XX.—*On the Colouring Matters of Madder.*

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The root of the *Rubia tinctorum,* commonly called madder, consti-
tutes one of the most valuable dyeing materials employed in the
arts.   Though probably known to the ancients, it is only in modern
times that it has come to be extensively used.   At the present
time, there is, perhaps, no dye-stuff, with the exception of indigo,
employed to so great an extent in imparting various colours to
calico and other fabrics as madder ; and a knowledge of its proper-
ties and the most advantageous mode of treating it is indispensable
to any one engaged in the arts of dyeing and printing.   It stands
in about the same relation to other dye-stuffs, in the eyes of the
dyer and calico-printer, as iron does to other metals in the eyes of
the engineer.

The principal advantages which madder presents are the follow-
ing :—1. It is capable of producing, according to the mordants
employed and the method of treatment, a great variety of different
colours and shades, such as black, red of different kinds from a dull
brownish-red to a bright red and a delicate pink, besides the pecu-
liar colour of Turkey red, also purple of various shades from a dull
reddish-purple to a delicate bluish-purple or lilac, as well as cho-

colate of all shades.—2. Its colouring matters have but little affinity for cotton fibre and a great affinity for mordants, so that it is not difficult to secure a good white on the parts of the tissue to which no mordant has been applied.—3. The compounds which its colouring matter or matters yield with mordants possess an unusually stable character, so that it is possible, without causing much detriment to the colour, to expose them to the action of various agents for the purpose of improving or modifying the shade. They are also capable of resisting the action of air and light in a remarkable degree, so much so that I am inclined to believe that the fading which we observe in colours produced by madder is caused rather by the mechanical wear and tear of the fabric than by any chemical decomposition of the colours themselves. It is these properties, chiefly, which have led to the extensive employment of madder in the arts of dyeing and calico printing.

The art of employing madder to the greatest advantage had, like many other arts, attained to a considerable degree of perfection, before any attempt was made to elucidate the principles involved in it. Indeed the art of Turkey-red dyeing affords a striking instance of a very complicated process of manufacture arriving at a state of great perfection, without one step in the process being really understood and without the least improvement having been made in it by any one conversant with the principles of chemical science. All processes in which the action of colouring matters are concerned, are in fact of so complicated a nature, and depend on the action of bodies for the most part so remote from the ordinary experience of the chemist, that their elucidation could only be attempted when the science had attained a high degree of developement. The process of fermentation, for instance, which plays a considerable part in the formation of many colouring matters, is one that could not possibly be understood in the early ages of the science of chemistry. All that could be accomplished was to describe the processes actually in use in the arts, without any successful attempt at their explanation. Chevreul, whose interesting and important labours on colouring matters are so well known, seems not to have occupied himself with any chemical examination of madder. The first discovery of any importance in this branch of chemistry was made by Robiquet and Colin, who succeeded in preparing from madder a substance, which on being exposed to heat gave a sublimate consisting of beautiful reddish-yellow needles, and to which they gave the name of *Alizarine*.

This substance they found to be very little soluble in water, but soluble in alcohol and ether. Its alkaline solutions were of a beautiful violet or purple colour, and it gave with earths and metallic oxides lakes of various colours. The method of preparation which they adopted, left it quite uncertain whether alizarine pre-existed in madder or whether it was a product of decomposition of some other body formed by the action of heat. It is only by recent researches that its pre-existence in the ordinary madder of commerce has been established. But finding that all the usual madder colours could be produced by its means, and moreover of great brilliancy and purity, Robiquet and Colin were right in attaching to it a considerable degree of importance. The same series of experiments led to the discovery of another colouring matter in madder, to which these chemists gave the name of *Purpurine*. This they found to be distinguished from the preceding chiefly by being soluble in alum-liquor, the solution having a beautiful pink colour. In other respects it did not differ very much from alizarine. It yielded a crystalline sublimate when heated; it was very sparingly soluble in water, but more soluble in alcohol, and its alkaline solutions were reddish-purple.

The red and pink colouring matters of madder obtained by Gaultier de Claubry and Persoz are, as Persoz himself confesses, identical with the alizarine and purpurine of Robiquet and Colin. To the former chemists however clearly belongs the merit of a very important discovery in the chemistry of madder, viz., that of the effect produced on madder by strong mineral acids. They found that when madder was treated with boiling dilute sulphuric acid, it was converted into a dark brown powder, which could afterwards be completely washed with cold water without any of the colouring matters being removed, the latter remaining in the residue, while many impurities were washed away by the water. The residue was found to yield in dyeing better results, in some respects, than madder itself, the colours being more brilliant and requiring very little after-treatment, while the white portions of the fabric remained unsullied. This process has since then been carried out on a large scale, the product having obtained the name of *Garancine*. This was the first instance that had occurred of the labours of the scientific chemist having been applied to the improvement of the art of madder-dyeing. Persoz as well as Robiquet, explained the action of the acid on madder by supposing that the saccharine, gummy and extractive matters contained in the root and pre-

sumed to be injurious during the process of dyeing, were charred or otherwise decomposed by the acid, or afterwards removed during the washing, the undecomposed colouring matters being left behind in a state of greater purity. This explanation, though it had at the time every appearance of probability, was afterwards discovered to be only partially correct, the acid having been found to produce other effects in addition to this.

Besides these two colouring matters, another was discovered in madder by Kuhlmann and called by him *Xanthine*. It was described by him as a substance resembling extractive matter, having a taste between bitter and sweet, and a yellow colour, being very easily soluble in water, and giving rise by the action of strong acids to the formation of a dark green powder.

About the year 1835, a memoir was published by Runge, containing a description of the properties and method of preparation of three distinct colouring matters from madder, which he named respectively *Madder-red, Madder-purple,* and *Madder-orange.* There can be no doubt that the two first are identical with the alizarine and purpurine of Robiquet. The discovery of madder-orange was the first indication of the existence of crystallized yellow colouring matters in madder. The memoir of Runge, which contained also an account of other substances not of any importance, as far as the process of dyeing was concerned, was for a number of years referred to as an authority on the subject, and for a long time no facts of any great importance were added to those previously known.

This short account may serve to give an idea of the state of our knowledge on this subject at the time when I entered on its investigation. My efforts were in the first place directed to the separation, as far as possible, of all the substances contained in the ordinary madder of commerce from one another, their preparation in a state of purity, and their mutual action and reaction during the process of dyeing. After much labour I succeeded in obtaining Robiquet's alizarine in a well crystallized state without having recourse to sublimation. The alizarine thus obtained differed from sublimed alizarine in containing several atoms of water of crystallization, which were lost even on heating the crystals to 100°C. Its colour inclined also more to yellow and had less of the reddish tinge seen in sublimed alizarine. Hence it followed that ordinary madder, in the state in which it is employed by the dyer, does in reality contain ready formed alizarine, and that the latter

is not a product of decomposition formed from some other substance by heat.   My experiments regarding the tinctorial power of alizarine, which have often been repeated since then, fully confirmed those of Robiquet.   I found that, by means of alizarine, I could produce all the usual madder colours, and moreover that the colours so produced were distinguished for their brilliancy and purity, being as beautiful as the ordinary madder colours, after they have been subjected to a long course of treatment with soap, acids &c., for the purpose of rendering them more brilliant. This simple fact, like many others connected with the chemistry of madder, has been the subject of much controversy.   It has been asserted by D. Köchlin that alizarine is not strictly speaking a colouring matter, but a mixture of a colourless crystallised resin with a red colouring matter, and that it owes to the latter its tinctorial power.   That this view is entirely erroneous must be obvious to any person possessing any knowledge of chemistry, who has occupied himself with this subject.   Its unvarying properties and the uniformity of its composition prove alizarine to be a pure unmixed substance.   That it plays a principal, if not the only part, in the production of the colours for which madder is employed, seems probable from the circumstance that the finer madder colours contain little besides alizarine in combination with the mordants. If, for instance, a few yards of so-called madder-pink calico be treated with muriatic acid to remove the alumina of the mordant, then well washed and treated with caustic alkali, a violet-coloured solution is obtained from which acids precipitate yellow flocks, consisting of almost pure alizarine, which may be obtained in long crystalline needles by solution in boiling alcohol and evaporation of the alcoholic solution.   This constitutes, indeed, the easiest method of preparing pure alizarine on a small scale.   The colours produced by pure alizarine do not yield to ordinary madder colours in their power of resisting decomposition by alkalies, soap, &c., they are equally fast, as was observed long since by Robiquet and others.   I have, in fact, after a long course of experiments, been led to the conclusion, that the final result of dyeing with madder and its preparations is simply the combination of alizarine with the various mordants employed, and that consequently if an economical method of preparing alizarine on a large scale could be discovered, a great gain would result to the arts.

