sponds to a loss of one molecule of water from each molecule of the dihydroxy ketone.

3. The polymerization taking place is probably closely related to that occurring in the formation of inulin from fructose.

New Haven, Connecticut

[Contribution from the Chemical Laboratory of the University of Illinois]

TRIHYDROXY-METHYL-ANTHRAQUINONES. I

By G. D. Graves[1] with Roger Adams

Received July 23, 1923

Hydroxy-methyl-anthraquinones and their methyl ethers occur widely, either in the free state or as glucosides, in the leaves, bark and roots of various plants, forming natural drugs and coloring matters. Six natural trihydroxy-methyl-anthraquinones have been reported in the literature, the most important being emodin, found in *Cascara sagrada*, *Frangula*, rhubarb and other plants. The probable structures which have been suggested for a few of these anthraquinones contain two hydroxyl groups in one ring, with the methyl and remaining hydroxyl in the other. A study of a practical method of synthesis of this type of substituted anthraquinones has been undertaken with the ultimate object of synthesizing the natural products.

In general, the best method available for the preparation of substituted anthraquinones with definite structures is the condensation of phthalic anhydride or its derivatives with benzene derivatives to form substituted benzoyl-benzoic acids; these can then be dehydrated to give anthraquinones. To prepare the desired trihydroxy-methyl-anthraquinones it was proposed to condense dimethoxy-phthalic anhydrides with the cresols, to dehydrate the resulting benzoyl-benzoic acids, and to demethylate the anthraquinones.

But few condensations involving methoxy-phthalic anhydrides have been reported. Bistrazycki[2] condensed 3,4-dimethoxy-phthalic anhydride (hemipinic anhydride) with anisole by means of aluminum chloride, using benzene as a solvent. The same anhydride was condensed by Weizmann[3] with veratrol, pyrogallol-trimethyl ether and *o*-xylene, using aluminum chloride with carbon disulfide as a solvent. Simonsen condensed this anhydride with *o*-cresol by means of aluminum chloride in acetylene tetrachloride.[4] With the exception of the condensation product of hemipinic anhydride with anisole, the exact structure of the resulting products

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[1] This communication is an abstract of a thesis submitted by G. D. Graves, DuPont Fellow for 1922–1923, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Bistrazycki, *Ber.*, **31**, 2796 (1898).

[3] Weizmann, *J. Chem. Soc.*, (a) **91**, 1626 (1907); (b) **93**, 435 (1908); (c) **105**, 2748 (1914).

[4] Simonsen, *ibid.*, **119**, 1339 (1921).

was not determined. In the particular case just mentioned it was shown without question that the carboxyl group adjacent to the methoxy group entered into reaction and that it condensed *para* to the methoxy group of the anisol.

Weizmann[3] condensed 4-methoxy-phthalic anhydride with *o*-xylene and *p*-cresol methyl ether by means of aluminum chloride in carbon disulfide, and with the free cresols by means of boric acid; Dimroth and Fick[5] condensed 3-methyl-5-methoxy-phthalic anhydride with hydroxy-hydroquinone triacetate by means of boric acid. The exact course of these condensations was also left undetermined. Moreover, in almost all of the condensations just reviewed the results were quite unsatisfactory.

A systematic study of the synthesis of such trihydroxy-methyl-anthraquinones of definite structures from methoxy-phthalic anhydrides must involve a thorough knowledge of four points: the best method for the initial condensation to form the benzoyl-benzoic acid derivatives; the best method for dehydrating the benzoyl-benzoic acids to form anthraquinones; the position in the cresol ring (whether *ortho* or *para* to the hydroxyl) taken by the entering benzoyl radical; the determination of which of the two carboxyl groups in an unsymmetrical phthalic anhydride reacts first with the cresol.

This research has involved a study of the condensation of 3,6-dimethoxy-phthalic anhydride with *o*-, *m*- and *p*-cresols. The structure of the benzoyl-benzoic acids formed has been determined and a study of their conversion into anthraquinones has been made. Preliminary work upon the condensation of 3,5-dimethoxy-phthalic anhydrides and cresols has been carried out.

On account of its ease of preparation, 3,6-dimethoxy-phthalic anhydride was chosen as a convenient methoxy-phthalic anhydride to employ in determining a satisfactory method of condensation with the various cresols. It has the further advantage of being symmetrical in structure, thereby eliminating a problem which is involved with unsymmetrical phthalic anhydrides, namely, the determination of which carboxyl reacts first with the cresol.

Many of the commoner methods of effecting condensation of phthalic anhydrides with various types of cresols gave unsatisfactory results with the 3,6-dimethoxy derivative. Thus, boric acid gave very poor yields, and the method of Ullmann and Schmidt,[6] using aluminum chloride and acetylene tetrachloride, caused the decomposition of the anhydride. Satisfactory results were obtained by using excess of cresol as a solvent[7] and a rather

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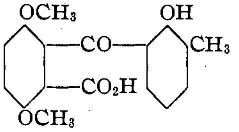
[5] Dimroth and Fick, *Ann.*, **411**, 315 (1915).

[6] Ullmann and Schmidt, *Ber.*, **52**, 2098 (1919).

[7] During the preparation of this manuscript an article has appeared by Widmer [*Helvetica Chim. Acta*, **6**, 421 (1923)] in which a similar method of condensation of certain phthalic anhydrides with phenols was employed with success.

large proportion of aluminum chloride. Under these conditions consistent results were obtained. 3,6-Dimethoxy-phthalic anhydride formed benzoyl-benzoic acid derivatives when condensed with the cresols and at the same time yielded diphenyl-phthalide derivatives as by-products.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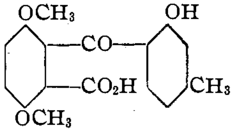
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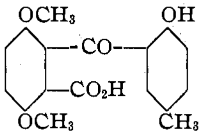
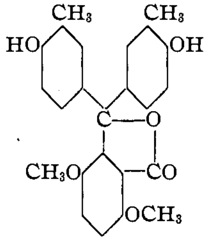

III

Acids I, II and III were obtained from *o*-, *m*- and *p*-cresols in 22%, 50% and 16% yields, respectively. In each reaction, a certain amount of diphenyl-phthalide derivative formed, a phthalein from both *o*- and *m*-cresol (IV and V) and a fluoran from *p*-cresol (VI).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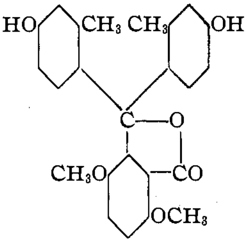
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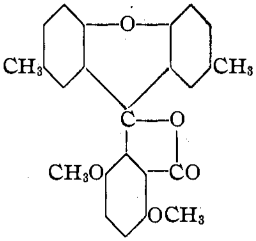
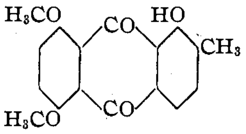
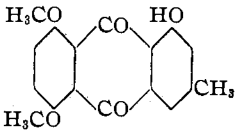

VI

Although the yields of benzoyl-benzoic acids appear small, the ease with which they could be separated and purified rendered the processes practicable.

