

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

Received June 13,—Read June 21, 1855.

## PART III.

*Combined Action of Alkalies and Oxygen on Rubian.*

IN the preceding part of this paper I have given an account of the action of alkalies on rubian and of the products of decomposition thereby formed. I have shown that these products are, with one exception, identical with those which the action of strong acids gives rise to, the rubianine produced by acids being merely replaced by rubiadine when alkalies are employed. Now though I found this to be in all cases the final result of the action of alkalies, there still remained a possibility of the existence of bodies intermediate between rubian and the final products of decomposition. Such bodies do in reality exist, but their formation is dependent, at least in part, on the simultaneous action of oxygen.

If to a solution of pure rubian baryta water be added in excess, if a current of carbonic acid gas be passed through the solution, until the whole or a great part of the baryta has been converted into bicarbonate of baryta, and the filtered solution be left exposed in a shallow vessel to the atmosphere, its surface becomes covered in a short time with a thin film of a beautiful scarlet colour, which, when viewed under a lens, is seen to consist of small interlaced crystals. If this film be broken so as to cause it to sink to the bottom, a new one is formed on the surface of the liquid. This process continues for some time, but at last ceases. On gently evaporating the solution, an additional quantity of this red substance separates in thick flocks. After being collected on a filter and washed with cold water, it appears of a fine scarlet colour. On drying it becomes brown, but if then reduced to powder the colour changes to a cinnabar-red. If it be suspended while still moist in water, and a current of carbonic acid gas be passed through the liquid, it dissolves again entirely, forming a yellow solution; but if this solution be evaporated, its colour changes to red, and it again deposits red flocks, after which it becomes almost colourless. The red flocks contain two organic substances in combination with baryta. On adding to them dilute sulphuric acid the former dissolve, giving a yellow solution. The excess of sulphuric acid having been removed by means of carbonate of lead, the solution is filtered, and the insoluble matter left on the filter is treated several times with boiling water, after which it generally retains only a slight pink tinge. The filtered solution deposits on evaporation a quantity of yellow crystalline needles. After evaporating to dryness there is left a yellow mass, the surface and edges of

which have a dark yellowish-brown tinge. On adding to this mass a small quantity of cold water, part of it dissolves with a deep yellow or reddish-yellow colour, while a yellow powder remains undissolved. The latter consists of a peculiar acid, to which I shall give the name of *Rubianic Acid*. After being collected on a filter and washed with cold water, it is purified by solution in boiling water, to which a little animal charcoal may be added. On filtering the solution boiling hot and allowing to cool, it crystallizes in beautiful lemon-yellow needles, which if the solution was at all concentrated entirely fill the liquid. The substance dissolved by the cold water is left on evaporation in the shape of a reddish-yellow or brownish-yellow substance, resembling rubian itself in appearance and all its properties. As analysis showed it to be formed from rubian by the elimination of several equivalents of water, I shall call it *Rubidehydran*.

The liquid filtered from the red flocks, consisting of the baryta compounds of the two substances just named, has still a dark brownish-yellow colour, and contains a third organic substance in solution. In order to ascertain whether the whole quantity of the two former substances has been separated, and whether the solution still contains any unchanged rubian, it is well to add caustic baryta to the liquid, to supersaturate the latter with carbonic acid and to evaporate again. If no more red flocks separate on evaporation, but only a deposit of carbonate of baryta is formed, then the process is completed. On now adding to the filtered solution basic acetate of lead a red precipitate falls, while the liquid becomes colourless. The former being separated by filtration and washed with water, is to be decomposed with sulphuric acid in the cold, and the excess of acid having been removed with carbonate of lead, sulphuretted hydrogen is passed through the filtered liquid, and the latter, after being filtered again from the sulphuret of lead, is evaporated to dryness, when it leaves a dark brownish-yellow substance, resembling rubian in appearance, but differing in being somewhat deliquescent. To this substance I will give the name of *Rubihydran*. The liquid filtered from the lead compound of this substance sometimes contains sugar, but this is entirely a secondary product of decomposition, formed at the cost of one or more of the primary products, and indicates the formation at the same time either of rubiadine or alizarine.

The same products of decomposition may be obtained by adding to the solution of rubian a solution of bicarbonate of baryta made from chloride of barium and bicarbonate of soda, and evaporating in contact with the air until red flocks begin to appear, or by adding caustic baryta to the solution, allowing the mixture to stand exposed to the air for some time and filtering, when the insoluble baryta compound left on the filter will yield rubianic acid and rubidehydran, and the liquid rubihydran. The same process of decomposition takes place, if caustic soda, ammonia, or lime water be added to a watery solution of rubian, and the mixtures be allowed to stand exposed to the air for some time. On now adding chloride of barium to any one of them a dark red precipitate falls, which being collected on a filter, washed with water

and then treated in the same manner as the red flocks obtained by means of bicarbonate of baryta, affords in each case rubianic acid and rubidehydran, while the liquid contains rubihydran. If a small quantity of any acid be added to a watery solution of rubian, and if the acid be then neutralized with carbonate of baryta, the small quantity of bicarbonate of baryta formed is sufficient to induce a decomposition of the rubian, for the filtered solution on exposure to the air very soon begins to deposit red flocks, which consist of rubianic acid and rubidehydran in combination with baryta. It is for this reason that I have recommended the employment of carbonate of lead instead of carbonate of baryta for the purpose of neutralizing the sulphuric acid used in purifying rubian\*. Even oxide of lead is a sufficiently strong base to cause rubian to undergo this process of decomposition, when oxygen is present at the same time. If rubian be precipitated from its watery solution by means of basic acetate of lead, and the lead compound be left exposed to the air for a short time, it will be found no longer to contain unchanged rubian. If the compound be decomposed with sulphuric acid in the cold, and the excess of acid be neutralized with carbonate of lead, the filtered solution deposits during evaporation crystals of rubianic acid, and leaves at last a brown deliquescent mass, which unless it be strongly dried is with difficulty removed from the vessel containing it†. In short, whenever rubian is brought into contact at the same time with oxygen and an alkaline or other strong base, it undergoes decomposition. Hence it follows, that in preparing the so-called xanthine according to the methods proposed by KUHLMANN, BERZELIUS, RUNGE and HIGGIN, as well as the ruberythric acid of ROCHLEDER, the use either of alkaline earths or basic acetate of lead being prescribed by all these chemists, products of the decomposition of rubian must in every case be formed.

For the purpose of preparing the three bodies which result from this process of decomposition, it is not necessary to employ pure rubian. If madder be extracted with boiling water, and sugar of lead be added to the extract, a purple precipitate is produced, and ammonia being added to the filtered liquid, the whole of the rubian is precipitated together with some chlorogenine in combination with oxide of lead. The precipitate is decomposed with sulphuric acid in the cold, and the excess of the acid is removed by means of carbonate of lead. To the filtered solution a quantity of baryta-water is to be added, and the baryta is then converted into bicarbonate of baryta by a stream of carbonic acid gas. The solution is then left exposed to the air for some time and then slowly evaporated. The red flocks which are deposited are collected on a filter as they form, and after being treated in the same way as the flocks from pure rubian, yield rubianic acid and rubidehydran. The liquid filtered

\* See Philosophical Transactions for 1851, p. 440.

† In purifying rubian by precipitation with basic acetate of lead, as described in the first part of this paper, care must be taken to wash the precipitate with alcohol and not with water. If the former be employed, decomposition is almost entirely prevented, whereas in using water the rubian in the precipitate undergoes complete decomposition during the short time necessary for edulcoration.

from these flocks contains chlorogenine as well as rubihydran, and the separation of the latter becomes therefore rather more difficult. This may however be effected by precipitating it with basic acetate of lead, filtering, washing the precipitate with water, then redissolving it in warm acetic acid, and again precipitating by means of a little ammonia. The last precipitate contains hardly any chlorogenine, and after being put on a filter and washed, is decomposed with sulphuric acid in the cold. The excess of acid is removed by carbonate of lead, the liquid is filtered, sulphuretted hydrogen is passed through it, it is again filtered from the sulphuret of lead, and on being evaporated leaves the rubihydran free from chlorogenine. Should it still contain a little of the latter substance, in which case its watery solution turns green on being boiled with muriatic or sulphuric acid, the precipitation with basic acetate of lead must be repeated. It frequently happens, that besides the usual products of decomposition, a quantity of rubiadine is also formed. In this case the red flocks deposited on evaporating the barytic solution yield, on being decomposed with sulphuric acid, besides the substances soluble in water, a yellow powder, which is insoluble both in cold and boiling water, and which consists of impure rubiadine; but this, like the sugar, which is also sometimes formed during the process, is without doubt a secondary product of decomposition. Indeed the formation of the one is most probably dependent on that of the other.

The process of decomposition just described is always accompanied by an absorption of oxygen. In order to ascertain the quantity of the latter which an alkaline solution of rubian was capable of absorbing, I took 4.2280 grms. of rubian, which after deducting the inorganic matter with which it was contaminated, was equivalent to 4.1049 grms. of the pure substance, dissolved it in hot water, poured the solution into a graduated tube, added to it a solution of about 6 grms. hydrate of baryta, filled the rest of the tube with mercury, and then inverted it over mercury. Oxygen gas was then introduced, and the liquid was from time to time agitated with the gas, in order to bring every portion, and especially the red flocculent precipitate produced by the baryta, and which sank to the bottom of the solution, into frequent contact with it. After 143 days I found that 147 cubic centimetres of gas had been absorbed. The contents of the tube were then removed and filtered. There remained on the filter a red baryta compound, which, on being treated as usual, yielded rubianic acid and rubidehydran, as well as a small quantity of alizarine. To the red liquid sulphuric acid was added; the excess of acid was removed with carbonate of lead, and sulphuretted hydrogen having been passed through the filtered liquid, the latter, after being filtered again from the sulphuret of lead, was submitted to distillation. The distillate was acid, and after being neutralized with carbonate of soda and evaporated, left a saline residue having all the characters of acetate of soda. Acetic acid is therefore another product formed in this process, but whether this acid is an essential product of decomposition or not, still remains doubtful. The residue of the distillation contained rubihydran, which was separated by precipitation with basic acetate of lead, as

before described, and a little sugar, which was obtained from the liquid filtered from the lead precipitate. The sugar and the alizarine were probably secondary products of decomposition formed from the rubianic acid by the action of the alkali.

