XXVI.—*On the Red Colouring Matters of Madder.*

BY ADOLPH STRECKER.

There is scarcely any class of bodies in organic chemistry, the investigation of which is attended with so many difficulties as that of the colouring matters; this may account for the imperfect knowledge we as yet possess of these substances, excepting indigo, which has been studied in every direction. Of many colouring matters we scarcely know more than the existence, while of others we possess the percentage-composition, translated into a more or less fitting empirical formula; a few only of these substances have become of late so far accessible to us, as to enable us to acquire a knowledge of them, corresponding to the present demands

* The same results are obtained in the distillation of *valeric acid*. *Comp. Chem. Soc. Q₁ J. III.*

of the science. This circumstance may be owing in some measure to the difficulty experienced in obtaining these substances in quantity sufficient for more accurate investigations, as they generally occur distributed in small proportions only, over a large amount of other matter, besides which, on the other hand, the feebly defined and generally acid character of the colouring matters renders the preparation of definite compounds of them a matter of difficulty.

Madder ranks in importance before all other colouring principles; the cultivation of the *Rubia tinctoria*, the preparation of the madder, and, above all, its manifold applications in the dyeing of cotton and in calico-printing, in which it affords the most varied, beautiful, and durable colours, form important branches of agriculture and manufactures.

Since Kuhlmann* first took up the chemical investigation of madder, many chemists have applied their talents and powers to this subject; and it must be gratefully acknowledged that the labours of Robiquet and Colin† Runge,‡ Schunck§ and Debus,|| have thrown much light on the chemical deportment of the active principles of the madder-root.

A superficial contemplation of the results of these researches would certainly appear to point out a great want of accordance between them; but on a more strict examination, the identity of the results may be discerned, and the differences in the statements easily explained and adjusted.

The study of the various researches on madder, together with comparative experiments made with this substance and with the splendid preparations of Messrs. Robiquet, Schunck and Debus, for the use of which I am indebted to Professor Liebig and Dr. Debus, have shown me that madder contains—besides the yellow or orange colouring matters, which do not play any important part in dyeing—two red colouring matters, which have been obtained by chemists in a state of greater or less purity, and have received from them various names.

The one of these, first prepared by Robiquet and Colin, and named by them *Alizarine*, was afterwards obtained in a state of perfect purity by Runge, who called it *Madder-red*. Persoz and

* Ann. Ch. Phys. [2], XXIV, 225.

† Ann. Ch. Phys. [2], XXXIV, 225; LXIII, 306.

‡ J. Pr.Chem. V, 362.

§ Ann. Ch. Pharm. LXVI, 174.

|| Ann. Ch. Pharm. LXVI, 351.

Gaultier de Claubry,* obtained it in a state of less purity, and described it under the name of *Matière colorante rouge*; and finally it was prepared perfectly pure by Schunck and Debus, and called, by the latter, *Lizaric acid*.

The second red colouring matter was first distinguished by Robiquet and Colin, by the name of *Purpurine*, although they did not obtain it pure; it was first isolated by Runge and called by him *Madder-purple*. Debus afterwards described it as *Oxylizaric acid*, and lately Higgin† obtained it mixed with alizarine, and described it under the latter name. Schunck has overlooked this substance; the correspondence of his analytical results with those of Debus, and some comparative experiments that I have instituted with the preparations of Schunck, Debus and Robiquet, show, however, that the alizarin of the first-named chemist is free from purpurine; and it is very probable that, in the treatment with concentrated solution of carbonate of potassa, the purpurine was dissolved, and only separated again in a decomposed form (possibly as alpha- or beta-resin).

ALIZARINE.

Alizarine is possessed of the following properties: it may be obtained in two forms, differing from each other in the amount of water which they contain. Hydrated alizarine occurs in small scales, having the appearance of mosaic gold. The anhydrous substance has a red colour, passing more or less into yellow, according to the thickness of the crystals. This explains the difference in the statements of Debus, Runge and Robiquet, who describe it, successively, as occurring in aurora-red needles, as a brownish-yellow powder, and of the colour chromate of lead. It fuses when heated, and sublimes in orange-coloured needles, a portion being decomposed with deposition of carbon, which may arise merely from the too rapid action of heat. It is moistened with difficulty by water, and, when boiled with the latter, dissolves with a deep yellow colour. The slightest trace of alkali (as ammonia or lime) colours the solution red; hence arises the fallacious statement of Robiquet that it dissolves in water with a rose-colour. It is considerably soluble in alcohol, to which it imparts a yellow colour, the solution becoming red under the same conditions as the aqueous solution. It dissolves likewise in ether with a yellow colour, which is not altered by the addition of small quantities of an

* Ann. Ch. Phys. [2], XLVIII, 69.

