XII.—*An Oxidation Product of Gallic Acid.*

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THIS work originated from the desire to determine if it was possible to prepare cœruleo-ellagic acid (dihydroxyellagic acid) (T., 1911, **99**, 1442) by the direct oxidation of gallic acid. Cœruleo-ellagic acid can be readily obtained in this manner from ellagic acid, whereas it has long been known that ellagic acid is produced to some extent by the interaction of gallic and arsenic acids. This compound possesses much stronger dyeing properties than the lower hydroxylated members of the ellagic acid series, and would, no doubt, find technical employment could it be prepared in a more economical manner. No attention appears to have been devoted to the action of oxidising agents on gallic acid dissolved in sulphuric acid at temperatures from 100° upwards, and this may have arisen from the fear of the formation at first of rufigallic acid, which is itself more or less immune when submitted to this treatment.

Oxidation in the Presence of Concentrated Sulphuric Acid.

To a solution of 1·5 parts of arsenic acid in 16 parts of 96 per cent. sulphuric acid at 110°, 1 part of gallic acid was added and the mixture heated in an oil-bath to 120° for six hours. The brown-coloured liquid was poured into much water, the precipitate

washed by decantation, collected, and dried at 160°. The finely powdered product was now digested with 5 parts of boiling acetic anhydride and a trace of pyridine for two and a-half hours, and the crystalline deposit (A) removed. By recrystallisation from much acetic anhydride this was obtained colourless, but was evidently a mixture, as its melting point, 290—305°, indicated. Further crystallisation being ineffectual, it was hydrolysed with sulphuric acid in boiling acetic acid, and after three hours the grey, crystalline powder was collected and converted into the benzoyl compound, employing benzoic anhydride (5 parts) with a little pyridine at 210—230°. On gradual cooling the solution commenced to deposit crystals, and at about 120° these were collected on a heated funnel and washed, first with a concentrated solution of benzoic anhydride in alcohol, and finally with alcohol. By recrystallisation from benzoic anhydride, colourless needles were obtained, which melted fairly sharply at 340°.

Found: C=70·51; H=3·04.

$C_{56}H_{30}O_{16}$ requires C=70·17; H=3·13 per cent.

The benzoyl compound when hydrolysed by long boiling with sulphuric acid, 8 parts, and acetic acid, 25 parts, yielded the colouring matter as a crystalline powder, which by means of the deep blue coloration it produced with dilute alkali and the melting point of its acetyl derivative was found to consist, without doubt, of cœruleo-ellagic acid.

The acetic anhydride mother liquors from (A) on partial concentration gave a further amount of acetyl derivative, melting indefinitely at about 290°. As it appeared likely that this consisted of a mixture of acetylcœruleo-ellagic and acetylflavellagic acids, its behaviour with boiling potassium hydroxide solution was studied for, in this manner, whereas flavellagic acid gives the 2:2'-lactone of 3:4:5:6:2':3':4'-heptahydroxydiphenyl-2-carboxylic acid (I), which is insoluble in water, cœruleo-ellagic acid yields only the readily soluble octahydroxydiphenyl (II):

The substance was digested with 5 parts of boiling 50 per cent. potassium hydroxide solution for a few minutes, and after dilution with water the liquid was immediately neutralised. The colourless needles, which separated on keeping, were soluble in dilute alkali with a bluish-violet coloration, and yielded an acetyl derivative

which melted at 232—234°. It evidently consisted of the compound (I), and this affords proof that the product from which it was derived contained acetylflavellagic acid.

The acetic anhydride mother liquor when again concentrated yielded after several days a small amount of an indefinitely crystalline deposit. By fractional crystallisation from acetic anhydride and by means of the benzoyl derivative, a bright yellow, crystalline compound was eventually isolated, which gave a crystalline sulphate, and is described in detail under the name of flavogallol in the second section of this paper.

The yield of mixed colouring matters obtained in this manner from gallic acid was unfortunately poor, the maximum (27·5 per cent.) being that obtained by heating the mixture to 110—120° for six hours, whereas the minimum (8 per cent.) was given at 100—110°.

