

VI.—*On Morindin and Morindon.*

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THE roots of various species of *Morinda*, particularly *M. citrifolia* and *M. tinctoria*, are extensively employed in various parts of India, under the general trade name of *Suranji*, as a dye-stuff, more especially for dyeing reds, purples, and chocolates. These plants are to be met with in nearly all the provinces of India, either wild, as in the jungles of Bengal, or cultivated in small patches in betel-nut plantations, or near the homesteads of the dyers.

In Bengal, the plant is usually propagated by slips or cuttings, but in other parts it is raised from seed, as well as from cuttings. When the plants have attained a height of some 5 or 6 feet, that is, as a rule, at about the end of the third year, the straight spindle-shaped roots, which extend into the ground to a depth of 3 or 4 feet, are dug out, and the upper portions of the plant are cut into slips to serve for the propagation of the next crop.

The colouring matter is found principally in the root-bark, and is developed in greatest quantities at about the end of three or four years, depending upon the character of the soil. After this time, the dyeing-matter gradually disappears, and the matured trees, which eventually attain the height of a mango tree, contain hardly a trace of it. The thin roots are the most valuable, roots thicker than half an inch being thrown away as worthless.

A'l, or Aich, as the root is called in Bengal, is mainly used for dyeing the thread or yarn from which the coloured borders of the cotton garments worn by the lower classes are woven, but it is also occasionally employed for dyeing the coarse cotton fabric called "Khárua," or for dyeing the silk thread which forms the border of the silk fabric known as "Endi" cloth. The colours given by A'l range from a reddish-yellow through pink and various shades of red to a dark brown-red. The tint seems primarily to depend upon the age of the root, and upon the proportion of root-bark to root-stem which is employed. The root-bark gives the best reds; the dye in the woody part of the root is yellow, and hence when the wood preponderates over the bark the resulting dye is reddish-yellow. The methods of A'l-dyeing differ considerably in various parts of India. The usual plan in Bengal is to steep the cloth or yarn in a mixture of powdered castor-oil seeds and the ashes of plantain leaves or other alkaline ashes and water, for some days with alternate washing and drying,

after which it is boiled with the dyeing solution prepared by treating the pounded roots, or sometimes the root-bark only with water.

Myrabolans, turmeric, the bark or leaves of *Symplocos racemosa*, alum, certain gums, and various other substances are occasionally used as mordants or auxiliaries either immediately after the cleansing process or along with the dye-stuff; frequently, however, the cloth is transferred directly from the cleansing liquor to the decoction of the root, and no mordant is employed. Purple and chocolates are obtained by adding sulphate of iron to the dyeing liquor.*

It will be observed that this process bears considerable resemblance in its main features to that of Turkey-red dyeing by means of madder, and it is not surprising therefore that some attempts should have been made to introduce *Suranji* into this country as a substitute for the roots of *Rubia tinctorum*. *Morinda citrifolia*, indeed, belongs to the same natural order as the madder plant. The trials made nearly half-a-century ago by Turkey-red dyers in the neighbourhood of Glasgow, to make use of *Suranji* as a dye-stuff were, however, without success.

The first inquiry into the nature of the colouring matters of A'1 was made by the late Dr. Anderson (*Trans. Roy. Soc. Edin.*, **16**, iv; *Annalen*, **71**, 216). Anderson found that on boiling the powdered root-bark with alcohol a deep brownish-red solution was obtained, which on cooling deposited the greater part of the colouring matter in brown flocks, mixed with a small quantity of a red substance which was not further examined. By repeated crystallisation from dilute alcohol (50 per cent.), the admixed red substance was removed, and the main product, which Anderson named *morindin*, was obtained in fine needle-shaped lustrous crystals of a yellow or orange-yellow colour. On analysis they gave numbers from which Anderson deduced the formula $C_{28}H_{30}O_{15}$.

On heating *morindin* in closed tubes, it fused to a deep brown liquid; this at a higher temperature decomposed with the formation of an orange-coloured vapour which condensed to long red needle-shaped crystals, leaving a residue of light porous charcoal. This crystalline product was termed *morindon* by Anderson. The crystals were insoluble in both hot and cold water, but readily soluble in alcohol and ether. Caustic alkalis and also strong sulphuric acid dissolved them with the production of an intense violet colour. With alum, an ammoniacal solution gave a beautiful red lake, and with baryta-water a cobalt-blue precipitate. Anderson's analytical numbers obtained from confessedly imperfectly purified material, led him to express the composition of *morindin* by the formula $C_{28}H_{30}O_{10}$.

* For further details, see Liotard "On Indian Dyes;" also McCann, "Dyes and Tans of Bengal."

