

LXXIX.—*Colouring Matter of Sicilian Sumach, Rhus Coriaria.*

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It is well known that numerous tannin matters such as sumach, catechu, divi-divi, &c., dye fabrics mordanted with aluminium pale yellow shades, and this, taken in conjunction with the dark bluish-black that they yield with iron mordant, has frequently been considered as a property of the tannin substance they contain. As numerous members of the tannin class have been but superficially examined, and many of their principles have probably not yet been obtained in a pure condition, some of these, it is possible, may behave as mordant yellow dye-stuffs; on the other hand, however, Löwe has stated that both catechu and sumach contain quercitrin and quercetin (*Zeit. anal. Chem.*, 1874, **12**, 127), and it is thus evident that, in some cases at least, this dyeing property is due to the presence of a distinct colouring matter rather than to the tannin itself.

With the object of determining how far this is the case, and with the desire of ascertaining the class of colouring matters they contain, such as are available are undergoing investigation.

Sumach consists of the dried and powdered leaves of the genus *Rhus* (order Terebinthacæ), especially *R. coriaria* and *R. cotinus*. The former constitutes Sicilian sumach, the best known and most frequently used variety, the latter Venetian sumach, and it is interesting to notice that it is the wood of this tree (*R. cotinus*) which constitutes young fustic, the tinctorial properties being due to fisetin. Sumach is useful for tanning the finer kinds of leather, and also in dyeing and

calico printing on account of the tannin matter present in it. According to Chevreul, it contains a yellow colouring matter which separates in crystalline grains from a concentrated decoction on cooling (*Watts' Dict. Chem.*, 1874, 5, 614).

We were unaware at the commencement of this investigation that Löwe (*loc. cit.*) had previously investigated this subject; had this been the case its re-examination would probably not have been attempted. In his paper, "Ueber das Vorkommen des Quercetins und Quercitrins in Catechu und Sumach," Löwe states that from the different varieties of sumach, yellow, crystalline substances can be obtained if these be extracted with methylated spirit, and the extracts evaporated and treated with water. Crystals are thus obtained which differ from quercetin in that they are soluble in a large volume of boiling water, and this solution, on cooling, redeposits them, sometimes in needles, but more often in yellow flocks. Sicilian sumach was found to contain them in somewhat greater quantity than the other varieties. An average of the analyses of the products gave C = 52.60; H = 4.83 per cent., and they had further the properties of quercitrin. Our investigation shows that Sicilian sumach contains neither quercitrin nor quercetin, but the colouring matter described below, and the difference between our results and those of Löwe can only be accounted for by the supposition that either his sample of Sicilian sumach was not genuine, or that the close resemblance between the appearance of this colouring matter and that of quercitrin caused him to believe them to be identical.

The tannin of sumach has also been investigated by Löwe, who found it to be identical with the gallotannic acid contained in nut-galls.

One thousand grams of ground Sicilian sumach was extracted for six hours with ten times its weight of boiling water, filtered through calico, and the filtrate, while still hot, treated with a solution containing 55 grams of lead acetate; the precipitate, which at first was pale yellow, on continued boiling, gradually became dirty white, and as on examination it was found to contain no colouring matter, but to consist almost entirely of a lead compound of the tannin matter, it was removed by filtration and washed with hot water. To the filtrate, excess of lead acetate solution was now added, the yellow precipitate thus formed being collected, washed with water, suspended in boiling water, and decomposed with dilute sulphuric acid. After removal of the lead sulphate, the clear liquid was extracted with ether, the ethereal extract evaporated to dryness, the crystalline residue dissolved in alcohol, and the solution treated with boiling water. On cooling, a small quantity of a crystalline matter separated, which was

collected, but as it was evident that by this treatment the quantity of the original product had considerably decreased, the filtrate was reserved for further examination. The residue was purified by crystallisation from dilute alcohol. The yield was 1.173 gram, or 0.1173 per cent.

0.1230, dried at 160°, gave 0.2557 CO₂ and 0.0400 H₂O. C = 56.69; H = 3.61.

C₁₅H₁₀O₈ requires C = 56.60; H = 3.14 per cent.

It was obtained as a glistening mass of light yellow needles, closely resembling quercetin in appearance, but was readily distinguished from the latter by its reaction with solutions of the alkali hydroxides. Dilute potassium hydroxide dissolves it with a green coloration which, on exposure to or shaking with air, rapidly assumes a deep blue tint; this, in its turn, gradually changing to dull violet. Strong alkali dissolves it with an orange-yellow coloration, which is fairly permanent; this solution, on dilution, becomes green, and passes through the colour changes recorded above. With lead acetate in alcoholic solution, an orange-red precipitate is formed, whilst alcoholic ferric chloride gives a brown-black coloration. Upon wool mordanted with chromium, aluminium, and tin, it gives respectively red-brown, brown-orange, and bright red-orange shades, which closely resemble those obtained from quercetin and fisetin in a similar way.

