# CCII.—The Iodination of Phenols and the Iodometric Estimation of, and Action of Reducing Agents on, Tannic Acid.

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THE chief object of the work described in this paper \* was to devise a rapid quantitative and absolute method for the estimation of tannic and gallic acids.

#### Action of Reducing Agents on Tannic and Gallic Acids.

From the known constitution of gallic acid, and from the formulæ ascribed to tannic acid, a quantitative yield of benzoic acid might be expected on reduction. Böttinger (Annalen, 1890, **258**, 252), acting with metallic sodium on a solution of tannic or gallic acid in absolute alcohol, obtained no reduction product, but Guignet (Compt. rend., 1891, **113**, 130) found that both tannic and gallic acids yield benzoic acid when treated with zinc dust in acid or alkaline solution.

After repeating these experiments, tannic acid was submitted to the action of reducing agents under various conditions, and it was found that, whilst little or no reaction takes place in neutral or acid solution, tannic acid is very reactive towards alkaline reducing agents. In no case, however, was a quantitative yield of benzoic acid obtained, this being due to the fact that benzoic acid itself is slowly destroyed by alkaline reducing agents. No higher yield of benzoic acid was obtained by carrying out the process in an

<sup>\*</sup> This paper corresponds with the abstracts "The action of reducing agents on tannic and gallic acids" and "The action of iodine on phenols and a modified process for the estimation of tannic acid" (Proc., 1908, **24**, 272, 273).

atmosphere of hydrogen or carbon dioxide, and in all cases the complete reduction of tannic and gallic acids occupied a considerable time.

## I.-Reducing Action of Zinc.

Zinc and Ammonia (Guignet's process).—To 2.5 grams of zinc dust in hot aqueous ammonia was added, with constant shaking, 1 gram of tannic acid dissolved in warm water. After boiling under a reflux condenser for three hours, tannic and gallic acids were absent. Potassium carbonate was then added, the solution boiled to convert the excess of zinc and ammonia into carbonates, then evaporated to dryness and extracted with absolute alcohol. On evaporation, 0.2 gram of pure potassium benzoate was obtained.

With zinc and ammonium chloride, 1 gram of tannic acid gave 0.13 gram of potassium benzoate, whilst zinc with acetic, sulphuric, or hydrochloric acid gave incomplete reduction even after many hours' heating.

With zinc-copper couple, thirteen hours were required for complete conversion, the amount of potassium benzoate obtained from 0.5 gram of tannic acid being 0.14 gram.

Action of Zinc and Ammonia on Benzoic Acid.—One gram of benzoic acid was heated under a reflux condenser for one hour with 2.5 grams of zinc in aqueous ammonia solution. The yield of potassium benzoate was 0.69 gram, an amount which diminished on further heating, thus demonstrating the slow destruction of benzoic acid under the conditions employed.

#### II.—Reducing Action of Sodium.

Sodium and Absolute Alcohol (Böttinger's process).—Two grams of sodium and 1 gram of tannic acid were separately dissolved in absolute alcohol. After heating the mixed solutions for two and a-half hours, no benzoic acid was found, but 0.23 gram of gallic acid was obtained.

Sodium and Moist Ether.--In this case no reduction took place, but gallic acid was formed by hydrolysis.

## III.—Reducing Action of Magnesium.

Magnesium and Hydrochloric Acid.—One gram of tannic acid gave 0.25 gram of gallic acid, but no benzoic acid.

Magnesium and Ammonium Chloride.—In this case the reaction was very violent, and amounts of potassium benzoate, varying from 0.08 to 0.23 gram, were obtained from 0.5 gram of tannic acid.

Magnesium and Potassium Carbonate.—Here the reaction was moderate, and after heating for five hours on the water-bath the

yield of potassium benzoate was 0.2 gram from 0.5 gram of tannic acid.

Magnesium Powder.—In the above experiment, when magnesium powder was added to the hot solution of tannic acid, a slight action was observed, and therefore the effect of magnesium powder alone was tried. On heating for several hours on the water-bath in a neutral atmosphere, 0.5 gram of tannic acid gave 0.08 gram of potassium benzoate.

IV.—By reaction with aluminium powder and potassium hydroxide, sodium hyposulphite, or hydriodic acid, no formation of benzoic acid occurred.

It is thus seen that in a number of the above experiments the production of benzoic acid was demonstrated, but in no case were the results of quantitative importance, and, although the conditions of concentration, time of reaction, and nature of atmosphere, were widely varied, the results were always unsatisfactory. One general observation was, however, of interest, namely, the tendency of tannic and gallic acids to form reduction products under alkaline conditions, and this is further borne out by experiments made with alkali iodides, which have given much more satisfactory results.

