XVIII. *On Rubian and its Products of Decomposition.* *By* EDWARD SCHUNCK, *F.R.S.*

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PART I.

AMONG the many discussions to which the subject of madder has given rise among chemists, there is none which is calculated to excite so much interest as that concerning the state in which the colouring matter originally exists in this root, and there is no part of this extensive subject which is at the same time involved in such obscurity. It is a well-known fact that the madder root is not well adapted for the purposes of dyeing until it has attained a growth of from eighteen months to three years, and that after being gathered and dried it gradually improves for several years, after which it again deteriorates. During the time when left to itself, especially if in a state of powder, it increases in weight and bulk, in consequence probably of absorption of moisture from the air, and some chemical change is effected, which, though not attended by any striking phenomena, is sufficiently well indicated by its results. There are few chemical investigations that have thrown any light on the nature of the process which takes place during this lapse of time, and in fact most of the attempts to do so have merely consisted of arguments based on analogy. It has been surmised that the process is one of oxidation, and that the access of atmospheric air is consequently necessary. We are indeed acquainted with cases, in which substances of well-defined character and perfectly colourless, as for instance orcine and hematoxyline, are converted by the action of oxygen, or oxygen and alkalies combined, into true colouring matters. A more general supposition is, that the process is one of fermentation, attended perhaps by oxidation, and in confirmation of this view the formation of indigo-blue from a colourless plant, by a process which has all the characters of one of fermentation, may be adduced. What the substance is however on which this process of oxidation or fermentation takes effect, what the products are which are formed by it, whether indeed the change is completed as soon as the madder has reached the point when it is best adapted for dyeing, or whether further changes take place when it is mixed with water and the temperature raised during the process of dyeing, are questions which have never been satisfactorily answered, if answered at all. It has indeed been suspected by several chemists, that there exists originally some substance in madder, which by the action of fermentation or oxidation is decomposed and gives rise by its decomposition to the various substances endowed either with a red or yellow colour, which have been discovered during the chemical investigations of this root. That several of these substances are merely mixtures, and some of them in the main identical, has been satisfactorily proved by late investigators. But there still remain a number, which, though extremely similar, have properties sufficiently marked to entitle them to be considered as distinct.

In my papers on the colouring matters of madder[*], I have described four substances derived from madder, only one of which is a true colouring matter, but all of them capable, under certain circumstances, as for instance in combination with alkalies, of developing red or purple colours of various intensity. To seek for a common origin for these various bodies so similar to one another and yet distinct, is very natural, and the discovery of it no improbable achievement.

PERSOZ[†] asserts the probability of this view in the following words:—"We may hence venture to conclude that the colouring matters which we extract from fabrics dyed with madder, as well as the alizarine which is obtained by submitting the products derived from madder to sublimation, do not exist ready formed in this root, and are only products derived from another substance which has not yet been isolated..... From numerous experiments which I have made on this subject, it follows that the colouring matter of madder may be compared, in respect to the derivatives to which it gives rise, to tannin, so that I do not despair of being able, as far as regards their metamorphoses, to establish a parallel between the products derived from madder and those obtained from tannin. If it should be possible to confer on the former that tendency to assume regular forms with which the latter are endowed, the separation of the proximate colouring or colour-giving (*colorable*) matters of madder will be easy, and it will thus be possible to establish their elementary composition and thence their relation to one another."

To Mr. J. HIGGIN is due the merit of having first called attention to the fact, that important changes take place during the process of dyeing with madder, which can only be explained by supposing that an actual formation of colouring matter takes place during the process. In his paper 'On the Colouring Matters of Madder[‡],' Mr. HIGGIN has detailed his experiments on that peculiar substance discovered in madder by KUHLMANN and called by him *Xanthine*. I have shown, on a former occasion, that the xanthine of KUHLMANN and other investigators is not a pure substance, but a mixture of two distinct substances. This fact however does not affect the correctness of Mr. HIGGIN's conclusions, the general accuracy of which I shall have great pleasure in confirming in the course of this paper. The presence of xanthine is easily ascertained by the deep yellow colour and intensely bitter taste which it communicates to cold water. Guided by these two tests, Mr. HIGGIN arrived at the conclusion, that in an infusion of madder, made with cold or tepid water, when left to itself, or more rapidly when heated to 120° or 130° FAHR., the xanthine gradually disappears and there is formed a gelatinous or flocculent substance, which possesses all the tinctorial power originally belonging to the infusion, while the liquid has lost

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[*] See Reports of the British Association for 1847 and 1848.

[†] Traité de l'Impression des Tissus, t. i. p. 501.

[‡] Philosophical Magazine for Oct. 1848.

all trace of any such power, and that as alizarine is the only substance contained in madder capable of dyeing, the xanthine must, during this process, have been changed into alizarine. Mr. HIGGIN found that this process is completely arrested by heating the infusion to the boiling-point, or by adding alcohol, acids or acid salts to it, and hence he concludes that the decomposition of the xanthine is caused by the action of a peculiar ferment contained in madder, and which is extracted together with xanthine by cold water. Mr. HIGGIN did not however succeed in converting his xanthine into alizarine or effecting any change in it by means of fermentation, in consequence, as he supposed, of not being able to obtain the exciting substance in a soluble and consequently active condition. His inferences were all derived from experiments made by either removing from an extract of madder the xanthine contained in it, or by adding to it an additional quantity of that substance, and then ascertaining the effects produced by dyeing in the usual way with liquids thus artificially prepared. By the action of sulphuric acid on xanthine, Mr. HIGGIN obtained a dark brown powder, which he seems to consider as devoid of any tinctorial power.

A very simple experiment suffices to prove that madder, in its dry state, contains very little, if any alizarine ready-formed. If an extract of madder be made with cold water, it will be found that the brownish-yellow liquid thus obtained when gradually heated will dye as well and as strongly as the madder from which it has been prepared. Now if the colouring matter were originally present in the form of alizarine, this could not take place, since alizarine is almost insoluble in cold water; and in employing it for the purpose of dyeing, it is necessary to dissolve it in warm or boiling water before it begins to exert any effect, as is plainly seen in the case of garancine, which contains alizarine ready-formed. Nor is there much colouring matter left behind in the madder after extraction with cold water, for after converting the residue in the usual manner into garancine by means of sulphuric acid, it is found to be capable of dyeing only very slightly. Nay more, if madder be extracted with hot water instead of cold, I have found the residue to give a garancine which dyed darker colours than that obtained from the residue of an equal weight of madder extracted with cold water, so that it appears that the colour-producing substance is more completely removed by cold than by hot water. If an extract of madder with cold water be left to stand, there is formed in it, as Mr. HIGGIN has shown, a flocculent substance, while the liquid loses its bitter taste, part of its yellow colour and the whole of its power of dyeing, which is now found to reside in its whole extent in the flocculent substance. This change takes place equally well with or without the access of atmospheric air.

By adding a variety of substances to an extract of madder with cold water, I was enabled to ascertain under what circumstances and by what means the tinctorial power of the liquid is destroyed, and consequently what is the general character of the substance or substances to which it is due. I found that by adding sulphuric or muriatic acid to the extract and heating, the liquid, after neutralization of the acid, was no longer capable of dyeing. The tinctorial power was also destroyed by the addition of hydrate of alumina, magnesia, protoxide of tin and various metallic oxides, but not by carbonate of lime or carbonate of lead. In all cases in which the property of dyeing in the extract was destroyed, I invariably found that its bitter taste and bright yellow colour were lost. Now in my former papers on this subject, I have shown that the intensely bitter taste of madder and its extracts is due to a peculiar substance, to which I have given the name of *Rubian*; and as it appeared from these preliminary experiments that this substance, though itself no colouring matter, is in some way concerned in the changes whereby a formation of colouring matter is induced in aqueous extracts of madder, I proposed to myself to examine its properties and products of decomposition more in detail than I had hitherto done.

