

CXLI.—*Some Oxidation Products of the Hydroxybenzoic Acids and the Constitution of Ellagic Acid. Part I.*

By ARTHUR GEORGE PERKIN, F.R.S., and, in part, MAXIMILIAN NIERENSTEIN, Ph.D.

DURING an examination of ellagic acid which has been in progress for some time both in the Dyeing and Leather Departments of this University, it was desirable to obtain some ready method by which this could be prepared in quantity, for although the synthetical methods of Löwe (*Zeitschrift für Chemie*, 1868, 4, 603) and Ernst and Zwenger (*Annalen*, 1871, 159, 32) were available and the substance is not difficult to obtain from numerous natural tannin products, much time and labour would be involved in isolating the necessary amount. In the earlier stage of the work these processes were in part adopted,

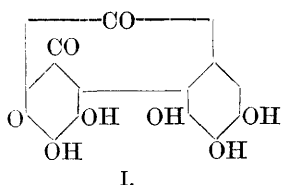
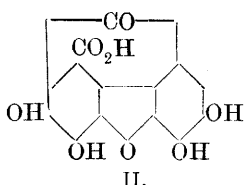
but later the desired object was effected in that it was found that by oxidising gallic acid in acetic acid solution by addition of potassium persulphate and sulphuric acid, ellagic acid could be produced both rapidly and in moderate quantity. As a consequence of this result, it was of interest to submit other hydroxybenzoic acids to a similar treatment, for it was expected that compounds bearing a simple relationship to this interesting substance would thus be formed. In this respect, the behaviour of protocatechuic acid, *p*-hydroxybenzoic acid, and in part *m*-hydroxybenzoic acid has been studied, for although some other acids of this class yield interesting products, these appear to be of a complex character, and are reserved for a later communication.

Ellagic Acid.

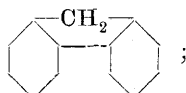
Of all the natural yellow colouring matters, ellagic acid, or rather ellagitannic acid, from which it is readily produced on hydrolysis, is probably the most widely diffused, as it is almost invariably found to accompany gallotannin in the numerous vegetable products in which the latter is known to occur. In certain instances, it has been shown to exist in conjunction with tannins of the catechol class, as for instance in the *Quebracho colorado* (Trans., 1896, 69, 1307), although as gallic acid can be isolated from this product, the presence of gallotannin is also likely. The most suitable source of this colouring matter is either "divi-divi" (*Cæsalpinia coriaria*), "agarobilla" (*Cæsalpinia brevifolia*), "myrabolans" (*Terminalia Chebula*), or "valonia" (*Quercus ægilops*), and extracts of these fruits on long standing frequently deposit ellagic acid, due apparently to the action of a ferment which is said to exist in these plants. This behaviour is a source of much trouble to the extract manufacturers, and large quantities of ellagic acid, unsuitable as it is in the free state for tanning purposes, are yearly thrown to waste. As regards ellagitannic acid, but little is known, and no work of importance has been done on the subject since its isolation by Löwe from divi-divi, who (*Zeit. anal. Chem.*, 1875, 14, 40) assigned to it the formula $C_{14}H_{10}O_{10}$, and described an acetyl derivative, $C_{14}H_5O_{10}(C_2H_3O)_5$. The ready solubility of this compound in water, together with the ease with which it is hydrolysed, leads one to infer that it is either a glucoside of ellagic acid or the glucoside of a gallic ester of this substance.

Ellagic acid has been studied by numerous workers, but the most important investigation of the subject is embodied in the very admirable work of Barth and Goldschmidt (*Ber.*, 1879, 12, 1237), which was supplemented in 1892 (*Monatsh.*, 1892, 13, 51) by Goldschmidt and Jahoda. As a result, the following constitutions

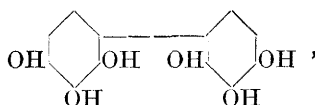
were proposed for this substance, the second of which was finally adopted: [View Article Online](#)



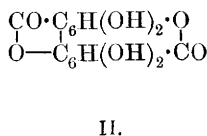
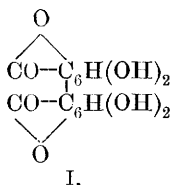
The reasons for this suggestion were mainly that ellagic acid, $C_{14}H_2O_4(OH)_4$, on distillation with zinc dust gives fluorene,



by fusion with alkali, it yields hexahydroxydiphenyl,

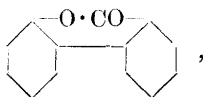


and by the more gentle action of the alkali gives rise to a compound, $C_{13}H_8O_7$, from which fluorene could also be obtained and which was considered to be hexahydroxydiphenylene ketone. Subsequently, Schiff (*Ber.*, 1879, 12, 1534), who had been previously engaged on this subject, proposed the following formulæ:



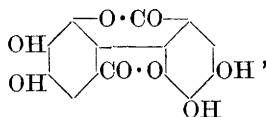
although he was also to some extent in sympathy with that of Barth and Goldschmidt.