*Rubianic Acid.*—This substance really merits the name of an acid, for though its acid properties are not well marked, the fact of its giving crystallized compounds with the alkalis is a sufficient indication of the class in which it should be placed. It crystallizes from its watery solution in silky needles of a pure lemon-yellow colour, which when dry form a light, bulky interwoven mass. Sometimes it is slowly deposited from its watery solution in grains and masses of an indistinctly crystalline form, which leave an orange tinge. This difference in appearance is due to some impurity, which may be removed by redissolving the acid in boiling water and adding a little animal charcoal, when the acid crystallizes rapidly from the filtered solution in needles, as just mentioned. The watery solution has a light yellow colour, reddens litmus paper slightly, and has a distinctly bitter taste, though not so intensely bitter as that of a solution of rubian. It is soluble in alcohol, but not in ether. When heated on platinum foil it melts and then burns with a smoky flame, leaving a slight carbonaceous residue. When heated in a tube it melts to a brownish-red liquid, which on being allowed to cool becomes solid and crystalline, but on being heated again more strongly gives fumes, which condense on the colder parts of the tube to a liquid, which soon solidifies, forming a mass of shining needles. When slowly heated between two watch-glasses, there is formed on the upper glass a sublimate of shining orange-coloured crystals, having the appearance and all the properties of alizarine, while a considerable carbonaceous residue is left on the lower glass. Concentrated sulphuric acid dissolves rubianic acid easily even in the cold, forming a dark red solution, which on being boiled becomes of a dark reddish-brown colour, without evolving much sulphurous acid. If sulphuric acid be added to a watery solution of rubianic acid, and the solution be boiled, dark yellow or orange-coloured flocks begin to be deposited, which increase as the boiling continues. On allowing to cool they often separate in such quantities as to render the liquid quite thick. These flocks are quite uncrystalline, though sometimes small yellow crystalline grains are found among them, which consist of undecomposed acid, and disappear on continuing the action for some time longer. These flocks consist of alizarine almost in a state of purity. On dissolving them in alcohol and evaporating spontaneously, a quantity of beautifully crystallized alizarine is obtained. The liquid filtered from the flocks contains sugar, which is obtained with its usual appearance and properties on neutralizing the acid with carbonate of lead, filtering, passing sulphuretted hydrogen through the liquid, filtering again, and evaporating. Muriatic acid acts in precisely the same manner on rubianic acid as sulphuric acid. Nitric acid dissolves rubianic acid even in the cold, forming a yellow solution, which on being boiled disengages nitrous fumes and becomes colourless. The solution on evaporation leaves a brown syrup, which contains oxalic acid. Rubianic acid is not decomposed on being treated

with boiling solutions of phosphoric, acetic, oxalic or tartaric acids; it merely dissolves in them, and crystallizes out again unchanged on the solutions cooling. If chlorine gas be passed through a watery solution of rubianic acid, the yellow colour of the solution slowly disappears. If there are any crystals of undissolved acid floating in the liquid, these disappear very slowly, and the gas must be passed through for a long time in order to effect their decomposition. The solution now appears colourless, but slightly milky. No yellow flocks are formed, as in the case of rubian, but the solution, on standing for some time, usually deposits a quantity of brownish-yellow crystals. If a solution of chloride of lime be added to a watery solution of rubianic acid, the latter turns blood-red, but in a few moments the colour disappears, and the solution becomes quite colourless.

Rubianic acid dissolves in caustic potash and soda in the cold with a lively cherry-red colour. If caustic potash be added to a strong watery solution of the acid, nothing separates on standing; but if carbonate of potash be employed instead of caustic potash, there is deposited almost immediately a quantity of dark-coloured crystalline needles. These needles are the potash salt. When collected on a filter, slightly washed with water and dried, they form a beautiful puce-coloured silky mass. When dried either in the water-bath or *in vacuo*, the colour changes to a bright red, but after a few minutes' exposure to the atmosphere the original colour is restored. Rubianic acid is so weak an acid, that water alone is sufficient to separate it from its combination with potash. When the potash salt is treated with boiling water it dissolves with a red colour, but the solution on cooling and standing deposits yellow crystals of the acid itself. Mere treatment with cold water produces to some extent the same effect; for if the salt be placed on a filter and washed with cold water, numerous small yellow specks, caused by the separation of the acid, become visible. When caustic or carbonate of soda are added to a boiling watery solution of the acid, the solution deposits on cooling a quantity of small bright red spherical grains, which generally form a mass so bulky as to render the liquid thick and gelatinous. When this mass, which consists of the soda salt, is placed on a filter, an almost colourless liquid runs through, leaving the salt on the filter in a soft spongy state, from its retaining mechanically a large quantity of water. The round grains of which it consists, though they have a somewhat crystalline appearance, are not in reality crystalline. In consequence of its sparing solubility in water, which is less than that of the potash salt, it may be washed with cold water without dissolving. When dry it is dark red, and gives a red powder. It dissolves again in boiling water with a red colour, and the solution on cooling forms a thick jelly, which however is converted, on standing, into a mass of yellow crystalline grains consisting of acid. If a solution of rubianic acid in caustic potash or soda be supersaturated with any stronger acid, the solution becomes yellow without depositing anything, but after some time the acid separates in yellow crystals. But if the alkaline solution, containing a considerable excess of alkali, be boiled, its colour changes gradually from red to purple, and

after prolonged boiling to violet, similar to that of a solution of alizarine in caustic alkali, the colour being generally so intense as to deprive the solution of its transparency. Acids now produce an immediate precipitate of dark yellow flocks, while the liquid becomes almost colourless. If the action of caustic alkali has not been continued long enough to produce a complete decomposition of the acid, then after some time crystals of the latter appear in the midst of the flocculent precipitate. The flocks consist of alizarine, but less pure than when the decomposition is effected by means of sulphuric or muriatic acid. On decomposing a considerable quantity of the acid by means of caustic soda, and treating the precipitated flocks in the same manner as those formed by the decomposition of rubian with acids or alkalies, I obtained, besides alizarine, a trace of verantine and a small quantity of a substance resembling rubianine or rubiadine\*. The liquid filtered from the flocks contains sugar. Rubianic acid dissolves in caustic ammonia with the same colour as in caustic potash or soda, but with much greater difficulty than in the latter. The solution does not change its colour, however long it may be boiled, and on adding an excess of a stronger acid, the rubianic acid crystallizes out unchanged. On evaporating the ammoniacal solution to dryness it loses part of its ammonia, leaving some yellow crystals of acid surrounded by a red uncrystalline coating like gum. The latter dissolves in cold water, but on evaporation the solution again gives yellow crystals. If to a boiling watery solution of the acid carbonate of ammonia be added, the solution becomes red, and deposits on cooling crystals of the ammonia salt, which have the same colour and appearance as the potash salt. These crystals may be dried without losing their ammonia, but, like the other alkaline salts, are decomposed on redissolving them in boiling water, the solution depositing on cooling crystals of the acid.

Baryta water gives in a watery solution of rubianic acid a beautiful crimson flocculent precipitate, while the liquid becomes colourless. If carbonic acid be passed through the liquid the precipitate gradually dissolves, forming a clear yellow solution; but if this solution be left exposed to the air, its surface becomes covered with a red film, and on evaporation it deposits a quantity of red flocks, until at length the whole of the acid seems to be again precipitated in combination with baryta. Lime water produces in a watery solution of the acid a light red precipitate, while the liquid becomes colourless. If carbonic acid be now passed through the liquid the precipitate dissolves, forming a yellow solution, which on exposure to the air becomes red, but gives no red film, and on evaporation deposits no flocks, but leaves at last a red mass, which dissolves again in boiling water. Acetate of alumina and peracetate of iron produce no change in a watery solution of the acid. Nevertheless the latter

\* This substance is light yellow and crystalline. When heated it is volatilized, giving a sublimate of yellow shining needles and scales. It is insoluble in boiling water, but dissolves in boiling nitric acid, and crystallizes out of the solution again on cooling in yellow needles. It is precipitated from its alcoholic solution by acetate of copper, but not by acetate of lead.

is entirely removed from its solution by hydrate of alumina, to which it communicates a light red colour, and also by hydrated peroxide of iron, though not so easily as by alumina. Rubianic acid dissolves easily in a boiling solution of perchloride of iron, forming a dark greenish-brown liquid, which contains protochloride of iron. The solution deposits nothing on standing, and on evaporation only a small quantity of black powder separates, which is probably a compound of alizarine and oxide of iron. Acetate of copper gives in watery and alcoholic solutions of the acid a brownish-red precipitate, which is soluble in boiling acetic acid. Neutral acetate of lead turns the watery solution of the acid red, but produces no precipitate; basic acetate of lead, however, gives a copious red flocculent precipitate, just as in a solution of rubian. An alcoholic solution of the acid gives with an alcoholic solution of acetate of lead a light red precipitate, which after filtration of the alcoholic liquid dissolves in pure water. On adding nitrate of silver to an aqueous solution of the acid and boiling no change takes place, but on the addition of a few drops of ammonia a dark reddish-brown precipitate slowly subsides as a fine powder, which is soluble in an excess of ammonia, forming a red solution, which does not change, and shows no signs of any reduction taking place when it is boiled. On adding chloride of gold to a watery solution of the acid no change takes place even on boiling, but on the addition of a little caustic alkali metallic gold is deposited, partly as a brown powder, partly in shining scales. If rubianic acid be mixed with water to which a quantity of erythrozym has been added, the yellow crystals of the acid gradually disappear, and are converted into alizarine. The liquid is found to contain sugar.