The analyses of pure alizarine made by myself and others have led to pretty nearly the same elementary composition.   The formula

which I gave to it in the first instance, viz. $C_{14}H_5O_4$ or $C_{28}H_{10}O_8$, I have never seen any cause to deviate from. Indeed all my subsequent researches have appeared to me only to confirm it. It is at all events certain that, the purer the alizarine, the more nearly does its composition approach what it should be according to this formula. By the action of nitric acid, alizarine is converted into a colourless beautifully crystallised acid, which subsequent investigations have proved not to be new, as I at first supposed, but identical with phthalic acid, one of the many products of decomposition of naphthaline discovered by Laurent. From this fact, conclusions have been drawn regarding the composition of alizarine, which I cannot but consider as erroneous. Since chloronaphthalic acid and alizarine both yield phthalic acid by decomposition with nitric acid, Strecker has inferred that there must be a similarity in the composition of the two bodies, that the formula of alizarine is $C_{20}H_6O_6$, and that consequently chloronaphthalic acid is simply alizarine with 1 At. of hydrogen replaced by chlorine; and he has adduced many ingenious arguments in favour of this view. If this view of the composition of alizarine were correct, it would lead to very important conclusions, as the possibility of converting a refuse product like naphthaline, into one of great value and importance would in that case not be so very remote. The attempts made by Strecker to replace the atom of chlorine in chloronaphthalic acid by hydrogen and thus convert it into alizarine did not succeed. The far easier experiment of converting alizarine into chloronaphthalic acid by the action of chlorine he does not seem to have attempted. In order to complete the presumed analogy between chloronaphthalic acid and alizarine, Strecker supposes the latter, like the former, to yield oxalic acid as well as phthalic acid by decomposition with nitric acid. This is however not the case, as no trace of oxalic acid is formed from alizarine by oxidising agents.

By a process similar to that adopted by Runge for the preparation of his madder-orange, I succeeded in obtaining a body crystallising in beautiful golden yellow needles and scales, to which I gave the name of *Rubiacine*. This was the first to be discovered of a series of yellow colouring matters from madder, having very similar properties and a similar composition. These colouring matters are all capable of crystallising, and though yellow themselves, yield red compounds with bases. They do not contribute to the production of fast colours during the process of madder dyeing,

but are, on the contrary, as my experiments show, very injurious
to the strength and beauty of those colours. The most cha-
racteristic property of rubiacine is the facility with which it
is converted by the action of persalts of iron into a new acid,
rubiacic acid, which yields definite crystallised compounds with
alkalies. By means of these compounds, it was possible to determine
the composition and formula of the acid with a tolerable degree of
certainty ; and as the acid was again convertible into rubiacine by
the action of sulphuretted hydrogen, it followed that the number
of equivalents of carbon in both bodies must be the same. This
number I found to be 32. In what relation, however, the compo-
sition of rubiacine stood to that of alizarine was at first not all
apparent, as the link uniting the two bodies had still to be dis-
covered. According to the old classification of colouring matters,
rubiacine would belong to the division called resinous, from being
insoluble in water, but soluble in alkaline liquids and alcohol, and
from its power of resisting the action of strong reagents such as
nitric and sulphuric acids. It is a remarkable fact that rubiacine
is oxidised and converted into rubiacic acid by means of persalts
of iron, whereas the same change is not produced by nitric acid.
It is improbable that this difference is owing to any predis-
posing affinity of the peroxide of iron for rubiacic acid, though
there is no doubt that some combination does take place; for on
treating rubiacine with boiling solutions of persalts of iron, it
dissolves with a dark brownish-red colour, and the solution, after
being boiled for some time, contains rubiacic acid, which is
precipitated in yellow flocks on the addition of muriatic or nitric
acid, the solution itself becoming yellow.

Two other bodies still more nearly resembling resins, yielding
red compounds with bases, but not themselves capable of crystal-
lising, were discovered in madder. These I found to be equally
injurious with rubiacine in the process of dyeing. It is only a
consideration of the source whence they are derived which lends
to these bodies the least interest.

For the purpose of completely understanding all the phenomena
which take place during the process of madder dyeing, I considered
it necessary to ascertain what other constituents the root contains
besides colouring matters. Several of these, such as sugar and
pectic acid, have for a long time been known as constituents of
madder. The latter may under certain circumstances act very
injuriously in dyeing. The xanthine of Kuhlmann is a mixed

substance. It contains a body which by the action of strong acids becomes dark green, and yields a green powder. It is this body, to which I have given the name of *Chlorogenine*, and which Rochleder calls *Rubichloric Acid*. It is a species of extractive matter. Its watery solution, when heated and exposed to the air, acquires a brown colour, and in this state is capable of imparting a brown tinge to calico, whether mordanted or unmordanted. Hence the uniform dirty reddish-brown tint which a piece of calico exhibits both on the printed and unprinted portions, after having been dyed with madder; to remove this tinge is one of the objects of the after treatment with soap and other materials. In the process of manufacturing garancine, this substance is partly decomposed, partly removed by the subsequent washing. Hence may, in a great measure, the greater purity and brilliancy of gerancine colours, as compared with madder colours, be explained.

There is a point connected with the chemistry of madder dyeing which has puzzled many, especially practical, persons who have devoted their attention to the subject, that is the apparent necessity of having a certain proportion of lime or its carbonate, either mixed with the material. or contained in the water of the dye-bath, in order to produce colours which shall resist the subsequent action of soap and other agents. It is a fact well known, since the time of Hausmann, that in order to insure fastness of colour, it is necessary, either to employ calcareous water or to add chalk to the dye-bath, the effect of so doing being to impoverish the colours, but at the same time to add to their permanency. Hence, too, madder grown in a calcareous soil is superior to any other, and for some colours dyers generally make up for a deficiency of lime in the root by the addition of chalk. Now the experiments of Robiquet, as well as my own, have demonstrated that in dyeing with pure alizarine, the least addition of lime is rather injurious than otherwise, as it merely weakens the colours without adding to their durability. Hence the beneficial effect of lime can only be accounted for by some action which it exerts on other constituents of the root. Now I found that the addition of rubiacine, or of any of the resinous colouring matters to alizarine, during the dyeing produced very prejudical effects. They weakened the colours and rendered them impure and unsightly. The red acquired an orange, the purple a reddish hue, while the black became brownish, and the white parts assumed a yellowish tinge. These effects disappeared, however, completely, as soon as the foreign colouring