† Phil. Mag. XXXIII, 282.

alkali, the resulting red alkaline compound being insoluble in ether. Alizarine is easily soluble in alkalies; its solution in hydrate of potassa or of soda appears, if sufficiently concentrated, of a deep purple colour by transmitted light and pure blue by reflected light; when highly diluted, the solution assumes a uniform violet colour. This readily explains why Robiquet and Runge state the solution to be violet-coloured, while Schunck calls it purple-coloured. Alizarine dissolves in ammonia and carbonate of ammonia with a colour similar to orchil, the solution possessing no blue appearance on the surface. The cause of the difference in colour of the solutions of alizarine in caustic or carbonated alkalies, evidently lies in the formation of different compounds of alizarine with the alkali. I prepared one of these in the following manner: Alizarine was dissolved, by the aid of heat, in a solution of carbonate of soda, saturated in the cold; the filtered solution deposited, on cooling, the compound of alizarine with soda, insoluble in concentrated soda-solution. This was dried, purified from an admixture of carbonate of soda by solution in absolute alcohol, and precipitated from this solution in purple flakes by addition of ether. It dissolved easily in water and alcohol with the colour of orchil; the solution was coloured blue by addition of caustic soda.

The compounds of alizarine with the alkalis are insoluble in cold concentrated salt solutions; the ammoniacal solution of alizarine gives with chloride of barium a nearly pure blue flocculent precipitate; the solution from which the precipitate has been separated by filtration is colourless. Acetate of lead gives a purple-red precipitate. A characteristic of alizarine is its insolubility in a cold solution of alum. When alizarine is boiled with a concentrated solution of alum, the liquid assumes a yellow colour, like that of an aqueous solution of alizarine; on cooling, the small quantity of alizarine that was dissolved separates again, the liquid becoming almost colourless. Alizarine forms a red solution in hydrated sulphuric acid, and is reprecipitated unchanged on the addition of water. Robiquet and Schunck have shown that alizarine is capable of producing, on mordantized cloth, all the colours obtained from madder. To conclude from this, that alizarine is the only active dyeing principle in madder, would certainly be going too far; for it will be presently shown that purpurine likewise yields durable and beautiful colours on mordantized cloths.

The results of the analysis of alizarine by Schunck and Debus, correspond exactly—nor does the older analysis by Robiquet differ considerably from their numbers. Schiel's results, however,

cannot be made to correspond with them. The percentage-composition of alizarine may perhaps be considered as established by the more recent analyses; but in the construction of its chemical formula, we meet with the difficulty of determining the equivalent of a weak acid by the preparation of neutral compounds. Schunck was led by the analysis of a lead-salt to the formula,

while Debus assigns to another lead-compound the formula,

and represents alizarine itself by the formula,

I believe I can prove that the chemical formula of alizarine is

which corresponds with sufficient accuracy with the percentage-composition of this substance and its compounds, and is likewise confirmed by the results of the decomposition of alizarine. The composition of alizarine, dried at 100° — 120° , is as follows:

Equiv.	Calc.	Schunck.			Found.	Debus.		
C_{20}	68.96	69.09	69.15	69.14	68.95	68.98	68.98	
H_6	3.45	3.88	4.04	4.11	3.79	3.80	3.78	
O_6	27.59	27.03	26.81	26.75	27.26	27.22	27.20	
	100.00	100.00	100.00	100.00	100.00	100.00	99.96	

Schunck has also submitted hydrated alizarine to analysis; it lost on desiccation 18.3 p. c. of water, which, when calculated upon the above formula, corresponds nearly to 4 equivalents of water, calculated (17.1 p. c.). The composition of hydrated alizarine is, therefore,

Equivalent.	Calc.	Found (Schunck).		
C_{20}	57.14	58.97	56.94	57.02
H_{10}	4.76	4.19	5.13	5.87
O_{10}	38.10	—	—	—
	100.00			

The amount of carbon found corresponds exactly with the calculated number; the discrepancy in the amounts of hydrogen found arises from the use of warm chromate of lead in the first analysis, while in the two latter the substance was even mixed in a cold mortar.

