CCXXXIV.—*The Colouring Matter of Cotton Flowers. Gossypium Herbaceum. Part II.*

By Arthur George Perkin.

Some years ago (Trans., 1899, **75**, 825) it was shown that the flowers of the Indian variety of the cotton plant contained as a glucoside a hitherto unknown colouring matter, which was called gossypetin, but a lack of material did not allow of a more than cursory study of this compound. More recently (this vol., p. 1855), it has been observed that gossypetin also exists as a glucoside in the flowers of the *Hibiscus sabdariffa*, and the results of this later investigation have indicated that the true formula of this dyestuff is $C_{15}H_{10}O_8$ rather than $C_{16}H_{12}O_8$, which was originally proposed for it. There was evidence that the rather higher analytical figures formerly obtained arose from a contamination of the gossypetin with a trace of a similar yellow colouring matter containing a higher percentage of carbon, and it is considered likely that this may consist of quercetin. The formula and general reactions of gossypetin suggest that it is possibly a hexahydroxyflavone isomeric with myricetin (Trans., 1902, **81**, 205), but the study of this substance is certain to be difficult, because, even could the flowers be procured in abundance, the amount of gossypetin which they yield is very small. With the desire of further investigating this compound, some quantity of Egyptian cotton flowers were obtained through the kindness of Mr. W. Lawrence Balls, of the Khedival Agricultural Society of Cairo, and although as a result the original intention of the work could not be carried out, some interesting new products

have been obtained. The flowers (corollas) were gathered from the ground, where they had fallen a day or two after the flower had opened out. They all came from one field of Afifi cotton, which is the main Egyptian variety and resembles all the other Egyptian kinds in its general habit of growth and in its flowers, differing only as regards the tint. The flower is golden-yellow, with a crimson spot at the base of the petal; this spot is not, however, so large as it is in many varieties of *Gossypium herbaceum*, using the word to signify the Asiatic type of cotton with small, round-lobed leaves. The Egyptian cottons appear, according to the recent researches of Messrs. Fletcher and Balls, to be derived from natural crosses of brown Peruvian cottons with the Sea Island variety.

Experimental.

The flowers were digested with ten times their weight of boiling alcohol for six hours, and the pale brown extract was evaporated to a small bulk. The residual liquid deposited, on cooling, an orange-brown precipitate, which was collected and washed two or three times with alcohol (the filtrate and washings (A) being reserved for examination). This product, which, when allowed to dry, consisted mainly of a semi-crystalline powder, was possessed of strong tinctorial property, and was of a glucosidal nature. It dissolved fairly readily in cold water, and this rather unusual property suggested that it was probably a salt of the dyestuff, which, on examination, proved to be the case. As the use of acid for the neutralisation of the compound was, in the circumstances, to be avoided, an aqueous solution of the substance, which had been freed from insoluble matter by filtration, and from wax by agitation with ether, was treated with lead acetate, causing the production of a dull red-coloured precipitate, which was collected, the filtrate being colourless or nearly so and free from dissolved glucoside. The precipitate, after being very thoroughly washed with boiling water, was mixed to a thin cream with water, and decomposed by means of hydrogen sulphide; the mixture was then heated to boiling, and the lead sulphide removed by filtration. The dull orange-coloured liquid, on being kept in a vacuum, slowly deposited a mixture of crystals and gelatinous matter, and the evaporation was continued until nothing further separated. This product was collected and crystallised two or three times from water, and then consisted of a yellow, micro-crystalline powder, melting at 196—197°. As further purification in this manner but little affected the melting point, it was at first considered to be pure, but subsequent experiment proved that this was far from

being the case, and that the substance was in reality a mixture. A recrystallisation from methyl alcohol and water caused the melting point to rise to 213—215°, by a second treatment in this manner it fused at 231—233°, and by two crystallisations from pyridine and water a further rise to 245—246° then occurred. Finally, it was ascertained that the true melting point of this more sparingly soluble constituent of the mixture was 247—249° (uncorr.).