matter was completely saturated with lime, the tinctorial power
of the alizarine then appearing again with all its original intensity,
while the other colouring matter was rendered innocuous.   The
same prejudicial effect was produced by adding free pectic acid to
the alizarine, but disappeared entirely on neutralising the pectic
acid with lime.   The phenomenon seems, therefore, to resolve itself
into a simple case of elective affinity.   The resinous colouring
matters and other bodies having a stronger affinity for bases than
alizarine, seize hold of the alumina and other mordants when all
are uncombined, but when lime is added, they combine with it as
the stronger base, leaving the alizarine at liberty to unite with the
mordants.   At the same time, I do not suppose, even if a speci-
men of madder contain exactly sufficient lime to unite with the
resinous colouring matters, pectic acid and other injurious sub-
stances existing in it, that the distribution of these substances and
the alizarine among the bases will be precisely as my theory pre-
supposes; for if even in a mixed solution containing various salts
of strong mineral acids and bases, it still remains a subject of
speculation with chemists, in what manner the acids and bases are
mutually distributed, and whether every base is not combined with
every acid, how much less can we expect it to be a settled matter
according to what law a certain number of complex organic bodies
existing in solution together will distribute themselves among a
certain number of bases.   In the case just mentioned I believe,
on the contrary, that however large an excess of lime or other
base be taken, a certain quantity only of the resinous colouring
matters, &c., will combine with the lime or other base, while the
remainder will go to the mordants and can only be separated by
after-treatment, a small portion of the alizarine at the same time
uniting with the lime or other base, and a larger portion with the
mordants.   Indeed this view of the case may be proved to be
correct ; for if a piece of printed calico be dyed in the usual
manner with madder to which chalk has been added, the colour is
found on examination to contain, in combination with the mor-
dants, not only alizarine, but also a small quantity of resinous
colouring matter as well as pectic acid, and a brown substance
insoluble in alcohol, which I suppose to be a product derived by
oxidation from xanthine or chlorogenine.   These impurities are
subsequently removed by means of soap, acids, &c., leaving a com-
pound containing only alizarine and a little fatty acid on the
fabric.   Now the residual madder left after the dyeing is com-

pleted, though apparently exhausted of colouring matter, may be proved to contain alizarine; for if it be treated with acids, a quantity of lime, magnesia, &c., is removed, and after being washed it is found to be capable of dyeing anew, and a fresh portion of alizarine and other substances may now be extracted by means of caustic alkalies. On this depends the manufacture of so-called *garanceux* from the waste madder of dye-houses, a product which used formerly to be thrown away.

When fresh madder is subjected to the action of strong acids for the purpose of manufacturing *garancine*, the following effects take place: 1. The sugar, xanthine, and other injurious substances soluble in water are either washed away or decomposed by the acid and so removed. 2. The lime, magnesia, and other bases which would prevent the colouring matter from exerting its full effect are removed, and thus, after the washing is completed, a suitable quantity of lime, soda or some base is added in order to combine with and render innocuous the resinous colouring matters, as well as the pectic acid, which, as is well known, is capable of taking up a certain quantity of mineral acids, forming with them compounds not easily soluble in water. There is another effect produced by the acid, in addition to those just named, which I shall refer to presently. To the view here taken it may be objected, in the first place, that the fact of the colours produced by alizarine being more durable and resisting better the action of alkalies, &c., than the compounds of the other colouring matters of madder with mordants, is inconsistent with the supposition of its having less affinity for bases than the other colouring matters. Secondly, that ordinary garancine, even when a sufficient quantity of base has been added to it to combine with the impurities which prevent the alizarine from uniting with the mordants, does not in practice produce exactly the same effect as madder. Garancine colours are notoriously not as fast as madder colours, and hence garancine cannot be made to replace madder completely, however great its advantages are in other respects. To the first objection it is certainly difficult to frame a convincing reply. The second will fall to the ground at once, when I state that, by a very simple process, garancine may be so modified as to be capable of affording colours as permanent as those from madder itself—nay, even more so. This process, which was patented by Mr. Pincoffs and myself several years ago, consists simply in subjecting garancine to the action of high pressure steam, or in heating it in a closed vessel

while slightly moistened, to a temperature of 200°C. or there-abouts. What takes place during this process, which is accom-panied by a loss of weight amounting to about 10 per cent., I have never been able exactly to ascertain; but I have reason to believe that it consists in the total or partial destruction of one or more of the resinous colouring matters which act so prejudicially during the process of madder dyeing. Be this as it may, the effect is so great that if a certain quantity of madder be converted, first into garancine, and then by means of high pressure steam into the new product, the latter is found to act more efficiently, as far as the depth of permanent colour which it is capable of yielding, is concerned, than the original material from which it was prepared; or, in other words, a larger proportional quantity of madder must be used to produce the same ultimate effect.

As this subject is one, our knowledge of which is still far from complete, I have preferred on this occasion treating it historically rather than systematically, stating as concisely as I have been able, in what manner and by whom the various facts connected with it have been discovered. In doing so I must not pass over the labours of Dr. Debus, who in his interesting memoir on madder has given us the results of his investigation on its colour-ing matters, of which he distinguishes two, viz., *lizaric* and *oxylizaric acids*, which are identical with the alizarine and purpurine of other chemists.

There is another part of this subject which far exceeds in its intricacy as well as in the interest attaching to it that portion of which I have just given a short account; indeed much of it still remains involved in obscurity. The researches of modern chemists have made us acquainted with a number of highly complicated processes in which bodies derived from the organic world are concerned. Of these processes perhaps few are so difficult to comprehend, both as to their efficient causes and their results, as those in which fermentation plays a part. The process of alcoholic fermentation, one of the simplest cases, has been the object of study with many eminent chemists without any definite notion of its true nature being arrived at. Various other phenomena of fermentation besides the conversion of sugar into alcohol and carbonic acid have been discovered and investi-gated, such as the transformation of salicine into saligenine and sugar, of amygdaline into oil of bitter almonds, &c. That some process of this nature goes on in madder has long been suspected,

from the circumstance that when ground madder is kept for several years, it gradually improves in quality until it reaches a certain point, after which it again deteriorates. But what body it was that was acted on during this process, or what was the nature of the process remained quite unknown. Strecker supposes that the change which goes on consists in the conversion of alizarine into purpurine; but this would constitute anything but an improvement in quality, since the colours produced by purpurine are in most respects inferior to those of alizarine. Besides this, alizarine is a body not easily decomposed, unless exposed to the action of very potent agents, and any portion of it once formed in the root, would probably resist the action of air and moisture for a very long period of time, if not entirely. Mr. Higgin states, as the result of his experiments on this subject, that there exists in madder a peculiar albuminous ferment, which, by acting on the xanthine gives rise to the formation of colouring matter, and that this process takes place to some extent even during the short period of time occupied by dyeing. This statement I subsequently found to be a correct representation of the truth in its main features, and I think that to Mr. Higgin is due the first distinct enunciation of it.

