

COLOURING MATTER OF THE FLOWER PETALS OF *BAUHINIA TOMENTOSA* LINN.

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Bauhinia tomentosa Linn. is a short shrubby garden plant (family Leguminosæ) occurring in central and south India and bears pale sulphur yellow flowers. The flower pigments of the *Bauhinia* species do not seem to have been examined so far. From the leaves of *Bauhinia reticulata*, however, was isolated quercitrin in 0.5% yield by Rabate.¹

In the present investigation the sun-dry *Bauhinia* flowers were extracted with alcohol. On concentration, the main colouring matter was obtained. The ethereal extract of the mother liquor yielded quercetin. No crystalline substance could be isolated from the mother liquor by means of the lead salt method.

The main colouring matter was a quercetin glycoside and on hydrolysis with acid gave rise to quercetin and an equimolecular mixture of *d*-glucose and *l*-rhamnose. From its properties and reactions it was considered to be rutin. This was confirmed by complete methylation and subsequent hydrolysis whereby was obtained 3-hydroxy-5:7:3':4'-tetramethoxy flavone.

The yield of rutin from the *Bauhinia* flowers is 4.6% and compares favourably with that of the American buckwheat² (6%). In view of the reported beneficial action of rutin on capillary fragility in man,³ the flowers of *Bauhinia tomentosa* may be a useful source of rutin.

EXPERIMENTAL

The flowers used in this investigation were collected from the local gardens in Waltair during the period of July to September. The sun-dried flowers (225 g.) were refluxed with alcohol (1,000 c.c.) for six hours and decanted hot. This was repeated three times. The combined extracts (1,800 c.c.) deposited some wax on cooling which was filtered and the filtrate distilled to recover most of the solvent. The residual liquid (120 c.c.) deposited a large quantity of a yellow solid (marked A) on leaving for a week along with excess of ether. It was filtered and washed with ether; yield 9.5 g. The ether layer was separated and marked B,

The alcoholic mother liquor was evaporated to remove all alcohol and the residue stirred up with boiling water (200 c.c.) and the solution filtered from waxy and resinous matter. It was concentrated to half its volume, treated with an equal volume of ether and left in the ice-chest for about a fortnight. About 1 g. more of A was obtained.

The ether solution B: Quercetin. When evaporated, it left behind a pale brown crystalline solid (0.8 g.) which after two crystallisations from alcohol gave yellow needles decomposing at 313-15°, not depressed by admixture with an authentic sample of quercetin. The acetate crystallised from alcohol as colourless needles melting at 193.5°, unchanged when mixed with penta-acetyl quercetin.

Sugar product by Bismar. When crystallised first from alcohol and then from aqueous pyridine it came out as pale yellow short needles melting at 188-90°. It did not depress the melting point of an authentic sample of rutin (found in the sample dried at 100° *in vacuo*: C, 53.0; H, 5.0. $C_{27}H_{34}O_{16}$ requires C, 53.1; and H, 5.0%). In 85% alcoholic solution, it had $[\alpha]_D^{25} = +88.8$ (Plouffe¹ reported $[\alpha]_D^{25} = +39$ for rutin in pyridine solution).

An alcoholic solution of the glycoside yielded an yellow precipitate with neutral lead acetate, a deep green colour with ferric chloride and a deep pink colour with manganous and hydrochloric acid. A solution in concentrated sulphuric acid exhibited a greenish fluorescence.

Hydrolysis. The pure glycoside (1 g.) was refluxed with 9% sulphuric acid for two hours. The aglycone, which separated even during the course of refluxing, was filtered and crystallised from alcohol; bright yellow needles (m.p. 313-15° (decomp.)), undepressed by admixture with an authentic sample of quercetin; yield 0.55 g. It answered all the colour reactions for quercetin. Methylation of the aglycone with dimethyl sulphate and potassium carbonate in anhydrous acetone solution yielded O-pentamethyl quercetin, m.p. 150-51° identical with an authentic sample.

The pale yellow acid nitrate from quercetin was extracted twice with ether and then neutralized with barium carbonate. It was evaporated at 30° *in vacuo* and the sugar residue extracted with absolute alcohol. The alcoholic extract was evaporated under reduced pressure and the sugar converted into osazone directly in the usual manner. When crystallised from aqueous alcohol it melted at 195-200°. Under the microscope, it was not homogeneous but the characteristic sheave-like clusters suggested the presence of phenyl glucosazon. Further the neutral sugar syrup answered the methyl furfural test for D-rhamnose. The acid hydrolysate (from 36.6 mg.

made up to 25 c.c.) gave a specific rotation of $+30.03^\circ$. Plouvier⁴ gave a value of $+29^\circ$ for the hydrolysate from rutin.

Methylation of the glycoside and hydrolysis: O-Tetramethyl Quercetin.

A suspension of finely powdered glycoside (2 g.) in dry acetone (150 c.c.) was refluxed with dimethyl sulphate (10 c.c. added in two lots) and potassium carbonate (20 g.) for 30 hours. The mixture was filtered, the pale brown acetone filtrate concentrated and the oily brown residue directly hydrolysed by refluxing with 7% sulphuric acid for two hours. On cooling, the solution deposited pale yellow needles melting at $197-98^\circ$, which was not depressed by an authentic sample of 3-hydroxy-5:7:3':4'-tetramethoxy flavone.⁵ Yield 0.8 g. (Found: C, 63.9; H, 5.3. $C_{16}H_{16}O_7$ requires C, 63.7; and H, 5.0%). It was easily soluble in aqueous alkali to give a yellow solution and exhibited dark brown colour with ferric chloride in alcoholic solution.

The above hydroxy flavone (1 g.) was refluxed for six hours with diethyl sulphate (1 c.c.) and anhydrous potassium carbonate (4 g.) in acetone solution. The ethyl methyl ether crystallised from alcohol as colourless narrow rectangular needles melting at $154-55^\circ$, undepressed by a synthetic sample of 3-ethoxy-5:7:3':4'-tetramethoxy flavone.⁵ (Found: C, 65.2; H, 5.8. $C_{21}H_{22}O_7$ requires C, 65.3; and H, 5.7%).

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SUMMARY

Rutin was isolated in an yield of 4.6% from the flowers of *Ranunculus tomentosus* Linn. They contained quercetin also in small quantities.

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