LXXVI.—*The Colouring Principle contained in the Bark of* Myrica nagi. Part I.

By Arthur George Perkin and John James Hummel.

In the course of examining the tinctorial properties of some Indian dye-stuffs (*J. Soc. Chem. Ind.*, 1895) our attention was especially attracted by the behaviour of the bark of *Myrica nagi*. Not only did the colouring power compare favourably with that of such well-known dye-stuffs as old fustic and quercitron bark, but in some respects it seemed to differ from all other yellow mordant dye-stuffs. Having subsequently received a larger supply through the kindness of the authorities of the Imperial Institute, London, the chemical examination of this dye-stuff was undertaken, and the results are recorded below.

Myrica nagi, also called *M. sapida*, *M. Integrifolia*, *M. rubra*, &c., belonging to the Myricaceæ, is the box-myrtle or *yangmæ* of China. It is an evergreen dicœcious tree possessing an aromatic odour, and is met with in the subtropical Himalayas from the Ravi eastwards, also

in the Khasia Mountains, Sylhet, and southwards to Singapore, and distributed to the Malay Islands, China, and Japan. The bark is said to have been exported from the North-West Provinces, Kumaou, &c., to other parts of India in recent years to the extent of about 50 tons per annum. In Bombay, it is met with under the name of *kaiphal*, and is there worth 1—2 rupees per maund of 41 lbs., being entirely imported from Northern India. According to Mr. W. Coldstream it is used in Sirmur (Simla district) for dyeing pink, and also as a tanning agent for fancy leather work and for medicinal purposes.

The bark has an astringent taste, and in the powdered condition acts as an irritant on the mucous membrane of the nostrils, indeed it is said to be used occasionally as a snuff in catarrh with headache (*Dictionary of the Economic Products of India*, G. Watt, Vol. V, p. 309). So far as we are able to learn, the chemical examination of this bark is here made for the first time.

Experimental Part.

The ground bark (1,000 grams) was digested for six hours with 10 times its weight of boiling water, the mixture strained through calico, and the residue treated again in a similar manner. Experiment showed that by extracting the filtrate with ether a small amount of colouring matter could be thus obtained; the ethereal extract separated, however, with difficulty from the aqueous liquid, and as also a very large quantity of ether was necessary for this process, the following method appeared preferable. To the combined boiling aqueous extracts, a solution of 60 grams of lead acetate was added, when a bulky, yellowish precipitate was obtained, which, on prolonged boiling, became dirty white; this consisted almost entirely of the lead compound of tannin matter, and contained but a trace of colouring matter. This was removed by filtration, washed with water, and the filtrate treated with more lead acetate solution until a precipitate was no longer formed; the lemon-yellow lead compound was then collected, washed, and decomposed while still moist by means of boiling dilute sulphuric acid. The brown liquid, which now contained the colouring matter, was removed from the lead sulphate by decantation, and extracted twice with ether; the yellow crystalline residue left on evaporating the ethereal extract was dissolved in a little alcohol, and the solution diluted with boiling water. The crystals which separated on cooling, were collected, and extracted two or three times with small quantities of boiling acetic acid in order to remove a colourless wax-like substance which was present in some quantity. By recrystallisation from dilute alcohol, the pro-

duct was obtained in a pure condition. The yield of colouring matter from 100 grams of bark averaged from 0·23 to 0·27 gram.

0·1139, dried at 160°, gave 0·2380 CO_2 and 0·0350 H_2O. C = 56·97; H = 3·41.

0·1199, dried at 160°, gave 0·2480 CO_2 and 0·0385 H_2O. C = 56·46; H = 3·57.

$C_{15}H_{10}O_8$ requires C = 56·60; H = 3·14 per cent.