For the dehydration of the benzoyl-benzoic acids to form anthraquinones, concd. or fuming sulfuric acid, sometimes with boric acid, has almost always been used. These reagents have proved satisfactory for many of the methoxy compounds studied. Concd. sulfuric acid with a trace of boric acid readily converted the condensation products from *o*- and *p*-cresol (I and III) into the corresponding anthraquinones (VII and IX) in 30% and 88% yields, respectively. In the case of the *m*-cresol, however, ordinary concd. sulfuric acid gave no results and only by the use of 7% fuming acid was it possible to obtain a 6% yield of the corresponding anthraquinone (VIII).


VII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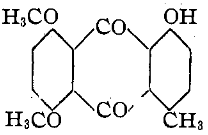
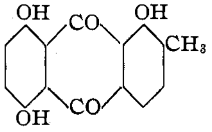
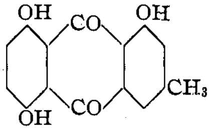

IX

A similar difficulty in the formation of anthraquinones from those benzoyl-benzoic acids which contain an *ortho* or *para* directing group *meta* to the position in which condensation must take place was observed by Weizmann.[8] This difficulty was particularly pronounced in the case of phenol derivatives probably on account of the ease with which sulfonation took place. Widmer[9] reports the formation of an anthraquinone from a *m*-cresol-benzoyl-benzoic acid by means of fuming sulfuric acid, but does not state his yield.

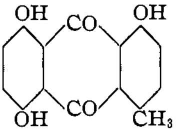
Under the conditions used for forming the anthraquinones from the benzoyl-benzoic acids, there was only a slight splitting of the methyl ethers during the condensation. In general, if temperatures higher than 100° were employed, the splitting of the ethers became appreciable and sulfonation took place to a greater extent. For the conversion of the methylated anthraquinones to the corresponding hydroxy anthraquinones (X, XI and XII), aluminum chloride in benzene may be used. It was found, however, that better results could be obtained by heating with constant-boiling hydrobromic acid in acetic acid solution.



X



XI



XII

The structure of the benzoyl-benzoic acids was determined by a comparison of the compounds obtained from the free cresols and the cresol ethers. The assumption was made that the entering group would be either *ortho* or *para* to the hydroxyl, since no condensations of this type have ever been known to enter the *meta* position. Nourrisson[10] and Weizmann[3] have already shown in a number of instances that phthalic anhydride and certain derivatives condensed with phenol ethers in the *para* position to the methoxyl group. Other investigators[11] have found that with free phenols the entering group goes *ortho* to the hydroxyl. By analogy, it seems reasonably certain that the structures of the compounds obtained in this investigation are correct as given. To confirm this conclusion the benzoyl-benzoic acids from 3,6-dimethoxy-phthalic anhydride and *o*- and *m*-cresols were methylated to give the trimethyl ethers. These products differed from the trimethyl ethers[12] obtained by the condensation of phthalic anhydride and cresol ethers, showing definitely that a different position was taken in each of the condensations. The condensation product from *p*-cresol, when methylated, gave the same substance as that obtained by the condensation product from *p*-cresol methyl ether. This would be expected because the *para* positions to the hydroxyl and methoxyl

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[8] Weizmann, Ref. 3a; *J. Chem. Soc.*, **95**, 279 (1909).

[9] Widmer, *Helvetica Chim. Acta*, **5**, 1 (1922).

[10] Nourrisson, *Ber.*, **19**, 2103 (1886).

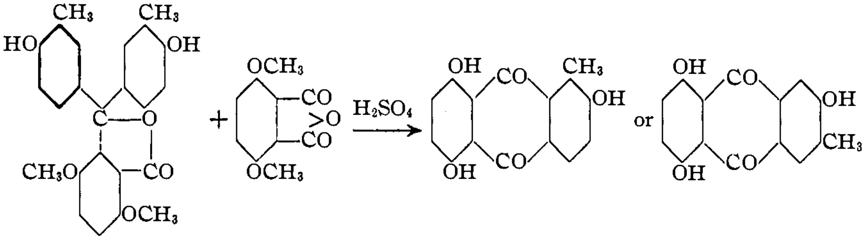
[11] Bentley, Gardner and Weizmann, *J. Chem. Soc.*, **91**, 1626 (1907). Ref. 6.

[12] See the following paper by Gardner and Adams.

groups in *p*-cresol and *p*-cresol methyl ether, respectively, are filled, and consequently the *ortho* position will be taken in both condensations.

Further evidence concerning the character of the condensation products came from a study of the decomposition of the phthaleins. It has already been mentioned that when the cresols were condensed with 3,6-dimethoxy-phthalic anhydride, diphenyl-phthalide by-products were obtained. The phthaleins from the *o*- and *m*-cresol condensations resemble phenol- and cresolphthalein very closely and the products, therefore, unquestionably have the structure represented by Formulas IV and V. In the case of the *p*-cresol, phthalein condensation must take place in the *ortho* position to the hydroxyl, thus allowing the formation of a fluoran by dehydration (VI). If, for any reason, the phthaleins had formed in the *ortho* position to the hydroxyl in either the *o*- or *m*-cresol condensations, it is extremely probable that fluorans would also have formed spontaneously.

The phthalein (IV) from the *o*-cresol condensation, when heated with 3,6-dimethoxy-phthalic anhydride in sulfuric acid, was converted according to the general method of Baeyer[13] into an anthraquinone derivative. This anthraquinone (XIII), however, should be different from that (X) obtained by the dehydration of the benzoyl-benzoic acid from 3,6-dimethoxy-phthalic anhydride and the free *o*-cresol and then demethylation of the anthraquinone produced; but it should be identical with the trihydroxy-methyl-anthraquinone[14] formed by the condensation of 3,6-dimethoxy-phthalic anhydride with *o*-cresol methyl ether, followed by condensation to the anthraquinone and demethylation.



XIII XIV

The experimental results were exactly those expected, the substances obtained checking up in every particular. The fact that the anthraquinone formed according to the above equation has the structure XIII and not the possible isomeric structure XIV is proved in the following paper.[14]

The condensation of 3,5-dimethoxy-phthalic anhydride and *m*-cresol (XV) was carried out. It went smoothly as might be expected from the

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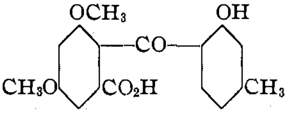
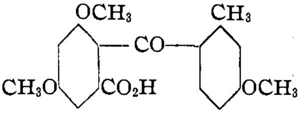
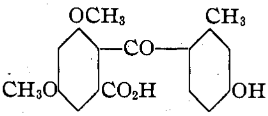
[13] Baeyer and Freude, *Ann.*, **202**, 137, 165 (1880).

[14] Gardner and Adams, THIS JOURNAL, **45**, 2455 (1923).

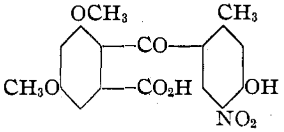
results with the 3,6-dimethoxy-phthalic anhydride and *m*-cresol. It seems probable that the condensation took place through the carboxyl adjacent to the methoxyl group judging by analogy to hemipinic anhydride condensations, but this has not yet been proved.

