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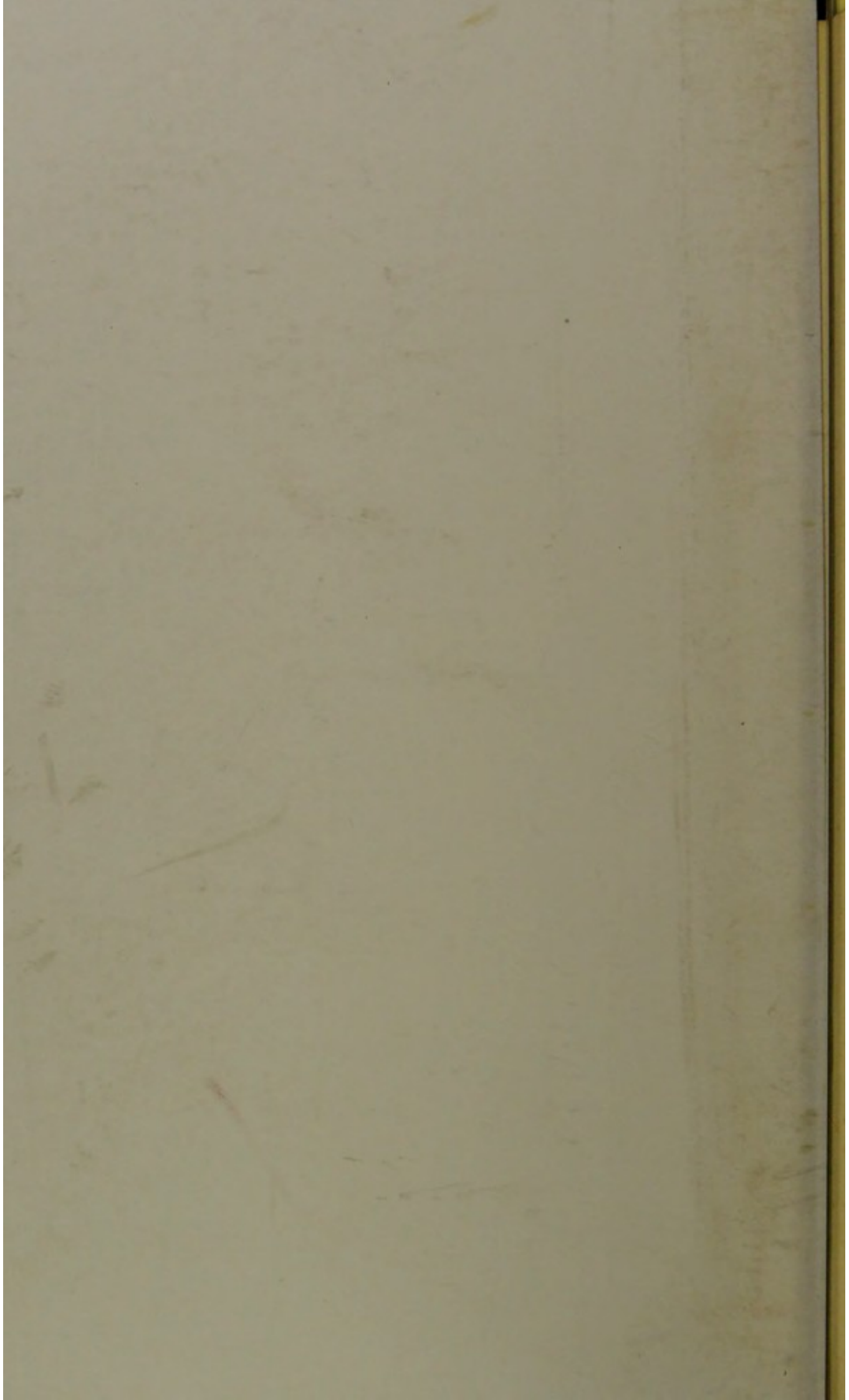
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ON SOME
SALTS AND PRODUCTS
OF
DECOMPOSITION OF PYROMECONIC ACID.

BY

MR. JAMES F. BROWN*.