Quite recently, Graëbe (*Ber.*, 1903, 36, 212) described the interesting result that diphenylmethyloid, the lactone of 2-hydroxydiphenylene-2'-carboxylic acid,



on distillation with zinc dust gave fluorene in addition to diphenyl

and methyldiphenyl, and in a theoretical discussion of the subject [View Article Online](#) suggested the following formula for ellagic acid,



which was identical with one of those proposed by Schiff. Accordingly, Barth and Goldschmidt's compound, $C_{13}H_8O_7$, would not be a hexahydroxydiphenylene ketone, and Graebe considers it probable that this may in reality be a pentahydroxydiphenylmethyloid.

Löwe (*Zeitschrift für Chemie*, 1868, 4, 603) was the first to prepare ellagic acid synthetically by oxidising gallic acid with arsenic acid, and this was subsequently accomplished by Ernst and Zwenger (*Annalen*, 1871, 159, 32) by heating the acid ethyl gallate with sodium carbonate solution in the presence of air, and by Griessmayer (*Annalen*, 1871, 160, 55) by heating gallic acid with water and iodine.

These reactions apparently indicate a simple formula for ellagic acid, and in case the fluorene difficulty is now removed, Graebe's formula is much to be preferred to that of Barth and Goldschmidt. The tinctorial properties of ellagic acid appear to have been recognised only recently, and it is unusual to find a reference to this subject in the older dyeing manuals. In 1887, it was placed on the market by Messrs. Meister, Lucius, & Brüning under the name of "Alizarine Yellow in Paste," and was recommended as yielding with chromium mordants shades of considerable permanence. So far as one can judge, it is but sparingly employed for this purpose.

In the tanning process, the ellagitannic acid absorbed by the hide undergoes at least partial hydrolysis, and the ellagic acid thus deposited adds weight and bloom to the finished article. On the other hand, it has not been determined whether ellagic acid is a tanning matter in the true sense of the word, and its extremely insoluble nature renders this a difficult question to solve.

EXPERIMENTAL

A solution of 10 grams of gallic acid in 100 c.c. of boiling acetic acid was treated with 5 c.c. of sulphuric acid, and 10 grams of finely-powdered potassium persulphate were then added a little at a time. A somewhat energetic reaction ensued and from the clear liquid, which rapidly assumed a brown colour, minute, prismatic needles gradually separated. As soon as the ebullition had moderated, the mixture was gently heated for a few minutes, allowed to stand for half an hour, then poured into water, and the resulting sandy precipitate collected,

washed, and dried. Owing to the sparing solubility of this product in the usual solvents, it was at first purified by means of its acetyl derivative, and this after recrystallisation was hydrolysed by acid, but this slow and tedious process was subsequently avoided by the employment of boiling pyridine* in which it was found to dissolve somewhat readily. On cooling, prismatic needles separated which were collected and recrystallised from the same solvent with the aid of animal charcoal. This substance, which in the pure condition was almost colourless, consisted of an unstable salt of the original compound, or contained pyridine of crystallisation, for on washing with alcohol these crystals were disintegrated and a pale yellow powder resulted, and again this change slowly occurred on standing at the ordinary temperature. On the other hand, it retained traces of pyridine with some avidity, for this was only completely removed on drying at 160°.

Found C = 55.53; H = 2.26. $C_{14}H_6O_8$ requires C = 55.62; H = 1.98 per cent.

Thus obtained it formed a crystalline powder, melting above 360°, soluble in dilute alkaline solutions with a pale yellow colour. It possessed somewhat feeble dyeing properties, similar to those given by ellagic acid, and, as subsequent experiment showed, there was no doubt as to its identity with this colouring matter. With nitric acid containing nitrous acid and subsequent dilution it gave the well-known blood-red coloration (Griessmayer's reaction), and it is evident that this is a reaction of ellagic acid and not due to some special impurity, as we have heard privately suggested. The yield of crude substance by the above process varied from 2.5 to 3 grams, and numerous unsuccessful experiments have been carried out with the object of improving the method. That this may be still effected seems possible and the matter is reserved for further study.

The *acetyl* derivative was prepared by boiling the finely-powdered substance with a large volume of acetic anhydride for several hours, and then recrystallising the product from the same solvent with the use of animal charcoal.

Found C = 56.24; H = 3.16. $C_{11}H_2O_8(C_2H_3O)_4$ requires C = 56.17; H = 2.98 per cent.

It formed glistening, colourless, flat needles which commenced to sinter about 335° and melted at 343—346° (the melting point 313—316° given in Proc., 1905, 21, 185, is a clerical error) and was identical with the product of the acetylation of natural ellagic acid. Goldschmidt and his colleagues (*loc. cit.*) were not successful in

* Kahlbaum's Pyridine II was employed for this purpose.