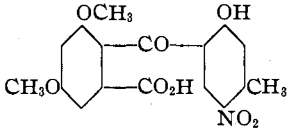

XV

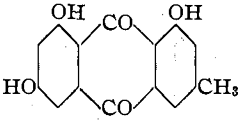

XVI


XVII

In order to show that condensation with the 3,5-dimethoxy-phthalic anhydride followed the same course as the condensation with 3,6-dimethoxy-phthalic anhydride, that is *ortho* to the hydroxyl and *para* to the methoxyl, 3,5-dimethoxy-phthalic anhydride was condensed with *m*-cresol methyl ether. A different trimethoxy-benzoyl-benzoic acid (XVI) was obtained from that formed by the methylation of the condensation product XV obtained from the free *m*-cresol. Proof of the structure of the condensation products was indicated by condensing 3,5-dimethoxy-phthalic anhydride with *o*-nitro-*m*-cresol, obtaining undoubtedly the acid XVIII because there would be practically no tendency for the benzoyl group to enter between the hydroxyl and methyl groups, and the other *ortho* position to the hydroxyl group is filled. This was not identical with the nitration product from the acid XV which, doubtless, then has the structure XIX. Had condensation with *m*-cresol gone *para* to the hydroxyl group to form the acid XVII, nitration would undoubtedly have given the acid XVIII.


XVIII


XIX


XX

The condensation product of 3,5-dimethoxy-phthalic anhydride and *m*-cresol (XV) should by dehydration and demethylation give emodin, provided the structure[15] XX which has been assigned to it after a careful study of its reactions is correct. When the ring closure was attempted, however, even poorer yields were obtained than with the *m*-cresol condensation product from 3,6-dimethoxy-phthalic anhydride. The product was methylated to form the trimethyl ether and this was compared with the trimethyl ether from emodin. Natural emodine and the synthesized dimethyl ether dissolved in alkali with the development of a red color. The synthetic trimethyl ether and that from cascara emodin dissolved

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[15] *Arch. Pharm.*, **250**, 301 (1912). Hesse [*Ann.*, **309**, 73 (1899)] had previously suggested that emodin might have the structure of the anthraquinone (XII) prepared as described above.

in concd. sulfuric acid with the same red color. The absorption spectra of the trimethyl ethers showed close similarity in their curves.

Although only a very small amount of the anthraquinone was obtained, all indications pointed toward its being an emodine derivative. Further work is now under way modifying this latter condensation in such a manner that the preparation of emodine in satisfactory yields should be possible and the constitution of this substance thus be proved without question.

Absorption Spectra of the Anthraquinones and Phthaleins[16]

The absorption spectra and color reactions of anthraquinones are accepted as furnishing very reliable evidence concerning the orientation of hydroxyl groups. Absorption-spectra curves for all of the anthraquinones prepared were obtained by the method recommended by the United States Bureau of Standards.[17,18] As abscissas are plotted wave lengths in (mμ) and as ordinates, $-\log_{10}$ transmission, which is defined as the ratio of the intensities of the light leaving to the light entering the absorbing layer, that is, $bck = -\log T$, where b is the concentration and c the thickness. The concentration of the solutions used was not determined so that the values of the ordinates have no significance; this does not interfere with the determination of the wave length of the absorption bands.

The absorption of slightly acid and alkaline alcoholic solutions was determined, the alcohol being used to accentuate the peaks of the curves.[19] The solutions for determination were prepared by adding to the alcoholic solutions of the anthraquinones just enough alcoholic alkali to change the color, or a drop of alcoholic hydrochloric acid. All of the curves of the anthraquinones having the quinizarin grouping (two α-hydroxyl groups in the same ring) have the same general form, the acid absorption band being nearer the blue than the alkaline band (Fig. 1). The maxima of the dimethoxy-hydroxymethyl-anthraquinones were 15–20mμ nearer the blue than those of the corresponding trihydroxy compounds (Fig. 2). The bands shifted toward the red in the 1,5,8-trihydroxy-anthraquinones as the methyl group moved from Position 2 to 4 to 3.

The phthaleins (IV and V) are very similar to phenolphthalein, giving blue-red colors with alkali. They are indicators, changing color at P_H values of 9.1 and 9.8, respectively, phenolphthalein and *o*-cresolphthalein changing at Sörensen values of 8.3 and 8.2, respectively.

The alkaline absorption curves were very similar, Phthaleins V and VI showing maxima at $\lambda 580$ and $\lambda 585$, respectively, while the maxima of

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[16] The authors are indebted to Mr. Wallace R. Brode for his assistance in determining the absorption spectra.

[17] *Bull.*, **440**, 128 (1922).

[18] A Keuffel and Esser spectrophotometer was used.

[19] Meek, *J. Chem. Soc.*, **109**, 554 (1916).

phenolphthalein and *o*-cresolphthalein are at λ555 and λ572, respectively. The curves are of the same general type as that obtained from phenolphthalein.

Experimental Part

Preparation of 3,6-Dimethoxy-phthalic Anhydride. 2,3-Dicyanohydroquinone, $C_6H_2(OH)_2(CN)_2$.—This substance was prepared by the method of Thiele and Meisenheimer[20] by the action of hydrocyanic acid on quinone in alcoholic solution. No product could be obtained by the method of Helferich.

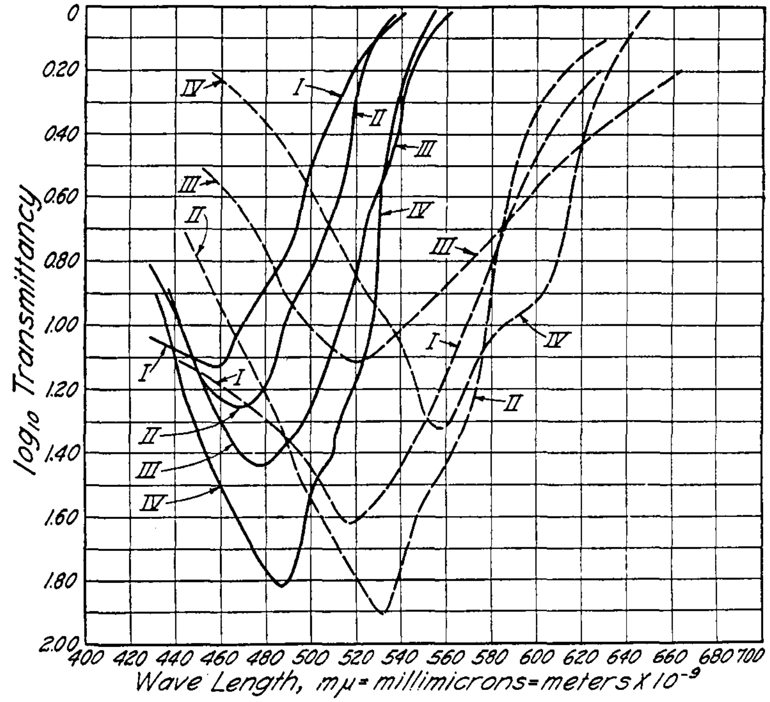

Fig. 1.—The solid lines represent the curves obtained from the alcoholic hydrochloric acid solutions, and the dotted lines the curves from the alcoholic sodium hydroxide solutions of the various anthraquinones. Readings were taken every 0.1 log *T*.

