

# PIGMENTS OF COTTON FLOWERS

## Part IX. A Note on the Occurrence of Populnetin in Indian Cotton Flowers

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IN the course of their study of the colouring matter of the flowers of *Gossypium indicum*, Neelakantam and Seshadri reported the isolation of a new non-glycosidic compound.<sup>1</sup> The total pigment of the flowers was separated into five fractions according to the general scheme and studied. The first alcohol fraction contained mainly gossypin, a complex glycoside of gossypetin and the second (aqueous) fraction gave a small amount of the new substance which was not given any name at that time since it could not be studied in detail and its individuality was not quite definite. In the course of our examination of various samples of *G. herbaceum* flowers this substance has been again met with in small quantities and hence it occurs in this source also. Its main characteristics are (1) stability to aerial oxidation in alkaline solution thus indicating that it is a flavone, (2) lack of any colour changes in buffer solutions of pH on the alkaline side, (3) dissolution in concentrated sulphuric acid forming a yellow solution with a bright green fluorescence, (4) absence of any precipitate when an alcoholic solution is treated with neutral lead acetate, (5) formation of a yellow precipitate with basic lead acetate and (6) absence of methoxyl in its composition. These seemed to indicate that it was probably populnetin<sup>2</sup> and the idea was supported by the fact that populnetin occurs along with herbacetin in the flowers of *Thespesia populnea*<sup>3</sup> and hence could be expected to accompany it in the Indian cotton flowers also. But the melting point of the substance was rather low and the results of analysis were not definite due probably to the presence of inseparable impurities and the existence of hydration which seemed to vary with different conditions. The preparation and study of the acetyl derivative were not more helpful. The quantity available after these experiments was too small for further repeated purification and a detailed study independently. Consequently it was subjected to complete methylation using an acetone solution and excess of dimethyl sulphate and dilute sodium hydroxide. The product could be crystallised from alcohol from which it came out in the form of rectangular plates which were almost colourless. In its melting point, reactions and analysis, it was found to be identical with a sample of tetramethyl populnetin (described below) obtained by methylating an

authentic sample of populnetin isolated from *T. populnea*. It appears that definite purification is effected during methylation leading to the isolation of a pure methyl ether. The non-glycosidic substance should therefore consist mostly of populnetin.

#### Methylation of Populnetin

The flavone (1 g.) was dissolved in acetone (40 c.c.) and treated alternately in small quantities with 10% aqueous sodium hydroxide (50 c.c.) and dimethyl sulphate (10 c.c.). Finally the medium was made alkaline by the further addition of the alkali (50 c.c.) with vigorous shaking. In an hour an almost colourless crystalline compound separated out. It was filtered and recrystallised from alcohol using a little animal charcoal. Under the microscope it appeared as rectangular plates which were almost colourless. On heating it shrank at 95–100° (dehydration) and melted at 164–66°. It was insoluble in dilute alkali and did not yield any colour with ferric chloride. Its solution in concentrated sulphuric acid had a weak green fluorescence. [Found in the air-dried sample: C, 60.6; H, 6.2, and loss (H<sub>2</sub>O) on heating at 110° for 2 hours *in vacuo*, 9.2%. C<sub>15</sub>H<sub>6</sub>O<sub>2</sub> (OCH<sub>3</sub>)<sub>4</sub>, 2H<sub>2</sub>O requires: C, 60.3; H, 5.8 and H<sub>2</sub>O loss, 9.5%. Found in the dehydrated sample: C, 66.2; H, 4.9%; C<sub>15</sub>H<sub>6</sub>O<sub>2</sub> (OCH<sub>3</sub>)<sub>4</sub> requires C, 66.6; H, 5.2%.] The mixed melting point with the methyl ether obtained from the sample derived from the cotton flowers was undepressed.

From the experiments described above it is clear that populnetin occurs free in the Indian cotton flowers along with gossypetin, herbacetin and quercetin which are present mostly as glycosides. Thus there is a further case of the association which was first found in the flowers of the *Thespesia populnea*. It has already been shown that the substance is a tetrahydroxy flavone having a hydroxyl in the 4'-position. The disposition of the other groups in the benzopyrone part is still a matter of investigation. Its occurrence along with compounds having the 5:7:8-orientation of hydroxyls seems to suggest a similar disposition of the hydroxyl groups in it also.

#### Summary

The new non-glycosidic substance obtained from the Indian cotton flowers has been shown to consist mostly of populnetin from a comparison of the methyl ethers. The characteristics of the methyl ether of populnetin are described.

#### REFERENCES

1. Neelakantam and Seshadri .. *Proc. Ind. Acad. Sci. (A)*, 1936, **4**, 54.
2. Neelakantam, Rao and Seshadri *Ibid.*, 1943, **17**, 26.
3. Rao and Reddy .. *Ibid.*, 1940, **12**, 372.