It is impossible to dye with rubianic acid. Mordants acquire in boiling solutions of the acid no more colour than in solutions of rubian or rubianine.

On submitting the acid to analysis the following results were obtained:—

I. 0.4605 grm., formed by the action of bicarbonate of baryta on rubian, dried in the water-bath and burnt with chromate of lead, gave 0.9445 carbonic acid and 0.2250 water.

II. 0.4030 grm. of another preparation, obtained by the action of bicarbonate of baryta, gave 0.8240 carbonic acid and 0.2020 water.

III. 0.2750 grm., formed by the action of caustic soda on rubian, gave 0.5605 carbonic acid and 0.1390 water.

IV. 0.4750 grm., obtained by means of ammonia, gave 0.9670 carbonic acid and 0.2295 water.

V. 0.2920 grm., obtained by means of caustic lime, gave 0.6000 carbonic acid and 0.1490 water.

These analyses give in 100 parts—

	I.	II.	III.	IV.	V.
Carbon . . . .	55.93	55.76	55.58	55.52	56.04
Hydrogen . . .	5.42	5.56	5.61	5.36	5.66
Oxygen . . . .	38.65	38.68	38.81	39.12	38.30



corresponding to the formula  $C_{52}H_{29}O_{27}$ , as the following calculation shows:—

	Eqs.		Calculated.
Carbon . . . .	52	312	56·01
Hydrogen . . . .	29	29	5·20
Oxygen . . . .	27	216	38·79
		<hr/> 557	<hr/> 100·00

Rubianate of potash was prepared by dissolving the acid in as small a quantity of water as possible, adding an excess of carbonate of potash, allowing the salt to crystallize, collecting it on a filter, washing it with just sufficient water to remove the excess of alkali, and drying. On analysing it I obtained the following results:—

I. 0·3580 grm., dried in the water-bath and burnt with chromate of lead, gave 0·6830 carbonic acid and 0·1590 water.

0·5590 grm. gave 0·0780 sulphate of potash.

II. 0·4850 grm. of another preparation, dried *in vacuo*, gave 0·9250 carbonic acid and 0·2070 water.

0·8140 grm. gave 0·1150 sulphate of potash.

These numbers lead to the following composition:—

	Eqs.		Calculated.	I.	II.
Carbon . . . .	52	312	52·42	52·03	52·01
Hydrogen . . . .	28	28	4·70	4·93	4·74
Oxygen . . . .	26	208	34·97	35·50	35·62
Potash . . . .	1	47·2	7·91	7·54	7·63
		<hr/> 595·2	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

The soda salt, prepared in the same way as the potash salt, was also analysed, but the analysis led to no satisfactory results.

A compound with baryta was obtained by dissolving the acid in water and adding ammonia and chloride of barium. The precipitate, which was bulky and of a fine crimson colour, was placed on a filter and washed with water. During the washing its bulk diminished and the colour changed to red, probably in consequence of its losing part of its baryta. Analysis showed it to be a basic compound, in which the acid is to the base as 2 : 3. The neutral baryta salt was obtained by adding chloride of barium to a watery solution of rubianate of potash, when a red precipitate fell, which was collected on a filter, washed with water, and dried *in vacuo*.

I. 0·6020 grm. of the latter compound, burnt with chromate of lead, gave 1·0800 carbonic acid and 0·2580 water.

0·5180 grm. gave 0·0925 sulphate of baryta.

II. 0·4440 grm. gave 0·7870 carbonic acid and 0·1900 water.

0·4890 grm. gave 0·0870 sulphate of baryta.

These numbers lead to the formula  $C_{52}H_{28}O_{26} + BaO + HO$ , as the following comparison of the experimental results with the theoretical composition shows:—

	Eqs.		Calculated.	I.	II.
Carbon . . .	52	312	49·24	48·92	48·34
Hydrogen . .	29	29	4·57	4·76	4·75
Oxygen . . .	27	216	34·11	34·60	35·24
Baryta . . .	1	76·6	12·08	11·72	11·67
		<u>633·6</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>

A lead compound was prepared by adding to an alcoholic solution of the acid acetic acid and acetate of lead and then a little ammonia, taking care to leave an excess of rubianic acid in solution. The red precipitate was collected on a filter, washed with alcohol and then dried, at first *in vacuo*, and then for several hours in the water-bath. Its analysis gave the following results:—

0·5490 grm. gave 0·6760 carbonic acid and 0·1580 water.

0·6600 grm. gave 0·3760 sulphate of lead.

These numbers correspond in 100 parts to—

Carbon . . . . .	33·58
Hydrogen . . . . .	3·19
Oxygen . . . . .	21·32
Oxide of lead . . . . .	41·91

The most probable formula for this compound is  $2C_{52}H_{28}O_{26}+7PbO$ , though the numbers found by experiment agree better with the formula  $2C_{52}H_{27}O_{25}+7PbO$ , as will be seen from the following calculation:—

	Eqs.		Calculated.	Eqs.		Calculated.
Carbon . . .	104	624	33·22	104	624	33·55
Hydrogen . .	56	56	2·98	54	54	2·90
Oxygen . . .	52	416	22·17	50	400	21·51
Oxide of lead .	7	781·9	41·63	7	781·9	42·04
		<u>1877·9</u>	<u>100·00</u>		<u>1859·9</u>	<u>100·00</u>

Another specimen of the lead salt, prepared by precipitating an alcoholic solution of the acid with an alcoholic solution of basic acetate of lead, was found to have a composition agreeing tolerably well with the formula  $C_{52}H_{28}O_{26}+9PbO$ . When this precipitate was redissolved in a mixture of alcohol and acetic acid, and a fresh precipitate was produced by means of a little ammonia, the latter was found to contain acid and oxide of lead in the proportion of 1 equiv. of the former to 6 equivs. of the latter. It appears, therefore, that these lead precipitates are by no means uniform in composition.

The silver salt was obtained by dissolving the acid in boiling water, adding a small quantity of ammonia and then nitrate of silver, when it fell in the form of a dark chocolate-coloured flocculent precipitate, which, when viewed under a lens, was sometimes seen to consist of small crystalline needles. The precipitate was collected

on a filter and slightly washed with water. As it was found to dissolve in water with a reddish-brown colour, as soon as the excess of nitrate of silver was removed, the edulcoration was completed with alcohol, in which the salt is insoluble. After being dried *in vacuo*—

0·6300 grm. gave 0·1370 grm. chloride of silver, equivalent to 0·11076 or 17·58 per cent. of oxide of silver. The formula  $C_{52}H_{28}O_{26} + AgO$  requires 17·47 per cent.

The alizarine and sugar obtained by the decomposition of rubianic acid with acids and alkalies, I found to have the usual composition, as the following analyses will show:—

I. 0·2190 grm. alizarine, obtained by the action of sulphuric acid on rubianic acid, dried at 100° C., yielded 0·5550 carbonic acid and 0·0850 water.

II. 0·3320 grm. alizarine, formed by the decomposition of rubianic acid with caustic soda, dried at 100° C., gave 0·8480 carbonic acid and 0·1195 water.

These numbers give in 100 parts—

	I.	II.
Carbon . . . . .	69·11	69·66
Hydrogen . . . . .	4·31	4·00
Oxygen . . . . .	26·58	26·34

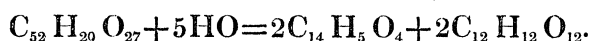
The sugar derived from the decomposition of rubianic acid with sulphuric acid was prepared for analysis by heating it, after the solution had been evaporated to a syrup, for some time at 100° C. until it became sufficiently brittle to be pulverized, when

0·3600 grm. yielded 0·5840 carbonic acid and 0·2060 water, corresponding with the following composition:—

	Eqs.		Calculated.	Found.
Carbon . . . . .	12	72	44·44	44·24
Hydrogen . . . . .	10	10	6·17	6·35
Oxygen . . . . .	10	80	49·39	49·41
		<hr/> 162	<hr/> 100·00	<hr/> 100·00

This specimen of sugar had therefore the same composition as that obtained by the action of erythrozym on rubian\*.

The analysis of the acid, its compounds and products of decomposition just detailed, lead to the conclusion that its composition must be expressed by the formula  $C_{52}H_{29}O_{27}$ , and that it belongs to the class of the so-called glucosides, the copula contained in it being alizarine. Its decomposition, by means of strong acids and alkalies into alizarine and sugar, is symbolized by the following equation:—



In order to remove all doubt concerning the true formula of this substance, I deter-

\* Philosophical Transactions for 1853, p. 79.

mined the quantities of alizarine which were obtained by decomposition of weighed quantities of the acid with sulphuric acid and with caustic soda.

1.7210 grm. rubianic acid, dried at  $100^{\circ}\text{C}$ ., gave, when decomposed with sulphuric acid, 0.7310 grm. dry alizarine = 42.47 per cent.

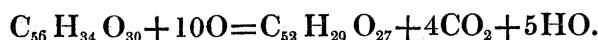
1.2020 grm. rubianic acid yielded, when decomposed with pure caustic soda, on precipitation with sulphuric acid, 0.5430 grm. alizarine = 45.17 per cent.

