

## LXII.—*Colouring Matter from the Flowers of Delphinium Consolida.*

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IN a previous communication (Trans., 1898, 73, 267) it was shown that the flowers of *Delphinium zaili* contain as glucosides isorhamnetin, quercetin, and a trace of a third colouring matter. With the desire at the time to study the latter compound more closely, attention was directed to *Delphinium Consolida*, a plant more readily procurable, in the hope that it might contain the same constituents. Experiment showed that the blue flowers contained a moderate quantity of yellow colouring matter which differed in composition from that present in *Delphinium zaili*. This, judging from the melting point of its acetyl derivative, appeared to be a mixture, and as attempts to effect a separation of the substances failed, the subject was laid aside for some time. Recently it was found that the colouring matter was a single substance, and its investigation was therefore proceeded with. *Delphinium Consolida* is a common European plant belonging to the Larkspur family; its name refers to its powers, real or imaginary, of healing or consolidating wounds.

### EXPERIMENTAL.

The flowers themselves were first employed, but subsequently, to economise time and labour, an extract was obtained by purchase from Merck of Darmstadt.

Four hundred grams of this product dissolved in  $4\frac{1}{2}$  litres of boiling water were digested at the boiling point with 30 c.c. of sulphuric acid, causing the separation of a light coloured, viscous deposit and a considerable quantity of calcium sulphate. The hot liquid decanted from this was treated with 100 c.c. of sulphuric acid, again boiled for an

hour, and allowed to stand overnight. A dark brown, resinous precipitate containing the colouring matter was thus formed, and this was collected on calico, washed with water, extracted with boiling alcohol, and the extract evaporated to a small bulk. Addition of ether caused the deposition of a tarry product, and the ethereal solution was continuously washed with water until no further impurity separated in this manner. On evaporation, a semi-crystalline mass of the crude colouring matter was obtained, which was collected, well washed with water, and crystallised from dilute alcohol. In this way, 500 grams of the flowers gave 5.13 grams of crude colouring matter or approximately 1 per cent. The product was now converted into its acetyl derivative, and this, when colourless, reconverted into the colouring matter in the usual manner:

0.1128 at 160° gave 0.2614 CO<sub>2</sub> and 0.0319 H<sub>2</sub>O. C = 63.20; H = 3.14.  
 0.1086       "       0.2503 CO<sub>2</sub>   "   0.0345 H<sub>2</sub>O. C = 62.85; H = 3.53.  
 C<sub>15</sub>H<sub>10</sub>O<sub>6</sub> requires C = 62.93; H = 3.49 per cent.

It consisted of pale yellow needles resembling quercetin in appearance, melted at 276—277°, was readily soluble in boiling alcohol and dissolved in alkaline solutions with a pale yellow colour. Alcoholic lead acetate gave an orange precipitate, and alcoholic ferric chloride a greenish-black coloration. It contained no methoxy-group. Addition of potassium acetate to its boiling alcoholic solution caused the separation of minute, orange-yellow, prismatic needles, which were collected with the aid of the pump, washed with alcohol, then with a little water, and finally with alcohol, and dried at 160°:

0.3265 gave 0.0875 K<sub>2</sub>SO<sub>4</sub>. K = 12.01.  
 0.5085   "   0.1345 K<sub>2</sub>SO<sub>4</sub>. K = 12.04.  
 C<sub>15</sub>H<sub>9</sub>O<sub>6</sub>K requires K = 12.03 per cent.

This *monopotassium* salt closely resembles those of quercetin, morin, &c. (Trans., 1899, 75, 433), and is decomposed by water with separation of the free colouring matter.

On adding sulphuric acid to the substance suspended in boiling acetic acid, a *sulphate* was obtained crystallising in orange-red, glistening needles:

0.1159 gave 0.1985 CO<sub>2</sub> and 0.0354 H<sub>2</sub>O. C = 46.70; H = 3.39.  
 C<sub>15</sub>H<sub>10</sub>O<sub>6</sub>.H<sub>2</sub>SO<sub>4</sub> requires C = 46.87; H = 3.12 per cent.

The *hydrochloride* and *hydrobromide* were similarly prepared, but were not analysed, as they suffer decomposition at 100°. The *hydroiodide* was somewhat more stable:

0.1148 gave 0.1863 CO<sub>2</sub> and 0.0310 H<sub>2</sub>O. C = 44.25; H = 3.00.  
 C<sub>15</sub>H<sub>10</sub>O<sub>6</sub>.HI requires C = 43.48; H = 2.65 per cent.

