

VIII.—*Notes on some Natural Colouring Matters.*

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THIS investigation contains an account of the yellow colouring matters which are present in the flowers of *Prunus spinosa* and the Japanese dyestuff "Fukugi," together with some results which have been obtained during the further study of morin, myricetin, hesperitin, and curcumin.

*The Colouring Matter of the Flowers of Prunus spinosa.*

Some years ago, while examining the dyeing properties of certain natural products, it was noted that some quantity of yellow colouring matter exists as a glucoside in the flowers of *Prunus spinosa* or common blackthorn. A cursory examination carried out at the time resulted in the isolation of a product which was apparently a mixture, because its acetyl derivative did not melt sharply, the melting point being

very low for this class of substance. The attempts then made to effect a separation were not successful, but more recently, in the hope that a new colouring matter might be present, the subject has been again investigated, and the difficulty overcome in an exceedingly simple manner. In order to facilitate the work, an extract of these flowers prepared by Merck of Darmstadt was chiefly employed.

Two hundred grams of the extract dissolved in 2 litres of water were treated with 50 c.c. of hydrochloric acid, boiled for three hours, and, after cooling, extracted with ether to remove the colouring matter, which was thus obtained as a brownish-yellow, crystalline mass (3.5 grams). This was purified by two or three crystallisations from dilute alcohol, and a portion then converted into the acetyl compound in order to determine whether its melting point coincided with that of the corresponding derivative of some known substance of this class. It was found to melt somewhat indefinitely at 133—134°, and gave on analysis C = 60.09; H = 4.28, these figures indicating that it was most probably a mixture. The main bulk of the colouring matter was now dissolved in a small quantity of boiling acetic acid, and the crystals which separated on cooling were collected and recrystallised from the same solvent until no alteration in the melting point could be observed; the yield was 0.8 gram.

Found C = 62.93; H = 3.89.

$C_{15}H_{10}O_6$  requires C = 62.94; H = 3.49 per cent.

The substance, which consisted of pale yellow, glistening leaflets melting at 276°, dissolved in dilute aqueous alkalis with a pale yellow coloration.

The *acetyl* compound crystallised from methyl alcohol in colourless needles which melted at about 116°, resolidified at a higher temperature, and melted again at 181—182°.

Found C = 60.77; H = 3.97.

$C_{15}H_6O_6(C_2H_3O)_4$  requires C = 60.79; H = 3.96 per cent.

On fusing the colouring matter with caustic alkali, phloroglucinol (m. p. 210°) and *p*-hydroxybenzoic acid (m. p. 208—210°) were obtained.

These facts, together with an examination of its dyeing properties, indicated without doubt that this colouring matter was *kampherol*. As this dyestuff has recently been found in at least four other plants, it is likely to occur in many other vegetable species.

The acetic acid mother liquors from which the kampherol had separated were allowed to absorb moisture by exposure to the

atmosphere, which caused the deposition of a small quantity of a mixture of a kampherol and a second substance. This precipitate was removed, the filtrate treated with a small quantity of hot water, and the yellow precipitate, which slowly separated, was collected and purified by conversion into its *acetyl* derivative.

Found C = 58.67 ; H = 4.26.

$C_{15}H_5O_7(C_2H_3O)_5$  requires C = 58.59 ; H = 3.90 per cent.

This substance, which melted at  $191^\circ$ , was decomposed with acid in the usual manner, and the regenerated colouring matter crystallised from dilute alcohol.

Found C = 59.56 ; H = 3.61.

$C_{15}H_{10}O_7$  requires C = 59.60 ; H = 3.31 per cent.

It formed glistening yellow needles soluble in alkali solutions with a yellow coloration ; on fusion with caustic potash, it gave phloroglucinol (m. p.  $210^\circ$ ) and protocatechuic acid (m. p.  $193-195^\circ$ ). It was evidently *quercetin*, and to this colouring matter and kampherol the dyeing property of these flowers is evidently due.

A cursory examination of the flowers of the violet (*Viola odorata*) and the white clover (*Trifolium repens*) by a method similar to that employed above indicated in each case the presence of *quercetin* in the form of a glucoside. This colouring matter was recognised by the melting point of its acetyl derivative, and its decomposition products with caustic alkali, and in consequence of these observations a fuller investigation appeared unnecessary.

#### *The Japanese Dyestuff "Fukugi."*

We are indebted to the kindness of Professor E. Yoshitake, of Tokio, for this material, which consists of the wood of a tree, and was obtained in the form of an almost colourless, coarse powder ; it appears, at least until recently, to have been employed to a considerable extent as a yellow mordant dyestuff, principally in the form of extract. A preparation of this kind was also procured and consisted of brittle, rectangular cakes ( $4'' \times 2\frac{1}{2}'' \times 1\frac{1}{2}''$ ) of a yellowish-brown colour, which weighed approximately 410 grams.