Assuming the formula  $\text{C}_{52}\text{H}_{29}\text{O}_{27}$  to be correct, 100 parts of acid should, according to theory, afford 43.44 of dry alizarine. If STRECKER's formula for alizarine,  $\text{C}_{20}\text{H}_6\text{O}_6$ , were the correct one, then the only possible formula for rubianic acid, though the calculated composition would then not agree very well with that found in my experiments, would be  $\text{C}_{52}\text{H}_{27}\text{O}_{27}$ , in which case the quantity of alizarine derived from 100 parts of acid would be 62.70. It will be seen, therefore, that the view which I have adopted of the constitution of the acid derives considerable support from these determinations.

A comparison of the composition of rubian and rubianic acid shows that the latter can only be derived from the former by means of oxidation. In order however to remove all doubt on this point, I made the following experiment. A solution of rubian was divided into two equal parts. One half was boiled to expel all the air it might contain, then mixed with a certain quantity of caustic soda, and immediately put into a bottle, which the liquid just sufficed to fill, and which was then closed airtight. The other half was mixed with the same quantity of caustic soda and left exposed to the air. After twenty-one days, both liquids were examined in the same manner. The soda was supersaturated with acetic acid, the liquid was again rendered alkaline with ammonia, and then chloride of barium was added, which gave in each case a red precipitate. This precipitate was treated as usual with sulphuric acid and carbonate of lead, and the filtered liquid was evaporated to dryness. From that part of the solution which had been enclosed in the bottle I obtained in this manner a quantity of a substance resembling rubian, which was probably rubidehydran, but not a trace of rubianic acid; whereas, by adding baryta water to the liquid filtered from the precipitate with chloride of barium, leaving the mixture to stand exposed to the air for some time, filtering and treating the substance left on the filter with sulphuric acid as usual, I obtained a small quantity of the acid. On the other hand, the precipitate with chloride of barium from the second half of the solution, which had been left in an open vessel, yielded at once 0.60 grm. of rubianic acid as well as a quantity of rubidehydran, but the liquid filtered from this precipitate, on being mixed with baryta water and treated as before, gave no more acid. Hence it follows that the presence of oxygen is as essential as that of alkalies to the formation of this acid.

As regards the manner in which the formation of rubianic acid takes place, we may suppose it to be effected in two ways. Assuming 1 equivalent of rubian to absorb 10 equivalents of oxygen, it may then yield 1 equivalent of rubianic acid,

4 equivalents of carbonic acid, and 5 of water, as the following equation will show:—



But since acetic acid is found among the products of decomposition, it is possible that this acid takes the place of carbonic acid, and the equation will then appear as follows:—



It is a very remarkable circumstance, that a body like rubianic acid, which belongs to a class of a highly complex nature, and having in general a high atomic weight, should owe its formation to a process of oxidation. It is probably the first known instance in which the formation of a body of this class by means of oxidation has actually been observed.

Some years since ROCHLEDER described a body obtained from madder to which he gave the name of *ruberythric acid*\*. This body, like rubianic acid, is decomposed by strong acids into alizarine and sugar, and the other properties mentioned by ROCHLEDER are similar to those of rubianic acid. It is therefore very probable that the two acids are identical. But the description given by ROCHLEDER of his acid is not sufficiently minute to enable me to come to a decision as to their identity, and the composition ascribed to it by him (C 54.48, H 5.16, O 40.36 per cent.) differs so much from that of rubianic acid as almost to lead one to believe that they are not the same. Until therefore the properties and composition of ruberythric acid have been more accurately studied, it will be impossible to arrive at any positive conclusion on this point, and for the present the two acids must be considered as distinct†. ROCHLEDER has ventured to express his conviction that rubian is nothing but impure ruberythric acid‡. The experiments which I have here described must lead to the conclusion that such an opinion cannot for an instant be entertained. If rubianic acid and ruberythric acid are identical, then ROCHLEDER has only committed the common error of mistaking a product for an educt.

*Rubidehydran*.—As obtained by the method above described, this body is not perfectly pure. It may be purified by redissolving it in water, evaporating the solution to a syrup, and then adding a quantity of alcohol, which precipitates a reddish-yellow glutinous substance mixed with sulphates of lime, magnesia, and soda. The alcoholic liquid having been allowed to clear, is decanted and evaporated to dryness, when it leaves a dark yellow or reddish-yellow, brittle, transparent residue like gum or varnish, which cannot be distinguished from rubian in appearance. It still gives, when burnt, a quantity of ash, consisting of sulphates of lime and magnesia, but I did not attempt

\* Berichte der Wiener Academie, April 1851.

† The easiest way of arriving at a conclusion would be by determining the amount of alizarine which ruberythric acid by its decomposition is capable of yielding. If ROCHLEDER's formula  $\text{C}_{72}\text{H}_{40}\text{O}_{40}$  be accepted, it should give 67.04 per cent. of alizarine. Variations of several per cent. in the amount of alizarine obtained would still allow a positive decision to be arrived at.

‡ Ann. der Chem. und Pharm. B. lxxxii. S. 215.

to purify it any further, for fear of inducing a change in its composition. Rubidehydran resembles rubian exactly in most of its properties. It is not in the least deliquescent. If it shows any tendency to deliquesce on exposure to the air, this must be attributed to its containing some impurity. It has a strongly bitter taste. The watery solution is yellow, and when boiled, with the addition of sulphuric or muriatic acid, deposits yellow flocks, and after cooling appears almost colourless. Like rubian, is also decomposed on boiling the watery solution with the addition of caustic potash or soda, the solution becoming purple and depositing yellow flocks on supersaturating the alkali with acid. It is not precipitated from its aqueous solution by any earthy or metallic salt, with the exception of basic acetate of lead, which produces a red precipitate, while the liquid becomes colourless. The alcoholic solution, however, gives, with an alcoholic solution of neutral acetate of lead, a red precipitate, similar to the last, which is soluble in water. When exposed in a dry state to the action of heat, and to that of chlorine in its watery solution, rubidehydran behaves exactly like rubian. It may, however, be distinguished from rubian by its not yielding a trace of rubianic acid, when its watery solution is mixed with caustic soda or baryta and left exposed to the atmosphere for some time. Its products of decomposition with acids differ also from those of rubian. If a solution of the substance in water be boiled with the addition of sulphuric acid, yellow flocks are deposited, which consist principally of alizarine, with some rubiadine and a little verantine and rubiretine, but not a trace of rubianine, while the filtered liquid contains sugar. Rubidehydran yields therefore the same products with acids as rubian does with alkalies, which makes it very probable that rubian, when acted on by alkalies, is first changed, in part at least, into rubidehydran.

In calculating the composition of this substance from the analysis, I took it for granted that the lime and magnesia found in the ash are contained originally in it as sulphates, and therefore always treated the ash obtained in the first instance with sulphuric acid, in order to replace that portion of the sulphuric acid which might have been reduced during the process of ignition, and then made the corrections accordingly.

I. 0.4360 grm. rubidehydran, formed by the action of bicarbonate of baryta on rubian, dried at 100° C. and burnt with chromate of lead, gave 0.8005 carbonic acid and 0.2130 water.

0.2790 grm., on being incinerated, left 0.0150 grm. ash, which after being treated with sulphuric acid and heated again, weighed 0.0325 grm. = 11.64 per cent.

II. 0.4950 grm., formed by the action of lime-water on rubian, gave 0.9750 carbonic acid and 0.2320 water.

0.6220 grm. left 0.0200 grm. ash, which after treatment with sulphuric acid weighed 0.0340 grm. = 5.46 per cent.

III. 0.4795 grm., obtained by means of caustic baryta, gave 0.9540 carbonic acid and 0.2320 water.

1·0785 grm. left 0·0245 grm. ash, which after treatment with sulphuric acid, weighed 0·0455 grm. = 4·21 per cent.

IV. 0·4990 grm., obtained by means of ammonia, gave 0·9780 carbonic acid and 0·2320 water.

0·7385 grm. left 0·0155 grm. ash, which after treatment with sulphuric acid, weighed 0·0395 grm. = 5·34 per cent.

After making the due corrections for the ash in the way just described, these numbers correspond in 100 parts to—

	I.	II.	III.	IV.
Carbon . . . . .	56·66	56·81	56·06	56·46
Hydrogen . . . . .	6·13	5·50	5·54	5·45
Oxygen . . . . .	37·21	37·69	38·40	38·09

leading to the formula  $C_{56}H_{32}O_{28}$ , as the following calculation shows:—

	Eqs.		Calculated.
Carbon . . . . .	56	336	56·75
Hydrogen . . . . .	32	32	5·40
Oxygen . . . . .	28	224	37·85
		<hr/> 592	<hr/> 100·00

The lead compound was prepared by dissolving the substance in a small quantity of water, adding an alcoholic solution of acetate of lead, separating the red precipitate which was formed, by filtration, adding a little ammonia to the filtered liquid, taking care to leave an excess of rubidehydran in solution, filtering the precipitate and washing it with alcohol.

0·5705 grm. of this precipitate, dried in the water-bath, gave 0·6110 carbonic acid and 0·1465 water.

0·3180 grm., treated with sulphuric acid and heated, left 0·2200 grm. residue, which on being treated with hot water, yielded to the latter 0·0140 grm. sulphate of magnesia, leaving 0·2060 sulphate of lead.

These numbers lead to the following composition:—

	Eqs.		Calculated.	Found.
Carbon . . . . .	56	336	29·20	29·20
Hydrogen . . . . .	32	32	2·78	2·85
Oxygen . . . . .	28	224	19·48	„
Oxide of lead . . . . .	5	558·5	48·54	47·66
		<hr/> 1150·5	<hr/> 100·00	

The deficiency in the oxide of lead in this analysis arose without doubt from the oxide being in part replaced by magnesia.

It appears therefore that rubidehydran differs from rubian merely by containing the elements of two equivalents of water less, and the origin of the different products

of decomposition to which it gives rise may therefore be explained in the same manner as in the case of rubian.