THIS acid was discovered by Sertuerner, and long viewed as sublimed meconic acid, till Robiquet in 1832 obtained the meconic acid from which it is produced, and showed that the acid existing in opium differed in its properties from the sublimed acid: he also prepared and analysed its lead salt, from which he deduced the formula $PbO, C^{10}H^3O^5$. Liebig has observed that its composition is the same as that of pyromucic acid, and thought it probable these acids might prove identical. This assertion, however, has been refuted by Dr. Stenhouse in his paper on the subject, to some of the details in which I shall have occasion to refer.

The pyromeconic acid employed in the following experiments was obtained by distilling, at a temperature of about 500° and 600° F., the impure meconic acid got by treating the crude meconate of lime twice with hydrochloric acid, which, though much coloured, answered sufficiently well. For the purification of the acid, which when first sublimed is in the form of an oily semifused mass, Stenhouse recommends pressure between folds of filtering paper, redistillation, and frequent crystallization from boiling alcohol. I found, however, that simple pressure, and sublimation at a comparatively low temperature in a cylindrical glass vessel provided with a number of diaphragms of filtering paper, rendered the acid perfectly colourless, and pure enough for the preparation of all its salts and products of decomposition.

As thus obtained, it is in beautiful large transparent plates, of ready solubility in water and alcohol, both hot and cold, from

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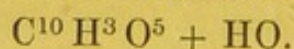
which it crystallizes in four-sided prisms of considerable size. It is slightly acid to litmus, and even after three crystallizations from boiling water it retained its acidity. It is completely volatile at 212° . A quantity having been exposed to that temperature for about fourteen hours, was found to have entirely disappeared. This property may serve as a test of its purity from paracomenic acid, with which pyromeconic, as first sublimed, is always contaminated, that acid requiring a much higher heat to volatilize it. It gives, as is well known, a deep red colour with persalts of iron, and does not precipitate chloride of calcium, barium, manganese, nor sulphate of magnesia, either hot or cold, even on the addition of a small quantity of ammonia. Bichloride of mercury gives after some time a white amorphous precipitate, soluble on boiling the fluid. When a hot aqueous solution of pyromeconic acid is treated with strong caustic potash in excess, and allowed to stand some hours, crystals soon begin to form, which upon examination proved to be the acid unaltered; a similar experiment was made with ammonia, but with the same result, the fluids in both cases becoming nearly black.

To ascertain the purity of the acid, the following analysis was made of it, dried *in vacuo*, after one sublimation.

5.74 grains substance gave 11.133 carbonic acid and 1.905 water.

	Experiment.	Calculation.		
Carbon . . .	53.23	53.57	C ¹⁰	60
Hydrogen . . .	3.71	3.57	H ⁴	4
Oxygen . . .	43.06	42.86	O ⁶	48
	<hr/> 100.00	<hr/> 100.00		<hr/> 112

The formula of the acid is therefore represented by



Pyromeconate of Baryta.—This salt may be obtained by mixing a warm ammoniacal solution of pyromeconic acid with acetate of baryta, when it makes its appearance after a short time in small colourless silky needles. In dilute solutions they do not appear immediately, but after standing some time they commence forming and rapidly increase. It is the most soluble in water of all the earthy salts of this acid,—181.90 grains of a saturated solution at 60° F. gave on evaporation at 212° a residue of 4.50 grains = 2.50 per cent. It is of sparing solubility in alcohol. Like the other pyromeconates, it reacts strongly alkaline, and gives a slight red colour with chloride of iron, which may be made much more apparent if the crystals be employed instead of a solution of the salt. By evaporation *in vacuo* it deposits itself in short prisms of a yellowish colour. When ex-

posed to a temperature of 212° , it loses no weight; but heated to a higher temperature, it burns with a slight deflagration without previous fusion. The following are the results of analysis after the salt had been thoroughly washed with alcohol, and dried at 212° . The other salts of this acid were also dried at 212° previous to analysis.

4.81 grains substance gave 5.55 carbonic acid and 1.06 water.
4.33 grains substance gave 2.24 carbonate of baryta.

	Experiment.	Calculation.		
Carbon . . .	31.46	31.82	C ¹⁰	60.00
Hydrogen . . .	2.43	2.12	H ⁴	4.00
Oxygen . . .	25.56	25.47	O ⁶	48.00
Baryta . . .	40.55	40.59	BaO	76.55
	<u>100.00</u>	<u>100.00</u>		<u>188.55</u>

The composition of the salt is therefore represented by the formula BaO, C¹⁰ H³ O⁵ + HO.

