

CVI.—*The Yellow Colouring Principles of various
Tannin Matters.*

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THIS investigation, a continuation of those already communicated to the Society (Trans., 1896, 1289, 1299, and 1303), was undertaken with the object of studying the yellow colouring principles which appear in numerous cases to accompany the natural tannin matters. It seemed probable that, as both the *Myrica nagi* and *Rhus Coriaria* (*loc. cit.*) were found to contain the new colouring matter, myricetin, which is apparently an hydroxyquercetin, other missing members of the quercetin and allied series might thus be brought to light. At the same time, it was interesting to determine, by the character of their decomposition products, how close the relationship is which exists between the colouring principle and tannin matter accompanying one another in the same plant.

Cape Sumach.

My attention was drawn to this material by Professor Procter during its examination as a tanning material in the Leather Industries department of this College, and to him I am also indebted for the subjoined description of its general properties.

The leaf of *Colpoon compressum* (also known as *Osyris compressa*, *Fusanus compressus*, *Thesium Colpoon*) is much used in South Africa under the Dutch name of "Pruim-bast," as a substitute for sumach for tanning. The bush is found in the mountains, where it grows to the height of about six feet, and only the younger leaves are gathered.

According to analyses made in the Leather Industries laboratory, and also by Mr. A. N. Palmer, it contains about 23 per cent. of a catechol-tannin giving green-blacks with ferric salts, a precipitate with bromine water, and with ammoniacal cupric solutions a precipitate which is soluble in excess of ammonia. It is quite as strong as the average Sicilian sumach (*Rhus Coriaria*), and although its tannin is very different chemically from that in the latter, it produces a very similar leather. Its employment, like that of the true sumach, is confined to the tannage of light leathers and to brightening the colour of goods which have been tanned with the bark of *Rhus Thunbergii* and other darker coloured materials. Alone, it produces a somewhat soft but light-yellow leather. In South Africa, the leaves are exhausted with hot water and the liquor alone is used, whilst in the case of the true sumach both leaves and liquor are usually brought in contact with the leather. For the supply of the leaves employed in this investigation, I am indebted to the kindness of Mr. R. H. Coaton, of Wellington, Cape of Good Hope.

The leaves, roughly broken by hand, were extracted in a Soxhlet's apparatus, first with ether to remove wax and chlorophyll, and subsequently with alcohol, which dissolved both colouring matter and tanning principles. The light brown alcoholic extract, after being evaporated to a small bulk, was poured into water, the mixture extracted with ether, and the small quantity of alcohol present removed from the aqueous liquid by distillation, which on cooling became semi-solid owing to the separation of crystals; these were collected with the aid of the pump, and washed repeatedly with ether, chloroform, and dilute alcohol until the washings were colourless. The yellow product thus obtained was further purified by two or three crystallisations from dilute alcohol, and a final crystallisation from boiling water. The substance was dried at 130° and analysed.

0.1136 gave 0.2152 CO₂ and 0.0497 H₂O. C = 51.66; H = 4.86.

0.1103 „ 0.2102 CO₂ „ 0.0526 H₂O. C = 51.97; H = 5.29.

C₂₇H₃₀O₁₇ requires C = 51.76; H = 4.79 per cent.

It was obtained as a glistening mass of pale yellow needles, almost insoluble in cold, and only sparingly soluble in boiling water, but readily in alcohol. When heated, it sinters at 180° , and at 185° melts to a thick, treacly liquid. The addition of ferric chloride to its aqueous solution produced a dark green coloration, and with lead acetate an orange-yellow precipitate was formed. Dilute alkalis dissolved it, yielding orange-yellow liquids.

Experiment having shown that this substance was a glucoside, its decomposition with acid was studied in the following manner.

0.7658 gram, dissolved in 600 c.c. of boiling water, was digested with 5 c.c. of sulphuric acid for 2 hours at this temperature; a yellow, crystalline product had then commenced to separate, and more of it was deposited on cooling. This was collected (the filtrate being reserved for further examination), washed with water, and dried at 160° . In this way, 0.3710 gram of a yellow colouring matter was obtained.

0.1111 gave 0.2427 CO_2 and 0.0370 H_2O . $\text{C} = 59.58$; $\text{H} = 3.70$.

