

CXIII.—*Some Constituents of the Root of Polygonum cuspidatum.*

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AMONG the different varieties of the species Polygonum, that best known is perhaps the *P. tinctorium*, the leaves of which are used as a source of indigo in China, Japan, and some parts of Russia. Of others, the *P. aviculare* and *barbatum* yield a blue colour, probably indigo, and the *P. hydropiper* and *tortosum* are said to contain a yellow colouring matter; moreover, the roots of some of these varieties possess medicinal value.

The *P. cuspidatum*, which is common in parts of India, China, and Japan, has evidently attracted but little attention, the only reference found bearing on its properties being the following, contained in a

paper (*Journal Royal China Branch of Royal Asiatic Society*, **22**, New Series, No. 5, 1887), by A. Henry, M.A., L.R.C.P., entitled "Chinese Names of Plants," "*Kan-yeu, wu-tzu*, name at Patung for the root of *P. cuspidatum*, which is said to be used for dyeing yellow."

During the removal of some of this plant from my garden, my attention was directed to the root on account of its strong colour internally and its somewhat close resemblance to madder and morinda root. As much as could be obtained was therefore collected for examination, and for a further quantity I am indebted to Mr. Richard Reynolds, F.I.C., of Leeds, by whom the plant was originally introduced into this district. The roots vary in diameter from $\frac{1}{4}$ in. to 1 in. when fresh, and consist of a thick succulent bark, internally of an orange-red colour, and a central light yellow, woody portion; the former, on drying, shrivels considerably and becomes lighter in tint. As examination showed that the woody portion contained but little extractive matter, the bark only was preserved, and of this in the dry condition 600 grams was obtained.

EXPERIMENTAL PART.

The Glucoside Polygonin.

The ground root bark was extracted twice with 10 times its weight of boiling alcohol for six hours, and the resulting orange-brown extracts evaporated to a small bulk. The residual liquid, from which nothing separated out on standing, was treated with water and extracted with ether, the ethereal solution being placed aside for subsequent examination. The addition of baryta water to the aqueous liquid produced a dirty white precipitate, which was removed by filtration, and washed with water until the washings were nearly colourless. The deep red filtrate, after being neutralised with acetic acid and saturated with common salt, was extracted with a large volume of ethylic acetate, and the extract evaporated; as the solution became concentrated, a brown gelatinous precipitate commenced to separate, and a further quantity was deposited on cooling. This product, which appeared under the microscope as a mixture of gelatinous and crystalline matter, was collected, rinsed with ethylic acetate, pressed, and dissolved in boiling alcohol, it being necessary, however, to previously grind the mass into a thin cream with the solvent, otherwise complete solution could only be obtained by protracted digestion. On evaporating to a small bulk and cooling, the liquid deposited a gelatinous matter; directly this ceased to form, it was rapidly filtered, and the crystalline substance which separated from the filtrate was collected and purified by crystallisation from acetic acid. The gelatinous portion, when dissolved in boiling alcohol

and treated in the manner above described, yielded more of the crystalline matter, the operation being repeated until at length crystals could no longer be obtained from the gelatinous matter which separated; the latter was then placed aside for subsequent examination. Analyses of distinct preparations of the crystalline substance gave the following numbers.

0.1151 gave 0.2460 CO₂ and 0.0510 H₂O. C = 58.28; H = 4.92.

0.1091 „ 0.2340 „ „ 0.0495 „ C = 58.48; H = 5.04.

0.1095 „ 0.2325 „ „ 0.0495 „ C = 57.90; H = 5.02.

C₂₁H₂₀O₁₀ requires C = 58.33; H = 4.63 per cent.

It consisted of a glistening mass of orange-yellow needles, which, when heated, softened at 200° and melted at 202—203°. From its solution in boiling alcohol, in which it is but sparingly soluble, it is deposited in a gelatinous condition if rapidly cooled, but when left to cool slowly it separates as a bulky mass of hair-like needles. Boiling water and ethylic acetate dissolve it sparingly, and it is almost insoluble in ether. With cold dilute alkalis or baryta water, it yields orange-red liquids, and by treating a boiling alcoholic solution of the substance with alcoholic potash, the potassium derivative separates, on cooling, in the form of red, flat, microscopic needles. The lead salt, an orange-red amorphous powder somewhat soluble in boiling water, is formed when lead acetate is added to an alcoholic solution of the substance.

Emodin.