#### The Action of Iodine on Phenols.

Messinger and Vortmann have shown (*Ber.*, 1890, **23**, 2753) that phenol absorbs iodine in the presence of alkali hydroxides, but were unable to obtain satisfactory quantitative results.

F. Musset (*Chem. News*, 1885, **51**, 42) has described a method of titrating tannin with iodine, but the absorption required twelve hours. The "non-tannins" were estimated in a second experiment after precipitating the tannic acid by means of gelatin.

A. Moullade (J. Pharm. Chim., 1905, [vi], 22, 153), who titrated tannic acid with iodine in presence of sodium hydrogen carbonate, using carbon disulphide as indicator, states that it is necessary to take the mean of several titrations in order to ensure accuracy, and estimates the non-tannins in the usual manner. All the abovementioned methods are thus defective, Musset's process requiring at least twelve hours, and that of Moullade being deficient in accuracy.

The modified method which the authors propose, apart from the gelatin precipitation, can be carried out in a few minutes, and concordant results are obtained, not only with tannic acid, but with many other phenolic substances. Within the range of phenols dealt with, a number were found to require one molecule

of iodine for each hydroxyl group, whereas in other cases, although the results were strictly quantitative, they were empirical in the sense that no ratio could be traced between the iodine absorbed and the number of hydroxyl groups.

The general method is as follows. A standard aqueous solution of the phenol is prepared (in the case of tannic acid 1 gram per litre), and to a known volume of this solution (20 c.c., diluted to 200 c.c. with water) N/10-iodine solution is added in excess (20 c.c.). A few drops of starch solution are then added, and afterwards aqueous sodium hydroxide is run in drop by drop until the colour due to the iodine disappears. By this means, excess of alkali, which has an injurious effect on the accuracy of the process, is avoided. Dilute hydrochloric or sulphuric acid (1 in 4) is added in sufficient excess (say 50 c.c.) to separate the unabsorbed iodine, the amount of which is estimated by N/10thiosulphate.

In the case of phenol, catechol, quinol, pyrogallol, and gallic acid, the amount of iodine absorbed is exactly one molecule for each hydroxyl group present.

The presence of such groups as  $NO_2$ ,  $NH_2$ , or OMe, as well as the position of the hydroxyl groups in the benzene nucleus, was found to have a determining effect on the course of the reaction. For example, the weak phenolic properties of the hydroxyl groups in *p*-hydroxybenzoic acid result in there being no absorption of iodine. The presence of nitro- or methoxy-groups also protects the hydroxyl group from attack, while in *p*-aminophenol a definite quantitative absorption was observed, which, however, did not correspond with one hydroxyl group. The alcoholic hydroxyl group, for example, in benzyl alcohol, is also unaffected under the conditions of the process.

Phloroglucinol, which possesses both phenolic and quinonoid properties, gave an absorption equivalent to two hydroxyl groups, whereas the isomeric pyrogallol behaved normally, the three hydroxyl groups absorbing three molecules of iodine. A similar normal result is obtained with gallic acid.

In the case of gallotannic acid, a large number of experiments were made under varying conditions of concentration, amount of excess of iodine, etc., and perfectly concordant results were always obtained. The process is, therefore, available for the quantitative estimation of gallotannic acid, and is applicable to the commercial tannins. Two estimations are, of course, necessary. First, that of the total iodine absorbed by the standard solution of the tannin, and, secondly, that of the iodine absorbed after removing the tannic acid from the solution by precipitation with gelatin or absorption by hide powder, the difference in the two estimations giving the iodine absorbed by the tannic acid itself.

In the case of pure tannic acid, the absorption was found to correspond with 11 atoms of iodine for each molecule of tannic acid. On the supposition that tannic acid may be regarded as digallic acid,



it may be assumed that the chain connecting the benzene nuclei is responsible for the absorption of the additional atom of iodine, the molecule undergoing fission at the chain and forming two molecules of sodium gallate, in one of which an OH group is replaced by OI.

The works of Wys (Zeitsch. angew. Chem., 1898, 11, 291), Koene (Pogg. Ann., 1845, 66, 302), and others on the action of Hübl's solution is interesting in connexion with the above recorded observations. Wys attributes the absorption of iodine by unsaturated fatty acids to the presence of iodine monochloride:

$$HgCl_2 + 4I = HgI_2 + 2ICl,$$

which reacts with water, yielding hypoiodous and hydrochloric acids. The hypoiodous acid is slowly transformed into iodic acid and free iodine, the latter again forming iodine monochloride by reacting with the liberated hydrochloric acid. A complicated equilibrium is thus established, the really active substances being contained in the cycle, iodine-iodine chloride-hypoiodous acid.

