

Unpublished results from this Laboratory show that the foregoing statement is probably true in some cases at least. Of course, the converse may also be true, that is, different salts may extract the same amount of nitrogen from a meal and yet may not be extracting a chemical entity.

This study is being extended to include other seeds known to yield crystalline globulins, and different salts at varying concentrations are also being used.

Conclusions

1. The alkali halide salts in normal concentration all extract the same amount of nitrogen from orange seed meal. There is no evidence for the existence of a lyotropic series in the extracting power of different salts on orange seed meal.

2. The protein isolated from orange seed meal by extraction with different salts is probably the same in every case.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

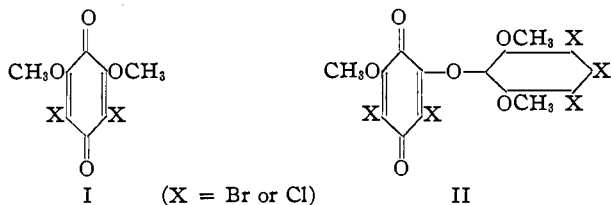
A NEW TYPE OF OXIDATION PRODUCT DERIVED FROM QUINONES¹

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During a study of the oxidation of tribromo- and trichloropyrogallol-2, 6-dimethyl ether, Hunter and Levine² showed that when treated with any of a number of oxidants, these phenols gave both a yellow mononuclear quinone (I) and a red (or purple) phenoxy quinone (II).



However, when the oxidations were carried out with chromium trioxide in 50% acetic acid³ there were obtained, in addition to these expected products, small amounts of colorless compounds. These compounds seemed to be of a nature different from any of the oxidation products previously isolated during this series of investigations. Their further study therefore

¹ The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Murray M. Sprung in partial fulfillment of the requirements for the degree of Doctor of Philosophy, September, 1928.

² Hunter and Levine, *THIS JOURNAL*, **48**, 1608 (1926); cf. Hunter and Morse, *ibid.*, **48**, 1615 (1926).

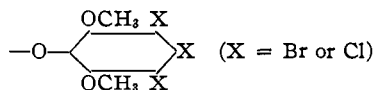
³ Hunter and Levine, *Ref. 2*, p. 1612.

appeared to be of interest, and was undertaken, leading to the results described in the present paper.

A quantity of each of the colorless oxidation products was prepared and very carefully purified. On subjecting them to ultimate analyses and molecular weight determinations, a pair of empirical formulas was obtained which at first sight do not seem to be related. For the colorless oxidation product of tribromopyrogallol-2,6-dimethyl ether the best formula is $C_{23}H_{22}O_{15}Br_8$ (calculated molecular weight, 1238); for the colorless oxidation product of trichloropyrogallol-2,6-dimethyl ether the best formula is $C_{14}H_{11}O_8Cl_4$ (calculated molecular weight, 449). Nor do these formulas have any apparent relation to either of the normal products of oxidation of the phenols, for the mononuclear quinones have the composition, $C_8H_6O_4Br_2(Cl_2)$, while the dinuclear quinones have the composition, $C_{18}H_9O_8Br_5(Cl_5)$. Furthermore, the colorless substances are much richer in oxygen than any of the expected products. We were therefore led to suspect that oxidative rupture had occurred at some stage of these oxidations.

It was later discovered that the colorless compounds could also be obtained directly from the corresponding dinuclear quinones (II) of Hunter and Levine, by oxidizing the latter with chromium trioxide under conditions identical with those used in the synthesis of the colorless compounds from the trihalogenated pyrogallol-dimethyl ethers, showing that the colorless compounds are probably secondary products, derived from oxidation of the primary quinones.

A second very significant reaction was found to occur when dilute alkali was added to the colorless substances. Both compounds went into solution quite rapidly. On acidification of the solution, immediate precipitates of colorless materials were produced which were, *in both cases, different from the starting materials*. Investigation proved them to be the *original trihalogenated pyrogallol-dimethyl ethers* from which the colorless oxidation products, themselves, are derived. This action was very rapid, and in the case of the brominated compound it was demonstrated that the yield of phenol obtained was constant, that is, 63.2% of the weight of the brominated oxidation product used. It is therefore evident that the white compounds contain the residue