Experiment soon revealed the fact that the above-described substance was a glucoside, and, in order to determine its nature, its solution in 60 per cent. alcohol was digested at the boiling heat with a small quantity of hydrochloric acid. During this operation, the light yellow liquid quickly became orange-red, and crystals separated; when the action had ended, boiling water was added a little at a time, and the mixture allowed to cool. The product was collected, washed with water, and dried at 120°.

0.1224 gave 0.2980 CO₂ and 0.0450 H₂O. C = 66.39; H = 4.08.

C₁₅H₁₀O₅ requires C = 66.66; H = 3.70 per cent.

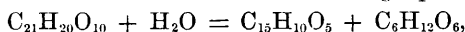
Thus obtained, it formed orange-red needles readily soluble in alcohol; it melted at 253—254°, and sublimed at higher temperatures with partial carbonisation. When distilled with zinc dust, a sublimate of greenish leaflets was produced, which, after crystallisation from alcohol, melted at 203°, and appeared to be identical with α -methylanthracene. Dilute alkalis and ammonia dissolved it with a red coloration, but it was almost insoluble in baryta water. The alkaline solutions when boiled with zinc dust became yellow,

but on exposure to air regained their original tint. When it was dissolved in nitric acid (sp. gr. 1·54) and the solution evaporated to a small bulk and cooled, a semi-solid mass was obtained which crystallised from acetic acid in long, thin, orange-yellow needles. This product dissolved in solutions of the alkali hydroxides with a red coloration, decomposed with a slight explosion when strongly heated, and evidently consisted of a nitro-derivative. To convert the substance $C_{15}H_{10}O_5$ into its acetyl compound, it was digested at the boiling temperature with a small quantity of acetic anhydride for three hours. On cooling, crystals separated, which, after recrystallisation from alcohol, formed lemon-yellow needles melting at 189° . Sufficient was not available for analysis. These results showed that the substance $C_{15}H_{10}O_5$ is *emodin*, a trihydroxy- α -methylanthraquinone, existing in rhubarb root (De la Rue and Muller, *J. Chem. Soc.*, 1857, **10**, 298), and also in the bark of *Rhamnus frangula*, as a glucoside (Trans., 1892, **61**, 1, Thorpe and Miller). The acetyl-emodin melts at 190° (Liebermann, *Ann.*, 1876, **183**, 161), and it has been previously shown (Trans., 1894, **65**, 934) that emodin reacts with nitric acid to form a nitro-derivative.

A determination of the amount of emodin produced by the hydrolysis of the glucoside gave the following result.

0·3858 glucoside yielded 0·2385 emodin, or 61·82 per cent.

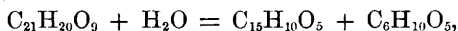
This result is in accordance with the following equation:—



which requires 62·50 per cent. of emodin.

The filtrate from the emodin, after neutralisation with silver carbonate and evaporation, yielded an almost colourless syrup, but obviously in too small a quantity for purification. A solution of the substance reacted with phenylhydrazine acetate, on gently warming; lemon-yellow aggregates of an osazone being deposited on cooling. The examination of this glucose must be deferred until more raw material is forthcoming.

Frangulin, the only glucoside of emodin hitherto known, and found in *Rhamnus frangula*, is not identical with the above. When hydrolysed, for instance, it yields emodin and rhamnose (Thorpe and Miller, *loc. cit.*),



a reaction which requires 64·9 per cent. of emodin, and its difference in composition ($C_{21}H_{20}O_9$ requires C = 60·57; H = 4·80), crystalline appearance, solubility, and other properties from the glucoside found in *Polygonum cuspidatum*, show clearly that they are distinct substances. I propose to give the name *polygonin* to this new glucoside of emodin from the *Polygonum cuspidatum*.

Emodin Monomethyl Ether.

