

XXVII. *Notes on Madder Colouring Matters.*

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WE propose in these notes to give an account of some recent experiments on colouring matters derived from madder, which were undertaken by us, for the purpose of elucidating some points which are still involved in obscurity. We shall not attempt to give a systematic arrangement to the account, but simply describe the results as they were obtained.

1. *Detection of Small Quantities of Alizarin in Mixtures of Alizarin and Purpurin.*

It is well known that alizarin and purpurin may be recognised by means of their absorption-spectra, even when only minute quantities of either substance, pure or impure, are examined. In the case of a mixture of both substances it is easy to discover purpurin in the presence of much alizarin, but not so if the purpurin greatly preponderates. If the amount of alizarin present is less than 5 p.c., the ordinary optical method does not suffice for its detection. Alkaline solutions of purpurin show a much greater power of absorption than do those of alizarin. That of the former extends, with a certain degree of concentration, to that part of the spectrum at which the bands of alizarin lie. If the amount of alizarin present in the mixture is below 5 p.c., its characteristic bands do not appear on diluting the solution.

The known methods of separating alizarin from purpurin are not to be depended on, and give, especially when operating on small quantities, unsatisfactory results. In any case it is necessary to crystallise repeatedly from alcohol, in order to obtain each substance in a state of purity. Purpurin is soluble in boiling alum-liquor, but it frequently occurs that all or nearly all the purpurin is deposited as the solution cools, in combination with alumina, instead of remaining in solution, as is generally asserted. Alizarin is also soluble in boiling alum-liquor, but far less so than purpurin, and is always deposited on the solution cooling and standing.

The different behaviour shown by alizarin and purpurin when their solutions in caustic alkali are exposed to the air, affords an easy means of detecting the minutest quantities of alizarin in a mixture of the two. In making the experiment, the mixture is dissolved in caustic soda-lye, and the solution is left exposed to the air in a shallow

vessel until it has become almost colourless, and the absorption-bands of purpurin are no longer seen on the addition of more alkali. During this process the purpurin is decomposed, the alizarin remaining unchanged. The latter is set at liberty by adding an excess of hydrochloric acid, and is then taken up by ether. It may now be easily recognised by its absorption-spectrum, which is not in the least affected by the products resulting from the decomposition of the purpurin. By this method it is possible to detect alizarin in 0.005 gm. of a mixture of purpurin and alizarin, containing 1 p.c. of the latter.

2. *Purpuroxanthic Acid, a Colouring Matter found in Commercial Purpurin.*

In preparing pure purpurin by treating the commercial product with boiling alum-liquor, adding hydrochloric acid to the solution and treating the precipitate produced by the acid with boiling alcohol, we observed that a portion of the precipitate remained undissolved in the form of a brown powder containing alumina. By treating this powder with boiling alcohol, to which a little hydrochloric acid was added, it dissolved, yielding a small quantity of a crystallised substance which was free from purpurin and was not identical with any of the substances accompanying purpurin described by Schützenberger and Schiffert. We propose to call it *purpuroxanthic acid*.

Having crystallised our purpurin from boiling alcohol, we examined the mother-liquor, and found it to contain an additional quantity of the new substance, along with purpurin, alizarin, purpuroxanthin and a small quantity of a body soluble in boiling baryta-water, which we have not been able to identify. The residue left on evaporation of the liquid was treated with boiling water, in which purpuroxanthic acid dissolves much more readily than the other substances. The filtered liquid gave, on addition of hydrochloric acid, an abundant orange-coloured precipitate which was filtered off and treated with boiling baryta-water, in order to remove the purpuroxanthin and the unknown body accompanying it, the barium purpuroxanthate remaining undissolved. The latter was decomposed with hydrochloric acid, and the purpuroxanthic acid set at liberty was crystallised from boiling alcohol. The traces of alizarin and purpurin accompanying it remained in the alcoholic mother-liquor. After two or three crystallisations from glacial acetic acid, its melting point became constant. It had exactly the same properties as the substance prepared from the alumina compound mentioned above.

