavomycelin and luteoskyrin gave the same Rf Value (0.52) on the paper chromatogram developed with the upper layer of a mixture of acetone : benzine : water (5 : 5 : 3.5).

Finally, the identity of flavomycelin and luteoskyrin was established by the comparison of their infrared spectra (in Nujol) which were completely superimposed. It was also confirmed by the infrared spectral analysis that purpurmycelin is identical with the irradiated luteoskyrin.

Summary

The identity of flavomycelin of *Mycelia sterilia* and luteoskyrin of *Penicillium islandicum* Sopp was established by the comparison of their physical and chemical properties.

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