I. 1,5,8-Trihydroxy-2-methyl-anthraquinone. II. 2,5,8-Trihydroxy-1-methyl-anthraquinone. III. 1,5,8-Trihydroxy-4-methyl-anthraquinone. IV. 1,5,8-Trihydroxy-3-methyl-anthraquinone.

2,3-Dicyanohydroquinone Dimethyl Ether, $C_6H_2(OCH_3)_2(CN)_2$.—This substance has previously been made by the action of methyl iodide on 1,3-dicyanohydroquinone.[21] A solution of 60 g. of potassium hydroxide in 300 cc. of water was made in a 5-liter flask. Before this had cooled, 60 g. of dicyanohydroquinone was dissolved in it, and 240 g. of dimethylsulfate added. The flask was shaken vigorously until the reaction mixture

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[20] Thiele and Meisenheimer, *Ber.*, **33**, 675 (1900); *Frdl.*, VI, 113. Ger. pat. 117,005. Helferich, *Ber.*, **54**, 155 (1921).

[21] Thiele and Günther, *Ann.*, **349**, 59(1906).

solidified, and the yellow color changed to a white, indicating that the reaction had become acid. A second 300cc. portion of 20% potassium hydroxide was then added and the flask shaken vigorously. When the yellow color had again changed to a white, a third 300cc. portion of alkali was added, the flask shaken, and set aside to cool. After several hours the product was filtered off and washed thoroughly with cold water. The yield was 64 g. (85%) of a product which after a crystallization from acetic acid melted[22] at 275°.

3,6-Dimethoxy-phthalic Anhydride, $C_6H_2(OCH_3)_2(CO)_2O$.—Thiele and Günther[23] hydrolyzed dicyanohydroquinone dimethyl ether to the corresponding phthalimide by means of sulfuric acid. The phthalimide was converted to the anhydride by alcohol and hydrochloric acid.

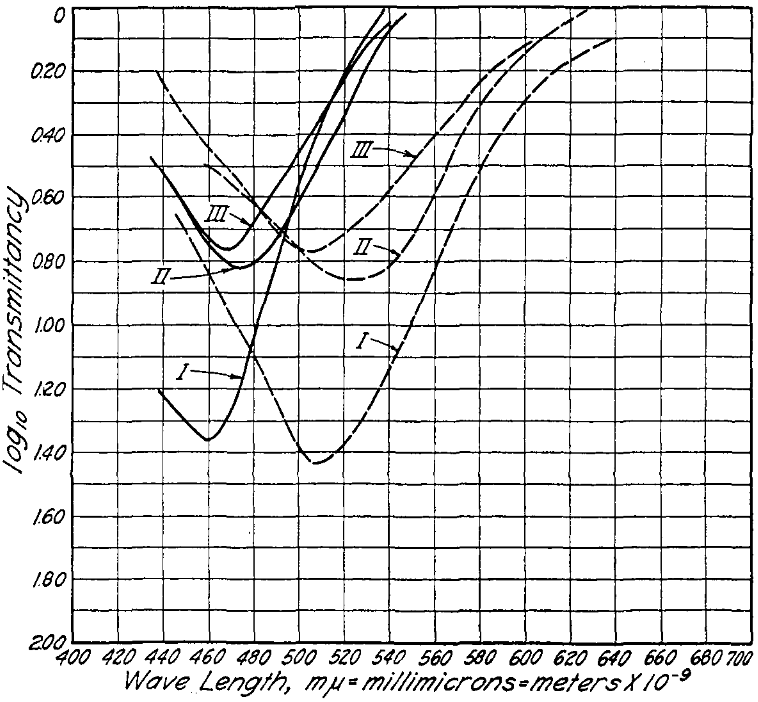

Fig. 2.—The solid lines represent the curves obtained from the alcoholic hydrochloric acid solutions, and the dotted lines the curves from the alcoholic sodium hydroxide solutions of the various anthraquinones. Readings were taken every 0.1 log T.

I. 1-Hydroxy-2-methyl-5,8-dimethoxy-anthraquinone. II. 1-Hydroxy-3-methyl-5,8-dimethoxy-anthraquinone. III. 1-Hydroxy-4-methyl-5,8-dimethoxy-anthraquinone.

The same results could not be obtained by following the directions given. It has been found possible to convert the nitrile directly to the anhydride by means of sulfuric acid.

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[22] All melting points given in this paper are corrected unless otherwise stated.

[23] Ref. 21. Zincke and Schmidt [*Ann.*, **286**, 37 (1895)] also obtained this anhydride by oxidation of 1,4,5,6-tetramethoxy-naphthalene with potassium permanganate.

A mixture of 60 g. of crude dicyanohydroquinone dimethyl ether, 300 cc. of concd. sulfuric acid, and 15 cc. of water was heated on the steam-bath for 1.5 hours. At the end of this time the solution was poured into 500 cc. of water and boiled for two hours. After the mixture had cooled the dimethoxy-phthalic anhydride was filtered off. The yield was 45 g. (64%) when the 2,3-dicyanohydroquinone dimethyl ether was of reasonably good grade. The product, after purification from benzene, melted at 259–261°. Sometimes the total amount did not precipitate at once. It was often necessary to evaporate the filtrate in an open dish overnight on the steam-cone in order to complete the hydrolysis of the nitrile. On the addition of water, the remainder of the anhydride was precipitated.

Condensation of 3,6-Dimethoxy-phthalic Anhydride with the Cresols

_p_-Cresol Derivatives. 3,6-Dimethoxy-2-(2-hydroxy-5-methylbenzoyl)benzoic Acid (III).—A mixture of 10 g. of 3,6-dimethoxy-phthalic anhydride, 10 g. of aluminum chloride, and 30 cc. of *p*-cresol was stirred mechanically and heated slowly up to 70° (oil-bath temperature) during the course of 4 hours, then held at that temperature for 9 hours. Water was cautiously added to decompose the excess of aluminum chloride, then 10 cc. of hydrochloric acid, and the excess of cresol was distilled with steam. The liquid remaining in the flask was decanted from the gummy residue which was dissolved in 10% sodium hydroxide solution. The alkaline solution was red, due to phthalein by-products. It was saturated with carbon dioxide to precipitate the phthalein (2 g.), which was filtered off. The filtrate was acidified with hydrochloric acid to precipitate the benzoylbenzoic acid; yield, 2.5 g. (16%). The product was purified from methyl alcohol, forming white plates; m. p., 218°.

Analyses. Subs., 0.1330; CO_2, 0.3146; H_2O, 0.0620. Calc. for $C_{17}H_{16}O_6$: C, 64.59; H, 5.06. Found: C, 64.51; H, 5.17.

Subs., 0.2243: required, 0.712 cc. of *N* NaOH. Calc.: neutr. equiv., 316. Found: 315.

2,7-Dimethyl-12,15-dimethoxyfluoran[24] (VI).—The phthalein by-product was dissolved in glacial acetic acid. The solution was treated with bone black and allowed to stand in the open for a week or more in order to avoid the separation of amorphous material by rapid precipitation and to allow crystals to form slowly. This material was recrystallized from glacial acetic acid, from dil. acetic acid, and from an acetone-ether mixture, to constant melting point. It was found to be insoluble in alkali, the acetic acid apparently having dehydrated the *ortho*-phthalein to a fluoran. The product formed white crystals that melted at 290°.