The first step necessary to be taken for the attainment of this object, was of course to find a method of procuring this substance in quantities sufficiently large for the purposes of examination. I was at the commencement however far from appreciating the difficulties with which its preparation in a state of purity is attended. The process which I had formerly described, by precipitation with sulphuric acid, is not well adapted to the purpose, since rubian in a state of perfect purity is not precipitated by sulphuric acid, besides which it is easily decomposed by an excess of that acid. Neither is it precipitated by any metallic salt, with the exception of basic acetate of lead, which, from the circumstance of its precipitating also other substances from the extract, is not applicable to the purpose. It is decomposed by alkalies and alkaline earths. Even bicarbonate of lime exerts a decomposing effect on it in conjunction with the oxygen of the atmosphere. These substances must therefore be discarded in its preparation. Besides its great tendency to decomposition, there is another circumstance which presents obstacles to almost all attempts to prepare rubian in a state of purity. There is no investigation of madder which does not make mention of a substance, which when its solution in water is mixed with sulphuric or muriatic acid and boiled, gives rise to the formation of a dark green powder. To this substance, which possesses no bitter taste, and is in fact devoid of any characteristic property except the one mentioned, I have restricted the name of xanthine. The xanthine of most other chemists is however a mixture of rubian with this substance, and possesses therefore the bitter taste of the former, while showing the characteristic behaviour of the latter towards acids. To avoid confusion, I shall no longer employ the name of xanthine, and I shall call the substance which gives the green powder with acids *Chlorogenine*. Now these two substances, though of very different nature, behave similarly towards many reagents. If, for instance, basic acetate of lead be added to a watery extract of madder, according to the method proposed by Berzelius for the preparation of xanthine, and adopted with a slight modification by Mr. Higgin, there is produced a red precipitate, which after being washed and decomposed with sulphuretted hydrogen or sulphuric acid, gives a solution containing rubian; but the presence of chlorogenine is also indicated by its turning dark green when boiled with the addition of sulphuric or muriatic acid. Hence it follows that chlorogenine, though it is not thrown down by basic acetate of lead when present alone in a solution, is still in part precipitated thereby when rubian is present at the same time. The same circumstance takes place with other precipitants.

After numerous experiments I discovered a property of rubian, which is perhaps more characteristic of it than any other, and that is the remarkable attraction which is manifested by it towards all substances of a porous or finely-divided nature, and it was this property by means of which I was at length enabled to obtain it in a state of purity. If to a watery extract of madder a quantity of protochloride of tin be added, a light purple lake is precipitated. Most of the rubian remains in the solution, which still retains its yellow colour and bitter taste. If, however, after filtering, sulphuretted hydrogen be passed through it, then, provided the quantity of tin still in solution be sufficiently large, the sulphuret of tin, at the moment of precipitation, carries down the whole of the rubian, and the solution loses its bitter taste and the greater part of its yellow colour. The whole of the chlorogenine remains in solution, and may easily be detected in the filtered liquid by means of acids. If the sulphuret of tin, after being collected on a filter and well washed with cold water until the percolating liquid no longer gives a green colour on being mixed with acid and boiled, be treated with boiling alcohol, a yellow solution is obtained, which on evaporation gives pure rubian, without any admixture of chlorogenine, in the shape of a dark yellow, brittle substance. The same effect is produced by sulphuret of lead. If sugar of lead be added to an extract of madder, a dark reddish-brown precipitate falls, the liquid still containing the rubian of the extract, as seen by its deep yellow colour and bitter taste. If sulphuretted hydrogen be now passed through the filtered liquid, a great part of the rubian goes down with the sulphuret of lead, and may again be separated from it by means of boiling alcohol. That this action of the sulphurets on rubian depends very much on their state of division, and is therefore mainly of a mechanical, and not chemical nature, is proved by the fact, that the sulphurets of tin and lead, if prepared by precipitation from solutions of salts in water, and then allowed to settle and repose for some time before being added to a watery extract of madder, remove far less rubian from it than they do, if they are formed in the extract itself, whence it follows that it is only in the minute state of division, in which they exist at the moment of precipitation, before the particles have time to cohere, that these sulphurets exert any great attraction for rubian. That they do however combine with some portion of the rubian is proved by the fact, that the power of dyeing in an extract of madder is very much diminished by adding to it sulphuret of tin or lead, previously precipitated. Of the two sulphurets, the sulphuret of tin, which is always precipitated in much finer particles than the other, is by far the most powerful absorbent of rubian. If equivalent quantities of protochloride of tin and acetate of lead be added to equal measures of watery extract of madder, the sulphuret of tin from the former absorbs at least twice as much rubian as the sulphuret of lead from the latter. Sulphuret of copper acts differently. If sulphate of copper be added to the extract of madder, a precipitate is produced, as in the case of almost all metallic salts. On passing sulphuretted hydrogen through the filtered liquid, the latter becomes dark brown, but no sulphuret of copper is precipitated.

This attraction of surface exerted towards rubian by bodies in a state of minute division is not confined to metallic sulphurets. There are few bodies which exceed animal charcoal in porosity, or which, in other words, possess for the same bulk a greater extent of surface. I found accordingly that animal charcoal exhibits a still greater attraction for rubian than even sulphuret of tin. A very small quantity of animal charcoal is sufficient to deprive an aqueous extract of madder of its bitter taste and of its tinctorial power. Lamp-black acts in the same manner, though much less powerfully. Wood charcoal however has no absorbent effect whatever on rubian. All these substances attract rubian alone, leaving the other substances contained in the extract, such as chlorogenine, sugar and pectine, untouched. By means of boiling alcohol part of the rubian in combination with them is again removed, and thus an easy and efficient means is given of obtaining rubian in a state of purity. Of these substances none is so well adapted in all respects as animal charcoal. In employing sulphuret of tin, which is the only one that at all approaches it in efficiency, much time is consumed in the process of filtration and washing. Besides this, I found that on operating with it on a large scale, the rubian obtained was in great part decomposed on evaporating the alcoholic solution, just as if it contained a quantity of acid; and even on treating a portion of the solution with carbonate of lime, for the purpose of neutralizing any free acid that might be present, and evaporating over sulphuric acid at the ordinary temperature, there was obtained a deliquescent mass, which, as further experiments showed, could not be considered as pure rubian. After many trials I at length adopted the following method of preparation, which surpasses all others in facility and certainty of execution.

A weighed quantity of madder* being placed on a piece of calico or fine canvas stretched on a wooden frame, boiling water, which is preferable to cold water, as all decomposition of the rubian by means of fermentation is thereby arrested, is poured on it, four quarts of the latter being sufficient for every pound of madder. A dark yellowish-brown liquor is obtained, to which there is added, while hot, for every pound of madder taken 1 ounce of animal charcoal, prepared in the usual way from bones. This proportion of charcoal should not be exceeded, for if an excess of it be taken, as for instance 1½ ounce for every pound of madder, the whole of the rubian is certainly removed from the solution; but on afterwards treating the charcoal with alcohol very little rubian is dissolved, from which it appears that the solvent power of the alcohol only overcomes the attraction of the charcoal for rubian in part. In

* Avignon madder, of the variety called *Rosa*, was the kind used.

using the first proportion, part of the bitter taste of the extract remains, showing that the rubian is in excess. The liquid being well stirred with the charcoal, the latter is allowed to settle, which it does in a very short time, and the liquid, which still retains a brown colour, is decanted. The charcoal is then placed on a piece of calico or on a paper filter and washed with cold water, until the percolating liquid, when mixed with muriatic acid and boiled, no longer acquires a green colour, which is a sign that the chlorogenine is removed. These operations occupy a very short time, in consequence of the rapidity with which the animal charcoal may be washed. The animal charcoal is now treated with boiling alcohol, which is filtered boiling hot, and the treatment is repeated until it no longer communicates to the alcohol any yellow colour. The rubian obtained by evaporating the alcoholic liquid is however impure; it contains a considerable quantity of chlorogenine, however carefully the charcoal may have been washed with water, and consequently gives a green powder when treated with boiling sulphuric or muriatic acid. This proceeds from the circumstance that fresh animal charcoal, when used in the preparation of rubian, invariably takes up, besides rubian, a quantity of chlorogenine, which is not removable by cold water, but which afterwards dissolves together with the rubian in boiling alcohol. Nevertheless, on using the charcoal which has been once employed, after treatment with alcohol, a second time for the same purpose, it seems to take up rubian alone and no chlorogenine, notwithstanding its being, as might be supposed, in the same condition for again absorbing the latter as it was in the first instance. At all events, the alcohol dissolves only rubian out of the charcoal, when it is used a second time; and if the alcohol should still contain chlorogenine, there will certainly not be a trace of the latter in the alcoholic solution, when the charcoal is used for the third time. That the attraction of the charcoal for rubian is not diminished after it has been once used and then exhausted with alcohol, however indifferent it then becomes towards chlorogenine, is proved by the fact that far more rubian is obtained when the charcoal is employed for the second time than in the first instance. If the animal charcoal, after being once used and exhausted, be heated red-hot so as to destroy all organic matter contained in it, it again behaves towards the two substances in the same manner as in the first instance, that is, it absorbs a mixture of rubian and chlorogenine. It is therefore advisable to reject the rubian which is obtained from the charcoal that has been used for the first time*. If a small portion of the alcohol with which the charcoal has been treated no longer gives a green colour when mixed with acid and boiled, but remains of a pure yellow, it is distilled or evaporated. During evaporation a small quantity of a dark brown flocculent substance is deposited, which is separated by filtration. The solution now contains, besides rubian, another substance in small quantity, which is a product of decomposition of rubian itself, and is