Of its products of decomposition with acids I only obtained alizarine in quantities and of the degree of purity requisite for analysis. It had the usual composition of that substance, as the following analysis will show :—

0·2500 grm. of the crystallized substance lost, on being heated in the water-bath, 0·0460 water = 18·40 per cent.

0·2800 grm. of the dry substance gave 0·7110 carbonic acid and 0·1030 water, corresponding in 100 parts to—

Carbon . . . . .	69·25
Hydrogen . . . . .	4·08
Oxygen . . . . .	26·67

*Rubihydran*.—This substance, like rubidehydran, bears a great resemblance to rubian, the body from which it is derived. It is obtained on evaporation of its solutions as an uncrystalline, transparent mass like gum, having a dark brownish-yellow colour and a bitter taste. When quite dry it is brittle and may be easily pulverized, but on exposure to the atmosphere at the ordinary temperature it rapidly attracts moisture and becomes soft, a property by which it may be distinguished from rubian and rubidehydran. On being heated in a tube it gives less crystalline sublimate than rubian does. Its watery solution, on being boiled with the addition of sulphuric or muriatic acid, becomes muddy, and slowly deposits a quantity of yellow flocks mixed with some brown resinous drops. The liquid must be boiled for a considerable time in order to effect the entire decomposition of the rubihydran contained in it and make it appear colourless. The flocks on being collected on a filter are found to consist chiefly of rubiretine, verantine, and rubiadine, with only a very small quantity of alizarine, while the filtered liquid contains sugar. The products of decomposition with acids are therefore the same as those of rubidehydran, the only difference being in the relative proportions of the products formed. It is not decomposed, when treated with boiling phosphoric, oxalic, tartaric or acetic acids. If a watery solution of rubihydran be boiled with caustic potash or soda, the colour of the solution, which was red on the first addition of alkali, changes to reddish- or yellowish-brown, but only a few purple flocks are deposited. This circumstance also serves to distinguish this substance from rubian and rubidehydran, the watery solutions of which, when mixed with caustic alkali and boiled, deposit an abundance of the purple compound of alizarine and alkali. Nevertheless the rubihydran is completely decomposed by the caustic alkali, for on adding an excess of acid to the liquid a quantity of yellow or light brown flocks are precipitated like those produced by the action of acids, while the liquid becomes almost colourless. When chlorine gas is passed through the watery solution, it produces exactly the same effects as in watery solutions of rubian or rubidehydran. It is the behaviour to chlorine, which more than any other



reaction proves that these substances have a similar composition, and forms perhaps the most characteristic mark of distinction between them and rubianic acid. Rubihydran is not precipitated from its aqueous solution by any reagent except basic acetate of lead, which produces a light brownish-red precipitate, which is paler and less bright than the precipitates produced by the same reagent in solutions of rubian or rubidehydran. The liquid filtered from this precipitate has still a light yellow colour, and ammonia produces in it a fresh precipitate of a pale pink colour, after which it appears colourless. Rubihydran is soluble in alcohol, but not very easily. From the manner in which it is prepared it may be inferred, that it is incapable of yielding rubianic acid by the influence of the same agents which lead to the formation of the latter from rubian. In order to obtain this substance in a perfectly dry state, it is necessary to heat it in the water-bath continuously for a day or two. In two analyses I obtained numbers corresponding respectively with the formulæ  $C_{56}H_{45}O_{41}$  and  $C_{56}H_{42}O_{38}$ . I only succeeded once in obtaining it of the same composition, or as free from water as when in combination with oxide of lead. On this occasion it gave the following results:—

0·3940 grm. gave 0·7440 carbonic acid and 0·2130 water, numbers which lead to the following composition:—

	Eqs.		Calculated.	Found.
Carbon . . . .	56	336	51·29	51·50
Hydrogen . . . .	39	39	5·95	6·00
Oxygen . . . .	35	280	42·76	42·50
		<hr/> 655	<hr/> 100·00	<hr/> 100·00

On being burnt this specimen left no ash.

The lead compound was prepared by dissolving the substance in alcohol and then adding acetate of lead and ammonia, taking care to leave an excess of rubihydran in solution, filtering, washing the precipitate with alcohol and drying, at first *in vacuo*, and then for several hours in the water-bath.

I. 0·8740 grm. of this compound gave 0·6720 carbonic acid and 0·1970 water.

0·7270 grm. gave 0·5850 sulphate of lead.

II. 0·8860 grm. gave 0·6820 carbonic acid and 0·1930 water.

0·8465 grm. gave 0·6805 sulphate of lead.

In 100 parts:—

	I.	II.
Carbon . . . . .	20·96	20·99
Hydrogen . . . . .	2·50	2·42
Oxygen . . . . .	17·34	17·44
Oxide of lead . . . .	59·20	59·15
	<hr/> 100·00	<hr/> 100·00

The amount of oxide of lead here stands in no simple relation to that of the other

constituents. If the oxide of lead be deducted, then the rubihydran combined with it will have the following composition in 100 parts:—

	I.	II.
Carbon . . . . .	51·37	51·38
Hydrogen . . . . .	6·12	5·92
Oxygen . . . . .	42·51	42·70
	<hr/> 100·00	<hr/> 100·00

It will be seen that this is exactly the composition of the substance itself according to the analysis given above, and it follows that the composition of rubihydran, both in a perfectly dry state and when in combination with oxide of lead, is expressed by the formula  $C_{56}H_{39}O_{35}$ . It differs therefore from rubian by containing the elements of 5 equivalents more of water. That it should yield the same products of decomposition as rubian and rubidehydran is therefore not at all extraordinary.

The rubiadine which is formed by the decomposition of rubihydran with acids may be obtained in a state of greater purity and with much greater facility from this, than from any other source. It is separated from the other products of decomposition in the manner I have described when treating of the action of alkalies on rubian. It is purified by dissolving it in boiling alcohol and adding to the boiling solution hydrated oxide of lead, when it crystallizes from the filtered solution in beautiful golden-yellow, glittering scales, some of which assume the form of regular four-sided tables, possessing all the properties of rubiadine\*, but evidently freer from impurities than when obtained by the action of alkalies on rubian.

I. 0·3060 grm. of this substance, dried at  $100^{\circ}C$ ., gave 0·7795 carbonic acid and 0·1380 water.

II. 0·2580 grm. of the same, recrystallized from boiling alcohol, gave 0·6600 carbonic acid and 0·1190 water.

From these numbers it may be inferred that its composition is as follows:—

			Calculated.	I.	II.
Carbon . . . . .	32	192	69·31	69·47	69·76
Hydrogen . . . . .	13	13	4·69	5·01	5·12
Oxygen . . . . .	9	72	26·00	25·52	25·12
		<hr/> 277	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

The formula  $C_{32}H_{13}O_9$ , to which these analyses lead, differs from the one formerly given,  $C_{32}H_{12}O_8$ , by 1 equivalent of water. I prefer the former, since the substance employed in the last analyses was evidently purer than that used in any previous one. It will be seen also, that the formula just given is confirmed by an examination of the products of decomposition of rubian with chlorine.

\* In examining these crystals I discovered a property of rubiadine which I had not previously observed. If the ammoniacal solution, which is red, be mixed with chloride of barium, it deposits a quantity of dark brownish-red needle-shaped crystals, which are evidently the baryta compound of rubiadine, while the liquid loses almost all its colour. The rubiadine derived directly from rubian also yields these crystals.

*Action of Chlorine on Rubian.*—If a current of chlorine gas be passed through a watery solution of rubian, the latter begins immediately to deposit flocks of a lemon-yellow or orange colour. These flocks continue to be formed as long as the solution retains any portion of its yellow colour. When the action is completed the liquid appears colourless. The flocks, the quantity of which is considerable compared with that of the rubian employed, consist almost entirely of one substance, which I shall call *Chlororubian*, though this name is not perfectly appropriate, since it is not formed from rubian simply by the substitution of hydrogen by chlorine. If these flocks, after being collected on a filter and washed until all the acid and chlorine are removed, be treated with a little cold alcohol, the latter dissolves a small quantity of a substance, which after the evaporation of the alcohol is left as a yellow or yellowish-brown resinous residue. This substance melts at the temperature of boiling water; it contains chlorine, and dissolves in caustic alkalies with a dirty purple colour. The chlororubian may be purified by simply dissolving it in boiling alcohol. It crystallizes on the solution cooling in small orange-coloured needles, which increase very much in quantity after standing for several hours. The acid liquid, filtered from the yellow flocks formed by the action of chlorine, contains sugar, which may be obtained by neutralizing the acid with carbonate of lead, filtering, evaporating the liquid to a small volume, decolorizing with animal charcoal, filtering, evaporating to dryness, and treating the residue with alcohol. The alcohol after filtration and evaporation leaves a yellow syrup having all the properties of sugar, as usually obtained by the decomposition of rubian. Chlororubian may be prepared as well from impure as from pure rubian. It is only necessary to extract madder with boiling water, add sugar of lead to the extract, add ammonia to the liquid filtered from the precipitate, decompose the red precipitate produced by ammonia with sulphuric acid, and pass chlorine gas through the filtered liquid. The first portions of chlorine generally produce a dirty yellow flocculent precipitate, which, being separated by filtration, is found to consist of the resinous easily fusible substance just mentioned. On passing chlorine through the filtered liquid, pure yellow flocks of chlororubian are precipitated, which are purified as before by crystallization from boiling alcohol.