Pyromeconate of Strontia.—When alcoholic solutions of nitrate of strontia and pyromeconic acid, made ammoniacal, are mixed, there immediately ensues a precipitate of minute silky needles, which by solution in water are obtained in stellar groups of a yellowish colour. As precipitated, it is colourless, sparingly soluble in cold water and alcohol, more so in hot, and reacts strongly alkaline. 2.24 grains aqueous solution at 68° gave 3.00 grains on evaporation at 212° = 1.3 per cent. It loses nothing at 212° , and at a higher temperature is infusible, but burns with a slight explosion.

The well-washed substance gave the following results on analysis, the strontia being determined as carbonate.

5.875 grains substance gave 7.79 carbonic acid and 1.35 water.
7.97 grains substance gave 3.58 carbonate of strontia.

	Experiment.	Calculation.		
Carbon . . .	36.16	36.63	C ¹⁰	60
Hydrogen . . .	2.74	2.44	H ⁴	4
Oxygen . . .	29.61	29.31	O ⁶	48
Strontia . . .	31.49	31.62	SrO	51.78
	<u>100.00</u>	<u>100.00</u>		<u>163.78</u>

The formula of the salt is therefore SrO, C¹⁰ H³ O⁵ + HO.

Pyromeconate of Lime.—This salt is obtained in the form of small colourless silky needles when a warm ammoniacal solution of pyromeconic acid is added to acetate of lime in excess. It is slightly soluble in boiling alcohol, but rather more so in water, from which it deposits itself by gradual cooling of the solution

in crystals of considerable size. 3.41 grains aqueous solution of this salt at 60° gave 1.08 grain of residue at 212° = 0.31 per cent.

6.15 grains substance gave 10.26 carbonic acid and 1.56 water.
6.34 grains substance gave 2.34 carbonate of lime.

	Experiment.	Calculation.	
Carbon . . .	42.94	42.85	C ¹⁰ 60
Hydrogen . . .	2.60	2.85	H ⁴ 4
Oxygen . . .	34.02	34.30	O ⁶ 48
Lime . . .	20.44	20.00	CaO 28
	100.00	100.00	140.00

Hence the composition of the salt is represented by the formula CaO, C¹⁰ H³ O⁵ + HO.

Pyromeconate of Magnesia.—A warm aqueous solution of pyromeconic acid gives with acetate of magnesia a white amorphous precipitate, insoluble in water and alcohol. In its properties it closely resembles the other pyromeconates. The following is the analysis of the salt, the magnesia being determined by ignition of it, and weighing the residue. It loses nothing at 212°.

4.925 grains substance gave 8.735 carbonic acid and 1.235 water. 4.595 grains substance gave .76 magnesia.

	Experiment.	Calculation.	
Carbon . . .	48.37	48.51	C ¹⁰ 60
Hydrogen . . .	2.76	2.41	H ³ 3
Oxygen . . .	32.34	32.37	O ⁵ 40
Magnesia . . .	16.53	16.71	MgO 20.67
	100.00	100.00	123.67

From which it appears that this is the only earthy salt of pyromeconic acid which is anhydrous, the composition of it being expressed by the formula MgO, C¹⁰ H³ O⁵.

Pyromeconate of Lead.—When a warm concentrated solution of pyromeconic acid, made ammoniacal, is added to acetate of lead, it causes an immediate precipitate of a dense crystalline powder, which rapidly increases upon violent agitation of the fluid. This salt, as has already been mentioned, was prepared and analysed by Robiquet, who formed it by adding hydrated oxide of lead to a hot solution of pyromeconic acid; he found it to be anhydrous, and to consist of PbO, C¹⁰ H³ O⁵.

The crystals require a considerable quantity of hot water for their solution; they are not so soluble in alcohol either hot or cold. It is colourless when thrown down, but rapidly becomes yellow by exposure for any length of time to bright daylight.

It loses nothing at 212° , even after being kept for three or four hours at that temperature.

The following is the result of analysis, the lead being determined as sulphate by ignition of the salt with a few drops of strong sulphuric acid.

5.48 grains substance gave 5.65 carbonic acid and 0.815 water. 5.29 grains substance gave 3.74 sulphate of lead.