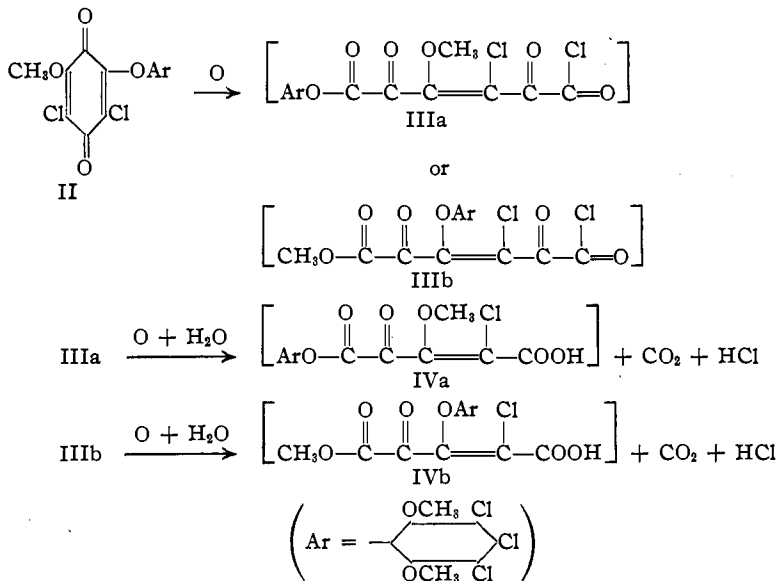


and that this residue attaches to the rest of the molecule by some easily saponifiable linkage, for which only two simple possibilities suggest themselves: an ester linkage, and an acetal or hemiacetal linkage.

If now we consider the chlorinated oxidation product first (because of its simpler analytical formula, $C_{14}H_{11}O_8Cl_4$) we may arrive at a theory for its formation on the basis of the above information only. Three significant

facts must be accounted for at this time: first, one carbon atom is lost when the white compound is produced from the phenoxy quinone; second, the colorless compound still contains the phenoxy group as a distinct unit, easily lost by saponification; third, when the phenoxy residue is removed from the colorless compound, the resulting residue is easily and apparently completely destroyed by the reagent.⁴

A series of steps leading from the purple dinuclear quinone (II) to a product (IV) of the desired empirical composition is outlined below.



On the basis of the well-known oxidation of quinone to maleic acid,⁵ it might reasonably be expected that if the chlorinated phenoxy quinone (II) were subjected to the action of a sufficiently strong oxidant, the first effect would be to split the quinonoid ring open at one of the double bonds. One oxygen atom would add to each side of the ruptured bond, and there would result one of two compounds, IIIa or IIIb, depending upon which double bond of the quinone ring was ruptured. Either of the hypothetical compounds thus produced is a di-acid derivative: the first a substituted phenyl ester and an acid chloride; the second a methyl ester and an acid chloride. It is important, also, that each is *twice an alpha oxo acid* derivative, that is, an alpha oxo acid chloride and an alpha oxo ester. Now alpha oxo esters are quite stable toward oxidation (pyruvic ester, for example). However, we have been able to find no mention in the literature

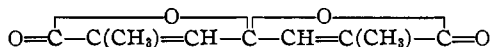
⁴ Many attempts were made to isolate this residue after the "hydrolytic" reaction, but in no case could a single, homogeneous product be obtained. In all such cases, large amounts of halogen acid and some oxalic acid were found in the solution.

⁵ Kempf, *Ber.*, 39, 3719 (1906).

of the existence of alpha oxo acid chlorides. We consider it quite probable that such a compound, under the conditions of our experiments, would either be hydrolyzed to the free alpha oxo acid and then further oxidized, or oxidized directly as the oxo chloride. In either case, we should expect to find the carbon chain lessened by one carbon atom, to give a C_{14} compound. There would result, then, a complicated alpha oxo ester of an unsaturated 5 carbon di-acid (IVa or IVb).

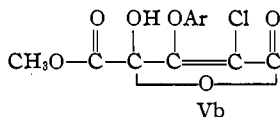
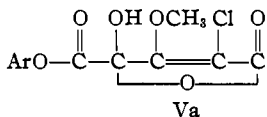
The formulas IVa and IVb are of course isomeric, and correspond empirically to the composition $C_{14}H_{10}O_8Cl_4$. The experimental formula for the chlorinated colorless oxidation product is $C_{14}H_{11}O_8Cl_4$, identical with the above except for one hydrogen, a discrepancy which could easily be accounted for by a relatively slight error in hydrogen analysis.