Chlororubian has the following properties. After crystallization from alcohol and drying, it forms a mass of a light orange colour, consisting of small crystalline needles. It has no perceptible taste at first, but on chewing it for some time it produces a slightly bitter taste. When heated on platinum it melts and burns with a smoky flame slightly tinged with green, and leaves a considerable quantity of charcoal. On being heated in a tube it melts to a brown liquid, and gives fumes which condense on the colder parts of the tube to a white crystalline sublimate, consisting of star-shaped masses, while much carbonaceous residue is left. On being treated with boiling water chlororubian dissolves in considerable quantity, forming a yellow solution, which on cooling deposits a great part of the substance, not in crystals, but

in amorphous masses consisting of spherical grains. The boiling alcoholic solution, if very concentrated, also deposits part of the substance on cooling in amorphous, spherical, translucent grains, which have the appearance of drops of oil, but by redissolving these in fresh alcohol, crystals of the usual appearance are obtained. The alcoholic solution does not redden litmus paper in the least. The watery solution gives no precipitate with nitrate of silver, but if chlororubian be treated with boiling nitric acid it is decomposed with an evolution of nitrous acid, forming a colourless solution, in which nitrate of silver produces a precipitate of chloride of silver. The action of sulphuric and muriatic acids, caustic alkalies and chlorine on chlororubian, I shall treat of presently. Chlororubian dissolves in boiling solutions of the carbonates of potash, soda and ammonia, forming blood-red solutions, which deposit nothing on cooling. Baryta water imparts to the watery solution a deep red colour, and on boiling dark red flocks are deposited, while the liquid becomes almost colourless. Lime water turns the watery solution red without producing any precipitate, but the ammoniacal solution gives with chloride of calcium a light red flocculent precipitate, while the supernatant liquid becomes colourless. The watery solution gives no precipitate with the acetates of alumina and peroxide of iron. On being treated with a boiling solution of perchloride of iron, chlororubian dissolves with a brownish-yellow colour, which after some time becomes dark brown, while a black powder is deposited. The alcoholic solution of chlororubian does not change on being mixed with an alcoholic solution of acetate of lead, but the watery solution gives with basic acetate of lead a light red precipitate, the liquid retaining a reddish colour. The alcoholic solution gives no precipitate with acetate of copper. An alkaline solution of chlororubian reduces chloride of gold to the metallic state, even in the cold. Chlororubian produces no effect on mordants, on trying to dye with it in the usual manner.

On submitting chlororubian to analysis the following results were obtained :—

I. 0·4100 grm., dried in the water-bath and burnt with chromate of lead, gave 0·7690 carbonic acid and 0·1860 water.

0·4760 grm., burnt with lime, gave 0·1260 chloride of silver.

II. 0·4780 grm. of the same, recrystallized from boiling alcohol, gave 0·8950 carbonic acid and 0·2100 water.

III. 0·5470 grm. of another preparation gave 1·0270 carbonic acid and 0·2400 water.

0·7720 grm., burnt with lime, gave 0·2015 chloride of silver.

IV. 0·4425 grm. of the same preparation as the last gave 0·8320 carbonic acid and 0·1960 water.

0·5450 grm., on decomposition with fuming nitric acid to which a little nitrate of silver was added, gave 0·1380 chloride of silver.

V. 0·4975 grm. of a new preparation gave 0·9330 carbonic acid and 0·2240 water.

0·8580 grm., burnt with lime, gave 0·2180 chloride of silver.

VI. 0·5320 grm. gave 1·0000 carbonic acid and 0·2380 water.

0·9370 grm., burnt with lime, gave 0·2450 chloride of silver.

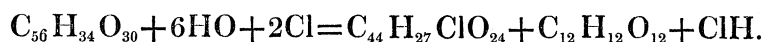
These numbers correspond in 100 parts to—

	I.	II.	III.	IV.	V.	VI.
Carbon . . .	51·15	51·06	51·20	51·27	51·14	51·26
Hydrogen . .	5·04	4·88	4·87	4·92	5·00	4·97
Chlorine . .	6·54	„	6·45	6·26	6·28	6·46
Oxygen . . .	37·27	„	37·48	37·55	37·58	37·31

There are several formulæ which give a composition in 100 parts agreeing tolerably well with these numbers, but only one which at the same time explains the manner in which chlororubian is formed. This formula is  $C_{44}H_{27}ClO_{24}$ , which gives the following composition:—

	Eqs.		
Carbon . . .	44	264	50·92
Hydrogen . .	27	27	5·20
Chlorine . . .	1	35·4	6·82
Oxygen . . .	24	192	37·06
		<hr/> 518·4	<hr/> 100·00

Assuming this formula to be correct, then rubian, when acted on by chlorine, loses 1 equivalent of hydrogen, which is replaced by chlorine, at the same time taking up 6 equivalents of water and splitting up into chlororubian and sugar, as will be seen from the following equation:—



*Action of Acids on Chlororubian.*—If chlororubian be treated with boiling dilute sulphuric or muriatic acid, it first dissolves to a yellow liquid, but on continuing to boil, the solution suddenly becomes milky and deposits a large quantity of yellow crystalline flocks. The filtered liquid is almost colourless, and contains sugar. The flocks consist entirely of a body, to which, as it has the composition of rubiadine in which 1 equivalent of hydrogen is substituted by chlorine, I shall give the name of *Chlororubiadine*. It is purified by collecting the flocks on a filter, washing them with water, and dissolving them in boiling alcohol, which on cooling and standing, deposits yellow shining crystals, which are larger than those of chlororubian.

Chlororubiadine has the following properties. When crystallized from alcohol and dried, it has the appearance of a yellow mass, consisting of small shining crystalline needles and scales. When heated on platinum it melts to a brown liquid, and then burns with a yellow flame bordered with green, leaving much carbonaceous residue. When heated in a tube it melts and gives penetrating fumes, smelling of muriatic acid, and forming on the colder parts of the tube a sublimate which is at first oily but soon becomes crystalline. It is insoluble in boiling water. Dilute nitric acid does not affect it, even on boiling. Nitric acid of sp. gr. 1·52, however, dissolves it, even

in the cold, forming a dark orange-coloured solution. If nitrate of silver be added to this solution, no precipitate is produced; but if the solution be boiled, an evolution of nitrous acid takes place, the solution becomes turbid, and gives a copious deposit of chloride of silver. Concentrated sulphuric acid dissolves it in the cold, forming an orange-coloured solution, from which it is precipitated again by water in bright yellow flocks. If the solution in the acid be boiled its colour changes to a deep purple, without much sulphurous acid being evolved, a small quantity of a white crystalline sublimate making its appearance after some time on the sides of the vessel near the surface of the liquid. Chlororubiadine is easily dissolved by caustic soda with a purplish-red colour, and by ammonia and the carbonates of potash, soda and ammonia, with a blood-red colour. The ammoniacal solution loses its ammonia on evaporation, and leaves the substance behind as a bright yellow residue. On adding chloride of barium to the ammoniacal solution, the baryta compound crystallizes out on standing in long needles, arranged in large fan-shaped or star-shaped masses of a beautiful red colour, while the liquid becomes almost colourless. The baryta compound, when treated with boiling water, only dissolves in part, some chlororubiadine being left undissolved. If a current of carbonic acid be passed through the filtered solution, the whole of the chlororubiadine is precipitated in yellow flocks, the liquid becoming colourless. The ammoniacal solution gives with chloride of calcium, after some time, a dark red uncrystalline deposit, and also loses its colour. A boiling solution of perchloride of iron does not dissolve chlororubiadine, nor does the colour of the solution change during boiling. The alcoholic solution of chlororubiadine reddens litmus paper. The solution gives no precipitate with acetate of lead, not even on the addition of ammonia, but with acetate of copper it gives after some time a copious light brown precipitate. Acetate of alumina and peracetate of iron produce no change in the alcoholic solution. An alkaline solution of chlororubiadine reduces chloride of gold to the metallic state.

The composition of chlororubiadine was determined by the following analyses:—

I. 0·5650 grm., dried at 100° C. and burnt with chromate of lead, gave 1·2630 carbonic acid and 0·2130 water.

0·4850 grm., burnt with lime, gave 0·2200 chloride of silver.

II. 0·4620 grm. of a second preparation gave 1·0260 carbonic acid and 0·1760 water.

III. 0·5475 grm., made from the last by dissolving it in ammonia, adding chloride of barium, filtering the liquid from the dark flocks which were precipitated, allowing the baryta compound to crystallize, decomposing it with muriatic acid, and crystallizing what was left by the acid from boiling alcohol, gave 1·2280 carbonic acid and 0·2100 water.

0·6260 grm. gave 0·2775 chloride of silver.

IV. 0·4980 grm. of another preparation, obtained like the last from the baryta compound, gave 1·1130 carbonic acid and 0·1905 water.

0·7680 grm. gave 0·3455 chloride of silver.

Hence the following composition may be deduced:—

	Eqs.		Calculated.	I.	II.	III.	IV.
Carbon .	32	192	61·65	60·96	60·56	61·17	60·95
Hydrogen .	12	12	3·85	4·18	4·23	4·26	4·25
Chlorine .	1	35·4	11·36	11·21	„	10·95	11·10
Oxygen .	9	72	23·14	23·65	„	23·62	23·70
		<u>311·4</u>	<u>100·00</u>	<u>100·00</u>		<u>100·00</u>	<u>100·00</u>

The baryta compound I found to have no very simple composition. It was prepared, as above described, by dissolving crystallized chlororubiadine in ammonia, adding chloride of barium, filtering from a few flocks that were precipitated, and allowing to crystallize in an air-tight flask, filtering, washing with water, and drying *in vacuo*.

0·8370 gram. of the crystals lost, on being heated for some hours in the water-bath, 0·0690 water=8·24 per cent.

0·5770 gram. of the substance thus dried gave, when burnt with chromate of lead, 1·0965 carbonic acid and 0·1790 water.

0·5660 gram. gave 0·1350 sulphate of baryta.