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determining the acetyl groups in this substance, and eventually resorted to an examination of the benzoyl compound. Experiment, however, showed that the hydrolysis may be carried out by the indirect method with good result, employing 2 c.c. of sulphuric acid, 15 c.c. of acetic acid, and 1 gram approximately of the acetyl derivative.

Found $C_{14}H_6O_8 = (a)$ 63.74 and (b) 64.19. $C_{14}H_2O_8(C_2H_3O)_4$ requires $C_{14}H_6O_8 = 64.25$ per cent.

In these estimations (a) refers to the acetyl compound prepared from artificial and (b) from natural ellagic acid.

It has been recently found that a convenient source of natural ellagic acid is the "Alizarine yellow in paste" of Messrs. Meister, Lucius, & Brüning, previously referred to; and this, after drying, can be readily purified by crystallisation from pyridine, and constituted the natural ellagic acid which was latterly employed to a considerable extent in this work.

Ellagic acid prepared by the hydrolysis of its acetyl compound is much more faintly yellow than when purified by the pyridine method, and at first sight might be presumed to be colourless. On comparison with its acetyl derivative, however, its yellow tinge is at once evident, from which it appears that this must be regarded as a characteristic of the pure substance. Experiment showed that protocatechuic, *p*-hydroxybenzoic, and *m*-hydroxybenzoic acids do not react so readily as gallic acid in the manner described and but traces of products insoluble in water could be thus obtained. If sulphuric acid, however, undiluted with acetic acid was employed as a solvent, this difficulty was avoided, and the oxidation of the above acids was accordingly studied by this method.

Catellagic Acid.

Schiff (*Ber.*, 1882, 15, 2590), on heating protocatechuic acid with arsenic acid, obtained a substance which he named catellagic acid, and to this he assigned the formula $C_{14}H_{10}O_7$ or $C_{14}H_8O_7$. No analyses, however, are given in the paper, and no description of the compound can be found beyond the statement that it is like ellagic acid.

As ellagic acid is so readily obtained from gallic acid by the persulphate method, it was likely that in the case of protocatechuic acid a similar substance, containing, however, only two hydroxyls, would be produced. Five grams of protocatechuic acid dissolved in 50 c.c. of sulphuric acid were treated gradually with 7.5 grams of potassium persulphate, not allowing the temperature to rise above 45°, and the resulting deep green liquid was allowed to stand overnight. On pouring into water, a finely-divided, greenish-yellow precipitate separated, which, after washing and drying, weighed 3.77 grams. As the sub-

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stance in this condition, owing to its sparing solubility, could not be purified by crystallisation from the ordinary solvents, it was finely powdered and acetylated with acetic anhydride with the aid of a drop of sulphuric acid. The product, on cooling, became semi-solid owing to the separation of crystals, which were collected and purified by crystallisation from large volumes of acetic anhydride, in which it is very sparingly soluble. The yield was 1.45 grams.

Found, C = 61.22; H = 3.02. $C_{14}H_4O_6(C_2H_3O)_2$ requires C = 61.01; H = 2.82 per cent.

It was obtained as colourless, prismatic needles resembling acetyl-ellagic acid, melting at 322—324°, and almost insoluble in the ordinary solvents. An acetyl determination by the indirect method, employing sulphuric and acetic acids, gave a result indicating two such groups.

Found, $C_{14}H_6O_6 = 76.23$. $C_{14}H_4O_6(C_2H_3O)_2$ requires 76.27 per cent.

The catellagic acid thus formed consisted of minute, prismatic needles, which were anhydrous at 100°, and differed in this respect from ellagic acid prepared by a similar method.

Found, C = 62.04; H = 2.60. $C_{14}H_6O_6$ requires C = 62.22; H = 2.22 per cent.

Subsequent experiment showed that as in the case of ellagic acid, the crude catellagic acid is readily purified by crystallisation from pyridine. The colourless, prismatic needles which separate on cooling contain pyridine, and are decomposed by alcohol with the formation of a pale yellow, crystalline powder.

When heated, it does not melt below 360°, but at higher temperatures sublimes with but moderate carbonisation, a distinction again from ellagic acid, which behaves much less readily in this manner. Catellagic acid dissolves in nitric acid (sp. gr. 1.42), forming a magenta-coloured liquid, which, on standing, changes to dull brown, and from which, on dilution with water, a yellow, crystalline precipitate, probably consisting of a nitro-compound, is deposited. Solutions of the alkali hydroxides dissolve it with a pale yellow colour, which is discharged on warming, but these liquids, on neutralisation with acid, deposit unchanged catellagic acid, which again dissolves in the alkali with a yellow tint. It does not dye mordanted calico.

It has been previously mentioned that, when distilled with zinc dust ellagic acid gives fluorene, and it was therefore to be expected that catellagic acid would behave similarly. This was found to be the case, for, proceeding in the usual manner, a small quantity of oily distillate came over, which solidified on standing, and, after three crystallisations from alcohol, melted at 110—111° and closely resembled fluorene

(m. p. 112—113°). A certain amount of a more fusible substance [View Article Online](#) was found to be present in the mother liquors, but too little for identification.