Analyses. Subs., 0.0791, 0.1029: CO_2, 0.2128, 0.2771; H_2O, 0.0378, 0.0493. Calc. for $C_{24}H_{20}O_5$: C, 74.22; H, 5.16. Found: C, 73.37, 73.43; H, 5.30, 5.32.

The material analyzed had not undergone the final purification with acetone and ether and apparently held acetic acid, so that the analyses were not as accurate as might be expected.

About 4 g. of uncondensed dimethoxy-phthalic anhydride was recovered by adding $^1/_3$ the volume of sulfuric acid to the liquors remaining over the gummy condensation product after steam distillation, and boiling the solution until the anhydride separated. Thus, from the 6 g. of anhydride that reacted, 4.5 g. of mixed product was isolated.

3,6-Dimethoxy-2-(2-methoxy-5-methylbenzoyl)benzoic Acid.—This substance was prepared in quantitative yields by refluxing 1 g. of the 3,6-dimethoxy-2-(2-hydroxy-5-methylbenzoyl)benzoic acid (III), 4 g. of potassium hydroxide, 5 g. of dimethyl sulfate and 75 cc. of water for an hour, filtering, and precipitating the trimethoxy compound with hydrochloric acid. It was recrystallized from dil. methyl alcohol, forming white

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[24] The nomenclature used is that recommended by *Chemical Abstracts*.

needles that melted at 203°. It proved to be identical with the compound made from 3,6-dimethoxy-phthalic anhydride and *p*-cresol methyl ether and described in the following paper by Gardner and Adams.

1-Hydroxy-4-methyl-5,8-dimethoxy-anthraquinone (IX).—Two g. of the 3,6-dimethoxy-2-(2-hydroxy-5-methylbenzoyl)benzoic acid (III), a pinch of boric acid, and 40 cc. of concd. sulfuric acid were heated on the steam-bath for one hour. The color changed from green to bluish red. The solution was poured over ice to precipitate the anthraquinone. It was purified by dissolving in alkali and reprecipitating with carbon dioxide; yield, 1.5 g. (88% of the calculated amount). The material was purified from acetone, forming red needles; m. p., 224°. It gave a red solution in alkali and a blue to blue-red color in concd. sulfuric acid, depending on the concentration.

Analyses. Subs., 0.0620: CO_2, 0.1566; H_2O, 0.0247. Calc. for $C_{17}H_{14}O_5$: C, 68.46; H, 4.70. Found: C, 68.89; H, 4.47.

1,5,8-Trihydroxy-4-methyl-anthraquinone (XII).—1-Hydroxy-4-methyl-5,8-dimethoxy-anthraquinone (IX) was refluxed with equal parts of constant-boiling hydrobromic acid and glacial acetic acid for 6 hours. The anthraquinone was precipitated by pouring the solution into water and purified by recrystallization from glacial acetic acid. It dissolved in alkali with the development of a blue-red color. In concd. sulfuric acid it showed a blue color in dilute solutions, and a blue-red color in greater concentrations.

Analyses. Subs., 0.0734: CO_2, 0.1784; H_2O, 0.0250. Calc. for $C_{15}H_{10}O_5$: C, 66.66; H, 3.70. Found: C, 66.29; H, 3.78.

o-Cresol Derivatives. **3,6-Dimethoxy-2-(2-hydroxy-3-methylbenzoyl)benzoic Acid (I).**—A mixture of 15 g. of 3,6-dimethoxy-phthalic anhydride, 24 g. of aluminum chloride and 60 cc. of *o*-cresol, stirred mechanically, was heated in an oil-bath at 75° for 19 hours. The products were worked up as in the *p*-cresol condensation: yield, 5 g. of benzoyl-benzoic acid (22%) and 18 g. of crude phthalein by-product. The benzoyl-benzoic acid was purified from methyl alcohol, forming white needles; m. p., 194°.

Analyses. Subs., 0.0748: CO_2, 0.1958; H_2O, 0.0352. Calc. for $C_{24}H_{22}O_6$: C, 70.33; H, 5.17. Found: C, 71.02; H, 5.22.

***o*-Cresol-3,6-dimethoxy-phthalein (2,2-Bis(4-hydroxy-5-methylphenyl)3,6-dimethoxyphthalide) (IV).**—This substance was purified in the same way as was 2,7-dimethyl-12,15-dimethoxy-fluoran (VI). It was treated, however, with hot alkali after recrystallization from acetic acid in order to saponify any acetyl derivative which might have formed. The product forms white needles; m. p., 258°. The substance is an indicator, changing from colorless to red at P_H 9.1. The alkaline absorption spectrum showed a peak at $\lambda 580 m\mu$.

Analyses. Subs., 0.0748: CO_2, 0.1948; H_2O, 0.0352. Calc. for $C_{24}H_{22}O_6$: C, 70.93; H, 5.17. Found: C, 71.02; H, 5.22.

3,6-Dimethoxy-2-(2-methoxy-3-methylbenzoyl)benzoic Acid.—This was prepared by methylation of 3,6-dimethoxy-2-(2-hydroxy-3-methylbenzoyl)benzoic acid (I) exactly as described under the preparation of 3,6-dimethoxy-2-(2-methoxy-5-methylbenzoyl)benzoic acid. It was purified from methyl alcohol, forming white needles; m. p., 178°. It was not identical with the benzoyl-benzoic acid obtained by condensing 3,6-dimethoxy-phthalic anhydride with *o*-cresol methyl ether, which has the constitution 3,6-dimethoxy-2-(4-methoxy-5-methylbenzoyl)benzoic acid.

Analyses. Subs., 0.1438: CO_2, 0.3430; H_2O, 0.0700. Calc. for $C_{18}H_{18}O_6$: C, 65.45; H, 5.45. Found: C, 65.12; H, 5.40.

Subs., 0.4642: required, 0.139 cc. of *N* NaOH. Calc.: neutr. equiv., 330. Found: 333.

o-**Cresol-3,8-dimethoxy-phthalein-dimethyl Ether, (2,2-Bis(4-methoxy-5-methylphenyl)3,6-dimethoxyphthalide).**—This substance was prepared by refluxing 1 g. of the corresponding phthalein with 5 g. of potassium hydroxide and 4 g. of dimethyl sulfate. The red color disappeared and the ether precipitated from the alkaline solution. It was filtered off and crystallized from acetic acid. It formed white needles; m. p., 202°. This was the same substance as that formed in the condensation of 3,6-dimethoxyphthalic anhydride with *o*-cresol methyl ether.

Analyses. Subs., 0.0808: CO_2, 0.2115; H_2O, 0.0433. Calc. for $C_{26}H_{26}O_6$: C, 71.99; H, 5.99. Found: C, 71.37; H, 5.95.

1-Hydroxy-2-methyl-5,8-dimethoxy-anthraquinone (VII).—This was prepared from 3,6-dimethoxy-2-(2-hydroxy-3-methylbenzoyl)benzoic acid, sulfuric acid and boric acid in the same way as was the 1-hydroxy-4-methyl-5,8-dimethoxy-anthraquinone (IX). It was recrystallized from glacial acetic acid, giving red needles; m. p., 165°. Its solution in alkali was red; in concd. sulfuric acid it was blue to blue-red, depending on the concentration.

