

LXXIX.—*The Colouring Matters contained in Dyer's Broom (*Genista tinctoria*) and Heather (*Calluna vulgaris*).*

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IN addition to the well known natural dyestuffs now found in commerce, numerous other plants were formerly employed in Europe for dyeing purposes; as some of these have not been previously studied, it was of interest to submit them to examination, and an account is here given of the colouring matter of dyer's broom and heather.

I. DYER'S BROOM.

Genista tinctoria (dyer's broom, dyer's greenweed; genet, genestrole, trentanel, Fr.; Ginster, Germ.) is found in the pastures, thickets, and waste places throughout Central and Southern Europe, across Russian Asia to the Baikal, and northward to Southern Sweden. It is frequent in the greater part of England, but rare in Ireland and Scotland. Although not previously studied, the fact that it contains a yellow colouring matter is recorded by numerous writers, and the following embody the principal references to the dyeing and general properties of the plant: Bancroft (*Philosophy of Permanent Colours*, 1813, 2, 108), Gmelin (*Handbook of Chemistry*, 16, p. 517), Berthelot (*On Dyeing*, 1824, 2, p. 242), Gonfreville (*Art de la teinture de laines*, p. 501), Leuchs (*Farben u. Farbekunde*, 1846, 2, 309), and Schutzenberger (*Traite de matieres colorantes*, 1867, 4, 422). The following interesting statement occurs in Kane's *Elements of Chemistry* (1849, p. 933), and no doubt owes its origin to the very similar dyeing properties of both plants: "Luteolin is the colouring matter of the weld, and probably of the dyer's broom."

For purposes of extraction, the plant is best cut into small pieces; it should not be ground, for in this condition it is converted by hot water into a viscous mass extremely difficult to manipulate. Quantities of 1 kilo. at a time were digested for 6 hours with 10 kilos. of boiling water, the extract treated with 10 c.c. of glacial acetic acid, and then with excess of lead acetate solution. A pale yellow, viscous precipitate separated, and this was collected and washed with water, the filtrate A being reserved for examination. The product, made into a thin cream with water, was decomposed by boiling dilute sulphuric acid, the lead sulphate removed, and the filtrate allowed to cool; the dull yellow precipitate which separated was collected, dissolved in a little alcohol and poured into ether, which caused the separation of a

dark coloured, resinous substance; this was removed, and the clear liquid washed with water until the washings were colourless. On evaporating the ether, a yellow, crystalline mass remained containing two substances, one yellow, B, and the second, C, colourless or nearly so. The latter, being more soluble, could be partially removed by fractional crystallisation from dilute alcohol, and this process was resorted to at first, but subsequently advantage was taken of the fact that B with sulphuric acid, in the presence of acetic acid, forms a sparingly soluble sulphate, whilst C does not react with the acid and remains in solution.

The sulphate of B was collected, washed with acetic acid, decomposed by water, and the regenerated colouring matter crystallised from dilute alcohol.

0.1091 gave 0.2526 CO_2 and 0.0381 H_2O . C = 63.14; H = 3.87.

$\text{C}_{15}\text{H}_{10}\text{O}_6$ requires C = 62.93; H = 3.50 per cent.

It was obtained in glistening, yellow needles, readily soluble in alcohol, and soluble in alkali solutions with a yellow coloration. With alcoholic lead acetate, a yellow precipitate was formed, and alcoholic ferric chloride yielded first a green and then a brownish-red coloration. Potassium acetate, in the presence of alcohol, gave a gelatinous precipitate of a potassium salt too soluble for examination.

Tetracetyl Compound.—When the substance B was digested with acetic anhydride and sodium acetate in the usual manner, an acetyl compound was obtained, crystallising from alcohol, in which it was very sparingly soluble, in colourless needles melting at 221—223°.

0.123 gave 0.273 CO_2 and 0.046 H_2O . C = 60.52; H = 4.15.

$\text{C}_{15}\text{H}_6\text{O}_6(\text{C}_2\text{H}_3\text{O})_4$ requires C = 60.79; H = 3.96 per cent.

The acetyl groups were estimated by hydrolysis with sulphuric acid.

0.8665 gave 0.551 $\text{C}_{15}\text{H}_{10}\text{O}_6$. Found, 63.58.

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

On fusion of the substance B with alkali at 220°, *phloroglucinol* (m. p. 210°) and *protocatechuic acid* (m. p. 194—196°) formed the main products of the decomposition.