From the acid filtrate obtained during the foregoing preparation of catellagic acid, some quantity of unattacked protocatechuic acid was isolated by means of ether.

The Oxidation of p-Hydroxybenzoic Acid.

For this purpose, 30 grams of *p*-hydroxybenzoic acid, ground into a thin cream with 150 c.c. of sulphuric acid, was gently heated to effect solution, and after cooling to 20° treated gradually with 90 grams of potassium persulphate, avoiding much rise of temperature. The dark liquid, which had been allowed to stand overnight, was poured into water, and the resulting deep brown amorphous precipitate was collected, washed, and well drained. The moist product was digested with about five times its volume of boiling alcohol, the mixture treated with a large volume of ether, and the clear liquid (B) decanted from some quantity of insoluble matter (A).

The latter product, when rinsed two or three times with ether, was mixed with a little water, heated to boiling until free from ether, and after cooling collected, allowed to dry for some days at the ordinary temperature, and finally in the oven. As the black, resinous product (3·68 grams), which resembled hard pitch, was too insoluble to be purified by crystallisation, it was acetylated by means of acetic anhydride and a few drops of sulphuric acid. When cold, alcohol was cautiously added, and after standing overnight, the crystals were collected and washed, first with acetic acid and then with alcohol. Examination showed that this substance (2·8 grams) was a mixture of two acetyl compounds, one of which (C) was only slightly soluble in boiling acetic acid, whereas the second was much more so (D). Proceeding in this manner, it was possible to obtain (C) in an almost chemically pure condition, and when finally crystallised from a large volume of acetic anhydride in the presence of animal charcoal, it was isolated in minute, colourless prisms melting at 322—324°.

Found, C = 61·15 ; H = 3·07. $C_{14}H_4O_6(C_2H_3O)_2$ requires C = 61·01
H = 2·82 per cent.

An acetyl determination gave $C_{14}H_6O_6 = 75·76$ per cent., whereas the above formula requires 76·27 per cent. The product of the hydrolysis was obtained in minute, colourless prisms, which did not melt below 360°.

Found, C = 61·84 ; H = 2·60. $C_{14}H_6O_6$ requires C = 62·22 ; H = 2·22 per cent.

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Heated between watch glasses, it readily sublimed, and had the properties of the *catellagic acid* previously obtained from protocathechuic acid. To be certain of this point, equal portions of the acetyl compound, prepared from both sources, were crystallised together from acetic anhydride, and as a result it was found that the product gave the correct melting point, 322—324°. The formation of this substance from *p*-hydroxybenzoic acid was interesting, and indicated that either protocathechuic acid had been first formed by the oxidation, or that the catechol nuclei had been produced at a later stage of the reaction.

The acetic acid extracts which were obtained during the isolation of the acetylcatellagic acid, and which contained principally the more soluble compound (D), on concentration and cooling, deposited crystals still containing a trace of the former substance. The product was collected, and by two or three fractional crystallisations from acetic acid, setting aside in each case the first portions as impure, a compound of definite melting point was isolated.

This acetyl derivative was more readily obtained pure from the product contained in the ethereal extract (B, page 1419), which on evaporation yielded a brown, semicrystalline mass (5.4 grams). The acetyl compound, prepared with acetic anhydride and sulphuric acid, was repeatedly crystallised from acetic acid, employing animal charcoal until its melting point was constant. No doubt a trace of a third substance is present in these mixtures, which could only be removed by several operations of this kind, and this was unfortunate, as the yield of pure product was of necessity considerably decreased. To determine if the compound was completely acetylated, it was digested with acetic anhydride and sodium acetate, but no change occurred thereby.

Found, C = 60.57; 60.65; H = 3.60; 3.60. $C_{14}H_6O_6(C_2H_3O)_2$ requires C = 60.67; H = 3.37 per cent.

It formed long, glistening needles, melting with effervescence at 267—268°. Hydrolysis with sulphuric acid in the presence of acetic acid gave the following result:

Found, $C_{14}H_8O_6 = 76.73$ and 75.74. Theory requires $C_{14}H_8O_6 = 76.40$ per cent.

The product of the reaction consisted of minute, colourless needles, which did not melt below 360°, but commenced to darken about 300°. At higher temperatures it does not sublime.

Found, C = 61.68; H = 3.08. $C_{14}H_8O_6$ requires C = 61.76; H = 2.94 per cent.