When deposited from aqueous liquids, this substance contains water of crystallisation, which is evolved at 100°, but is regained in contact with moist air for some days. For the purpose of analysis, a determination of the gain in weight thus experienced by the dried substance gave the most satisfactory result:

Found, $H_2O = 10{\cdot}64$; 10·53.

An analysis both of the dried (*a*) and undried glucoside (*b*) was carried out:

Found, (*a*) C = 54·22; H = 4·76; (*b*) C = 48·82; H = 5·07.

$C_{21}H_{20}O_{12}$ requires C = 54·31; H = 4·31.

$C_{21}H_{20}O_{12},3H_2O$ requires C = 48·65; H = 5·02; H_2O = 10·42 per cent.

It consists of small, glistening, bright yellow plates, almost insoluble in cold and fairly readily soluble in boiling water. Its alkaline solutions possess a deep yellow tint; with aqueous lead acetate it gives a bright red precipitate, and with ferric chloride an olive-green coloration. The high melting point of this glucoside is remarkable, for such has been unusual in connexion with the hitherto described members of this special group. A study of its hydrolysis with mineral acids revealed that it possessed considerable stability in this respect, for when a solution of 0·766 gram of the substance in 500 c.c. of water was digested at the boiling point for one and a-half hours with addition of 1 c.c. of sulphuric acid, on cooling, 0·733 gram of a yellow powder separated, which, on examination, was found to consist almost entirely of unaltered glucoside.

In a second experiment, 0·6905 gram of the dried substance, dissolved in 100 c.c. of hot water, was boiled for fifteen minutes with addition of 1 c.c. of sulphuric acid, but as hydrolysis did not even then appear to have occurred, a further 2 c.c. of the acid was added, and the solution boiled for two hours. During the latter operation a dull yellow precipitate gradually separated, and this was collected and dried at 160°:

Found, $C_{15}H_{10}O_7 = 63{\cdot}94$.

$C_{21}H_{20}O_{10}$ requires $C_{15}H_{10}O_7 = 65{\cdot}08$ per cent.

Finally, it was observed that the most efficient strength of acid for the hydrolysis of the glucoside was 4 c.c. of sulphuric acid in

100 c.c. of water, and although a slight discoloration of the product had occurred after a two hours' digestion, this was not very material. An analysis of the air-dried substance by this method gave as follows:

Found, $C_{15}H_{10}O_7 = 58{\cdot}05$.

$C_{21}H_{20}O_{10},3H_2O$ requires $C_{15}H_{10}O_7 = 58{\cdot}30$ per cent.

The product consisted of yellow needles, contaminated with a trace of a brown impurity, and on account of this it was first converted into its acetyl derivative, which formed colourless needles, melting at 191—194°.

The hydrolysis of this compound was carried out by means of sulphuric acid in the presence of acetic acid, in the manner usually employed in these investigations (Trans., 1905, **87**, 107):

Found, $C = 58{\cdot}32$; $H = 3{\cdot}97$; $C_{15}H_{10}O_7 = 58{\cdot}75$.

$C_{15}H_5O_5(C_2H_3O)_5$ requires $C = 58{\cdot}59$; $H = 3{\cdot}91$; $C_{15}H_{10}O_7 = 58{\cdot}96$ per cent.

An analysis of the free colouring matter gave the following result:

Found, $C = 59{\cdot}43$; $H = 3{\cdot}64$.

$C_{15}H_{10}O_7$ requires $C = 59{\cdot}60$; $H = 3{\cdot}31$ per cent.