The coarsely powdered extract, dissolved in ten times its weight of water, was boiled with 100 c.c. of hydrochloric acid for two hours in order to decompose the glucoside. A somewhat viscous precipitate of the impure colouring matter thus separated, which, when cold, was washed by decantation, drained on a tile, and allowed to dry at the ordinary

temperature. The product was extracted with boiling alcohol, the extract evaporated and poured into a large bulk of ether, which caused the separation of a resinous impurity, and on evaporating the ethereal liquid the colouring matter now obtained was of a much lighter colour. For further purification, it was dissolved in boiling alcohol containing a trace of acetic acid, lead acetate solution added, the resulting yellow precipitate removed, the filtrate evaporated to a small bulk and poured into ether. The pale yellow, ethereal liquid was well washed with water, evaporated to dryness, and the viscid residue left for some days. Minute crystals slowly separated, which were collected, washed with a small amount of ether, and crystallised first from dilute ethyl alcohol and then from methyl alcohol until the melting point was constant. The product frequently contained a trace of the lead compound, which adhered somewhat tenaciously, and was best removed by means of ether, in which it dissolved with difficulty.

Found, (i) C = 65.03 ; H = 4.04. (ii) C = 65.17 ; H = 3.97.

$C_{17}H_{12}O_6$  requires C = 65.37 ; H = 3.84 per cent.

It consisted of a mass of minute, prismatic, canary-yellow needles, which melted at 288—290°. When crystallised from dilute alcohol, the air-dried product contains one and a half molecules of water of crystallisation.

Found,  $H_2O = 7.56$ .

$C_{34}H_{24}O_{12}, 3H_2O$  requires  $H_2O = 7.35$  per cent.

This new colouring matter, for which the name *fukugetin* is proposed, is readily soluble in hot alcohol and dissolves in aqueous alkalis or in cold sulphuric acid with a pale yellow coloration. The solution in the latter solvent, on heating, becomes dull violet-red, and finally assumes an orange-brown tint, and, on dilution with water, now deposits a brown, amorphous precipitate soluble in aqueous alkalis to a dull red solution. With lead acetate in alcoholic solution, an orange-yellow precipitate is formed, whilst alcoholic ferric chloride develops a brownish-black coloration ; on the other hand, alcoholic potassium acetate gives no insoluble salt, and mineral acids do not react to form the usual compounds. When examined by Zeisel's method, it was found to contain no methoxyl groups.

Fukugetin readily dyes mordanted fabrics, and it was at once observed that the shades produced were almost identical, except as regards the iron mordanted portion, with those given by luteolin.

	Cr.	Al.	Sn.	Fe.
Fukugetin.	Dull orange-yellow.	Orange-yellow.	Bright ye'low.	Olive-brown.
Luteolin.	Brown orange-yellow.	„	„	Olive-black.

Crystalline acetyl and benzoyl derivatives of this new colouring matter could unfortunately not be obtained either by the usual processes or by the pyridine method. Methylation also led to the formation of a viscous product, although it is possible that these difficulties might have been surmounted if a larger quantity of substance had been available for experiment.

*Bromine Compound.*—One gram of fukugetin was added to a solution of one gram of bromine in a little glacial acetic acid. After twenty-four hours, the product was drained on porous tile, ground up with a small amount of acetic acid, filtered at the pump, washed once or twice with acetic acid, and purified by crystallisation from nitrobenzene, two or three drops of acetic acid being added to the solution when cooling. Two distinct preparations were made.

Found, (i) C = 43.47 ; H = 2.43. (ii) C = 43.53 ; H = 1.95.

$C_{17}H_{10}O_6Br_2$  requires C = 43.22 ; H = 2.54.

*Dibromofukugetin* forms minute, flat needles melting at 280°, readily soluble in hot alcohol, more sparingly so in acetic acid.

On fusion with alkali in the usual manner, fukugetin gave protocatechuic acid (m. p. 194—196°) and phloroglucinol (m. p. 210°).

