

XX. *Examination of the proximate Principles of some of the Lichens.*—PART II.

By JOHN STENHOUSE, F.R.S.

Received February 14,—Read March 29, 1849.

*Gyrophora pustulata**.

THIS lichen has been long employed in the manufacture of archil, though the quantity of colouring matter contained in it is by no means considerable, being little more than a twelfth of that in the *Roccella Montagnei*.

The *Gyrophora pustulata* is the Tripe de Roche of the Canadian hunters, who, notwithstanding its disagreeably bitter taste, occasionally use it as an article of food in seasons of scarcity. A memorable instance of this occurred in the case of Messrs. FRANKLIN and RICHARDSON, who during their disastrous journey to the shores of the Polar sea, after the failure of their supplies, subsisted almost entirely upon this lichen during several weeks. The *Gyrophora pustulata*, on which I operated, was brought from Norway, where it is annually collected in considerable quantity for the manufacture of archil. The colouring principle was extracted by maceration with milk of lime, and was precipitated in a gelatinous state by neutralizing the lime solution by muriatic acid, precisely in the way so frequently described in the first part of this paper. I may mention however that the most convenient mode of effecting this operation on a considerable scale, is to steep the lichens, previously cut into small pieces, for some hours in water till they are thoroughly soaked. They should then be stratified with a great excess of slacked lime in a large barrel furnished with a false bottom pierced with small holes, under which a spigot is placed; in fact, in exactly such an arrangement as is employed by the soap-makers for preparing caustic lyes. Water is then poured into the top of the barrel, and when it has remained on the mixture of the lime and the lichens for an hour or so, it is drawn off by opening the spigot, when the solution runs off quite clear of a deep brownish colour. Water is still added in successive quantities so long as the lime solution, when neutralized by muriatic acid, continues to afford a precipitate. The great advantage of this arrangement is, that it can be easily and rapidly executed on a large scale, and that the extraction and filtration are effected by a single operation.

The gelatinous precipitate from the lichen, which had a reddish brown colour after being washed with cold water by decantation to remove adhering muriatic acid, was collected on a cloth filter and dried by a very gentle heat. When the greater portion

* I am indebted to the kindness of JOHN KING, Esq., of GEORGE M^cINTOSH and CoY, chemical manufacturers, Glasgow, for the lichens employed in this part of the investigation.

of the moisture it contained had been removed, it was found advisable to treat it for a short time with a small quantity of dilute spirits of wine at nearly a boiling temperature. This had the effect of freeing it from a greenish-coloured resinous substance. The undissolved portion of the precipitate, which had now become much whiter, was next digested with strong alcohol and a considerable quantity of purified animal charcoal, great care however being taken to prevent the liquid from boiling. The solution was then filtered, and on standing for some hours the colouring principle was deposited in small prisms arranged in stars. By repeated digestions with alcohol and animal charcoal it was rendered colourless, when it had a silky lustre. A considerable portion of the original precipitate however did not dissolve in the alcohol, and consisted of a brownish coloured humus-like substance.

The colouring principle of the *Gyrophora pustulata*, which I shall call gyrophoric acid, when pure forms small white soft crystals, which have neither taste nor smell. It is almost insoluble both in cold and in boiling water. It is also but sparingly soluble both in ether and in alcohol. It is much less soluble therefore in hot alcohol than either orsellic, lecanoric or erythric acids. Its solutions have no action upon test-paper. Gyrophoric acid has no saturating power, for the smallest quantity of either potash or ammonia gives its solutions an alkaline reaction. When gyrophoric acid is boiled for a short time with a considerable excess of any of the alkalies or alkaline earths, it gives off carbonic acid and is converted into orcine. When, on the other hand, it is boiled with a very small portion of alkali only, it is decomposed in the same way as the orsellic, erythric and other similar acids, and yields a corresponding intermediate acid, which is more soluble in water and exhibits more distinctly acid properties than the gyrophoric acid from which it has been derived. Gyrophoric acid strikes the same bright red fugitive colour with hypochlorite of lime which appears to be characteristic of this class of colouring matters. The red solution which it yields is however rather more durable than those of the above-mentioned acids. Gyrophoric acid is very slightly soluble even in a large excess of a cold aqueous solution of ammonia, and it is precipitated by ammonia from its alcoholic solution, without however combining with any of that alkali. When gyrophoric acid is heated with an alcoholic solution of ammonia it readily dissolves, but at the same time it is decomposed with the formation of an intermediate acid. When gyrophoric acid is macerated with an excess of ammonia and exposed for a considerable time to the air, it is slowly converted into a purplish-red colouring matter similar to that which the analogous acids furnish in the same circumstances.