Sulphuric acid Compound.—When treated with mineral acids in the presence of acetic acid, the colouring matter yielded orange to orange-red crystalline compounds, readily decomposed by water. The sulphuric acid compound was analysed.

0.1278 gave 0.2037 CO₂ and 0.0350 H₂O. C = 43.46; H = 3.03.

C₁₅H₁₀O₈.H₂SO₄ requires C = 43.26; H = 2.88 per cent.

Acetyl Compound.—In order to prepare the acetyl compound the colouring matter was digested with three parts of acetic anhydride and one of anhydrous sodium acetate at the boiling point for one hour. The product was poured into water, and after standing 12 hours, the precipitate was collected and crystallised from alcohol.

0.1201 gave 0.2497 CO₂ and 0.0420 H₂O. C = 56.70; H = 3.88.

C₁₅H₄O₈(C₂H₃O)₆ requires C = 56.84; H = 3.86 per cent.

It was obtained as colourless needles, melting at 203–204°, and sparingly soluble in alcohol.

Action of Fused Alkalis.—The colouring matter was heated at 150–170° for half an hour with 10 times its weight of potassium hydroxide dissolved in a little water. The melt was dissolved in water, neutralised with acid, extracted with ether, the extract evapo-

rated, and the residue dissolved in a little boiling water and treated with lead acetate solution. The precipitate was collected, washed with water, decomposed in the usual way, the clear solution extracted with ether, and the extract evaporated. The residue, when purified by crystallisation from water, was obtained as needles melting at 235° to 240° , with evolution of gas. It was found to be *gallic acid*.

The filtrate from the lead precipitate was treated with sulphuric acid to decompose lead compounds present, extracted with ether, and the extract evaporated. The residue left was too small for complete purification, but as its aqueous solution gave, with fir-wood and hydrochloric acid, the *phloroglucinol* reaction, it evidently contained this substance.

From these results it is evident that the colouring matter of Sicilian sumach is *myricetin*, $C_{15}H_{10}O_6$, which, as demonstrated in a preceding paper, exists in the Indian dye-stuff, *Myrica nagi* (this vol., p. 1289).

The acetyl compound of this substance melts at 203 – 204° ; on fusion with alkali, it yields phloroglucinol and gallic acid, moreover, its dyeing properties are identical with those of the colouring matter of Sicilian sumach.

It is remarkable that its existence in a product so largely used should have been so long undetected, for although in external properties it is very similar to quercetin, yet its characteristic reaction with dilute alkali at once distinguishes it from this colouring matter.

As previously stated, it was evident that the ethereal extract obtained during the isolation of the myricetin contained a second substance distinguished by its ready solubility in dilute alcohol. The filtrate from the myricetin was, therefore, extracted with ether, the extract evaporated, and the crystals which separated from the residue on standing, collected and drained upon a porous tile. It was purified by crystallisation from water.

0.1079 gave 0.1972 CO_2 and 0.0350 H_2O . C = 49.84; H = 3.60.

0.1216 „ 0.2223 „ „ 0.0406 „ C = 49.85; H = 3.70.

$C_7H_6O_5$ requires C = 49.41; H = 3.52 per cent.

The product consisted of nearly colourless needles melting at 238 – 240° , with evolution of gas. With ferric chloride, in aqueous solution, it gave a blue-violet coloration, and when heated with sulphuric acid at 140° , a product was obtained having the reactions of rufigallic acid. It was evidently *gallic acid*.

In order to determine whether myricetin existed in this sample of sumach chiefly in the free state, or whether its isolation in the

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manner above described was due to the decomposition of a glucoside, an aqueous extract was extracted with ether. The residue obtained on evaporating the extract consisted principally of myricetin* and gallic acid, and in such quantity that it was evident that little or no glucoside could be present in the sumach. It is probable that in the fresh leaves a glucoside exists, for there seems to be little doubt that this is the original condition of all vegetable colouring matters.

In investigating the dyeing properties of sumach, wool mordanted with chromium, aluminium, and tin was employed. The shades produced were respectively pale olive, olive-yellow, and pale yellow, but these were extremely weak when compared with the well-known natural yellow dye-woods.

We feel it desirable to reinvestigate the other varieties of sumach, and hope to do so if we can obtain them of guaranteed purity.

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