The examination of the properties of this substance indicated that it consisted of quercetin, and it was therefore evident that the compound $C_{21}H_{20}O_{12}$ is a hitherto unknown glucoside of this colouring matter. To identify, if possible, the sugar which is produced by the hydrolysis of this glucoside, the sulphuric acid present in the aqueous filtrate from the quercetin was removed by means of barium carbonate, and the clear liquid evaporated to dryness. The viscid residue was extracted with alcohol, the alcoholic solution evaporated, and the now almost colourless product was treated with phenylhydrazine in the usual manner. An osazone was thus obtained crystallising in needles, and this was collected and washed with a little ether. Considerable trouble was experienced in the complete purification of this substance by crystallising it either from alcohol or from alcohol and water, a point which has been referred to by Tutin (Proc., 1907, **23**, 250) as sometimes occurring with phenylglucosazone; but by the employment of alcoholic pyridine and water, as recommended by this author, the substance previously melting at 196—198° then fused and decomposed at 204—205°. Owing to the small quantity of the glucoside which was available, it was not possible to examine the pure crystalline sugar, but, on the other hand, as a mixture of the osazone and phenylglucosazone also melted at 204—205°, there is every reason to consider that it consists of dextrose.

The hydrolysis of this glucoside, for which the name *quercimeritrin* * is proposed, proceeds therefore according to the equation:

$$C_{21}H_{20}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6,$$

which requires a yield of 65·08 per cent. of quercetin.

When quercimeritrin is added to boiling acetic anhydride, it slowly dissolves, and if, after a two hours' digestion at this temperature, the solution is treated with its own volume of alcohol, colourless crystals of the acetyl derivative gradually separate out. The product is purified by recrystallisation from a mixture of alcohol and acetic acid:

Found, C = 55·31; H = 4·69.

$C_{21}H_{12}O_{10}(C_2H_3O)_8$ requires C = 55·50; H = 4·50 per cent.

Acetylquercimeritrin consists of needles, which melt at 214—216°, and is very sparingly soluble in boiling alcohol.

A determination of the number of acetyl groups which this substance contains was carried out by the acetic ether method (Trans., 1905, **87**, 107), employing a solution of 3 c.c. of sulphuric acid in 30 c.c. of alcohol. At the conclusion of the operation, an examination showed that hydrolysis of the glucoside had also occurred, and the quercetin, which had been thus produced, was isolated by treating the residual alcoholic liquid with hot water and cautiously distilling off the greater portion of the alcohol:

Found, $C_2H_4O_2$ = 61·07; $C_{15}H_{10}O_7$ = 37·76.

$C_{21}H_{12}O_{10}(C_2H_3O)_8$ requires $C_2H_4O_2$ = 60·00; $C_{15}H_{10}O_7$ = 37·75 per cent.

It was therefore an octa-acetyl derivative.

Although quercimeritrin itself is almost insoluble in cold water, it has been shown above that it exists in these flowers, in a readily soluble condition, probably in the form of a salt. An examination of the residue given by an incineration of this plant product indicated the presence of a trace of iron, together with a considerable quantity of potassium, so that evidently the compound in question is mainly the potassium salt of the glucoside. A trace of copper was also present in the ash, but no importance could be attached to this point, because the alcoholic extraction of the flowers was performed in a copper vessel.

If a hot alcoholic solution of quercimeritrin is treated with potassium acetate, a yellow precipitate of a *potassium* salt at once separates. As this, when collected, congealed together, it was not completely freed from the excess of acetate by washing with alcohol:

* Derived from the "Quercimerinsäure" of Hlasiwetz and Pfaundler (*Jahresb.*, 1864, 569), the existence of which appears to be doubtful.

Found, K = 9·1.

$C_{21}H_{19}O_{12}K$ requires K = 7·77 per cent.,

but it was evidently a monopotassium compound, analogous to that which was previously prepared from rutin, a glucoside of quercetin (Trans., 1899, **75**, 439). This quercimeritrin compound was readily soluble in water, and almost insoluble in alcohol, and may be identical with the potassium salt of the glucoside which is present in the flowers.

The fact that quercimeritrin is an extremely stable glucoside is rendered obvious by a comparison of its behaviour in this respect with such well-known quercetin glucosides as quercitrin and rutin. These latter can be readily hydrolysed by digestion for about an hour with boiling dilute sulphuric acid of the concentration of 1 c.c. in 250 c.c. of water, whereas, as previously shown, quercimeritrin is best attacked by an acid which is ten times this strength.