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* This impure rubian cannot be purified by means of basic acetate of lead, since when rubian is present in a solution together with chlorogenine, the latter is, though not entirely, still in great part precipitated together with the rubian by that salt.

probably formed by the application of too great a heat in the process of drying the madder. There are two ways in which this substance may be removed. The first consists in adding to the solution sugar of lead, which precipitates it in dark reddish-brown flocks. These being separated by filtration, the rubian is precipitated by means of basic acetate of lead, and the light red compound or lake, after being washed with alcohol to remove all excess of lead salt, is decomposed either with sulphuretted hydrogen, or better still with sulphuric acid, the excess of the latter being removed by carbonate of lead. The other method, which is more expeditious, consists in adding sulphuric acid to the cold solution, after the greatest part of the alcohol has been evaporated. The sulphuric acid completely decomposes the foreign substance, provided a sufficient quantity is employed, and converts it into a substance which renders the solution milky, and then falls in the shape of brown resin-like drops. The sulphuric acid being neutralized with carbonate of lead, the filtered solution, which is yellow and now contains pure rubian, is evaporated to dryness. It is necessary to employ carbonate of lead, and not carbonate of baryta, for the neutralization of the sulphuric acid in both cases ; for if carbonate of baryta be used, the bicarbonate of baryta which is usually formed, even if present only in small quantity, causes part of the rubian to undergo decomposition. In evaporating the solution of rubian, care must be taken not to employ too great a heat when the evaporation approaches to a conclusion. The ordinary heat of a sand-bath is sufficient to decompose rubian in great part, especially if a large quantity of the substance be present. It is therefore advisable, when the solution is nearly evaporated, to complete the evaporation either in a water-bath or in a moderately warm place. The free access of atmospheric air need not be feared, as rubian is not thereby decomposed, unless some other substance be present at the same time. The quantity of rubian which I have obtained, according to this method of preparation, amounts to about 1000 grs. from 1 cwt. of madder. It may be mentioned that the method of preparing rubian, as above described, by means of animal charcoal and alcohol, is not new in principle. LEBOURDAIS* has proposed the same method for the preparation of several vegetable substances, such as colocynthine, strychnine, quinine, &c.

Properties of Rubian.—When prepared according to the method just described, rubian is obtained as a hard, dry, brittle, shining, perfectly uncrystalline substance, similar in appearance to gum or dried varnish. It is not in the least deliquescent, as xanthine is described to be. In thin layers it is perfectly transparent and of a beautiful dark yellow colour. In large masses it appears dark brown. It is very soluble in water and alcohol, more so in the former than the latter, but insoluble in ether, which precipitates it from its alcoholic solution in brown drops. Its solutions have an intensely bitter taste. When it is pure, its solution in water gives no precipitates with the mineral or organic acids, nor with salts of the alkalies or alkaline earths.

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* On the Nature and Preparation of the Active Principles of Plants, Annal. de Chim. et de Phys. 3^{me} ser. t. xxiv. p. 58.

Acetate of alumina, alum, protacetate and peracetate of iron, acetate of zinc, neutral and basic acetate of copper, acetate of lead, nitrate of silver, perchloride of tin, protonitrate of mercury, perchloride of mercury and chloride of gold produce no precipitate whatever in a watery solution of pure rubian, nor does any reaction take place, except a darkening of the solution in the case of some of these salts. If the rubian be impure, which is always the case when the solution has been incautiously evaporated and the rubian has been exposed to too great a heat after evaporation, then its solution, though it does not differ in appearance from one of pure rubian, when mixed with any mineral or organic acid, even acetic acid, or the salts of the alkalies or alkaline earths, is rendered milky, and a quantity of dark brown transparent resinous drops, mixed with yellow flocks, are deposited. These drops, in the case of the salts, consist merely of a substance insoluble in saline liquids, which dissolves again in pure water; but in the case of acids, they are, though similar in appearance, a product of decomposition of the latter substance, and do not redissolve in pure water. Sugar of lead gives, in a solution of impure rubian, a dark reddish-brown precipitate. Most metallic salts also give precipitates, consisting either of the substance itself which accompanies the rubian, or of compounds of this substance, with the respective metallic oxides. I shall return to these reactions when I come to treat of the action of heat on rubian. Basic acetate of lead gives a copious light red precipitate in a solution of pure rubian, the solution becoming colourless. This is the only definite compound of rubian with a base that I am acquainted with. Concentrated sulphuric acid dissolves rubian with a blood-red colour; on boiling the solution it becomes black and disengages sulphurous acid gas in abundance, after which water precipitates a black carbonaceous mass. If sulphuric acid be added to a watery solution of rubian, and the mixture be boiled, the solution, if dilute, becomes opalescent, and on cooling a quantity of light yellow flocks are deposited; and if the solution was concentrated, these are formed in such abundance on cooling as to render the liquid thick. If these flocks exhibit the least tinge of green, the presence of chlorogenine is indicated. Muriatic acid acts in precisely the same manner. Nitric acid produces in the cold no effect in a solution of rubian, but on boiling a disengagement of nitrous acid takes place, the liquid becomes light yellow, and now contains the acid which I called in my former papers alizaric acid, and which LAURENT and GERHARDT consider as identical with naphthalic acid. Phosphoric, oxalic, tartaric and acetic acids produce no effect on the solution, even on boiling for some time. When a stream of chlorine gas is passed through a watery solution of rubian, the solution immediately becomes milky and begins to deposit a lemon-yellow powder, into which, on continuing the action, the whole of the rubian is converted, the liquid becoming colourless. Caustic soda turns the colour of the solution from yellow to blood-red, and on neutralizing the alkali with acid, a clear yellow solution is again obtained. By boiling the solution to which the soda has been added, the colour changes from blood-red to purple; and on now supersaturating the alkali with acid, a reddish yellow precipitate falls, while the supernatant liquid becomes almost colourless. Ammonia changes the colour of a solution of rubian to blood-red; the colour is not changed by boiling; and by supersaturating the ammonia with acid either before or after boiling, no precipitate is formed. Lime and baryta water give dark red precipitates in a solution of rubian, which are soluble in pure water, forming dark red solutions. Magnesia turns the solution dark red; the solution contains magnesia. The carbonates of lime and baryta produce no perceptible effect on a solution of rubian; they do not change its colour, nor do they take up any rubian. Hydrate of alumina, when placed in a solution of rubian, acquires a brownish-yellow colour. If sufficient alumina be taken, the liquid is rendered almost colourless. Hydrated peroxide of iron acts in a similar manner. Oxide of copper also removes most of the rubian from its solution. Alkaline solutions of rubian do not reduce the oxides of silver and copper on the addition of salts of these oxides, but they reduce salts of gold to the metallic state. When heated on platinum foil, rubian melts, swells up very much, burns with a flame and gives a carbonaceous residue, which does not entirely disappear on being further heated, but leaves a quantity of ash. When heated gradually in a tube it begins to undergo decomposition, accompanied by loss of water at a temperature of about 130° C., and is converted into another substance, which I shall describe further on. When heated to a still higher degree in a tube or retort, it gives fumes of an orange colour, which condense on the colder parts of the vessel to a crystalline mass, consisting chiefly of alizarine.

Rubian cannot be considered as a colouring matter in the ordinary sense of the word. It imparts hardly any colour to mordanted cloth, when an attempt is made to dye with it in the usual way, the alumina mordant only acquiring a slight orange, the iron mordant a light brown colour.

Composition of Rubian.—In determining the composition of rubian, I found it necessary to take into consideration the fact of its leaving when burnt a considerable quantity of ash. This ash consists almost entirely of carbonate of lime. The amount of ash is not uniform in different specimens; it is greatest when the rubian has been purified by means of sulphuric acid, but I have never been able to obtain it in a state in which it burns without any residue. Even after being precipitated with basic acetate of lead and again separated from the oxide of lead, rubian leaves some ash on being burnt, so that it appears as if the lime which it contains were an essential constituent, or at all events, that it follows it into the lead compound, from which it cannot be removed by means of water or alcohol.

The following results were obtained on analysis:—

I. 0·3880 grm. rubian, which had been purified by means of sulphuric acid, dried at 100° C., gave, when burnt with oxide of copper, 0·7210 carbonic acid and 0·1745 water.

II. 0·4780 grm. of the same preparation, burnt with oxide of copper, gave 0·8865 carbonic acid and 0·2180 water.

III. 0·4755 grm. of the same preparation, burnt with oxide of copper, gave 0·8835 carbonic acid and 0·2180 water.

0·1690 grm., on being incinerated, left 0·0130 grm. of ash=7·69 per cent.

IV. 0·3910 grm. rubian, purified by means of acetate and basic acetate of lead, burnt with chromate of lead, gave 0·7455 carbonic acid and 0·1880 water.