The composition of the compounds obtained by precipitating an ammoniacal solution of alizarine with chloride of calcium and chloride of barium, and when dried at 100° , corresponds to the following formula :

	Calc.	Found.	(Schunck.)
Percentage of lime . . .	18.3	18.30	18.58

	Calc.	Found.
Percentage of baryta . . .	38.0	38.03

Schunck's lead-compound corresponds most nearly with the formula,

	Calc.	Found (Schunck.)	
Carbon	36.1	37.5	36.9
Hydrogen	1.5	1.7	1.6
Oxygen	12.1	—	—
Protoxide of lead . . .	50.3	49.1	49.8

100.0

The lead-compound, analysed by Debus, contains the alizarine and protoxide of lead in another proportion, which (when the substance is dried at 120°) may be expressed by the formula,

	Calc.	Found (Debus.)	
Carbon	38.2	38.18	38.51
Hydrogen	1.6	1.97	1.98
Oxygen	12.8	—	—
Protoxide of lead . . .	47.4	47.62	—

100.0

Of the products of decomposition of alizarine, one only is accurately known, that namely which is produced by various oxidizing agents, and has been described by Schunck under the name of *Alizaric acid*. Laurent and Gerhardt* have recently pointed out the close correspondence of alizaric acid, in its properties and composition, with *Phtalic acid*. By treating garancine with nitric acid, these chemists obtained an acid, the ammonia-salt of which yielded, on sublimation, a substance similar to phtalimide in all its properties.

* Compt. Rend. par Gerhardt et Laurent, 1849, 222.

Hence they are of opinion that no doubt can exist with respect to the identity of alizaric and phtalic acids.

I am enabled to quote some quantitative determinations which prove the identity of the acid obtained from alizarine and of phtalic acid. I am indebted to Professor Liebig for a specimen of alizaric acid, prepared by Schunck himself. It accords perfectly in its physical properties with the acid obtained from naphthaline. The silver-salt of the acid, dried at 100° , furnished, on analysis, the following numbers:

I.	0.4465	grms. of the salt, burnt with chromate of lead, gave:
	0.4195	„ „ carbonic acid, and
	0.0455	„ „ water.
II.	0.4475	„ „ gave, on careful ignition:
	0.2540	„ „ of silver.
III.	0.5443	„ „ gave:
	0.3090	„ „ of silver.

The silver-salt explodes when rapidly heated; this may be avoided by heating it gently and lighting it with a piece of burning paper.

These numbers correspond, in 100 parts, with the composition of the phtalate of silver.

	Equiv.	Calculated.		I.	Found.	III.
Carbon . .	16	96	25.3	25.6	—	—
Hydrogen .	4	4	1.0	1.1	—	—
Oxygen . .	8	64	16.9	—	—	—
Silver . .	2	216	56.8	—	56.7	56.8
	<hr/>	<hr/>	<hr/>			
	30	380	100.0			

Schunck's analysis of his *alizaric acid* and *pyro-alizaric acid* (anhydrous phtalic acid) may be quoted as further proofs of the identity of the two acids.

The formula of phtalic acid is $C_{16}H_6O_8$, and that of anhydrous phtalic acid is $C_{16}H_4O_6$.

		Phtalic acid.		Anhydrous phtalic acid.	
		Calc.	Mean	Calc.	Found.
In 100 parts,	C_{16}	57.8	57.5	C_{16}	64.9
„ „	H_6	3.6	3.9	H_4	2.7
„ „	O_8	38.6	—	O_6	32.4
		<hr/>		<hr/>	
		100.0		100.0	

If we compare the formula of alizarine with that of its product of

oxidation, it will be found that 4 equivalents of carbon have been eliminated and that 2 equivalents of oxygen have entered into the compound.

The 4 equivalents of carbon are probably eliminated in the form of oxalic acid, as the latter is obtained in considerable quantity in the treatment of madder with nitric acid. The decomposition of alizarine by nitric acid is expressed by the following equation :

The new formula of alizarine brings to light a close connection between this colouring matter and a substance obtained by Laurent,* in his elaborate research on the metamorphoses of naphthaline, namely, *Chloronaphthalic acid*. The latter substance is *Chlorinated Alizarine*, as will be seen by the comparison of their formulæ :

That the apparent relation exhibited by the formulæ of these substances really exists, is proved by the close analogy of their properties and products of decomposition. The acid character of alizarine is only feeble, that of chloronaphthalic acid is more strongly marked, as is generally the case with chlorinated compounds.

