49. **Yellow Coloring Matters in the Flower of Meratia praecox.**

By Kôzô Hayashi and Kazuhiko Ōuchi.

Botanical Department, Research Institute for Natural Resources in Tokyo.

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According to the suggestion of Prof. K. Shibata, that the yellow flowers of *Meratia praecox* Rehder et Wilson (Calycanthaceae) might contain a flavone pigment, we have recently studied the coloring principles of this plant, and could confirm, that a flavonol glucoside really exists in petals. Moreover, was found in them a small amount of another pigment, which appears to be $\alpha$-carotene itself after some qualitative tests.

The principal component, which shows all the characteristics of a flavonol glucoside, is isolated as yellow needles, Fp. 179–180°. As the result of further examinations it was found, that this pigment is quercetin 3-diglucoside, which has hitherto never been found in nature and for the sake of convenience is named "meratin". The amount of meratin at hand was, however, too small for a comprehensive experimentation to determine the position and nature of sugar-linkage by the usual method of hydrolysis of the methylated glucoside. Otherwise a full account of our observations, on which the above stated constitution of glucoside is based, will be given below in experimental part.

As is well known, the flower petals of *Meratia praecox* are covered with a considerable amount of waxy substance. This is soluble in petroleum ether, from which it can be obtained in colorless needles, Fp. 77–78°. After saponification with boiling 10% alcoholic potash, the wax was seemingly decomposed into two substances, *i.e.* alcoholic and acidic. Owing to a small quantity available, the identification of these substances could not be performed.

**Experimental.**

(Under collaboration of D. Ōhata and (Miss.) T. Isaka.)

*Extraction and fractionation of the constituents of flower petals.*

On the flowering season in midwinter the yellow petals were collected...
and cautiously separated from the red and brown colored portions, 90 gr. of fresh material being thus obtained. For extraction 500 cc of methyl alcohol was used at first and then 300 cc. of the same solvent. By these two extractions at room temperature almost all of the flavone pigment and a small amount of carotenoid came into solution.

The residue contained much more carotenoid, which was extracted with 300 cc. of petroleum ether at ordinary temperature, and after filtration was evaporated under reduced pressure into about 60 cc.

\[\text{Fraction (A)}\]

The combined methyl alcoholic extracts were filtered and after standing over night evaporated \textit{in vacuo} into a volume of about 200 cc. The solution was shaken repeatedly with petroleum ether; the petroleum ether extract amounting to about 400 cc. was colored intensively yellow. By vacuum distillation its volume was reduced into about 80 cc.

\[\text{Fraction (A')}\]

The methyl alcoholic layer was again evaporated \textit{in vacuo} at about 60° and 25 cc. of aqueous solution were thus obtained. This was extracted 5 times by shaking with an equal volume of ethyl acetate.

\[\text{Fraction (B)}\]

The remaining aqueous solution was then washed with fresh ether (no substance was extracted by this solvent). This final fraction is colored reddish brown and becomes deep red on reduction with magnesium powder and hydrochloric acid.

\[\text{Fraction (C)}\]

\textit{Fraction (A + A') (carotenoid fract.).}

The combined solution of the above two fractions (A + A') was washed with 10% aqueous sodium hydroxide and water. After drying with anhydrous sodium sulfate, the solution was passed through an aluminium oxide column (complete adsorption was observed), and then the column was washed repeatedly with petroleum ether (130 cc.). The solution became pale yellow and the orange colored substance remained in the column. The latter was eluted with 100 cc. of benzene. The petroleum ether solution was evaporated \textit{in vacuo}, and the residue was recrystallized from ligroin, from which it separated out in colorless, slender needles, Fp. 77–78°. About 30 mg of the pure substance were thus obtained. It shows much of the waxy character. On saponification with boiling 10% alcoholic potash we obtained an alcoholic substance as white needles, while an acidic component was separated in amorphous form. Owing to the scarcity of material, further examinations could not be carried out.
The above mentioned benzene eluate (about 100 cc.), which probably contains carotenoid pigment, was evaporated to dryness (in vacuo, below 40° and in CO₂). The syrupy residue was dissolved in petroleum ether and adsorbed again on alumina. An upper portion, which was orange yellow and appeared to retain much of the pigment, was then eluted with the least possible quantity of warm benzene and evaporated by standing in the air. The substance could not, however, be obtained in crystalline form, so that some qualitative reactions observed are given below: distribution between petroleum ether and methyl alcohol epiphasic; easily soluble in benzene, petroleum ether and carbon bisulfide; two absorption maxima, 508 and 480 μμ (in CS₂). From these observations it appears to be most probable, that the coloring matter is nothing else than α-carotene (509 and 477 μμ(1)).