A quantity of gyrophoric acid, prepared in the way already described and repeatedly washed with boiling water to free it from any trace of the ether compound which might have adhered to it, was subjected to an analysis:—

I. 0.2785 grm. substance dried *in vacuo*, and burned with chromate of lead, gave 0.621 carbonic acid and 0.123 water.

II. 0.175 ditto gave 0.3925 Co^2 and 0.082 water.

III. 0.1798 substance gave 0.403 carbonic acid and 0.081 water.

Calculated numbers.			Found.		
		per cent.	I.	II.	III.
36 C	2700	61.02	60.81	61.16	61.12
18 H	225	5.09	4.90	5.20	5.00
15 O	1500	33.89	34.29	33.64	33.88
	<u>4425</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>

These numbers therefore give $C_{36} H_{18} O_{15}$ as the formula of gyrophoric acid.

Ether compound.

When gyrophoric acid is boiled for some hours in strong spirits of wine it is readily converted into an ether, a considerable quantity of a resinous matter and orcine being also formed during the operation. The ether is very soluble in hot water, and is purified from adhering resinous matter exactly in the same way as the ethers of the orsellie, lecanoric and analogous acids, which in its external properties it very closely resembles.

I. 0.2532 grm. ether dried *in vacuo*, gave with chromate of lead 0.570 Co^2 and 0.144 Ho.

II. 0.278 substance gave 0.625 carbonic acid and 0.155 water.

Calculated numbers.			Found numbers.	
			I.	II.
C	40 3000	61.39	61.33	61.31
H	23 287	5.87	6.31	6.19
O	16 1600	32.74	32.36	32.50
	<u>4887</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>

These numbers give $C_{36} H_{18} O_{15} + C_4 H_5 O_1$ as the rational formula of the gyrophoric ether.

Gyrophoric acid also readily forms a corresponding methyl compound when it is boiled for some hours with wood-spirit. In all its characters it perfectly agrees with the analogous compounds of lecanoric and orsellie acids.

Gyrophoric acid dissolves very readily in a slight excess of baryta, and when the solution is supersaturated by an acid the gyrophoric acid precipitates unchanged. A quantity of gyrophoric acid was dissolved in a cold solution of baryta and the excess of the base removed by a stream of carbonic acid. The precipitate, which consisted of a mixture of carbonate of baryta and the organic salt, was collected on a filter and dried by a gentle heat. The dried precipitate was then repeatedly digested in strong spirits of wine, in which the organic salt dissolved, though with difficulty, the carbonate of baryta remaining on the filter. On standing for some time, the clear solution deposited the baryta compound in silky crystals. This salt is insoluble in cold alcohol. The hot spirits appear to have partially altered it, for on subjecting it to analysis, though it appeared to have an uniform composition, yet on decomposing it

by an acid and recrystallizing, the organic acid it contained was found to have a different composition from that of gyrophoric acid; from which it also differed in its properties, being much more soluble in water and also more distinctly acid.

An alcoholic solution of gyrophoric acid gives no precipitate with an alcoholic solution of sugar of lead, but it yields a pretty bulky precipitate with both an aqueous and an alcoholic solution of subacetate of lead. Though I made many trials I was unable to obtain these precipitates of anything approaching to an uniform composition. Neither was I more successful in forming any other definite compounds of gyrophoric acid by which its atomic weight might have been more definitely ascertained.

Lecanora tartarea.

This lichen, like the *Gyrophora pustulata*, has been employed from a very early period in the manufacture of archil. The *Lecanora tartarea* is found in considerable abundance in the hilly districts of the northern parts of both Scotland and Ireland, though what is usually met with in commerce is chiefly obtained from Norway and its neighbouring countries. The lichen on which I operated was from Norway. Its colouring principle was extracted by milk of lime, exactly in the way already described. The quantity of colouring principle it contained was, comparatively speaking, small, not exceeding that in the *Gyrophora pustulata*. The precipitate thrown down from the lime solution by muriatic acid had a brownish-red colour. It was washed with cold water, collected on a cloth filter and cautiously dried. It was then digested with a little dilute spirits, which removed a greenish coloured resinous substance precisely similar to that contained in the *Gyrophora pustulata*. The portion of the precipitate which did not dissolve in the weak spirits was next digested in strong alcohol assisted by a considerable quantity of animal charcoal. The filtered solution deposited the colouring principle in small silky prisms arranged in stars. These crystals at first had a yellowish tinge, but by being repeatedly digested with animal charcoal, they were rendered quite colourless. A considerable portion of the original gelatinous precipitate did not dissolve in the hot alcohol, and appeared, as in the case of the preceding lichen, to consist of a brownish coloured humus-like substance. The purified acid from the *Lecanora tartarea* was dried *in vacuo* and burned with chromate of lead.