Purpuroxanthic acid possesses properties by which it may readily be distinguished from pseudopurpurin, purpuroxanthin, and the other colouring matters described by Schützenberger and Schiffert. It

melts at 231° . At $232-233^{\circ}$, however, it splits up into purpuroxanthin and carbonic acid, and it is therefore hardly possible to sublime it without decomposition. The gas evolved during fusion gives a white precipitate when passed into lime water, while the residue has the properties of purpuroxanthin, the melting point being 264° . No other products are formed. Purpuroxanthic acid is more soluble in boiling water than most madder colouring matters. The solution has a yellow colour, and deposits crystalline flocks on standing. It dissolves easily in hot spirits of wine, giving a yellow solution, which on cooling deposits yellow lustrous needles. These needles, on exposure to the air, gradually become dull, apparently from loss of water of crystallisation. Concentrated alcoholic solutions however frequently yield crystalline plates, which retain their lustre on heating, and are therefore probably anhydrous. The substance dissolves easily in glacial acetic acid on boiling, giving a yellow solution with a slight green fluorescence, which on cooling deposits yellow shining micaceous scales resembling iodide of lead. Dilute solutions deposit on standing long crystalline needles of a deep yellow or reddish-yellow colour. On one occasion we obtained in place of needles flat triangular plates, which on drying became completely opaque. Purpuroxanthic acid is soluble in ether, chloroform and benzene. It dissolves in concentrated sulphuric acid, giving an intensely yellow solution, which shows no absorption-bands. It is easily decomposed on treatment with boiling nitric acid of ordinary strength. It dissolves in caustic potash, yielding a solution resembling in colour alkaline solutions of purpuroxanthin, but with a more decided red tinge; it shows no trace of absorption-bands. When treated for some time with boiling caustic potash-lye, purpuroxanthic acid yields purpurin, but whether purpuroxanthin is formed as an intermediate product we have not been able to ascertain. It is quite insoluble in baryta- and lime-water. The ammoniacal solution gives red precipitates with the chlorides of barium and calcium. An alkaline solution gives with alum a precipitate which dissolves completely in an excess of boiling alum-liquor, yielding a yellow solution which is not fluorescent, and shows no absorption-bands; on standing it deposits a quantity of orange-coloured flocks. The substance dissolves in boiling concentrated perchloride of iron solution, with a deep reddish-brown colour, and is reprecipitated by hydrochloric acid in yellow flocks. The alcoholic solution gives with acetate of lead an orange-coloured precipitate, the supernatant liquid being colourless. Since purpuroxanthin is not precipitated from its alcoholic solution by acetate of lead, the two substances may by this means be distinguished as easily as by the difference in their barium compounds. Purpuroxanthic acid in a freshly precipitated state dyes alumina mordants an orange and iron

mordants a brown colour. These colours are, however, very fugitive, and disappear entirely on treatment with boiling soap-liquor.

On comparing this description with the account given by Rosenstiehl of his ϵ -purpurin (*Compt. rend.*, lxxxiii, 827), it will be found that in most respects the two substances exactly coincide. In two particulars only will any essential difference be observed, the ϵ -purpurin being described as an orange-coloured powder, and its melting point given at 180° .

The analysis of our substance dried at 120° led to the following results :—

I. 0.2374 grm. of substance gave 0.5482 grm. of CO_2 and 0.0638 grm. H_2O .

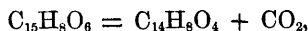
II. 0.2264 grm. of substance from a different preparation gave 0.5222 grm. CO_2 and 0.0644 grm. H_2O .

III. 0.2526 grm. of substance prepared on a third occasion gave 0.5836 grm. CO_2 and 0.0720 grm. H_2O .

These numbers lead to the following composition :—

		Calculation.	I.	II.	III.
C_{15}	180	63.38	62.98	62.90	63.01
H_8	8	2.82	2.98	3.16	3.16
O_6	96	33.80	—	—	—
		<hr/>			
		284	100.00		

The formula $\text{C}_{15}\text{H}_8\text{O}_6$ or $\text{C}_{14}\text{H}_7\text{COOH}\text{O}_4$, to which these analyses lead, explains the decomposition of the substance into purpuroxanthin and carbonic acid, since



a process similar to that which other acids of the aromatic series, such as hydroxybenzoic acid, undergo under the same circumstances.