These results suggested that the colouring matter $\text{C}_{15}\text{H}_{10}\text{O}_6$ was identical with the luteolin of weld, and its acid compounds were examined, for it has been shown by one of us (*Trans.*, 1896, 69, 208) that, whereas the sulphate and hydriodide of luteolin have the formulæ $\text{C}_{15}\text{H}_{10}\text{O}_6, \text{H}_2\text{SO}_4$ and $\text{C}_{15}\text{H}_{10}\text{O}_6, \text{HI}$ respectively, the hydrochloride and hydrobromide are peculiar in crystallising with $1\text{H}_2\text{O}$, and differ in this respect from the acid compounds of all other yellow colouring matters at present examined.

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The *sulphate* formed orange-red needles, rapidly decomposed by water.

0.1332 gave 0.2285 CO_2 and 0.0345 H_2O . C = 46.78 ; H = 2.87.

$\text{C}_{15}\text{H}_{10}\text{O}_6, \text{H}_2\text{SO}_4$ requires C = 46.87 ; H = 3.12 per cent.

The *hydriodide* was obtained in glistening, orange plates.

0.1304 gave 0.2065 CO_2 and 0.0308 H_2O . C = 43.18 ; H = 2.62.

$\text{C}_{15}\text{H}_{10}\text{O}_6, \text{HI}$ requires C = 43.47 ; H = 2.65 per cent.

The *hydrochloride* was an ochre-coloured mass of fine needles, and, as is the case with luteolin, an excess of acid was necessary for its formation. It is decomposed by water somewhat slowly.

0.1137 gave 0.2177 CO_2 and 0.0325 H_2O . C = 52.30 ; H = 3.17.

$\text{C}_{15}\text{H}_{10}\text{O}_6, \text{HCl} + \text{H}_2\text{O}$ requires C = 52.70 ; H = 3.81 per cent.

These reactions prove without doubt that the colouring matter $\text{C}_{15}\text{H}_{10}\text{O}_6$ of the *Genista tinctoria* is *luteolin*, and a comparison of its dyeing properties with those of luteolin prepared from weld (*Reseda luteola*) further corroborated this fact. Woollen cloth mordanted with chromium, aluminium, tin, and iron compounds was employed, and the shades, which have not been described previously, are given, together with those of quercetin, for the sake of comparison.

Chromium.	Aluminium.	Tin.	Iron.
Luteolin..	Brown-orange.	Orange-yellow.	Bright yellow.
Quercetin	Red-brown.	Brown-orange.	Bright orange.

The yield of luteolin by the above method was small, 1000 grams of the plant giving only 3.7 grams of the crude substance, which was reduced to about 2.8 grams on purification. It is interesting to note that, previously, luteolin has only been known to occur in weld.

The More Soluble Colouring Matter.

The substance C (page 831) contained in the dilute alcoholic mother liquors from the purification of the luteolin was also present in considerable quantity in the filtrate (A) from the lead precipitate, from which it was isolated as follows. To the boiling liquid, ammonia was added, causing the separation of a voluminous lemon-yellow precipitate, which was collected, washed with water, and decomposed with boiling dilute sulphuric acid. The clear liquid, decanted from the lead sulphate, was extracted with ether, and the extract evaporated, leaving a brownish, crystalline mass, which was washed on the pump, first with water, then with dilute alcohol, and dried. The crude product isolated by these methods was dissolved in boiling acetic acid, the brown solution treated with animal charcoal, and evaporated to a

small bulk ; when left overnight, a semi-solid mass of needles separated, which was collected, washed with a little acetic acid, and then with water. With the object of removing any traces of luteolin, a small quantity of lead acetate was added to an alcoholic solution of the product, and the filtrate, after the addition of acetic acid, was evaporated to a small bulk and diluted with boiling water. The long, glistening needles which separated on cooling had still a faint brown tint, and to remove this the compound was converted into its acetyl derivative, which, after purification, was hydrolysed in the usual manner, the regenerated colouring matter being finally crystallised from dilute alcohol.

0.1152 gave 0.2746 CO_2 and 0.0380 H_2O . C = 65.00 ; H = 3.66.

0.1131 ,, 0.2706 CO_2 ,, 0.0420 H_2O . C = 65.25 ; H = 4.12.

$\text{C}_{14}\text{H}_{10}\text{O}_5$ requires C = 65.11 ; H = 3.87 per cent.