On wool mordanted with aluminium, tin, chromium, and iron, quercimeritrin gave the following shades:

Aluminium.	Tin.	Chromium.	Iron.
Orange-yellow	Bright orange	Reddish-brown	Olive-brown

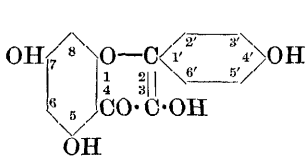
and these results were interesting, because, with the exception of the colour of the iron mordanted pattern, which is of a rather browner character, these shades closely resemble those which are given by quercetin * itself when dyed in a similar manner. On the other hand, they are widely different from the colours thus yielded by quercitrin and rutin, which have been described in an earlier communication (Trans., 1902, **81**, 480).

It has been previously pointed out (*loc. cit.*) that quercitrin is not hydrolysed during the dyeing operation, and it is most improbable that the more stable quercimeritrin would suffer decomposition during this process. The fact therefore that very similar shades are given both by the latter glucoside and quercetin itself is of importance, in regard to the location of the sugar nucleus.

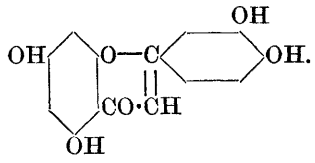
A study of the dyeing properties of kaempferol and luteolin (Trans., 1902, **81**, 590), employing woollen cloth, has shown that the colours given by the chromium, aluminium, and tin mordants are almost identical in each case. On the other hand, the dyeings produced by quercetin are not only stronger, but much redder than those characteristic of kaempferol and luteolin, and this result is evidently the joint effect of the 3′- and 4′-hydroxyl groups and the

* This was to be anticipated, owing to the fact that both this glucoside and quercetin yield, with lead acetate solution, similarly coloured precipitates.

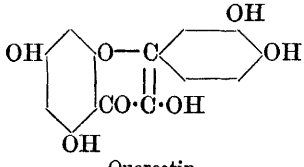
pyrone 3-hydroxyl group, contained by the former colouring matter. Again, it has been rendered certain by the location of the methoxy-



Kaempferol.

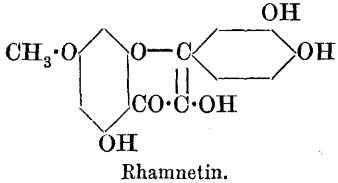


Luteolin.



Quercetin.

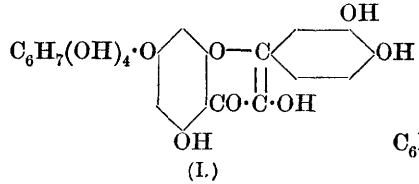
group in rhamnetin (quercetin monomethyl ether) (Trans., 1902, **81**, 471):



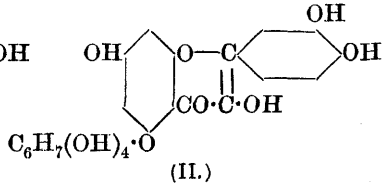
Rhamnetin.

which dyes similarly to quercetin, that the hydroxyl groups present in the phloroglucinol nucleus have little or no effect as regards the shades produced from the latter compound.

There is every reason, therefore, to suppose that quercimeritrin contains the quercetin hydroxyl groups in the 3′-, 4′-, and 3-positions intact, and therefore its constitution will be represented by one of the two following formulæ:



(I.)



(II.)

The solution of this problem should not be difficult, and experiments on this point will be carried out as soon as the necessary quantity of the glucoside is available.

The alcoholic filtrate (A) (p. 2182), from which the crude potassium quercimeritrin had been removed, was treated with water, the alcohol evaporated, and the solution then agitated with ether

to remove waxy matter. The addition of lead acetate caused the formation of a deep red precipitate, which was collected, and the filtrate (B) placed aside for subsequent examination. When decomposed with hydrogen sulphide, this product gave, by the method above described, a further quantity of quercimeritrin, the identity of which was confirmed by analysis:

Found, C = 54·00; H = 4·48.