It formed a mass of light yellow, glistening needles closely resembling quercetin in appearance, and melting above 300° with decomposition. When heated between watch glasses, the mass became carbonised, and a small quantity of yellow vapour was evolved, which, on cooling, condensed to minute needles of the unchanged substance. It is very sparingly soluble in boiling water, somewhat readily in alcohol, and almost insoluble in chloroform and acetic acid. Though closely resembling in appearance the colouring matters of the quercetin group, it is readily distinguished from those at present known by the colour changes it produces when dissolved in alkaline solutions. With dilute potassium hydroxide, a green solution is first formed; this, on exposure to air, rapidly assumes a deep blue tint, which in its turn gradually becomes dull red-violet. With strong alkali a fairly permanent orange-coloured liquid is obtained which, when diluted, passes through the colour changes recorded above. A solution of ammonia produced somewhat similar results, the colours obtained having, however, a redder tint. The addition of lead acetate to its alcoholic solution throws down a reddish-orange precipitate which becomes yellower on boiling. The colouring matter dissolves in cold sulphuric acid, forming a deep red solution, which deposits the unchanged substance on adding water. Its alcoholic solution is coloured brownish-black by ferric chloride. In examining the dyeing properties of this new colouring matter, for which we propose the name *myricetin*, experiments were carried out with it side by side with equal weights of pure preparations of quercetin, fisetin, morin, gentisin, and euxanthone, using woollen cloth mordanted with chromium, aluminium, and tin. It was at once apparent that a strong resemblance existed between the shades given by myricetin, quercetin, and fisetin, in fact, so similar were they, that unless placed side by side one might easily be mistaken for the other. These differences are best seen in the table, p. 1290.

This table shows that, so far as its dyeing properties are concerned, morin belongs to a distinct group, and the same may be said regarding gentisin and euxanthone.

By examination in Ziesel's apparatus, myricetin was found to contain no methoxy-groups.

		Chromium.	Aluminium.	Tin.
1	Myricetin	Red-brown	Brown-orange	Bright red-orange.
	Fisetin	,, ...	Brown-orange, inclining to red	Slightly less red.
	Quercetin	,, ...	Brown-orange, inclining to yellow	Bright orange.
2	Morin	Olive-yellow	Dull yellow.....	Bright yellow.
3	Gentisin	Green - yellow, dull and pale	Bright yellow tint, very pale, scarcely dyed	Cream colour, scarcely dyed.
	,, ...			
	Euxanthone ..	Dull brown, yellow	Bright yellow, pale	Bright yellow tint, very pale, scarcely dyed.

Myricetin Sulphate.—In order to determine the molecular weight of myricetin, its behaviour towards mineral acids was studied, this method, as shown in former communications, having proved of considerable service for this purpose.

The addition of sulphuric acid to myricetin suspended in boiling acetic acid caused the formation of an orange-coloured, crystalline compound, which was collected, washed with acetic acid, and dried.

0·1336 gave 0·2120 CO_2 and 0·0425 H_2O. C = 43·27; H = 3·53.
0·1273 ,, 0·2020 ,, ,, 0·0345 ,, C = 43·27; H = 3·01.
$C_{15}H_{10}O_8,H_2SO_4$ requires C = 43·26; H = 2·88 per cent.

It was obtained as a glistening mass of slender needles somewhat redder than the corresponding quercetin compound. By treatment with water, it is decomposed into myricetin and sulphuric acid, as the following result shows.

0·4892 gave 0·3760 $C_{15}H_{10}O_8$ and 0·2747 $BaSO_4$. $C_{15}H_{10}O_8$ = 76·85; S = 7·71.
$C_{15}H_{10}O_8,H_2SO_4$ requires $C_{15}H_{10}O_8$ = 76·44; S = 7·69 per cent.

Myricetin hydrobromide is obtained in orange-red needles on adding hydrobromic acid to myricetin suspended in boiling acetic acid.

0·1256 gave 0·2057 CO_2 and 0·0385 H_2O. C = 44·66; H = 3·39.
0·1417 ,, 0·2358 ,, ,, 0·0417 ,, C = 45·38; H = 3·25.
0·1258 ,, 0·2095 ,, ,, 0·0318 ,, C = 45·41; H = 2·81.
$C_{15}H_{10}O_8,HBr$ requires C = 45·11; H = 2·75 per cent.

By treatment with water, it is decomposed into myricetin and hydrobromic acid, as the following result shows.

0·4590 gave 0·3690 $C_{15}H_{10}O_8$ and 0·2120 AgBr. $C_{15}H_{10}O_8$ = 80·39 · Br = 19·64.
$C_{15}H_{10}O_8,HBr$ requires $C_{15}H_{10}O_8$ = 79·69; Br = 20·05 per cent.

Myricetin hydrochloride, $C_{15}H_{10}O_8,HCl$, closely resembles the above compound. When heated at 100°, it is slowly decomposed into myricetin and hydrochloric acid, and was consequently not analysed. In the instability of its compound with hydrogen chloride, myricetin resembles quercetin, fisetin, and morin (Trans., 1895, **67**, 646), but differs from that of luteolin (this vol., p. 208), which is stable at this temperature.

Myricetin hydriodide, $C_{15}H_{10}O_8,HI$, crystallises beautifully in glistening needles of a red orange colour. The above results show that the true formula of myricetin is $C_{15}H_{10}O_8$.