*Action of Bromine.*—To the colouring matter suspended in acetic acid sufficient bromine was added to convert it into a tetrabromo-derivative, rise of temperature being avoided. After standing for 3 days, the product was drained on a porous tile, washed with alcohol, and purified by crystallisation from acetic acid with the aid of animal charcoal:

0.1177 gave 0.1492  $\text{CO}_2$  and 0.0190  $\text{H}_2\text{O}$ .  $\text{C} = 34.57$ ;  $\text{H} = 1.79$ .

0.1525 „ 0.1944  $\text{CO}_2$  „ 0.0185  $\text{H}_2\text{O}$ .  $\text{C} = 34.76$ ;  $\text{H} = 1.34$ .

$\text{C}_{15}\text{H}_7\text{O}_6\text{Br}_3$  requires  $\text{C} = 34.41$ ;  $\text{H} = 1.34$  per cent.

The *tribromo*-compound crystallises in pale yellow needles, sparingly soluble in boiling acetic acid and soluble in alkaline solutions with an orange-yellow coloration. It melts at  $275-277^\circ$ .

The colouring matter has thus the formula  $\text{C}_{15}\text{H}_{10}\text{O}_6$ , and from its reactions is probably a member of the quercetin group.

The *acetyl* derivative, prepared by heating the colouring matter with one part of anhydrous sodium acetate and three of acetic anhydride, crystallised from methyl alcohol in colourless needles. These, when heated, commenced to melt at  $116^\circ$ , became completely fluid at  $120^\circ$ ; on further heating, however, gradual solidification ensued, and the product subsequently melted at  $181-182^\circ$ . When ethyl alcohol was employed, this preliminary liquefaction was not so pronounced, and only a slight sintering at  $120^\circ$  was observed. Investigation showed that no loss in weight occurred during the preliminary fusion, and the resolidified product was not viscous as would be expected if an impurity of low melting point were present. The amount of impurity, if present, must have been infinitesimal, and all attempts to eliminate it were unsuccessful; moreover, there is evidence to show the product was a pure substance:

0.1065 gave 0.2368  $\text{CO}_2$  and 0.0400  $\text{H}_2\text{O}$ .  $\text{C} = 60.64$ ;  $\text{H} = 4.17$ .

$\text{C}_{23}\text{H}_{18}\text{O}_{10}$  requires  $\text{C} = 60.79$ ;  $\text{H} = 3.96$  per cent.

Acetyl determinations in the usual manner gave the following results, indicating that the compound was a *tetracetyl* derivative:

0.9453 gave 0.6018  $\text{C}_{15}\text{H}_{10}\text{O}_6$ .  $\text{C}_{15}\text{H}_{10}\text{O}_6 = 63.66$ .

4.2595 „ 2.6560  $\text{C}_{15}\text{H}_{10}\text{O}_6$ .  $\text{C}_{15}\text{H}_{10}\text{O}_6 = 62.36$ .

$\text{C}_{15}\text{H}_6\text{O}_6(\text{C}_2\text{H}_3\text{O})_4$  requires  $\text{C}_{15}\text{H}_{10}\text{O}_6 = 63.00$  per cent.

*Fusion with alkali* at  $200-220^\circ$  gave *phloroglucinol* (m. p.  $210^\circ$ ) and a crystalline acid melting at  $208-210^\circ$ . The identity of the latter with *p-hydroxybenzoic acid* was confirmed by analysis:

0.1114 gave 0.2480  $\text{CO}_2$  and 0.0394  $\text{H}_2\text{O}$ .  $\text{C} = 60.71$ ;  $\text{H} = 3.93$ .

$\text{C}_7\text{H}_6\text{O}_3$  requires  $\text{C} = 60.86$ ;  $\text{H} = 4.34$  per cent.

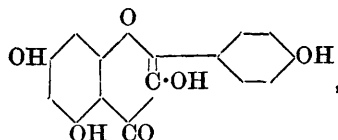
*Dyeing Properties.*—In investigating these, mordanted woollen cloth

was employed, and the shades obtained are described, together with those of morin, for the sake of comparison :

	Chromium.	Aluminium.	Tin.	Iron.
Colouring matter of } <i>Delphinium Consolida</i> }	Brownish-yellow.	Yellow.	Lemon-yellow.	{ Deep olive-brown.
Morin .....	Olive-yellow.	Dull yellow.	Bright yellow.	{ Deep olive-brown.