Hence it might be assumed to be derived from morindin by the elimination of 5 mols. of water, a view of its origin which Anderson held to be substantiated by the mode of action of oil of vitriol upon morindin. After treatment with the acid, the solution of morindin gave on dilution with water a yellow flocculent precipitate, insoluble in water, but soluble in alkalis with the violet colour characteristic of morindon.

According to Rochleder (*Wien. Akad. Ber.*, **7**, 806), Anderson's morindin is probably identical with rubererythric acid, $C_{26}H_{28}O_{14}$, the formula of which agrees practically as well with Anderson's analytical numbers as that which he himself deduced from them. Hence, therefore, morindon would probably be identical with alizarin, to which, indeed, from Anderson's description of its physical properties, it bears considerable resemblance. This view of the nature and relation of morindin and morindon was supported by Stenhouse (*Chem. Soc. J.* [1864], **17**, 333), mainly from a comparison of the absorption spectra of morindon and alizarin. It would appear, therefore, that the colouring matters of Al and of madder were probably identical.

Several facts, however, seem to be inconsistent with this supposition. We have first the circumstance of the inability of the Glasgow dyers to procure madder colours from *Suranji*. Anderson, also, was unable to obtain more than a brownish-red colour in a trial of the Turkey-red process with pure morindin. Morindon, on the other hand, he found to combine readily with mordants, giving with alumina a deep rose-red, and a violet or black colour with oxide of iron. Stein also (*J. pr. Chem.*, **97**, 234) has adduced evidence to show that Anderson's morindin is not identical with rubererythric acid, and that morindon is not identical with alizarin. According to Stein, morindin is distinguished from rubererythric acid by its insolubility in ether, by the violet colour of its barium-compound, and by its behaviour with caustic potash. It is, like rubererythric acid, a glucoside, and by heating alone, or by the action of alkalis, is converted into products which reduce an alkaline solution of copper oxide. It melts at 245° , but even below this temperature it gives a crystalline sublimate of morindon.

Stein found that the readiest way of preparing morindon was to hydrolyse a dilute alcoholic solution of morindin with hydrochloric acid, when the greater part of the morindon is deposited, on cooling, as a bright reddish-yellow flocculent precipitate. In this manner morindin yields about half its weight of morindon, whereas rubererythric acid if decomposed in accordance with the equation $C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6$, gives only 42.5 per cent. of alizarin.

Morindin dissolves in oil of vitriol, forming a solution which is at

first indigo-blue, but this gradually changes to a reddish-purple, and eventually becomes yellowish-red. Alizarin gives a reddish-purple coloured solution at once. With ferric chloride, an alcoholic solution of morindon gives a dull green colour, whereas with alizarin the colour is reddish-brown. When oxidised with nitric acid, morindon gives no phthalic acid but only oxalic acid. According to Anderson (*loc. cit.*), however, the nitric acid solution of morindon, after long continued boiling and subsequent neutralisation with ammonia, gives no precipitate with salts of lime. Stein found that the optical behaviour of solutions of morindon agreed perfectly with the description given by Stokes, and on which Stenhouse based his assumption of the identity of morindon and alizarin.

This conflict of testimony respecting the real nature of the colouring matter of A'1 seemed to warrant fresh investigation. Thanks to the kindness of the Director of the Royal Gardens, Kew, who was good enough to make application to the India Office on our behalf, we obtained about 10 lbs. of the roots of *M. citrifolia*. The method of extraction we employed was substantially that described by Anderson, the powdered root-bark being repeatedly treated with hot dilute alcohol so long as anything seemed to be dissolved. The roots as received from the India Office were in two parcels, the one parcel consisting of thick and evidently old roots, the other of thin roots as a rule not more than $\frac{1}{4}$ inch thick: these alone appeared to contain any sensible quantity of the colouring matter. The alcoholic extracts were concentrated by evaporation, and the precipitates which formed on standing, were collected and treated first with benzene, and then with absolute alcohol, so long as any red colouring matter passed into solution. The residue was then dissolved in hot 50 per cent. alcohol, and purified by repeated crystallisation. In this manner about a gram of pure morindin was obtained. After being dried at 100° , it yielded the following numbers on analysis:—

I. 0.2024 gram gave 0.4098 gram CO_2 and 0.0930 gram H_2O .
 II. 0.2088 " 0.4236 " " 0.0951 "

	Calculated for $\text{C}_{26}\text{H}_{28}\text{O}_{14}$ (rubererythric acid).	Calculated for $\text{C}_{28}\text{H}_{30}\text{O}_{15}$.	Anderson's analysis.	I.	II.
C.	55.33	55.44	55.43	55.27	55.37
H.	4.96	4.95	5.11	5.11	5.06
O.	39.71	39.60	—	—	—
	<hr/> 100.00	<hr/> 100.00			

It will be observed that our analytical results are in close agreement with those of Anderson, and that both sets of numbers are

almost as well expressed by the formula $C_{28}H_{30}O_{15}$ as by that of rubererythric acid.