0·4050 grm. of this preparation left 0·0215 grm. of ash=5·30 per cent.

V. 0·4235 grm. rubian, purified in the same way as I. and burnt with chromate of lead, gave 0·7890 carbonic acid and 0·2020 water.

0·6400 grm. of this preparation left 0·0465 ash=7·26 per cent.

VI. 0·4390 grm. rubian, purified in the same way as IV., burnt with chromate of lead, gave 0·8370 carbonic acid and 0·2120 water.

0·8400 grm. of this preparation left 0·0440 ash=5·23 per cent.

After making the necessary corrections for the ash, these numbers correspond in 100 parts to—

	I.	II.	III.	IV.	V.	VI.
Carbon	54·89	54·79	54·89	54·90	54·78	54·84
Hydrogen . . .	5·41	5·48	5·51	5·64	5·71	5·66
Oxygen	39·70	39·73	39·60	39·46	39·51	39·50

Rubian contains no nitrogen. On burning it with oxide of copper and collecting the gas over mercury, I found the latter to be entirely absorbed by caustic alkali. When burnt with lime and soda, only a minute trace of chloride of platinum and ammonium was obtained. The statement contained in my former paper, which was made at a time when I had not obtained rubian in a state of absolute purity, that nitrogen is one of its constituents, must therefore be corrected.

From the above analyses the following composition may be deduced:—

	Eqs.		Calculated.
Carbon	56	336	55·08
Hydrogen	34	34	5·57
Oxygen	30	240	39·35
		610	100·00

The compound with oxide of lead, which was the only one that could be employed for the determination of the atomic weight, was prepared by dissolving rubian in alcohol, adding acetate of lead, precipitating with a little ammonia, taking care to leave an excess of rubian, and washing with alcohol. If it be prepared by precipitation from a watery solution by means of basic acetate of lead, great difficulties are experienced in the course of filtration; the liquid begins to run through slowly, the precipitate becomes somewhat mucilaginous and adheres to the paper, and sometimes even it seems to be decomposed and no longer gives unchanged rubian, but a dark brown viscid substance. Its analysis gave the following results:—

I. 0·3670 grm., dried at 100° C. and burnt with chromate of lead, gave 0·3520 carbonic acid and 0·0875 water.

0·3360 grm. gave 0·2390 sulphate of lead.

II. 0·4440 grm. of another preparation, burnt with chromate of lead, gave 0·4190 carbonic acid and 0·1115 water.

0·4320 grm. gave 0·3100 sulphate of lead.

III. 0·4635 grm. of the same preparation as the last gave 0·4450 carbonic acid and 0·1050 water.

0·5405 grm. gave 0·3880 sulphate of lead.

These numbers lead to the following composition:—

	Eqs.		Calculated.	I.	II.	III.
Carbon	56	336	26·25	26·15	25·73	26·18
Hydrogen	34	34	2·65	2·64	2·87	2·51
Oxygen	30	240	18·76	18·89	18·62	18·51
Oxide of lead . . .	6	670	52·34	52·32	52·78	52·80
		1280	100·00	100·00	100·00	100·00

Hence it appears that oxide of lead in combining with rubian does not replace any basic water, as is usually the case.

It may easily be conceived that a body so readily decomposed as rubian gives a number of different products of decomposition. It is decomposed by acids, alkalies, chlorine, heat and ferments; and I shall now proceed to describe the products of decomposition to which these various reagents give rise.

Action of Sulphuric and Muriatic Acid on Rubian.—The action of these two acids is precisely the same; but for the purpose of studying it, it is better to employ sulphuric acid, as it is more easily removed again afterwards. On adding sulphuric acid in considerable quantity to a watery solution of rubian and boiling the liquid, no perceptible change takes place at first, except that the solution loses a little of its transparency and becomes slightly opalescent. If the solution was not very dilute, there begin to appear very soon a number of orange-coloured flocks. After boiling for some time and allowing to cool, these flocks are deposited in large quantities, and the liquid is now found to be much lighter in colour than before. After allowing to cool and filtering, the liquid, on being mixed with fresh acid and boiled again, often deposits on cooling a fresh quantity of these flocks. When after repeated boilings no more flocks separate on cooling, the process is completed. The last portions of rubian are usually more difficult to decompose than the first, and an additional quantity of acid is therefore necessary to effect their decomposition. The liquid retains to the last a light yellow colour. I shall return to it presently. The orange-coloured flocks are washed on the filter with cold water until all the acid is removed. They now consist of four different substances, three of which are bodies previously known, the fourth one which has not hitherto been observed. The three former are,—1st, *Alizarine*; 2ndly, the substance which in my former papers I have called *alpha-resin*, but to which I prefer giving the name of *Rubiretine*; 3rdly, the substance which I formerly termed *beta-resin*, but I shall now call *Verantine* from *Verantia*, the name applied to madder in the middle ages. The fourth substance I shall denominate *Rubianine*.

The presence of alizarine in this mixture is indicated by the dark and beautiful colours which are produced when it is employed for dyeing a piece of mordanted cloth, and which contrast forcibly with the faint and dull tints produced by rubian. It may also easily be separated from the other substances by dissolving the mixture in alcohol, adding hydrate of alumina to the solution, filtering, treating the alumina compound repeatedly with a solution of carbonate of potash or soda, until nothing more is dissolved by the latter, decomposing the alumina compound with acid, and dissolving the residue in alcohol, when on evaporating the latter crystals of alizarine with its usual characters are obtained. In order however to obviate all objections which might arise from the use of alkalies in regard to the effect which the latter might be supposed to have in causing the formation of the alizarine, I determined if possible to use acids and salts only in the separation of the substances mentioned above. Of the four substances contained in the orange-coloured flocks, two, viz. alizarine and rubianine, are soluble in boiling water, and may thereby be separated from the two others which are insoluble in water. This method of separation is however tedious, on account of the sparing solubility of alizarine and rubianine in boiling water. I therefore prefer using the following method. The orange-coloured flocks containing the four substances are treated with boiling alcohol, in which they dissolve with a dark reddish-yellow colour. The alcohol is filtered boiling hot, and deposits on cooling a small quantity of yellow crystalline particles, consisting chiefly of rubianine. The treatment with alcohol is repeated as long as the latter acquires a dark yellow colour. The greatest part of the rubianine remains behind as a yellow or brownish-yellow crystalline mass, which is treated repeatedly with boiling alcohol, in which the whole at last dissolves, the greatest part again separating on the solution cooling, either in yellow needles or as a brownish-yellow crystalline mass. If its colour is not a pure yellow, or if it is imperfectly crystallized, it contains verantine and must be purified. For this purpose the whole of the mass which has been deposited on the alcohol cooling, after being collected on a filter, is again dissolved in boiling alcohol, and sugar of lead is added to the solution, by which means the verantine is precipitated in combination with oxide of lead, while the rubianine remains in solution and is again deposited, when the solution, after being filtered boiling hot, is allowed to cool, in long, lemon-yellow silky needles, which may be rendered perfectly pure by recrystallization. The compound of verantine and oxide of lead may be decomposed with sulphuric acid, and the verantine separated from the sulphate of lead by boiling alcohol. The alcoholic liquid from which the rubianine has been deposited contains the three other substances besides a portion of the rubianine. By adding acetate of alumina to it, the whole of the alizarine as well as a part of the verantine are precipitated, in combination with alumina, in the shape of a dark red powder, while the liquid retains a dark brownish-red colour. This precipitate, after being collected on a filter and washed with alcohol until the latter runs through colourless, is decomposed with muriatic acid, which dissolves the alumina, leaving behind red flocks consisting of alizarine and verantine. These flocks, after being filtered off and washed with water, are again dissolved in alcohol, to which is then added a solution of neutral acetate of copper. This instantly changes the colour of the liquid to a beautiful dark purple. The copper compound of alizarine remains dissolved, while the verantine is entirely precipitated, in combination with oxide of copper, as a dark reddish-brown powder. The dark purple liquid, after filtration and evaporation, leaves a purple mass of alizarine-oxide-of-copper, which is decomposed with muriatic acid. Yellow flocks, consisting of alizarine, remain behind, which after being washed with water are dissolved in alcohol. The alcoholic solution on evaporation gives crystals of alizarine, which may be purified by recrystallization. The compound of verantine with oxide of copper is decomposed with muriatic acid. The liquid filtered from the alumina compound of alizarine and verantine is evaporated to dryness, muriatic acid is added to the residue, which is placed on a filter and washed with cold water until all the acid and salts of alumina are removed. On being now treated with boiling water, a quantity of dark brown resinous drops sink to the bottom of the vessel and cohere into a semi-fused mass, while brownish-yellow flocks float in the water. The water is decanted from the mass at the bottom, carrying with it the flocks. This process is repeated with fresh quantities of water until no more flocks are carried away by it. The resinous mass at the bottom now consists principally of rubiretine. It may be purified by dissolving in cold alcohol, which leaves behind a quantity of verantine. The brownish-yellow flocks consist chiefly of verantine and rubianine; they are treated with boiling water, in which the rubianine dissolves, and from which it is again deposited, on filtering the water boiling hot and allowing to cool, in orange-coloured flocks. The process is repeated until the water dissolves nothing more. The orange-coloured flocks of rubianine are collected on a filter and dissolved in boiling alchohol, out of which the rubianine crystallizes on cooling in yellow needles. The mother-liquor is somewhat darker than a mere solution of rubianine would be. It contains a little alizarine and rubiretine, which may be separated by means of acetate of alumina, as before described. The verantine which is left behind by the boiling water is mixed with the other portions obtained from the lead and copper compounds, and the whole is dissolved in a small quantity of boiling alcohol, out of which the verantine is deposited on cooling as a dark reddish-brown or yellowish-brown powder, which may be purified by a second solution in alcohol.