In this respect, therefore, these colouring matters are almost identical, morin, however, being stronger to a slight extent.

The reactions of the colouring matter  $C_{15}H_{10}O_6$  harmonised closely with those given by Gordin (*Diss., Berne*) to *kampherol*, which he prepared from the monomethyl ether, kampheride, contained in galanga root (*Alpinia officinarum*). Thus the melting points of these compounds and those of their acetyl derivatives are practically identical, and the decomposition products are the same in both cases. To kampherol, Kostanecki has given the following constitution as probable (*Ber.*, 1901, 34, 3723) :



it being thus the connecting link between apigenin (*Trans.*, 1897, 71, 805) and quercetin. An unsuccessful attempt was made to procure a copy of Gordin's dissertation, but an extract evidently taken from it is given in *Der Chemie der natürlichen Farbstoffe*, 1900, p. 80. In this description, the only distinction of importance between the colouring matter under discussion and kampherol is to be found in the account given of the dyeing properties of the latter, regarding which the following sentence occurs: "Kämpferid sowohl wie Kämpferol färben Thonerdebeize schwach gelb an." As this is not in harmony with the above results, it was necessary to prepare some kampheride, and from this kampherol.

In isolating the constituents of galanga root, its ethereal extract was treated according to the method given by Ciamician and Silber (*Ber.*, 1899, 32, 861). Possibly the quality of the root varies, for the process employed by these authors was not entirely satisfactory. Thus the extract diluted with benzene gave a semi-crystalline precipitate, devoid of kampheride, which, after purification, melted at 292—295°, gave an acetyl compound melting at 175—176°, and was identical with the galangin monomethyl ether described by Testoni (*Gazzetta*, 1900, 30, ii, 327—329). The filtrate, on addition of light petroleum, deposited a brown tar, and this, on solution in hot chloroform, gave, on cooling, a precipitate containing kampheride and galangin, which were

separated by fractional crystallisation from alcohol. The kampheride thus obtained melted at  $223\text{--}226^\circ$ , and the kampherol prepared from it at  $271\text{--}272^\circ$ . The latter possessed well marked dyeing properties, identical in all respects with those of the colouring matter of *Delphinium Consolida*, and there can be no doubt that the two are identical.

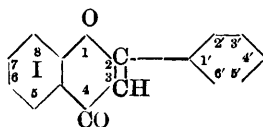
A study of the acetyl derivative of kampherol from kampheride showed that this, when crystallised from methyl alcohol, had the same double melting point as that described above; further, the acetyl compound of kampherol obtained from robinin (this vol., p. 475) behaved similarly. It thus appears that this is a definite property of the substance.

Molisch and Goldschmiedt (*Monatsh.*, 1901, 22, 679) have recently described a colouring matter, scutellarein, which exists in the form of its glucoside, scutellarin, in the *Scutellaria altissima*. This has the same formula and general reactions as kampherol, and yields the same decomposition products, but melts at above  $300^\circ$ . To be certain that the melting point of kampherol here given was correct, a sample was treated in numerous ways; for example, with hydriodic acid, then converted into its sulphate and into its potassium compound, then crystallised from acetic acid, &c., but the melting point was practically unaltered, the final product melting at  $276\text{--}277^\circ$ . Scutellarein and kampherol, therefore, cannot be identical.

Attempts to isolate the glucoside of kampherol which exists in the *Delphinium Consolida* have not yet been successful, but the results show that this compound is not robinin.