The small quantity of substance at our disposal (the purpurin employed in its preparation containing only about 1 p.c.) was not sufficient for the preparation of any compounds.

We propose making experiments to obtain it synthetically, proceeding from a bioxyanthraquinone. We think it probable that it is formed by the oxidation of some body pre-existing in the plant.

3. *Munjistin, ϵ -Purpurin and Purpuroxanthic Acid.*

We owe to the kindness of Dr. Stenhouse a specimen of munjistin, the beautiful substance discovered by him several years ago in Munjeet. We found it to bear a striking resemblance to the body described by us in the preceding note, and on examination discovered that its principal properties were exactly those of purpuroxanthic acid.

On being heated it began to soften at 225° , and fused completely at 230° . When further heated it evolved carbonic anhydride, and was converted into purpuroxanthin. By fusion with caustic alkali it yielded purpurin. Hence there can be little doubt that munjistin and purpuroxanthic acid are identical. The analyses of Dr. Stenhouse differ however considerably from ours, and we therefore propose to re-examine munjistin from munjeet in order to remove all doubts as to its identity with our substance.

Some time ago M. Rosenstiehl (*Compt. rend.*, lxxxiii, 827) described, under the name of *ε-purpurin*, a body which he found accompanying pseudopurpurin in a commercial product. This body, which he considers as a fifth isomeride of purpurin, may be formed, according to him, by the simple oxidation of purpuroxanthin, into which it is reconverted by reducing agents. By fusion with caustic potash it yields ordinary purpurin, in consequence of some internal molecular change. Although the properties of this substance strongly resemble those of purpuroxanthic acid, we did not venture to suppose the two bodies could be identical, since the behaviour of his *ε-purpurin*, as given by Rosenstiehl, was in many respects so different, that we were compelled to conclude they must be distinct. In a recent note (*Compt. rend.*, lxxxiv, 559), however, Rosenstiehl admits that *ε-purpurin* and purpuroxanthic acid are the same body, and that our view of its composition explains the reactions observed in a more satisfactory manner than his own. Having maintained that our substance has already been observed, which we by no means deny, Rosenstiehl proceeds to say, that it is identical with the madder orange of Runge. This is quite possible, since many of the properties of madder orange, as described by the discoverer, resemble those of purpuroxanthic acid. The process of preparing it given by Runge (*Journ. f. prak. Chem.*, v, 362) is however one that under varying circumstances might yield different substances, and when repeated by one of us many years ago, it gave in fact, not purpuroxanthic acid, but rubiacin, a colouring matter, which according to the researches of Stenhouse and Stokes (*Proc. Roy. Soc.*, xii, 363), differs essentially from munjistin.

M. Rosenstiehl is of opinion that our substance is or may be formed from pseudopurpurin, for which he now gives a new formula, based on the assumption that it is decomposed on heating into purpurin and carbonic anhydride. By heating pseudopurpurin to 180° , Rosenstiehl finds that it does indeed evolve carbonic anhydride, and that it therefore belongs to the same class of compounds as purpuroxanthic acid. We rejoice to hear that the further investigation of this somewhat anomalous body, of which so little is known in spite of numerous researches, is in such able hands. Having, however, been the first to discover, among this series of bodies, one containing

a carboxyl group, we for our part claim to be left, for the present, in undisturbed possession of the field we have opened up, *i.e.*, the preparation and examination of such members of the series as are formed from alizarin and its isomerides, as well as from the isomerides of purpurin, by the replacement of H by COOH.

4. *Purpurin.*

Since its discovery by Robiquet, nearly fifty years ago, purpurin has been the subject of numerous investigations. The accounts given of its properties and composition by various chemists differ however very considerably. The analyses, with the exception perhaps of those of Schützenberger and Schiffert, indicate a more or less considerable admixture of alizarin. Graebe and Liebermann were the first to remove all doubts regarding the formula of purpurin, by showing that it is a derivative of anthracene, and must be considered as a trioxyanthraquinone. The methods formerly adopted for separating alizarin and purpurin were indeed imperfect, and though chemically pure alizarin had previously been obtained by the decomposition of its glucoside, it was only after the introduction of Kopp's method of preparation that chemists were enabled to procure purpurin in large quantities in a state of tolerable purity. Commercial purpurin however still contains a certain amount of alizarin, besides several other impurities. Even in a specimen which had been purified in the manufactory of Kahlbaum at Berlin by solution of the crude product in boiling alum liquor, we were able to detect traces of alizarin by the method described by us in a previous note. By again treating this product with boiling alum liquor, adding acid to the filtered solution, and dissolving the precipitated purpurin in boiling alcohol, we obtained a pure crystallised substance. Pure purpurin cannot be obtained by sublimation from the crude product, since alizarin sublimes at nearly the same temperature as purpurin.