Koene (*loc. cit.*) has shown that correct iodine values are rapidly obtained by means of the solution produced by shaking alcoholic iodine with finely divided mercuric oxide, which solution contains only mercuric iodide and hypoiodous acid, and Wys has further shown that in the presence of any substance favourable to the formation of hypoiodous acid, for example, iodine, mercuric chloride, or water, iodine absorption takes place more rapidly, whereas the presence of hydrochloric acid or mercuric iodide, which retard the production of hypoiodous acid, have an opposite effect.

The very rapid absorption of iodine in presence of alkali, which occurs in the method for the estimation of phenols suggested in this paper, is very probably due to the formation of hypoiodates.

The action of Hübl's solution on tannic acid has been studied with the view of throwing further light on the question, and a direct connexion between the iodine absorbed from Hübl's solution and that taken up from an alkaline solution has been established. Attempts were also made to isolate iodotannin compounds, but without success. Similar lack of success in this direction has been

recorded by F. B. Power and F. Shedden (*Pharm. J.*, 1901, [iv], **13**, 147). These authors consider that true compounds of tannic or gallic acid with iodine cannot be formed by the simple interaction of these compounds in the presence of water, the resulting products containing the iodine in the form of hydriodic acid associated with more or less unaltered tannic or gallic acid and their oxidation products.

Comparison between the results obtained with the iodine process and the Löwenthal method, when applied to a number of the commercial tannin-containing materials, showed a close agreement in all cases.

## Experimental Results.

*Phenol.*—0.1 Gram of phenol was dissolved in 100 c.c. of water. To 10 c.c. of this solution, 5 c.c. of N/10-iodine were added, and then a few drops of starch solution. Sodium hydroxide solution was then cautiously added, drop by drop, until the solution became colourless. After stirring, concentrated hydrochloric acid was added, and the separated iodine estimated by standard thiosulphate. The mean of six titrations gave 2.15 c.c. of iodine solution absorbed (=0.0273 gram of iodine). On the supposition that one hydroxyl group requires one molecule of iodine, 0.0272 gram of iodine is theoretically required.

Salicylic A cid.—0.01 Gram of salicylic acid in aqueous solution absorbed 1.85 c.c. (0.0234 gram) of iodine. Calculated for one hydroxyl group, the theoretical absorption is 0.0184 gram of iodine. The result in this case is, therefore, empirical, although repeated estimations proved it to be quantitative.

Messinger and Vortmann (loc. cit.), following Kopperschaar's process for the estimation of phenol by bromine, proposed to estimate salicylic acid by precipitating it in alkaline solution, as sodium di-iodoiodososalicylate, by addition of iodine and titrating the excess of iodine with sodium thiosulphate. W. Fresenius and Grünhut (Zeitsch. anal. Chem., 1899, **38**, 292) have criticised this method adversely, but in our experiments the results were remarkably consistent, and the results were unaffected by the concentration of the solution or the amount of excess of iodine or of sodium hydroxide. Moreover, the method is available for the estimation of salicylic acid in the presence of benzoic acid.

Resorcinol.—0.01 Gram of resorcinol absorbed 5.2 c.c. (0.06604 gram) of iodine. The theoretical amount of iodine representing three molecules is 0.0694 gram.

Catechol.—0.01 Gram required 3.65 c.c. of N/10-iodine (0.0461 gram). Theory for two hydroxyl groups=0.0463 gram. In this case, therefore, the reaction may be considered normal.

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Quinol.—0.01 Gram required 3.6 c.c. of N/10-iodine (0.0456 gram). Theory requires 0.0463 gram. Of the three isomeric dihydroxybenzenes, therefore, the ortho- and para-compounds behave normally, whereas the meta-derivative gives somewhat empirical results.

Pyrogallol.—0.01 Gram required 6.1 c.c. of N/10-iodine, which corresponds almost exactly with three hydroxyl groups on the supposition that one molecule of iodine is required for each hydroxyl group.

Gallic A cid. -0.01 Gram required 3.55 c.c. of N/10-iodine (0.0448 gram). Theory for three hydroxyl groups = 0.0450 gram.

Catechu-tannic Acid.—0.01 Gram in four titrations absorbed 3 c.c., 2.9 c.c., 3.1 c.c., and 2.9 c.c. respectively of N/10-iodine. The method is, therefore, available in this case.

Catechin.—0.01 Gram required 2.4 c.c. of N/10-iodine (0.033 gram). Calculation for five hydroxyl groups gives 0.035 gram of iodine.