These substances can, as may be supposed, be obtained without any difference in properties by adding sulphuric or muriatic acid to an extract of madder made with boiling water, boiling the liquid, and treating the dark green precipitate obtained in the same way as the orange-coloured flocks, from the decomposition of rubian. The dark green colour of the precipitate in this case proceeds from the decomposition of chlorogenine by the acid; the product of decomposition does not however in any way interfere, as it is insoluble in alcohol. It may be remarked, however, that very little rubianine is obtained in this manner, its place being supplied, from a cause which I shall mention hereafter, by rubiacine.

There still remains in the acid liquid filtered from the orange-coloured flocks, a substance which is an essential product of the action of acids on rubian. This liquid has, as I mentioned before, a light yellow colour. After neutralizing the acid with carbonate of lead it becomes almost colourless, while the carbonate of lead acquires a pink tinge. After filtration it is found to contain neither sulphuric acid nor lead; nor does it give any precipitate with neutral or basic acetate of lead, nor with alkalies, either before or after neutralization, unless it be boiled with an excess of the latter. This absence of reaction proves that no substance of a basic nature has been formed during the process. The liquid however contains a considerable quantity of an organic substance, which is obtained by carefully evaporating at the ordinary temperature over sulphuric acid. It is not advisable to evaporate with the assistance of heat, as the solution then becomes dark brown from the action of the air. After evaporation over sulphuric acid there is left at last a brownish-yellow, transparent syrup, having a sweetish taste, which I shall prove by its properties and composition to be a species of sugar.

I shall now describe more in detail the properties of the substances just mentioned.

Alizarine.—The alizarine obtained from the decomposition of rubian exhibits all the usual properties of this well-known substance. Its colour is dark yellow without any tinge of brown or red. The crystals possess a lustre which I have never seen equalled in this substance. Its analysis gave the following results:—

0·3200 grm. of the crystals, on being heated in the water-bath, lost 0·0580 grm. of water=18·12 per cent. According to the formula $C_{14} H_5 O_4 + 3HO$, they should lose 18·24 per cent.

0·2575 grm. of the dry substance, burnt with chromate of lead, gave 0·6550 carbonic acid and 0·0945 water.

These numbers lead to the following composition:—

	Eqs.		Calculated.	Found.
Carbon	14	84	69·42	69·37
Hydrogen	5	5	4·13	4·07
Oxygen	4	32	26·45	26·56
		121	100·00	100·00

0·1050 grm. of the lead compound, prepared by precipitating the alcoholic solution with sugar of lead, gave 0·0720 sulphate of lead, equivalent to 0·0529 oxide of lead

=50·44 per cent. The formula $C_{14} H_4 O_3 + PbO$ requires 49·90 per cent. oxide of lead.

The formula here given is the same to which I was led by my former experiments, and it now receives a new confirmation from the relation in which it stands to that of rubian.

The formation of alizarine from rubian admits of a very easy explanation. By simply losing 14 equivs. of water, 1 equiv. of rubian is converted into 4 equivs. of alizarine, as the following equation shows:—

$$C_{56} H_{34} O_{30} = 4(C_{14} H_5 O_4) + 14HO.$$

The action of sulphuric acid in the preparation of garancine from madder now becomes more intelligible. It consists simply, as far as the practical effect is concerned, in the conversion of rubian into alizarine.

MM. Wolff and Strecker, in a late paper 'On the Red Colouring Matters of Madder*,' have given another formula for alizarine, which they prefer on account of the relation in which they suppose this substance to stand to naphthaline. This formula is $C_{20} H_6 O_6$, which requires in 100 parts—

Carbon	68·96
Hydrogen	3·45
Oxygen	27·59

In confirmation of this formula they adduce one analysis, in which they obtained from 0·0650 grm. alizarine 0·163 carbonic acid, equivalent to 68·4 per cent. If it be permitted to deduce any safe inference from the analysis of so small a quantity of substance, I should be inclined to say that the substance analysed was impure. Even when perfectly well crystallized, alizarine may contain an amount of impurity sufficient to affect its composition. This impurity generally consists of verantine. A large admixture of the latter substance entirely prevents alizarine from crystallizing, but a small quantity merely gives the crystals a brownish or reddish tinge. Alizarine can never be considered as perfectly pure unless it exhibits a pure dark yellow colour without admixture of red. In proof of this statement I may adduce the following experiments. In the course of my investigation I obtained from madder a specimen of alizarine in perfectly well-defined crystals, containing apparently no foreign substance, but having a brownish-red colour instead of the dark yellow characteristic of pure alizarine.

0·3530 grm. of these crystals, dried at 100° C., gave 0·8855 carbonic acid, equivalent to 68·41 per cent. of carbon.

The remainder of the substance was recrystallized from alcohol, and

0·2940 grm. now gave 0·7360 carbonic acid, equivalent to 68·27 per cent. of carbon.

On dissolving the rest in alcohol and adding to the solution acetate of copper, a dark reddish-brown precipitate of verantine-oxide-of-copper fell. From the dark

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* Ann. der Chem. u. Pharm., vol. lxxv. p. 1.

purple solution, after being treated in the manner before described, there were obtained some beautiful dark yellow crystals of alizarine, which on analysis yielded the following result:—

0·1270 grm., dried at 100° C., gave 0·3245 carbonic acid, equivalent to 69·68 per cent. of carbon.

It appears therefore that alizarine cannot be separated from the last portions of impurity by recrystallization merely.

Were the above formula the correct one, it would be difficult to account for the circumstance that the purer the substance the greater is the excess, not only of hydrogen, but also of carbon. An excess of 0·6 per cent. of hydrogen, as this formula would pre-suppose, is unusually large; an excess of 0·4 per cent. of carbon seldom or never obtained in the analysis of a pure substance. The most common impurity of alizarine is verantine; and since the latter contains, as I shall presently show, more oxygen for the same amount of carbon and hydrogen, it follows that if a portion of it be mixed with the alizarine, the amount of carbon and hydrogen in the latter will be reduced, and the composition will approximate to that given by **Wolff** and **Strecker**.

Again, if the correct formula for alizarine be $C_{20}\,H_6\,O_6$, the formula of rubian must necessarily be $C_{20}\,H_{11}\,O_{11}$, which requires in 100 parts—

Carbon	54·79
Hydrogen	5·02
Oxygen	40·19

These numbers, as will be perceived, do not agree so well with those of the analyses as those corresponding to the formula which I have given above. The lead compound of rubian can, under this supposition, only be represented by the formula $6(C_{20}\,H_{11}\,O_{11})+13PbO$, which requires in 100 parts—

Carbon	26·03
Hydrogen	2·38
Oxygen	19·10
Oxide of lead	52·49

Here also it will be seen there is less accordance with the numbers found by experiment than in the case of the other formula. But besides this, the latter formula is of too complicated a nature to be received; I therefore consider the formula $C_{14}\,H_5\,O_4$, or perhaps $C_{28}\,H_{10}\,O_8$, for alizarine to be as firmly established as it can be with the means at present at our command.

