

II.—*Action of Bromine on Protocatechuic Acid, Gallic Acid, and Tannin.*

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A PRELIMINARY notice appeared some time ago (*Chem. News*, xxix, 95) on this subject, of which the details are now given, together with some additional matter.

*Action of Bromine on Protocatechuic Acid.*

Barth has shown (*Ann. Chem. Pharm.*, cxlii, 246) that when protocatechuic acid is treated with excess of bromine in the cold, one equivalent of the hydrogen in the acid is replaced by bromine, giving rise to monobromoprotocatechuic acid,  $C_7H_5BrO_4$ . If, however, this bromoprotocatechuic acid, or protocatechuic acid itself, be heated in sealed tubes to  $100^\circ$  with excess of bromine, I find that the reaction which

takes place is quite different—hydrobromic acid and carbonic anhydride are evolved, and tetrabromopyrocatechin is produced.



As is well known, protocatechuic acid at a high temperature splits up into pyrocatechin and carbonic anhydride, but this reaction does not take place at 100°. The presence of bromine, however, determines the decomposition of the acid, with simultaneous production of the highly brominated tetrabromopyrocatechin. The latter substance, produced in this way, crystallises in long silky needles, and possesses all the properties ascribed to it by Hlasiwetz (*Ann. Chem. Pharm.*, cxlii, 246). The best solvent from which to crystallise it is ordinary acetic acid of density 1·050. It melts at 187°, and when submitted to analyses gave the following results:—

- I. ·229 gram substance gave ·406 of silver bromide.  
 II. ·329           "           "           ·580           "           "  
 III. ·267           "           "           ·165 gram of carbonic anhydride and  
 ·016 gram of water.

			I.	II.	III.
C <sub>6</sub>	= 72 ....	16·90	—	—	16·86
H <sub>2</sub>	= 2 ....	·47	—	—	·66
Br <sub>4</sub>	= 320 ....	75·12	75·44	75·01	—
O <sub>2</sub>	= 32 ....	7·51	—	—	—
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	426	100·00			

Although the action of bromine alone on protocatechuic acid, when gently heated with it, does not go further than the formation of bromo-protocatechuic acid, iodine bromide under similar circumstances causes a more complete decomposition, giving rise to bromopyrocatechin.

#### *Preparation of Protocatechuic Acid.*

Of the numerous sources from which protocatechuic acid may be obtained, East India kino is by far the best, and that which yields it most readily. One part of the kino in fine powder is gradually added to three parts of fused sodic hydrate, stirring the mixture constantly during the introduction of the kino, the most convenient method being to sift the fine powder over the surface of the hydrate, which is kept fused at a gentle heat. When the mixture has acquired a bright orange-brown colour it is poured out on a stone or an iron plate, and allowed to cool. The cake is then broken up and dissolved in about 20 parts of hot water, to which dilute sulphuric acid is added from time to time, so as to render the solution slightly acid. The dark

brown solution is then allowed to stand for 24 hours, when it deposits a large quantity of sodic sulphate in the crystalline state; the mother liquors which contain the protocatechuic acid, after being filtered to remove a small quantity of tarry matter, are agitated with ether. The ethereal solution is then separated, and the ether recovered by distillation in the water-bath: the dark-coloured syrupy residue on standing deposits the protocatechuic acid in the crystalline state. The mother-liquors may be readily separated from the crystals by means of the vacuum pump, and the acid is then easily purified by one or two crystallisations from a small quantity of hot water, with the addition of some freshly precipitated lead sulphide, which removes the brown colouring matter.

If kino be dissolved in hot water, and the solution boiled for an hour after being strongly acidified with sulphuric acid, a bright red powder (kino red) is deposited, which is insoluble in water. This, when fused with about four times its weight of sodic hydrate, yields a purer protocatechuic acid than the original kino. A similar crimson powder (larch red) is obtained by boiling the extract of larch bark with dilute acid (*Phil. Mag.*, xxiii, 336), and this also, when fused with an alkaline hydrate, yields protocatechuic acid with facility. The extract itself does not yield such good results. The amount of protocatechuic acid obtained from catechu is but small, and it is very difficult to purify. Pure catechin, however, is a much better source, but not superior to ordinary East India kino or to larch red.

#### *Action of Bromine on Gallic Acid and on Tannin.*

As gallic acid bears the same relation to pyrogallol that protocatechuic acid does to pyrocatechin, it seemed probable that when treated with bromine at 100° it might undergo a similar decomposition. On making the experiment, this was found to be the case—hydrobromic acid and carbonic anhydride are evolved, and tribromopyrogallol is formed—



Here also the action of bromine on gallic acid, when the two are gently heated together, is to convert it into dibromogallic acid,  $\text{C}_7\text{H}_4\text{Br}_2\text{O}_5$  (Grimaux, *Bull. Soc. Chim.* [2], vii, 479), but at 100°, in presence of excess of bromine, this acid is decomposed, carbonic anhydride being eliminated, and tribromopyrogallol produced.

When tannin is heated to 100° in a sealed tube with excess of commercial bromine, large quantities of hydrobromic acid and carbonic anhydride are liberated, and the product, after the removal of the

excess of bromine, is found to consist of bromopyrogallol. If, however, both the tannin and the bromine be very carefully dried, the reaction is quite different—hydrobromic acid and some carbonic anhydride are evolved, but the product consists of a dark-coloured amorphous substance, totally different in appearance from the colourless crystals of the bromopyrogallol. I have not as yet investigated the nature of the product obtained by the action of dry bromine on dry tannin, but the result strongly confirms Schiff's view (*Ann. Chem. Pharm.*, clxx, 43), that tannin is merely digallic anhydride.

In the experiment made with undried tannin and commercial bromine, the small amount of water naturally present in these substances was sufficient to convert the tannin into gallic acid, which was then decomposed, with formation of bromopyrogallol, and elimination of carbonic anhydride.

*Action of Chlorine on Protocatechuic Acid and on Pyrogallol.*

When protocatechuic acid is heated to 100° with a saturated solution of chlorine in carbon tetrachloride, in sealed tubes, a chlorinated compound is produced, which, after being purified by crystallisation from carbon disulphide, forms colourless needles. A similar reaction takes place when pyrogallol is treated with a carbon tetrachloride solution of chlorine.

I cannot conclude this paper without expressing my obligations to Mr. Charles E. Groves for the valuable assistance he has rendered me in conducting this investigation.

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