It has been previously shown that the purification of crude quercimeritrin is a matter of considerable difficulty, indicating that in this condition other compounds of a similar nature are present. To investigate this point, the combined mother liquors which had been derived from it were fractionally evaporated, and the deposits thus obtained were redissolved and submitted to a similar treatment. Eventually a middle fraction was isolated of a gelatinous nature, and this was allowed to dry, and digested with a little boiling acetic acid, which caused it to become granular, whereas the supernatant liquid acquired a rich dichromate colour. It was collected, again digested with the boiling acid, and, after extraction with methyl alcohol, repeatedly crystallised from dilute acetic acid. For analysis it was dried at 160°:

Found, C = 52·50; H = 4·31.

$C_{21}H_{20}O_{13}$ requires C = 52·50; H = 4·17 per cent.

It consisted of pale orange-yellow needles, melting at about 200—202°, very sparingly soluble in absolute alcohol or acetic acid. With aqueous lead acetate, it gives a deep red precipitate almost identical in appearance with that produced by quercimeritrin, and with ferric chloride an olive-green coloration. Alkalis dissolve it with a deep yellow tint, which becomes greener when the solution is diluted with water. As there could be no doubt that this substance was a glucoside, it was digested with boiling dilute sulphuric acid (1 c.c. in 25 c.c. of water) for two hours. During the reaction, crystals slowly separated, and after keeping overnight these were collected and weighed:

Found, $C_{15}H_{10}O_8$ = 65·60.

$C_{21}H_{20}O_{13}$ requires $C_{15}H_{10}O_8$ = 66·25 per cent.

This product formed glistening, yellow needles, which dissolved with a green colour in very dilute alkali, and appeared to be gossypetin. To settle this point, an acetyl derivative was prepared; this consisted of colourless needles, melting at 226—228°, and was without doubt identical with acetylgossypetin.

The sugar produced by the hydrolysis of this glucoside was isolated in the usual manner, and an osazone prepared from it. This was obtained in yellow needles, which, after crystallisation

from alcoholic pyridine and water, melted at 203—205°, and was most probably phenylglucosazone.

The hydrolysis of *gossypitrin*, the name which is proposed for this glucoside, can therefore be represented as follows:

$$C_{21}H_{20}O_{13} + H_2O = C_{15}H_{10}O_8 + C_6H_{12}O_6.$$

As but slightly less than one gram of this compound has as yet been isolated, it was not possible to investigate its acetyl derivative or its dyeing properties. Similarly, however, to quercimeritrin, it appears to be a somewhat stable glucoside, and it is likely that further experiment will show that the sugar nucleus occupies an analogous position in both these compounds. That gossypitrin, like quercimeritrin, also exists in these flowers as a potassium salt follows from its method of preparation.

The aqueous filtrates and other residues obtained during the isolation of this latter glucoside yielded, on further treatment, a gelatinous mixture, from which but a trace of sparingly soluble substance could be isolated by means of acetic acid. As a further separation appeared to be very difficult, especially as the quantity of the material available was small, it was dissolved in water and hydrolysed by the addition of sulphuric acid (1 c.c. in 25 c.c. of water), and digestion at the boiling point for two hours. A dull yellow-coloured precipitate gradually separated, which was collected, and converted into hydrochloride by means of hydrochloric acid in the presence of boiling acetic acid, and the semi-solid mass of red needles, which thus separated, was collected, washed with acetic acid, and decomposed with water. The product thus purified proved to be a mixture, the constituents of which were best separated in the form of their acetyl compounds. By repeated crystallisation, first from alcoholic acetic acid and subsequently from acetic anhydride, a small quantity of a very sparingly soluble acetyl derivative was isolated, which melted at 229—230°, and had the properties of acetylgossypetin. This was hydrolysed by means of hydrochloric acid, and gave the following result:

Found, $C_{15}H_{10}O_8 = 55{\cdot}50$.

$C_{15}H_4O_8(C_2H_3O)_6$ requires $C_{15}H_{10}O_8 = 55{\cdot}78$ per cent.