Verantine.—This substance coincides in most of its properties with the substance to which I formerly gave the name of the beta-resin of madder. When prepared according to the method above described, it is obtained in the shape of a reddish-brown powder, similar in colour to snuff or roasted coffee. It has the following properties. When heated on platinum-foil it melts and then burns away without leaving any residue. When heated in a glass tube it gives a small quantity of an oily sublimate without a trace of anything crystalline. When however it contains alizarine, as it very often does, it gives on being heated a crystalline sublimate consisting of the latter substance. It dissolves in concentrated sulphuric acid with a brown colour, and is reprecipitated by water in brown flocks. On heating the solution in concentrated sulphuric acid it becomes black, sulphurous acid is disengaged, and the substance is decomposed. Concentrated nitric acid dissolves it on boiling with a disengagement of nitrous acid, forming a yellow liquid, from which nothing separates on cooling. Dilute nitric acid does not affect it sensibly on boiling. It is almost insoluble in boiling water, but readily soluble in boiling alcohol with a dark brownish-yellow colour, and is again deposited, on the alcohol cooling, as a brown powder, which is its most characteristic property. It is soluble in alkaline liquids with a dirty brownish-red colour, and is reprecipitated by acids in brown flocks. If it be mixed with alizarine, then its solutions in alkalies have a reddish-purple colour. The ammoniacal solution loses its ammonia on evaporation, and leaves the substance behind as a brown transparent pellicle. The ammoniacal solution gives precipitates with the chlorides of barium and calcium. The alcoholic solution gives dark brown precipitates with the acetates of lead and copper, as I mentioned before. When it is free from alizarine, it does not communicate any colour to mordanted cloth, and is therefore no colouring matter in the usual sense.

In the opinion of most chemists who have examined madder, this root contains two distinct colouring matters, viz. alizarine and another, to which the names of *purpurine, oxylizaric acid* and *madder-purple* have been applied by different chemists. This opinion has been advocated with considerable ability by MM. Wolff and Strecker. I have however reason to suppose that purpurine is in fact no distinct substance, but a mixture of alizarine and verantine. The latter substance accompanies almost all the products which are obtained from madder, and it is this body which renders them so difficult to purify. It adheres so pertinaciously to alizarine, as to induce the belief that the two actually form a chemical compound. The mixtures of the two vary in appearance from that of dark red crystals to that of a red crystalline powder. In these mixtures the verantine may easily be detected by dissolving in alcohol and adding acetate of copper, which precipitates the verantine, as before described. It also accompanies rubianine and renders it difficult to crystallize, as I mentioned above, and I have never been able to obtain rubiretine without some trace of it. As a characteristic of purpurine is mentioned its property of giving a cherry-red solution with alkalies, having none of the violet appearance belonging to alkaline solutions of alizarine; and also its forming, when treated with boiling alum-liquor, a red opalescent solution, from which it separates again in orange-coloured flocks on the solution cooling. Now by adding to a solution of alizarine in caustic alkali a little verantine, the beautiful violet colour of the solution may be instantly changed to reddish-purple; and by dissolving in it still more of that substance the colour may be rendered cherry-red, these colours being evidently mixtures of the violet due to alizarine and the brownish-red produced by verantine. Pure alizarine is not more soluble in boiling alum-liquor than in water, as has been repeatedly shown; it only communicates to the liquor a yellow colour, and crystallizes out again on the liquid cooling. Verantine is still less soluble in alum-liquor. If this substance be dissolved in caustic alkali and be then precipitated with a solution of alum, the precipitate does not dissolve in the least degree, however much alum be added; it only communicates a slight yellow tinge to the liquid. If, however, a mixture of alizarine and verantine be dissolved in caustic alkali and they be then precipitated together by means of a solution of alum added in excess, then on boiling the precipitate with the liquid, a bright red solution is obtained, and on filtering and allowing to cool, orange-coloured flocks are deposited, while the liquid still remains red, but gives a yellow precipitate on the addition of acid. By treating the residue with additional quantities of alum-liquor more is dissolved with the same colour, and this continues until either the alizarine or the verantine, whichever of the two was present in the smallest quantity, is removed. From this experiment I am inclined to conclude that alizarine and verantine are capable of forming a double compound with alumina soluble in boiling water, and that a mixture of the two in the proportion in which they exist in this compound, constitutes what has been called purpurine. At all events, it follows that alum is not adapted as a means of separating the substances derived from madder. The fact of rubianine also dissolving in boiling alum-liquor and crystallizing out again on cooling, is an additional objection to its use.

The difficulty of obtaining pure verantine in sufficient quantity for the purposes of analysis, has prevented me from determining its composition with the requisite accuracy. I have however obtained approximations sufficiently near to remove almost all doubts on the question.

I. 0·3280 grm. verantine, dried at 100° C. and burnt with chromate of lead, gave 0·7865 carbonic acid and 0·1215 water.

II. 0·3220 grm. gave 0·7740 carbonic acid and 0·1205 water.

III. 0·2890 grm. gave 0·6995 carbonic acid and 0·1040 water.

IV. 0·1255 grm. gave 0·3010 carbonic acid.

These numbers agree best with the following composition:—

	Eqs.		Calculated.	I.	II.	III.	IV.
Carbon	14	84	65·11	65·39	65·55	66·01	65·41
Hydrogen . . .	5	5	3·87	4·11	4·15	3·99	
Oxygen	5	40	31·02	30·50	30·30	30·00	
		129	100·00	100·00	100·00	100·00	

The composition here given approaches that of the oxylizaric acid of DEBUS, who obtained in analysing that substance as a mean of his experiments in 100 parts,—

Carbon	66·40
Hydrogen	3·82
Oxygen	29·78

The baryta compound, prepared by precipitating the ammoniacal solution with chloride of barium, gave on analysis the following results:—

0·2605 grm., dried at 100° C. and burnt with chromate of lead, gave 0·4640 carbonic acid and 0·0740 water.

0·4055 grm. gave 0·1835 sulphate of baryta.

In 100 parts:—

Carbon	48·57
Hydrogen	3·15
Oxygen	18·60
Baryta	29·69

The formula $C_{42}H_{13}O_{13}+2BaO=2(C_{14}H_4O_4+BaO)+C_{14}H_5O_5$ requires in 100 parts—

Carbon	48·27
Hydrogen	2·49
Oxygen	19·93
Baryta	29·31

The compound with oxide of copper gave the following results:—

0·3680 grm., dried at 100° C. and burnt with chromate of lead, gave 0·7050 carbonic acid and 0·1030 water.

0·4710 grm. gave 0·1200 oxide of copper.

These numbers correspond very nearly to the following composition:—

	Eqs.		Calculated.	Found.
Carbon	14	84	52·50	52·24
Hydrogen	4	4	2·50	3·10
Oxygen	4	32	20·00	19·19
Oxide of copper	1	40	25·00	25·47
		160	100·00	100·00

Another specimen, prepared in exactly the same manner and having the same appearance, gave a different composition.

0·4375 grm. gave 0·8910 carbonic acid and 0·1345 water.

0·5530 grm. gave 0·1080 oxide of copper.

This gives the following composition:—

	Eqs.		Calculated.	Found.
Carbon	56	336	55·17	55·54
Hydrogen	17	17	2·79	3·41
Oxygen	17	136	22·34	21·53
Oxide of copper	3	120	19·70	19·52
		609	100·00	100·00

The formula of this compound must be expressed in the following manner:

$$3(C_{14}H_4O_4+CuO)+C_{14}H_5O_5.$$

These analyses show that verantine, like many substances, the acid character of which is not well-marked, combines with bases in various and complicated proportions.

It appears therefore that verantine differs from alizarine by containing 1 equiv. more of oxygen. According to DEBUS, the same relation exists between alizarine and his oxylizaric acid. He gives for alizarine the formula $C_{30} H_{10} O_9$, and for oxylizaric acid $C_{15} H_5 O_5$, so that 2 quivs. of the latter contain 1 equiv. more oxygen than 1 equiv. of the former. If my view of the composition of these substances be the correct one, the relation subsisting between the two is still more simple. Nevertheless I have some hesitation in asserting that verantine is to be considered as a higher oxide of the same radical as alizarine, or in supposing that it may be formed by oxidation from the latter. Its formation is due, as I shall presently show, not to any process of oxidation, but rather to the splitting up of an atom of rubian into two bodies.

Rubiretine.—This substance is identical with that which I formerly called the alpha-resin of madder, from which it does not differ in properties. It is obtained as a dark brown, opake, resinous mass, brittle when cold, but becoming soft and almost melting in boiling water. On being heated to a higher degree, it melts completely without being decomposed. It is generally found to be mixed with a small quantity of verantine, from which it may be separated by solution in cold alcohol, which leaves the greatest part of the verantine behind; I have however found it impossible to remove the last traces of that substance. It is almost insoluble in boiling water. Its solution in alcohol is dark yellow. It dissolves in concentrated sulphuric acid with a yellowish-brown colour, and is decomposed on boiling the solution with blackening and disengagement of sulphurous acid. Boiling nitric acid changes it into a yellow substance, which no longer softens at the temperature of boiling water, and is very little soluble in alcohol. It dissolves in alkaline liquids with a brownish-red colour, and is reprecipitated by acids in brown flocks, which on boiling the liquid cohere into dark-brown semifluid masses. When heated in a glass tube, it usually gives a small quantity of sublimed alizarine mixed with a brown oil. It is not capable of dyeing when quite free from alizarine. Its analysis yielded the following results:—

I. 0·5300 grm. from the decomposition of rubian, dried at 100° C. and burnt with chromate of lead, gave 1·3190 carbonic acid and 0·2405 water.

