CI. GALUTEOLIN, A NEW GLUCOSIDE FROM *GALEGA OFFICINALIS*.

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DURING the preparation of galegine from the seeds of *Galega officinalis* (see the preceding paper) a yellow colouring matter was detected and identified as a new glucoside of luteolin, for which the name *galuteolin* is suggested. It gave a green coloration with ferric chloride, characteristic of catechol derivatives, and was accordingly precipitated by normal lead acetate in the preliminary purification for the isolation of galegine.

Isolation. The precipitate with normal lead acetate, obtained from the extract of six kilos. of seeds, was air-dried, finely ground and extracted several times with boiling dilute acetic acid, in which it was almost wholly soluble. After removal of the lead by hydrogen sulphide and concentration of the filtrate to a small bulk, a yellow solid separated, in a yield of 2 g. This was insoluble in water, and very slightly soluble in absolute alcohol, but more so in hot dilute alcohol from which it crystallised in aggregates of yellow needles melting with decomposition at 280°. These crystals gave the original olive green coloration with ferric chloride, and a yellow precipitate with normal lead acetate, soluble in hot dilute acetic acid. They reduced Fehling's solution and ammoniacal silver nitrate, and dissolved in alkalis with a deep yellow colour. On boiling a small portion with dilute sulphuric acid, cooling and filtering, the filtrate gave Molisch's reaction, suggesting that the colouring matter was a glucoside.

Galuteolin crystallises with 3 molecules of water, of which $2\frac{1}{2}$ are lost at 120–130°, but the remaining $\frac{1}{2}\text{H}_2\text{O}$ is only removed with great difficulty. This behaviour is similar to that of the glucosides osyretin and violaquercitrin recorded by A. G. Perkin [1902] which both lose $2\frac{1}{2}\text{H}_2\text{O}$ at 130° but the remaining $\frac{1}{2}\text{H}_2\text{O}$ only at 160°. As our glucoside was not stable at the latter temperature, we preferred to dry it at the temperature of boiling tetrachloroethane *in vacuo* over phosphorus pentoxide.

0.1254 air-dry lost 0.0111 at 120–130°;	$\text{H}_2\text{O} = 8.85\%$.
Calculated for $\text{C}_{21}\text{H}_{20}\text{O}_{11} \cdot 3\text{H}_2\text{O}$	$2\frac{1}{2}\text{H}_2\text{O} = 8.96$.
0.1137, dried as above, lost 0.0022 <i>in vacuo</i> over P_2O_5 ;	$\text{H}_2\text{O} = 1.93$.
Calculated for $\text{C}_{21}\text{H}_{20}\text{O}_{11} \cdot \frac{1}{2}\text{H}_2\text{O}$	$\frac{1}{2}\text{H}_2\text{O} = 1.97$.

For analysis the glucoside dried at 120–130° was employed.

0.1480 gave 0.2978 CO₂ and 0.0594 H₂O; C = 54.9; H = 4.5%.

0.1538 „ 0.3104 CO₂ „ 0.0635 H₂O; C = 55.0; H = 4.6.

Calculated for C₂₁H₂₀O₁₁ · $\frac{1}{2}$ H₂O C = 55.1; H = 4.6.

A methoxy determination yielded a negative result.

Hydrolysis of galuteolin. This proceeds readily with quite dilute sulphuric acid [compare A. G. Perkin, 1909].

0.2904 (dried at 120°) was boiled with 20 cc. of 3 % sulphuric acid for 3 hours. The solution was cooled and the precipitate collected and dried; it weighed 0.1808 = 62.3 %.

Calculated for C₂₁H₂₀O₁₁ · $\frac{1}{2}$ H₂O C₁₅H₁₀O₆ = 62.6 %.

The hydrolysis is therefore represented by the equation:

After removal of the sulphuric acid, the filtrate yielded a phenylosazone, which on recrystallisation from alcoholic pyridine melted at 203°. Mixed with a sample of phenylglucosazone it melted at 204°. The sugar is therefore glucose.

The greater part of the available glucoside was now hydrolysed, the resulting insoluble colouring matter crystallising from dilute alcohol in small needles of indefinite melting point, blackening at 290–300°.

After several crystallisations it was dried at 120° and analysed:

0.1305 gave 0.3002 CO₂ and 0.0451 H₂O; C = 62.7; H = 3.8 %.

0.1306 „ 0.3008 CO₂ „ 0.0463 H₂O; C = 62.8; H = 3.9.

Calculated for C₁₅H₁₀O₆ C = 62.9; H = 3.5.

The fission product is readily and completely acetylated by boiling for a minute with acetic anhydride and a drop of pyridine or trace of concentrated sulphuric acid. The acetyl compound, crystallised from absolute alcohol, forms long colourless needles, m.p. 221–223°.

0.1400 gave 0.3104 CO₂ and 0.0496 H₂O; C = 60.4; H = 3.9 %.

Calculated for C₁₅H₆O₆(C₂H₃O)₄ C = 60.8; H = 4.0.

The composition and melting point of the acetyl derivative suggested that the fission product was *luteolin*, and this identity was confirmed by comparison with a specimen of luteolin, for which we are indebted to the kindness of Prof. A. G. Perkin, F.R.S. A portion of the latter specimen was acetylated, and the acetyl derivative, from both sources as well as the mixture, melted at 221–223°.

Sublimation of hydroxyflavones. Before the definite identification of the fission product of our glucoside with luteolin we had already compared it with other hydroxyflavones by a method which does not seem to have been previously employed in this group. We found that in a high vacuum most hydroxyflavones may be sublimed without decomposition. We simply heated minute quantities in a test tube in a metal bath, evacuating with a rotary oil pump (pressure < 1 mm.). The temperature (of the bath) at which sub-

limation takes place, as well as the colour shade of the sublimate, is characteristic, for instance:

	Chrysin	Luteolin	Apigenin	Fisetin
Sublimes at	220°	250–270°	230–290°	230–330°
Resublimes at	220	230–235	260–270	280–290
Colour of sublimate	Almost white	Faint yellow white	Yellowish white	Brownish yellow

Since the melting points of hydroxyflavones are often very high their “mixed” melting points are unsatisfactory. Comparative sublimation (two tubes in the same bath) can be readily carried out with minute quantities.

We found that when galuteolin was similarly heated *in vacuo* a sublimate of luteolin appeared on the sides of the tube at the same temperature as before, and a tarry residue of decomposed sugar remained on the bottom.

In addition to galuteolin, luteolin itself was present in the extract of the seeds. Luteolin has been found previously in a number of plants (*Reseda luteola*, *Genista tinctoria*, *Digitalis purpurea*) but no glucoside of luteolin seems to have been isolated hitherto.

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REFERENCES.

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