However, our colorless compound has no effect upon saturated sodium hydrogen sulfide, and it, therefore, cannot be a carboxylic acid. Furthermore, it forms a well-defined acetyl derivative, which can be crystallized unchanged from ethyl alcohol, and is, therefore, not a mixed anhydride. We conclude from this that our acid, which would be a gamma oxo acid, exists in the oxy-lactone form, similar to the alternate formula for levulinic acid, $\text{CH}_3\text{C}(\text{OH})\text{CH}_2\text{CH}_2\text{C}=\text{O}$. Levulinic acid, too, is known to form an acetyl derivative, which also can be crystallized unchanged from ethyl alcohol, and to which the formula $\text{CH}_3\text{C}(\text{OCOCH}_3)\text{CH}_2\text{CH}_2\text{C}=\text{O}$ has been assigned.⁶ Unsaturated gamma oxo acids show the same tendency toward lactone formation. Thus acetone dipyrucic acid exists only in the form of a dianhydro compound to which the formula



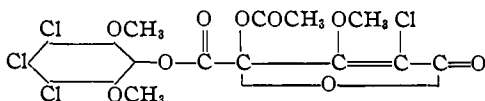
has been assigned.

If our white oxidation product is a gamma oxy lactone, it may have either of the following formulas



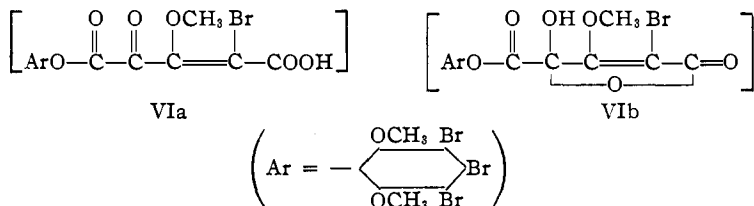
To choose between these two formulas, it need only be remembered that the substituted phenoxy group is easily saponified, the methoxy group not. Therefore the substituted phenyl group must be tied by an ester linkage, and the methyl group by an ether linkage. All this evidence points to formula Va as representing the most probable structure for the colorless oxidation product of trichloropyrogallol-2,6-dimethyl ether. Its acetyl derivative would then have the structure

⁶ Bredt, *Ann.*, **236**, 225 (1886); *ibid.*, **256**, 314 (1890); Autenrieth, *Ber.*, **20**, 3191 (1887); Thiele, Tischbein and Lussow, *Ann.*, **319**, 184 (1901).



The colorless brominated oxidation product is similar to the chlorinated compound both as regards mode of formation and chemical behavior. The two compounds behave analogously in respect to a variety of chemical reagents. However, a series of carefully checked analytical data and molecular weight determinations has established the previously mentioned C_{28} formula, *i. e.*, $C_{28}H_{22}O_{15}Br_3$. Assuming the hydrogen analyses to be high again, we may modify this formula (for reasons which will shortly be clear) to $C_{28}H_{18}O_{15}Br_3$. If the brominated compound were exactly analogous to the chlorinated compound it would have the composition $C_{14}H_{10}O_8Br_4$. It is then evident that the formula $C_{28}H_{18}O_{15}Br_3$ represents a *dimolecular anhydride* of the simpler formula $C_{14}H_{10}O_8Br_4$.

The most reasonable mechanism by which to explain the formation of the brominated oxidation product is as follows: as in the case of the analogous chlorine compound, a monomolecular derivative is first formed. This may possess either the free acid structure (VIa), or the gamma oxy-lactone form (VIb).



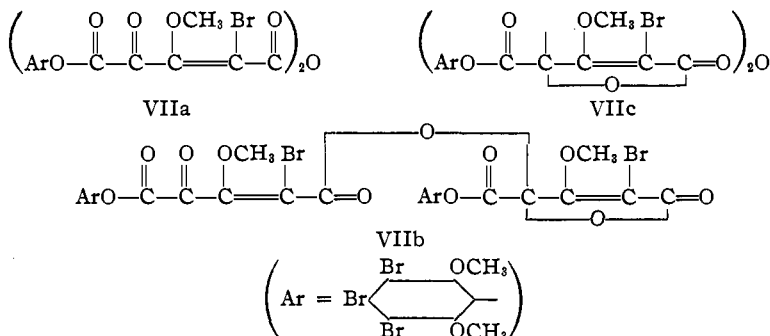
But, as we have previously mentioned, there is a definite tendency for the hydroxyl group of a gamma oxy lactone to become esterified through dilactone formation. When this is impossible, dehydration sometimes occurs, by loss of the hydroxyl group along with an alpha hydrogen atom. The above hypothetical gamma oxo acid, however, has neither a second gamma carboxyl group nor an alpha hydrogen atom. The tendency toward reaction can only be satisfied, in this case, by elimination of water between two molecules,⁷ and this leads to the *dimolecular anhydride* which is actually isolated.⁸

There are at least three possible mechanisms by which the formation of a dimolecular anhydride may be explained, assuming that such anhydride formation actually does occur. There may be formed in the solution both

⁷ Stating this in another way, the only "available" hydrogen atom which can split out with the hydroxyl group of one molecule is the hydroxyl hydrogen of a second molecule.