*Oxidation in the Presence of Dilute Sulphuric Acid.**

In this connexion very many experiments were carried out, involving variations in the temperature, the time, dilution of the acid, and quantity of oxidising agent. As a result the following process appears to give the best result.

One and a-half parts of arsenic acid were dissolved in 2·5 parts of water, 16·5 parts of 96 per cent. sulphuric acid added, and the mixture was heated in an oil-bath to 110—115°. One part of gallic acid was now slowly added, causing the temperature to rise to 120°, at which it was maintained for six hours. The solution, which was at first of a reddish-brown colour, soon darkened, and effervescence occurred. The product was poured into twenty times its volume of water, the mixture allowed to remain overnight, and the resulting dull yellowish-green deposit washed by decantation and dried on the steam-bath. It was obtained in this way as a brownish-black, amorphous mass, the weight of which on the average was equivalent to 62 per cent. of the gallic acid employed. In the paste form it readily dyes mordanted fabrics, and, employing woollen cloth, the following shades are produced:

Chromium.	Copper.	Tin.	Iron.
Dull olive-yellow.	Pale brown.	Pale orange-yellow.	Brownish-black

These are of the type of those given by alizarine-yellow-A (tri-hydroxybenzophenone), and quite distinct from those yielded by flavellagic or cœruleo-ellagic acids. The isolation of the main constituent of this product in a pure condition was difficult, and in the earlier experiments a preliminary treatment with warm sodium

* A provisional patent for these processes has been secured.

hydrogen carbonate solution was employed. A yellow, amorphous sodium salt thus separates, which by filtration can be freed from the brownish-black liquid simultaneously produced, and when neutralised gives a dull yellow powder. Eventually, however, an acetylation process was adopted. The crude product (dried at 160°) was heated with 3 parts of acetic anhydride, and when the first violent reaction had subsided a trace of pyridine was added and the digestion continued for three hours. After remaining overnight, the crystalline deposit was collected, redissolved in 5.5 parts of boiling acetic anhydride, and allowed to remain for several hours without disturbance. A fine red powder thus separated in small amount, and this was rapidly collected, as the clear liquid on agitation soon commenced to deposit crystals. The residue was again treated in a similar manner with acetic anhydride, the trace of red substance which separated removed,* and the crystalline deposit, produced on evaporating the filtrate purified by recrystallisation from nitrobenzene. (Found, $C=56.25$; $H=3.31$, $C_{14}H_2O_8(C_2H_3O)_4$ requires $C=56.17$; $H=2.98$ per cent.) It consisted of needles melting at 343° , and was found to consist of acetyllellagic acid.

The filtrate (A), after keeping for some hours, had deposited some quantity of cream-coloured crystals, and by evaporating the mother liquor fractionally, further amounts of a similar product could be isolated. The final dark-coloured, viscid liquid contained a considerable amount of an amorphous substance, and from this no definite compound was obtained.

By recrystallisation from acetic anhydride the fractions of acetyl compound could be obtained apparently pure, but the melting points varied from 240° to about 260° , and these were far from sharp. A benzoyl compound, however, of definite melting point could be isolated either from the hydrolysed acetyl compound or from the acetyl compound itself. The solution obtained by heating the latter with 3 parts of benzoic anhydride at $230-240^{\circ}$ for three hours, on cooling to about 120° deposited crystals, which were collected, washed with fused benzoic anhydride, and finally with alcohol.† The hydrolysis of this compound, which required

* This was too trifling for examination. On heating with sulphuric acid it gave a deep olive-green solution.

† This reaction is a general one, acetic anhydride being evolved. Thus acetanilide at 260° gives benzanilide (Found, $N=7.1$ per cent.). Acetyl- β -naphthol yields the benzoyl derivative at 220° (m. p. 206°), (Found, $C=82.14$; $H=5.03$), and is isolated by removing excess of benzoic anhydride with steam distillation, followed by washing with dilute alkali. Dibenzoyl-alizarin, m. p. $177-178^{\circ}$ (Found, $C=75.14$; $H=3.73$), and pentabenzoyl-quercetin, m. p. $187-188^{\circ}$ (Found $C=72.77$; $H=3.59$), were readily prepared in this manner from the corresponding acetyl compounds.

considerable care, otherwise darkening occurred, was carried out as follows: One gram of the benzoyl derivative was dissolved by gentle warming in 3 c.c. of sulphuric acid, the solution heated at 60° for two hours, and after remaining overnight, diluted with four volumes of acetic acid and briskly boiled. The milky liquid quickly became clear, and crystals of the oxonium sulphate separated. These were collected, hydrolysed by water, and converted into the acetyl derivative, which now melted at 278—280°.