$\text{C}_{15}\text{H}_{10}\text{O}_7$ requires $\text{C} = 59.60$; $\text{H} = 3.31$ per cent.

It formed a glistening mass of yellow needles sparingly soluble in water, somewhat readily in alcohol. In alcoholic solution ferric chloride caused a dark green coloration, and lead acetate gave an orange-red precipitate.

The *acetyl* derivative, prepared in the usual manner, crystallised from alcohol in colourless needles melting at 189 — 191° .

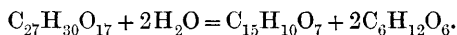
0.1195 gave 0.2567 CO_2 + 0.0462 H_2O . $\text{C} = 58.65$; $\text{H} = 4.29$.

$\text{C}_{15}\text{H}_5\text{O}_7(\text{C}_2\text{H}_3\text{O})_5$ requires $\text{C} = 58.59$; $\text{H} = 3.90$ per cent.

By fusion with alkali, two crystalline decomposition products were obtained melting respectively at 210° and 195 — 196° ; these consisted of *phloroglucinol* and *protocatechuic acid*. The colouring matter resulting from the decomposition of the glucoside was evidently, therefore, *quercetin*, a fact also corroborated on examining its dyeing properties.

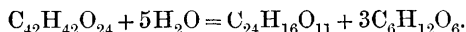
The Sugar.—In order to obtain some insight as to the nature of the sugar liberated in the above action, the acid filtrate from the quercetin was neutralised with barium carbonate, filtered, and evaporated to a small bulk. The amount of the sugar present in this solution being obviously too small to allow of its identification by means of crystallisation and analysis, the liquid was treated with phenylhydrazine acetate in the presence of sodium acetate in order to obtain the osazone, and the crystalline product formed was purified by extraction with small quantities of acetone and subsequent crystallisation from dilute alcohol. It consisted of glistening, yellow needles melting at 205° , apparently *dextrosazone*.

The decomposition of the glucoside with acid can be therefore represented by the equation



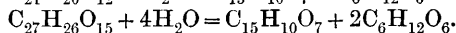
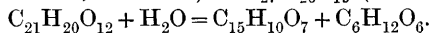
This reaction requires a yield of 48.24 per cent. of quercetin, whereas the amount actually obtained (see above) is equal to 48.44 per cent.

Three distinct glucosides of quercetin have been described, of which quercitrin and rutin are the best known. The former, which occurs in quercitron bark, is decomposed by acid into quercetin and one molecule of rhamnose, whereas the latter, a constituent of rue (*Ruta graveolens*), when so treated, yields quercetin and two molecules of the same sugar. Viola-quercitrin, the third, obtained by Mandelin (*Jahresber.*, 1883, 1369) from the flowers of *Viola tricolor variensis*, gave, in a similar way, quercetin and glucose, as indicated by the following equation, which is based upon the old formula of this colouring matter.



As Mandelin's full paper is published in the Russian *Pharmaceutical Journal*, to which I have not access, it is not possible to be certain whether this equation is based upon the quantity of quercetin liberated when this glucoside is decomposed by acid. Consequently, the formula of viola-quercitrin, $\text{C}_{42}\text{H}_{42}\text{O}_{24}$ (C = 54.19; H = 4.51), if corrected according to the true formula of quercetin, may be expressed in two ways.

$\text{C}_{21}\text{H}_{20}\text{O}_{12}$ (C = 54.31; H = 4.31) or $\text{C}_{27}\text{H}_{26}\text{O}_{15}$ (C = 54.91; H = 4.40).



Of these, the latter formula, though possessing a somewhat high percentage composition, would appear more probable, giving, as it does, a yield of quercetin (51.19 per cent.) which closely agrees with that required by Mandelin's own equation (51.61 per cent.). These figures, however, prove without doubt that the glucoside present in Cape sumach cannot be identical with viola-quercitrin, and must therefore be a new glucoside of quercetin. It is proposed to name this substance *Osyritrin*, derived from one of the names of Cape sumach (*Osyris compressa*).