That the whole of the colouring matter of madder does not exist ready-formed in the article as used by the dyer, may be rendered evident by a simple experiment. If madder be extracted with cold water, the clear watery extract does not contain any alizarine or other colouring matter, since these are almost insoluble in cold water. Nevertheless the extract when gradually heated is found capable of dyeing in the same way as madder itself. If the extract be made tolerably strong, it possesses a deep yellow colour and a very bitter taste; but if it be allowed to stand in a warm place for a few hours, it gelatinises, and the insoluble jelly which is formed is found to possess the whole of the tinctorial power of the liquid, while the latter has lost its yellow colour and bitter taste. Hence, it may be inferred that the substance which imparts to the extract its bitter taste and yellow colour is capable of giving rise to the formation of a certain portion of colouring matter. This simple fact formed the starting point of a fresh series of researches, of which I will in as few words as possible state the results. By extracting madder with boiling water, the subsequent gelatinisation or coagulation is prevented, and the extract retains its yellow colour and bitter taste, a proof that the

coagulation observed in the extract with cold water is a result of
some process of fermentation which is arrested when the tempera-
ture is sufficiently raised. When the extract is agitated with a
little animal charcoal, the latter absorbs the bitter principle and
gives it up again to boiling spirits of wine, which on evaporation
leaves it in an almost perfect state of purity. In this manner I
obtained a substance, to which I have given the name of *Rubian,*
and of which the principal characteristics are these:—It is amor-
phous and shining like gum, has a deep yellow colour and an
intensely bitter taste, is easily soluble in water and alcohol. It is
not a colouring matter in the practical sense of the word, for it
gives to mordants in dyeing only the faintest shades of colour.
But if its watery solution be mixed with sulphuric acid and boiled,
it gradually deposits a quantity of insoluble yellow flocks and
becomes almost colourless. These flocks after being well washed,
are found to dye exactly the same colours as alizarine. In fact
they contain alizarine. The liquid gives the reactions of sugar.
Taking this fact into consideration, it becomes possible to give an
account of all that takes place in the process of manufacturing
garancine. It is evident that during this process, the easily
soluble rubian becomes converted into the difficultly soluble
alizarine, that there is in this case, in fact, an actual formation of
colouring matter which is added to that which already exists in
the root. A similar change takes place, when caustic alkali is
used instead of the acid. A solution of rubian on being
mixed with caustic potash or soda simply turns red, but on being
boiled it becomes dark purple and deposits a purple powder
which consists chiefly of a compound of alizarine with alkali,
insoluble in caustic lye. Fermentation also decomposes rubian
with great facility; but in order to effect its decomposition it is
not indifferent what ferment be taken; a peculiar ferment is
essential for the purpose. A solution of rubian may be left for
several days in contact with yeast, decomposing albumen, casein,
emulsin, &c., without showing any sign of change. But if an
extract of madder with cold water be mixed with a large excess
of alcohol, flocks of a dirty red colour are precipitated, which,
after being well washed with alcohol are found to consist chiefly
of an azotised principle which exerts a peculiar and powerful
decomposing effect on rubian. If some of this substance be mixed
with a watery solution of rubian, and the mixture be left to stand
at the ordinary temperature, the rubian is found after a few hours

to be as completely decomposed as if it had been treated with a strong acid or caustic alkali, though no evolution of gas or any of the usual signs of fermentation have been manifested. The solution, if tolerably strong, gelatinises just as an extract of madder with cold water does under the same circumstances. The jelly when mixed with cold water is found to be almost insoluble. The water acquires only a slight colour, but contains sugar in solution, while the insoluble portion contains alizarine mixed with the ferment. With a knowledge of this process of decomposition it becomes possible to explain several curious phenomena, the true cause of which was previously unknown. It is well known to madder dyers that if the dye-bath be heated up rapidly to the boiling point, instead of gradually, as is the usual practice, prejudicial effects ensue. It is evident, from what I have just said, that the sudden heating puts a stop to the action of the ferment, as would be the case in any other process of fermentation, whereas the gradual heating allows it to exert its full decomposing power on the rubian. Hence, too, the advantage of mixing together several sorts of madder, one containing for instance an excess of rubian in proportion to ferment, the other a superabundance of ferment to counterbalance it, will be apparent. The improvement which takes place in the quality of madder after long keeping is probably also an effect of the same cause. Indeed, it seems highly probable that the alizarine, which undoubtedly exists ready formed in ordinary madder, owes its formation to the action of fermentation on rubian ; and an experiment which I made with fresh madder roots goes far to prove that this is in fact the case, and that, surprising as it may seem, the fresh root contains no trace of ready-formed colouring matter. The experiment was as follows : Some madder roots having been taken out of the ground and cut small without being dried, produced the ordinary colours when used for dyeing in the common manner. But on treating the roots, after being cut into pieces as quickly as possible, with boiling alcohol, a yellow extract was obtained, which contained rubian, but which, even after all the alcohol had been driven away, was found incapable of imparting to mordants any but the slightest shades of colour ; while the portion of the root left undissolved by the alcohol, on being subjected to the same test as the extract, imparted to mordants no more colour than the latter. It was evident, therefore, that the alcohol in this case had effected a separation between the colour-producing body and the agent

which under ordinary circumstances is destined to effect its transformation into colouring matter.   The same relation, it is apparent, subsists between rubian and *erythrozym*, as I have called the ferment of madder, as between amygdaline and emulsine.   It affords another of the instances of the mutual fitness of things and adaptation of means to an end, which we find occurring so often in all departments of nature, and which point so unmistakeably to an intelligence superior to our own.   What, it may be asked, would have been the consequence if there had not been placed in close proximity with the colour-producing body of this plant another substance peculiarly fitted to effect its decomposition? Why, that probably one of the most valuable of our dyeing materials, and some of the most beautiful of our dyes would have remained for ages unknown, for it may be doubted whether, supposing this peculiar fermentative substance to have been absent in the root, we should ever, except by mere chance, have discovered the valuable properties of the latter.

The property which principally distinguishes erythrozym from other ferments is the power which it possesses of effecting the decomposition of rubian.   When allowed to act on a watery solution of cane-sugar, the latter yields alcohol, carbonic acid, and hydrogen.   The liquid is found to contain also a minute quantity of succinic acid, the formation of which I at one time supposed to be characteristic of this process of decomposition.   Pasteur has however, since then discovered that this acid is always formed in small quantities during the ordinary fermentation of sugar by yeast.   In its composition, erythrozym differs from all other known ferments.   It contains carbon, hydrogen, nitrogen, and oxygen, but the proportion of nitrogen is remarkably small, as it hardly exceeds 4 per cent.

At first sight the change which rubian undergoes when decomposed by means either of acids, alkalies, or ferments, would seem to be simple enough.   It might be supposed to consist simply in a splitting up of its complex molecule into alizarine and sugar, and to resemble many analogous processes with which we are acquainted, and which result in the formation of sugar and another body, the two together having formed originally a conjugate-compound.   Nevertheless, the process is by no means so simple as might at first be supposed.   The products of decomposition formed in these cases never consist of alizarine and sugar only. The part insoluble in cold water contains in all cases, besides

alizarine, two resinous bodies, one easily soluble in alcohol, which I call *Rubiretine*, the other less soluble in that liquid and to which, I have applied the name of *Verantine*. These bodies, though resembling resins in some respects, must be classed as colouring matters, since their colour seems to be inherent, and not a merely accidental property. But in addition to these, there is uniformly found accompanying the alizarine, a third body, belonging, as far as general appearance and properties are concerned, to the same class of substances as rubiacine. This third body is, however, in each case quite distinct. When acids have been employed for the decomposition of rubian, then this third body is found to have the following properties: It is tolerably soluble in boiling water, and crystallises in lemon-yellow, silky needles; it is decomposed on being heated, but resists the action of nitric and concentrated sulphuric acids; I have called it *Rubianine*. When alkalies are used instead of acids, then rubianine is replaced by *Rubiadine*, which is a body crystallising in beautiful, golden-yellow scales, insoluble in water, but soluble in alcohol, and is completely volatilised when heated. But when rubian is decomposed by fermentation, it yields neither of these two, but in their place *Rubiafine*, a substance resembling rubiadine in most of its properties, but essentially distinguished from it by passing into rubiacic acid when treated with perchloride of iron. This substance is usually accompanied by another of similar properties, of which it is difficult to say whether it must be considered as distinct from the others, since I have not succeeded in obtaining it in a state of perfect purity. I call it *Rubiagine*. Now all these bodies which accompany alizarine make their appearance so invariably on the occasions which I have named, that their occurrence cannot be considered as accidental. Let us see, therefore, how their simultaneous formation from rubian is to be explained. I assume for rubian the formula $C_{56}H_{34}O_{30}$. Hence it follows that rubian is converted into alizarine simply by the loss of 14 eqs. of water. The formation of verantine and rubiretine is due to another kind of decomposition. The formulæ of these two bodies being respectively $C_{28}H_{12}O_{8}$ and $C_{28}H_{10}O_{10}$, it will be seen that by adding both together we obtain 1 eq. of rubian, minus 12 of water. The composition of the class of bodies to which rubianine belongs is rather doubtful. It is probable that the formula of rubianine is $C_{44}H_{24}O_{20}$. If so, it is formed from rubian by the separation from the latter of 1 eq. of grape sugar. Rubiafine, however, being