Through the kindness of Dr. Schunck, who forwarded us a specimen of rubererythric acid, we have been enabled to make a comparison of the properties and modes of decomposition of that substance with those of morindin. In appearance, the two substances were almost exactly similar. When heated in capillary tubes placed side by side, they both decomposed with charring at about the same temperature, and yielded reddish or violet vapours condensing to crystalline sublimates. Contrary to the statements of Rochleder and Stein, rubererythric acid was found to be practically insoluble in ether. Rubererythric acid and morindin are however at once distinguished by their reaction with potash: both give bright red solutions, but, on boiling, that of rubererythric acid at once changes to a dark purple, whilst that of morindin does not alter even after long-continued boiling: this reaction is very striking and characteristic.

A further proof that rubererythric acid and morindin are not identical is afforded by their behaviour on hydrolysis. 0.4354 gram rubererythric acid and 0.4884 gram morindin were separately dissolved in 80 c.c. boiling 50 per cent. alcohol together with 8 c.c. strong hydrochloric acid solution. The solutions were heated by steam under a reflux condenser for about four hours, when the hydrolysis was found to be complete. The precipitates were then collected, washed with water, dried at 120° , and weighed. The weights were—

From rubererythric acid,	0.1832 gram	=	42.1 per cent.
„ morindin	„ 0.2369 „	=	48.5 „

The proportion of the hydrolysed product to the morindin employed agrees closely with the result obtained by Stein: the amount of the hydrolysed product in the case of the rubererythric acid is nearly $6\frac{1}{2}$ per cent. lower, and is almost identical with that required by the equation $C_{26}H_{26}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6$, which gives 42.5 per cent. of alizarin.

Moreover the two products behaved very differently towards reagents. That from rubererythric acid gave a blue-purple colour with potash, unchanged on standing; in the case of that from morindin, the colour was reddish-purple and gradually faded. With ferric chloride, the rubererythric acid product gave a dull brownish-yellow coloration; with the morindin product, the colour was sage-green. With concentrated sulphuric acid, the product from rubererythric acid gave a bright yellowish-red; whereas in the case of the morindin product the coloration was first dark-blue and then purple. Seen under the microscope, the forms of the two products as crystallised from benzene were quite distinct. The two products were then submitted to

analysis, after being heated, side by side, at 130°, with the following results:—

Product from rubererythric acid:—

0·1457 gram gave 0·3726 gram CO₂ and 0·0458 gram H₂O.

	Found.	Calculated for alizarin, C ₁₄ H ₈ O ₄ .
C	69·74	70·00
H.....	3·49	3·33
O	26·77	26·67
	<hr/> 100·00	<hr/> 100·00

Product from morindin—

0·1604 gram gave 0·3906 gram CO₂ and 0·0554 gram H₂O.

	Found.	Calculated for trihydroxymethylantra- quinone, C ₁₅ H ₁₀ O ₅ .	Calculated for isopurpurin, C ₁₄ H ₈ O ₅ .
C	66·41	66·66	65·62
H.....	3·83	3·70	3·12
O	29·76	29·64	31·26
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

There would seem therefore to be no doubt that morindin and rubererythric acid are not identical as was supposed by Rochleder and Stenhouse. The true nature of morindon has still to be determined; the amount of material at our disposal was unfortunately insufficient for its further investigation. In many of its reactions morindon closely resembles isopurpurin, although the numbers afforded by its analysis agree more nearly with those required by trihydroxymethylantraquinone. In either case, its formation by hydrolysis is not very readily explained. We made attempts to determine the quantity of sugar yielded by the decomposition of a known weight of the morindon, but the amount obtained (35 per cent.) threw no light upon the mode in which the morindin is derived, or upon its probable formula. It is, however, quite certain that morindin is not identical with the only trihydroxymethylantraquinone at present known, viz., the *Emodin* discovered by Warren De la Rue and Hugo Müller in rhubarb root (*Chem. Soc. J.*, 10, 304). Our thanks are due to Dr. Hugo Müller for his kindness in affording us the opportunity of comparing the properties of the two products. Since the experimental work in connection with this communication was concluded, Mr. Thomas Wardle, of Leek, has kindly placed a quantity of the roots of *M. citrifolia* and *M. tinctoria* at our disposal. As, however, we are unable to prosecute the work

in common any further, we have ventured to bring the results obtained up to now before the Society. One of us hopes to be shortly in a position to present the results of a fuller investigation.

A portion of the work was done in the laboratory of the Yorkshire College: our thanks are due to Mr. C. W. Gamble, a former student of that institution, for his assistance in the extraction of the crude colouring matter from the roots.
