

of the rotatory power of cinchonine hydrochloride and cinchonine acetate, respectively, with increasing concentration of bivalent alkaloid ion.

By extrapolation the rotatory power of the univalent cinchonine ion in the concentration and at the temperature used may be given as 17.45° Ventzke and that of the bivalent ion as 21.48° Ventzke. The specific rotation of the two ions, in circular degrees under these conditions, would then be $[\alpha] = 205.6^\circ$ and $[\alpha] = 253.1^\circ$, respectively. The corresponding values for the univalent and bivalent cinchonidine ions are -11.94° Ventzke and -15.75° Ventzke. From these values the specific rotation in circular degrees at the temperature employed may be represented as $[\alpha] = -141.1^\circ$ and $[\alpha] = 185.6$.

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THE CONSTITUTION OF XANTHOGALLOL.

By F. J. MOORE AND RUTH M. THOMAS.

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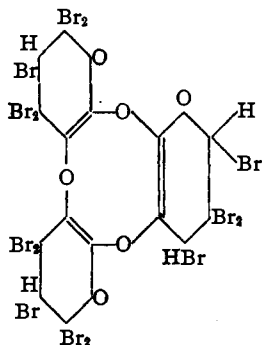
Xanthogallol was discovered by Stenhouse¹ who in 1875 prepared it by the action of bromine and water upon tribromopyrogallol, and afterward more conveniently by the action of the same reagents upon pyrogallol. He also prepared one or two derivatives and made an analysis on the basis of which he assigned to xanthogallol the empirical formula $C_{18}H_4O_6Br_{14}$.

In 1888 Theurer,² working in Zincke's laboratory, made an extensive investigation of the substance, with the express object of determining whether a simpler formula (perhaps $C_6HO_2Br_5$) might not be admissible. His analyses, however, confirmed those of Stenhouse, and he provided additional evidence in favor of the latter's formula by preparing a whole series of derivatives whose genetic relationships he interpreted on the same basis. Some of these interpretations appeared a little forced, but the composition of the derivatives seemed so well borne out by analytical data that Theurer's article has remained essentially the last word upon the subject. It included a tentative structural formula for which, however, the author made no claim for accuracy in matters of detail. This appears below in the modified form suggested by Zincke's foot-note.

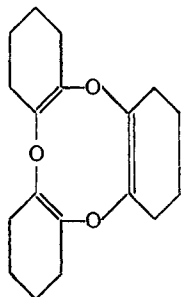
Of this formula it may be said that, on the one hand, it harmonized fairly well with the experimental results described by Theurer, and, on the other, that the task of establishing its details with accuracy promised more labor than profit. This is perhaps the reason why the subject has since been so much neglected.

¹ *Ann.*, 177, 191 (1875).

² *Ibid.*, 245, 327 (1888).



The present investigation was not begun with any thought of revising the work of Theurer (which, indeed, impresses the reader with an unusual sense of finality) but rather for the sake of preparing other compounds containing the somewhat unusual complex:



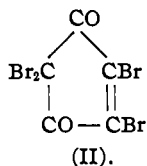
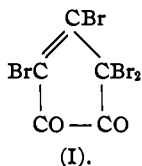
Since, however, no previous investigators had determined any molecular weights in this field, we began by determining that of xanthogallol, and were not a little surprised when three series of results obtained by the freezing-point method in benzene ranged from 379 to 403 whereas the formula of Stenhouse requires no less than 1436. This contradiction became more puzzling when an analysis was made and the results of Stenhouse and Theurer apparently confirmed. The percentages are, however, reasonably compatible with the formula $C_5O_2Br_4$ which is consistent with the molecular weight and finds additional confirmation in the fact that xanthogallol *contains no hydrogen*. This has been established by two combustions using a one-gram sample, a procedure which makes negligible the error caused by adventitious moisture when a substance containing little hydrogen is burned in the ordinary way.

If, however, the formula $C_5O_2Br_4$ is to be substituted for the old, it must give a better account than the latter for the composition and relationships of all Theurer's derivatives. To test this meant a thorough revision of his work. His more important compounds have, therefore, been again prepared and analyzed, new ones have been added, and all find natural

places in a system consistent with itself and with the new formula, which we believe will be found convincing. Since the relationships are somewhat complex an outline chart has been prepared which is printed on page 977. By its aid the reader will be able to follow without difficulty the details of the following general discussion. This will be devoted to a concise exposition of the relationships involved from our own point of view, though Theurer's interpretation of the same facts will also be mentioned as we proceed. Generally speaking, it will be found that we do not differ seriously from him concerning the properties and qualitative behavior of the compounds we both have studied. That we have come to very different conclusions is due in part to the discovery of some relationships which he had overlooked, and partly to differences in the results of analysis. Our figures, compared with those of all previous investigators, will be found fully set forth in the experimental part of this paper.

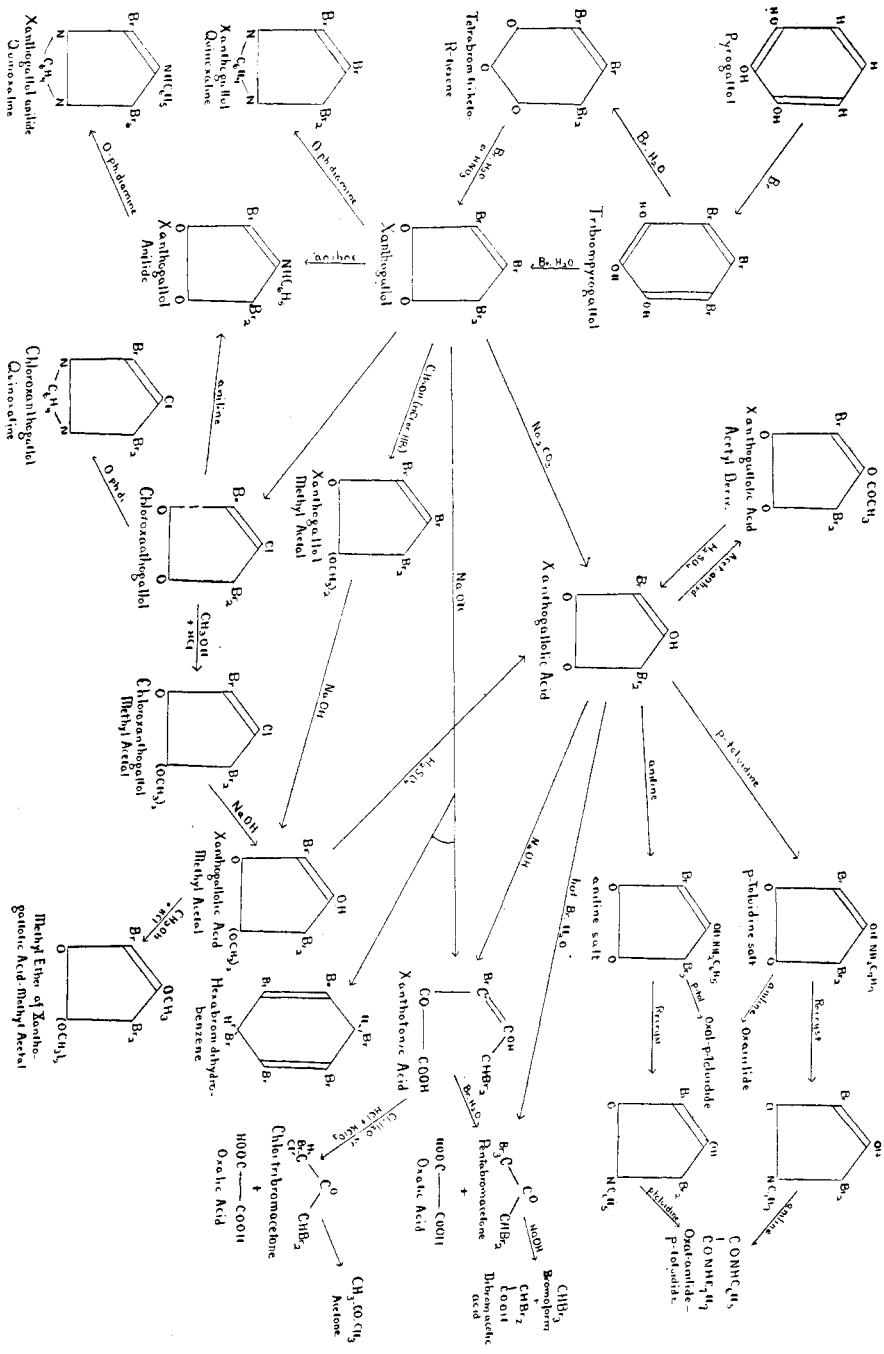
Xanthogallol

If we disregard grotesque possibilities, the formula $C_5O_2Br_4$ naturally takes one of the structural forms:



Of these II has already been applied by Jackson and Russe¹ to the compound which they prepared by the action of fuming nitric acid upon tetrabromo-*o*-benzoquinone. They justified this formula by hydrolyzing their compound to dibromomaleic acid and methylene bromide. Formula I, on the other hand, we have selected for xanthogallol and we shall see that it is supported by no mean positive evidence. In the first place, an adjacent position of the carbonyl groups would naturally be expected in a substance prepared from pyrogallol. Further, no less than three independent decompositions of xanthogallol lead to oxalic acid or its derivatives, and the substance itself reacts with *o*-phenylene diamine to form a quinoxaline free from oxygen. This compound was not studied by Theurer. Its molecular weight corresponds closely with the formula $C_5Br_4, N_2C_6H_4$ and this in turn confirms the simpler formula for xanthogallol. We shall see that the molecular weights of other derivatives furnish similar evidence. Of the reactions leading to oxalic acid we may first mention the one to which we have given least attention, that of bleaching powder and sodium hypobromite. These reagents decompose xanthogallol, yielding oxalic acid and certain other products which much resemble xanthogallic and xanthotonic acids—to be described later.

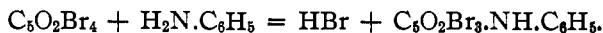
¹ *Am. Chem. J.*, 35, 154 (1906); 43, 135 (1910).