I. 0.153 substance gave 0.342 Co² and 0.071 water.

II. 0.250 substance gave 0.561 Co² and 0.115 water.

Calculated numbers.			Found numbers.	
		per cent.	I.	II.
36 C	2700	60.02	61.96	61.20
18 H	225	5.09	5.15	5.10
15 O	1500	33.89	33.89	33.70
	4425	100.00	100.00	100.00

These numbers give $C_{36} H_{18} O_{15}$ as the formula of the acid in the *Lecanora tartarea*, which is exactly the formula of gyrophoric acid. In fact the acid in the *Lecanora tartarea* is identical in all its properties and reactions with the acid in *Gyrophora pustulata*, so that no doubt can be entertained that both lichens contain one and the same colouring principle, viz. gyrophoric acid.

The Ether Compound.

Gyrophoric ether was also formed by boiling the acid from the *Lecanora tartarea* in strong spirits. As might have been expected, it proved also identical in composition and properties with that obtained from the acid of the *Gyrophora pustulata*. The following are the results of its analysis:—

I. 0.337 grm. ether dried *in vacuo* and burned with chromate of lead, gave 0.7595 carbonic acid and 0.191 water.

II. 0.296 grm. gave 0.6658 carbonic acid and 0.165 water.

Calculated numbers.			Found numbers.	
		per cent.	I.	II.
C 40	3000	61.39	61.46	61.30
H 23	287	5.87	6.29	6.19
O 16	1600	32.74	32.25	32.51
	<hr/>	<hr/>	<hr/>	<hr/>
	4887	100.00	100.00	100.00

The rational formula for the gyrophoric ether from the acid in the *Lecanora tartarea* is therefore $C_{36} H_{18} O_{15} + C_4 H_5 O_1$.

It is certainly not a little singular that the ether compounds of this whole series of acids, the lecanoric, the erythric, the alpha and beta orsellic acids, and here again the gyrophoric acid, should approach each other so closely in their general properties and in their per cent. composition. Mr. SCHUNCK has been induced by this circumstance to think it probable that all this class of acids are coupled acids containing lecanoric acid and an adjunct, and that the ethers which they yield are in fact only one compound, viz. lecanoric ether. Mr. SCHUNCK's hypothesis is, however, much weakened from the fact that we possess no means of reproducing lecanoric acid from the so-called lecanoric ether, for when any of these ethers are acted on by an alkali, the organic acid they contain undergoes decomposition as well as the compound itself. Besides, it appears somewhat gratuitous to infer merely from the per cent. composition of these ethers that they all contain lecanoric acid, and are in fact lecanoric ether, as any person may easily convince himself, by a few trials, that considerable alterations may be made on the formulæ of these acids without materially affecting the per cent. composition of their ethers.

Brom-orcine.

In the former paper on the proximate Principles of some of the Lichens, read before this Society on the 3rd of February 1848, I described a crystalline body ob-

tained by cautiously pouring bromine into a concentrated aqueous solution of orcine, giving at the same time an analysis of the compound and a description of its properties. An abstract of the paper containing most of these particulars was published in the Athenæum and Chemical Gazette for March, and in the London Philosophical Magazine for April 1848. Notwithstanding all this, in the Comptes Rendus for August 1848, Messrs. LAURENT and GERHARDT describe this very compound with exactly the same properties, and obtained in precisely the same way, without so much as ever hinting that it had been previously discovered. Messrs. LAURENT and GERHARDT, however, give a different formula for the compound, which I am also disposed to adopt, as on repeating my analysis of it I find I had somewhat over-estimated the amount of bromine contained in it, while its other constituents were determined correctly enough. The following are the results of the corrected analysis of brom-orcine:—

I. 0·361 grm. substance dried *in vacuo* gave 0·5628 Ag Br=0·2395 Br=66·34 per cent. Br.

II. 0·3615 gave 0·565 Ag Br=0·2404 Br=66·50 per cent. Br.

III. 0·281 gave 0·438 Ag Br=0·1864 Br=66·33 per cent. Br.

0·264 substance dried *in vacuo*, and burned with chromate of lead, gave 0·227 carbonic acid and 0·0367 water.