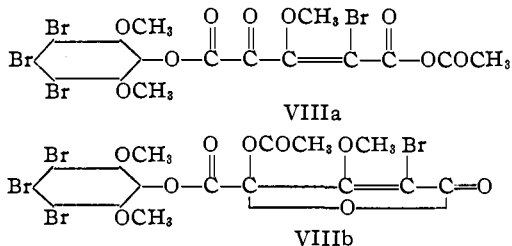
⁸ The chloro and the bromo hypothetical intermediates, then, behave differently under the same experimental conditions. It is not entirely clear just why they should do so; but there is, on the other hand, no *a priori* reason to assume that they must behave the same.

the free acid form and the lactone form (formulas VIa and VIb). The free acid, instead of becoming esterified intramolecularly, as in the case of the analogous chloro compound, may become esterified intermolecularly, and this may occur either by union with a second molecule of the free acid itself, or by union with a molecule in the oxy lactone form. In the first case, the ordinary type of acid anhydride (formula VIIa) would result; in the second case, the product would be an unsymmetrical molecule (formula VIIb).



The third possibility is that only the lactone form of the acid (VIb) is involved in intermolecular anhydride formation. The dimolecular anhydride would then have the structure VIIc. It is possible to eliminate the first of these structures (formula VIIa) by virtue of the fact that the compound can be crystallized unchanged from ethyl alcohol, and therefore cannot be a normal acid anhydride. It is impossible at present to make a choice between formulas VIIb and VIIc.

The colorless oxidation product of tribromopyrogallol-dimethyl ether, like the analogous chloro compound, forms an acetyl derivative, when subjected to the action either of acetic anhydride and glacial acetic acid, or acetyl chloride and concentrated sulfuric acid.⁹ This acetyl derivative has the composition $\text{C}_{16}\text{H}_{12}\text{O}_9\text{Br}_4$, and is therefore derived from the *monomeric form* of the acid. Its structure may be either that of a mixed anhydride VIIIa or an acetylated gamma oxy lactone VIIIb, again.

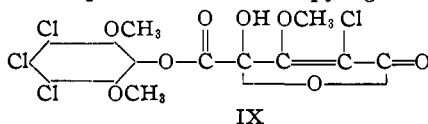


⁹ The hydrogen necessary for this reaction may come from the sulfuric acid used during the acetylation. Very little water is required, due to the very large molecular weight of the colorless oxidation product.

We are once more inclined to favor the gamma oxy-lactone formula (VIIIb), by analogy with the acetyl derivative of levulinic acid and of our chlorinated oxidation product. Moreover, this acetyl derivative also may be crystallized unchanged from alcohol, which is evidence against the mixed anhydride formula. Further evidence for structure VIIIb is that whereas the acetyl derivative is broken down to the original phenol by dilute alkali, as is the white compound itself, in the former case the hydrolysis requires boiling alkali, while the unacetylated derivative breaks down quite easily in the cold. In formula VIIIb the oxo group alpha to the substituted ester grouping is modified in such a way as would be expected to stabilize the ester group toward hydrolysis, while in formula VIIIA no such modification is suggested.

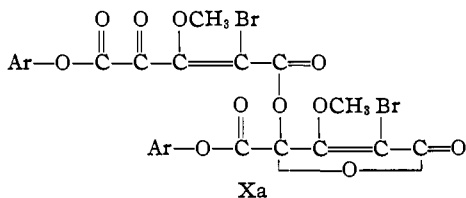
Conclusions

1. From these considerations we suggest IX as the most probable formula for the colorless oxidation product of trichloropyrogallol-2,6-dimethyl ether

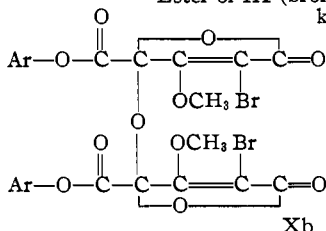


the oxy-lactone of α -chloro- β -methoxyquinonic¹⁰ acid [(3,4,5-trichloro-2,6-dimethoxy)-phenyl ester].

2. Either Xa or Xb then becomes the best formula for the colorless oxidation product of tribromopyrogallol-2,6-dimethyl ether.



Ester of IX (bromine analog)
keto form



Ether of IX (bromine analog)
Ar = -C₆Br₃(OCH₃)₂

¹⁰ In order to simplify the naming of these structures, it is convenient to designate the parent acid (α -keto-glutaconic acid, COOHCOCH=CHCOOH) by some suitable trivial name. We have adopted the name "quinonic acid," since a like oxidation of parabenzoquinone would yield this acid, if it could be carried out.