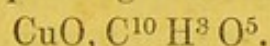
	Experiment.	Calculation.		
Carbon . . .	28.12	27.94	C ¹⁰	60
Hydrogen . . .	1.65	1.39	H ³	3
Oxygen . . .	18.21	18.77	O ⁵	40
Oxide of lead . . .	52.02	51.90	PbO	111.56
	100.00	100.00		214.56

The formula is therefore represented by $\text{PbO}, \text{C}^{10} \text{H}^3 \text{O}^5$.

Pyromeconate of Copper.—The ammonio-sulphate of copper mixed with a warm aqueous solution of pyromeconic acid causes an immediate precipitate of this salt in bright green crystalline needles, which are extremely brittle and easily pulverized. This salt has also been examined by Stenhouse*, who prepared it by boiling the acid with hydrated oxide of copper, and allowing the filtered solution to cool. The crystals require a considerable amount of hot water for their solution, and are very slightly soluble in cold water or alcohol.

The copper was determined as oxide by heating the salt to redness, and then igniting the residue with nitric acid. It loses nothing at 212° .

6.00 grains substance gave 1.66 oxide of copper, which calculated per-centage gives 27.66 of oxide of copper, the number 27.79 being that corresponding with the formula



Pyromeconate of Iron.—Dr. Stenhouse has observed in the paper before mentioned, that when pyromeconic acid is boiled with hydrated peroxide of iron, and also with the persulphate, it combines with the oxide and forms a brownish-red powder, which when neutral is very little soluble in cold water. It may also be obtained, and perhaps more conveniently, by adding perchloride of iron to a hot concentrated solution of the acid in water, when the cinnabar-red crystals begin to make their appearance, adhering firmly to the sides and bottom of the vessel.

Its properties have been so fully described by Stenhouse, that further remark is unnecessary.

The crystals were well washed with cold water, until the fluid

* Mem. and Proc. Chem. Soc. vol. ii. [Phil. Mag. S. 3. vol. xxiv. p. 128.]

which passed through ceased to precipitate nitrate of silver, and then subjected to analysis in the usual way.

6.53 grains substance gave 1.32 peroxide of iron.

The per-centage calculated from the number is 20.21, while 20.56 is that corresponding to the formula $\text{Fe}^2\text{O}^3, 3\text{C}^{10}\text{H}^3\text{O}^5$.

Products of decomposition of Pyromeconic Acid.—If some crystals of the acid be moistened with strong nitric acid in the cold, they immediately assume a white gelatinous appearance, and bubbles of nitrous acid are soon evolved; by the application of a gentle heat the action becomes excessively violent, and continues so even though the heat be withdrawn, with the production of oxalic and hydrocyanic acids. Sulphuric acid in the cold has no action on pyromeconic acid; but when gently warmed, it dissolves it to a colourless fluid, which upon cooling deposits the pyromeconic acid again.

Several experiments were made by passing chlorine into a solution of pyromeconic acid with the view of obtaining a chlorine substitution compound, but without success, that reagent acting too powerfully on it. Complete decomposition always ensued, and oxalic acid was detected in the fluid, but not in large quantity. I may here mention that I failed in obtaining an æther of pyromeconic acid by passing dry hydrochloric acid gas into a solution of the acid in absolute alcohol, the crystals which deposited from the fluid proving on analysis to be the acid unaltered.

Action of Bromine on Pyromeconic Acid.—When bromine water is added to a strong aqueous solution of pyromeconic acid, leaving the latter in excess, it is rapidly absorbed, yielding a colourless fluid, which after standing for an hour or even less, deposits the new acid in beautiful small colourless prisms. In one experiment a large excess of bromine failed to yield any of the new acid, even after standing a considerable time; more bromine was then added, but no crystals made their appearance. The solution, which had acquired a yellowish colour, was evaporated to a small bulk, still without the formation of any bromopyromeconic acid. It had now become perfectly black, and oxalic acid was found in fluid.

The crystals obtained by the action of a limited quantity of bromine, after thorough washing with cold water, gave the following results on analysis:—

4.97 grains substance gave 5.82 carbonic acid and 0.925 water.

4.845 grains substance gave, when burned with lime, 4.71 grs. bromide of silver.