Brom-orcine.		per cent.	Found numbers.		
Calculated numbers.			I.	II.	III.
14 C	1050·00	23·27	23·44		
5 H	62·50	1·39	1·54		
3 Br	2998·89	66·47	66·34	66·50	66·33
40	400·00	8·87	8·68		
	<hr/>	<hr/>	<hr/>		
	4511·39	100·00	100·00		

The rational formula of brom-orcine is therefore $C_{14}H_5Br_3O_4$, or orcine in which three equivalents of hydrogen are replaced by bromine.

The following is the composition of anhydrous orcine:—

0·349 grm. orcine dried *in vacuo* over So_3 for some weeks, and burned with chromate of lead, gave 0·8675 carbonic acid and 0·205 water.

	Calculated numbers.	per cent.	Found numbers.
C 14	1050·0	67·75	67·80
H 8	99·8	6·44	6·52
O 4	400·0	25·82	25·68
	<hr/>	<hr/>	<hr/>
	1549·8	100·00	100·00

Beta-orcine.

The London Philosophical Magazine for July 1848 contains a description of a compound to which I have given the name of beta-orcine, from the great analogy

which it bears to oricine both in the mode of its formation and in most of its properties. Beta-oricine may be obtained by two processes; either by destructively distilling usnic acid, or by acting on that body by alkalies. It crystallizes very beautifully in four-sided prisms surmounted at either end by well-defined four-sided pyramids. It is very soluble in water, alcohol and ether. Its solutions are perfectly neutral. Its crystals are hard and brittle, have a brilliant lustre, and are usually from an inch to three quarters of an inch long.

Beta-oricine has a faintly sweetish taste. In the course of a few minutes it assumes with ammonia a beautiful blood-red colour, which on standing becomes deeper. Beta-oricine is therefore much more rapidly acted on by ammonia than ordinary oricine. The smallest portion of beta-oricine instantly strikes a bright blood-red colour with a solution of hypochlorite of lime; just as alpha and beta orsellic acids, erythric, lecanoric and gyrophoric acids do with the same reagent. Ordinary oricine, on the other hand, yields a violet purple colour with hypochlorite of lime. The formula which I now propose for beta-oricine is $C_{16}H_{10}O_4$, that of oricine being $C_{14}H_8O_4$. I have inserted this short notice of beta-oricine merely to complete the series of this class of bodies.

Quintonitrated-erythromannite.

In the former paper on the lichens, already so often referred to, I have described under the name of pseudo-oricine, a remarkably beautiful crystalline body, which is obtained by boiling either picro-erythrin or erythric acid itself, with an excess of lime or baryta. I have subsequently been induced to change the name of this compound to that of erythromannite, as indicating at once its origin and its most characteristic properties. It was mentioned in the previous paper that I then regarded erythromannite as very analogous to mannite in its properties, and from an experiment I have recently made this conjecture has received very ample confirmation. About two years ago, MESSRS. FLORES DOMONTE and MENARD obtained a curious detonating compound by dissolving mannite in fuming nitric acid kept carefully cooled, and then adding an equal bulk of sulphuric acid to the solution. The compound, which is crystalline, is deposited on the cooling of the liquid. It is first washed with cold water, in which it is insoluble, to free it from adhering acid, and then dissolved in boiling spirits of wine, out of which it crystallizes in long silky needles. Mannite-quintinitrique, as these French chemists have called it, possesses the remarkable property of detonating so violently when struck with a hammer, that M. SOBRERO has proposed employing it for the manufacture of percussion caps instead of fulminate of mercury.