At the present time we wish to present these formulas provisionally only. Although these structures are as yet by no means rigorously established, we nevertheless consider them to be entirely plausible, in so far as they agree with *every one* of the known experimental facts and satisfy the analytical requirements admirably. We hope to be able to test these suggested structures by further chemical investigation of the substances and of analogous materials.

Experimental Part

Oxidation of Tribromopyrogallol-2,6-dimethyl Ether.—A representative procedure was as follows. Nine grams of tribromopyrogallol-2,6-dimethyl ether (m. p. 134.2°) was covered with 900 cc. of 50% acetic acid and warmed on a water-bath to 80°, at which temperature the dimethyl ether went into solution. Six and six-tenths grams (3 molar equivalents) of chromium trioxide was stirred in. An immediate precipitate of the purple phenoxy quinone was usually obtained. This varied somewhat in quantity, and in one or two cases no phenoxyquinone was formed. The temperature was maintained at 80° for fifteen to twenty minutes, after which the mixture was cooled, and filtered from the phenoxyquinone. It was then poured, slowly and with stirring, into 1200 cc. of cold water, and allowed to stand. The white oxidation product appeared as a very flocculent precipitate, which slowly settled to the bottom of the vessel. After several hours, most of the supernatant liquid was decanted, and the white compound filtered onto a good grade of coarse filter paper made into a "fluted filter." It was washed with dilute acetic acid, water and dilute (*ca.* 25%) alcohol and allowed to dry between filter papers. Eight oxidations, each starting with 9 g. of the phenol, gave an average of 2.9 g. of the colorless compound, or about 32% of the weight of the starting material. The yield was greatly reduced when the oxidation was carried out with larger amounts of the phenol.

The colorless compound melted, when crude, at 193–197°. A sample was purified by recrystallization, as follows: four times from dilute ethyl alcohol, once from aqueous ethyl acetate, three times from dilute methyl alcohol, twice from aqueous methyl acetate and finally once again from dilute methyl alcohol. Starting now with a bath temperature of 200°, the substance showed a melting point of 206–206.6° (with decomposition). A sample obtained from the last methyl alcohol-water filtrate by evaporating to dryness melted with decomposition at 206–207° (Jackson's test for purity).

Anal. Subs., 0.1842, 0.1977: AgBr (Carius), 0.2258, 0.2413. Subs., 0.1955, 0.2022: CO₂, 0.1940, 0.2006; H₂O, 0.0318, 0.0325. Subs., 0.1747, 0.1709: AgI (Zeisel), 0.1936, 0.1922. Calcd. for C₂₅H₁₈O₁₆Br₃(6 OCH₃): C, 27.23; H, 1.46; Br, 51.86; O, 19.45; OCH₃, 15.08; C₈H₆O₃Br₃ (hydrolyzable), 63.2; mol. wt., 1234. Found: C, 27.06, 27.04; H, 1.81, 1.80; Br, 52.17, 52.04; O (by difference), 19.96, 20.12; OCH₃, 14.64, 14.86; C₈H₆O₃Br₃ (hydrolyzable), 63.2, 63.3; mol. wt. (in ethylene dibromide), 1241, 1208, 1215, 1110, 1150, 1260; mol. wt. (in camphor), 1226, 1515.

Properties of the Colorless Oxidation Product of Tribromopyrogallol-2,6-dimethyl Ether.—This substance crystallizes from dilute ethyl alcohol in pure white, microscopic needles, melting, when very pure, at 206–206.6° (decomp.). It is very soluble in acetone, acetic acid, ethyl acetate, methyl acetate and chloroform; moderately soluble in methyl alcohol, and ethyl alcohol; slightly soluble in amyl alcohol, toluene, benzene, xylene, ethylene dibromide, acetophenone and hot carbon tetrachloride; practically insoluble in cold carbon tetrachloride, water and ligroin.

It is oxidized only very slowly by hot alkaline permanganate, hot acid permanganate and boiling concentrated nitric acid. Boiling silver nitrate in 95% alcohol pro-

duces only a slight murkiness. It dissolves in concentrated sulfuric acid to a clear solution. Such a solution was diluted with water, leading to the precipitation of a white material, which was shown to be tribromopyrogallol-2,6-dimethyl ether (m. p. 131–136°).

The original oxidation product is entirely unaffected by any of the following reagents: boiling bromine in chloroform, phosphorus pentabromide in hot chloroform or carbon disulfide, liquid bromine without a solvent, dilute or concentrated hydrochloric acid, dilute nitric acid, saturated sodium hydrogen sulfide.