The free colouring matter, as was anticipated, was found to be gossypetin:

Found, $C = 56{\cdot}71$; $H = 3{\cdot}41$.

$C_{15}H_{10}O_8$ requires $C = 56{\cdot}60$; $H = 3{\cdot}14$ per cent.

The more soluble constituent of the acetylated mixture, which proved to be the main bulk of this product, was obtained in colourless needles, melting at 191—194°, and consisted of acetylquercetin.

That the original condition of the gossypetin thus prepared from

the plant was the glucoside gossypitrin above described seems probable, but, on the other hand, it cannot be considered that the quercetin isolated in such comparatively large amount had been produced by the hydrolysis of quercimeritrin. That so sparingly soluble a substance should have resisted isolation by the methods given above is not probable, and this point will be further investigated.

A study was now made of the aqueous filtrate from the second lead precipitate, and this, on treatment at the boiling point with basic lead acetate, gave a small quantity of a bright yellow precipitate. This was collected, suspended in water, and decomposed with hydrogen sulphide, and the mixture filtered hot. The pale yellowish-brown filtrate slowly deposited gelatinous nodules, and after several days these were collected and allowed to drain. This product, in the moist condition, was dissolved in a little boiling acetic acid, and the crystals, which separated on cooling, were recrystallised from dilute acetic acid, from water, and finally from pyridine and water:

Found, C = 54·09; H = 4·64.

$C_{21}H_{20}O_{12}$ requires C = 54·31; H = 4·31 per cent.

It consisted of pale yellow needles, melting at 217—219°, which were much less highly coloured than those of quercimeritrin, and in this respect somewhat resembled rutin. It is almost insoluble in cold and but sparingly in boiling water, soluble in alkaline solutions with a deep yellow tint, but its most interesting property is the fact that with aqueous lead acetate it gives a bright yellow precipitate entirely distinct from the deep red deposit which is produced in this manner from quercimeritrin. Again, this yellow lead compound is fairly readily dissolved in the moist condition by hot dilute acetic acid, whereas the quercimeritrin lake is much more stable under this treatment. With dilute alcoholic ferric chloride, it gives a deep olive-green coloration.

An important distinction between the two glucosides is observed also by an examination of their behaviour during hydrolysis, for when iso*quercitrin*, the name proposed for this new compound, is submitted to the action of boiling dilute sulphuric acid (1 c.c. in 25 c.c. of water), a crystalline product rapidly separates, and the reaction is quickly completed. On the other hand, the comparative stability of quercimeritrin in these circumstances has been previously discussed.

The following result was given by the hydrolysis of *iso*quercitrin:

Found, $C_{15}H_{10}O_7$ = 64·56.

$C_{21}H_{20}O_{12}$ requires $C_{15}H_{10}O_7$ = 65·08 per cent.

The product consisted of yellow needles, soluble in dilute alkalis

with a yellow coloration, and on acetylation gave an acetyl compound, which formed colourless needles, and melted at 191—194°. Further experiment indicated that this colouring matter was quercetin.

The sugar produced during the hydrolysis of this glucoside was isolated in the usual manner, and converted into osazone. This, when purified by crystallisation from alcoholic pyridine and water, consisted of yellow needles, melting at 203—205°, which, when admixed with pure phenylglucosazone, did not affect the fusion point of the latter, and thus appeared to be identical with it.

