The natural coloring matters of the greenish domestic cocoon (Bombyx mori, var. Seihaku) had hitherto been investigated by several authors, but no one had carried out the complete identification upon the chemical entity of the pigments. I have investigated to isolate the pigments in their purest state and gained new compounds, named by the author as “Bombycin” (glucoside) and “Bombycetin” (aglucose of bombycin), which were characteristic to have each one atom of nitrogen and show many reactions and absorption bands like flavone derivatives. There were another flavone-like pigments in small quantity which were ether soluble and that found in the mother liquor of bombycin, but the author could not precisely study them owing to the shortness of material.

Bombycin is a monoglucoside of bombycetin which has a molecular formula near as C_{20}H_{19}O_{7}N and has three hydroxyl groups. Bombycetin shows two absorption bands of which maximum are near 2700 and 3750 1/\mu and shows flavone-like reaction. Acetyl bombycetin was obtained through acetylation by acetic anhydride and sodium acetate. It has a molecular formula near as C_{26}H_{25}O_{10}N and has three acetyl groups. Its absorption band shows horizontal portion between 3100 and 3600 1/\mu and differs utterly from that of flavone or flavonol acetate.

The following items are discussed.

(1) The origin of bombycin can be asked in the mulberry leaves but it must be synthesized biochemically in the body of silk worm (Bombyx mori, var. Seihaku) owing to the fact that the author tried negative to isolate the nitrogenous flavone-like substances from the leaves. The presence of nitrogenous flavone-like pigments, bombycin and bombycetin, in animal products is, indeed, very noticeable and interesting fact, because no one has yet found flavone-like substances from the animal origin except from the butterfly (Melanargia galatea).
(2) The physiological function of the presence of bombycin in the cocoon layers is perhaps to protect the pupa from the injurious action of the ultraviolet ray.

(3) Bombycin and bombycetin are with bombilupeol deemed as characteristic components found in the green cocoon (Bombyx mori, var. Seihaku).

Experimental.

The yellowish green cocoon layers were extracted by cold 70% alcohol several times and the extract was concentrated and divided into two fractions, ether soluble and water soluble. From the former fraction bombilupeol and ether soluble pigment were searched, to the latter fraction was added neutral lead acetate and the orange yellow precipitates formed were digested with dilute hydrochloric acid. Crude bombycin was precipitated by neutralizing the filtrate by sodium hydroxide. As crude bombycin could not be obtained in any crystal form, it was purified by dissolving in dilute hydrochloric acid and reprecipitated by neutralization. Bombycin is a monoglucoside of bombycetin and melts and decomposes over 300°C and shows many analogous character with flavone-glucosides except that it contains nitrogen. It is brownish yellow powder and shows some imbibitional properties.

Bombycin was hydrolysed by 5% H₂SO₄ and its aglucone, bombycetin, was obtained. From mother liquor of bombycetin, glucose was detected as glucosazone.

As bombycetin could not be obtained in any crystal form by any method, it was first converted into its acetyl derivative and then regenerated by saponification.

Acetyl bombycetin is a slightly yellowish powder which melts between 135~142°C and has a molecular formula near as C₉₀H₅₆O₄(CH₃CO₃)₃N. By inspection of its absorption bands, it has a characteristic feature to have absorption horizontal between 3100~3600 1/λ (in alcohol) and differs utterly from that of flavone or flavonol acetates. It is easily soluble in glacial acetic, alcohol and acetic ether; insoluble in water, alkalies and acids. Color reaction by FeCl₃ is negative but reduction color by Mg+HCl is after a long time positive (red).

Bombycetin was obtained as follows: after boiling acetyl bombycetin in the mixed solution of glacial acetic acid and few drops of sulphuric acid, the mixture was poured into cold water and the precipitates formed were recrystallized from 50% alcohol. It could not be obtained in crystal form and was yellowish brown amorphous powder. It shows following reaction.

Reduction color by Mg+HCl.............intense red.
FeCl₃............... dark green→dark brown.
Lead acetate........... orange red precipitates.

It is easily soluble in alcohol, aceton and pyridin but insoluble in ether, water and dil. HCl and changes brownish red by touching to alkalies. It melts between 170~180°C and at the same time decomposes by foaming. It has a molecular formula near as C₂₉H₁₉O₇N and has three hydroxyl groups. It could not be methylated easily by dimethyl sulphate and the decomposition substances by alkali fusion could not be obtained in sufficient quantity to identify. It has two absorption maximum 2700 and 3750 1/₀ (in alcohol) which resemble that of quercetin.

Bombycetin is a flavone-like pigment and yet has nitrogen. That this nitrogen cannot be deemed as mere impurity but as a element of bombycetin is sure from the fact that it is estimated as one atom from both acetyl bombycetin and the regenerated bombycetin.

Ether soluble pigment was obtained from mother liquor of bomibilupeol which was hitherto obtained by the author and published in this bulletin. The pigment has many analogous properties with bombycetin.

Mother liquor of bombycin was concentrated and after adding alcohol, the filtrate was condensed to syrupy and hydrolysed by 5% H₂SO₄. After repeating the extraction with ether, ether solution was evaporated and the residue was dissolved in alcohol. From that solution, brownish yellow crystal appeared in needles in small quantity which showed many analogous properties with bombycetin especially in respect to the absorption bands.

Chemical Studies on “Bukuryo”, Sclerotia of
Pachyma Hoelen Rumph. (VII).

The Production of Tetracetyl Glucuronic Acid by Acetolysis
of β-Pachyman in the Presence of Perchloric Acid.

By

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(Received September 6, 1934.)

In completely acetylated pachyman (C₁₁H₂₂O₁₀, about 14%) obtained in the previous study (I) was treated with acetic acid, acetic anhydride and the small amount of perchloric acid, and acetolysis was carried out by controlling