Fraction (B).

Combined ethyl acetate extracts were filtered and dried. After evaporation to about 10 cc., a small amount of alcohol and water was added and left to stand over night. Only a trace of yellow, minute prismatic needles, which are practically insoluble in ether, has appeared. With ferric chloride an olive green color with a brownish tinge and with magnesium and hydrochloric acid a beautiful cherry red coloration is produced. Owing to the insufficient crop of specimen further examination could not be achieved.

Fraction (C). (Isolation and description of meratin.)

From this fraction the crystallization of meratin soon commenced. Af-

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ter standing two days the crystals were filtered off with suction and dried on porcelain plate. Yield 0.85 gr. (about 0.9% of fresh flower material). The recrystallization from 50% alcohol was repeated three times. Pale yellow needles (Fig. 1); Fp. 179–180° (decomp.). It gives a dark olive green color with ferric chloride and a cherry-red color with magnesium powder and hydrochloric acid in alcoholic solution. The substance contains no methoxyl group. Water of crystallization was determined by drying over phosphorous pentoxide at 100° at a pressure of 3 mm.

Calc. for C_{21}H_{30}O_{17}·3\frac{1}{2}H_2O: H_2O 9.14. Found: H_2O 9.03.

**Hydrolysis of meratin.** The anhydrous glucoside pigment, 111.9 mg., was hydrolyzed by boiling in 10 cc. 2% sulfuric acid for two hours. The solution was cooled and the sugar-free pigment (quercetin) was collected, washed with a small amount of water and dried over calcium chloride. It weighed 59.2 mg.

The filtrate from the aglucone was combined with wash water, transferred to a volumetric flask and filled up with water to 20 cc. With one half of this solution the sugar was quantitatively determined according to the method of Bertrand, and the another half was used to identify it with glucose\(^{(1)}\). Thus we found, that 61.5 mg. glucose are obtainable from 111.9 mg. of anhydrous meratin.

$$C_{27}H_{30}O_{17} + 2H_2O \longrightarrow C_{15}H_{10}C_7\cdot1\frac{1}{2}H_2O + 2C_6H_{12}O_6.$$  
meratin  
quercetin  
glucose

Calc. 52.6  
Found 52.9 57.2 %,

Sugar-free pigment (quercetin). The aglucone obtained on hydrolysis was

\(^{(1)}\) Color reactions, i.e. Seliwanoff-, Bial- and phlorogluconol-reaction, were all negative; and the osazone was, from its characteristic crystal form (Fig. 3) and melting point (193°), identified as that of glucose alone. A contamination of another kind of sugar could not be detected.

\(^{(2)}\) The substance, which separated out directly from the hydrolysate, contains 1\frac{1}{2} mol. of water of crystallization: Calc. H_2O 8.20; Found 8.13% (H_2O, 118°, 3 mm.).
recrystallized from dilute alcohol. Slender, yellow needles (Fig. 2), Fp. above 300°. The substance contained two molecules of water of crystallization. (Calc. for C_{15}H_{10}O_{7}·2H_{2}O: H_{2}O 10.65. Found: H_{2}O 10.89 [P_{2}O_{5}, 118°, 3 mm.].)

The pigment gave all the qualitative reactions of quercetin; reactions with ferric chloride and with magnesium-hydrochloric acid were also identical with those of the latter.

On acetylation with acetic acid anhydride and a drop of pyridine we obtained colorless needles (from alcohol), which melted at 193°. This melting point was not depressed by admixture with authentic specimen of penta-acetyl quercetin.

*The position of sugar attachment.* Since meratin and rutin (3-O-rhamnopyranosyl quercetin) give, as is shown in Fig. 4, coincident absorption curves, it must be concluded, that the meratin has a configuration of 3-O-diglucosidyl quercetin.

![Fig. 4](image-url)