The properties of purpurin have not been so minutely and accurately described as would seem desirable in the case of a body, of which several isomerides are already known. We have therefore ourselves carefully examined its properties, taking for the purpose a specimen of which the melting point remained constant after it had been converted into the acetyl-compound and again liberated. An analysis of the substance yielded the following results:—

0.2336 grm. of substance dried at 110° gave 0.5596 grm. CO₂, and 0.0730 grm. H₂O, corresponding in 100 parts to—

C	65.33
H	3.47

The formula $C_{14}H_8O_5$ requires—

C.....	65.62
H.....	3.12

Purpurin dissolves easily in boiling spirits of wine, yielding a yellow solution, from which it crystallises on cooling in thin flattened prisms, sometimes 3 millims. long, having a deep orange colour and much lustre. On being heated at 100° , these crystals become dark red from loss of water. From a solution of purpurin in strong alcohol dark red needles are deposited, which are anhydrous.

The determination of the water of crystallised purpurin led to the following results :—

0.4602 grm. of substance dried over sulphuric acid lost on being heated at 110° 0.0302 grm. $H_2O = 6.56$ p.c.

0.4110 grm. of substance lost 0.0260 grm. $H_2O = 6.32$ p.c.

The formula $C_{14}H_8O_5.H_2O$ would require a loss of 6.56 p.c., and the crystals therefore contain 1 molecule of water.

The melting point of purpurin is at 253° . It begins however to sublime at 150° (according to Schützenberger at 250°). The sublimate consists of red, plumose or needle-shaped crystals. Much carbonaceous residue is left. The crystals obtained by dissolving sublimed purpurin in spirits of wine are generally anhydrous, but occasionally hydrated crystals of the usual appearance are obtained. After purpurin has been repeatedly sublimed, its melting point becomes considerably depressed, indicating some kind of decomposition, but after recrystallising several times from alcohol, the melting point again becomes constant at 253° .

Purpurin is slightly soluble in boiling water, the solution having a yellow colour with a tinge of red, and depositing crystalline yellow flocks on cooling. It dissolves in ether, giving a yellow fluorescent solution, which shows two bands of absorption, as described by Professor Stokes (*Chem. Soc. Journ.*, xii, 219). It also dissolves readily in boiling carbon disulphide, benzene and glacial acetic acid, yielding yellow solutions which deposit crystalline needles on cooling. These solutions show two bands of absorption coinciding with those of the ethereal solution. Purpurin dissolves in concentrated sulphuric acid, giving a rose-red solution, which shows three bands of absorption, one in the yellow, the others in the same position as those of the ethereal solution. Purpurin dissolves in caustic potash and soda-lye, in sodium carbonate solution, and in ammonia. The solutions have a deep red colour, inclining to purple, and show the absorption-bands described by Professor Stokes and other observers. In alcoholic potash or soda, purpurin is almost insoluble. On being treated with boiling baryta-water, it forms a purple lake quite insoluble in water.

By treatment with lime water it yields a compound which resembles that with barium, and is also insoluble.

A solution of purpurin in caustic alkali loses its colour on exposure to the air, becoming pale yellow, and the purpurin disappears entirely. Vogel (*Deut. Chem. Ges. Ber.*, x, 159) ascribes the change which takes place in this case to the sensitiveness of the solution towards light, and thinks it is due chiefly to an absorption of the yellow rays. There can be little doubt however that the decomposition of the purpurin is caused by oxidation, since the alkaline solution remains unchanged for weeks, if kept in a well stoppered bottle even on exposure to direct sunlight, whereas the same solution soon becomes decolorised on exposure in an open vessel in the dark. If the solution be left to stand in a test-tube, it will be seen that the change of colour commences at the surface and proceeds gradually downwards.