This new colouring matter, for which the name *genistein* is proposed, crystallises in long, glistening, colourless needles sparingly soluble in cold alcohol or acetic acid, and almost insoluble in water. An alcoholic solution gives, with basic lead acetate, a lemon-yellow precipitate, but with the neutral salt, except in large excess, only a slight separation is obtained. It is soluble in alkalis or in cold sulphuric acid, forming pale yellow solutions, and in cold nitric acid of sp. gr. 1.42, giving a dull brown coloration. With alcoholic potassium acetate, no potassium salt is produced, and with mineral acids in the presence of acetic acid, no acid compounds separate ; the conclusion is therefore drawn that the hydroxyl groups in this compound are not present in relatively ortho-positions (this vol., 450). Alcoholic ferric chloride gives a dull reddish-violet coloration, which, on addition of excess of the reagent, becomes somewhat olive in tint. Genistein does not contain a methoxy-group.

Triacetylgenistein.—In the preparation of this derivative, the use of sodium acetate was not beneficial ; the colouring matter was therefore digested with boiling acetic anhydride for 6 hours, the solution evaporated to a small bulk, alcohol added, and the crystalline separation collected and digested with a fresh quantity of the anhydride for 2 hours. The product, purified by crystallisation from alcohol, consisted of colourless needles melting at 197—201° and sparingly soluble in alcohol.

0.1145 gave 0.2622 CO_2 and 0.0448 H_2O . C = 62.45 ; H = 4.34.

$\text{C}_{14}\text{H}_7\text{O}_5(\text{C}_2\text{H}_3\text{O})_3$ requires C = 62.50 ; H = 4.17 per cent.

The acetyl groups were estimated by hydrolysing the compound with hydrochloric acid in the presence of boiling acetic acid, a method previously found serviceable in the analysis of tetracetylmorin (this

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vol., 448), and necessary owing to the tendency of the product to become sulphonated when sulphuric acid is employed.

0.5396 gave 0.3670 $C_{14}H_{10}O_5$. Found, 68.01.

$C_{14}H_7O_5(C_2H_3O)_3$ requires $C_{14}H_{10}O_5 = 67.19$ per cent.

To obtain with some certainty a clue to the molecular weight of this colouring matter, its behaviour towards diazobenzene was studied, but the reddish-brown product was unfortunately of a resinous nature and not readily purified. Sufficient material was not available for further work in this direction, but if possible the reaction will be again investigated.

Tetrabromogenistein.—The colouring matter, made into a thin paste with acetic acid, was treated with bromine in excess; hydrogen bromide was at once evolved, and the mixture was allowed to stand for three days with frequent stirring. The product was drained on a porous tile, washed with boiling alcohol, crystallised first from a large volume of acetic acid, and finally from nitrobenzene. It forms a glistening mass of colourless needles melting above 290° , dissolves in dilute alkalis with a pale yellow colour, and is very sparingly soluble in boiling alcohol or acetic acid, but more readily in nitrobenzene. It does not dye mordanted calico.

0.1133 gave 0.1237 CO_2 and 0.0162 H_2O . $C = 29.77$; $H = 1.58$.

$C_{14}H_6Br_4O_5$ requires $C = 29.27$; $H = 1.04$ per cent.

Decomposition Products of Genistein.

The substance was digested with boiling aqueous caustic potash of sp. gr. 1.46 for half an hour, or until the solution, which at first was yellow, had become brown, and on treatment with acid no longer gave a crystalline precipitate on cooling. The product, after neutralisation, was extracted with ether, the extract evaporated, the crystalline residue dissolved in water, and the solution saturated with sodium bicarbonate. Agitation with ether removed from this liquid a crystalline substance which after purification formed colourless needles melting at 210° and having the reactions of *phloroglucinol*. From the residual aqueous solution by acidification, and extraction with ether, a crystalline acid was isolated, which, after repeated crystallisation from water, formed long, thin, colourless leaflets melting at $147-149^\circ$.

0.0998 gave 0.2314 CO_2 and 0.0513 H_2O . $C = 63.23$; $H = 5.71$.

$C_8H_8O_3$ requires $C = 63.15$; $H = 5.26$ per cent.

To ascertain its constitution, the acid was submitted to prolonged fusion with caustic potash at 240° . The product, isolated by solution in water, acidification, and extraction with ether, formed almost colour-

less needles melting at 208—210°, and was identified as *parahydroxybenzoic acid*. There is little doubt therefore that the acid melting at 147—149° was identical with Salkowski's *parahydroxyphenylacetic acid* (*Ber.*, 1879, 12, 1438), obtained by the action of nitrous acid on paramidophenylacetic acid.