The Tannin.—Although it is not intended in these investigations to study thoroughly the tannin matters which are present in the plants under investigation, it is desirable to determine the general characteristics of those not previously isolated, as in the case of Cape sumach, for comparison with the accompanying colouring matters. For this purpose, the light-brown filtrate from the osyritrin, after removal of final traces of this glucoside by further evaporation and cooling, was treated with lead acetate solution drop by drop until, on filtration from the dark-coloured precipitate, a pale orange-coloured liquid was ob-

tained; the latter was then treated with sulphuretted hydrogen to remove lead, and evaporated to dryness.

In this way, an orange-coloured, hygroscopic, transparent, glassy mass was obtained which, in aqueous solution, coagulated albumin and gave a dark green coloration with ferric chloride. Dilute alkalis dissolved it, forming orange-yellow solutions which became darker on heating, and on exposure to air developed a blood-red tint. It was found to be a *tannin glucoside*, for on treatment with boiling dilute sulphuric acid there was formed, together with a sugar, a reddish-brown, insoluble product closely resembling the so-called anhydrides or phlobophanes which are produced from so many tannin matters in this way. On fusion with alkali, both glucoside and anhydride yielded *protocatechuic acid*.

This tannin closely resembles, both in description and properties, quinotannic acid (Schwarz, *Jahresber.*, 1851, 411) and quinovatannic acid (Hlasiwetz, *Annalen*, 79, 129), which are decomposed by acid into a sugar and an anhydride, and yield protocatechuic acid on fusion with alkali.

Dyeing trials with Cape sumach were carried out on woollen cloth mordanted with chromium, aluminium, tin, and iron; full buff, pale orange yellow, pale yellow, and pale greenish-black shades were obtained, respectively.

Catechu.

Two varieties of this well-known commercial product exist, namely, gambier and acacia catechus, which are derived respectively from the leaves and twigs of the *Ungarica gambier* and the stem of the *Acacia catechu*. The yellow colouring matter present in the former was isolated by Löwe (*Zeit. anal. Chem.*, 1874, 12, 127) and considered by him to be identical with quercetin, whereas the latter has apparently not been examined in this respect. Owing to the close similarity in appearance of the principal members of the quercetin group, and the lack of confirmatory evidence given by Löwe in his paper, as to the identity of his colouring matter with quercetin, it was considered advisable to re-examine the gambier variety in order to determine the accuracy of this result. For the material employed in this portion of the investigation, I am indebted to the authorities of the Imperial Institute.

Gambier Catechu.—Two hundred grams dissolved in 1500 c.c. of water were boiled with 100 c.c. of sulphuric acid for 15 minutes. The clear liquid was decanted from the brown deposit while hot, cooled, extracted with ether, and the extract evaporated. The yellow, crystalline mass thus obtained was purified by crystallisation from dilute alcohol.

0.1117 gave 0.2445 CO_2 and 0.0365 H_2O . C = 59.69; H = 3.63.

$\text{C}_{15}\text{H}_{10}\text{O}_7$ requires C = 59.60; H = 3.31 per cent.

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The acetyl compound, prepared in the usual manner, formed colourless needles melting at 189—191°.

0.1209 gave 0.2594 CO₂ and 0.0451 H₂O. C = 58.51; H = 4.14.

C₁₅H₅O₇(C₂H₃O)₅ requires C = 58.59; H = 3.90 per cent.

On fusion with alkali, *protocatechuic acid* and *phloroglucinol* were obtained, and from these and its general properties no doubt could exist as to the identity of this colouring matter with *quercetin*.

Acacia Catechu.—Experiments at first indicated that this product contained no yellow colouring matter; but eventually a trace was isolated in the following manner.

The ethereal extract corresponding with that obtained from the gambier catechu, on evaporation, yielded an almost colourless, sticky product soluble in water. This, after treatment with aqueous sodium hydrogen carbonate, was again extracted with ether, and the extract evaporated; on adding water to the residue, a very small quantity of yellow precipitate separated, which was collected and crystallised from dilute alcohol. In this manner, 400 grams of the catechu yielded but 0.05 gram of colouring matter, consequently its analysis could not be attempted. As, however, its acetyl compound melted at 189—191°, and its dyeing and other properties corresponded with those of *quercetin*, it evidently consisted of this colouring matter.

Rhus Cotinus.