Having now ascertained the characteristics of the pure substance, a more economical method of purification was devised. The purified acetyl derivative was made into a cream with nitrobenzene containing a little acetic anhydride, and the mixture heated until solution was obtained. When cold, the crystals were collected, washed with nitrobenzene followed by acetic anhydride, and hydrolysed by sulphuric acid in the presence of acetic acid. The oxonium sulphate which thus separated was washed with acetic acid, decomposed by water, and the colloidal mass of free colouring matter drained, made into a cream with alcohol, and gently poured into a very large volume of boiling alcohol. A part of the substance without dissolving thus became crystalline, and by evaporating the filtrate to about one-sixth of its bulk, a further quantity separated from the boiling liquid. In the crystalline condition it is almost insoluble in boiling alcohol, and for further purification if necessary the acetyl derivative was employed. For analysis it was dried at 160°.*

Found: C = 55.35; H = 1.98.

$C_{21}H_8O_{12}$ requires C = 55.74; H = 1.77 per cent.

These figures closely approximate with those required by ellagic acid, $C_{14}H_6O_8$ (C = 55.62; H = 1.98), but for reasons given later the higher formula is adopted.

This colouring matter, for which the name *flavogallol* is proposed, forms fine, hair-like, canary-yellow needles, which when heated to a high temperature carbonise without melting, with the production of a trace of a yellow sublimate. It is very sparingly soluble in the usual solvents, and dissolves in 10 per cent. sodium hydroxide solution with an orange-yellow colour, which slowly becomes brown by oxidation. With very dilute alkali a pure yellow coloration is produced. Alcoholic lead acetate gives an orange precipitate, and ferric chloride a dull green liquid, whereas sulphuric and nitric acids respectively give yellow and orange-coloured solutions. By means of the latter it does not give the Griessmayer

* When air dried it contains $4H_2O$. (Found H_2O = 11.3, 11.38. $C_{21}H_8O_{12} \cdot 4H_2O$ requires H_2O = 11.57 per cent.)

reaction. On mordanted woollen cloth it dyes shades of a purer character than those given by the crude paste:

Chromium.	Aluminium.	Tin.	Iron
Old gold.	Pale brownish-yellow.	Pale greenish-yellow.	Brownish-grey.

When flavogallol, in the form of a paste with alcohol, is boiled with a 25 per cent. solution of potassium acetate in alcohol for three hours an orange-coloured, crystalline powder is obtained, and this is washed with alcohol and dried at 160°.

Found: $K = 20.13$.

$C_{21}H_5O_{12}K_3$ requires $K = 20.67$ per cent.

This tripotassium salt dissolves in hot water, giving an orange-yellow solution, which gives with acids a precipitate of flavogallol. Concentrated boiling aqueous potassium acetate behaves similarly, giving at first a curdy, yellow precipitate of fine needles (Found, $K = 13.61$), which appears to be a mixture of mono- and di-potassium salts, and eventually a tripotassium compound (Found, $K = 20.48$). The solution of the latter gives respectively with barium chloride and lead acetate yellow and orange precipitates.

Flavogallol anhydrosulphate can be obtained from the acetyl compound, or by adding glacial acetic acid to a solution of flavogallol in sulphuric acid. The product is collected and washed with acetic acid.

Found: $C = 46.91$; $H = 2.42$.

$C_{21}H_6O_{11}, H_2SO_4$ requires $C = 47.36$; $H = 1.50$ per cent.

It crystallises best when obtained from the benzoyl compound by the method above described, and thus forms a glistening mass of orange-yellow prisms. By the action of cold water it is readily transformed into flavogallol and sulphuric acid.

Found, $C_{21}H_8O_{12} = 84.26, 84.88$; $H_2SO_4 = 18.73, 18.70$.

