PIGMENTS OF COTTON FLOWERS.

Part I. Cambodia (*Gossypium hirsutum*).

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A. G. Perkin has studied the colouring matter of cotton flowers belonging to several species and shown that most of them contain flavonols in the form of glucosides. The ordinary Indian yellow cotton flower, *Gossypium herbaceum*, contains Gossypitrin and Isoquercitrin whereas the Egyptian, *G. barbadense* contains besides the above two substances Quercimeritrin as the main component. The red flowers of *G. arboreum* contain Isoquercitrin; the yellow flowers *G. neglectum* contain the same pigments as the *Herbaceum* whereas the white variety possesses only a very small quantity of a glycoside resembling Apiin. The pink flowers of *G. sanguinum* contain only traces of flavones. The flowers of the American upland cotton *G. hirsutum* which are described as yellow have been examined by Viehoever who isolated from them Quercimeritrin and Isoquercitrin.

The Cambodia which is widely grown in South India under irrigated conditions is of American origin and belongs to the species *Hirsutum*. The fresh petals have only an ivory colour and the yellow is not prominent. As the flower withers, it turns red due to anthocyanin formation. We collected the fresh flowers from CO_2, a selection made in Coimbatore during two seasons, 1932 and 1933. The petals were isolated and dried in the sun as rapidly as possible and preserved. The first collection gave a good yield of Quercimeritrin (about 3% of the dry flowers) along with a very small quantity of Quercetin. No trace of Isoquercitrin could be detected. From the second collection, about 75% of the pigment was found to be Quercetin, the remainder being Quercimeritrin. It could therefore be concluded that the composition of the pigment from the flower petals varies with the variety, with the locality and with the season.

Experimental.

Sample Collected in 1931.

The sun-dried powdered petals (1 kg.) were extracted with boiling 96% ethyl alcohol. Each batch was twice extracted for eight hours each time.

The combined extracts were distilled over a water-bath in order to remove most of the alcohol. Water was then added to the distilling flask, the whole transferred to a large basin and heated again to evaporate the remaining alcohol. A large quantity of brown resin was formed and the clear yellowish brown solution containing the pigment was separated from it by decanting it while hot on to a filter and rapidly filtering. On leaving overnight a crystalline yellow deposit was formed. This amounted to about 2·5% of the dry petals.

After repeated crystallisation from aqueous pyridine, the substance was obtained in the form of yellow flat needles, m.p. 246–248° C. (Found :— C 47·8%, H 5·6% ; $C_{21}H_{20}O_{12}$, 3 H_2O requires C 48·6%, H 5·1%.) A solution of the pure substance in aqueous alcohol gave a scarlet red precipitate with neutral lead acetate and an olive green colour with ferric chloride. These properties agree with those of Quercimeritrin. The identity was further confirmed by acetylation with acetic anhydride and sodium acetate, when the acetyl derivative was obtained, m. p. 216–217° (octacetyl derivative according to Perkin melts at 214–216° C.), and by hydrolysis with boiling 7% aqueous sulphuric acid (2 hours) yielding an aglucone, m. p. 310–312° (decom.) which gave all the reactions for Quercetin. Its acetyl derivative melted at 197–198° C. (Perkin gives for pentacetyl Quercetin 197° C.). (Found :—In air dried specimen, C 52·6%, H 4·6%, $C_{15}H_{10}O_7$, 2 H_2O requires C 53·2%, H 4·2%; Specimen dried at 110° C 59·0%, H 3·8%, $C_{15}H_{10}O_7$ requires C 59·6%, H 3·3%.)

The acid filtrate after the hydrolysis was treated with an excess of Barium Carbonate, filtered and the filtrate was concentrated and examined for the sugar. It gave glucosazone having the characteristic crystalline shape and melting at 205–206° C.

The aqueous mother liquor obtained after the separation of the crystalline deposit of Quercimeritrin was twice extracted with ether. Except for a little resinous matter, no pigment was taken up by the ether. Excess of neutral lead acetate was now added to the aqueous solution, the bulky red precipitate was filtered, washed with water, made into a thin paste with a large volume of water and decomposed by repeatedly saturating with hydrogen sulphide. Lead sulphide was then filtered off, and the filtrate concentrated to a small bulk over a steam-bath and finally in a desiccator over sulphuric acid. A yellow solid (yield 0·5% of the weight of the flowers) was deposited ; this was readily obtained crystalline from aqueous pyridine, m.p. 248° and was found to be identical with Quercimeritrin obtained above. No other crystallisable substance could be obtained from this fraction.

It was noticed that Quercimeritrin crystallises in two forms depending upon the conditions, either as fine needles or as plates which were partly rectangular and partly triangular. On allowing the hot solution in aqueous pyridine to stand undisturbed a light brown oil came down and when the supernatant liquid was decanted off, the oil rapidly turned into a mass of yellow needles. The decanted liquid slowly deposited plates. The latter form seems to be more common. However, the two forms have identical properties.

The filtrate obtained after the removal of the neutral lead acetate precipitate was treated with basic lead acetate. The resulting precipitate was rather small in quantity. It was decomposed just as above and the resulting pigment repeatedly recrystallised from aqueous pyridine. It melted at 312° (decomp.), gave an acetyl derivative, m.p. 196° C. and resembled Quercetin in all its reactions.

Sample Collected in 1933.

The material was extracted with alcohol and after removing the alcohol, the aqueous extract was obtained as before. But this time it did not deposit any Quercimeritrin on standing. When it was extracted with ether, the ether layer was brownish red and hence extraction with ether was repeated till the ether failed to remove any appreciable quantity of colouring matter. The combined ether extract on evaporation gave a yellow solid which after recrystallisation from alcohol and then pyridine yielded flat needles, m.p. 312° and was found to be identical with Quercetin obtained from the previous experiment. On acetylation it gave acetyl Quercetin, m.p. 197°.

The aqueous solution after ether extraction, however, gave a crystalline precipitate on leaving for 24 hours. It was recrystallised from aqueous pyridine and subsequently from aqueous alcohol, m.p. 246–248° C. It gave an acetyl derivative melting at 216° C. and in all reactions was identical with Quercimeritrin obtained already.

After separating Quercimeritrin, the aqueous solution was treated first with neutral lead acetate and then with basic lead acetate and the precipitates were separately collected and decomposed as usual. The first precipitate was rather bulky and the pigment obtained from its decomposition was found to be almost pure Quercetin. After recrystallisation from aqueous pyridine, it melted at 312° C. and gave an acetyl derivative melting at 197° and no other substance could be obtained from it.

The basic lead acetate precipitate was rather small and the pigment obtained from it was also Quercetin and no glucoside could be isolated from this fraction.

Summary.

The Cambodia cotton flowers (*G. hirsutum*) contain a good amount of pigment (3%) in spite of their feeble ivory colour. In one sample the pigment was found to be mainly Quercimeritrin along with a small quantity of Quercetin, whereas in another sample collected next year Quercetin formed 75% of the total pigment and Quercimeritrin only 25%. In the nature of the pigments these flowers differ from the yellow American upland cotton (*G. hirsutum*) which have been reported to contain Quercimeritrin and Isoquercitrin. It is therefore concluded that the nature of the pigments vary with (1) the variety, (2) the locality, and (3) the season.

REFERENCES.

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