The above results are, unfortunately, too meagre to allow of the prediction of the constitution of this substance with any certainty, but the similarity of most of the general properties of the compound with those of luteolin, and the fact that it contains similar nuclei, point to the probable close relationship between these colouring matters. Interesting in this respect is the stability of alkaline solutions of fukugetin when exposed to the air, for these do not undergo oxidation even after many days. This property, as shown in former investigations, is somewhat characteristic of flavone compounds such as apigenin and luteolin, but is not possessed by flavanol derivatives, of which fisetin and quercetin may be quoted as examples. It is possible that the distinction between luteolin and fukugetin consists chiefly in the manner by which the catechol nucleus is connected with the pyrone ring, and one or two formulæ suggest themselves as very probable representatives of this colouring matter. It is intended, should a further supply of raw material be forthcoming, to continue these experiments in the hope of elucidating with certainty the constitution of this interesting substance.

An examination of the dyeing properties of "fukugi" showed, as was to be expected, that it behaved in this respect in an analogous manner to weld (*Reseda luteola*). The similarity in shade was so marked that, except in point of strength—for fukugi is a stronger dye than weld—

it is impossible to distinguish between them, and there can be little doubt that prior to the introduction of the synthetical colouring matters this dyestuff would have been a valuable addition to those already in use.

*Ethylation of Morin.*

Although quercetin and other members of the flavanol class readily give, on alkylation, well-defined crystalline substances, morin has only yielded a methyl ether in a state of purity (Trans., 1896, 29, 192), for on ethylation in the usual manner, viscous products result which have hitherto refused to crystallise. As it seemed possible that the impurities might be more readily removed after acetylation, the residue from former experiments carried out some years ago was treated in the following manner.

The resinous mass was digested with boiling acetic anhydride for some hours, the solution evaporated to a small bulk, and diluted with about twice its volume of methylated spirit. After several days, a small quantity of crystalline matter separated, and the mixture was now set aside for some weeks; the product was then collected, crystallised two or three times from methyl alcohol, and thus obtained in colourless needles, readily soluble in hot alcohol and melting at 121—123°.

Found, C = 65.70; H = 6.22.

$C_{15}H_5O_3(OEt)_4 \cdot C_2H_5O$  requires C = 65.78; H = 6.06 per cent.

To prepare the free tetraethyl ether, the acetyl compound was digested with boiling alcoholic potassium acetate, the solution poured into a small quantity of dilute hydrochloric acid and the product crystallised from methyl alcohol.

Found, C = 66.50; H = 6.63.

$C_{15}H_6O_3(OEt)_4$  requires C = 66.65; H = 6.28 per cent.

*Morin tetraethyl ether* forms pale yellow, prismatic needles, sparingly soluble in cold methyl alcohol, and melting at 126—128°. In general properties, it closely resembles the tetramethyl ether previously described (*loc. cit.*).

*The Bromination of Myricetin in the presence of Alcohol.*

A most interesting property of morin,  $C_{15}H_{10}O_7$ , the colouring matter of old fustic, is that when brominated in the presence of alcohol it yields tetrabromomorin ethyl ether,  $C_{15}H_5O_6Br_4 \cdot OEt$ . This peculiar behaviour, which is apparently not possessed by other flavanol derivatives, is considered by Herzig (*Monatsh.*, 1897, 18, 700) to render doubtful the constitution assigned to it by one of the authors (*Trans.*, 1896, 29, 792).

Being in possession of a small quantity of myricetin, which is apparently a flavanol derivative capable of yielding a tetrabromo-compound (*Trans.*, 1896, 69, 1287), the authors have studied its behaviour in these circumstances.

Myricetin (1.9 grams) in 20 c.c. of alcohol was treated with 3.4 grams of bromine and the mixture left for forty-eight hours, when on cautiously diluting with water a small quantity of crystalline precipitate gradually separated and was recognised as tetrabromomyricetin (*loc. cit.*); this was removed after some hours, the filtrate treated with a large volume of water, and a second deposit collected and crystallised two or three times from dilute alcohol.

Found, C = 31.29; H = 1.68; Et = 4.36.

$C_{15}H_5O_6Br_4Et$  requires C = 50.81; H = 1.51; Et = 4.38 per cent.

*Tetrabromomyricetin ethyl ether* formed colourless needles very soluble in alcohol; it becomes red at  $110^\circ$ , commences to sinter at  $132^\circ$ , and melts with decomposition at  $146^\circ$ . This melting point is given with reserve, owing to the possibility that a trace of tetrabromomyricetin itself may be associated with the product. The lack of raw material did not permit of further experiment, but the result indicates that in these circumstances myricetin behaves in an analogous manner to morin, though somewhat less readily.