$C_{21}H_6O_{11}, H_2SO_4$ requires $C_{21}H_8O_{12} = 84.96$; $H_2SO_4 = 18.42$ per cent.

Flavogallol does not yield a hydrochloride in the usual manner with 33 per cent. hydrochloric acid, but with hydriodic acid (D 1.7) the formation of a very unstable hydriodide appears to take place.

Acetylflavogallol, $C_{21}H_2O_{12}(C_2H_3O)_6$, consists of small, prismatic needles possessing a faint yellow colour. When slowly heated it melts and decomposes at 278—280°.

Found: $C = 56.11, 56.00$; $H = 3.17, 3.00$.

$C_{33}H_{20}O_{18}$ requires $C = 56.25$; $H = 2.84$ per cent.

It is sparingly soluble in acetic anhydride, which either alone or in conjunction with nitrobenzene forms the only solvent from which it can be satisfactorily crystallised. Alcohol or acetic acid,

for reasons to be given later, must not be employed in this operation. Its solution in acetic anhydride possesses a pale blue fluorescence.

The acetyl groups in this compound were determined by a modification of the acetic ether method, the indirect process proving to be unsuitable. Being but slowly hydrolysed in the ordinary way, the substance was first dissolved in sulphuric acid, and the solution then rapidly admixed with the alcohol.

Found: $C_2H_4O_2 = 51.06, 50.73$.

$C_{21}H_{12}O_{12}(C_2H_5O)_6$ requires $C_2H_4O_2 = 51.13$ per cent.

Benzoylflavogallol, $C_{21}H_{12}O_{12}(C_7H_5O)_6$, separates from its solution in benzoic anhydride in small, canary-yellow prisms, which melt at $326-328^\circ$, and are sparingly soluble in the usual solvents.

Found: $C = 70.00, 70.40$; $H = 3.00, 3.25$.

$C_{63}H_{32}O_{18}$ requires $C = 70.26$; $H = 2.97$ per cent.

These figures, therefore, correspond with those given by the acetyl determinations, and indicate the presence of six hydroxyl groups. The benzoyl compound was soluble in warm naphthalene, and did not separate, at least to any extent, on cooling, except after a considerable period:

0.5143 , in 10.82 naphthalene, gave $\Delta t = 0.300$. M.W. = 1109 .

$C_{63}H_{32}O_{18}$ requires M.W. = 1076 .

This result is thus in fair agreement with the formula, $C_{21}H_8O_{12}$, assigned to flavogallol.

Flavogallolanilide, $C_{21}H_7O_{11} \cdot NH \cdot C_6H_5$.—When flavogallol is heated with boiling aniline, the gelatinous product at first obtained gradually changes into minute crystals. After digestion for one hour the product was collected and washed with alcohol.

Found: $C = 61.46$; $H = 2.49$; $N = 3.14$.

$C_{27}H_{13}O_{11}N$ requires $C = 61.48$; $H = 2.46$; $N = 2.65$ per cent.

It consisted of yellow needles possessing a slightly more orange tint than flavogallol, which melted at above 345° . It was soluble in dilute alkali hydroxides with an orange-yellow coloration.

Flavogallonic Acid.

When acetylflavogallol is hydrolysed by the acetic ether method, the residual alcoholic liquid on treatment with water deposits after several hours faintly yellow nodules. By recrystallisation from dilute alcohol it was obtained in fine needles.

Found: $C = 54.79, 55.05$; $H = 3.17, 3.00$; $Et = 5.69$.

$C_{23}H_{14}O_{13}$ requires $C = 55.42$; $H = 2.81$; $Et = 5.82$ per cent.

This compound, for which the name *ethyl flavogallonate* is sug-

gested, melts at above 300° , and when dried at 160° is hygroscopic. Dilute alkali hydroxides dissolve it with a pale yellow coloration. Its formation evidently arises from hydrolysis, a lactone group being thus opened, and the carboxyl group subsequently undergoing esterification.

Acetyl Derivative.—The ester was digested with boiling acetic anhydride and a little pyridine, and the crystals which separated overnight were redigested with acetic anhydride. On adding alcohol, prismatic needles were deposited which melted at 214° .