easily convertible into rubiacic acid, must contain 32 eqs. of carbon, and its formula is therefore, probably, $C_{32}H_{13}O_9$, that of rubiadine being the same.   In its conversion into these bodies, rubian therefore loses 2 eqs. of sugar, since $C_{56}H_{34}O_{30} + 3HO = C_{32}H_{13}O_9 + 8C_{12}H_{12}O_{12}$.   It appears from this, that rubian undergoes, not one, but three different processes of decomposition when acted on by acids, alkalies, or ferments; that the formation of sugar is connected, not with that of alizarine, but with that of rubianine and its allies, and that in fact there is no reason why only one of these processes should not take place to the exclusion of the others,; why, for instance, rubian should not be so decomposed as to yield alizarine alone without any of the accompanying bodies, which are from this point of view, not only a source of loss, but also positively prejudicial in practice.

I am aware that the view which I take of the composition of rubian and its products is open to some objection.   In the case of this, as of all other uncrystallisable organic bodies with very high atomic weights, doubts will arise in the mind of the chemist as to its right to be considered a pure unmixed substance.   It might be supposed, for instance, that rubian, instead of being a pure substance, is a mixture, containing among other things a conjugate compound of alizarine and sugar, a view which has indeed been taken by Rochleder, and that the other products of decomposition are purely accidental.   I may, therefore, very naturally be called on to adduce, if possible, further arguments in favour of the view I have taken, instead of basing it solely on such as are derived from an examination of the composition of these very complex bodies.   I will, therefore, state in few words such as have occurred to me.   In the first place, then, I have found that if the action of the ferment on rubian be retarded by means of antiseptic substances, the decomposition of the latter is not prevented, but there is then found no trace of alizarine among the products of decomposition, which then consist almost entirely of rubiretine and verantine.   Now if rubian were a conjugated compound of alizarine and sugar, or contained any such compound, alizarine must of necessity appear among the products of the fermentation, however much this might be retarded.—2. If rubian contained the elements of sugar, it ought when decomposed with nitric acid to yield oxalic acid. Such is, however, not the case, when perfectly pure rubian is employed. The only product is phthalic acid, so that in this case rubian behaves as if

it contained alizarine only. The same takes place when hypo-chlorite of lime is the decomposing agent.—3. It is found that when chlorine is made to act on rubian, the phenomena are of a totally different description. By means of chlorine, rubian is converted into a yellow crystallised substance, almost insoluble in water, but soluble in alcohol, and almost neutral in its character, which I have called *Chlororubian*. Its formula is $C_{44}H_{27}ClO_{24}$, and it is consequently formed from rubian by the elimination of 1 atom of sugar and the replacement of 1 atom of hydrogen by 1 of chlorine. But chlororubian is itself also a glucoside; for by the action of strong acids, it splits up into grape sugar, which may be obtained from it with its usual crystalline appearance and other properties, and into a chlorinated body, possessing the properties of a weak acid, and which has the composition of rubiadine with 1 atom of hydrogen replaced by chlorine, hence called *chlororubiadine*. Rubian then, when decomposed by chlorine, behaves exactly as if it were a glucoside; it yields an atom of sugar and chlororubian, the latter of which, by decomposition with acids, gives another atom of sugar and a substitution product of one of the rubiadine series containing 32 atoms of carbon. No products of substitution standing in any relation to alizarine make their appearance, as far as my observations extend.* Now, if rubian behaves, when decomposed in one particular way, as if it contained alizarine only; when subjected to another kind of decomposition, as if rubiretine and verantine were its sole con-stituents; and when exposed to a third species of action, as if it were made up of sugar and one of the rubiadine class of bodies:

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* ,Among the many anomalies with which this subject abounds, the following is deserving of mention. By the long-continued action of chlorine, chlororubian is converted into *perchlororubian*, a colourless crystallised substance, the formula of which is $C_{44}H_9Cl_9O_{15}$. Now it is singular that the 9 atoms of chlorine of this body are far more firmly combined with the other constituents than the 1 atom in chloro-rubian; for the latter, by the action of strong caustic alkalies loses the whole of its chlorine, which may also be detected by silver salts after treatment with nitric acid, whilst perchlororubian is not affected in the least degree either by caustic alkalies or by strong nitric acid. Chlororubian also is capable of combining with bases and plays the part of a weak acid, whilst perchlororubian, though contain ng 8 more atoms of chlorine, is a perfectly neutral substance, quite insoluble in caustic alkalies and not uniting with any base. Lastly, chlororubian is a glucoside, easily decom-posed by strong acids and yielding sugar as one of its products of decomposition; whilst perchlororubian is not in the least affected by the strongest acids, the atoms which in chlororubian go to form sugar being, from some cause or other, prevented from doing so, after having entered into the composition of perchlororubian.

I think I am justified in arriving at the conclusion that not one of these different bodies pre-exists in rubian, that the molecules of the latter arrange themselves in a different manner according to the decomposing agent employed, and that in fact we know nothing whatever of the internal constitution of that body. This is not a question of mere speculative interest, which concerns only the theoretical chemist; it may become one of great practical importance. The quantity of alizarine which a certain quantity of rubian is under ordinary circumstances capable of yielding amounts to between 10 and 20 per cent. of the rubian employed; but if my views be correct, it would be possible in theory to obtain nearly 80 per cent. The remaining 60 per cent. appear in the form either of useless or even injurious products. In my opinion a wide field is here opened for further experiment and research.

If our knowledge of the products of decomposition of rubian were confined to the points to which I have adverted, the matter would be simple enough, but a great additional complication has been introduced into it by the fact of the discovery of an acid, which is actually a conjugate compound of alizarine and sugar. This discovery we owe to Rochleder, who has described the acid under the name of *Ruberythric acid*. I have given it the name of *Rubianic acid*, because the composition given by Rochleder is so very different from that to which my experiments have led, that I cannot help supposing the two acids to be distinct, though it is not probable that there should exist two different acids having properties so nearly alike. It is a true acid, giving definite crystalline compounds with alkalies, a circumstance not observed by Rochleder. It is tolerably soluble in boiling water and crystallises in beautiful silky needles of a lemon-yellow colour. It is decomposed by the same agents, which effect the decomposition of rubian into alizarine and sugar, no secondary products in this case making their appearance. Now nothing could apparently be simpler than to attempt to explain the results obtained in my experiments, as Rochleder has endeavoured to do, by supposing that rubian contains rubianic acid ready formed, and that the alizarine observed in the decomposition of the former is due to that of the acid only. Nevertheless I have obtained, I believe, clear proofs that rubianic acid does not pre-exist either in madder or in rubian. It is formed from the latter by the simultaneous action of alkalies or other bases and oxygen. Oxygen is

essential to its formation. In a closed vessel, however great the excess of alkali which may be employed at the same time, not a trace of it is formed. Its composition, which is easily ascertained from that of its potash salt, which crystallises in beautiful puce-coloured needles, is a confirmation of the correctness of this view : for, as its formula is $C_{52}H_{29}O_{27}$, it will be seen that its formation is due to the elimination from rubian of 4 atoms of carbon and 2 of hydrogen, which must have been removed in the shape of carbonic acid and water. By decomposition it yields, as will be evident from the formula, 1 atom of alizarine and 2 atoms of grape sugar. Its existence then is no argument against the correctness of the view which I take of the composition of rubian and its derivatives. I do not claim the discovery of this interesting and beautiful acid, which is due to Rochleder, if his substance and mine are identical. I merely claim the discovery of the circumstances on which its formation depends. If, as I suppose, it does not pre-exist in the root, then it will afford the first instance in which the formation of a true glucoside or conjugate compound of sugar from a still more complex body by the action of oxygen has been observed.