These numbers lead to the formula  $4C_{32}H_{12}ClO_9 + 3BaO$ , as the following comparison between the theoretical composition and the experimental results will show:—

	Eqs.		Calculated.	Found.
Carbon . . . .	128	768	52·05	51·82
Hydrogen . . . .	48	48	3·25	3·44
Chlorine . . . .	4	141·6	9·59	„
Oxygen . . . . .	36	288	19·54	„
Baryta . . . . .	3	229·8	15·57	15·65
		<u>1475·4</u>	<u>100·00</u>	

The sugar which is formed from chlororubian together with chlororubiadine may be obtained in a crystallized state, which is not the case with the different specimens of sugar derived from the other processes of decomposition to which I have subjected rubian. If sulphuric acid be employed for the decomposition of chlororubian, and the acid after filtration of the flocks of chlororubiadine be neutralized with carbonate of lead, the filtered liquid yields on evaporation a sweet syrup. If this syrup be treated with alcohol, a part of it dissolves with a yellow colour. If the alcoholic solution, after separation from the insoluble part, be mixed with several times its volume of ether, it becomes milky and deposits again a yellow syrup, which after standing some time becomes filled with small yellowish crystals, so as almost to form a solid mass. This mass is pressed between blotting-paper, in order to remove the mother-liquor, and the crystals are dissolved in boiling alcohol, to which a little animal charcoal is added. The filtered solution on evaporation gives a syrup, which

is soon converted into a mass of white crystals. These crystals have the properties and composition of crystallized grape sugar.

0.5015 grm. of the crystals, dried *in vacuo*, gave 0.6830 carbonic acid and 0.3380 water.

These numbers lead to the following composition:—

	Eqs.		Calculated.	Found.
Carbon . . .	12	72	36.36	37.14
Hydrogen . . .	14	14	7.07	7.48
Oxygen . . .	14	112	56.57	55.38
		<hr/> 198	<hr/> 100.00	<hr/> 100.00

It will now admit, I think, of little doubt, that the uncrystallizable sugar obtained from rubian in other processes of decomposition is merely modified grape sugar.

The formation of chlororubiadine and sugar from chlororubian is a very simple process. The latter loses three equivalents of water and splits up into chlororubiadine and sugar, as will be evident from the following equation:—



I have adopted the name of chlororubiadine, under the assumption that the true formula for rubiadine is  $C_{32}H_{13}O_9$ . Nevertheless I have not succeeded in converting the latter into chlororubiadine by means of chlorine, nor in substituting the chlorine in chlororubiadine by hydrogen and thus forming rubiadine. If chlororubiadine be suspended in water to which an amalgam of potassium (1 part of potassium to 100 mercury) is added, it dissolves with a dirty red colour without much hydrogen being evolved. The liquid gives a greenish-yellow flocculent precipitate on the addition of nitric acid. This precipitate contains no chlorine, but it does not contain any rubiadine, since it gives, after being dried and heated between two watch-glasses, none of the crystalline sublimate characteristic of rubiadine. The liquid filtered from this precipitate gives an abundant precipitate with nitrate of silver.

Hydrosulphate of ammonia dissolves chlororubiadine, forming a red solution, which on standing becomes of a fine purple, and after some hours brownish-red. If nitric acid be added to the solution as soon as it has acquired a purple colour, an orange-coloured flocculent precipitate falls. This precipitate is free both from sulphur and chlorine, the chlorine of the chlororubiadine being found in the filtered liquid, but it contains no rubiadine. It is only partly soluble in boiling alcohol, but dissolves easily in boiling nitric acid, the solution depositing on standing some long dark yellow sword-shaped crystals.

If crystallized rubiadine, obtained by the decomposition of rubihydran with acid, be dissolved in caustic alkali and reprecipitated with acid, and if the precipitated flocks after filtering and washing be suspended in water, and a current of chlorine gas be passed through the liquid, the flocks become somewhat paler in colour. If they be now collected on a filter and washed with water and then treated with cold alcohol,



the greatest part dissolves, leaving undissolved a small quantity of a white powder, which has all the properties of a body which I shall describe presently, and which is formed by the action of chlorine on chlororubian. If the alcoholic solution be evaporated to dryness and a little cold alcohol be again added to the residue, the alcohol again dissolves a great part, leaving undissolved a yellowish-green granular powder, which resembles but is not identical with chlororubiadine. The alcoholic solution leaves on evaporation a brown, transparent, resinous substance. This substance contains a large quantity of chlorine. It dissolves in caustic soda with a brown colour, and is reprecipitated by acids in yellow flocks, which melt in the boiling liquid to brown oily drops. I found it to contain the following quantities of carbon and hydrogen:—

0·3090 grm., dried at 100° C. and burnt with chromate of lead, gave 0·6090 carbonic acid and 0·1060 water, corresponding in 100 parts to—

Carbon . . . . .	53·75
Hydrogen . . . . .	3·81

The formula  $C_{32}H_{13}Cl_2O_{10}=C_{32}H_{12}Cl_2O_9+HO$  requires in 100 parts—

Carbon . . . . .	53·96
Hydrogen . . . . .	3·65
Chlorine . . . . .	19·89
Oxygen . . . . .	22·50

I may mention by the way, that the brown resinous substance, which, as I stated above, is formed in small quantities along with chlororubian by the action of chlorine on rubian, is very similar both in properties and composition to this substance. It was prepared simply by passing chlorine through a solution of rubian, collecting the yellow flocks which were formed in the first instance separately, washing them with water, and treating with cold alcohol. The filtered solution was evaporated to dryness, when it left a resinous substance resembling rubiretine.

0·4130 grm. of this substance, dried in the water-bath, gave 0·8200 carbonic acid and 0·1500 water.

0·3010 grm., burnt with lime, gave 0·2160 chloride of silver.

These numbers correspond in 100 parts to—

Carbon . . . . .	54·14
Hydrogen . . . . .	4·03
Chlorine . . . . .	17·74
Oxygen . . . . .	24·09

By the action of chlorine on chlororubiadine, a body very similar to these but differing in composition is formed. If finely pounded chlororubiadine be suspended in water and a stream of chlorine gas be passed through the liquid for some time, the powder becomes lighter in colour, but not white. If it now be collected on a filter, washed with water, and treated with boiling alcohol, it dissolves in the latter,

forming a yellow solution, which deposits nothing on cooling, but on evaporation leaves a transparent dark yellow amorphous substance like resin, which remains soft for a long time, and only becomes hard and brittle after being heated in the water-bath for some time. This substance, when heated on platinum, burns with a yellow flame, leaving much charcoal. When heated in a tube, it melts and gives acid fumes and a yellow oily sublimate, in which on cooling some white crystals make their appearance. The alcoholic solution gives no precipitate with nitrate of silver, but the substance on being treated with boiling nitric acid is dissolved and decomposed, and nitrate of silver now gives an abundant precipitate. It is soluble in concentrated sulphuric acid with a brown colour, but on boiling the solution no sulphurous acid is evolved. Caustic soda dissolves it easily with a brown colour. On being analysed it yielded the following results:—

0.3910 grm., dried in the water-bath, gave 0.6675 carbonic acid and 0.1100 water.  
0.4055 grm. gave 0.4990 chloride of silver.

In 100 parts it contained therefore—

Carbon . . . . .	46.55
Hydrogen . . . . .	3.12
Chlorine . . . . .	30.42
Oxygen . . . . .	19.91

Since the carbon here is to the chlorine as  $32\text{C} : 3\frac{1}{2}\text{Cl}$ , this substance must either have been a mixture, or it must have lost chlorine during the process of drying.

*Action of Caustic Alkalies on Chlororubian.*—The action of alkalies on chlororubian differs essentially from that of acids. The chlorine in chlororubian is so loosely combined that the affinity of the alkaline metal is sufficient to remove it, and hence all the organic products of decomposition formed by the alkali are free from chlorine.

If chlororubian be treated with a solution of caustic soda it dissolves easily, forming a red solution. If this solution be heated for some time, it deposits a quantity of dark reddish-brown flocks. When these flocks cease to be formed, the liquid, which is still red, is filtered, the flocks are washed with water until the excess of soda is removed, and they are then treated with boiling muriatic acid, by which their colour is changed to yellowish brown. After being collected on a filter and washed with water, they are then treated with boiling alcohol, in which they are but little soluble, placed on a filter, washed with alcohol and dried. After drying, there is obtained a yellowish-brown powder which has the following properties. It is almost insoluble both in alcohol and in caustic alkalies, though the latter impart to it a dark reddish-brown colour. It is not dissolved by hydrosulphate of ammonia. It contains no chlorine. When heated in a tube it gives a yellow crystalline sublimate, which dissolves easily in caustic alkalies. Its composition was determined by the following analyses:—

I. 0.3980 grm., dried at  $100^{\circ}\text{C}$ . and burnt with chromate of lead, gave 1.0330 carbonic acid and 0.1390 water.