They are, however, apparently not identical with either. Free hypobromous acid does not produce oxalic acid.

The Reactive Bromine Atom.

Xanthogallol reacts with primary amines like aniline and *p*-toluidine in the sense of the equation



On account of the complex formula which Theurer assumed for xanthogallol he was obliged to interpret this reaction with aniline as a substitution of three bromines by $\text{—NH.C}_6\text{H}_5$ groups, while a fourth aniline is added to the molecule. The difference between the theoretical percentages for the elements in the two formulas is not large, but rather outside the usual range of experimental error. We found the product not sufficiently soluble to permit a determination of the molecular weight, but it yields a quinoxaline free from oxygen, showing that the aniline radical has no influence upon the carbonyls. We had hoped to obtain the same quinoxaline from xanthogallol quinoxaline but the latter does not react with aniline.

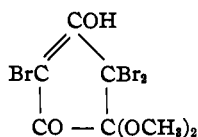
The reactive bromine in xanthogallol can be replaced by chlorine. The product, chloroxanthogallol ($\text{C}_5\text{O}_2\text{Br}_3\text{Cl}$), was prepared by Theurer in several ways: by passing dry hydrochloric acid into a solution of xanthogallol in glacial acetic acid, by the saponification of the chlorinated methyl acetal about to be described, and as a by-product in the preparation of the latter when hydrochloric acid is passed into a solution of xanthogallol in methyl alcohol. This proved to be the most advantageous method. The product, which Theurer formulates $\text{C}_{18}\text{H}_4\text{O}_6\text{Br}_{11}\text{Cl}_3$, is interesting because its chlorine atom shows the same reactivity as the bromine it has replaced. Chloroxanthogallol and xanthogallol, therefore, react alike with caustic soda, with the alkaline carbonates and with aniline. The aniline derivative is particularly easy to prepare, and its identity with that from xanthogallol has been demonstrated by a mixed melting point. Chloroxanthogallol also yields a quinoxaline which contains all the halogen of the mother substance, and so doubtless has the same constitution as that of xanthogallol.

The Methyl Acetals.

We have seen that when hydrochloric acid is passed into a methyl alcohol solution of xanthogallol a partial transformation to chloroxanthogallol takes place. At the same time there is an exchange of one oxygen for two methoxyls in each of these compounds to form acetals. As might naturally be expected the acetal of xanthogallol itself is the product which predominates at first. Then chloroxanthogallol and its acetal are formed. The best yields of the last are therefore obtained by re-treating the residues (consisting of a mixture of crude chloroxanthogallol and

xanthogallol) from the acetal preparation with fresh methyl alcohol and hydrochloric acid as before. When this was once realized, no serious difficulty was found in preparing all of the products in a state of reasonable purity though troubles were at first experienced when it was attempted to follow Theurer's directions too literally. He, too, recognizes that the compounds are acetals, but in accordance with his higher system of molecular weights formulates them $C_{18}H_4O_3Br_{14}(OCH_3)_6$ and $C_{18}H_4O_3Br_{11}Cl_3(OCH_3)_6$.

We do not know which carbonyl group is involved in the formation of these compounds. Alkali, however, replaces their reactive halogen by hydroxyl forming an acetal of xanthogallic acid,



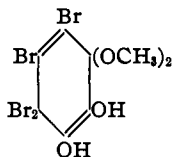
and since xanthogallic acid itself is not stable toward alkali it might be argued that the methoxyl groups are attached to that carbon atom where that acid splits to form xanthotonic acid. This reasoning accounts for the way these acetals are formulated in the chart, but we attach little weight to it, and nothing else in our discussion depends upon the position of these methoxyl groups.

That the acetal whose formula appears above is really a derivative of xanthogallic acid is shown by the fact that it yields the latter when treated with fuming sulfuric acid. Theurer also carried out this very reaction but apparently did not recognize the product. This is not so surprising as it seems on account of its irregularities of melting point. He therefore made another analysis and now gave it the formula $C_8H_2O_2Br_4$. He also prepared addition products of the acetal with aniline and toluidine. The analyses of the products were not repeated as they are obviously 'salts, and regenerate the acetal when treated with alkali.

When the acetal of xanthogallic acid is treated with hydrochloric acid in methyl alcohol the hydroxyl group is replaced by methoxyl, forming an ether from which the acetal can be again regenerated with alkali. Our product here had the same melting point as that of Theurer but there was a striking difference in the analysis. Our substance contained only 0.5% chlorine (obviously a contamination) while his analyses show no less than 8%.

A glance at the chart will show that the new formula for xanthogallol accounts for the somewhat complex relationships of these alcohol derivatives simply and rationally by transitions of ordinary type. Theurer's interpretations, are, however, more confusing here than in any other part of his paper. We have already seen that he formulates xanthogallol acetal

$C_{18}H_4O_3Br_{14}(OCH_3)_6$. When this is treated with alkali he assumes—rather gratuitously—the collapse of his three-ring system, and ascribes to the acetal of xanthogallic acid the formula $C_8H_2O_2Br_4(OCH_3)_2$ —perhaps



which cannot be derived from the other by any simple hydrolysis. He treats this with sulfuric acid, to which he ascribes a reducing action, and obtains xanthogallic acid, which he fails to recognize and formulates $C_8H_2O_2Br_4$. Finally he obtains the methyl ether of the acetal and writes it $C_8HBr_4Cl(OCH_3)_4$.

Xanthogallic Acid.

This substance was first studied by Stenhouse¹ who prepared it by allowing xanthogallol to stand with sodium carbonate. He assigned to the acid the formula $C_{18}H_4O_6Br_{11}(OH)_3$ and his percentages for carbon and hydrogen agree very well with our formula, while that for bromine varies by nearly 2%. Theurer's figures are close to those of Stenhouse but we are unable to confirm either in this respect. In 1887, just before Theurer's paper appeared, Hantzsch and Schniter² prepared the compound. They considered the free acid unsuitable for analysis, so they prepared the barium salt and determined barium in that, finding in this way a figure which corresponded to Stenhouse's formula for the acid. Stenhouse himself, however, rejected his own barium determination in this salt, partly, no doubt, because it failed to confirm his theories, but explicitly on the ground that the salt turns yellow on drying and hence was unsuitable for analysis. His results, however, agree very well with our own as well as with our theory though they differ to the same extent from those of Hantzsch and Schniter. The same investigators also prepared an acetyl derivative of xanthogallic acid in order to fix the number of hydroxyl groups it contained. With reference to this compound, also, our results show a similar divergence.

Our own formula for xanthogallic acid has been already anticipated. Briefly stated, it rests upon the following evidence: Several decompositions leading to oxalic acid speak for an adjacent position of the carbonyl groups in xanthogallol, and this in turn involves the distribution of the four bromine atoms upon three adjacent carbons. Furthermore, since both xanthogallol and chloroxanthogallol yield xanthogallic acid when treated with sodium carbonate the hydroxyl group of the latter must occupy the same position as the reactive bromine in xanthogallol. Finally, the hydroxyl group is situated on the middle carbon of the three, because,

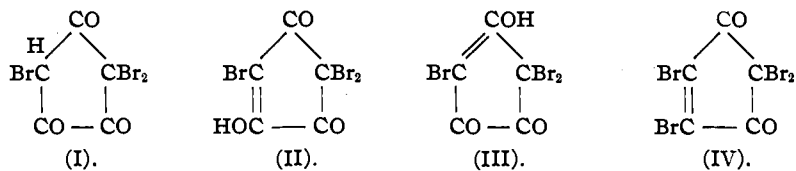
¹ *Loc. cit.*

² *Ber.*, 20, 2038 (1887).

as we shall see, bromine water decomposes xanthogallic acid into oxalic acid and pentabromoacetone. This proof is analogous to that used by Hantzsch¹ in the case of tribromo-triketo-pentamethylene which he split in the same way into oxalic acid and hexabromoacetone.



Satisfactorily as this accounts for all the relations of the acid with which we are here concerned there are nevertheless two arguments against it which must be frankly considered. The first of these is that this very formula has already been applied by Nef² to the tribromo-triketo-pentamethylene of Hantzsch just referred to above and accepted by the latter³ in the sense that Nef's formula represented the enol form of his own. Inspection, however, shows that Hantzsch's formula (I) is susceptible of



two enol forms (II) and (III). Of these it is safe to assume that (II) is the true enol because Henle⁴ by treating Hantzsch's compound with phosphorus pentabromide obtained from it compound (IV) already referred to on page 976. As there stated, Jackson and Russe⁵ fixed the constitution of this substance by hydrolysis to methylene bromide and dibromomaleic acid. For these reasons we feel justified in regarding I and II as a true tautomeric pair while Formula III, as that of an independent isomer, remains open for xanthogallic acid.

Another difficulty is found in the molecular weight. Our formula requires 349, but determinations both in benzene and nitrobenzene yielded results approximating 600. These fell off, it is true, when the solutions were allowed to stand, but the values never reached 450 and the changes were obviously due to decomposition so no conclusions could be drawn. We found solace, however, in the behavior of the acetyl derivative. This compound, when treated with concentrated sulfuric acid, promptly regenerates xanthogallic acid, showing that its formation has wrought no fundamental changes in the constitution of the latter, and it shows a

¹ *Ber.*, 21, 2439 (1888).

² *J. prakt. Chem.*, [2] 42, 178 (1890).

³ *Ber.*, 25, 836 (1892).

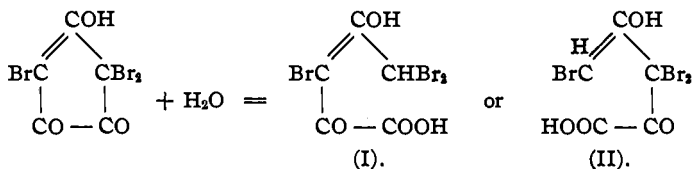
⁴ *Ann.*, 352, 47 (1907).