*The Molecular Weights of Hesperitin and Curcumin.*

In a previous communication (*Trans.*, 1898, 31, 1031), it was shown that the properties of hesperitin were in accord with the constitution  $OH \cdot C_6H_3(OCH_3) \cdot CH:CH \cdot CO \cdot O \cdot C_6H_3(OH)_3$ , previously indicated by Hoffmann (*Ber.*, 1876, 9, 685) and Tiemann and Will (*ibid.*, 1881, 14, 848). The fact, however, that this substance gave well-defined crystalline salts having the formulæ  $(C_{16}H_{14}O_6)_2C_2H_3O_2K$  and

$C_{32}H_{27}O_{12}K$  suggested that its molecular weight was  $C_{32}H_{28}O_{12}$ , or twice that assigned to it by these authors.

More recently it was shown (Trans., 1903, 88, 127) that certain substances, the molecular weights of which were well known, also gave somewhat peculiar salts by similar methods. Thus from gallacetophenone,  $C_8H_8O_4$ , the salt  $C_{24}H_{23}O_{12}K$ , and from daphnetin,  $C_9H_6O_4$ , the salt  $C_{18}H_{11}O_8K$  resulted, and other cases might be cited. It was accordingly evident that these salts do not in all cases furnish trustworthy indications of the molecular weight, and cryoscopic experiments were therefore carried out, advantage being taken of the ready solubility of acetylhesperitin in naphthalene.

0.3351 in 13.90 naphthalene gave  $\Delta t - 0.375^\circ$ . Found,  $M = 449$ .

0.4310 ,, 13.87 naphthalene gave  $\Delta t - 0.490^\circ$ . Found,  $M = 443$ .

$C_{16}H_{11}O_6(C_2H_3O)_3$  requires  $M = 428$ .

It is consequently evident that the molecular weight of hesperitin is represented by the formula  $C_{16}H_{14}O_6$ , and that the above-mentioned potassium and sodium salts belong to the class of "semi-substituted" compounds (*loc. cit.*).

It has been shown by Ciamician and Silber (*Ber.*, 1897, 30, 192) that the molecular weight of curcumin is most probably represented as  $C_{21}H_{20}O_6$  rather than  $C_{14}H_{14}O_4$ , the formula originally assigned to it by Jackson and Menke (*Amer. Chem. J.*, 1882, 4, 77). Analyses of its mono-potassium salt (*loc. cit.*), although agreeing approximately with the formula  $C_{21}H_{19}O_6K$ , were not completely satisfactory, owing to the difficulty of purifying this somewhat soluble compound. It therefore appeared interesting to confirm these results, if possible, by the cryoscopic method, for which purpose a benzoylcurcumin would probably be suitable.

This derivative was readily prepared by treating 2 grams of curcumin dissolved in 30 grams of pyridine with 23 grams of benzoyl chloride. The product was washed with water, the viscous residue dissolved in alcohol, and the crystals, which gradually separated, were purified by crystallisation from a mixture of this solvent and benzene.

Found,  $C = 73.87$ ;  $H = 4.48$ .

$C_{21}H_{17}O_6(C_7H_5O)_3$  requires  $C = 74.11$ ;  $H = 4.70$  per cent.

*Benzoylcurcumin* consists of fine, lemon-yellow needles melting at  $176-178^\circ$ .

0.3256 in 13.23 naphthalene gave  $\Delta t - 0.25^\circ$ . Found,  $M = 688$ .

$C_{21}H_{17}O_6(C_7H_5O)_3$  requires  $M = 680$ .

These results therefore indicate that the molecular weight assigned



to curcumin by Ciamician and Silber is correct, and point to the fact that this colouring matter contains three hydroxyl groups, although only two have hitherto been suspected.

Curcumin itself is somewhat soluble in naphthalene, but apparently not sufficiently so for molecular weight determination; the cryoscopic experiments gave  $M = 429$ , whereas the formula  $C_{21}H_{20}O_6$  requires  $M = 368$ .

The isolation of curcumin from turmeric is at best a tedious operation, and as the yields obtained by the published methods were not satisfactory, the following process was adopted.

An alcoholic extract of turmeric was treated with lead acetate solution (Daube, *Ber.*, 1870, 3, 709), and the precipitated lead compound of the colouring matter collected, thoroughly washed with alcohol, and then with water. The product suspended in warm water was decomposed with dilute sulphuric acid, and the resulting mixture of curcumin and lead sulphate well washed, drained on porous tile, and extracted with boiling alcohol. After concentration, the extract was poured into ether, the solution decanted from tarry matter, evaporated to a small bulk, and diluted with carbon disulphide. The mixture, when left exposed to the air at the ordinary temperature, gradually deposited crystals, which were collected from time to time, and in this way a yield of approximately 0.56 per cent. of curcumin was isolated from the sample of root employed. Little or no loss should occur by this process, and the mother liquors contain only a trace of the so-called turmeric resin.

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