Found: C=56.22, 56.00; H=3.99, 3.70.

$C_{37}H_{28}O_{20}$ requires C=56.06; H=3.54 per cent.

It is readily soluble in acetic anhydride, and sparingly so in alcohol. When acetylflavogallol is dissolved in acetic anhydride and alcohol is added to the solution, it is reprecipitated at first, but afterwards slowly passes into solution. In order to study this reaction a solution of the acetyl compound in acetic anhydride was boiled for one hour with addition of alcohol, the liquid evaporated, and the viscid residue repeatedly boiled with small quantities of alcohol. The product, which crystallised on keeping, was purified by means of alcohol and acetic anhydride. (Found, C=56.16; H=4.02.) It melted at 215 – 217° , and consisted of the acetylflavogallonic ester described above.

The *acetyl methyl ester* was prepared in the same manner, employing methyl alcohol, and was purified by crystallisation from a mixture of alcohol and benzene.

Found: C=55.50; H=3.58.

$C_{36}H_{26}O_{20}$ requires C=55.52; H=3.31 per cent.

It formed small, prismatic needles melting at 181 – 183° .

Flavogallonic Acid.—When flavogallol is added to boiling 30 per cent. potassium hydroxide solution, preferably diluted with a little alcohol to lower the boiling point, the liquid soon loses its colour, a property which is also possessed by the ellagic acid group of colouring matters. By cautious acidification with hydrochloric acid a grey-coloured precipitate is deposited, which is removed, and from the filtrate colourless needles slowly separate. These gradually become greyer in colour, and when dried at 160° are somewhat hygroscopic.

Found: C=53.35; H=2.63.

$C_{21}H_{10}O_{13}$ requires C=53.61; H=2.13 per cent.

It melts above 300° and dissolves in very dilute alkali hydroxides with a pale yellow colour, becoming browner on keeping in air. Acetic anhydride in the presence of pyridine readily yields an acetyl compound crystallising in prisms which melt at 278 – 280° ,

and have all the properties of acetylflavogallol. (Found, C=56.20; H=3.22.)

The re-formation of the lactone group originally opened by the action of the alkali thus occurs in the presence of boiling acetic anhydride, and a similar result is produced by digesting flavogallonic acid with sulphuric acid in the presence of boiling acetic acid. Anhydroflavogallol sulphate gradually separates, which can be transformed into flavogallol by the action of water.

Interesting is the behaviour of acetylflavogallol with boiling acetic acid, for although at first it remains almost insoluble, a solution is slowly produced, and from this on cooling no separation occurs. The product, which has only been isolated as an amorphous powder, is of a readily soluble nature, and consists probably of acetylflavogallonic acid. With sulphuric and acetic acid anhydroflavogallol sulphate separates. For these reasons alcohol and acetic acid cannot be used in the purification of acetylflavogallol, and the ignorance of these facts caused much inconvenience during the earlier stages of this work.

Flavogallone.

If flavogallonic acid or flavogallol itself (2 grams) is digested with boiling 50 per cent. potassium hydroxide solution for about ten minutes, avoiding air oxidation, cautious acidification causes the deposition of a grey-coloured precipitate, which according to the concentration may be amorphous, or consist of minute needles (1.43 grams). The dried product when acetylated yielded an acetyl derivative in the form of leaflets which were readily soluble in acetic anhydride and melted at 257—259°.

Found: C=56.88; H=3.58.

$C_{34}H_{24}O_{18}$ requires C=56.66; H=3.33 per cent.

A solution of the acetyl compound in boiling acetic acid was hydrolysed by the gradual addition of 33 per cent. hydrochloric acid, causing the separation of a colourless precipitate, which was washed and dried at 160°.

Found: C=56.10; H=2.65.

$C_{20}H_{10}O_{11}$ requires C=56.33; H=2.34 per cent.