On treatment with boiling alum-liquor, purpurin dissolves, giving the well-known pink fluorescent solution, the optical properties of which have been frequently described. The solution, on cooling, generally yields a deposit, consisting of yellow crystalline needles of purpurin mixed with amorphous particles of an alumina-compound, as may easily be seen by treating the deposit, after filtration, with boiling alcohol, which dissolves the purpurin with a yellow colour, leaving the alumina-lake undissolved as a dark-red powder. The solution, doubtless, contains purpurin in combination with alumina, for, on agitation with ether, it remains quite unchanged, whereas, after the addition to it of hydrochloric acid, ether takes up purpurin, forming a yellow solution, and leaving the liquid below only slightly coloured. Nevertheless, the combination is a very loose one, for if alcohol be added to the solution, to precipitate the excess of alum present, and the filtrate be evaporated, a mixture of alum crystals and needles of purpurin is obtained, from which the purpurin may be extracted by treatment with absolute alcohol, in which it dissolves with a yellow colour, an almost colourless crystalline mass being left. The solution in alum-liquor, when mixed with a little sodium carbonate or ammonia, the liquid still retaining an acid reaction, gives a flocculent precipitate, having the pink colour peculiar to the so-called madder lakes, which, as Robiquet long ago showed, are essentially compounds of purpurin with alumina. The precipitate is quite insoluble in a strong boiling solution of sodium carbonate, but dissolves easily in sodium hydrate.

An alcoholic solution of purpurin gives, with lead acetate, a dark crimson precipitate, which, on treatment with an excess of alcoholic lead acetate solution, dissolves, yielding a fine crimson solution. This solution shows three bands of absorption. This behaviour is characteristic, and may serve to distinguish purpurin from alizarin, which gives a lead-compound quite insoluble in alcoholic lead acetate.

An alcoholic solution of purpurin gives, with copper acetate, a dark reddish-yellow precipitate, whereas an alcoholic solution of alizarin becomes purple on the addition of copper acetate, and gives no precipitate, provided the alizarin is quite pure.

The derivatives of purpurin cannot be obtained with the same ease as those of alizarin and its isomerides. On endeavouring, for instance, to prepare methylpurpurin or ethylpurpurin, the difficulties encountered in consequence of the formation of various by-products are so great as to render the purification of the product almost impossible when only moderate quantities of material are taken. Schützenberger and Schiffert (*Traité des matières colorantes*, ii, 129) have described an ethyl-purpurin, but the composition given by them leaves it doubtful whether the compound contains one, two, or three molecules of ethyl.

Triacetylpurpurin.

This compound, first described by Liebermann and Giesel (*Deut. Chem. Ges. Ber.*, ix, 332), was prepared by heating purpurin with acetic anhydride at 180°. When heated, it begins to soften at 193°, and melts completely at 198—200°, which is somewhat higher than the temperature given by Liebermann and Giesel. It is decomposed even in the cold by dilute caustic potash lye, yielding purpurin. It is dissolved by concentrated nitric acid, giving a yellowish-brown solution, which, on the addition of water, deposits yellow flocks. These flocks dissolve in caustic potash lye, giving a fine pink solution which shows the absorption-bands of purpurin.

On analysis, the following results were obtained :—

0.3546 grm. of substance dried at 110°, gave 0.8154 grm. CO₂ and 0.1218 grm. H₂O, corresponding in 100 parts to

C	62.71
H	3.81

The formula C₁₄H₅(C₂H₃O)₃O₅ requires

C	62.82
H	3.66

Bromopurpurin.

When purpurin is digested with carbon disulphide containing bromine, hydrobromic acid is immediately evolved. Unless the temperature is raised to 150—200°, however, a portion of the purpurin remains unattacked. The product crystallises from glacial acetic acid in dark red lustrous needles, melting at 276°. Its properties are very similar to those of purpurin. It is, however, less soluble in

alcohol and glacial acetic acid than purpurin, and on being heated sublimes, leaving hardly any residue. In order to ascertain its composition, the amount of bromine contained in it was determined, the following results being obtained:

I. 0.1738 grm. of substance gave 0.0950 grm. AgBr, corresponding to 23.26 p.c. of bromine.

II. 0.2500 grm. of substance gave 0.1374 grm. AgBr, corresponding to 23.38 p.c. of bromine.

The formula $C_{14}H_7BrO_5$ requires 23.88 p.c. of bromine.