This compound is almost insoluble in the usual solvents, and

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cannot be recrystallised in this way, but if it be suspended in boiling alcoholic potash, with which it interacts to form an insoluble salt, and the mixture be then diluted with a little water, the clear liquid thus formed on neutralisation with acid will deposit the substance in silky needles. It dissolves in aqueous alkalis with a pale yellow colour, which on boiling is discharged, but if acid is now added the original substance is precipitated, and after washing, again dissolves in a solution of the reagent with a pale yellow tint. It is soluble in solutions of the alkali hydrogen carbonates and in a hot aqueous solution of potassium acetate, and this behaviour, which is not possessed by ellagic or catellagic acid, indicates the presence of a *carboxyl* group. The compound $C_{14}H_8O_6$ is readily soluble in warm pyridine, and from concentrated solutions prismatic needles separate on long standing. The behaviour of these crystals indicates that they consist of a true pyridine salt, for on diluting their solution with water or alcohol no deposit is formed, and only by neutralisation with acid is the original compound liberated. The sparing solubility of catellagic acid in pyridine and the ready solubility of the substance $C_{14}H_8O_6$ in this liquid indicates at once a more ready method for separating these compounds than that which has been described, and this, it is expected, will much facilitate the further work in this direction. Alcoholic potassium acetate gives a potassium salt, which has not as yet been obtained crystalline, and a similar compound separates as a colourless jelly when the acetyl derivative is digested at the boiling point with the same reagent. Sulphuric acid dissolves it with a pale yellow colour, and nitric acid gradually attacks it with the formation of an orange-red liquid. It does not dye mordanted calico.

Distilled with zinc dust in the usual manner, it yielded a crystalline distillate, which separated from alcohol in colourless leaflets, melted at $110-111^\circ$, and evidently consisted of flourene.

A preliminary study of the action of fused alkali on the substance $C_{14}H_8O_6$ has shown that it is only slightly attacked at 200° , but at $280-310^\circ$ two compounds are formed the properties of which indicate that they contain carboxylic groups. Whereas the first (A) melts at about $305-306^\circ$, and the second (B) at about $248-249^\circ$, both are easily soluble in alcohol, a fact which distinguishes them from the parent substance. Although analyses of these products have been carried out, these are reserved for a further communication, because, owing to the difficulties of preparing a quantity, some time must elapse before their constitution is satisfactorily elucidated.

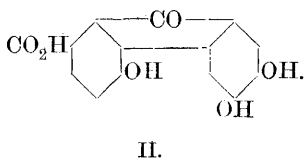
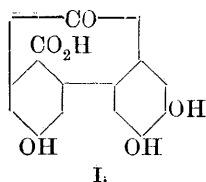
The close resemblance between the formulæ of catellagic acid, $C_{14}H_6O_6$, and the substance $C_{14}H_8O_6$ suggested the possibility that this latter was an intermediate product of the reaction which on further oxidation might pass into the former. An experiment in this direction

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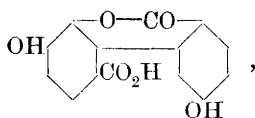
was, however, unsuccessful, for 0.5 gram of the compound, 0.5 gram of persulphate, and 5 c.c. of sulphuric acid under previous conditions gave 0.4 gram of unchanged substance. The employment of larger amounts of persulphate merely resulted in a decreased yield of the original compound, and a stage was reached when the acid liquid gave no precipitate on dilution with water. This behaviour probably accounts for the small yield which has been obtained from *p*-hydroxybenzoic acid, the substance being further oxidised with formation of soluble products. It was interesting to note also that catellagic acid in this manner is but little attacked, and no higher oxidation compound of the nature of ellagic acid is thus formed.

As there can be no doubt that the substances under consideration are derivatives of diphenyl, it seemed likely, judging by the above experiments, that this linkage had occurred subsequently to the oxidation of the phenol to the catechol nucleus. This appeared to be at least in part the case, as an examination of the acid filtrate from the crude, insoluble product of the oxidation of *p*-hydroxybenzoic acid showed. On extracting this solution with ether, some quantity of *p*-hydroxybenzoic acid was isolated, but a trace of a more soluble acid was also present, which gave a green coloration with aqueous ferric chloride. It was separated by fractional crystallisation, was found to melt at 194—196°, and had the properties of protocatechuic acid.

It is not possible to formulate the substance $C_{14}H_8O_6$ on the lines of Goldschmidt's formula for ellagic acid, for such a compound (I) would contain three hydroxyl groups. For the same reason, the diphenylene ketone formula (II) is not available, and moreover, as ortho-hydroxyls are here indicated, tinctorial property would be observed.

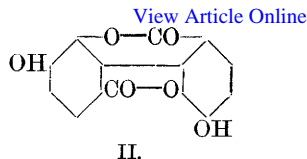
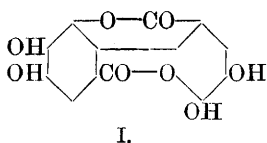


The only reasonable constitution for this substance appears to be as follows :

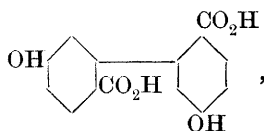


with which its reactions are in agreement.