Analyses. Subs., 0.0360: CO_2, 0.0910; H_2O, 0.0162. Calc. for $C_{17}H_{14}O_5$: C, 68.45; H, 4.69. Found: C, 68.43; H, 5.00.

1,5,8-Trihydroxy-2-methyl-anthraquinone (X).—This was prepared from the ether in the same manner as 1,5,8-trihydroxy-4-methyl-anthraquinone (XII) was prepared from its ether. It was purified from glacial acetic acid, forming red needles that sublimed at 250–60°. It dissolved in alkali with the development of a red, and in concd. sulfuric acid to give a blue-red solution.

Analyses. Subs., 0.1153: CO_2, 0.2821; H_2O, 0.0385. Calc. for $C_{15}H_{10}O_5$: C, 66.66; H, 3.70. Found: C, 66.74; H, 3.71.

2,5,8-Trihydroxy-1-methyl-anthraquinone (XIII).—A solution of 3 g. of *o*-cresol-3,6-dimethoxy phthalein (IV) and 1.5 g. of 3,6-dimethoxy-phthalic anhydride in 60 cc. of concd. sulfuric acid was heated for 40 hours in a bath at 125°. The anthraquinone (1 g.) was precipitated by pouring the solution into water and purified by precipitation from alkaline solution by carbon dioxide. It was recrystallized from chloroform, forming dark red needles; m. p., 270°. It was identical with the anthraquinone obtained by condensing 3,6-dimethoxy-phthalic anhydride with *o*-cresol methyl ether, dehydrating the benzoyl-benzoic acid thus obtained, and demethylating the anthraquinone. The substance dissolved in alkali and in concd. sulfuric acid to give a bluish red solution.

Analyses. Subs., 0.0795: CO_2, 0.1935; H_2O, 0.0255. Calc. for $C_{15}H_{10}O_5$: C, 66.68; H, 3.70. Found: C, 66.38; H, 3.58.

m-Cresol Derivatives. **3,6-Dimethoxy-2-(2-hydroxy-4-methylbenzoyl)benzoic Acid (II).**—A mixture of 20 g. of dimethoxy-phthalic anhydride, 40 g. of aluminum chloride, and 120 cc. of *m*-cresol, after standing for 2 hours, was heated for 12 hours in a bath at 75° with mechanical stirring. The products were worked up as in the analogous *p*-cresol condensation. The yield of crude benzoyl-benzoic acid was 15 g. (50%), and of phthalein, 17 g.

On recrystallizing the crude benzoyl-benzoic acid from methyl alcohol, two substances were obtained. The least soluble fraction formed white needles that melted at 233° and proved to be the above-mentioned substance.

Analyses. Subs., 0.0933: CO_2, 0.2204; H_2O, 0.0450. Calc. for $C_{17}H_{16}O_6$: C, 64.59; H, 5.66. Found: C, 64.44; H, 5.35.

Subs., 0.3767: required, 1.19 cc. of *N* NaOH. Calc.: neutr. equiv., 316. Found: 314.

3-Hydroxy-6-methoxy-2-(2-hydroxy-4-methylbenzoyl)benzoic Acid.—A second, much more soluble substance was obtained from the filtrates in the crystallization of the crude benzoyl-benzoic acid. This when pure melted at 147° (uncorr.) losing water and resolidifying. A second melting point was reached at about 179°. It was impossible to remove all the water by heating the substance at 120°. At 140° for 48 hours the water was removed completely and the product then melted at 187°. This was analyzed and shown to be a monomethyl ether. It probably has the structure assigned it, but this was not proved.

Analyses. Subs., 0.0557, 0.0860: CO_2, 0.1307, 0.2005: H_2O, 0.0245, 0.0391. Calc. for $C_{16}H_{14}O_6$: C, 63.57; H, 4.63. Found: C, 63.99, 63.57; H, 4.90, 5.02.

Hydrated subs. (m. p., 147°), 0.1468: CO_2, 0.3275, H_2O, 0.0697. Calc. for $C_{16}H_{14}O_6.H_2O$: C, 60.00; H, 5.00. Found: C, 60.84; H, 5.27.

Hydrated subs. 0.1673: required, 0.529 cc. of *N* NaOH. Calc.: neutr. equiv., 320. Found: 316.

3,6-Dimethoxy-2-(2-methoxy-4-methylbenzoyl)benzoic Acid.—This substance was prepared from each of the benzoyl-benzoic acids obtained from *m*-cresol, by the action of alkali and dimethyl sulfate, in a manner similar to the methylation of the analogous *o*- and *p*-cresols. The identity of the trimethyl ethers was proved by a mixed melting point. The product forms white needles from methyl alcohol; m. p., 189°.

Analyses. Subs., 0.0668: CO_2, 0.2078; H_2O, 0.0428. Calc. for $C_{18}H_{18}O_6$: C, 65.45; H, 5.45. Found: C, 65.24; H, 5.48.

Subs., 0.5355: required, 1.61 cc. of *N* NaOH. Calc.: neutr. equiv., 330. Found: 331.

***m*-Cresol-3,6-dimethoxy-phthalein; (2,2-Bis(4-hydroxy-6-methylphenyl)3,6-dimethoxy phthalein) (V).**—This substance was purified in the same way as was 2,2-bis-(4-hydroxy-5-methylphenyl) 3,6-dimethoxy-phthalein (IV). The product formed white needles; m. p., 271°. It is an indicator, the solution changing from colorless to red at P_H 9.8. The alkaline absorption spectrum showed a peak at $\lambda 585 m\mu$.

Analyses. Subs., 0.0708: CO_2, 0.1843; H_2O, 0.0338. Calc. for $C_{24}H_{22}O_6$: C, 70.93; H, 5.17. Found: C, 71.10; H, 5.30.

1-Hydroxy-3-methyl-5,8-dimethoxy-anthraquinone (VIII).—A solution of 5 g. of 3,6-dimethoxy-2-(2-hydroxy-4-methylbenzoyl)benzoic acid (II) and 5 g. of boric acid in 100 cc. of 7% oleum was heated for one hour on the steam-bath. The solution was poured over ice and extracted with chloroform. The chloroform solution was washed with sodium bicarbonate solution and again with alkali, which removed the anthraquinone. Acidification precipitated the substance. It was purified from glacial acetic acid, forming red needles; m. p., 172°; yield, about 0.25 g. (6%). Not enough of the substance was obtained to analyze, but it was converted to the corresponding trihydroxy compound (XI).

1,5,8-Trihydroxy-3-methyl-anthraquinone (XI).—The corresponding dimethyl ether (VIII) was refluxed with glacial acetic and hydrobromic acids for 5 hours. As the mixture cooled the trihydroxy compound separated. It was purified from glacial acetic acid, forming red needles; m. p., 227°. The substance dissolved in alkali, giving a blue solution, while the dimethyl ether gave a red solution. Both gave blue-red solutions in concd. sulfuric acid.