Flavogallone melts at above 340° and is sparingly soluble in the usual solvents. In absence of air its solution in 10 per cent. sodium hydroxide is almost colourless, but by oxidation passes through yellowish-green to brownish-red. It is insoluble in cold sulphuric acid, but on heating an orange-yellow liquid is produced, which later develops a fine magenta-violet colour; this on dilution with water gives a blue-coloured precipitate. With alcoholic ferric

Whereas flavogallonic acid is produced from flavogallol by the opening of a lactone group, flavogallone is evidently derived from the former by an elimination of its carboxyl group, thus:

This reaction is analogous to that given by ellagic acid, which in these circumstances is transformed into the 2:2'-lactone of 4:5:6:2':3':4'-hexahydroxydiphenyl-2-carboxylic acid:

When flavogallone is prepared in the above-described manner, the alkaline liquid before neutralisation, when diluted with water, develops a fine magenta-violet colour, which eventually becomes brown. This is not a property of flavogallone itself, but is proof of the presence of a lactone group in this substance, which is opened by the action of the strong alkali, but closed when the solution is rendered acid. It accordingly appeared probable that flavogallol contains two lactone groups.

Flavogallone is but little attacked by prolonged boiling with potassium hydroxide solution, and suitable conditions for the production of a further degradation product have as yet not been ascertained. Potassium hydroxide at 200–220° yields a brown product very readily soluble in water, and from this no definite compound could be isolated.

Methylation of Flavogallol.

Flavogallol (5 grams) suspended in a mixture of 50 c.c. of methyl alcohol and 10 c.c. of water was treated with equivalent amounts of 40 per cent. methyl-alcoholic potassium hydroxide and methyl sulphate until little or no coloration was produced on addition of the former. The mixture was boiled from time to time, but the process, which occupied about an hour, was tedious, and a very large amount of the reagents was necessary. The product was diluted with water, causing the separation of a viscid mass, and this was removed by shaking with ether. After washing with dilute sodium hydroxide solution, the ethereal liquid was evaporated, and the residue, which slowly crystallised, was digested with boiling 5 per cent. alcoholic potassium hydroxide until a sample of

the liquid no longer became turbid on addition of water. By acidification an oily deposit was obtained, which hardened on keeping, and this was washed, well drained, and dissolved in boiling alcohol. Crystals (2 grams) slowly separated, which were purified by recrystallisation.

Found: C=57.75; H=5.16; Me=23.1, 22.9.

$C_{21}H_4O_5(OMe)_{10}$ requires C=57.58; H=5.27; Me=23.21 per cent.

This compound, which is produced from flavogallol by the addition of three molecular proportions of water and subsequent methylation of ten hydroxyl groups, crystallises in colourless prisms which melt at 206—208°. Sulphuric acid dissolves it to form a colourless liquid which, when heated, develops a fine magenta-red tint, and this by dilution with water gives a deep blue solution (compare flavogallone). A cold alkaline solution does not decolorise permanganate.

The hydriodic acid liquid from the Zeisel determination contained crystals which, when recovered in the usual manner, were found to consist of flavogallol, in that they yielded the acetyl derivative melting at 278—280°.

Employing *N*/10-sodium hydroxide, two samples of the substance required respectively 12.4 and 12.5 per cent. of sodium hydroxide for neutralisation, indicating the presence of two carboxyl groups. [$C_{29}H_{32}O_{11}(CO_2H)_2$ requires NaOH=12.38 per cent.]

The acid was esterified in the usual manner, and the solution allowed to evaporate in a vacuum. Colourless plates of considerable size gradually separated, which melted at 128—130°.

Found: C=58.5; H=5.6; Me=26.36.

$C_{29}H_{32}O_{11}(CO_2Me)_2$ requires C=58.75; H=5.63; Me=26.7 per cent.

The acid melting at 206—208° (1.2 grams) was unaffected by long digestion with a 7 per cent. potassium hydroxide solution at the boiling point, 1.05 grams being recovered, and the action of concentrated alcoholic potassium hydroxide in sealed tubes at 175° was therefore studied. On cooling, a semi-solid, crystalline product was obtained, and this was dissolved in water, the alcohol evaporated, and when cold the solution was neutralised. No deposition occurred, but on gently boiling crystals gradually separated in considerable amount. These were collected, dissolved in boiling water, and the small quantity of substance which crystallised on cooling and contained some unattacked compound was neglected. The filtrate on evaporation gradually deposited glistening leaflets, which were collected and dried at 160°.

Found: C=56.96; H=5.09; Me=20.90.