Before concluding, it remains for me to say a few words in regard to purpurine, the colouring matter which has by some chemists been supposed to be, in addition to alizarine, essential to the production of madder colours. The two chief properties, whereby, according to those chemists who have examined it, it is distinguished from alizarine are : 1. That it dissolves in alkalies with a cherry-red or bright red colour, alizarine giving with alkalies beautiful violet solutions. 2. That it is entirely soluble in boiling alum-liquor, forming a solution of a beautiful pink colour with a yellow fluorescence, whereas alizarine is almost insoluble in the same menstruum. These properties are, however, not of a sufficiently decided character to entitle it to rank as a distinct substance, as they might possibly be produced by an admixture of alizarine with some foreign substance. Having convinced myself by numerous experiments that almost all madder colours may be produced by means of alizarine only, and that the finer madder colours of the dyer contain little besides alizarine in combination with the mordants, I made some attempts to prove that purpurine contains ready-formed alizarine, to which its tinctorial power may be supposed to be due. The optical phenomena exhibited by solutions of purpurine are however so peculiar,

as to lead Professor Stokes, who has carefully examined them, to the conclusion that they cannot be produced by any compound of alizarine, or by a mixture of alizarine with any other substance hitherto obtained from madder. Nevertheless it is certain that alizarine and purpurine are nearly allied substances, since both of them yield phthalic acid when decomposed by nitric acid, a property which belongs, as far as is known, to no other substance with the exception of naphthaline. There is one property by which purpurine may be easily distinguished from alizarine, viz. that of being decomposed when its solution in caustic alkali is exposed to the air. The bright red colour of the solution, when left to stand in an open vessel, soon changes to reddish-yellow, and at length almost the whole of the colour disappears, after which the purpurine can no longer be discovered in the solution. This is probably the cause of the disappearance of purpurine, when the method given by me for the preparation of alizarine from madder and its separation from the impurities with which it is associated, is adopted. This method, which depends on the employment of caustic alkalies, is an imitation of that to which dyers have recourse for the purpose of improving and beautifying ordinary madder colours, and it is certain that during this process the purpurine is either decomposed or by some means disappears. The only advantage which purpurine presents over alizarine in dyeing is that it imparts to the alumina-mordant a fiery red tint which in some cases is preferred to the purplish-red colour from alizarine. To the iron mordant it communicates a very unsightly reddish-purple colour, presenting a disagreeable contrast with the lovely purple from alizarine. In all madder colours which have been subjected to a long course of after-treatment, the purpurine is found to have almost entirely disappeared.

For the purpose of convenient reference I have subjoined a table containing the formulæ, properties, and principal reactions of the various colouring matters, and their products of decomposition mentioned in the preceding pages.

Professor Stokes has had the kindness to draw up, for the purpose of being appended to this paper, the following account of the optical characters of purpurine and alizarine, containing the