⁵ *Am. Chem. J.*, 35, 154 (1906); 43, 135 (1910).

molecular weight very close to the theoretical. For this reason we do not hesitate to ascribe the high value obtained in the case of the mother substance to association in solution, a phenomenon not uncommonly shown by hydroxyl compounds.

Xanthotonic Acid.

When xanthogallolic acid is dissolved in aqueous or alcoholic caustic soda, another compound to which we have given the name of xanthotonic acid is produced. This substance can be obtained in the same way from xanthogallol but in this case a good deal of hexabromodihydrobenzene is also formed. The acid is not a very stable substance and readily undergoes further complex alteration by alkalis if exposed to their continued action. It gives a characteristic color reaction with ferric chloride, passing from purple-red through blood-red to yellow. The formation of the compound is to be interpreted as a hydrolytic splitting of the five-carbon ring in xanthogallolic acid in the sense of the equation:



Such a formula is supported by the analysis and the molecular weight. Theurer prepared the compound, and gave it the formula $\text{C}_5\text{H}_4\text{O}_3\text{Br}_2$ on the basis of an analysis of the barium salt. He did not, however, name it or observe the reaction which throws most light upon its constitution, *viz.*, decomposition by bromine water into oxalic acid and pentabromoacetone. This reaction is extremely smooth, 4.9 g. acid yielding, in one experiment, no less than 5 g. crude pentabromoacetone. The latter substance was identified in a great variety of ways, as its formation really furnished the fundamental idea to the whole investigation. In addition to the analysis and a determination of molecular weight, a strict comparison was made of the product with a sample of pentabromoacetone prepared by the action of bromine water upon acetone-dicarboxylic acid. The following qualitative reactions were also observed: Ammonia forms dibromoacetamide, and hydrolysis by alkali yields bromoform and dibromoacetic acid, the latter also being changed through the chloride to ester and amide.

These results still leave open, however, a choice between Formulas I and II above. While a choice between them is not of vital importance for our purposes we consider I more probable in accordance with the traditional view¹ that in such a case the ring opens between a carbonyl group and a carbon with two halogens. This is also in harmony with the action

¹ Compare Zincke, *Ber.*, 25, 2682 (1892).

of hydrochloric acid and potassium chlorate upon xanthotonic acid. This yields oxalic acid and a hitherto unknown chlorotribromoacetone which apparently has the structure $\text{CHBr}_2\text{CO.CHBrCl}$. If this is true, and we make the natural assumption that chlorine is added at the point where the chain is broken, then the formation of this substance is to be expected from a compound of Formula I, whereas one of Formula II would be more apt to yield $\text{CBr}_2\text{Cl.CO.CH}_2\text{Br}$. Our evidence concerning the constitution of the new substituted acetone may be summed up as follows: It is so hygroscopic that it presents difficulties of analysis but the ratio of bromine to chlorine is clearly three to one. Its relation to acetone is proved by the fact that it yields that substance on reduction, the product being identified by the formation of dibenzylidene acetone with benzaldehyde, and of indigo with *o*-nitrobenzaldehyde. Finally when boiled with alkali it yields neither bromoform nor chlorobromoform as might be expected of the other two possible isomers CHCl.CO.CBr_3 and $\text{CH}_2\text{Br.CO.CClBr}_2$. Of these, the former has been prepared and described by Ch. Cloez.¹ It may be mentioned that, by brominating epichlorohydrin, Grimaux and Adam² obtained an oil of the same empirical formula which gave a crystalline tetrahydrate, melting, however, at 55° , 10° lower than the one described in the present paper.

Before leaving this topic it should be stated that pentabromoacetone and oxalic acid can also be obtained directly from xanthogallic acid by the use of warm bromine water.

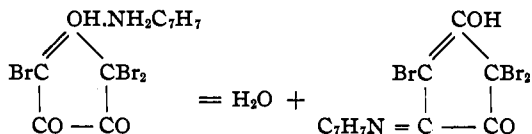
Decomposition of Xanthogallic Acid by Aniline and Toluidine.

Theurer states that when xanthogallic acid is treated with aniline in alcoholic solution oxanilide is formed and also an addition product of the acid and base to which he gives the formula $\text{C}_{18}\text{H}_7\text{O}_9\text{Br}_{11}(\text{NH}_2\text{C}_6\text{H}_5)_8$. He states that a perfectly analogous reaction takes place with *p*-toluidine but gives no melting point for either product. We can verify the formation of oxanilide (or toluidide) but the composition of the other substances we obtained bears no relation to the analytical results recorded by Theurer. The reactions actually observed, however, are peculiar, and sufficiently interesting to record here in spite of the fact that no complete interpretation is yet possible. We get the best insight into the reaction when xanthogallic acid is treated in turn with two different bases. If, for example, the acid is dissolved in alcohol and less than one molecule of *p*-toluidine is added, practically no oxal-*p*-toluidide is formed but a curdy precipitate, A, is thrown down, which when dried melts at $89-90^\circ$. If this is crystallized from dilute alcohol or dilute acetic acid a hydrated product, B, is formed, melting at $102-104^\circ$. Finally, if B is thoroughly dried we get C,

¹ *Ann. chim.*, [6] 9, 207 (1886).

² *Bull. soc. chim.*, 33, 257 (1880).

melting at 147–148°, which on recrystallization regenerates B. It follows that B and C are the same substance but they differ chemically from A, as is best shown in their behavior toward aniline. A is obviously the toluidine salt of xanthogallic acid, and when it is treated with aniline it yields oxanilide, the aniline apparently reacting with the carbonyl groups, while the toluidine molecule remains connected with hydroxyl. When B is treated with aniline, however, oxalanilide-*p*-toluidide is formed, showing apparently that in the transition from A to B the toluidine molecule has wandered from the hydroxyl to one of the carbonyls, perhaps in the sense of the following reaction:

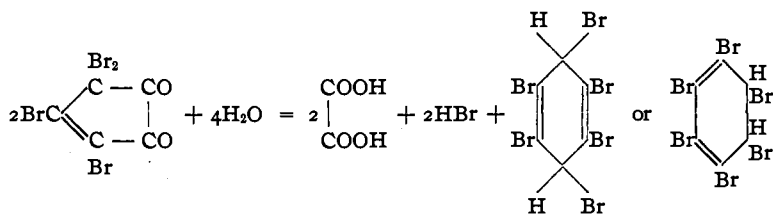


The analysis of C would agree well enough with such a formula, if we assume that the dried product still retains a half molecule of water. Water of crystallization did not seem likely, and some bimolecular combination involving water chemically combined was thought of, but a molecular weight determination in glacial acetic acid gives results which are low even for the simple formula. Other solvents were not available, but a comparative determination of the molecular weight of aniline oxalate in acetic acid yielded a similar low result. More troublesome still is the question of what becomes of the rest of the molecule when the oxanilide is formed. One might expect the formation of *p*-toluidine and 1,1,3-tribromoacetone but the evaporated mother liquors have thus far failed to yield any homogeneous product. It should be added that when xanthogallic acid is treated first with aniline and then with toluidine, an entirely analogous series of reactions is observed though the compounds here are a little less stable.

Hexabromodihydrobenzene.

We have seen that when xanthotonic acid is prepared from xanthogallol by the action of caustic soda, a by-product is formed to which we have alluded as hexabromodihydrobenzene, a name bestowed by Theurer. As the formation of a six-carbon ring seemed unlikely at this point we fully expected to find his results in error and were not a little surprised when the analyses and molecular weight determinations fully confirmed his empirical formula. We also have no different suggestion to make as to the constitution of the substance, although, so far as we know, no genetic relationships as yet exist connecting it with other benzene derivatives. We have ourselves heated it with quinoline in the hope of getting pentabromobenzene, but although a reaction takes place no product has been isolated. If the substance is hexabromodihydrobenzene its formation

might be interpreted as a splitting out of oxalic acid and hydrobromic acid from xanthogallol while the remaining fragments of two molecules unite:



Peculiar as this reaction looks, it is supported by the fact that a quantity of oxalic acid can be found in the mother liquors which is approximately that required by the equation. The objection that the oxalic acid might come from the action of alkali upon the xanthotonic acid has been met by special experiments in which this acid alone was treated with alkali. Only traces of oxalic acid could then be found.

The Formation of Xanthogallol.

It is believed that the considerations detailed in the foregoing pages make out a strong case for the new theory of the constitution of xanthogallol. It remains to show that this formula also offers a consistent interpretation for the mechanism of its formation from pyrogallol.

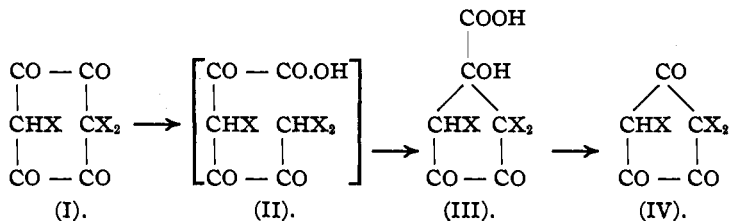
When Stenhouse¹ treated pyrocatechol with bromine water he obtained a product which was afterward recognized by Zincke² as tetrabromo-*o*-benzoquinone. Theurer therefore treated tribromopyrogallol carefully with the same reagents, apparently in the hope of obtaining the same compound or a close derivative. He was disappointed in this, but did obtain a substance to which, because it could be easily oxidized to xanthogallol, he gave the formula $\text{C}_{18}\text{H}_{14}\text{O}_{12}\text{Br}_{14}$. What he really had in hand now appears as a compound formed, in principle, in the same way as that of Stenhouse, namely, by the oxidation of the three hydroxyls to carbonyl groups and further bromination of the rest of the molecule. The compound is then tetrabromo-triketo-*R*-hexene. In repeating the work our product did not at first melt at the same point as that described by Theurer, but the explanation for this was soon found. The compound occurs in two forms, with two, and with four molecules of water, respectively. The latter melts a little higher and the former a little lower than the figure mentioned by Theurer. It is not unlikely that the presence of this water may have misled him as to the true composition of the substance, although the formation of hydrates is common among compounds of this class.

