

XXII. *On Pyrogallic Acid, and some Astringent Substances which yield it.* By Dr. JOHN STENHOUSE.

Read November 1, 1842.

THE usual method of procuring pyrogallic acid is by cautiously distilling either gallic or tannic acids. The pyrogallic acid is obtained partly as a crystalline sublimate and partly dissolved in the empyreumatic liquor which passes into the receiver. Pyrogallic acid thus procured is very seldom free from empyreumatic oil, from which it can only be puri-

fied by repeated distillations, in each of which much acid is unavoidably lost. The usual method, therefore, of procuring pyrogallic acid by distillation is troublesome and unproductive. The process which I have found most advantageous for preparing it in quantity, is the following:—

Finely pounded gall-nuts are to be treated with successive portions of cold water till they are exhausted. These extracts are then to be evaporated and strongly dried, till all their hygrometric water is driven off. In this state they form a spongy deliquescent mass, in taste and colour very much resembling catechu. Instead of distilling this dried extract in a retort, it is much better to employ Dr. Mohr's apparatus for subliming benzoic acid. It consists of a cast iron pan from three to four inches deep, and from eighteen inches to two feet wide. The dried extract is coarsely pounded and spread equally over its bottom to the depth of about half an inch. The top of the pan is then covered with a diaphragm of bibulous paper, fitting closely over it by being pasted round its rim. The diaphragm may be pierced by a few small pin-holes, which greatly facilitates the sublimation. The pan is surmounted with a paper cap twelve or eighteen inches high, fitted closely to its top, and fastened by means of a cord passed two or three times round it. The apparatus is to be cautiously heated for ten or twelve hours on a sand- or still better on a metallic bath. The temperature is to be kept as nearly as possible at about 400° F., though towards the end of the sublimation it may be raised a few degrees higher. The crystals of pyrogallic acid pass up through the bibulous paper, which absorbs the empyreumatic oil by which they are always accompanied. Should the heat have been carefully regulated, the crystals, which are either large scales or needles, are perfectly white; should they be slightly coloured, which sometimes happens, they may be easily purified by a second sublimation. This method possesses the great advantage that a pound or more of the extract can be operated on at once; the apparatus is extremely cheap, and as it is not liable to break it may be used for any number of times. On one trial 1380 grains of dried extract yielded 69 grs. of perfectly pure crystals, and 74 grs. which were slightly coloured, in all 143 grs., or 10·3 per cent. Now as galls yield rather more than half of their weight of soluble matter, the quantity of pyrogallic acid obtainable from them by this process is very considerable. I think it right to mention, however, that on a previous trial, when the sublimation was not so carefully conducted, I did not obtain more than half this quantity.

The following are some of the leading characters of pyro-

gallic acid. It has a very bitter taste, resembling that of salicine. When pure it does not redden litmus paper; but if it has been sublimed at too high a heat, it is accompanied with a little of some volatile acid, which causes it to redden litmus slightly. It gives a deep indigo-blue colour with solutions of protosulphate of iron, but no precipitate falls. If the proto-salt contains any peroxide, this colour soon changes to dark green; but if the salt is pure the deep blue colour remains for a considerable time. With persulphate of iron it gives a yellowish red; with perchloride a much brighter red, but in neither case any precipitate. When pyrogallic acid is dropt into milk of lime, a beautiful reddish purple colour appears, which however speedily changes to a dark brown. Caustic barytes produces a dark brown colour which quickly becomes black. Its reactions with salts of iron and milk of lime are the best tests for pyrogallic acid, and by these its presence even in very small quantity can be easily ascertained. It is very soluble in water, but its aqueous solution, if exposed to the air, speedily blackens. It is also very soluble in alcohol, though not so much so as in water. The taste of its alcoholic solution very much resembles laudanum. Dilute sulphuric acid first reddens pyrogallic acid and then blackens it. Iodine has no effect upon it. Dry chlorine instantly colours the crystals of pyrogallic acid bright red and then blackens them. Moist chlorine, when sent through a solution of pyrogallic acid, gives it a hyacinth-red colour, and evolves much muriatic acid; no precipitate fell, however, and when left to spontaneous evaporation it yielded no crystals, but left only a reddish gummy mass. Pyrogallic acid reduces the oxides of gold, silver and platinum to the metallic state, and precipitates them completely from their solutions. In order to test the purity of the pyrogallic acid I had obtained, it was dried at 212° F., and analysed in the usual way. 0.312 gram. gave 0.65 carbonic acid, and 0.1345 water.

Found.	Calculated.
C 57.60	8 C = 611.480 = 57.61
H 4.78	4 H = 49.918 = 4.70
O 37.62	4 O = 400.000 = 37.69
100.00	1061.398 100.00

This result agrees closely with the calculated numbers given above.

I next endeavoured to form the hydrate of pyrogallic acid by dissolving some very pure crystals in a small quantity of water, and evaporating the solution *in vacuo* over sulphuric acid. It gave large white needles of a silky lustre.