The *chloronaphthalic acid* of Laurent is a yellow substance, almost insoluble in water, dissolving in alcohol and ether in larger, but still not very considerable, quantity. It fuses at 200° , and may be sublimed without change. It dissolves in concentrated sulphuric acid without undergoing decomposition. Its combinations with metallic oxides exhibit lively colours, extending from yellow to bright red.

Solution of potassa dissolves chloronaphthalic acid with a deep red colour. A concentrated solution deposits, on cooling, a crimson salt, crystallized in needles, whose formula, according to Laurent, is :

The *ammonia-salt* is similar to the foregoing.

* *Revue Scientifique*, XIII.

The *baryta-salt* is obtained by double decomposition in the form of golden-yellow needles, of silky lustre, which, when dried at 100° , have the formula,

The *lime-salt* is obtained, like the other salts, by double decomposition; it crystallizes in orange-coloured needles. The *strontia-salt* has the same colour.

Protochloride of mercury gives a red-brown precipitate; solution of *alum* an orange-coloured; solution of *protoxide of lead* a reddish-yellow; and solution of *oxide of silver* a blood-red precipitate, becoming carmine red and crystalline when heated. Salts of the *protoxides of cobalt* and *copper* give carmine-coloured precipitates.

Chloronaphthalic acid dyes neither mordantized cloth, nor cotton mordantized or oiled for turkey red. This might have been expected, the acid character of the substance being already too strongly defined.

The close similarity of character between chloronaphthalic acid and alizarine—a similarity which is found only in the nearest substitution products—is further supported by the corresponding decomposition of these two substances by nitric acid. According to Laurent, chloronaphthalic acid is converted, by treatment with nitric acid, into *oxalic* and *phthalic acids*.

The only difference consists in the simultaneous elimination of chlorine and its substitution by hydrogen. It is possible, however, that, instead of phthalic acid, a chlorinated phthalic acid was formed, in which case the decomposition would correspond still more closely with that of alizarine:

Laurent has also obtained, besides this chloronaphthalic acid, a *pentachloronaphthalic acid* ($\text{C}_{20} \left\{ \begin{smallmatrix} \text{H} \\ \text{Cl}_5 \end{smallmatrix} \right\} \text{O}_6$), which likewise yields carmine-coloured salts insoluble in water. I have myself obtained in the preparation of naphthalic acid, an acid which did not yield with solution of baryta, the usual golden-yellow baryta-salt, but a splendid purple-red compound. I had too small a quantity of substance at my command for an analysis; it was probably a bi- or terchloronaphthalic acid. I obtained, simultaneously with this substance, a *chlorinated phthalic acid*, which has not been described

hitherto. I prepared the potassa-salt of this acid by saturating a boiling alcoholic solution with solution of potassa; it quickly separated in small plates of silvery lustre, which, when dried at 140° , gave, on analysis, the following numbers:

0.4045	gram. of potassa-salt gave:
0.2175	„ „ sulphate of potassa.
0.3495	„ „ potassa-salt, burnt with chromate of lead, gave:
0.3890	„ „ carbonic acid, and
0.0215	„ „ water.

These determinations correspond with the composition of *bi-chlorophthalate of potassa*.

	Calc.	Found.
C_{16} . . .	30.8	30.4
H_2 . . .	0.6	0.7
Cl_2 . . .	22.8	—
O_8 . . .	20.6	—
K_2 . . .	25.1	24.3
	<hr/> 100.0	

The question now arose whether it would be possible to expel the one equivalent of chlorine from chloronaphthalic acid and to replace it by hydrogen.

Two methods in particular are known for obtaining the original substance from chlorinated compounds. Melsens* reconverted *chloracetic* into *acetic acid* by the action of potassium-amalgam, (1 of potassium to 150 of mercury). The potassium dissolves without evolution of gas, as long as any chlorine is contained in the organic substance, in place of which hydrogen is taken up. Kolbe† made use of the galvanic current for the same purpose, and with great success; he passed the current into the neutral liquid by means of two amalgamated zinc plates.

I have endeavoured to obtain alizaric acid from chloronaphthalic acid by both these methods, without however arriving at the desired result. If potassium-amalgam is brought in contact with chloronaphthalic acid and water, the liberated potassa soon dissolves the acid, forming a dark red liquid, which however never exhibits the blue colour of the alizarine solution by reflected light. After a time, the solution contained chloride of potassium, and the colour of the solution diminished in intensity. A yellow precipitate was obtained

* Ann. Ch. Phys. [3] X, 233.