Accepting then this structure for the intermediate product, its easy transition to xanthogallol falls in line with what has been observed in other

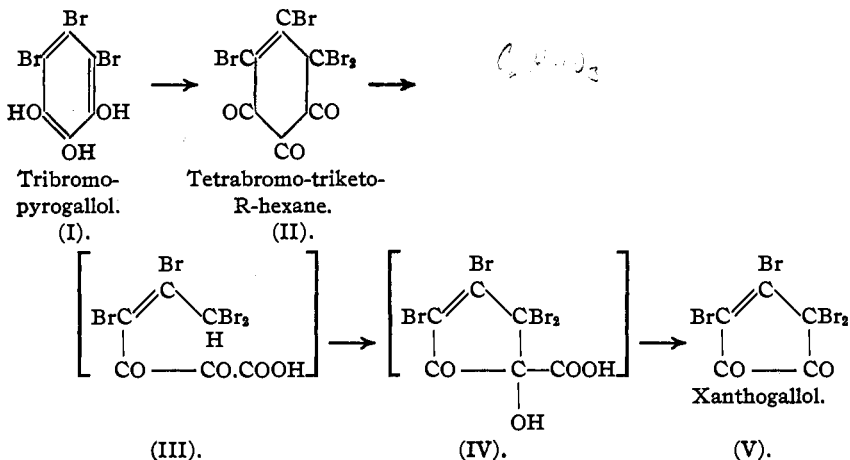
¹ *Ann.*, 177, 197 (1875).

² *Ber.*, 20, 1776 (1887).

cases. Hantzsch,¹ for example, when he studied the reaction of halogens and water upon bromoanilic acid, explained the mechanism of the final steps of the reaction (the only ones which concern us here) as follows:



It will be noticed that the transition from I to III is essentially a benzilic acid rearrangement, and Hantzsch points out one experimental fact which is of interest to us. He found that when the halogen was chlorine, the hydroxy acid (III) was stable enough to be isolated, but that in the case of bromine this could not be done, the transition taking place directly from I to IV. With these points in mind it is now possible to explain the formation of xanthogallol from tribromopyrogallol simply as follows:



Experimental Part.

By RUTH M. THOMAS.

Analysis.

The compounds studied in this investigation contain almost without exception large quantities of halogen and this makes some difficulties in the determination of the other elements.

In the case of carbon and hydrogen determinations both lead chromate and copper oxide and also a silver spiral were used, and for nitrogenous substances a reduced copper spiral. In some early analyses, copper bromide, formed in the customary spiral behind the substance, sublimed

¹ Ber., 21, 2421 (1888).

into the boat and prevented the complete combustion of the sample. In order to prevent this a second boat containing finely ground lead chromate was introduced between the two. This arrangement is illustrated below.



Fig. 2.

The nitrogen determinations were made in an open tube, using an auxiliary tube of manganese carbonate for the evolution of carbon dioxide. This saved refilling the tube for each determination, and since it was cooled in carbon dioxide, the reduced spiral could be used repeatedly without reduction. Some experiments were made to test the Kjeldahl method for determining nitrogen in substances of this class but it was found entirely unsuitable.

All melting points given in this paper are uncorrected. This affords a better comparison with the figures of previous investigators.

Tribromopyrogallol.

Tribromopyrogallol was prepared by dropping 25 cc. of bromine diluted with carbon tetrachloride into a suspension of 20 g. of pyrogallol in about 700 cc. of carbon tetrachloride. The mixture was warmed gently for two hours. It then contained a copious precipitate of the tribromo derivative. After cooling, this crude product was filtered off and used for the preparation of xanthogallol or of tetrabromo-triketo-R-hexene. The product always contained more or less of a purple, water-soluble impurity, which if present in very large amount interfered with the xanthogallol preparation. The carbon tetrachloride mother liquor was used over and over without purification.

The melting point of tribromopyrogallol is not given in Beilstein. After repeated recrystallization from dilute alcohol it darkened at about 160° and melted at $168-170^{\circ}$. It crystallizes from dilute alcohol in slender, slightly pinkish needles, which change on standing in the solvent for some hours into thicker prisms.

A little tribromopyrogallol moistened with sodium hydroxide or ammonia in a porcelain dish gives a pink color, changing through orange to brown. This distinguishes it from pyrogallol, but the behavior of the lower brominated pyrogallols is not known.

Tetrabromo-triketo-R-hexene Tetrahydrate.

According to Theurer's directions, 1 g. of tribromopyrogallol was suspended in 5 cc. of water and bromine added drop by drop until the precipitate entirely dissolved and the solution was orange with bromine. It was poured at once on a large watch glass to evaporate the bromine as rapidly as possible. In a few minutes, on scratching, a thick, flaky

white precipitate formed. This was spread on a tile, washed once with water and dried as rapidly and thoroughly as possible. Weight of product, 1.3 g. To recrystallize, it was dissolved in dry ether, in which it formed a moist lump before dissolving, the solution filtered, and treated with about four volumes of ligroin or enough to produce permanent cloudiness. The hexene crystallized at once in pearly gleaming flakes, melting at 70° with evolution of gas. Recrystallization did not change the melting point, though Theurer gives 79–80° for his substance prepared by the same method.

The compound is easily soluble in ether and in alcohol, difficultly in ligroin. With warm ligroin it decomposes, giving an oily residue. In warm water it dissolves with slight effervescence. The orange solution clouds in a few minutes, with the separation of a brown oily film on the side of the tube. This is also characteristic of xanthogallol.

Analyses were necessarily made on air-dried material. The compound was recrystallized twice from ether-ligroin, and dried in the air eighteen hours. It had no odor of ligroin or of bromine. The first carbon and hydrogen sample was weighed and analyzed at once. At the same time two Carius samples were weighed out and sealed up as soon as possible, and the second carbon sample weighed out into a small glass tube and sealed up. Another bromine determination was also made on another preparation of the compound.

0.1802 g. gave 0.0312 g. H₂O, 0.0931 g. CO₂; 0.1767 g. gave 0.0325 g. H₂O, 0.0909 g. CO₂; 0.1910 g. gave 0.2783 g. AgBr; 0.1827 g. gave 0.2658 g. AgBr; 0.1854 g. gave 0.2686 g. AgBr; 0.1897 g. gave 0.2747 g. AgBr.

	Theory.			Found.	
	C ₁₆ H ₁₄ Br ₁₂ O ₁₄ .	C ₂ Br ₄ O ₂ ·2H ₂ O.	C ₈ Br ₄ O ₃ ·4H ₂ O.	Theurer.	Thomas.
C.....	15.27	15.13	14.06	15.23, 15.30	14.09, 14.03
H.....	0.99	0.84	1.56	1.14, 1.15	1.92, 2.01
Br.....	67.89	67.22	62.50	67.80, 67.98	61.92, 62.02 61.65, 61.63

Tetrabromo-triketo-R-hexene Dihydrate.

Some preparations of the tetrahydrate decomposed rapidly on standing even in a desiccator. Others lost water smoothly to form a dihydrate. The latter compound seems to have been the substance studied by Theurer. In one preparation, after recrystallization of the air-dried material from ether-ligroin the crystals (m. p. 69–70°) were dried over calcium chloride overnight and now melted at 85°. When recrystallized they melted at 83°, and after drying three hours over calcium chloride at 85°. The material was dried overnight and analyzed for bromine.

0.1655 g. gave 0.2642 g. AgBr; 0.1633 g. gave 0.2619 g. AgBr. % Br = 67.93, 68.24.

Xanthogallol.

Xanthogallol was first prepared from pyrogallol, following the directions of Stenhouse, which were also used by Theurer. One part (20 g.)

of powdered pyrogallol was slowly added to ten parts (200 g.) of bromine, contained in a large round-bottomed flask fitted with a loosely fitting cork. The mixture was allowed to stand $3\frac{1}{2}$ hours, stirring up the material as well as possible, and then treated with thirty parts (600 cc.) of water. At this point there was vigorous action, with evolution of clouds of bromine and hydrobromic acid. The flask was now heated at $70-80^{\circ}$ for ten minutes in a water bath. There was a vigorous evolution of carbon dioxide and orange crystals of xanthogallol came down. These were filtered off, washed with water and dried. Yield 40-50 grams. Working with larger amounts of pyrogallol did not give so good results.

Xanthogallol was also prepared from tribromopyrogallol. Five g. crude tribromopyrogallol were treated with 3 cc. bromine (two parts). If there was any reaction when the bromine was added the mixture was left standing for an hour or so, otherwise it was treated at once with 30 cc. of water and warmed at $70-80^{\circ}$ for ten minutes. Four g. of xanthogallol were obtained. This yield reckoned on the pyrogallol required to make the tribromo derivative (15 g. give 40-45 g.) makes the percentage yield about the same as from the other method.

A method of formation not used for practical preparation is the oxidation of the intermediate R-hexene derivative, with hot bromine water or nitric acid. Warmed with 1.42 nitric acid, abundant fumes of oxide of nitrogen were evolved and xanthogallol came down in crystalline form.

As a rule the crude product was pure enough for use in making derivatives. The most satisfactory method of purification was crystallization from hot ligroin. The product crystallized on cooling in clean orange plates, melting at 123° . Stenhouse gives 122° .

Xanthogallol dissolves in methyl alcohol, and after three days' standing gives oily drops with water. On longer standing the solution gives a heavy silver bromide precipitate with silver nitrate. No solid could be isolated from the oily product of the reaction. Ethyl alcohol shows exactly the same behavior.

With aqueous potassium iodide iodine is slowly set free, more rapidly on warming or addition of acid. An attempt was made to use this reaction quantitatively, but no definite end point could be obtained.

Phenylhydrazine hydrochloride in glacial acetic acid gave no crystalline hydrazone, but only an amorphous red precipitate. Xanthogallol does not react with tribromopyrogallol or with xanthogallic acid.

Xanthogallol contains no water of crystallization. Heated at 100° there is a constant slow loss in weight due to sublimation.