Preparation of 3,5-Dimethoxy Phthalic Anhydride. The Acid Barium Salt of 3,5-Disulfo-benzoic Acid.—This substance was prepared by a slight modification of the method of Barth[25] and Hohenemser.[26] A mixture of 900 g. of benzoic acid, 300 g. of phosphorus pentoxide, and 1500 cc. of 50% oleum was sealed in an iron bomb and heated in an electric furnace for 5 hours at 240–250°. After it had cooled, the bomb was

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[25] Barth, *Ann.*, **159**, 222 (1871).

[26] Hohenemser, *Ber.*, **35**, 2305 (1902).

opened and the contents were poured into an excess of barium carbonate suspended in water. The mass was stirred thoroughly, heated to boiling, and filtered. The barium sulfate cake was washed with three portions of boiling water, being removed from the filter and stirred thoroughly with each portion of water. The combined filtrates were acidified with a large excess of hydrochloric acid and set aside overnight to crystallize. The acid barium salt crystallized in light yellow prisms; yield, 2630 g. (85%).

3,5-Dimethoxy-benzoic Acid.—The fusion of the sodium salt of benzoic acid-3,5-disulfonic acid with potassium hydroxide to give 3,5-dihydroxy-benzoic acid was described by Barth.[26] The methylation of this substance with dimethyl sulfate was described by Bülow.[27] A combination of these procedures was developed.

The acid barium salt isolated as described above was fused directly with 1.5 times its weight of potassium hydroxide for 8 hours at 200–220° (melt temperature). The fusion pot was heated in a bath of Wood's metal (240–250°). Efficient mechanical stirring was provided, and the fusion mixture was kept fluid by the addition of water from a dropping funnel during the entire fusion period and by the passing of a current of steam over the surface of the melt.

The fused mixture while still hot and pasty was transferred to a large flask containing enough water to dissolve the alkali used. The contents of the flask were heated to boiling and, after the flame was removed, one part by weight of dimethyl sulfate was added slowly from a dropping funnel through the reflux condenser. Care must be taken not to add the dimethyl sulfate too fast since the reaction is exothermic. About 2 hours should be taken for the addition. It is well to stir the reaction mixture with a current of air during the methylation, since any layer of dimethyl sulfate which may collect is likely to react too suddenly.

The mixture was refluxed gently for 2 hours after the addition of the dimethyl sulfate to saponify any ester which might have formed. It was then filtered hot and the residue of salts was removed from the filter and washed with 3 portions of hot water. The combined filtrates, while still hot, were poured into an excess of hydrochloric acid to precipitate the dimethoxy-benzoic acid, which was filtered off at once. The yield obtained varied over a wide range, averaging 30%. In runs using 375 g. of barium salt, as high as 60% yields were obtained, while in kilogram runs no higher than 25% yields were obtained. Doubtless the higher yields could be realized if an autoclave fusion pot were used, since the chief difficulty seemed to be a drying out of the fusion mixture and consequent elimination of carbon dioxide from the carboxyl group.

Many fusions were made, varying in both time and temperature. When a shorter fusion period was used the yields were smaller, while longer fusion resulted in a splitting out of carbon dioxide. Lower temperatures resulted in incomplete replacement while higher temperatures resulted in a loss of carbon dioxide.

The use of sodium instead of potassium hydroxide resulted in lower yields. No greater yields were obtained by fusing the sodium or potassium salt rather than the barium salt.

3,5-Dimethoxy-ethyl Benzoate.—This was made by esterification of the corresponding acid in the usual way. The product boiled at 199–200° at 50 mm.

3,5-Dimethoxy-trichloromethyl-phthalide.—Dimethoxy-benzoic ester was converted to dimethoxy-phthalic acid by the method of Fritsch.[28] Since certain details were discovered which made the preparation more easily carried out, the directions are repeated below.

A mixture of 630 g. of concd. sulfuric acid and 70 g. of water was added without

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[27] Bülow, *Ber.*, **35**, 3901 (1902).

[28] Fritsch, *Ann.*, **296**, 357 (1897).

cooling to 140 g. of ester and 115 g. of chloral hydrate. The solution was stirred vigorously. Separation of the trichloromethyl-phthalide soon began. The stirring was continued overnight, after which a liter of water was stirred slowly into the suspension. The solid which separated was filtered off, washed with hot 50% alcohol and dried; yield, 158 g. (93%).

Much time was spent in an effort to condense dimethoxy-benzoic acid, rather than its ester, with chloral hydrate. The ester has been most generally used[29] but the use of the free acid has been found successful in some cases.[30] It was found, however, that the chloral condensation product was not the expected substance, and that the product obtained from it in the succeeding steps could not be identified with the desired derivatives. Work with the free acid was, therefore, abandoned.

3,5-Dimethoxy-phthalide Carboxylic Acid.—To a solution of 160 g. of sodium hydroxide in 790 cc. of water was slowly added 158 g. of trichloromethyl-phthalide. Solution began with evolution of heat and was completed by warming for several hours at 80–90°. The solution was filtered and acidified. On standing, the phthalide carboxylic acid was completely precipitated; yield, 103 g. (93%).

3,5-Dimethoxy-phthalide.—The phthalide acid (100 g.) was melted at 180–185° in an oil-bath until no more carbon dioxide was evolved. The product was not further purified; yield, 78 g. (95%).

3,5-Dimethoxy-phthalic Acid.—A solution of 78 g. of dimethoxy-phthalide in 40 g. of sodium hydroxide was oxidized slowly at room temperature with 2860 cc. of 3% potassium permanganate solution. The mixture was stirred mechanically overnight. After the oxidation was complete, the solution was heated to 50°, decolorized with alcohol, filtered, evaporated to a volume of 500 cc. and acidified. The dimethoxy acid precipitated on standing; yield, 84 g. (quantitative).

3,5-Dimethoxy-phthalic Anhydride.—One part of dimethoxy-phthalic acid was refluxed for 2 hours with 4 parts of acetic anhydride. As the mixture cooled, part of the anhydride crystallized in a pure condition. Evaporation in a vacuum and cooling yielded another pure fraction. Finally, the solution was evaporated to dryness and the anhydride recrystallized by dissolving it in benzene and precipitating with petroleum ether. The yield was practically quantitative.

Condensation of 3,5-Dimethoxy-phthalic Anhydride with *m*-Cresol and *m*-Cresol Methyl Ether

3,5-Dimethoxy-2-(2-hydroxy-4-methylbenzoyl)benzoic Acid (XV).—A mixture of 20 g. of 3,5-dimethoxy-phthalic anhydride, 40 g. of aluminum chloride, and 120 cc. of *m*-cresol contained in a 500cc. flask was allowed to react for 2 hours without heating. It was then placed in a bath at 70° and stirred mechanically for 12 hours. The products were worked up as were the analogous compounds previously described. The acid (XV) crystallized from methyl alcohol in white needles; m. p., 233°. The yield of benzoyl-benzoic acid was 14 g. (45%) and of crude phthalein was 14 g.

Analyses. Subs., 0.0886: CO_2, 0.2093; H_2O, 0.0405. Calc. for $C_{17}H_{16}O_6$: C, 64.59; H, 5.06. Found: C, 64.43; H, 5.01.