The product is, therefore, monobromopurpurin. This fact is of some interest, since it shows that purpurin differs from its isomerides in its behaviour to bromine. Anthrapurpurin, according to Perkin, takes up 2 atoms of bromine, while flavopurpurin, as we have recently ascertained, yields a product containing 3 atoms.

5. Action of Heat on Purpurin.

According to Schiel (*Ann. Chem. Pharm.*, lx, 76), purpurin, when strongly heated, undergoes some peculiar change, since the sublimate which is obtained no longer gives a red solution with caustic alkaline lye like purpurin, but dissolves with a violet colour. Bolley (*Journ. f. prakt. Chem.*, xcix, 305), maintains that at a temperature of 210—220°, purpurin is partly converted into alizarin. Quite recently, however, Rosenstiehl (*Compt. rend.*, lxxix, 669) has asserted that the observations of the chemists just named are erroneous.

Having heated some purified commercial purpurin in sealed tubes at 300° for several hours, we found that the purpurin had been entirely decomposed, yielding a carbonised mass, though no pressure from evolved gas could be observed on opening the tubes. On treating a small quantity of the product with caustic alkali, we obtained a violet solution which showed absorption-bands having the same position as those of alizarin, but a little broader than the latter. We now treated the whole contents of the tubes with boiling alcohol, and added to the filtered liquid an alcoholic solution of lead acetate. This gave a precipitate of lead alizarate, leaving in solution a lead-compound of quinizarin. As it was possible that the alizarin and quinizarin which we found had not been formed from the purpurin, but pre-existed in the specimen employed, the purpurin being simply decomposed by the heat applied, while the two other substances were left intact, we examined the purpurin we had taken by the method described in a previous note. This method is applicable to mixtures of purpurin and quinizarin, since the latter, like alizarin, remains unchanged when its alkaline solutions are exposed to the air. Now, our material was, indeed, found to contain small quantities of alizarin,

but not a trace of quinizarin. We therefore repeated our experiment by heating perfectly pure purpurin in sealed tubes as before. The product was quite free from alizarin, but contained quinizarin, which we, therefore, concluded is really a product of the action of heat on purpurin.

The quinizarin produced in this way has all the properties ascribed to the substance by its discoverer, Grimm (*Deut. Chem. Ges. Ber.*, vi, 508). It crystallises in bright red needles, melting at 193–194°. Its ethereal solution is strongly fluorescent, and shows two well-defined absorption-bands. Its alkaline solution is violet, like that of alizarin, and shows, like the latter, two absorption-bands, situated, however, somewhat further away from the red end of the spectrum. It is soluble in alum-liquor, giving a red solution which resembles that of purpurin in alum, and, like the latter, shows two absorption-bands.

In conducting the process of decomposition, whereby quinizarin is formed, it is advisable to discontinue heating before the purpurin is completely decomposed. The tube containing the latter having been heated at 300° during 6 or 7 hours, the contents are removed and treated with a boiling dilute solution of sodic carbonate, which dissolves a great part of the undecomposed purpurin along with various by-products. The residue is now treated with dilute caustic potash-lye, and the quinizarin and purpurin in solution are separated by the method described by Auerbach for purifying alizarin, *i.e.*, by passing through it a current of carbonic anhydride as long as any precipitate is formed. The precipitate contains quinizarin with a little purpurin, the latter being, for the most part, left in solution. The precipitate is filtered off and treated with hydrochloric acid, and the flocks left by the acid are again dissolved in caustic lye, carbonic anhydride being a second time passed through the solution. The process is repeated until the filtrate no longer contains purpurin.

The yield of quinizarin is but trifling, and is surpassed by that of the by-products formed at the same time. The latter cannot be obtained in a form suitable for analysis, and we are, therefore, unable to give any explanation of the cause of this remarkable metamorphosis.