II. 0·3785 grm. of the same preparation as the last, heated to the melting-point, gave 0·9465 carbonic acid and 0·1730 water.

III. 0·4815 grm. obtained directly from madder, dried at 100° C., gave 1·2130 carbonic acid and 0·2335 water.

IV. 0·4290 grm. of the same preparation as the last, heated to the melting-point, gave 1·0735 carbonic acid and 0·2050 water.

V. 0·3120 grm. of another preparation obtained directly from madder, gave 0·7855 carbonic acid and 0·1460 water.

VI. 0·2350 grm. of the same preparation as the last, gave 0·5865 carbonic acid and 0·1065 water.

In 100 parts it therefore contains—

	I.	II.	III.	IV.	V.	VI.
Carbon	67·87	68·19	68·70	68·24	68·66	68·06
Hydrogen . . .	5·04	5·07	5·38	5·30	5·20	5·03
Oxygen . . .	27·09	26·74	25·92	26·46	26·14	26·91

I endeavoured in vain to determine the atomic weight of this substance. Neither the lead nor the baryta compound gave results which harmonized either with one another or with the analyses of the substance itself. There is however only one formula which is in accordance with the analyses, and at the same time satisfactorily explains its formation. This formula is $C_{14} H_6 O_4$, which requires in 100 parts—

Carbon	68·85
Hydrogen	4·91
Oxygen	26·24

It may be remarked that this is also the composition of benzoic acid; and even if the formula of rubiretine should not be exactly that given above, but perhaps the double or triple of it, it still remains remarkable that two such very different substances should have the same percentary composition.

The formation of rubiretine from rubian can only be explained in connection with that of verantine. If 2 equivs. of verantine, 2 equivs. of rubiretine and 12 equivs. of water be added together, the sum will be equal to 1 equiv. of rubian, as follows:—

2 equivs. of Verantine $=C_{28} H_{10} O_{10}$
2 equivs. of Rubiretine $=C_{28} H_{12} O_8$
12 equivs. of Water $= H_{12} O_{12}$

1 equiv. of Rubian $=C_{56} H_{34} O_{30}$

If this be the correct representation, it follows that verantine and rubiretine stand in an intimate relation to one another, that the formation of one always indicates that of the other. In confirmation of this view, I may state that I have never seen the formation of one of these substances taking place without it being possible to detect the presence of the other.

Rubianine.—This substance, as I mentioned before, has not hitherto been observed among the bodies derived from madder. It greatly resembles rubiacine in its appearance and many of its properties; it may however easily be distinguished by several characteristics, and above all by its composition. It is obtained from a solution in boiling alcohol in the form of bright lemon-yellow, silky needles, which, when dry, form an interwoven mass. It is soluble in boiling water, more so in fact than any of the products of decomposition hitherto mentioned. It crystallizes out again on the solution cooling in yellow silky needles. It is less soluble in alcohol than the preceding substances. Its colour is lighter than that of rubiacine. When heated on platinum-foil it melts to a brown liquid, then burns, leaving a carbonaceous residue, which on further heating disappears entirely. When heated in a glass tube it gives a small quantity of a yellow crystalline sublimate, but not by far so large a quantity as is obtained under the same circumstances from rubiacine, which, when carefully heated, may be almost entirely volatilized. It is soluble in concentrated sulphuric acid with a yellow colour; the solution on boiling becomes black and gives off sulphurous acid. A solution of rubiacine in concentrated sulphuric acid, remains quite unchanged on boiling. It is not affected either by dilute or concentrated nitric acid, even on boiling; it merely dissolves in them, and crystallizes out again on the acid cooling, just as from boiling water. When treated in the cold with a solution of carbonate of potash or soda, or liquid ammonia, it does not dissolve, nor is its colour at all changed. When the liquid is boiled, it dissolves however with a blood-red colour. Nevertheless it cannot be said to combine with the alkali, but merely to be dissolved by it; for on allowing these solutions to stand for some time, a yellow crystalline mass again separates, which is nothing but the substance itself. The ammoniacal solution gives red precipitates with the chlorides of barium and calcium. The alcoholic solution gives no precipitate with sugar of lead, whereas a solution of rubiacine gives a dark red precipitate with sugar of lead. It dissolves in a concentrated solution of perchloride of iron with a dark brown colour, but is not thereby converted into rubiacic acid. It communicates to mordanted cloth only a slight tinge of colour, similar to that produced by rubiacine.

Its analysis gave the following results:—

I. 0·3520 grm. substance, dried at 100° C. and burnt with chromate of lead, gave 0·7400 carbonic acid and 0·1750 water.

II. 0·3805 grm. of the same preparation gave 0·7990 carbonic acid and 0·1890 water.

III. 0·3965 grm. of another preparation gave 0·8330 carbonic acid and 0·1890 water.

IV. 0·2480 grm. of the same preparation as the last, recrystallized from alcohol, gave 0·5290 carbonic acid and 0·1280 water.

V. 0·3735 grm. of a third preparation gave 0·7925 carbonic acid and 0·1785 water.

VI. 0·3995 grm. of the same preparation gave 0·8450 carbonic acid and 0·1855 water.

These numbers correspond in 100 parts to—

	I.	II.	III.	IV.	V.	VI.
Carbon	57·33	57·26	57·29	58·17	57·86	57·68
Hydrogen . . .	5·52	5·51	5·29	5·73	5·31	5·15
Oxygen	37·15	37·23	37·42	36·10	36·83	37·17

I have as yet been unsuccessful in my attempts to determine the atomic weight of rubianine. The little affinity which it has for bases is proved by the fact above mentioned, of its crystallizing unchanged out of its alkaline solutions. The baryta compound, which is obtained by adding chloride of barium to its ammoniacal solution, is easily decomposed when it comes to be washed with pure water, the baryta being dissolved by the water, a yellow residue of rubianine being left at last. It is not capable of separating oxide of lead from acetic acid. In fact it nearly approaches the character of a perfectly neutral body, a circumstance which might be *à priori* foreseen from its containing more carbon and less oxygen than rubian itself, the properties of which are not far removed from those of an indifferent substance.

There are three formulæ which all of them give for 100 parts, numbers not widely differing from those found by experiment, viz. $C_{28} H_{17} O_{13}$, $C_{32} H_{19} O_{15}$ and $C_{44} H_{24} O_{20}$. These formulæ require for 100 parts of substance the following amount of constituents:—

	$C_{28} H_{17} O_{13}$.	$C_{32} H_{19} O_{15}$.	$C_{44} H_{24} O_{20}$.
Carbon	58·13	58·00	57·99
Hydrogen.	5·88	5·74	5·47
Oxygen	35·99	36·26	36·54

It will be seen that the last formula is that with which the analyses agree best.

If the first formula be the true one, then the formation of this substance from rubian is easily explained. It would then differ by 5 equivs. of water from 2 equivs. of rubiretine; and 1 equiv. of rubianine, 2 equivs. of verantine and 7 equivs. of water added together would be equal to 1 equiv. of rubian, as seen by the following equation:

$$C_{28} H_{17} O_{13}+2(C_{14} H_5 O_5)+7HO=C_{56} H_{34} O_{30}.$$

I shall presently show, however, that there is more probability in favour of one of the two latter formulæ.

Sugar.—That the substance obtained from the acid liquid after the complete decomposition of rubian is a species of sugar, will, I think, be apparent from an enumeration of its properties. It is always obtained in the form of a transparent yellow syrup, which neither crystallizes, however long its solution may be left to stand, nor becomes dry, unless heated to 100° C. Its taste is sweetish, accompanied by a bitter aftertaste, like that of burnt sugar. When heated for some time at 100° C. it loses a portion of its water, but remains soft and viscid. On allowing it however to cool, it becomes brittle and capable of pulverization. After a few moments' exposure to the air it again begins to attract moisture, which it does as rapidly as chloride of calcium, and is soon reconverted into syrup. This is a character which it has, in common with ordinary syrup, obtained by boiling a solution of cane-sugar in water. It is soluble in alcohol. It is not affected by dilute sulphuric acid, even on boiling; but on evaporating a solution to which sulphuric acid has been added, it is decomposed in proportion as the acid becomes concentrated, and is changed into a black powder like humus. Concentrated sulphuric acid destroys it immediately with disengagement of sulphurous acid. It is destroyed by nitric acid. By operating on a moderately large quantity of it, I was enabled to ascertain that the sole product of the action of nitric acid is oxalic acid. It is not precipitated from its watery solution by any metallic or other salt, not even by basic acetate of lead. On the addition of caustic potash or soda to its solution and boiling, the solution immediately becomes brown, and a brown powder falls, just as in the case of grape-sugar. It is capable of fermentation. The watery solution when mixed with yeast soon begins to ferment, though the process is not so lively as in the case of an equal quantity of common sugar; and by distilling the liquid and boiling the distillate with dry carbonate of soda, alcohol may be obtained.