Molecular weight determinations were made in benzene on material which had been twice recrystallized and which melted at 123° . The third set of results is on material dried at 100° .

0.5270 g. in 17.42 g. C_6H_6 gave lowering 0.388° ; 1.0111 g., 0.731° ; 1.4820 g., 1.056° .
 0.3640 g. in 17.42 g. C_6H_6 gave lowering 0.274° ; 0.8010 g., 0.599° .
 0.3170 g. in 17.42 g. C_6H_6 gave lowering 0.240° .

The analytical results agreed well with those previously obtained. A determination of hydrogen in one-gram samples of the dry material proved its absence in xanthogallol.

0.2148 g. gave 0.0027 g. H_2O , 0.1188 g. CO_2 . 0.1255 g. gave 0.2300 g. AgBr; 0.1035 g. gave 0.1902 g. AgBr. 1.0156 g. gave 0.0044 g. H_2O ; 1.0812 g. gave 0.0029 g. H_2O .

	Theory.		Found.		
	$C_{18}H_{14}Br_{14}O_4$.	Co_2Br .	Stenhouse.	Theurer.	Thomas.
C.....	15.04	14.58	14.89, 15.03, 15.03	15.06, 15.24	15.05
H.....	0.28	0.00	0.29, 0.36, 0.32	0.34, 0.49	0.14, 0.05, 0.03
Br.....	78.00	77.69	78.14, 77.98	78.07, 78.08	78.00, 78.21
M. Wt..	1436	412		390, 397, 403, 381,	384, 379

Xanthogallol Quinoxaline.

The quinoxaline of xanthogallol was undescribed by Theurer, though he mentions that it does react with diamines. Four parts of xanthogallol (1 g.) and one part of *o*-phenylene diamine (0.25 g.) were entirely dissolved in alcohol. Upon slight warming on the steam bath the solution was filled with crystals of the quinoxaline. On recrystallization from hot benzene and alcohol it came out in almost colorless, slender needles, melting at $186-187^\circ$.

The quinoxaline dissolves in concentrated sulfuric acid with a reddish color and is reprecipitated on dilution. Its ether solution is unattacked by sodium carbonate, and 25% sodium hydroxide has no effect on the solid, even on boiling. With aniline the quinoxaline does not react.

The material for analysis and molecular weight determinations was dried over sulfuric acid. Molecular weights were determined in benzene.

0.1860 g. in 15.78 g. C_6H_6 gave lowering 0.135° ; 0.3744 g., 0.266° ; 0.4785 g., 0.338° .
 0.1883 g. gave 0.2912 g. AgBr; 0.1833 g. gave 0.2866 g. AgBr. 0.1902 g. gave 0.0168 g. H_2O , 0.1889 g. CO_2 ; 0.1694 g. gave 0.0153 g. H_2O , 0.1709 g. CO_2 .

	Theory.	Found.
	$C_8Br_4N_2C_6H_4$.	
C.....	27.30	27.09, 27.50
H.....	0.83	0.99, 1.01
Br.....	66.11	65.82, 66.54
N.....	5.79	6.45, 6.34
M. Wt.....	484	437, 446, 449

Xanthogallol, Aniline Derivative.

This aniline derivative was prepared according to Theurer's directions, by mixing cooled glacial acetic acid solutions of xanthogallol (4 g.) and aniline (4 g.). The product which came out on standing consisted of thick, short, yellowish needles, which could be recrystallized from hot alcohol. Yield, 1.5 g. The product darkened about 190° and melted about 195° (uncorr.). Theurer gives $204-205^\circ$.

The aniline derivative is quite soluble in hot alcohol, much less in cold. It is very difficultly soluble in benzene (0.1 g. would not dissolve in 20 cc.) and in nitrobenzene. Owing to the slight solubility no molecular weight determinations could be made.

0.1620 g. gave 0.0226 g. H₂O, 0.1863 g. CO₂; 0.1823 g. gave 0.0248 g. H₂O, 0.2085 g. CO₂. 0.1828 g. gave 0.2405 g. AgBr; 0.1942 g. gave 0.2543 g. AgBr. 0.2473 g. gave 7.20 cc. moist nitrogen at 22.5°, 760.6 mm.; 0.2318 g. gave 7.00 cc. at 23°, 773.5 mm.

	Theory.		Found.	
	C ₁₈ H ₅ Br ₁₁ O ₆ (NHC ₆ H ₅) ₄ .	C ₁₈ O ₂ Br ₂ .NHC ₆ H ₅ .	Theurer.	Thomas.
C.....	32.22	31.13	31.98	31.36, 31.20
H.....	1.79	1.41	2.16	1.56, 1.52
N.....	3.58	3.30	3.39	3.29, 3.45
Br.....	56.28	56.60	56.53	55.99, 55.73

Xanthogallol, Quinoxaline of Aniline Derivative.

The quinoxaline was prepared by dissolving four parts of the aniline derivative (1 g.) and one part of *o*-phenylene diamine (0.25 g.) separately in glacial acetic acid and mixing the solutions. Slight warming produced an orange crystalline precipitate. It crystallized fairly well on diluting a hot glacial acetic acid solution with water. The material darkened on heating, was black by 210° and shrank on longer heating to 250° but did not melt.

The results of analysis give rather high bromine results, but the ratio of bromine to nitrogen is 1.04 : 1, indicating that the reaction has taken place at the CO groups.

0.1535 g. gave 0.1770 g. AgBr; 0.1521 g. gave 0.1759 g. AgBr. 0.1729 g. gave 12.70 cc. moist nitrogen, 19°, 755 mm.; 0.1923 g. gave 13.80 cc. at 19°, 769 mm.

	Theory.		Found.
	C ₈ Br ₂ (NHC ₆ H ₅) ₂ :C ₆ H ₄ .		
Br.....	48.39		49.09, 49.21
N.....	8.47		8.35, 8.31

Xanthogallol and Bleaching Powder.

Xanthogallol reacts with bleaching powder, giving, in addition to an orange oil, two acid products, resembling, respectively, xanthogallic acid and xanthotonic acid.

Four grams xanthogallol were treated with 150 cc. cold concentrated bleaching powder solution. The mixture clouded at once, the xanthogallol disappeared, and a flocculent white precipitate formed. The characteristic odor of xanthogallol with alkali developed. After about an hour the precipitate had settled, leaving a clear orange supernatant layer with a strong bromine odor. The precipitate consisted entirely of calcium oxalate (0.6 g.). On extraction of the mother liquor with ether there were obtained crystals which could be freed from the orange oil by washing with water. They resembled xanthogallic acid in their behavior, giving with sodium carbonate a yellow sodium salt, from which a flaky white barium

salt could be made with barium nitrate. The free acid melted, however, between 120 and 128°, and a mixture with xanthogallic acid (128-130°) at 75-85°.

After extraction the mother liquor was treated with sulfuric acid, filtered, and extracted repeatedly with ether. The residues consisted of a semi-crystalline acid, much more soluble in water than that just described. It differed from xanthotonic acid in giving no color with ferric chloride and in not decolorizing bromine water. It was converted to its barium salt by treating the aqueous solution with barium carbonate, filtering and adding alcohol. The results of analysis of this salt were unsatisfactory, except to indicate that chlorine is present only as an impurity.

Ba 29.92, 29.91, 30.10; Br 32.66, 32.32; Cl 0.05, 0.07. Ba : Br : Cl = 1:1.86: 0.008.

With aniline in alcohol the acid gave gleaming white flakes, decomposing about 150°. In one case xanthotonic acid gave a similar compound melting at 154-156°.

Xanthogallol and Sodium Hypobromite.

Sodium hypobromite was prepared by adding bromine to 33% sodium hydroxide, cooling with ice. When xanthogallol was added to this solution, it was instantly changed to a heavy white precipitate, the action being accompanied by a hissing sound. The solid was sodium oxalate. No other product of the reaction was isolated. A slight tarry residue was obtained.

Xanthogallol and Hypobromous Acid.

The solution was prepared by adding excess silver nitrate to bromine water and filtering off the silver bromide, xanthogallol was added to the pale yellow, slightly cloudy solution. After about an hour the xanthogallol had entirely disappeared, and a whitish precipitate had formed in the orange solution. A blank hypobromous acid solution did not change color in five hours. The white precipitate consisted essentially of silver bromide. The filtrate was treated with a little sulfuric acid and extracted with ether. The first extract contained more or less unchanged xanthogallol. The other product consisted of a solid acid mixed with considerable oil.

The acid resembled xanthotonic acid in its ready solubility in water, and in the formation of a barium salt with barium carbonate, readily soluble in water and crystallizing on the addition of alcohol. It gave no color with ferric chloride. With aniline in alcohol it gave a derivative which yellowed at 138° and melted at 140-141°. An acid obtained in one case by treating xanthogallol mother liquors with sodium hydroxide gave a similar aniline derivative melting at the same temperature, as did also a mixture of the two.

A later experiment did not give such simple results. There seemed to be *two* acid products, one of which gave a much more difficultly soluble barium salt than the one just described. In no case was any oxalic acid formed.

Chloroxanthogallol.

Theurer says that this may be prepared by passing hydrochloric acid gas into a glacial acetic acid solution of xanthogallol, by treating the chlorinated ester with acid, or as a by-product in the preparation of the ester. Our material was obtained in the last way. From 5 g. xanthogallol about 2.5 g. of the chloro compound were obtained.

Chloroxanthogallol was also prepared by warming xanthogallol (2 g.) with absolute methyl alcohol containing 3% hydrochloric acid for two hours with a return condenser. On evaporation there was left a dirty orange residue, which was treated with concentrated sulfuric acid, diluted, filtered and dried. 1.1 g. of crude chloroxanthogallol were obtained.

The product was fractionally recrystallized and melted at 99–101°. Theurer gives 104°.

With aniline it gave the same aniline derivative as xanthogallol, melting at 196° alone and also mixed with the xanthogallol compound. With sodium carbonate xanthogallic acid was formed.

A determination of mixed halogens gave the ratio 2.97 Br : 1 Cl.