The Acetyl Derivative.—One and two-tenths grams of the white oxidation product was covered with acetyl chloride, 2 drops of concd. sulfuric acid added and the mixture heated gently in an acetylation flask for three hours. Fumes of hydrogen chloride were evolved from the start. The contents of the flask, poured into 200 cc. of ice water, gave 1.1 g. of the white acetyl derivative. Three recrystallizations from dilute ethyl alcohol gave a pure white product, m. p. 141–144° (decomp.). A sample recrystallized twice more was used for analysis.

Anal. Subs., 0.1261, 0.1889: AgBr, 0.1437, 0.2146. Subs., 0.1861, 0.1655: CO₂, 0.1964, 0.1743; H₂O, 0.0345, 0.0315. Calcd. for C₁₆H₁₂O₅Br₄: C, 28.45; H, 1.81; Br, 47.91. Found: C, 28.78, 28.72; H, 2.07, 2.13; Br, 48.16, 48.34.

The same acetyl derivative is obtained by using acetic anhydride and glacial acetic acid as the acetylating agent. It crystallizes from dilute alcohol in minute, colorless needles. It is moderately soluble in ethyl alcohol, methyl alcohol, glacial acetic acid, chloroform and carbon disulfide; slightly soluble in fractol or ligroin.

Action of Dilute Alkali upon the Acetyl Derivative.—A sample of the acetyl derivative, when boiled with 6% potassium hydroxide, slowly went into solution. When the solution was cooled and acidified with a few drops of concentrated hydrochloric acid, a white material precipitated, which was shown, by the method of mixed melting points, to be tribromopyrogallol-2,6-dimethyl ether.

The Action of Dilute Alkali upon the Colorless Oxidation Product.—An example is given of one of the hydrolytic experiments in which quantitative technique was adopted. Ninety-eight hundredths gram of the pure colorless oxidation compound was dissolved in 90 cc. of cold 6% potassium hydroxide. Solution required only a minute or two. Immediate acidification at this point would give a good yield of the tribromodimethoxyphenol; however, for the sake of quantitative results, the solution was heated gently on the steam-bath for two hours, then nearly neutralized with glacial acetic acid and made slightly acid with dilute (1 normal) acetic acid. The precipitate which resulted was allowed to stand overnight, then filtered onto a weighed Gooch crucible and dried over calcium chloride in a vacuum desiccator. The tribromopyrogallol-2,6-dimethyl ether weighed 0.62 g., or 63.3% of the weight of the starting material. A check determination gave 63.2%.

A sample of the phenol thus prepared was crystallized twice from dilute ethyl alcohol, giving pure white, delicate needles, m. p. 133.8–134.0°; mixed melting point with a known sample of tribromopyrogallol-2,6-dimethyl ether, 134–134.2°. Since it was exceedingly important to establish, without question, the identity of this material, the purified material was subjected to analysis.

Anal. Subs., 0.2002, 0.2037: AgBr (Carius), 0.2881, 0.2943. Subs., 0.0695, 0.0925: CO₂, 0.0664, 0.0841; H₂O, 0.0151, 0.0177. Calcd. for C₆H₇O₅Br₃: Br, 61.34; C, 24.87; H, 1.80. Found: Br, 61.24, 61.48; C, 25.00, 24.80; H, 2.35, 2.15.

Investigation of the Filtrate from the Hydrolysis Reaction.—Examination of the solution from which the tribromopyrogallol-dimethyl ether was filtered led to the following results. Silver nitrate and concd. nitric acid gave a heavy precipitate of silver bromide, showing that further decomposition occurred when the phenol was split off.

Chlorine water and chloroform also disclosed the presence of much free bromide ion. From the filtrate from one sample of 0.57 g. of the white oxidation product, 0.25 g. of silver bromide, equivalent to 0.10 g. of bromine or 33% of the total bromine present in the starting material, was obtained. This, plus the bromine content of the dimethyl ether, accounts for approximately the total bromine available. Another portion of the solution, when neutralized with ammonia and treated with a solution of calcium chloride, gave a white precipitate which gradually darkened on standing, indicating the presence of some reducing acid residue. This was confirmed by the fact that permanganate acidified with dilute sulfuric acid was rapidly decolorized.

The filtrate from one hydrolytic experiment was extracted with ether and the ether extracts allowed to evaporate. There was obtained less than 0.1 g. of an impure white material, melting at 150–160°. The substance was exceedingly deliquescent; standing in the air for even a few moments rendered it of a sirupy consistency. It could not again be isolated, even in this state of impurity, although several attempts were made to do so.