	PHYSICAL PROPERTIES.	HEAT.	WATER.	ALCOHOL.	CHLORINE.	HYPOCHLORITE OF LIME.	CONCENTRATED SULPHURIC ACID.	DILUTE SULPHURIC OR MURIATIC ACID.	NITRIC ACID.	ALKALIES.	LIME AND BARYTA.	ALUMINA AND ITS SALTS.	PEROXIDE OF IRON AND ITS SALTS.	SALTS OF LEAD.	OTHER METALLIC SALTS.	FERMENTS.
Rubian $C_{56}H_{34}O_{30}$	Amorphous, shining, brittle, not deliquescent, dark yellow, and transparent in thin layers, very bitter.	Begins to be decomposed at 130°C, gives a sublimate of alizarine and much charcoal.	Very easily soluble in water, removed from the solution by animal charcoal.	Not so easily soluble in alcohol as in water; separated by alcohol from its combination with animal charcoal.	Decomposed by chlorine, giving chlororubian and grape sugar.	Decomposed, giving phthalate of lime.	Dissolved with a blood-red colour, and decomposed on boiling the solution with blackening.	Decomposed on boiling, giving phthalic acid.	Decomposed on boiling nitric acid, giving phthalic acid.	Gives blood-red compounds with alkalies; decomposed by excess of caustic alkali, giving alizarine, rubiretine, verantine, rubiadine and sugar.	With lime and baryta water dark red precipitates, soluble in pure water.	Not more soluble in a boiling solution of alum than in boiling water; compound with alumina, not decomposed on boiling with weak caustic lye.	Removed from its watery solution by excess of hydrate of alumina.	With acetate of lead, watery solution gives no precipitate; with basic acetate of lead light red precipitate.	Alkaline solutions reduce salts of silver or copper.	Not affected by yeast, or decomposing casein, albumen, &c., but easily decomposed by erythrozym, giving alizarine, rubiretine, verantine, rubiafine, rubiagine and sugar.
Alizarine $C_{28}H_{10}O_8+6HO$	Crystallises in long transparent dark yellow needles, with much lustre.	At 100°C, loses its water of crystallisation and becomes opaque, at 216°C, begins to sublime, partly decomposed, leaving much charcoal.	Slightly soluble in water with a yellow colour.	Soluble in boiling alcohol; solution is dark yellow, and when concentrated, deposits crystals on cooling and standing.	Decomposed by chlorine, converted into a colourless substance.	..	Dissolved in the cold with a yellow colour, and not decomposed on boiling the solution.	..	Decomposed by boiling nitric acid, giving phthalic acid.	Dissolves in alkalies with violet colour; solutions in caustic alkalies do not change colour in the air; that in ammonia loses its ammonia.	Ammoniacal solution gives with chlorides of calcium and barium, purple precipitates.	Not more soluble in a boiling solution of alum than in boiling water; compound with alumina, not decomposed on boiling with weak caustic lye.	Peroxide of iron removes it from its solution in caustic potash.	With acetate of lead, alcoholic solution gives a purple precipitate, which on standing becomes red.	Ammoniacal solution gives purple precipitates with salts of silver and copper; alcoholic solution becomes of beautiful purple with acetate of copper.	
Verantine $C_{29}H_{10}O_{10}$	Amorphous, pulverulent, reddish-brown.	Heated in a tube gives little oily sublimate and much charcoal.	Almost insoluble in cold and boiling water.	Soluble in boiling alcohol, and deposited again on cooling, as a brown powder.	..	..	Dissolved with a brown colour, and decomposed on boiling the solution, with blackening.	..	Decomposed by concentrated nitric acid on boiling, not by dilute acid.	Soluble in alkalies with a dirty brownish-red colour.	Ammoniacal solution gives precipitates with lime and baryta salts.	..	..	With acetate of lead, watery solution gives dark brown precipitate.		
Rubiretine $C_{28}H_{12}O_8$	Amorphous, resinous, brittle, opake, dark brown.	Softens at 100°C, then melts, then decomposed.	Very little soluble in cold and boiling water.	Easily soluble in cold alcohol.	..	..	Dissolved with a yellowish-brown colour, and decomposed on boiling the solution, with blackening.	..	Decomposed by boiling nitric acid, and converted into a yellow substance, little soluble in alcohol.	Soluble in alkalies with a brownish-red colour.						
Rubiretine $C_{44}H_{24}O_{20}$	Crystallises in bright lemon-yellow silky needles.	Heated in a tube gives little yellow crystalline sublimate and much charcoal.	Tolerably soluble in boiling water, crystallises out again on cooling.	Soluble in alcohol.	Decomposed by chlorine and converted into perchlororubian.(?)	..	Dissolved with a yellow colour, and decomposed on boiling the solution, with blackening.	..	Dissolved by boiling concentrated nitric acid, without being decomposed.	Dissolved with difficulty by alkalies, giving blood-red solutions.	Ammoniacal solution gives red precipitates with the chlorides of barium and calcium.	..	Soluble in perchloride of iron solution, but not converted into rubiacic acid.	With acetate of lead, alcoholic solution gives no precipitate.		
Rubiadine $C_{32}H_{13}O_9$	Crystallises in yellow needles or in golden-yellow, glittering scales, or four-sided tables.	When heated, entirely volatilised, giving sublimate of yellow, micaceous shining scales.	Almost insoluble in boiling water.	More soluble in alcohol than rubianine.	..	..	Dissolved with a dark yellow colour, which changes to yellowish-brown on boiling.	..	Decomposed by boiling nitric acid.	Behaves like rubianine.	The baryta compound crystallises in dark brownish-red needles soluble in water.	..	Insoluble in perchloride of iron.	With acetate of lead, alcoholic solution gives no precipitate.		
Rubiacine $C_{32}H_{11}O_{10}$	Crystallises in greenish-yellow needles, or in tables with much lustre.	When heated, entirely volatilised, giving sublimate of brilliant yellow scales.	Slightly soluble in boiling water.	Soluble in boiling alcohol and crystallises out on cooling.	..	..	Dissolved with a yellow colour; not decomposed on boiling the solution.	..	Dissolved by boiling dilute nitric acid without being decomposed.	Soluble in caustic alkalies, with a purple colour.	Ammoniacal solution gives with chlorides of calcium and barium red precipitates.	Removed from its alcoholic solution by excess of hydrate of alumina.	Dissolves in perchloride of iron with a dark brownish-red colour, and converted by boiling into rubiacic acid.	With acetate of lead, alcoholic solution gives a dark red precipitate.		
Rubiacic Acid $C_{32}H_9O_{17}$	Lemon-yellow powder, not crystalline.	When heated, gives no crystalline sublimate.	Slightly soluble in boiling water.	Slightly soluble in boiling alcohol.	..	..	Dissolved with a yellow colour, which becomes darker but not black on boiling the solution.	..	Decomposed by boiling concentrated nitric acid.	The potash salt crystallises on cooling of its solution in boiling water, in long silky, brick-red needles; the colour of its watery solution is red, but changes to purple on the addition of caustic potash; the salt is decomposed on heating, with a slight explosion.	Watery solution of the potash salt gives with chloride of calcium, a crystalline, orange-coloured precipitate, with chloride of barium a yellow precipitate.	Watery solution of the potash salt gives with an orange-red coloured precipitate.	Watery solution of the potash salt gives reddish-brown with perchloride of iron, but gives no precipitate.	..	Watery solution of the potash salt gives with nitrate of silver a yellow precipitate, not changed on boiling the liquid; with sulphate of copper a red precipitate; with perchloride of mercury a yellow crystalline precipitate.	
Rubiafine $C_{32}H_{13}O_9$	Crystallises in yellow shining needles and scales.	When heated, entirely volatilised, giving yellow crystalline sublimate.	Very little soluble in water.	Soluble in boiling alcohol and crystallises out on cooling.	..	..	Dissolved, not decomposed on boiling the solution.	..	Dissolved by boiling nitric acid, not decomposed.	Soluble in caustic alkalies with a reddish-purple, in carbonated alkalies with a red colour.	..	..	Dissolves in perchloride of iron with dark brownish-purple colour, and converted by boiling into rubiacic acid.	With acetate of lead, alcoholic solution gives a crimson precipitate.	With acetate of copper, alcoholic solution gives an orange-coloured precipitate.	
Rubiagine	Crystallises in yellow needles collected in grains and nodules.	When heated, gives little crystalline sublimate and much charcoal.	Insoluble in boiling water.	Easily soluble in boiling alcohol, not crystallising on cooling.	..	..	Dissolved with a reddish-brown colour, decomposed on boiling the solution, with blackening.	..	Dissolved by boiling nitric acid, solution on cooling depositing yellow shining needles.	Soluble in alkalies with a blood-red colour.	Soluble in lime and baryta water with blood-red colour.	..	Very little soluble in perchloride of iron.	With acetate of lead, alcoholic solution turns dark yellow, and after some time gives orange-coloured granular precipitates.	With acetate of copper, behaves like rubiafine.	
Rubianic Acid $C_{52}H_{29}O_{27}$	Crystallises in lemon-yellow silky needles.	When heated, gives sublimate of alizarine and much charcoal.	Soluble in boiling water and crystallises out again on cooling; watery solution is bitter and reddens litmus paper.	Soluble in alcohol.	Decomposed slowly by chlorine, products of decomposition being soluble in water.	..	Dissolved with a dark red colour, which becomes reddish-brown on boiling the solution, little sulphurous acid being evolved.	Decomposed on boiling, giving alizarine and sugar.	Decomposed by boiling nitric acid, with facility.	Dissolves in caustic alkalies with cherry-red colour, which on boiling changes to purple, alizarine and sugar being formed; with carbonate of potash, gives silky puce-coloured needles of potash salt.	Watery solution gives with lime water a light red precipitate; with baryta water a crimson precipitate.	Watery solution gives no precipitate with acetate of alumina.	Dissolves in perchloride of iron with a greenish-brown colour, the solution containing protochloride.	With acetate of lead, watery solution turns red without giving any precipitate; with basic acetate it gives a copious red precipitate.	Alkaline solutions reduce salts of gold, but not salts of silver.	Decomposed by erythrozym, giving alizarine and sugar.
Chlororubian $C_{44}H_{27}ClO_{24}$	Crystallises in orange-coloured needles, slightly bitter on being chewed.	When heated, gives a little white crystalline sublimate and much charcoal.	Soluble in boiling water and deposited on cooling in amorphous masses.	Soluble in boiling alcohol, crystallises out on cooling; solution does not redden litmus paper.	Converted by chlorine into perchlororubian.	..	..	Decomposed on boiling, giving chlororubiadine and grape sugar.	Decomposed by boiling nitric acid, giving colourless solution, from which nitrate of silver precipitates chloride of silver.	Soluble in alkalies with a blood-red colour; converted by excess of caustic alkali into oxyrubian, with loss of its chlorine.	Watery solution turns red with lime water; with baryta water it turns red, and on boiling deposits red flakes and becomes colourless.	Watery solution gives no precipitate with acetate of alumina.	Soluble in perchloride of iron with a brownish-yellow colour, becoming after some time dark brown.	With acetate of lead, alcoholic solution gives no precipitate; with basic acetate, watery solution gives red precipitate.	Watery solution gives no precipitate with nitrate of silver.	
Chlororubiadine $C_{32}H_{12}ClO_9$	Crystallises in small orange-coloured needles and scales.	When heated, gives acid fumes and a little crystalline sublimate, and leaves much charcoal.	Insoluble in boiling water.	Soluble in boiling alcohol and crystallises out again on cooling; solution reddens blue litmus paper.	Converted by chlorine into a dark yellow, amorphous substance, insoluble in water, but easily soluble in alcohol.	..	Dissolved with an orange colour, which becomes dark purple on boiling the solution.	..	Dissolved by nitric acid of sp. gr. 1.52 in the cold; the solution gives no precipitate with nitrate of silver, but on boiling chloride of silver precipitates.	Soluble in caustic fixed alkalies with a purplish-red colour, and in ammonia and carbonated alkalies with a blood-red colour.	The baryta compound, formed by double decomposition, crystallises from water in long red needles, arranged in fan-shaped masses.	Alcoholic solution gives no precipitate with acetate of alumina.	Insoluble in perchloride of iron.	With acetate of lead, alcoholic solution gives no precipitate, even on adding ammonia also.	Alcoholic solution gives with acetate of copper a copious light brown precipitate.	
Perchlororubian $C_{44}H_9Cl_9O_{15}$	Crystallises in colourless, transparent, flat, four-sided iridescent tables.	When slowly heated, entirely volatilised, giving a sublimate of bright micaceous scales; suddenly heated it is decomposed with slight explosion.	Insoluble in boiling water.	Soluble in boiling alcohol and crystallises out again on cooling.	..	..	Dissolved, not decomposed on boiling the solution.	..	Dissolved by nitric acid, of sp. gr. 1.52; not decomposed on boiling the solution.	Insoluble in alkalies.	..	..	..	With acetate of lead, alcoholic solution gives no precipitate.		
Purpurine	Crystallises in small orange-coloured or red needles.	When heated carefully, it is volatilised without much residue, giving a sublimate of shining scales and needles.	Slightly soluble in boiling water with a pink colour.	Soluble in boiling alcohol and crystallises out on cooling.	..	..	Dissolved, not decomposed on boiling the solution.	..	Decomposed by boiling dilute nitric acid, more easily than alizarine.	Soluble in alkalies with bright purplish-red colour; solutions in caustic fixed alkalies lose their colour by the action of oxygen.	Soluble in lime and baryta water with chlorides of calcium and barium, purple precipitates.	Ammoniacal solution gives purple precipitate with acetate of alumina.	Soluble in boiling alum-liquor with a pink colour, separating on cooling, but precipitated by muriatic acid.	With acetate of lead, alcoholic solution gives a purple precipitate, not changed on standing, which dissolves on boiling with excess of acetate of lead, giving a purple solution.		