0.2169 g. gave 0.4160 g. mixed Ag salt, loss with Cl 0.0783 g. = 0.3306 g. AgBr.
0.2130 g. gave 0.4084, loss 0.0770 g. = 0.3251 g. AgBr.

	Theory.		Found.	
	$C_{12}H_4Br_{11}Cl_2O_8$.	$C_6Br_2ClO_2$.	Theurer.	Thomas.
C.....	16.6	16.34	16.36
H.....	0.3	0.00	0.19
Br.....	67.5	65.31	70.98	64.86, 64.96
Cl.....	8.1	9.65	9.09	9.74, 9.68

Chloroxanthogallol Quinoxaline.

Chloroxanthogallol reacts with *o*-phenylene diamine just as xanthogallol does, giving an abundant precipitate of brownish white needles. The crystals melted at 170°, and after two recrystallizations from benzene-alcohol at 171–172°.

A determination of mixed halogens resulted as follows:

0.2497 g. gave 0.3974 g. mixed Ag salt; 0.2394 g. gave 0.3805 g. Ag salt.

	Theory.	Found.
	$C_8Br_2Cl:N_2:C_6H_4$.	
Br + Cl.....	62.64	62.72, 62.80

Xanthogallol Methyl Acetal.

According to Theurer, when hydrobromic acid gas is passed into a cooled methyl alcohol solution of xanthogallol, there form colorless crystals of the methyl acetal.

Twenty g. of xanthogallol and 40 g. of methyl alcohol were well cooled

and treated with hydrobromic acid gas, prepared by dropping bromine on naphthalene covered with kerosene, and purified by passing through red phosphorus and calcium chloride tubes. The solution became orange and a small amount of crystals separated. The amount did not increase in the ice chest overnight. The solution was allowed to evaporate and 0.57 g. of the acetal was obtained. On further evaporation 5 g. of xanthogallol were recovered.

When recrystallized from hot methyl alcohol the acetal melted at 113.5° . Theurer gives 113° . It could also be recrystallized by dissolving in glacial acetic acid and adding water. It was readily soluble in benzene. With cold concentrated sulfuric acid it gave xanthogallol.

When xanthogallol is treated with hydrochloric acid gas in absolute methyl alcohol solution the product consists, not as Theurer says, of the chlorinated acetal but of the bromine compound, mixed with more or less of the former. On fractional crystallization a product containing only 0.5% chlorine was obtained. If, instead of xanthogallol, the residue from the acetal preparation, consisting of xanthogallol and chloroxanthogallol, is used, the product obtained is correspondingly richer in chlorinated compound. The acetal obtained in this way melted about where Theurer's did and gave comprehensible results on analysis.

The details were as follows: Xanthogallol was dried over sulfuric acid before use, and the absolute methyl alcohol was freshly prepared. The gas was passed for about half an hour after saturation seemed complete, and in every case the acetal crystallized out on standing in the ice chest—in one case after only three hours. The proportion of alcohol to xanthogallol was changed, using only 18 cc. of alcohol for 10 g., whereas Theurer recommends double the weight of alcohol. The product separated in coarse, thick, shining, white crystals, which were washed with methyl alcohol. They were decidedly soluble in the alcohol and lost their luster. More of the acetal was obtained by rapid evaporation of the mother liquor or by careful dilution with water. The final residue was an orange oil which yielded chloroxanthogallol (mixed with xanthogallol) on standing. Ten g. xanthogallol gave 4.8 g. of the acetal and 2.8 g. of orange residue.

As a rule, the crude product from the methyl alcohol melted about $91-94^{\circ}$. Repeated crystallization from hot methyl alcohol gave bromoacetal melting at $110-112^{\circ}$. From the mother liquors the more soluble chlorine derivative was obtained, though in small amount. These residues melted at $83-85^{\circ}$.

The bromoacetal was analyzed, using material melting at $112.5-113^{\circ}$. It consisted of shining white flakes, dried over sulfuric acid. Methoxyl carbon was determined in addition to total carbon and hydrogen and mixed halogens. Molecular weights were determined in benzene.

0.1698 g. gave 0.0234 g. H₂O, 0.1157 g. CO₂. 0.2363 g. gave 0.3907 g. mixed Ag salts, 0.2363 g. gave 0.3907 g. mixed salts, which together lost 0.1825 g. = 0.7705 g. AgBr. 0.2666 g. gave 0.2663 g. AgI.

0.1913 g. in 17.5 g. C₆H₆ gave lowering 0.134°; 0.3762 g. gave 0.258°.

	Theory.		Found.	
	C ₁₈ H ₄ Br ₁₄ O ₂ (OCH ₃) ₂ .	C ₈ Br ₄ O(OCH ₃) ₂ .	Theurer.	Thomas.
C.....	18.8	18.34	18.58, 18.51	18.58
H.....	1.6	1.31	1.62, 1.62	1.54
Br.....	70.4	69.86	70.98 ...	69.39
Cl.....	0.0	0.0	0.57
C _{meth}	4.57	5.24	5.10
M. Wt.....	1574	458	408, 417

Chloroxanthogallol Methyl Acetal.

As mentioned above, the chlorinated acetal could be obtained by using chloroxanthogallol instead of xanthogallol as a starting point. In this case also the amount of alcohol was decreased (9.5 g. of fairly clean residues from the acetal preparation, dried over sulfuric acid, were dissolved in 15 cc. absolute methyl alcohol). Crystals formed more slowly than with the bromine compound and came out in large glassy lumps. Nine g. of residues gave 3.3 g. of acetal and 4.0 g. of orange residue.

The crude substance usually melted about 79–80°. Several recrystallizations from hot methyl alcohol gave clear glassy crystals melting at 83–84° (Theurer, 86°). This material was dried over sulfuric acid and analyzed.

0.1645 g. gave 0.0223 g. H₂O, 0.1204 g. CO₂; 0.1783 g. gave 0.0241 g. H₂O, 0.1310 g. CO₂. 0.2827 g. gave 0.3039 g. AgI; 0.2755 g. gave 0.2942 g. AgI. 0.2237 g. gave 0.3840 g. Ag salts; 0.2288 g. gave 0.3922 g. Ag salts, which together lost 0.1476 g. = 0.6231 g. AgBr.

	Theory.		Found.	
	C ₁₈ H ₄ Br ₁₁ Cl ₂ O ₂ (OCH ₃) ₂ .	C ₈ Br ₂ ClO(OCH ₃) ₂ .	Theurer.	Thomas.
C.....	20.0	20.34	20.37, 19.82, 20.16	19.96, 20.04
H.....	1.5	1.45	1.98, 1.65, 2.10	1.51, 1.52
Br.....	61.1	58.10	61.94, 61.82, ...	58.61 ...
Cl.....	7.3	8.47	5.47, 6.54 ...	8.37 ...
C _{meth}	4.9	5.81	5.45, 5.49

Xanthogallic Acid Acetal.

When prepared according to Theurer's directions, by heating the brominated or chlorinated acetal with successive portions of sodium hydroxide solution, the yield is not large and the product is dark in color. It was found that it was sufficient to warm the acetal with 10% sodium hydroxide (4.5 g. acetal : 25 cc. NaOH) for about fifteen minutes at 50–80°. The solid material consisted almost entirely of the sodium salt. This was filtered off and dissolved by washing with cold water. On acidification of the original mother liquor and of the washings with concentrated hydrochloric acid the acetal came out in a mass of white crystals. It was re-

crystallized from ether-ligroin or from methyl alcohol and water. It crystallized with water, melted at 96–102°, and on drying over sulfuric acid at 105–106° (Theurer, 105°).

Theurer treated the compound with fuming sulfuric acid and obtained on dilution a product melting about 65°, showing strongly acid properties, which he analyzed, giving it the formula $C_6H_2Br_4O_2$. This product, however, is xanthogallic acid. Our product obtained in this way melted when freshly recrystallized from alcohol and water at about 70°, when dried on a tile overnight at 91–130°, and when dried over sulfuric acid at 136–137°. A sample of xanthogallic acid crystallized from alcohol and water gave the same melting points and a mixture also melted at 135–137°.

Theurer made and analyzed an aniline derivative of xanthogallic acid acetal. He does not give the melting point. Qualitative experiment seemed to show that the aniline compound is simply the salt. It was made by adding aniline to the glacial acetic acid solution of the acetal, and was recrystallized from boiling alcohol. The fine white crystals melted with decomposition about 152–154°. It dissolved readily in very dilute sodium hydroxide, and on acidification the acetal was precipitated, melting when dried at 102–103°. A mixture with dry xanthogallic acid acetal melted at 105–106°.

As a derivative of xanthogallic acid the acetal might be expected to form an acetyl derivative. Theurer, heating with acetyl chloride at 180°, obtained brownish crystals which he did not investigate. With acetic anhydride on the steam bath the acetal did not react. It dissolved readily in the anhydride and no crystals formed after warming. On complete evaporation the original substance was recovered.

The material for analysis was dried over sulfuric acid in a vacuum two weeks. It had completely lost its luster and melted at 105–106°. The silver bromide was converted to chloride to make sure that the compound contained no chlorine.

0.1911 g. gave 0.0352 g. H_2O , 0.1471 g. CO_2 ; 0.1923 g. gave 0.0346 g. H_2O , 0.1489 g. CO_2 . 0.2764 g. gave 0.3373 g. AgI; 0.2439 g. 0.2782 g. AgI. 0.1979 g. gave 0.2792 g. AgBr, 0.2080 g. gave 0.2925 g. AgBr; combined, lost 0.1352 g. = 0.5707 g. AgBr, total ppt. 0.5717 g.

	Theory.		Found.	
	$C_6H_2Br_4O_2(OCH_3)_2$	$C_6Br_3O(OH)(OCH_3)_2$	Theurer.	Thomas.
C.....	19.66	21.27	19.39	20.99, 21.12
H.....	1.64	1.77	2.29	2.06, 2.01
Br.....	65.6	60.75	66.07	59.84, 60.03
C_{meth}	4.9	6.08	5.65	5.82, 6.23

Methyl Ether of Xanthogallic Acid Acetal.