Burnt with oxide of copper,—

I. 0.3265 gramme substance, dried *in vacuo*, gave 0.68 carbonic acid, and 0.138 water.

II. 0.2873 gramme, dried at 212° F., gave 0.600 carbonic acid, and 0.124 water.

I.	II.	Calculated.
C 57.58	57.83	57.61
H 4.97	4.79	4.70
O 37.45	37.38	37.69
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100.00	100.00	100.00

Pyrogallic acid, therefore, does not form a hydrate.

Pyrogallate of Lead.

In order to determine the atomic weight of pyrogallic acid, the lead salt was prepared by adding a solution of pyrogallic acid to an excess of neutral acetate of lead in the cold. A copious white flocculent precipitate immediately fell. It was washed repeatedly by decantation, then thrown upon a filter and rapidly washed, the air being excluded as much as possible, and when pressed between folds of blotting-paper was dried *in vacuo*. When dried it was still nearly white, having only a slight shade of yellow.

I. 0.7985 gramme, dried *in vacuo*, gave 0.269 oxide of lead and 0.174 metallic lead = 57.16 per cent. oxide.

II. 0.731 salt gave 0.252 oxide and 0.153 lead = 57.02 oxide of lead.

III. 0.6402 gave 0.1712 oxide and 0.1815 lead = 57.28 per cent. oxide.

IV. 0.709 salt, dried at 212° F., gave 0.252 oxide and 0.143 lead = 57.27 per cent. oxide.

0.5685 salt gave, when burnt with oxide of copper, 0.504 carbonic acid and 0.117 water.

		Calculated.
C = 24.51	8 C =	611.480 = 24.89
H = 2.28	4 H =	49.918 = 2.03
O = 16.03	4 O =	400.000 = 16.30
Pb O = 57.18	Pb O =	1394.500 = 56.78
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100.00	2455.898	100.00

The mean of these determinations gives 1044 for the atomic weight of pyrogallic acid, which corresponds pretty closely with the calculated number 1061. It is evident also that these analyses give $C_8 H_4 O_4$ as the formula of pyrogallic acid; and not $C_6 H_3 O_3$, that of Berzelius. The formula $C_8 H_4 O_4$ is that found by the late R. C. Campbell, as stated in Liebig's Geiger; but I am not aware that the details of his analysis have ever been published.

When even a single drop of caustic ammonia is added to a

solution of pyrogallic acid, it becomes alkaline and assumes a dark brown colour. A great excess of ammonia was added to a solution of pyrogallic acid, which was then evaporated *in vacuo*. The acid crystallized in confused tufts of a dark brown colour; when pounded, however, its colour was only light brown. It did not give the least indication of ammonia when heated either with a strong solution of potash or with quick lime. When dried *in vacuo* and subjected to analysis,

I. 0.4620 substance gave 0.9255 carbonic acid, and 0.201 water.

II. 0.3141 substance, also dried *in vacuo*, gave 0.6314 carbonic acid, and 0.1405 water.

I.	II.
C 55.38	C 55.58
H 4.83	H 4.96
O 39.79	O 39.46
100.00	100.00

Now pyrogallate of ammonia should have given only 44.44 per cent. carbon, and 6.34 per cent. hydrogen.

The substance of number II. was prepared at a different time from number I.; and in its preparation a still larger excess of ammonia was employed. The reactions of the supposed pyrogallate of ammonia with salts of iron and milk of lime were exactly the same as those of ordinary pyrogallic acid. It is evident, therefore, that pyrogallic acid does not combine with ammonia, but is slightly oxidized when brought in contact with it.

The addition of a little potash also rendered solutions of pyrogallic acid alkaline and even darker coloured than ammonia does. The colorization takes place first at the surface of the liquid, and is evidently the effect of oxidation. When evaporated *in vacuo* it became a black gummy mass, which showed no disposition to crystallize. When this black mass was dissolved in water, in which it is very soluble, and treated with sulphuric acid, it effervesced, apparently from the escape of carbonic acid. It also gave off the vapours of acetic acid in abundance. These were easily recognisable by their smell, and by their immediately reddening litmus paper when held over them. When the solution was very concentrated, a little of a dark brown matter precipitated; but if the solution was at all dilute no precipitate appeared. I made an unsuccessful attempt to collect this precipitate on a filter, and to free it from adhering sulphuric acid by washing it with cold water. The whole of the black matter was speedily dissolved and passed through the filter. Soda produced similar effects on pyrogallic acid. It is plain, therefore, that pyrogallic acid is

decomposed by the alkalies, but does not combine with them, and that its acid properties, if indeed it possesses any, are very feeble. In this and some other respects it closely resembles pyromeconic acid.

When pyrogallic acid is dropped into acetate of copper, it causes a dark brown precipitate, which however quickly becomes black, and is very soluble. When we attempt to collect it on a filter and to wash it, the greater portion of the salt is dissolved by the water. The liquid when it first passes through the filter is colourless, but on standing a few minutes it becomes dark brown and slowly deposits a new precipitate. The compound first formed appears to be decomposed by the water.

When pyrogallic acid is added to a solution of bichromate of potash, it immediately turns it yellowish brown, and then dark brown till the liquid is almost opaque, but no precipitate falls.