As was to be expected, the action of fused alkali at 240° on genistein gave phloroglucinol and parahydroxybenzoic acid.

Methylation of Genistein.

Genistein, dissolved in a solution of caustic potash (5 mols.) in methylic alcohol, was digested at the boiling point with excess of methylic iodide for three days. The product, after evaporation to a small bulk, became semi-solid, owing to the separation of crystals, which were collected by the aid of the pump, and washed first with a little dilute alcohol, and then with aqueous caustic potash. When crystallised from alcohol, the main bulk (D) melted at 137—139°, but a trace of a less soluble substance (E) melting at 187—189° was also present.

Analyses of D showed it to be *genistein dimethyl ether*. It crystallised in colourless leaflets, melted at 137—139°, and was readily soluble in alcohol, but insoluble in aqueous solutions of alkalis.

0.1039 gave 0.2547 CO₂ and 0.0433 H₂O. C = 66.85; H = 4.63.

0.1472 „, by Zeisel's method, 0.2560 AgI. CH₃ = 10.52.

C₁₄H₉O₃(OCH₃)₂ requires C = 67.13; H = 4.89; CH₃ = 10.48 per cent.

An analysis of the regenerated genistein from the Zeisel determination gave the following numbers:

0.1004 gave 0.2398 CO₂ and 0.0358 H₂O. C = 65.09; H = 3.96.

C₁₄H₁₀O₅ requires C = 65.11; H = 3.87 per cent.

As genistein contains three hydroxyl groups, it was evident that one had resisted methylation, and to confirm this point a small portion of the dimethyl ether was boiled with acetic anhydride and sodium acetate. The product crystallised from alcohol in minute, colourless needles melting at 202—204°

0.1140 gave 0.2773 CO₂ and 0.0485 H₂O. C = 66.33; H = 4.72.

0.1181 „, 0.2855 CO₂ „, 0.0520 H₂O. C = 65.93; H = 4.89.

C₁₄H₇O₃(C₂H₅O)(OCH₃)₂ requires C = 65.86; H = 4.84 per cent.

Sufficient material has not yet been available for an acetyl determination, but the compound was proved to be an acetyl derivative by hydrolysis in the usual manner; the regenerated product melted at 137—139°, and was identical with the dimethyl ether just described.

These reactions, whilst confirming the presence of three hydroxyl

groups in genistein, indicate that one of them is in the ortho-position relatively to a carbonyl group. An alcoholic solution of the ether, when treated with alcoholic potash, gives only a pale yellow liquid, and no insoluble potassium salt is precipitated.

The more insoluble substance, E, melting at 187—189° gave the following results on analysis:

0.1023 gave 0.2518 CO₂ and 0.0442 H₂O. C = 67.12; H = 4.80.

0.1537 „ 0.2440 AgI. CH₃ = 10.13.

C₁₄H₈O₅(OCH₃)₂ requires C = 67.13; H = 4.89; CH₃ = 10.48 per cent.

It is not dissolved by alkali solutions, and is apparently a second *genistein dimethyl ether*. As its melting point was very similar to that of the corresponding luteolin ether (Trans., 1896, 69, 211), and the contamination of the genistein employed with a trace of luteolin was possible, the regenerated colouring matter from the Zeisel determination was analysed, and proved apparently to be genistein.

0.0986 gave 0.2371 CO₂ and 0.0353 H₂O. C = 65.57; H = 3.97.

C₁₄H₁₀O₅ requires C = 65.11; H = 3.87 per cent.

As the yield of this second ether was exceedingly small, amounting in all to not more than 0.5 gram, its further study has been impossible. It is conceivable that it is a dimethyl ether of a methylgenistein, a methyl group having entered the ring during methylation.

Dyeing Properties.

Although genistein is but a feeble dye-stuff, its tinctorial properties are important in connection with its constitution. The shades on mordanted woollen cloth resemble in general character those given by apigenin and vitexin.

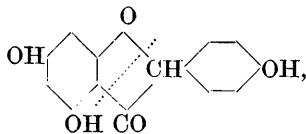
	Chromium.	Aluminium.	Tin.	Iron.
Genistein.	Pale greenish-yellow.	Very pale yellow.	Not dyed.	Chocolate brown.
Vitexin.	Greenish-yellow.	Pale bright yellow.	Very pale yellow.	Pale brown, somewhat dull.
Apigenin.	Yellow, with faint orange tint.	Pure yellow.	Not dyed.	Chocolate brown.

All these colouring matters yield parahydroxybenzoic acid on decomposition, and to the phenol nucleus which they contain must be due the power they have of producing chocolate brown shades with the iron mordant.