By analogy, therefore, ellagic acid has the constitution suggested for it by Graebe (*loc. cit.*), I :



and a natural consequence, that of catellagic acid, is represented by formula II. Whereas, therefore, ellagic acid is formed by the condensation of two molecules of gallic acid, and catellagic acid of two molecules of protocatechuic acid, the substance $C_{14}H_8O_6$ results from the interaction of one molecule of protocatechuic acid and one of *p*-hydroxybenzoic acid. A second lactone formation cannot here occur owing to the absence of the hydroxyl in the position (6) necessary for this purpose. It is remarkable that a compound having the constitution



which one would naturally expect to form the main product of the oxidation of *p*-hydroxybenzoic acid, has not yet been isolated. If present, it must be looked for among the more soluble portion of the mixed acetyl derivatives, and a search will be instituted in this direction.

The Action of Fused Alkalis on Ellagic Acid.

Being in possession of a method by which large quantities of ellagic acid could be rapidly prepared, it was thought desirable to study the products of this action, because the statement of Barth and Goldschmidt that hexahydroxydiphenylene ketone can be obtained in this manner from ellagic acid was not in harmony with the above results. According to these authors (*loc. cit.*), this product is formed when ellagic acid is digested for a few minutes with a boiling, very concentrated potassium hydroxide solution, and experiment corroborated this statement both as regards the natural and artificial products. Ten grams of ellagic acid dissolved in a solution of 75 grams of potassium hydroxide in 100 c.c. of water were boiled for ten minutes and the liquid then neutralised with acid.

The acid solution was extracted three times with large volumes of ether, and on evaporation yielded a crystalline residue which on examination was found to consist of three substances. On digestion with boiling water, a small quantity of the product remained undissolved; this, which was identified as ellagic acid, was removed, and the hot filtrate allowed to stand overnight. A precipitate of long,

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hair-like needles had then separated, which after drying at 100° readily dissolved in cold alcohol, and could not therefore consist of ellagic acid. In case, however, a trace of the latter should still be present, and this was likely, the product was extracted with insufficient boiling water for complete solution, and the residue rejected as impure. On cooling, the crystals were collected, dissolved in boiling alcohol, the liquid treated with animal charcoal and filtered, evaporated to a small bulk, diluted with boiling water, and after standing for some hours the deposited substance was collected and dried at 160°. The yield was approximately 1 gram, or 10 per cent.

Found, C = 56.68; H = 3.12. $C_{13}H_8O_7$ requires C = 56.52; H = 2.89 per cent.

In its colour reactions with solutions of the alkaline hydroxides and with ferric chloride, this substance possesses identical properties to those described by Barth and Goldschmidt in connection with their hexahydroxydiphenylene ketone, and there could be no doubt as to its identity with their product. As regards melting point, these authors state that "bis 250 tritt Schwärzung ohne Schmelzen ein," but experiments showed that this blackening is merely the effect of the alkali of the glass. It was found, for instance, that at 300° the substance was as a whole unaltered, though it was impossible at higher temperatures to observe the point at which fusion did occur.

An *acetyl* derivative is readily prepared by the action of boiling acetic anhydride during two hours. Addition of alcohol to the clear solution caused the separation of a crystalline precipitate, which was redigested with the anhydride for a few minutes, and again isolated in a similar manner. Thus obtained, it consisted of small, colourless prismatic needles melting at 224—226°. An acetyl determination by the ethyl acetate method gave the following result:

Found, $C_2H_4O_2$ = 61.34. $C_{13}H_8O_7(C_2H_3O)_5$ requires 61.73 per cent.
 $C_{13}H_2O_7(C_2H_3O)_6$ „ 68.18 „ „

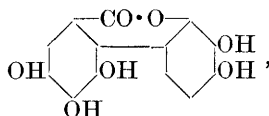
To corroborate this point, the *benzoyl* derivative was examined, as this substance was produced without difficulty by means of the pyridine method, employing 9 grams of pyridine, 7 grams of benzoyl chloride, and 0.6 gram of the substance. It was purified by crystallisation from a mixture of nitrobenzene and alcohol, and was obtained as small, colourless plates melting at 257—259°.

Found, C = 72.26; H = 3.81. $C_{13}H_8O_7(C_7H_5O)_5$ requires C = 72.36; H = 3.52 per cent.

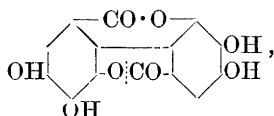
These results indicate therefore that the compound $C_{13}H_8O_7$ contains but *five* hydroxyl groups, and thus cannot be a hexahydroxydi-

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phenylene ketone, as its discoverers, Barth and Goldschmidt, suggest. By distillation with zinc dust, a small quantity of a hydrocarbon was obtained, which after purification formed colourless leaflets melting at 110—111°, and this corroborates the work of the above authors, who prepared fluorene in this manner from their compound. From these facts, it thus appears certain that this substance is the pentahydroxy-derivative of the lactone of 2-hydroxydiphenyl-2'-carboxylic acid (diphenylmethyloid) :



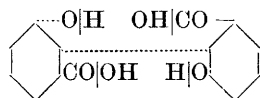
this as previously stated has been surmised by Graëbe, and is in harmony with the earlier results of this work. The formation of such a product from ellagic acid is readily understood in that by the action of the alkali,



a lactone group is opened and the carboxyl group subsequently eliminated.