The gelatinous residue obtained during the purification of the polygonin, had the properties of a glucoside, but as the quantity obtained did not exceed 0.1 gram, it could not be examined in this condition, but was at once hydrolysed by digestion with dilute hydrochloric acid, when a dirty, orange-coloured crystalline product was obtained; this, by crystallisation from alcohol was separated into emodin, which is readily soluble, and a second substance, characterised by its sparing solubility in this liquid. By recrystallisation, the latter was obtained in yellow needles melting at 199°, though from more dilute solutions it was deposited in leaflets. It differs from emodin, also, in that it is insoluble in dilute ammonia, and almost so in alkalis of moderate strength. Its solution in sulphuric acid is also slightly bluer than the corresponding solution of emodin. While examining this substance, I was struck not only by the nearness of its melting point to that of emodin methyl ether (m. p. 200°) found in the root bark of the *Ventilago madraspatana* (Perkin and Hummel, Trans., 1894, **65**, 932), but also by the similarity of their appearance and properties. The quantity of substance available for experiment was only 0.05 gram, and, as the question of its identity could not be decided by analysis only, it was thought better to test its behaviour with sulphuric acid at 160°; for, in case it were the emodin methyl ether, it would thus yield emodin. The product of the action of sulphuric acid was accordingly treated with water, and the dirty, orange-coloured precipitate thus produced was collected and purified, first by crystallisation from dilute alcohol, and, finally, from toluene. The orange-coloured needles thus obtained melted at 253—254°, dissolved readily in ammonia, and, without doubt, consisted of emodin. It therefore follows that the substance melting at 199°, obtained from *Polygonum cuspidatum*, is identical with the emodin monomethyl ether which exists in *Ventilago madraspatana*. In the former it is present in the condition of glucoside, but, as previously shown (*loc. cit.*), it exists in the latter root in the free state.

It is interesting to note that Schwabe (*Arch. Pharm.*, 1888, **26**, 569), and subsequently Thorpe and Miller (Trans., 1892, **61**, 6), isolated from the bark of *Rhamnus frangula* not only frangulin, but a second substance, to which they respectively assigned the melting points 199°, and 202—203°, and this was considered by the latter authors to be probably a trihydroxymethylanthraquinone isomeric with emodin. The properties of this substance agree very closely with those of the emodin methyl ether above described, and it appears possible that they may be identical. Experiments will be instituted with *Rhamnus frangula* to decide this point.

The Wax.

The ethereal extract, obtained during the isolation of the glucoside, was extracted with dilute alkali, the red-coloured extract neutralised with acid, and the orange-red flocks thus formed were collected and purified by crystallisation from toluene; the product consisted of orange-coloured needles melting at 253—254°, and had all the properties of emodin. The quantity of emodin obtained from the root in the free state was exceedingly small.

As the remaining ethereal solution appeared to contain a wax, it was evaporated to dryness, and the colourless, sticky residue dissolved in a small quantity of boiling alcohol. On standing, the solution deposited warty nodules, and these were collected and purified by further crystallisation. The product consisted of beautiful, colourless leaflets which resembled phenanthrene in appearance, and melted at 134—135°. In melting point* and properties it appeared identical with the wax existing in the root bark of the *Morinda umbellata* (Perkin and Hummel, Trans., 1894, **65**, 867), and, though the quantity obtained was very small (0.06 gram), it appeared evident that, if the two were identical, an analysis would yield numbers agreeing approximately with those formerly given (*loc. cit.*). This proved to be the case.

0.0536 gave 0.1635 CO₂ and 0.0560 H₂O. C = 83.19; H = 11.60.
C₁₈H₂₈O requires C = 83.08; H = 10.75 per cent.

The wax contained in the root of the *Polygonum cuspidatum* is, therefore, identical with that existing in the root of *Morinda umbellata*.

The chief constituents of the root of *Polygonum cuspidatum* are thus shown to be a glucoside polygonin, C₂₁H₂₀O₁₀, which yields emodin on hydrolysis, also free emodin, an emodin monomethyl ether, and a wax, C₁₈H₂₈O. In containing emodin, it shows a chemical connection with the rhubarb root, and with the bark of *Rhamnus frangula* in containing emodin methyl ether; also a connection with *Ventilago madraspatana* root, and a similar relationship with the *Morinda umbellata*, in that they both contain identical waxes.

Dyeing experiments with the root, using mordanted calico, showed, as was to be expected from the chemical examination, that it was devoid of useful tinctorial properties; faint, dull shades were obtained, evidently due to the presence of a small quantity of tannin matter. It is thus evident that no yellow colouring matter is present in this portion of the plant. Examination, however, showed that the *leaves* contain a small quantity of a substance which yields

* The melting point of this wax given in the former paper is 124—125°, an error which appears to have arisen during the correction of the proof sheets.

yellow shades with alumina mordant, and it is possible that some confusion has arisen between the leaves and the root with regard to this property.

It is my intention to study the constituents of the roots of the *Polygonum bistorta* and *Rumex nepalensis*—members of two closely-allied species.

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