Hexacetylmyricetin.—A solution of one part of myricetin and one part of anhydrous sodium acetate in three parts of acetic anhydride was boiled for one hour, the product poured into water, and, after being allowed to stand 24 hours, collected and purified by crystallisation from alcohol.

0·1162 gave 0·2420 CO_2 and 0·0448 H_2O. C = 56·80; H = 4·27.
$C_{15}H_4O_8(C_2H_3O)_6$ requires C = 56·84; H = 3·86 per cent.

It forms a silky mass of colourless needles melting at 203—204°, very sparingly soluble in alcohol, more readily in acetic acid. It is insoluble in cold alkaline solutions. In order to determine the number of acetyl groups present in this substance, a solution in acetic acid was boiled with the addition of a few drops of sulphuric acid. Boiling water was then added, and the crystals of myricetin which separated on cooling were collected and weighed.

0·8350 gave 0·4680 $C_{15}H_{10}O_8$. $C_{15}H_{10}O_8$ = 56·04.
$C_{15}H_4O_8(C_2H_3O)_6$ requires $C_{15}H_{10}O_8$ = 55·79 per cent.
$C_{15}H_5O_8(H_3O)_5$ „ „ = 60·22 „

It was therefore a *hexacetyl* compound.

Hexabenzoylmyricetin.—Owing to the readiness with which myricetin decomposes in alkaline solution, the method of Baumann and Schotten was not available. Myricetin was therefore heated with excess of benzoic anhydride at 160—170° for four hours, and the product dissolved in acetic acid and poured into alcohol. After 12 hours, a colourless precipitate had separated, which was collected, washed with alcohol, and purified by crystallisation from this solvent.

0·1005 gave 0·2663 CO_2 and 0·0353 H_2O. C = 7226; H = 3·90.
$C_{15}H_4O_8(C_7H_5O)_6$ requires C = 72·61; H = 3·60 per cent.

It was obtained as colourless needles, readily soluble in acetic acid, sparingly in alcohol.

Action of Fused Alkalis on Myricetin.—Myricetin was heated with 10 times its weight of potassium hydroxide at 150—170° until the melt, which was originally of an orange colour, had become brown. It was then dissolved in water, the solution neutralised with

acid, extracted with ether, the extract evaporated, and the crystalline residue dissolved in a little hot water. On adding lead acetate, a yellowish-white precipitate was formed, which was collected, and washed with hot water, the filtrate being placed aside for further examination.

The lead precipitate, suspended in a little water, was decomposed by sulphuric acid, the lead sulphate removed by filtration, the filtrate extracted with ether, and the extract evaporated. The brown residue, which became crystalline on standing, was treated with a very little hot water, in which most of it dissolved, the small quantity of insoluble product being collected. This, on examination, was found to be a trace of unaltered myricetin, and it is strange that any of this substance, which is so readily decomposed in dilute alkaline solution, should have resisted the action of concentrated alkali at such a high temperature.

The filtrate, on standing, deposited crystals, which, after being drained upon a porous tile and crystallised two or three times from boiling water, formed a mass of needles of a slightly brown tint, melting at 239—240°, with evolution of gas, and giving the reactions of gallic acid with ferric chloride. As, however, the reactions of phloroglucinolcarboxylic acid are very similar, according to Will and Albrecht (*Ber.*, 1884, **17**, 2103; 1885, **18**, 1323), it was necessary to institute further tests. It was found that the substances dyed iron mordanted calico like gallic acid, that it did not give with fir wood and hydrochloric acid the phloroglucinol reaction, and, further, that when heated to 240° the residue had the properties of pyrogallol, and not of phloroglucinol. It was therefore *gallic acid*.

The filtrate from the lead precipitate was treated with sulphuric acid to decompose lead compounds, the lead sulphate removed by filtration, the filtrate extracted with ether, and the extract evaporated. The residue thus obtained was too small for complete purification, but it gave the phloroglucinol reaction, and without doubt consisted chiefly of this substance.

The principal products of the action of fused alkali on myricetin are therefore *gallic acid* and phloroglucinol.