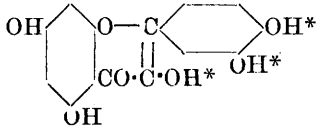
The hydrolysis of *iso*quercitrin proceeds therefore as follows:

$$C_{21}H_{20}O_{10} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6.$$

Dyeing experiments with this glucoside, employing mordanted wool, gave interesting results, because the shades produced were entirely distinct from those given by quercimeritrin, but, on the other hand, somewhat closely resembled those yielded by quercitrin, although slightly paler (Trans., 1902, **81**, 480):

Chromium.	Aluminium.	Tin.	Iron.
Brownish-yellow	Golden-yellow	Lemon-yellow	Brownish-olive

It is quite evident, therefore, that although quercimeritrin and *iso*quercitrin are isomeric, and when hydrolysed give identical products, they are distinct substances. For reasons previously discussed, and alluded to elsewhere (Trans., 1902, **81**, 210), it is clear that the sugar group in the latter glucoside is not attached to the phloroglucinol nucleus, but is probably constituted like quercitrin, which on hydrolysis yields, however, rhamnose. Three formulæ are possible for *iso*quercitrin, which may be briefly expressed by the statement that the position of the sugar residue in respect to the quercetin group is at one or other of the points in the following formula which are marked with an asterisk:



Further experiments with regard to *iso*quercitrin have not been at present possible, for the total amount as yet obtained has been merely one gram, but it has been ascertained that its acetyl derivative is much more soluble in alcohol than the quercimeritrin compound. In the hope of isolating a larger amount of this substance, an extract of the flowers, to which a small quantity of acetic acid had been added, was treated with lead acetate, and the precipitate removed, but the quantity of *iso*quercitrin present in the filtrate did not appear to be thereby increased.

The mother liquors obtained during the purification of this glucoside yielded nothing but quercetin (Found, C = 59·45; H = 3·49), and this result was further corroborated by the preparation of its acetyl derivative (Found, C = 58·21; H = 4·22), which melted at 191—194°.

General Properties of the Flowers.

The results of this investigation have shown that Egyptian cotton flowers contain three hitherto unknown glucosides, quercimeritrin, *iso*quercitrin, and gossypitrin, of which the first-named has been isolated in by far the largest amount.

To ascertain approximately the total amount of yellow colouring matter which could be produced from this sample of flowers, 100 grams of the material were exhausted with boiling water, and the glucosides present in this solution hydrolysed by means of acid. The mixture was then repeatedly extracted with ether, the ethereal solution evaporated, and the residue collected and washed with water. There was thus obtained 1·86 grams, or 1·86 per cent. of the crude colouring matter, consisting of a mixture of quercetin and gossypetin, and this, when acetylated and the product fractionally crystallised from a mixture of alcohol and acetic acid, gave 0·3 gram of pure acetylgossypetin (Found, C = 56·68; H = 4·30), which corresponds with 0·165 gram of gossypetin itself. Such a process of separation is, however, far from exact, but it seemed evident that not more than 10 per cent. of the total colouring matter consisted of gossypetin. Dyeing experiments carried out with the flowers themselves in the usual way gave shades which, although duller, were somewhat similar in character to those yielded by quercimeritrin, a result indicating that no great quantity of *iso*quercitrin could be present:

Chromium.	Aluminium.	Tin.	Iron.
Reddish-brown	Green-yellow	Orange-brown	Olive-brown

In comparison with the colours similarly produced from other natural dyes, these shades most nearly resemble those of the so-called "Patent Bark," a preparation of quercitron bark, in which quercetin and no quercitrin is present. Further experiment indicated that in colouring power two parts of the bark were about equal in strength to five parts of the flowers, and this result was to be anticipated, for it was ascertained some time ago that the former dyestuff contains on the average 5 per cent. of quercetin.

The fact that quercetin is the predominating colouring matter of the Egyptian cotton flowers suggests that in this respect it may differ from the Indian variety, which was first examined, for in

the latter case (*loc. cit.*) the presence of gossypetin only was detected. It has, however, been shown in this present work that the main constituent of the Egyptian material, quercimeritrin, is not readily susceptible to hydrolysis by acid, and it is possible that under the former experimental conditions the main bulk of this glucoside, if present, escaped decomposition. Through the kindness of Mr. I. H. Burkill, Reporter on Economic Products to the Government of India, a considerable quantity of the Indian material will be shortly available for investigation, and an opportunity will arise, not only for a study of the constitution of gossypetin, but for a direct comparison of the two varieties of flower, a matter which appears to be of considerable interest.

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