Hydrolytic Decomposition by Means of Other Alkalies.—The hydrolysis could be effected by the use of weaker bases than potassium hydroxide, for example, ammonia or aniline. The latter reagent had previously been used in attempts to obtain an anilide of the colorless compound, without success. It was now clear why these experiments had proved fruitless. If heated for a few minutes with aniline in alcoholic solution, the substance was unaffected. If heated for a somewhat longer time, a gummy product resulted, from which a quantity of the tribromodimethoxyphenol could be obtained. The effect of aniline when used without a solvent was either to leave the colorless material unaffected, or to cause deep-seated decomposition of the substance.

Oxidation of 3,5-Dibromo-6-methoxy-2-(3,4,5-tribromo-2,6-dimethoxyphenoxy)-*p*-benzoquinone.—A sample of the above compound, obtained as a by-product during the oxidation of tribromopyrogallol-2,6-dimethyl ether to the colorless oxidation product, was recrystallized three times from glacial acetic acid. It melted at 219–219.5° (Hunter and Levine report 214°). When recrystallized again it melted at 219.5° sharply. Thirty-five hundredths gram of this material was suspended in 50 cc. of 50% acetic acid, heated to 80° and 0.2 g. of chromium trioxide added. The heating was continued for one and one-half hours, after which the solution was cooled and the unchanged quinone filtered. The filtrate was diluted with 120 cc. of water. A white substance slowly precipitated. After being filtered, washed and dried at 100°, it showed a melting point of 200.5–201.5° (only the most highly purified samples of the white product melt above this temperature) with decomposition, and was found to be identical with the white oxidation product obtained in the original oxidation experiments.

Oxidation of Trichloropyrogallol-2,6-dimethyl Ether.—A representative procedure was as follows. Three grams of trichloropyrogallol-2,6-dimethyl ether was dissolved in 350 cc. of 50% acetic acid and heated on a water-bath to 78°. Two grams (1.7 molar equivalents) of chromium trioxide was stirred in and the heating continued for ten to fifteen minutes, after which the mixture was cooled and the red phenoxyquinone filtered off. (As in the case of the corresponding bromo compound, this phenoxyquinone usually precipitated immediately upon addition of the oxidant, but it varied in amount, and in one or two cases it failed to appear at all.) The filtrate was poured into 500 cc. of cold water and allowed to stand overnight, when the white oxidation product had settled to the bottom of the beaker. Most of the supernatant liquid was decanted, and the precipitate was filtered onto a fluted filter paper, washed with dilute acetic acid, water and dilute alcohol and dried between sheets of filter paper. The average yield of crude material was 31% of the weight of the starting material. The crude material melted at 177–182° (decomp.). After crystallizing twice from dilute acetic acid, twice from

dilute ethyl alcohol and twice from dilute methyl alcohol, it melted at 187.4–187.8°, with decomposition.

Anal. Subs., 0.1059, 0.1003, 0.1391, 0.1270: AgCl (Carius), 0.1380, 0.1284, 0.1779, 0.1627. Subs., 0.1657, 0.1669: CO₂, 0.2300, 0.2297; H₂O, 0.0357, 0.0365. Subs., 0.2040, 0.2027: AgI (Zeisel), 0.3220, 0.3175. Calcd. for C₁₄H₁₀O₉Cl₄ (3 OCH₃): Cl, 31.65; C, 37.53; H, 2.25; O, 28.57; OCH₃, 20.76; mol. wt., 448. Found: Cl, 32.24, 31.67, 31.64, 31.69; C, 37.85, 37.53; H, 2.41, 2.45; O (by difference), 28.10, 28.33; OCH₃, 20.84, 20.68; mol. wt. (in ethylene dibromide), 525, 476, 460; mol. wt. (in camphor), 515.

Properties of the Colorless Oxidation Product of Trichloropyrogallol-2,6-dimethyl Ether.—This substance crystallizes from dilute alcohol in small, white, delicate needles, which melt, when very pure, at 187.4–187.8°, with decomposition. The microscopic crystals are much better developed than those of the bromine analog, which gives reason to suspect, *a priori*, a much smaller molecule in the former case than in the latter. It is readily soluble in ethyl alcohol, methyl alcohol, glacial acetic acid, acetone, chloroform and ether; slightly soluble in carbon disulfide, benzene, toluene, xylene and ethylene dibromide; practically insoluble in water, carbon tetrachloride and fractol.¹¹

Like the bromine analog, the substance is inert to most common chemical reagents. It is unaffected by dilute or concentrated hydrochloric acid, dilute or concentrated nitric acid, saturated sodium hydrogen sulfide, bromine, pure or in solution, and is attacked only very slowly by hot acid or alkaline permanganate. The pure material dissolves in concentrated sulfuric acid to a clear solution. One such solution, on dilution, was found to give a precipitate of trichloropyrogallol-2,6-dimethyl ether (m. p. 121–122°). The same substance was produced by the action of 6% potassium hydroxide on the colorless product, and subsequent acidification, by dilute acetic acid, of the solution produced. It was identified by the method of mixed melting points. A large amount of free chloride ion was found to be produced during the hydrolytic reaction, and there was also present in the solution, after reaction, a substance which reduced acid permanganate. It could not be isolated.