Action of Bromine on Myricetin.—To a thin paste of myricetin in acetic acid, the amount of bromine necessary for the formation of a tetrabromo-compound was added. Hydrogen bromide was evolved, and a clear solution gradually formed; this, after standing over night, was poured into about six times its bulk of water. At first crystals were slowly deposited, but after some time a small quantity of flocculent matter also separated. The product was collected and purified by several crystallisations from dilute acetic acid. As the yield obtained in this way was somewhat unsatisfactory, experiments

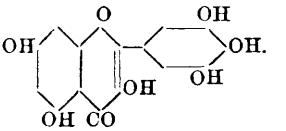
were carried out on the bromination of myricetin suspended in carbon bisulphide at 100°. By this means the quantity of product obtained was found to be considerably increased.

0·1275 gave 0·1325 CO_2 and 0·0155 H_2O. C = 28·34; H = 1·35.
0·2373 „ 0·2790 AgBr. Br = 50·02.
$C_{15}H_6O_8Br_4$ requires C = 28·47; H = 0·63; Br = 50·63 per cent.

It was obtained in the form of brownish-orange, prismatic needles, melting and decomposing at 235—240°, readily soluble in acetic acid, slightly less so in alcohol. Alkaline solutions dissolve it at first with a yellow coloration, which on exposure to air becomes red, and finally passes into dirty brown. Its alcoholic solution gives with ferric chloride a deep blue coloration. With mordanted calico, it dyes shades considerably yellower than those of myricetin itself, and more resembling those yielded by gallacetophenone.

Although the analytical numbers agree closely with those required by tetrabromomyricetin, and moreover the production of such a compound is in harmony with the probable constitution of this substance, yet on account of the peculiarity of its properties considered side by side with those of the bromine derivatives of quercetin, morin, and luteolin, some little doubt must be entertained as to its identity until a molecular weight determination can be carried out. By the introduction of bromine into the above colouring matters, their reactions with ferric chloride are but little altered, moreover these compounds are considerably less soluble than the colouring matters themselves.

In examining the results of this investigation, but little doubt can be entertained that myricetin is a member of the quercetin series. Its formula, its reactions with mineral acids, and the number of hydroxyl groups it contains, when considered with the results of its decomposition with alkali, are all in harmony with this suggestion. Moreover, its dyeing properties are very similar to those of quercetin and fisetin.* Before absolutely deciding its constitution, it will be necessary to examine its methyl and ethyl ethers and their decomposition products; unfortunately, the difficulty of isolating sufficient substance for this purpose may delay this investigation for some time. There appears, however, every probability that myricetin, $C_{15}H_{10}O_8$, will thus be shown to have the constitution of an hydroxy-quercetin,



* Quercetin and fisetin both contain a catechol, and myricetin a hydroxycatechol (pyrogallol) nucleus. In place of this, morin, on the other hand, possesses a

Its colour reactions in alkaline solution are evidently due to the oxidation of the pyrogallol nucleus it contains.

Tannin Matter.—We are indebted to Mr. H. R. Procter, Lecturer on Leather Industries, Yorkshire College, for the following, an average of four separate analyses of the bark of *Myrica nagi*.

Tannin matters absorbed by hide	27·3
Soluble non-tanning substances.....	7·9
Fibre and insoluble matters.....	52·3
Moisture.....	12·5
	100·0

Dyeing Properties.—The tinctorial power of the product now examined was much less than that of the small sample of bark with which the earlier experiments were made, and which had a much smoother exterior, and was labelled *Myrica rubra;* moreover, it gave somewhat different shades with the different mordants. On striped mordanted calico, the present sample gave with alumina a comparatively dull yellow, inclining to pink on a weak mordant, and with iron a purplish-grey, as if tannic acid were present. Its colouring power was much less than that of old fustic and quercitron bark. On the other hand, our former sample gave with alumina a full yellow, distinctly stronger, although somewhat duller, than those given by the dyewoods just mentioned, and the colour with iron mordant gave little or no indications of the presence of tannic acid. On wool mordanted with chromium, aluminium, and tin, and dyed with 40 per cent. of our latest sample, greenish-olive, olive-yellow, and yellow colours respectively were obtained, all very pale and dull, whereas with the same mordants our former sample yielded deep olive yellow, dull yellow, and bright red-orange, the two first reminding one of the corresponding colours obtained from quercitron bark, the latter being very similar to those given by Persian berries.

These results show either that the colouring properties of *Myrica nagi* are somewhat variable, according to the age of the tree or branch from which the bark is taken, or that there may be different species of *Myrica*, each with slightly different tinctorial properties. The comparative richness of some of the barks, however, warrants us in directing the attention of native dyers of India to its probable utility as a yellow dye-stuff.

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resorcinol group, and its distinctive dyeing properties when compared with the above three colouring matters must be due to this fact.