#### *The Dyeing Properties of some Members of the Flavone Group.*

Being in possession of the galangin prepared as above, we studied its dyeing properties, with the object of gaining further insight into the functions in this respect of the various hydroxyl radicles contained in the compounds previously studied. Woollen cloth similarly mordanted (mordanted calico, so frequently employed by others, is of little service for comparing the members of this group) was employed in each case, and the experiments were carried out, as far as possible, in an identical manner. The positions of the hydroxyl radicles are indicated by the numbers in the following formula:

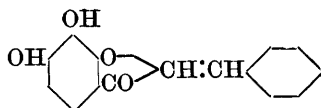


	Chromium.	Aluminium.	Tin.	Iron.
Chrysin, $C_{15}H_8O_2(OH)_2$ ..... [5:7]	Yellow, faint orange tint.	Pale yellow.	Undyed.	Pale chocolate.
Apigenin, $C_{15}H_8O_2(OH)_3$ ... [5:7:4']	„	Pale yellow, slightly stronger.	„	Chocolate- brown.
Luteolin, $C_{15}H_8O_2(OH)_4$ ... [5:7:4':5']	Brown- orange.	Orange- yellow.	Bright yellow.	Olive-black.
Galangin, $C_{15}H_8O_2(OH)_3$ ... [5:7:3]	Olive yellow.	Yellow.	Lemon- yellow.	Deep olive.
Kampherol, $C_{15}H_8O_2(OH)_4$ . [5:7:3:4']	Brown- yellow.	„	Lemon- yellow.	Deep olive- brown.
Morin, $C_{15}H_6O_2(OH)_6$ ..... [5:7:3:2':4']	Olive-yellow.	Dull yellow.	Bright yellow.	Deep olive- brown.
Quercetin, $C_{15}H_8O_2(OH)_5$ ... [5:7:3:3':4']	Red-brown.	Brown- orange.	Bright orange.	Olive-black.
Myricetin, $C_{15}H_4O_2(OH)_6$ ... [5:7:3:3':4':5']	„	„	Bright red- orange.	Olive-black.
Rhamnetin, $C_{16}H_8O_3(OH)_4$ . [5:8:3:4']	„	„	Bright orange.	Deep olive.
Fisetin, $C_{15}H_8O_2(OH)_4$ ..... [7:3:3':4']	„	Reddish- brown-orange	Bright red- orange.	Olive-black.

Certain other colouring matters, as apigenin monomethyl ether (Trans., 1900, 77, 430), kampheride, galangin monomethyl ether, *is*-rhamnetin, rhamnazin, &c., could be added to this list, but are omitted, as the above form a complete series. Only five of these colouring matters, luteolin, fisetin, rhamnetin, quercetin, and myricetin, contain two hydroxyl radicles in the ortho-position relatively to one another, a condition which Liebermann and Kostanecki noted to be essential in the case of the anthraquinone dyestuffs.

Although this factor, doubtless, exercises a strengthening effect in the dyestuffs of the flavone series, it is not a necessity, as is specially evident in the cases of morin and kampherol, the former of which, occurring as it does in old fustic, is still most extensively employed in the dyeing industry. An interesting point is the marked increase in tinctorial property associated with the presence of hydroxyl in position 3, as is at once observed between chrysin and galangin, apigenin and kampherol, and no doubt exists between lotoflavin,  $C_{15}H_6O_2(OH)_4$  [5:7:2':4'] (Dunstan and Henry, *Proc. Roy. Soc.*, 1901, 68, 374), and morin; this is again to be seen in the case of luteolin and quercetin, for its presence in the latter gives strength and redness to the shades. It will be noted from the above examples that a multiplication of hydroxyl radicles in the flavone series does not by any means exert such a marked tinctorial effect as is observed in the anthraquinone group (compare, for instance, alizarin, anthragallol, and alizarin-cyanine R); this is evident by the almost identical character of the shades given by apigenin and chrysin, by fisetin,

quercetin, rhamnetin, and myricetin, and by galangin, kampherol, and morin. The introduction of hydroxyl in the positions 4' and 4':2', in galangin, with the respective formation of kampherol and morin, certainly exerts some strengthening effect, but on the other hand fisetin, quercetin, and myricetin do not materially differ in strength of shade. It is likely, however, that hydroxyl radicals in ortho-positions relatively to one another in the nucleus I (p. 589) would exert a more marked effect on the shade, for the benzylideneanhydroglycogallol,



(Friedländer and Rudt, *Ber.*, 1896, 29, 878), a member of a closely allied group, yields powerful and characteristic colours. The dyeing properties of these and other phenolic compounds are intimately connected with their property of forming monosubstituted salts (*Trans.*, *loc. cit.*); this question will be discussed in a further communication, which it is hoped will be laid before the Society at an early date.

A preliminary investigation of the flowers of *Prunus spinosa* has shown that these contain an apparently new colouring matter, which in its general reactions resembles kampherol. This will be further investigated.

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