The analysis was attended with some difficulty on account of the great affinity which it has for water. By heating it however for some time at 100° C., then allowing to cool and pulverizing while in its brittle state as quickly as possible, it was obtained in a condition fit for analysis. Even then however the state of hydration was not uniform, so that the analyses differed considerably from one another. The following results were obtained:—

I. 0·4765 grm., burnt with chromate of lead, gave 0·6860 carbonic acid and 0·2905 water.

II. 0·3050 grm. gave 0·4450 carbonic acid and 0·1815 water.

III. 0·3820 grm. gave 0·5650 carbonic acid and 0·2205 water.

These numbers give in 100 parts—

	I.	II.	III.
Carbon	39·26	39·79	40·33
Hydrogen . . .	6·77	6·61	6·41
Oxygen	53·97	53·60	53·26

As this substance does not combine with bases, its atomic weight could not be determined by direct experiment. There are, however, two formulæ, both of which agree with the analyses and explain its formation, viz. $C_{14}H_{14}O_{14}$ and $C_{12}H_{12}O_{12}$. Both of these formulæ require in 100 parts—

Carbon	40·00
Hydrogen	6·66
Oxygen	53·34

If the formula $C_{14}H_{14}O_{14}$ be the true one, then its formation from rubian admits of an easy explanation. It would then differ from verantine by 9 equivs. of water; and by adding together 2 equivs. of it and 2 equivs. of rubiretine, the sum would be equal to 1 equiv. of rubian plus 6 equivs. of water, as the following equation shows:—

$$\begin{array}{lll} \begin{array}{l}\text{2 equivs. of Sugar . .}\\ \text{2 equivs. of Rubiretine}\end{array} & \left.\begin{array}{l}=C_{28}H_{28}O_{28}\\ =C_{28}H_{12}O_{8}\end{array}\right\}= & \left\{\begin{array}{l}C_{56}H_{34}O_{30}=1\text{ equiv. of Rubian.}\\ \quad H_{6}O_{6}=6\text{ equivs. of Water.}\end{array}\right. \\ & \overline{C_{56}H_{40}O_{36}} & \overline{C_{56}H_{40}O_{36}} \end{array}$$

If the formula of rubianine be $C_{28}H_{17}O_{13}$, it may replace rubiretine in the above equation; 11 equivs. of water instead of 6 being added to the rubian, as follows,—

$$\begin{array}{lll} \begin{array}{l}\text{2 equivs. of Sugar . .}\\ \text{1 equiv. of Rubianine .}\end{array} & \left.\begin{array}{l}=C_{28}H_{28}O_{28}\\ =C_{28}H_{17}O_{13}\end{array}\right\}= & \left\{\begin{array}{l}C_{56}H_{34}O_{30}=1\text{ equiv. of Rubian.}\\ \quad H_{11}O_{11}=11\text{ equivs. of Water.}\end{array}\right. \\ & \overline{C_{56}H_{45}O_{41}} & \overline{C_{56}H_{45}O_{41}} \end{array}$$

To this view however it may be objected that all the species of sugar capable of fermentation with which we are acquainted contain 12 equivs. of carbon. Indeed it is difficult to conceive how a body of the formula $C_{14}\,H_{14}\,O_{14}$ can be decomposed into alcohol and carbonic acid. It is therefore far more probable that the formula of this substance is $C_{12}\,H_{12}\,O_{12}$, which is also that of grape-sugar when dried at 100° C. In fact, were it capable of being crystallized, it would no doubt be considered as identical with grape-sugar. If this be granted, then it follows that the formula of rubianine must be either $C_{32}\,H_{19}\,O_{15}$ or $C_{44}\,H_{24}\,O_{20}$, as will be seen by the following equations:—

$$\left.\begin{array}{ll}\text{2 equivs. of Sugar . .} & =C_{24}\,H_{24}\,O_{24}\\ \text{1 equiv. of Rubianine .} & =C_{32}\,H_{19}\,O_{15}\end{array}\right\}=\left\{\begin{array}{l}C_{56}\,H_{34}\,O_{30}=1\text{ equiv. of Rubian.}\\ \quad H_{9}\,O_{9}=9\text{ equivs. of Water.}\end{array}\right.$$

$$C_{56}\,H_{43}\,O_{39} \qquad C_{56}\,H_{43}\,O_{39}$$

or

$$\left.\begin{array}{ll}\text{1 equiv. of Sugar . .} & =C_{12}\,H_{12}\,O_{12}\\ \text{1 equiv. of Rubianine .} & =C_{44}\,H_{24}\,O_{20}\end{array}\right\}=\left\{\begin{array}{l}C_{56}\,H_{34}\,O_{30}=1\text{ equiv. of Rubian.}\\ \quad H_{2}\,O_{2}=2\text{ equivs. of Water.}\end{array}\right.$$

$$C_{56}\,H_{36}\,O_{32} \qquad C_{56}\,H_{36}\,O_{32}$$

The formula $C_{44}\,H_{24}\,O_{20}$ seems to me the more probable of the two. It agrees best with the results of analysis, and the high atomic weight of rubianine which follows from it explains the very neutral character of that substance. Hence it appears that rubianine stands in the same relation to the sugar as rubiretine does to verantine. When added together they contain the elements of rubian plus the elements of water, while rubiretine and verantine added together contain the elements of rubian minus the elements of water.

On the whole, it appears that the action of acids on rubian is not of so complicated a nature as might at first sight be supposed. The number of substances produced by this action is five. Nevertheless it does not follow that these five substances are all formed together, or in other words, that one atom of rubian by its decomposition gives rise to all five at the same time. From the composition of these substances, as compared with that of rubian, it follows that the latter by the action of acids undergoes decomposition in three different directions, or more correctly speaking, that the decomposition affects three separate atoms of rubian. One of these atoms loses 14 atoms of water, and is converted into alizarine. The second loses 12 atoms of water, and then splits up into verantine and rubiretine. The third takes up the elements of water, and then splits up into rubianine and sugar. What the circumstances are under which either one or the other of these three processes takes place I am unable to say. That the loss of a greater or smaller proportion of water or the addition, on the contrary, of the elements of water to those of rubian, are the immediate efficient causes of one or the other of the three processes taking place is very probable; but what again determines the elimination of more or less water from rubian, or, on the other hand, its combination with more water, remains uncertain. It is not unlikely however that the degree of temperature at which the decomposition is effected may have something to do with it. It is probable that the lower the temperature at which the acid acts on the rubian, the more rubianine and sugar are formed, and that at a higher temperature more alizarine, verantine and rubiretine are produced. In all experiments hitherto mentioned I have always obtained all five products of decomposition, though by no means in equal proportions, the alizarine being formed in the smallest quantity, the amount of rubiretine and verantine being somewhat greater, and the rubianine and sugar being produced in the largest quantity. In the course of this paper I shall have occasion to mention circumstances in which a still greater preponderance takes place in the amount of several of these substances formed over that of the others. Whether it would be possible to confine the decomposition of rubian entirely to one of these processes, or whether all three are essential, is a question of the highest importance, not so much in a theoretical, as a practical point of view. That beautiful substance, alizarine, is the only one of these products which is capable of yielding dyes. It is this body which in my opinion gives rise to all the beautiful colours for the production of which madder is employed. The others are not only useless, they are positively injurious, as I have shown on a former occasion. Though experimentally alizarine is formed in the smallest proportion, it is nevertheless theoretically possible to convert rubian entirely into alizarine, without the least quantity of the other substances being produced. From this point of view the other substances may be considered as formed at the expense of alizarine. In fact, by adding together 1 equiv. of verantine and 1 equiv. of rubiretine, and subtracting 1 equiv. of water, we obtain the elements of 2 equivs. of alizarine, for

$$C_{14} H_5 O_5 + C_{14} H_6 O_4 = 2(C_{14} H_5 O_4) + HO.$$

Also by adding together 1 equiv. of rubianine and 1 equiv. of sugar, and subtracting 16 equivs. of water, we obtain the elements of 4 equivs. of alizarine, for

$$C_{44} H_{24} O_{20} + C_{12} H_{12} O_{12} = 4(C_{14} H_5 O_4) + 16HO.$$

If any chemist should succeed in changing rubian entirely into alizarine, an undertaking in which there is no occasion to despair of success, he would be the means of giving a great stimulus to many branches of manufacture and adding a large sum to the national wealth.