The Oxidation of m-Hydroxybenzoic Acid.

An examination of the behaviour of *m*-hydroxybenzoic acid in this respect was interesting, because, if viewed in the light of the previous results of this paper, there was a possibility that the parent substance of ellagic acid would be thus produced.



The acid, in quantities of 10 grams, was dissolved in 75 c.c. of sulphuric acid, and 30 grams of potassium persulphate were gradually added, the temperature being kept at about 30°, and after standing for 12 hours the orange-brown liquid was poured into water, and the resulting yellow precipitate collected, washed, and well drained on the pump. While still moist, the product was digested with five times its volume of boiling alcohol, cooled, and again collected at the pump, this process having for its object the removal of a resinous colouring matter readily soluble in the alcohol. When dry (2.5 grams), it was now extracted twice with some quantity of

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boiling acetic acid, and the combined extracts were partially evaporated. On cooling, a semicrystalline precipitate A (0.63 gram) separated, which was collected and the filtrate again evaporated, when a second crop B (0.39 gram) was deposited.

The latter fraction (B) was readily acetylated by means of acetic anhydride and sulphuric acid, and on adding alcohol to the solution thus obtained, the product was isolated in the form of colourless crystals. Examination showed that this was a mixture of two substances, one of which could be isolated by means of its sparing solubility in acetic anhydride. By repeated crystallisation from this solvent, it was obtained in beautiful, colourless leaflets melting at 269—271°, the yield being 0.16 gram.

Found, C = 64.41 ; H = 2.89. $C_{14}H_6O_5(C_2H_3O)$ requires C = 64.86 ; H = 2.70 per cent.

The substance was hydrolysed by means of sulphuric acid in the presence of acetic acid in the usual way.

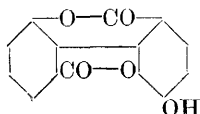
Found, $C_{14}H_6O_5$ = 84.45. Theory requires 85.81 per cent.

The product of the hydrolysis crystallised from acetic acid in colourless needles melting at 273—276°.

Found, C = 66.19 ; H = 2.62. $C_{14}H_6O_5$ requires C = 66.14 ; H = 2.36 per cent.

This new substance, for which the name *metellagic acid* is proposed, resembles catellagic acid in that at high temperatures it sublimes readily in the form of needles. It is soluble in boiling pyridine, and, on cooling, this solution deposits long, colourless, prismatic needles. Sulphuric acid dissolves it with a pale yellow coloration, and nitric acid on gentle warming with an orange-yellow tint, and on diluting this solution with water a yellow precipitate, probably consisting of a nitro-compound, is precipitated. With caustic alkaline solutions, it behaves similarly to catellagic acid, giving a yellow liquid, the colour of which is discharged on boiling. Distilled with zinc dust in the usual manner, a small quantity of a crystalline hydrocarbon was obtained, which appeared to be identical with fluorene. It does not dye mordanted calico.

The reactions of this substance are in harmony with those required by a member of the ellagic acid series, and the following formula assigned to it is probably correct :



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This, it will be noted, represents the compound as being formed by the interaction of *m*-hydroxybenzoic acid and protocatechuic acid. Although in this case we have no direct evidence of the latter and no catellagic acid has been isolated from the products of this reaction; the presence of the resinous colouring matter referred to above, which dyes mordanted fabrics, is suggestive in this respect.

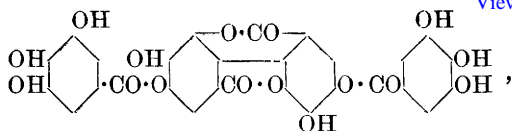
In the mother liquors obtained during the purification of the acetylmetellagic acid, a second compound of this nature was detected. This product (0.1 gram) crystallised in colourless needles, melted at 237—243°, and on hydrolysis with acid gave a substance crystallising in glistening, yellow needles.

A satisfactory examination of the principal substances which are formed by the oxidation of *m*-hydroxybenzoic acid has been found to present considerable difficulty, for not only are at least five of these contained in the mixture, but the quantity in each case is comparatively small.

The reaction in this case appears to proceed in a somewhat different manner to that observed with protocatechuic and *p*-hydroxybenzoic acids. On the other hand it is likely that the principal products thus obtained are related to those which are formed when gallic acid is oxidised in the presence of concentrated sulphuric acid (see below). Considerable time has been spent on this portion of the subject, and the two following substances have also been isolated: (*a*) yellow needles, which forms a colourless acetyl derivative (m. p. 331—335°), and (*b*) yellow needles, the acetyl derivative of which melts at 278—280°; these compounds, which are devoid of tinctorial property, together with the resinous colouring matter which dyes aluminium mordanted calico an orange-yellow shade, will be further investigated. No substance of the nature suggested at the commencement of this section appears to have been formed.