$C_{30}H_{32}O_{15}$ requires C=56.96; H=5.06; Me=21.20 per cent.

It melts at 183—184°, and when dried in the air contained one molecule of water of crystallisation.

Found: $\text{H}_2\text{O}=2.73$.

Theory requires $\text{H}_2\text{O}=2.77$ per cent.

The hydriodic acid liquid from the Zeisel determination contained flavogallol, which was identified by the acetyl derivative melting at 278—280°.

Titration indicated the presence of two carboxyl groups.

Found: $\text{NaOH}=12.92$.

$\text{C}_{28}\text{H}_{30}\text{O}_{11}(\text{CO}_2\text{H})_2$ requires $\text{NaOH}=12.34$ per cent.

By the action of alcoholic potassium hydroxide on the acid $\text{C}_{21}\text{H}_4\text{O}_5(\text{OMe})_{10}$ (m. p. 206—208°), one methoxy-group is therefore hydrolysed, with the formation of the acid $\text{C}_{21}\text{H}_5\text{O}_6(\text{OMe})_9$. With hot sulphuric acid the latter acid gives, like the former, a magenta-red solution passing to blue on dilution with water.

The alcoholic mother liquors from the crude methylation product, which had deposited the acid melting at 206—208°, when gradually evaporated, gave crystals which, after purification with the same solvent or from acetic acid, heated at 238—240°.

Found: $\text{C}=57.26$; $\text{H}=5.29$; $\text{Me}=22.73$.

$\text{C}_{21}\text{H}_4\text{O}_5(\text{OMe})_{10}$ requires $\text{C}=57.58$; $\text{H}=5.27$; $\text{Me}=23.21$ per cent.

From alcohol when slowly crystallised it forms large prisms, which contain alcohol of crystallisation. This is slowly evolved on keeping, the crystals becoming opaque.

Found at 160°: $\text{C}_2\text{H}_6\text{O}=6.49$.

$\text{C}_{31}\text{H}_{34}\text{O}_{15}, \text{C}_2\text{H}_6\text{O}$ requires $\text{C}_2\text{H}_6\text{O}=6.64$ per cent.

When heated with sulphuric acid it behaves similarly to the acid melting at 206—208°, a magenta-red solution being obtained which passes to blue when diluted with water. Its cold alkaline solution does not reduce permanganate.

Titration indicated the presence of two carboxyl groups.

Found: $\text{NaOH}=12.62$.

Theory requires $\text{NaOH}=12.38$ per cent.

The hydriodic acid liquid from the Ziesel determination appeared to contain crystals of flavogallol, in that these yielded an acetyl derivative melting at 278—280°.

The *methyl* ester, prepared in the usual manner, was precipitated by water as an oil, the solution of which in dilute alcohol slowly deposited large, prismatic needles. These melted at 86—87°, and were very soluble in alcohol.

Found: $\text{C}=58.60$; $\text{H}=5.64$; $\text{Me}=26.04$.

$\text{C}_{29}\text{H}_{32}\text{O}_{11}(\text{CO}_2\text{Me})_2$ requires $\text{C}=58.75$; $\text{H}=5.63$; $\text{Me}=26.7$ per cent.

The acid melting at 238—240° is thus isomeric with that melting at 206—208°, which is simultaneously produced with it by the methylation of flavogallol.

By digestion with boiling 10 per cent. alcoholic potassium hydroxide for six hours, little or no hydrolysis occurred. The main bulk of the recovered substance after crystallisation from dilute alcohol melted at 236—237°, and that isolated from the mother liquors at 233—234°. The action of alcoholic potassium hydroxide at higher temperatures has not yet been studied.

When distilled with zinc dust flavogallol yielded a small amount of an oily hydrocarbon, which did not crystallise on long keeping.

Preliminary experiments on the methylation of flavogallol with diazomethane have yielded a methyl ether crystallising in yellow needles melting at above 305°, and this is reserved for investigation.

The employment of ferric sulphate and manganese dioxide in the presence of sulphuric acid as oxidising agents, to replace arsenic acid, for the production of flavogallol from gallic acid has been studied, but the results have hitherto been unsatisfactory. In the former case ellagic acid in considerable amount is produced, and it seems possible that this may prove to be the most economical method hitherto devised for the preparation of this dyestuff.* The crude substance, however, contains traces of iron, but this can be readily removed by the preparation of the acetyl derivative.