Theurer described another compound, prepared by passing hydrochloric acid into the methyl alcohol solution of xanthogallic acid acetal. He analyzed it, obtaining a large percentage of chlorine. The present results

indicate that only a trace of this element is present, and that the substance is a simple ether in which the hydrogen of the hydroxyl group is replaced by a methyl. This explains the fact that dilute alkali regenerates the acetal.

In the first preparation the solution of acetal (3 g. in 10 cc. absolute methyl alcohol) was cooled with ice during saturation with dry hydrochloric acid. No crystals formed after standing overnight and the solution was warmed on a boiling water bath ten minutes. On cooling with ice and seeding with a crystal obtained by diluting a drop of solution with water, the solution was filled with crystals. 1.6 g. were filtered off and 0.2 g. more was obtained on evaporation to one-half volume. The product melted about 75°, and on recrystallization from dilute methyl alcohol at 75–76.5°.

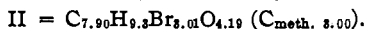
In the second preparation the solution (3 g. acetal in 7 cc. alcohol) was not cooled while the acid was passed in. After standing two days at room temperature it contained hard square transparent crystals (1 g.). They melted at 76.5–77°. On longer standing the mother liquor contained another crop of crystals (0.5 g.) of the same melting point, which was not raised by recrystallization. Theurer gives 77° as the melting point.

Both preparations of the ether were analyzed for carbon, hydrogen, methoxyl, carbon bromine and chlorine.

I. 0.1543 g. gave 0.0303 g. H₂O, 0.1305 g. CO₂; 0.1618 g. gave 0.0343 g. H₂O, 0.1372 g. CO₂. 0.2548 g. gave 0.3991 g. AgI; 0.3039 g. gave 0.4976 g. AgI. 0.1967 g. gave 0.2728 g. Ag salt; 0.2064 g. gave 0.2865 g. Ag salt, which combined lost 0.1306 g. = 0.5511 g. AgBr.

II. 0.1560 g. gave 0.0316 g. H₂O, 0.1316 g. CO₂. 0.2008 g. gave 0.3435 g. AgI. 0.2000 g. gave 0.2749 g. Ag salt; 0.2567 g. gave 0.3550 g. Ag salt, lost 0.1485 g. = 0.6270 g. AgBr.

	Theory.		Found.		
	C ₈ HBr ₄ Cl(OCH ₃) ₄ .	C ₈ Br ₂ O(OCH ₃) ₄ .	Theurer.	Thomas.	
				I.	II.
C.....	21.7	23.47	22.38	23.07, 23.13	23.00
H.....	2.5	2.20	3.00	2.20, 2.37	2.27
Br.....	57.8	58.68	57.55	58.20 ...	58.43
Cl.....	6.3	0.00	8.03	0.45 ...	0.16
C _{meth.}	8.7	8.80	...	8.36, 7.99	8.73



Xanthogallic Acid.

Two methods of preparation of xanthogallic acid were used: First, as described by Theurer, xanthogalloyl was rubbed in a mortar with cold, concentrated sodium carbonate till it formed a smooth paste, pale reddish yellow in color, then acidified with dilute sulfuric acid, filtered, washed and dried. To recrystallize, the product was dissolved in either benzene or ether and precipitated with ligroin. In order to obtain good crystals water must be present, otherwise the acid was obtained in a coarse powder

on evaporation. Five g. xanthogallol gave about 4 g. of crude acid, and about 1 g. of recrystallized acid. On acidification of the mother liquors more or less xanthotonic acid could be extracted with ether.

The second method of preparation was that originally described by Stenhouse. The xanthogallol was dissolved in a little ether and dilute sodium carbonate added with constant cooling. The pale yellow crystals of the sodium salt were filtered off, washed with a very little cold water, suspended in water and treated with dilute sulfuric acid. The acid was obtained in a papery mass of white crystals. Using this method the acid was cleaner and no xanthotonic acid was obtained on acidification of the carbonate solution.

Stenhouse gives the melting point of xanthogallic acid as 131° . Theurer mentions the fact that he obtained from benzene three kinds of crystals—long hairlike needles which melted at 72° and decomposed on rapid heating to 110° , and large prisms melting at 131° . Our acid melted at 70° , and when dried in a desiccator at 114° . When dried by treatment with concentrated sulfuric acid it melted at $132-133^{\circ}$, and once even as high as $136-137^{\circ}$.

The acid is readily soluble in ether and almost insoluble in ligroin. 0.15 g. dissolves in from 10 to 15 cc. benzene. It is much more soluble in nitrobenzene, 0.4 g. dissolving in 5 cc. It is almost insoluble in water.

Xanthogallic acid slowly disappears on long standing in water, the solution giving no color with ferric chloride, in contrast to xanthotonic acid. Warmed with water the acid melted to an oily layer which was partly crystalline on shaking. The solution now gave the xanthotonic acid color reaction with ferric chloride. An aqueous suspension of fresh xanthogallic acid gave a faint olive-green color with this reagent.

With cold bromine water the acid does not react. Warmed with bromine water it yields oxalic acid and pentabromoacetone. Potassium permanganate is quite rapidly decolorized, but no solid product is obtained. Nitric acid dissolves it to a yellow solution, milky on dilution. Sulfuric acid does not dissolve the acid but removes water of crystallization. With bleaching powder the acid reacts, giving apparently the same product as xanthogallol does. It gives a yellowish precipitate with silver nitrate, soluble in nitric acid. With phenylhydrazine hydrochloride it gives a dirty gray flocculent precipitate. No crystalline product was obtained. With *o*-phenylene diamine in alcohol it gives a crystalline orange product, which did not give concordant results on analysis.

No ether was obtained either by the action of hydrochloric acid upon its solution in alcohol, nor yet by treatment of its silver salt with methyl iodide.

By treatment with benzoic anhydride and also with 3,5-dinitro-benzoyl

chloride, attempts were made to prepare compounds corresponding to the acetyl derivative but none were obtained.

The sodium salt of the acid was made by dissolving the free acid in ether and adding sodium carbonate solution. The salt came down in yellow flakes. They were soluble in water and the solution decomposed on standing. The product was used in the preparation of the silver and barium salts.

Xanthogallic acid crystallizes with water. This can be removed by drying in a vacuum over sulfuric acid, by careful heating, or by treating the acid with concentrated sulfuric acid. A sample of good papery crystals was air-dried on a tile for one and a half hours, then weighed and dried to constant weight in a desiccator over sulfuric acid. After about two days the weight was constant and the sample was heated to constant weight at 55–60°.

Loss in desiccator 10.94%. Total loss 11.64%. $C_8H_5O_3Br \cdot 2H_2O = 9.35\%$; $3H_2O = 13.40\%$; $2.5H_2O = 11.42\%$. Another sample lost 9.33%.

Molecular weight determinations were made in benzene and in nitrobenzene, but in both cases the material decomposed. The first determination was made on desiccator-dried material.

0.0966 g. in 17.5 g. C_6H_6 gave lowering 0.081°, 0.2513 g. gave 0.152°. M. Wt. = 597, 526.

0.1602 g. in 23.44 g. $C_6H_5NO_2$ gave 0.079°, 0.2723 g. gave 0.132°. M. Wt. = 610, 622.

In the next determination the material was dried to constant weight at 50–75°. Considerable time elapsed before the second sample was introduced.

0.3146 g. in 22.63 g. $C_6H_5NO_2$ gave lowering 0.165°. M. Wt. = 596. 0.5318 g. gave 0.308°, 0.322° after 1/2 hour, 0.353° the next day. M. Wt. = 539, 516, 471.

Successive determinations were made on a single sample to see whether a constant value could be obtained, but the results did not indicate a simple breaking down of one molecule into two.

0.3525 g. in 20.18 g. $C_6H_5NO_2$.

Lowering 0.211° (15 min.)	M. Wt. = 585
0.227° (1 1/4 hr.)	M. Wt. = 544
0.234° (2 1/2 hr.)	M. Wt. = 528
0.247° (5 3/4 hr.)	M. Wt. = 500
0.264° (24 1/2 hr.)	M. Wt. = 468

Analytical results are given by both Stenhouse and Theurer on xanthogallic acid. Our bromine results do not agree at all with those of previous investigators, but two sets of determinations were made on two preparations of the acid which gave perfectly concordant results. The material was carefully prepared and recrystallized and dried in a vacuum desiccator over sulfuric acid to constant weight. It melted at 131°.

0.1939 g. gave 0.3137 g. AgBr; 0.1697 g. gave 0.2749 g. AgBr.

0.2004 g. gave 0.3238 g. AgBr; 0.1957 g. gave 0.3174 g. AgBr.

	Theory.			Found.		
	$C_{18}H_4Br_{11}O_8(OH)_2$.	$C_8HBr_3O_2$.	$(C_5Br_3O_2)_2O$.	Stenhouse.	Theurer.	Thomas.
C.....	17.33	17.20	17.65	17.36, 17.40	17.36
H.....	0.56	0.29	0.00	0.49, 0.54	0.78
Br.....	70.57	68.76	70.58	70.37, 70.17	70.27	68.84, 68.94 68.79, 69.04

Xanthogallic Acid—Barium Salt.

As mentioned above, the barium salt was prepared from the pure sodium salt. Clean, white recrystallized xanthogallic acid was dissolved in a little ether and treated with cold concentrated sodium carbonate solution. The heavy precipitate of sodium salt was filtered off, washed quickly with water and dried on a tile. It was then dissolved in water and treated with aqueous barium nitrate. The barium salt came down as a flaky white precipitate with a slight yellowish tinge. It could be washed with water, in which it was almost insoluble. The dry salt gradually became yellow. In a desiccator it lost 5.63% of its weight. At 100° the salt became brown and partly fused in less than twenty minutes. Another preparation of the barium salt came to constant weight in a vacuum desiccator after thirteen days, losing 13.7% of its weight.