† Ann. Ch. Pharm. LIV, 274.

by the addition of an acid, which proved to be unaltered chloronaphthalic acid, as it yielded, with solution of baryta, the beautiful golden-coloured needles already mentioned. A portion of the acid had undergone a decomposition, which was however not limited to the substitution of hydrogen for the atom of chlorine, but had at once proceeded further.

The insolubility of chloronaphthalic acid in slightly acidulated water precluded its decomposition in such a solution by the galvanic current. When subjected to the current in an alkaline solution, chloronaphthalic acid soon underwent a change, which was indicated by the decrease in the colour of the solution and the assumption of a brown coloration, as also by the presence of chlorine in the liquid. But in this case likewise, no alizarine could be detected at any period of the operation.

Although these experiments have led to no positive results, I have no doubt that continued exertions and the application of new agents, will lead to a reaction, the results of which will be more within reach of the means presented to us by the science.

Chloronaphthalic acid was prepared by Laurent, by treating the compound $C_{20}H_7Cl_5$ (*chlorure de chloronaphtase*) with nitric acid. Chlorine is passed over naphthaline, until the mass, at first in a state of fusion, has assumed an unctuous consistence, when the chloride of naphthaline is dissolved out by ether, and obtained, by evaporation of the ether, in the form of an oily liquid. This is submitted for several days to a current of chlorine, the resulting viscid matter being rendered more fluid, towards the end of the operation, by the application of heat. After the action is complete, the substance is dissolved in boiling ether, which, on cooling, deposits the chlorinated chloride of naphthaline; this is boiled with nitric acid till it no longer solidifies on cooling, but remains in the form of a viscid mass. A yellow powder is separated by the addition of ether, to which Laurent has given the name *oxyde de chloroxinaphtose*. When treated with an alcoholic solution of potassa, this substance is immediately converted into chloronaphthalic acid. These reactions may be expressed by the following equations :

Now it is evident that, if chloride of naphthaline ($\text{C}_{20}\text{H}_8\text{Cl}_4$) were to be submitted to these reactions, the final product would also contain 1 equivalent of chlorine less and 1 equivalent of hydrogen more; in fact, alizarine ($\text{C}_{20}\text{H}_6\text{O}_6$) must then be obtained instead of $\text{C}_{20}\text{H}_5\text{ClO}_6$. In the treatment of the chlorinated chloride of naphthaline by nitric acid, a large quantity of the substance is converted into further products of decomposition, namely into phthalic and oxalic acids. The chlorinated compounds withstand the oxidizing action of nitric acid much better than the normal substances, and this may be the reason why chloride of naphthaline yields, instead of $\text{C}_{20}\text{H}_6\text{O}_6$, only the products of decomposition of that substance, namely phthalic and oxalic acids. The experiments of Schunck have shown that alizarine, when boiled with nitric acid, splits up readily into phthalic and oxalic (?) acids.

I do not know whether I shall be able to follow up this subject; I believe, however, to have pointed out with sufficient clearness in the foregoing, the manner in which we may hope to obtain alizarine from naphthaline. The method would be to check the reaction at a certain point; this might be arrived at by the employment of a more feeble oxidising agent than nitric acid, as the latter always effects a further decomposition.

The theoretical and practical interest of the above question leads me to hope that chemists will bestow a little attention upon it. If it be considered, that, according to the experiments of Robiquet and Schunck, alizarine not only produces the same colours as madder, but even possesses advantages over the raw material; if, besides this, the small amount of alizarine required for dyeing, and the low price of naphthaline, obtained as it is in large quantities in the manufacture of coal-gas, be taken into consideration, it will be evident that, even if a very elaborate and circuitous method should be requisite for the conversion of naphthaline into alizarine, its practical application might still be found advantageous.

PURPURINE.