Acetylation.—Fifteen-hundredths gram of the colorless compound and 30 cc. of acetic anhydride, contained in a long-necked flask, was warmed gently over a free flame for two to three hours. The contents of the flask were cooled, neutralized with sodium hydroxide and diluted with water. The brown product was crystallized from dilute alcohol, giving white crystals, m. p. 135–136°, with decomposition. A chlorine analysis on the crude product indicated that it was a monoacetyl derivative.

Anal. Calcd. for C₁₆H₁₂O₉Cl₄: Cl, 29.0. Found: 27.7, 29.0.

Oxidation of 3,5-Dichloro-6-methoxy-2-(3,4,5-trichloro-2,6-dimethoxyphenoxy)-*p*-benzoquinone.—Five-tenths gram of the above compound was suspended in 100 cc. of 50% acetic acid, and treated at 78° with 0.35 g. of chromium trioxide. After heating at this temperature for one and one-half hours, the solution was cooled, the excess quinone filtered and the filtrate poured into 200 cc. of cold water. After twenty-four hours, the small amount of white material which had settled to the bottom of the vessel was collected, washed with water and dried. It melted at 186–188°, with decomposition, and was identical with the colorless oxidation product of trichloropyrogallol-2,6-dimethyl ether.

¹¹ The oxidation product sometimes appears in the colloidal condition, either when first precipitated from 50% acetic acid by dilution, or on subsequent recrystallization. Under these circumstances, purification cannot be effected and the material must be discarded.

Summary

The oxidation of halogenated pyrogallol-2,6-dimethyl ethers leads to the formation of colorless products. The same products are likewise obtained by the further oxidation of phenoxy quinones, derived from the halogenated phenols by oxidation. These colorless compounds differ from previously known quinone oxidation products by virtue of the fact that in their formation by rupture of the quinone ring, only one carbon atom of the ring is lost.

Structures are proposed for these compounds, and the mechanism by which they are formed is discussed.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

DERIVATIVES OF PHENYLBORIC ACID, THEIR PREPARATION AND ACTION UPON BACTERIA¹

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The fact that boric acid acts as a very mild antiseptic agent suggested that, in seeking new types of organic antiseptics, an investigation of the organic boric acids, $R-B(OH)_2$, would be of interest. Michaelis and Becker,² who first prepared phenylboric acid, observed that this substance was toxic toward microorganisms and relatively harmless toward higher animals. Notwithstanding the promising indications of this early work, no further investigations have been made upon the antiseptic action of the substituted boric acids. The present study was undertaken with the object of preparing a number of derivatives of phenylboric acid containing nitro and amino groups, and testing their action on microorganisms.

Since none of the usual methods for the preparation of aryl boric acids could be adapted readily to the direct synthesis of the nitrophenylboric acids,³ it seemed desirable to introduce the nitro group by the nitration of phenylboric acid. This compound is prepared conveniently by the interaction of boron trifluoride⁴ or methyl borate⁵ and phenylmagnesium bromide.

¹ This article is an abstract of a thesis submitted by William Seaman to the Faculty of the Graduate School of Cornell University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in March, 1929.

² (a) Michaelis and Becker, *Ber.*, **13**, 58 (1880); (b) *ibid.*, **15**, 180 (1882).

³ An adaptation of the method of preparation of aryl boric acids used by Michaelis and Becker would involve the interaction of boron trichloride or boron tribromide with a bis-(nitrophenyl)-mercury. Although it has been possible to prepare bis-(*m*-nitrophenyl)-mercury (unpublished work of R. S. Shelton in this Laboratory), the relative inaccessibility of such compounds led us to seek other methods.

⁴ Krause and Nitsche, *Ber.*, **54**, 2734 (1921); **55**, 1261 (1922); German patent 371,467 [*C. A.*, **18**, 992 (1924)].

⁵ (a) Khotinsky and Melamed, *Ber.*, **42**, 3090 (1909); (b) Gilman and Vernon, *THIS JOURNAL*, **48**, 1064 (1926).