	Experiment.	Calculation.		
Carbon . .	31.93	31.70	C ¹⁰	60
Hydrogen . .	2.05	1.58	H ³	3
Oxygen . .	24.68	25.65	O ⁶	48
Bromine . .	41.34	41.07	Br	78.26
	100.00	100.00		189.26

Which show that they consist of an acid produced by the substitution of an equivalent of hydrogen in pyromeconic acid by an equivalent of bromine.

This acid is of sparing solubility in cold water, more so in hot, and reddens litmus slightly. Boiling alcohol dissolves it readily, from which it crystallizes in beautiful fibrous plates; and if the cooling be carefully effected, in short prisms. It imparts to persalts of iron a deep purple colour, quite distinct from the red produced by the original acid. Nitric acid decomposes it with effervescence, but sulphuric dissolves it without any apparent decomposition. Submitted to destructive distillation, it fuses and then blackens, hydrobromic acid being evolved in large quantity; after the continuation of the heat, a white crystalline substance begins to collect on the cool part of the tube, but in quantity too small to admit of examination.

It gives no precipitate with nitrate of silver, neither when boiled does it reduce the oxide to the metallic state. It causes no precipitate in solutions of chloride of barium, calcium, or sulphate of magnesia, even in the presence of ammonia. Ammonio-sulphate of copper, though producing no effect in the cold, gives when heated a precipitate of a bluish tint.

Bromo-pyromeconic acid, like pyromeconic, is monobasic, forming only one series of salts. The salt employed for controlling the analysis and establishing the saturating power of the acid was that of lead.

Bromo-pyromeconate of Lead.—A warm alcoholic solution of the acid gives with acetate of lead, also dissolved in alcohol, a white precipitate of small dense crystalline needles which rapidly fall to the bottom of the vessel. From its insolubility in water and alcohol, recrystallization of the salt was impossible; thorough washing with alcohol was therefore resorted to. This salt may also be obtained by using aqueous solutions of the acid and salt of lead with the addition of ammonia, but the product is in this case very much coloured.

The lead in the following analysis was determined as sulphate by ignition of the salt with sulphuric acid. It loses nothing at 212°.

7.34 grains substance gave 5.54 carbonic acid and 0.56 water.
4.68 grains substance gave 2.29 sulphate of lead.

	Experiment.	Calculation.		
Carbon	20.57	19.91	C ¹⁰	60
Hydrogen	00.85	00.99	H ³	3
Oxygen	16.19	O ⁶	48
Bromine	26.01	Br	78.26
Oxide of lead	36.48	36.90	PbO	111.56
	<u>100.00</u>	<u>100.00</u>		<u>300.82</u>

The composition of this salt is therefore expressed by the formula $\text{PbO}, \text{C}^{10} \text{H}^2 \text{Br O}^5 + \text{HO}$.

I have also obtained a substitution product of iodine, by operating in a particular manner, which I shall describe in detail in a future paper. I shall conclude this communication with a list of the substances described in it along with their formulæ.

These experiments were performed in the laboratory of Dr. Anderson, to whom I am much indebted for assistance.

Pyromeconic acid	$\text{C}^{10} \text{H}^3 \text{O}^5 + \text{HO}$.
Pyromeconate of baryta	$\text{BaO}, \text{C}^{10} \text{H}^3 \text{O}^5 + \text{HO}$.
Pyromeconate of strontia	$\text{SrO}, \text{C}^{10} \text{H}^3 \text{O}^5 + \text{HO}$.
Pyromeconate of lime	$\text{CaO}, \text{C}^{10} \text{H}^3 \text{O}^5 + \text{HO}$.
Pyromeconate of magnesia	$\text{MgO}, \text{C}^{10} \text{H}^3 \text{O}^5$.
Pyromeconate of lead	$\text{PbO}, \text{C}^{10} \text{H}^3 \text{O}^5$.
Pyromeconate of copper	$\text{CuO}, \text{C}^{10} \text{H}^3 \text{O}^5$.
Pyromeconate of iron	$\text{Fe}^2 \text{O}^3, 3\text{C}^{10} \text{H}^3 \text{O}^5$.
Bromo-pyromeconic acid	$\text{C}^{10} \text{H}^2 \text{Br O}^5 + \text{HO}$.
Lead salt	$\text{PbO}, \text{C}^{10} \text{H}^2 \text{Br O}^5 + \text{HO}$.

Edinburgh, July 1, 1852.