Subs., 0.1300: required, 0.413 cc. of *N* NaOH. Calc.: neutr. equiv., 316. Found: 315.

3,5-Dimethoxy-2-(2-methoxy-4-methylbenzoyl)benzoic Acid.—This substance was prepared by methylation of the dimethoxy acid (XV) in the manner previously described under analogous compounds. It was purified from methyl alcohol, forming white needles; m. p., 219°.

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[29] Meldrum, *J. Chem. Soc.*, **99**, 1712 (1911). Bargellini and Molina, *Atti accad. Lincei*, [5] **21**, II, 146 (1912). Herzig, *Ann.*, **421**, 283 (1920).

[30] Meldrum, *J. Chem. Soc.*, **117**, 964 (1920).

3,5-Dimethoxy-2-(4-methoxy-2-methylbenzoyl)benzoic Acid (XVI).—By condensing *m*-cresol methyl ether with 3,5-dimethoxy-phthalic anhydride, this substance was obtained in 40% yield. It was recrystallized from dil. methyl alcohol, forming white needles; m. p., 233°.

A mixed-melting-point determination showed that this acid is different from the isomer (m. p., 219°) obtained by methylating the compound (XV), indicating that the rule of condensation *ortho* to hydroxyl and *para* to methoxyl groups holds for 3,5- as well as 3,6-dimethoxy phthalic anhydrides.

3,5-Dimethoxy-*m*-cresol-phthalein (2,2-Bis-(4-hydroxy-6-methylphenyl)3,5-dimethoxy Phthalide.—It was found impossible to crystallize this compound free from tarry impurities by the methods used successfully with the other phthaleins.

Attempts at Preparation of Emodin Dimethyl Ether.—A solution of 5 g. of 3,5-dimethoxy-2-(2-hydroxy-4-methylbenzoyl)benzoic acid (XV) and 5 g. of boric acid in 50 cc. of 7% oleum was warmed on the steam-cone for an hour. The anthraquinone was purified as described under the preparation of 1-hydroxy-3-methyl-5,8-dihydroxy-anthraquinone. A very small amount was obtained, sulfonation apparently taking place to a considerable extent. The product crystallized from dil. alcohol in yellow needles; m. p., about 185°. Its solution in alkali was red. This product was refluxed with excess of dimethyl sulfate and alkali for 2 hours. The trimethoxy compound was extracted from the alkaline solution with ether. On evaporation of the ether it was obtained in yellow needles; m. p., about 175–180°. Not enough was obtained to purify. It dissolved in concd. sulfuric acid with the development of a red color. This crude trimethyl ether was used for the absorption spectrum determinations.

Nitration of 3,5-Dimethoxy-2-(2-hydroxy-4-methylbenzoyl)benzoic Acid (XV). 3,5-Dimethoxy-2-(2-hydroxy-4-methyl-5-nitrobenzoyl)benzoic Acid (XIX).—A solution of 4 g. of the benzoyl-benzoic acid in 80 cc. of glacial acetic acid was treated with 1 cc. of nitric acid (sp. gr. 1.42) in 20 cc. of glacial acetic acid at 50–60° for 3 hours. On adding water the nitro acid was obtained in quantitative yield. It was recrystallized from alcohol in light yellow needles; m. p., 241°.

Analyses. Subs., 0.0823: CO_2, 0.1697; H_2O, 0.0325. Calc. for $C_{17}H_{15}O_8N$: C, 56.51; H, 4.15. Found: C, 56.23; H, 4.38.

Subs., 0.1195: required, 0.642 cc. of *N* NaOH. Calc.: neutr. equiv., 361, or 180 if the OH were neutralized. Found: 186.

Condensation of 3,5-Dimethoxy-phthalic Anhydride with *o*-Nitro-*m*-cresol. 3,5-Dimethoxy-2-(4-hydroxy-2-methyl-5-nitrobenzoyl)benzoic Acid (XVIII).—A mixture of 10 g. of 3,5-dimethoxy-phthalic anhydride, 35 g. of *o*-nitro-*m*-cresol,[31] and 20 g. of aluminum chloride was heated and stirred in a bath at 75° for 20 hours. The excess of nitrocresol was steam distilled and the product worked up as before; yield of acid, 9 g. (62%). It was purified from methyl alcohol, forming white needles; m. p., 181°. Only a trace of phthalein derivative was obtained.

Analyses. Subs., 0.1098: CO_2, 0.2299; H_2O, 0.0446. Calc. for $C_{17}H_{15}O_8N$: C, 56.51; H, 4.15. Found: C, 57.00; H, 4.51.

Subs., 0.1143: required, 0.620 cc. of *N* NaOH. Calc.: neutr. equiv., 361; or 180 if the OH were neutralized. Found: 184.

Summary

1. A satisfactory method has been developed for the condensation of phthalic anhydride containing methoxyl groups with cresols to form substituted benzoyl-benzoic acids.

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[31] Keller, *Ann.*, **259**, 223 (1890).

2. 3,6-Dimethoxy-phthalic anhydride was condensed with *o*-, *m*- and *p*-cresols.

3. The benzoyl-benzoic acids thus formed were condensed by means of sulfuric acid to the corresponding trihydroxy-methyl-anthraquinones or their ethers.

4. The exact structures of the benzoyl-benzoic acid derivatives and of the anthraquinones have been established: first, by comparison with the isomeric substances (described in the following paper) prepared by condensing 3,6-dimethoxy-phthalic anhydride with cresol ethers; and second, by comparison with the trihydroxy-methyl-anthraquinone of known structure prepared from 3,6-dimethoxy-*o*-cresolphthalein.

5. It has been established that the entering group takes the *ortho* position to the hydroxyl in the cresols.

6. The anthraquinones from the benzoyl-benzoic acids derived from *o*- and *p*-cresol form readily, and those from the *m*-cresol only with great difficulty.

7. A preliminary study of the condensation of 3,5-dimethoxy-phthalic anhydride with *m*-cresol and of the formation of the anthraquinone from the resulting benzoyl-benzoic acid derivative has been made, with the object of the synthesis and proof of the structure of the natural drug emodin.

8. The course of the condensation of the 3,5-dimethoxy-phthalic anhydride with *m*-cresol was determined by a comparison of the products obtained with this cresol and with *m*-cresol methyl ether and *o*-nitro-*m*-cresol.

9. The absorption spectra of the anthraquinones and phthaleins were obtained.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

TRIHYDROXY-METHYL-ANTHRAQUINONES. II

BY J. H. GARDNER[1] WITH ROGER ADAMS

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In the previous paper[2] a satisfactory method was developed for the condensation of certain phthalic anhydrides containing methoxyl groups with cresols. The resulting benzoyl-benzoic acids were converted to substituted anthraquinones. A detailed study of the condensation of 3,6-dimethoxy-phthalic anhydride with cresols showed that the reactions took place very readily by means of anhydrous aluminum chloride and an excess of cresol as a solvent with the formation of products in which the ketonic carbonyl of the benzoyl-benzoic acid was *ortho* to the hydroxyl group of the cresol. Sulfuric acid in the presence of a little boric acid

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[1] This communication is an abstract of a thesis submitted by J. H. Gardner in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Graves and Adams, THIS JOURNAL, **45**, 2439 (1923).