This second red colouring principle of madder differs from alizarine chiefly by its solubility in solution of alum. If a concentrated solution of alum be boiled with purpurine, the latter dissolves with a fine bright red colour; the solution has an orange colour by reflected light. Ammonia precipitated a red-lake, varying in

colour, when dry, from rose to *ponceau*, according to the quantity of alumina present. The solubility of purpurine in solution of alum has been applied by Runge and Debus to the separation of this substance from alizarine. Purpurine differs in appearance according to the conditions under which it crystallizes. It is deposited from its solution in strong alcohol, in red needles, and from weak spirits in thin, soft, orange-coloured needles, forming a matted mass, when dried. These orange-coloured crystals contain water of crystallization, which they part with at 100° , assuming a red colour. A specimen of pure purpurine, containing, however, some red crystals (anhydrous purpurine) in admixture, lost 4.9 of water at 120° . Runge describes his purpurine as occurring in orange-coloured crystallized grains, and Debus his oxylicaric acid as forming red needles, from $\frac{1}{6}$ to $\frac{1}{8}$ of an inch in length. Purpurine is more easily soluble in warm water than alizarine, and forms a red solution. It fuses when heated, and sublimes with deposition of carbon. Its solution in alcohol has likewise a much deeper red colour than that of alizarine; it dissolves in ether and in concentrated sulphuric acid. Purpurine* may be easily distinguished from alizarine by the colour of its solution in potassa; it is bright red, and does not possess the blue tint characteristic of alizarine. Purpurine gives purple-coloured precipitates with lime- and baryta-salts, which are easily distinguishable from those of alizarine. The lead-compound is likewise purple. Purpurine is also insoluble in a concentrated solution of carbonate of soda in the cold; it dissolves on ebullition, but separates again perfectly from the solution on cooling. The compound of purpurine with potassa- (?) alkali is also insoluble in other salt-solutions.

Runge has already shown that purpurine dyes cloth purple when mordantized with alumina, rose-coloured with tin-mordant, ponceau-coloured with lead-mordant, and violet with iron-mordant. I have convinced myself that purpurine imparts to stuffs mordantized with alumina, as well as to cotton which has been oiled and mordantized for turkey-red, a fine deep red dye without any blue tint, and that these colours are not altered by the process of raising with soap. It cannot, therefore, be doubted that purpurine plays a part in turkey-red dyeing, as well as in the common-madder dyeing.

Debus has published several concordant analyses of purpurine (oxylicaric acid), which correspond exactly to the formula,

* I am not able to confirm the statement made by Schiel, that sublimed madder-purple (purpurine) dissolves with a blue colour in solution of potassa. Purpurine, repeatedly sublimed, dissolved in potassa with a bright red colour.

To a lead-compound of purpurine, he has assigned the formula,

It has already been seen, with alizarine, how little reliance can be placed on the atomic weights derived from compounds of bodies like these, of feebly acid properties; the equivalent proportion $\text{C}_3 \text{H O}$, determined upon by Debus seems, however, undoubtedly correct, and the most probable formula appears to be $\text{C}_{18} \text{H}_6 \text{O}_6$. Hydrated purpurine would contain, according to the above determination, one equivalent of water of crystallization (calc. 5.3 per cent).

A certain connection between two substances, occurring in the same plant and so similar in properties to each other, might reasonably be expected. Debus interpreted the composition of alizarine and purpurine, as found by him, by assuming the presence of one atom more of oxygen in the former than in the latter; the endeavours to convert alizarine into purpurine by the action of oxygen, were not attended with the expected result. The following experiment would however seem to indicate a reconversion of alizarine into purpurine. Some madder from Elsars was suspended in water, mixed with fresh yeast, and kept for some time in a closed vessel at a temperature of about 30° . Fermentation was soon set up, as was indicated by the brisk evolution of carbonic acid. After the lapse of two days, the action terminated—the liquid was powerfully acid—and, when distilled, yielded alcohol and a trace of a volatile acid; the strongly acid residue contained much phosphoric acid.

The liquid was separated from the solid portion by a cloth; the solid matter removed, and treated with a boiling solution of alum, which assumed the exact colour of purpurine. On cooling, the solution deposited, besides crystallized alum, a red colouring matter, which dissolved again when boiled with more solution of alum, and contained, besides purpurine, a mere trace of alizarin. The addition of sulphuric acid to the alum-solution separated a considerable quantity of purpurine, which, after extraction with boiling hydrochloric acid, yielded from its alcoholic and ethereal solutions crystals of purpurine mixed with an amorphous substance. The alizarine appeared therefore to have disappeared, while a considerable quantity of purpurine was obtained. It would, however, be necessary, in order to prove decidedly whether alizarine is converted into purpurine by fermentation to submit pure alizarine mixed with yeast to fermentation.