Note on Hexahydroxybenzophenone.

In the earlier stages of this work it was considered possible that a compound having the formula:

might be formed. Biginelli (*Gazzetta*, 1909, **39**, ii, 68) states that among other products dihexahydroxybenzophenonearsinic acid is formed by the interaction of arsenic and gallic acids. Such a compound might presumably be formed by the oxidation of hexahydroxybenzophenone, although, as experiment indicated that flavogallol does not result from such a process, the product of the reaction was not carefully examined. The details for the preparation of hexahydroxybenzophenone are (D.R.-P. 49149) not to be found in the literature, but it was ascertained that the following process gives good results: One part of gallic acid, 1 part of pyro-

* A provisional patent for this process has been secured.

gallol, and 3 parts of zinc chloride are heated at 120° . From the product the ketone is precipitated by means of water, and is recrystallised from water with the employment of animal charcoal. It consists of faintly yellow needles melting at $272-273^{\circ}$. (The above patent gives "above 270° .") (Found, C=56.15; H=3.65 per cent.) The *acetyl* derivative not previously described crystallises in needles melting at 132° .

Found: C=56.66; H=4.25.

$C_{25}H_{22}O_{13}$ requires C=56.60; H=4.15 per cent.

Summary.

It seems clearly established from the composition of the potassium salt, $C_{21}H_5O_{12}K_3$, and of the anhydrosulphate, $C_{21}H_6O_{11}, H_2SO_4$, and also from the molecular weight determination of the benzoyl derivative, that flavogallol possesses the formula $C_{21}H_8O_{12}$. It contains apparently also six hydroxyl groups, and the percentage of these, as indeed the percentage composition of flavogallol itself, it is interesting to note, are almost the same as those of ellagic acid itself. A further resemblance between flavogallol and ellagic acid is shown by their behaviour with boiling concentrated alkali hydroxide solutions, for whereas flavogallonic acid, $C_{21}H_{10}O_{13}$, and flavogallone, $C_{20}H_{10}O_{11}$, are produced from the former, luteoic acid (I) and the 2:2'-lactone of 4:5:6:2':3':4'-hexahydroxydiphenyl-2-carboxylic acid (II) are yielded by the latter:

With methyl sulphate and alkali and hydrolysis of the ester, ellagic acid gives the acid:

which is closely analogous to the acid $C_{29}H_{32}O_{11}(CO_2H)_2$ produced in the same way from flavogallol. On the other hand, flavogallol gives the sulphate referred to above, whereas oxonium sulphates of the ellagic acid group cannot be prepared, at least in the usual manner. Again, flavogallol differs from ellagic acid in being yellow and in possessing strong dyeing properties towards mordants. That flavogallol may possibly be produced from ellagic acid by condensation with a molecule of gallic acid seems feasible, not only on

account of its formula, but from the fact that during its preparation some ellagic acid is always produced. Important is the fact that whereas during methylation galloflavol takes up three molecules of water, a dicarboxylic acid only is formed, for this not only precludes the presence of a free carboxyl group in the colouring matter itself, but its possession of the following semi-symmetrical constitution:

which at one time was apparently feasible. On the other hand, it seems probable that a pyrone group is present in flavogallol, and that this during the somewhat drastic methylation process is opened, and thereby takes up the third molecule of water under discussion,

with subsequent methylation. If such is the case the following formula can be devised:

which assumes the oxidation of gallic acid to tetrahydroxybenzoic acid and its subsequent condensation with ellagic acid. This constitution explains the main properties of flavogallol, but cannot be considered completely satisfactory until the relationship of the isomeric acids simultaneously produced during the methylation process has been elucidated. Should this prove to be a case of geometrical isomerism, the formation of flavogallol from gallic acid will be of a more complex nature than is above conjectured, and its true nature will still involve investigation of a prolonged character.

Unfortunately, owing to other duties, further work on the subject may be delayed for some time, but it is desired to reserve the study of this substance, which will be again undertaken when opportunity occurs.

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