II. 0·3910 grm. gave 1·0150 carbonic acid and 0·1370 water.

III. 0·4000 grm. of a new preparation gave 1·0350 carbonic acid and 0·1435 water.

In 100 parts it contained therefore—

	I.	II.	III.
Carbon . . . . .	70·78	70·79	70·56
Hydrogen . . . . .	3·88	3·89	3·98
Oxygen . . . . .	25·34	25·32	25·46

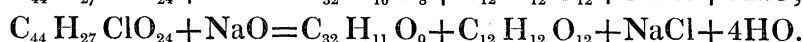
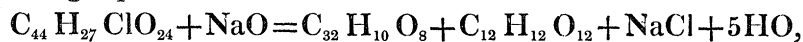
It is doubtful whether this body contains 44 or 32 equivalents of carbon. The formulæ  $C_{44}H_{14}O_{12}$ ,  $C_{32}H_{10}O_8$  and  $C_{32}H_{11}O_9$  require in 100 parts respectively the following amounts of the three constituents :—

	$C_{44}H_{14}O_{12}$ .	$C_{32}H_{10}O_8$ .	$C_{32}H_{11}O_9$ .
Carbon . . . . .	70·58	72·18	69·81
Hydrogen . . . . .	3·74	3·75	4·00
Oxygen . . . . .	25·68	24·07	26·19

If the first formula be adopted, then this substance is formed from chlororubian by the latter losing its chlorine, which combines with sodium and is replaced by oxygen, while 13 equivalents of water are eliminated, in accordance with the following equation :—



If one of the two latter formulæ be adopted, then chlororubian first splits up into chlororubiadine and sugar, and the former then loses its chlorine which is replaced by oxygen, while either five or four equivalents of water separate, as will be seen from the following equations :—



The first formula agrees best with the results of analysis. Nevertheless, it seems improbable that chlororubian, when subjected to the action of so potent an agent as caustic soda, should not, in the first instance at least, be decomposed in the same manner as with strong acids. On the other hand, if this were the case, chlororubiadine should, by the action of caustic alkalis, be converted into the same body as chlororubian, which is not the case. If chlororubiadine be treated with caustic soda in the same way as chlororubian, it first dissolves with a purple colour, but the solution on boiling slowly deposits reddish-brown flocks and loses the greatest part of its purple colour. The flocks, on being treated with boiling muriatic acid, acquire an orange colour, and after being collected on a filter and washed, are found to be almost insoluble in boiling alcohol; but notwithstanding their resemblance to the body formed from chlororubian, they differ from the latter in containing a large quantity of chlorine, only a small quantity of the latter having been abstracted by the alkali.

0·3610 grm. of this substance, dried at 100° C., gave 0·8620 carbonic acid and 0·1060 water.

0·2920 grm. gave 0·1110 chloride of silver.

In 100 parts it contained therefore—

Carbon . . . . .	65·12
Hydrogen . . . . .	3·26
Chlorine . . . . .	9·39
Oxygen . . . . .	22·23

Should the body formed from chlororubian by caustic alkalies be found to contain 44 equivalents of carbon, the most appropriate name for it would be *Oxyrubian*.

The liquid filtered from this body is still red. On adding to it sulphuric acid, a yellowish-brown flocculent precipitate falls. This precipitate consists of several bodies. If after being filtered and washed it be treated with boiling alcohol, a part dissolves, leaving undissolved a dark brown substance, which after drying becomes black. This substance is doubtless a product of the decomposition of sugar, as it has the same properties and very nearly the same composition as the body, insoluble in alcohol, which I obtained by the decomposition of rubian with caustic soda\*.

0·1760 grm. of this substance gave 0·4360 carbonic acid and 0·0650 water, corresponding in 100 parts to—

Carbon . . . . .	67·56
Hydrogen . . . . .	4·10
Oxygen . . . . .	28·34

On adding acetate of lead to the liquid filtered from this precipitate, a brown precipitate falls, which after being filtered off, washed with alcohol and decomposed with boiling muriatic acid, yields brown flocks. These, on being dried and treated with cold alcohol, yield to the latter a body resembling and probably identical with rubi-retine, while a brown powder is left undissolved, having the properties and composition of verantine.

0·1755 grm. of the latter, after being purified by redissolving in a boiling mixture of alcohol and ammonia, then adding an excess of acetic acid, collecting the pulverulent deposit formed on cooling, and washing with alcohol, gave 0·4170 carbonic acid and 0·0680 water.

In 100 parts it contained therefore—

Carbon . . . . .	64·80
Hydrogen . . . . .	4·30
Oxygen . . . . .	30·90

The liquid filtered from the lead precipitate is yellow. It gives with water a yellow precipitate, which, after being filtered off and washed with water, dissolves again in boiling alcohol, with the exception of a little brown flocculent matter. The alcoholic solution, on evaporation, leaves a yellow uncrystalline substance resembling impure rubiadine, which contains no chlorine, gives when heated a sublimate like that from

\* Philosophical Transactions, 1853, p. 71.

rubiadine, and forms with baryta a compound which crystallizes in dark reddish-brown needles. I obtained so small a quantity of this substance that I was unable to arrive at any positive conclusion as to whether it is identical with rubiadine or not. The residue left on evaporation of the alcoholic solution was analysed without any attempt being made to purify it, when it was found to have a composition nearly approaching that of rubiadine.

0.2980 grm. gave 0.7525 carbonic acid and 0.1450 water, corresponding in 100 parts to—

Carbon . . . . .	68.86
Hydrogen . . . . .	5.40
Oxygen . . . . .	25.74

The formation of this body, as well as that of verantine and rubiretine, from chlororubian, I am unable to explain in a satisfactory manner.

If the excess of sulphuric acid, with which the four last bodies have been precipitated, be neutralized with carbonate of lead, the filtered liquid leaves on evaporation a saline mass, which, on being pulverized and treated with warm alcohol, communicates to the latter a reddish-brown colour. The alcoholic liquid, after being filtered from the insoluble matter consisting of sulphate of soda, leaves on evaporation crystals of chloride of sodium surrounded by a brown syrup of sugar.

*Action of Chlorine on Chlororubian.*—If finely pounded chlororubian be mixed with water, and if, after the mixture has been placed in a large bottle or other suitable vessel, a current of chlorine gas be passed through it, no change is perceptible for some time; but if the bottle be closed, after the space above the liquid has been filled with chlorine, the latter is gradually absorbed, the colour of the chlororubian becomes paler, and after several days it appears perfectly white. The process is not accelerated by the action of sunlight, but frequent agitation of the liquid and powder with the gas assists it. The white powder into which the chlororubian is changed consists of a body to which I will give the name of *Perchlororubian*. After collecting it on a filter and washing out the chlorine and acid with water, it is to be dissolved in boiling alcohol, from which it crystallizes on the solution cooling in colourless, transparent, flat, four-sided tables, exhibiting a beautiful iridescence. If it should not be quite colourless, it must be redissolved in boiling alcohol, to which a little animal charcoal may be added. On filtering boiling hot and allowing to cool, the solution then yields perfectly colourless crystals. It may also be obtained directly from rubian, by continuing to pass chlorine through a watery solution of the latter, until the yellow precipitate produced at first has become white, but by this means it is not obtained as pure as from crystallized chlororubian.

Perchlororubian has the following properties. When heated on platinum it melts to a brown liquid, and then burns with a smoky yellow flame edged with green, leaving little carbonaceous residue. If slowly and carefully heated it may be entirely volatilized, yielding a sublimate of bright micaceous scales. But if it be suddenly

heated, if, for instance, it be thrown into a red-hot tube, it is decomposed with a kind of explosion, giving off an acid smell, and forming a large quantity of soot with little or no crystalline sublimate. It is insoluble in water, but soluble in alcohol and ether. The alcoholic solution does not redden litmus paper. Concentrated sulphuric acid dissolves it on heating, the solution, on being heated to the boiling-point, becoming slightly brown, but giving off very little sulphurous acid. The colder parts of the tube become covered with a crystalline sublimate, consisting probably of the substance itself. Nitric acid of sp. gr. 1·37 has no effect on it, even on boiling. Nitric acid of sp. gr. 1·52 dissolves it on boiling without decomposing it, for on adding water, the substance is precipitated unchanged in the shape of a crystalline deposit, and nitrate of silver produces in the liquid no precipitate of chloride of silver. Perchlororubian is quite insoluble in strong caustic soda lye, even on boiling, as well as in ammonia. It dissolves easily, however, in hydrosulphate of ammonia on boiling, and on now adding nitric acid and boiling, nitrate of silver produces an abundant precipitate. The alcoholic solution gives no precipitate with an alcoholic solution of acetate of lead. Its analysis led to the following results:—

I. 0·4945 grm., dried at 100° C. and burnt with chromate of lead, gave 0·6730 carbonic acid and 0·0610 water.

0·4350 grm., burnt with lime, gave 0·7770 chloride of silver.

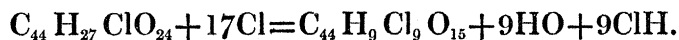
II. 0·3930 grm. of another preparation gave 0·5330 carbonic acid and 0·0585 water.

0·2730 grm. gave 0·4930 chloride of silver.

These numbers lead to the following composition:—

	Eqs.		Calculated.	I.	II.
Carbon . . .	44	264	37·09	37·11	36·98
Hydrogen . . .	9	9	1·26	1·37	1·65
Chlorine . . .	9	318·6	44·77	44·16	44·64
Oxygen . . .	15	120	16·88	17·36	16·73
		<hr/>	<hr/>	<hr/>	<hr/>
		711·6	100·00	100·00	100·00

It appears, therefore, that in passing into perchlororubian, chlororubian loses 9 equivalents of water and 9 of hydrogen, 8 of the latter being substituted by chlorine, since



It is a singular circumstance, that the 9 equivalents of chlorine in this compound are much more firmly combined with the other constituents than the 1 equivalent contained in chlororubian, which the mere action of alkali is sufficient to separate.

From the experiments just described it may be inferred, that chlororubian is a conjugate compound containing sugar. It resembles PIRIA's chlorosalicine, which, by the action of acids, yields chlorosaligenine and sugar, just as chlororubian gives chlororubiadine and sugar. Though chlororubian is not, strictly speaking, a pro-

duct of substitution of rubian, still it retains some of the properties of the latter; for instance, that of giving, with alkalies, products of decomposition differing from those formed by acids. In all the processes of decomposition previously described, rubian is decomposed in no less than three different modes, just as if it were a compound or mixture of three different bodies, whereas, when acted on by chlorine, it yields only one series of products. It behaves in the latter case as if it were simply a conjugate compound containing sugar. It splits up into sugar and a chlorinated body, and the latter, by the action of acids, again splits up into sugar and a second chlorinated compound. This series of products corresponds exactly with one of the three series in the other processes of decomposition, the bodies belonging to the two other series not making their appearance even in the form of products of substitution.