As might naturally have been expected, from the great similarity in composition and properties which mannite and erythromannite have to each other, erythromannite, when treated with fuming nitric acid, also yields a nitrated compound perfectly analogous to quintonitrated-mannite. In order to prepare this compound certain pre-

cautions are requisite, which I shall shortly describe. Erythromannite in the state of powder is to be slowly added to a quantity of fuming nitric acid kept at a low temperature. The erythromannite rapidly dissolves, while considerable heat is evolved. So soon as a complete solution is effected, rather more than an equal bulk of sulphuric acid must be cautiously added to the solution. When the mixture has stood for half an hour, it becomes filled with a magma of crystals. These are collected in a funnel stopped with asbestos, and are left to drain. They are next washed with cold water, in which they are insoluble, till all adhering acid is removed, and then dried by pressure between sheets of blotting-paper. The compound is then boiled with moderately strong spirits, in which it readily dissolves, and on the cooling of the liquid it is deposited in large flat crystals resembling those of benzoic acid, only larger, and exhibiting a great deal of a mother-of-pearl lustre.

It might naturally be supposed that this compound would also be formed by dissolving erythromannite in a mixture of equal parts of fuming nitric and sulphuric acids, and that it would be thrown down by adding a sufficient quantity of water. This is not the case, however, either with it or with the mannite compound, which can only be procured in the way already described, by employing the nitric acid first, and precipitating the nitrated compounds by adding the sulphuric acid afterwards. The solutions of nitrated erythromannite are quite neutral to test-paper. When nitrated erythromannite is heated to 61° C. it melts, but recrystallizes immediately when cooled a few degrees below that temperature; when strongly heated, it takes fire and burns with a gentle deflagration. When, however, the dried crystals are mixed with a little sand and are struck with a hammer, they detonate with great violence. This reaction clearly shows the close analogy that subsists between nitrated erythromannite and quintonitrated mannite, which will appear still more distinctly on comparing the results of their analysis. As however this relation equally subsists between mannite and erythromannite, I shall first subjoin the formulæ and analyses of these two bodies also, so that the intimate relation existing among these four compounds may be rendered more distinctly perceptible.

0·4702 grm. erythromannite, dried *in vacuo* and ignited with chromate of lead, gave 0·679 carbonic acid and 0·355 water.

Erythromannite.	per cent.	Found.	Mannite.	per cent.
11 C 825	39·29	39·36	C 12 900·0	39·57
14 H 175	8·33	8·60	H 14 174·7	7·67
11 O 1100	52·38	52·04	O 12 1200·0	52·76
<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
2100	100·00	100·00	2274·7	100·00

The rational formula of mannite is C₁₂ H₁₄ O₁₂.

The rational formula of erythromannite is . . C₁₁ H₁₄ O₁₁.

Mannite therefore only differs from erythromannite by containing one equivalent more of carbonic oxide.

I. 0·3755 grm. quintonitrated-erythromannite, dried *in vacuo* and burned with chromate of lead, gave 0·228 carbonic acid and 0·083 water.

II. 0·394 grm. quintonitrated-erythromannite, dried *in vacuo* and burned with chromate of lead, gave 0·241 carbonic acid and 0·089 water.

10 tubes gave 329 measures of mixed gases consisting of 227 carbonic acid and 102 measures nitrogen, or carbonic acid gas in the proportion of eleven to five nitrogen.

Quintonitrated-erythromannite.			Found.		Quintonitrated-mannite.		
Calculated numbers.		per cent.	I.	II.	Calculated numbers.		per cent.
11 C	825	16·75	16·56	16·68	12 C	900·0	17·66
9 H	112	2·27	2·46	2·50	9 H	112·3	2·21
5 N	885	17·98	17·83	17·83	5 N	885·0	17·36
31 O	3100	63·00	63·15	62·99	32 O	3200·0	62·77
	<u>4922</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>		<u>5097·3</u>	<u>100·00</u>

The rational formula of quintonitrated-erythromannite is therefore $C_{11} H_9 O_6 + 5NO_5 =$ erythromannite, in which five equivalents of water are replaced by five equivalents of nitric acid, and corresponding exactly in this respect with quintonitrated-mannite, in which five equivalents of water are also replaced by five equivalents of nitric acid. I conclude by subjoining the formulæ of these four compounds, which only differ from each other by one equivalent of carbonic oxide, that so their mutual relations may be seen at a glance.

Mannite $C_{12} H_{14} O_{12}$. Quintonitrated-mannite $C_{12} H_9 O_7 + 5NO_5$.
 Erythromannite $C_{11} H_{14} O_{11}$. Quintonitrated-erythromannite $C_{11} H_9 O_6 + 5NO_5$.

Glasgow, 12th February 1849.