results obtained by him on a renewed examination of their action on light.

Optical Characters of Purpurine and Alizarine.

The optical characters of purpurine are distinctive in the very highest degree; those of alizarine are also very distinctive. The characters here referred to consist in the mode of absorption of light by certain solutions of the bodies, and occasionally in the powerful fluorescence of a solution. They are specially valuable because their observation is independent of more than a moderate degree of purity of the specimens, and requires no apparatus beyond a test-tube, a slit, and a small prism, a little instrument which ought to be in the hands of every chemist.
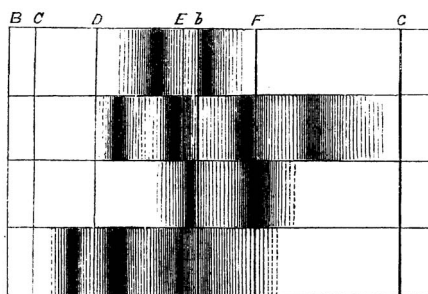
Alkaline solution of purpurine.—If purpurine be dissolved in a solution of carbonate of potash or soda, (it is easily decomposed by caustic alkalies,) the solution obtained absorbs with greatest energy the green part of the spectrum. In this and similar cases it is necessary to take care either to use a sufficiently small quantity of the substance, or else to dilute sufficiently the solution, or view it through a sufficiently small thickness; otherwise a broad region of the spectrum is absorbed, and the peculiar characters of the substance depending on its mode of absorbing light are not perceived. If the solution be contained in a wedge-shaped vessel, the effect of different thicknesses is seen at a glance; but a test-tube will answer perfectly well if two or three different degrees of dilution be tried in succession. When the light transmitted through an alkaline solution of purpurine of suitable

Fig. 1.—Solution of purpurine in carbonate of soda or potash, or in alum liquor.

Fig. 2.—Solution of purpurine in bisulphide of carbon.

Fig. 3.—Solution of purpurine in ether.

Fig. 4.—Alkaline solution of alizarine.

strength, after being limited by a slit, is viewed through a prism, two remarkable dark bands of absorption (Fig. 1) are seen about

the green part of the spectrum, comprising between them a band of green light, which, though much weakened in comparison with the same part of the unabsorbed spectrum, is bright compared with the two dark bands, which latter in a sufficiently strong solution appear perfectly black. The places of the dark bands, estimated with reference to the principal fixed lines of the spectrum, are given in the figure.

Solution in a solution of alum.—This solution has the same peculiar mode of absorption, and (Fig. 1) will serve equally well for it. But it has the further property of being eminently fluorescent, which the alkaline solution is not at all. The fluorescent light is yellow, but ordinarily appears orange from being seen through the fluid. The difference between the alkaline and alum-liquor solutions as to fluorescence does not depend on the acid reaction of the latter, but on the alumina. A solution exhibiting to perfection the peculiar properties of the alum-liquor solution may be obtained by adding to a solution of purpurine in carbonate of soda a solution of alum to which enough tartaric acid to prevent precipitation, and then carbonate of soda, has previously been added; and in this case the fluorescent solution is obtained at once and in the cold. This forms a very striking reaction in a dark room, according to the method described in the *Philosophical Transactions for* 1853, p. 385, with the combination, solution of nitrate of copper and a red (Cu_2O) glass. Some other colourless oxides besides alumina develop in this manner fluorescence, though to a less degree.

Solution in bisulphide of carbon.—This solution gives the highly characteristic spectrum (Fig. 2) exhibiting four bands of absorption, of which the first is narrower than the others, and the fourth is very inconspicuous, hardly standing out from the general absorption which takes place in that region of the spectrum. The second and third bands are the most conspicuous of the set.

Solution in ether.—This gives the characteristic spectrum (Fig. 3) exhibiting two bands of absorption. The solution is fluorescent, but not enough so to be perceptible by common observation.

The spectra of the solutions of purpurine in other solvents might be mentioned, but these are more than sufficient. In an optical point of view purpurine is remarkable for the general similarity of character, combined with diversity as to detail, which its various solutions exhibit as to their mode of absorbing light.

Alkaline solution of alizarine.—The solution of alizarine in caustic or carbonate of potash or soda, or in ammonia, exhibits on analysis the characteristic spectrum (Fig. 4) having a band of absorption in the yellow, and another narrower one between the red and the orange. There is a third very inconspicuous band at E, almost lost in the general darkening of that part of the spectrum.

Other solutions.—The solution of alizarine in ether or in bisulphide of carbon shows nothing particular. There is a general absorption of the more refrangible part of the spectrum, but there are none of those remarkable alternations of comparative transparency and opacity which characterize purpurine. Alizarine is hardly soluble in alum-liquor; and in the case of the red solution of mixed alizarine and verantine mentioned by Dr. Schunck at page 451 of the *Philosophical Transactions for* 1851, the absence of the remarkable absorption-bands (Fig. 1) and the absence of fluorescence, show instantly and independently of each other that it is distinct from purpurine.

Optical detection of purpurine and alizarine.—The characters of these substances are so marked that I do not know any substance with which either of them could be confounded, even if we restricted ourselves to *any one* of the solutions yielding the peculiar spectra. Not only so, but these properties enable us to detect small quantities, in the case of purpurine the merest trace, of the substance, present in the midst of a quantity of impurities. In the case of purpurine, a solution of alum is specially convenient for use, because the impurities liable to be present do not with this solvent absorb the part of the spectrum in which the bands occur. In this way I was able, though operating on only a very minute quantity of the root, to detect purpurine in more than twenty species of the family *Rubiaceæ* which were examined with this view, comprising the genera *Rubia, Asperula, Galium, Crucianella,* and *Sherardia.* The detection of alizarine by means of the characters of its alkaline solution is much less delicate, because many of the impurities liable to be present absorb the part of the spectrum in which all but the least refrangible of the absorption-bands occur; and as this band is not that which corresponds to the most intense absorption, a larger quantity of the substance must be present in order that the band may be perceived.