In a previous communication (*loc. cit.*), it was shown that, contrary to Lowe's statement, Sicilian sumach (*Rhus Coriaria*) contains myricetin and not quercetin; on this account, special interest attached to the examination of the Venetian variety (*R. Cotinus*) which Löwe also states to contain quercetin. Through the kindness of Signor A. Gilardini, of Turin, a commercial sample of this material was procured. From this, by proceeding in the manner previously adopted (*loc. cit.*), a yellow colouring matter was obtained closely resembling quercetin in appearance, but yielding with dilute alkalis a deep green solution. It thus appeared to be, not quercetin, but *myricetin*, and this was confirmed by the fact that its acetyl derivative crystallised in colourless needles melting at 203—204°. Owing, however, to the excessive adulteration which is practised with the various commercial sumachs, and the fact that this sample was in the form of powder, it appeared best to postpone the communication of the analytical and other details connected with this portion of the work until confirmatory evidence had been obtained with a specially gathered sample. Seeing, however, that this material was reported to be genuine, and that no trace of quercetin could be detected in the product, the result is extremely suggestive.

Other Tannin Matters.

During the study of the above tannins, my attention was directed to that well-known group of this class, which differ from those previously examined in that they consist of the *seeds* and *fruit* of various plants. As all, on examination, have given a similar result, they will be considered together.

These are, "Valonia," the acorn of *Quercus Ægilops*; "Dividivi," the seed pods of *Cæsalpina coriaria*; "Mryabolans," the unripe fruit of *Terminalia Chebula*; "Agarobilla," the seed pods of *Cæsalpina brevifolia*; Pomegranate rind, *Punica Granatum*, and gallnuts, *Quercus infectoria*.

An exhaustive investigation of these products, employing in each case numerous methods, showed clearly that they contained no member of the quercetin or allied series. As all are known to contain ellagic acid, or ellagitannic acid from which ellagic acid is readily obtained, it appeared probable that to this substance alone their yellow dyeing property was due. This was found to be the case, the shades yielded by pure ellagic acid being almost identical with those given by the natural products themselves.

The dyeing properties of all have been studied, but are so very similar that, for the sake of comparison, three only are here referred to. The material employed was woollen cloth mordanted with chromium, aluminium, tin, and iron.

—	<i>Chromium.</i>	<i>Aluminium.</i>	<i>Tin.</i>	<i>Iron.</i>
Ellagic acid.	Pale green olive-yellow.	Pale olive-yellow.	Scarcely dyed.	Somewhat olive grey-black.
Valonia nuts.	Green olive-yellow.	Faint olive.	Scarcely dyed.	Weak grey-black.
Pomegranate rind.	Yellow olive.	Faint olive.	Scarcely dyed.	Weak bluish grey-black.
Gallnuts.	Green olive.	Faint olive.	Scarcely dyed.	Purplish-black.

The fact that ellagic acid is possessed of dyeing property is not novel, for it forms the subject of a German patent, the material coming into the market in the form of a paste.

It is interesting to note that, whereas members of the quercetin group occur frequently in the flowers, leaves, and stems of plants, few instances are known of their existence in seeds and fruits, the most notable exceptions being Persian berries which contain rhamnetin and quercetin, and parsely seeds in which apiin is present. From the

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above and previous results, a very intimate connection is at once evident between the colouring principles and tannin matters occurring together in the plants at present examined, in that, on decomposition, the same acid, and in some cases the same phenol, is obtained from both.

—	Tannin.	Decomposition products of tannin.	Colouring matter.	Decomposition products of colouring matter.
<i>Querbracho colorado.</i>	Querbrachotannic acid.	Phloroglucinol and protocatechuic acid.	Fisetin.	Resorcinol and protocatechuic acid.
<i>Rhus Coriaria</i> <i>Rhus Cotinus</i> }	Gallotannic acid.	Gallic acid.	Myricetin.	Phloroglucinol and gallic acid.
Gambier Catechu Acacia Catechu }	Catechin. ,,	Phloroglucinol and protocatechuic acid.	Quercetin. ,,	Phloroglucinol and protocatechuic acid.
<i>Colpoon compressum.</i>	A catechol tannin.	Protocatechuic acid.	Quercetin.	Phloroglucinol and protocatechuic acid.
Dividivi, &c.	Ellagitannic acid.	—	Ellagic acid.	—

Whether so close a relationship will hold good in all cases is doubtful, although it is remarkable that the above group should contain no exception to this rule.

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