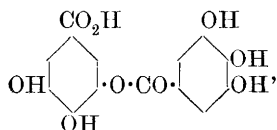
Preliminary experiments on the oxidation of salicylic acid in this manner have been carried out, but the product of the reaction, which is insoluble in water, has not yet been fully examined; on the other hand, β -resorecylic acid is apparently too susceptible to sulphonation to give a satisfactory result by the present method. It is anticipated that interesting results will be obtained by the oxidation of molecular proportions of two distinct acids; for instance, employing in this way both gallic and protocatechuic acids, it is possible that the trihydroxy-compound intermediate between ellagic and catellagic acids would be formed.

In view of the possibility that ellagitannic acid is derived from the condensation of 2 molecules of gallotannin or is a glucoside of this and possesses a constitution of the nature of



gallotannin has been oxidised by this method, and although no definite result can yet be announced there is indication that the matter is worthy of further study.

As it now appears certain that ellagic acid has the constitution previously discussed, it is worthy of note that its dyeing properties are somewhat anomalous in that the carbonyl group, when present as a portion of a lactone complex, is not usually associated with this characteristic. On the other hand, the diphenyl linkage has probably the effect of rendering these groups less susceptible to hydrolysis, so that a quinonoid form becomes possible. It is worthy of note that gallotannin, which appears to contain an analogous grouping,



and does not dye ordinary mordanted calico, will give a bright yellow shade if a titanium mordant be present. In this case, it may be considered that the special mordant is able to induce a quinonoid change, and further indicates that the carbonyl group when present in such a form has a tendency to assume chromophoric properties.

It was interesting to determine if pentahydroxydiphenylmethyloid was possessed of tinctorial properties, and experiment showed this was the case. The colours produced on woollen cloth mordanted respectively with chromium and iron possessed the general character of those given by ellagic acid; they were, however, considerably stronger, and with the first-named mordant a more olive shade was thus developed. These distinctions are readily accounted for by the fact that the substance in question is not only much more readily soluble in water, but contains five hydroxyls, whereas in ellagic acid but four such groups exist. Pentahydroxydiphenylmethyloid does not appear to possess tanning properties, for its warm aqueous solution gave no precipitate with gelatin, and from this result it appears doubtful whether ellagic acid can be regarded as a tannin matter in the true sense of the word.

Addendum.

When gallic acid dissolved in concentrated sulphuric acid is oxidised by means of persulphate at about 30° , a 66 per cent. yield of a crystalline product is obtained which, after purification, forms pale yellow needles identical in appearance with ellagic acid. As on distillation with zinc dust the new compound gives a hydrocarbon resembling fluorene, on fusion with alkali pentahydroxydiphenylmethylid and with nitric acid the Griessmayer reaction, it was assumed to consist of this colouring matter. An examination of the colourless acetyl derivative showed that on hydrolysis a yield of product (64.06 per cent.) identical with that expected from acetyllagic acid was obtained, and, again, the compound itself is possessed of feeble yellow dyeing property. In spite of these facts, it is, however, now certain that the two substances, although closely related, are not identical, for although ellagic acid dissolves somewhat readily in boiling pyridine, the substance in question (A) is very sparingly soluble in this liquid. Again by the action of boiling dilute alkali, a new compound not given by ellagic acid is obtained from the latter; this, which approximates in formula to $C_{14}H_{10}O_9$, crystallises in colourless needles, dissolves in alkali with a faint green coloration passing to bluish-violet on oxidation, possesses feeble dyeing property, and gives an acetyl compound melting at $232-234^{\circ}$. Experiments to determine if the substance in question was a mixture and contained ellagic acid have given a negative result, although there can be no doubt that the colouring matter thus formed is closely allied to this compound.

On the other hand, if gallic acid dissolved in sulphuric acid diluted with 10–20 per cent. of water is oxidised, a second colouring matter (B) not identical with the above is produced. The composition of this product approximates to the formula $C_{14}H_8O_9$. It has given a colourless acetyl compound melting at $310-312^{\circ}$, and this, on hydrolysis, yielded 61.78 per cent. of regenerated substance. With nitric acid, the Griessmayer coloration is readily formed, and on boiling with dilute alkali it is converted into the colourless compound mentioned above ($C_{14}H_{10}O_9$?), the acetyl derivative of which melts at $232-234^{\circ}$. Most probably the colouring matter (B) is identical with that described by A. G. and F. M. Perkin (Proc., 1905, 21, 212) as formed by the electrolytic oxidation of gallic acid. The close connection between the substances A and B and their relationship to ellagic acid is very evident, and as considerable analytical and other work has been carried out on this subject, it is hoped that their constitutions will shortly be elucidated.

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