## Influence of the Presence of other Groups on the Iodine Absorption.

Ortho- and para-nitrophenols do not absorb iodine under the conditions, showing the protective action of the nitro-group. Picric acid is also inactive. In the case of p-aminophenol, 0.01 gram absorbed only 0.35 c.c. of N/10-iodine (0.00444 gram). This corresponds with approximately one molecule of iodine for each four molecules of *p*-aminophenol. The result clearly shows the influence of the amino-group, and the method in this and similar cases is useless. Some absorption of iodine also takes place in the case of aminonaphthol-4-sulphonic acid. The non-absorption of iodine by mannitol, benzyl alcohol, and other compounds containing alcoholic groups, shows that the method is not available in the case of aliphatic hydroxyl groups. In the case of phloroglucinol, which can behave either as a phenol or as a quinone, 0.01 gram absorbed 0.04318 gram of iodine, which closely corresponds with two instead of the three hydroxyl groups actually present. The protective action of the methoxy-group is indicated in the case of vanillin, with which no absorption takes place. The influence of the position of the hydroxyl group is well shown in the case of the hydroxybenzoic acids. No reaction takes place with the p-derivative, but with salicylic acid, as already noted, quantitative results were obtained. This difference is probably associated with the pronounced phenolic character of salicylic acid exhibited in its antiseptic properties, its low melting point, its reaction with ferric chloride, its ready solubility in chloroform, and its slight solubility

in water, in which properties it is in marked contrast to its isomerides.

Cinnamic Acid.—This unsaturated acid, which contains no hydroxyl group, does not absorb iodine from alkaline solution.

Tannic Acid.—For the experiments with this substance, a sample of pure tannic acid (Kahlbaum) was used. 0.02 Gram required, as the mean of a large number of closely agreeing titrations, 7.15 c.c. of N/10-iodine. After precipitating the tannic acid by gelatin, an absorption of 0.3 c.c. of N/10-iodine was given by 20 c.c. of the residual solution. The corrected amount of iodine absorbed was therefore =0.08698 gram. 0.02 Gram of tannic acid requires for five hydroxyl groups 0.0788 gram of iodine (51<sub>2</sub>), and for six hydroxyl groups 0.0946 gram (61<sub>2</sub>). On the supposition that 11 atoms are absorbed by one molecule of gallotannic acid, the amount of iodine required by 0.02 gram of gallotannic acid is 0.0876 gram, which figure is in practical agreement with the experiments. The purity of the tannic acid was, however, not known.

In order to test the reliability of the method, a large number of results were obtained, using widely differing quantities of the substances. The method was also applied to a number of the ordinary tannin-containing materials, the results obtained being compared with those given by the Löwenthal process. The solution of tannic acid contained 1 gram per litre:

Volume of tannic acid solution, c.c... 40 35 30 25 20 15 10 5 ,, N/10-iodine, c.c. ........... 14.25 12.45 10.70 8.90 7.15 5.35 3.55 1.80

In each case the solution was diluted to 200 c.c. with water.

The experiments were repeated, using N/50-iodine and N/50-sodium thiosulphate:

Comparison of the Iodine with the Löwenthal Method.—The results (p. 1827) are expressed in percentages of tannic acid, Kahlbaum's pure tannic acid being taken as the standard.

Comparison of the Iodine Method with Hübl's Process.--0.2 Gram of tannic acid was dissolved in 25 c.c. of alcohol, and 25 c.c. of chloroform, followed by 25 c.c. of Hübl solution, were added. After standing twenty-four hours, the N/10-iodine absorbed was 33.55 c.c., the figures in sixteen experiments varying from 32.35 c.c. to 35.25 c.c. A similar series, in which the chloroform was omitted, gave 32.46 c.c. of N/10-iodine absorbed. The amount taken up by 0.2 gram of tannic acid under alkaline conditions is 71.5 c.c. of N/10-iodine, which is almost double the above figure.

<i>m</i> :		Löwenthal	Iodine
Tannins.		method.	method.
Gall-nuts	No. 1 Extract	66.47	65.3
	No. 2 ,,	64.02	65.63
	No. 3 ,,	60.40	60.28
	No. 4 .,	63.61	63.14
	No. 5 ,,	62.59	62.09
Sumac	No. 1 Extract	22.84	21.26
	No. 2	22.51	20.14
	No. 3	16.57	16.08
	No. 4 ,,	17.20	16.78
Myrabolams	No. 1 Extract	26.06	27.27
	No. 2	27.52	27.44
	No. 3	29.33	29.74
	No. 4 ,,	31.24	31.12
Valonia		28.11	28.67
Dividivi		33.00	31.47
Quebracho		13.63	13.28

#### General Conclusions.

The absorption of iodine by phenols in alkaline solution appears, in certain cases, to take place in definite molecular proportions, but in other cases in empirical, although quantitative, amount. The absorption takes place most readily in the case of compounds with pronounced phenolic properties, and is, in some cases, entirely prevented by the presence of other groups in the benzene nucleus. The method described is, however, available for the quantitative determination of tannic acid and other substances, and involves no complicated or lengthy process or the observation of an indefinite end-point. It appears, therefore, to be of practical importance.

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