Theoretical Considerations.

The results of this investigation indicate that genistein contains three hydroxyl groups, one being in the ortho-position relatively to a carbonyl group, and that on decomposition it yields phloroglucinol

and parahydroxyphenylacetic acid. Its dyeing properties, so closely resembling those of chrysin and apigenin, prove that it is not a simple ketone, for such a compound devoid of orthohydroxyl groups could not be a colouring matter. Most probably it is a trihydroxyphenylketocumarin.



the parent substance of which, ketocumarin, has been prepared and investigated by Friedlander and Neudörfer (*Ber.*, 1897, 30, 1077). This constitution explains the formation of phloroglucinol and parahydroxyphenylacetic acid, and is in harmony with the results at present obtained. Various points of interest have yet to be studied before the formula is completely established; the work, however, can proceed but slowly, on account of the long operations involved in the preparation of pure genistein.

Dyeing Properties of Genista tinctoria.—Experiments carried out in the usual manner indicated, as was to be expected, a close resemblance in this respect between dyer's broom and weld. The dyeing power of the former was distinctly the weaker of the two; otherwise, the only point of difference worthy of mention was that shown by the iron mordant, which, in the case of dyer's broom, gave a duller and more drab-coloured shade, and was evidently due to the genistein present.

II. HEATHER.

In former times, the common heath or heather, until recently named *Erica vulgaris*, was used as a dye-stuff, producing a yellow colour upon woollen goods (Crookes, *Dyeing and Calico Printing*, 1874, p. 511). Although now almost superseded, it was until recently employed in the home industries of outlying districts, such as the Highlands of Scotland. Bancroft (*Philosophy of Permanent Colours*, 1813, 2, 108) states that all five species of the erica or heather found in Great Britain are, he believes, capable of giving yellows much like those obtained with dyer's broom. According, however, to the experiments of J. J. Hummel (private communication), the *Erica tetralix* (bell-heather) and *E. cinerea* contain only traces of yellow colouring matter. Leuch refers to the tanning property of heather (*Farben u. Farbekunde*, 2, 320), and notes that the effect resembles in character that given by oak bark.

Experiment showed that the colouring matter was contained in the

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green portion of the plant, and this alone was therefore employed for investigation. One colouring matter only was present, and this was extracted with boiling water, isolated by the method described for the preparation of luteolin from dyer's broom, and purified by crystallisation from dilute alcohol.

0·1245 gave 0·2721 CO_2 and 0·0424 H_2O . C = 59·60 ; H = 3·78.

$\text{C}_{15}\text{H}_{10}\text{O}_7$ requires C = 59·60 ; H = 3·31 per cent.

It formed a glistening mass of yellow needles, sparingly soluble in water, but somewhat readily so in alcohol. In alcoholic solution, ferric chloride caused a dark green coloration, and lead acetate gave an orange-yellow precipitate. The *acetyl* derivative, prepared in the usual manner, crystallised from alcohol in colourless needles melting at 191°.

0·1102 gave 0·2368 CO_2 and 0·0381 H_2O . C = 58·60 ; H = 3·84.

$\text{C}_{15}\text{H}_9\text{O}_7(\text{C}_2\text{H}_3\text{O})_5$ requires C = 58·59 ; H = 3·90 per cent.

By fusion with alkali, two crystalline products were obtained, melting respectively at 210° and 195—196°; these consisted of *phloroglucinol* and *protocatechuic acid*. These results, together with comparative dyeing trials, prove that the colouring matter of the *Calluna vulgaris* is *quercetin*.

Dyeing Properties.

The dyeing properties of heather, although distinctly weaker, are so similar in character to those given by quercitron bark as to require no special description. Experiment showed that 36 parts of the heather were necessary to obtain as good a result as that given by 10 parts of quercitron bark.

Tanning Properties.—We are indebted to Prof. H. R. Procter for an analysis and examination of the tanning properties of heather :

Tanning matters absorbed by hide	6·4 per cent.
Soluble non-tanning matters	15·2 „
Insoluble at 60° F.	70·4 „
Water	8·0 „
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	100·0

The leather, produced in the usual manner, although of a good colour, was very imperfectly tanned, and it appears that a large quantity of material and long tannage would be necessary for the production of a practically useful material. An infusion gives

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a precipitate with bromine water and a green-black coloration with iron alum, reactions characteristic of a catechol tannin.

The investigation of dye-stuffs of a similar character will be undertaken as opportunity occurs.

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