$2H_2O = 4.14\%$; $3H_2O, 6.09\%$; $6H_2O, 11.47\%$; $7H_2O, 13.14\%$; $8H_2O, 14.74\%$.

Stenhouse and Hantzsch both analyzed the barium salt of the acid, obtaining results which did not agree. Stenhouse assumed that the yellowing of the salt represented extensive decomposition, thus rendering his results inaccurate. His results, however, fit the C_5 formula for a mono-basic acid.

0.2354 g. gave 0.0644 g. $BaSO_4$; 0.3045 g. gave 0.0830 g. $BaSO_4$; 0.3036 g. gave 0.0823 g. $BaSO_4$. 0.1929 g. gave 0.2554 g. $AgBr$; 0.1730 g. gave 0.2297 g. $AgBr$.

	Theory.		Found.		
	$(C_{18}H_4Br_{11}O_8)_2Ba_1$.	$(C_5Br_3O_2)_2Ba$.	Stenhouse.	Hantzsch.	Thomas.
Ba.....	14.18	16.45	15.93, 15.64	13.7	16.11, 16.05, 15.95
Br.....	60.70	57.62	56.35, 56.53 ...
					($Ba_1 : Br_{6.07}$)

Xanthogallic Acid—Acetyl Derivative.

The acetyl derivative was prepared according to the method of Hantzsch, by warming together xanthogallic acid (2 g.) and acetic anhydride (1.5 g.) on the steam bath for five minutes. On cooling the mixture became entirely solid. On recrystallization from hot glacial acetic acid 1.1 g. of good crystals were obtained. The compound is a white, well-crystallized solid, melting at 126–128°. Hantzsch gives no melting point. According to Hantzsch it is soluble in all the common solvents except water. It is much less soluble in cold glacial acetic acid than in hot. It dissolves readily in benzene (0.1 g. in less than 2 cc.) and in nitrobenzene.

The compound is hydrolyzed by concentrated sulfuric acid in the cold, giving xanthogallic acid. It yellows at once with strong ammonia and

dissolves more readily than in sodium hydroxide. On acidification the yellow color persists. The solution gives no color with ferric chloride.

The acetyl compound is attacked very slowly by sodium hydroxide. Strong alkali has scarcely more effect than dilute. The apparent product is xanthotonic acid, just as is obtained from xanthogallic acid. With alcoholic potash it reacted more readily, giving an infusible precipitate. Acidified and extracted with ether it gave the same acid, which gave the ferric chloride reaction, and pentabromoacetone and oxalic acid with bromine water.

Molecular weight determinations were made in benzene and in nitrobenzene. Hantzsch analyzed the acetyl compound, finding that three acetyl groups went in. On the C_5 basis this means that one is introduced and that one hydroxyl is present in the acid. Our analytical results do not agree with those of Hantzsch, but analyses made on two different preparations of the compound agree with each other. The material was freshly prepared and dried over sulfuric acid, and melted at $127-128^\circ$. Molecular-weight determinations were made in both benzene and nitrobenzene.

0.2055 g. gave 0.2974 g. AgBr; 0.2196 g. gave 0.3197 g. AgBr. 0.2009 g. gave 0.0153 g. H_2O , 0.1586 g. CO_2 ; 0.2187 g. gave 0.0166 g. H_2O , 0.1741 g. CO_2 .

0.1984 g. gave 0.2862 g. AgBr; 0.1792 g. gave 0.2597 g. AgBr.

0.2573 g. in 17.45 g. C_6H_6 gave lowering 0.209° ; 0.4747 g. gave 0.378° ; 0.5452 g. gave 0.434° .

0.2130 g. in 22.94 g. $C_6H_5NO_2$ gave 0.177° ; 0.4670 g. gave 0.381° .

	Theory.		Found.	
	$C_{18}H_{14}Br_{11}O_6(OC_2H_5O)_3$.	$C_3Br_3O_2 \cdot O_2C_2H_5$.	Hantzsch.	Thomas.
C.	20.98	21.49	21.22	21.54, 21.70
H.	0.95	0.77	1.00	0.85, 0.85
Br.	64.09	61.37	64.03	61.59, 61.97, 61.39, 61.67
M. Wt. . .	1373	391	...	353, 360, 360, 371, 378

Xanthogallic Acid—*p*-Toluidine Derivatives.

Theurer obtained from xanthogallic acid and *p*-toluidine in alcoholic solution oxalyl-*p*-toluidide and what he called the *p*-toluidine derivative of the acid. The present experiments indicate the formation of two successive derivatives, with the oxalyl-*p*-toluidide formation as a secondary reaction.

When concentrated alcoholic solutions of xanthogallic acid and *p*-toluidine were mixed, they instantly became solid with a curdy precipitate. This was filtered off by suction, washed rapidly on the filter with alcohol—with considerable loss of material—and dried in the dark on a porous tile. This product melted at $90-92^\circ$. It dissolved readily in hot glacial acetic acid and was not precipitated on cooling, but on dilution gave a product melting at $103-105^\circ$. On drying this substance in the hot closet it lost its luster and now melted at $147-148^\circ$. These three products will be dis-

cussed separately as Ppt. A, melting 89–90°, Ppt. B, melting at 102–104°, and Ppt. C, melting at 147–148°.

If the reaction mixture was allowed to stand without filtering, Ppt. A began to diminish at once, and after two days at room temperature gave a gummy brown residue, soluble in alcohol, from which no solid could be obtained. If an excess of *p*-toluidine was used and the mixture heated oxalyl-*p*-toluidide precipitated and it was difficult to obtain any solid on dilution.

Precipitate A.—1.5 g. acid and 0.5 g. of *p*-toluidine gave about 2 g. of product melting at 93–95°. Washed with alcohol till there was no odor of toluidine it melted at 87–88°, and another washing lowered the melting point to 84–85°. The dry substance decomposed slowly on standing. It dissolved more readily in hot glacial acetic acid than in alcohol, and, as mentioned above, gave Ppt. B. on dilution. With aniline in alcoholic solution it gave gleaming flakes of oxanilide, melting 244–245°.

Bromine determinations were made.

0.1948 g. gave 0.2438 g. AgBr; 0.1954 g. gave 0.2452 g. AgBr.

	Theory.	Found.
	$C_8H_9Br_3 \cdot NH_2 \cdot C_7H_7$.	
Br.....	52.63	53.26, 53.40

Precipitate B.—As mentioned above, this was made by recrystallizing A from dilute alcohol or acetic acid. It formed shining white rectangular plates from acetic acid (diluted with ten volumes of water) and melted at 102–104°. The crystals weathered very quickly in the air and lost water very rapidly over sulfuric acid or in the hot closet.

When B was treated with aniline in alcoholic solution the product was not oxanilide but the mixed oxalyl-anilide-*p*-toluidide, melting at 207°. With *p*-toluidine, B gave oxalyl-*p*-toluidide.

Several determinations of loss in weight gave varying results, depending on the time of drying before weighing. The first is probably the most reliable, as the second sample showed signs of weathering and the third was dried only a very short time before weighing.

Loss in weight = 20.41%, 18.17%, 23.24%.

$C_8H_9Br_3 \cdot NC_7H_7 \cdot 6H_2O = 19.78\%$; $7H_2O, 22.34\%$; $8H_2O, 24.74\%$.

Precipitate C.—The purest material obtained as C melted at 149–150°. Recrystallized from dilute acetic acid it gave B.

In alcoholic solutions it gave the mixed oxalyl-anilide-*p*-toluidide with aniline.

The substance was too difficultly soluble in benzene and in nitrobenzene to permit molecular-weight determinations in these solvents. An attempt was made to use glacial acetic acid, but, while the results checked among themselves, they were very low. A determination of the molecular weight of aniline oxalate in the acid gave similarly low results.

0.2840 g. in 21.84 g. acetic acid gave lowering 0.136° ; 0.5603 g. gave 0.265° ; 0.7258 g. gave 0.331° . M. wt., 373, 378, 392.

0.1568 g. aniline oxalate in 21.04 g. acetic acid gave 0.141° ; 0.1361 g. in 24.17 g. gave 0.106° . M. wt., 206, 207. Theory, 276.

The analytical results on this *p*-toluidine derivative are so different from those of Theurer that it seems possible that he had a different compound, although his method of preparation was the same. He gives no melting point.

I. 0.1547 g. gave 0.0318 g. H_2O , 0.1827 g. CO_2 ; 0.1565 g. gave 0.0343 g. H_2O , 0.1855 g. CO_2 . 0.1653 g. gave 0.2082 g. AgBr; 0.1481 g. gave 0.1860 g. AgBr.

II. 0.1725 g. gave 0.0377 g. H_2O , 0.2039 g. CO_2 ; 0.1552 g. gave 0.0356 g. H_2O , 0.1818 g. CO_2 . 0.1718 g. gave 0.2162 g. AgBr; 0.1543 g. gave 0.1945 g. AgBr. 0.2361 g. gave 7.10 cc. nitrogen, 24° , 772 mm.; 0.2668 g. gave 7.60 cc., 21° , 760 mm.; 0.2347 g. gave 6.70 cc., 21° , 760 mm.

	Theory.		Found.			
	$C_{18}H_{17}Br_{11}O_8(NH_2C_7H_7)_4$	$C_8H_9O_2Br_2NC_7H_7 \cdot \frac{1}{2}H_2O$	Theurer.	Thomas.		
				I.	II.	
C.....	42.1	32.21	41.7	32.20, 32.33	32.24, 31.94	
H.....	3.8	2.01	3.69	2.30, 2.45	2.44, 2.57	
Br.....	41.8	53.69	42.38	53.60, 53.45	53.56, 53.66	
N.....	5.3	3.13	5.88	...	3.41, 3.23, 3.23	

Xanthogallic Acid—Aniline Derivatives.

Theurer describes the action of xanthogallic acid with aniline in more detail than that with *p*-toluidine, obtaining similar results. He treated an alcoholic solution of the acid with aniline and warmed gently. There gradually formed crystals of oxanilide. These were filtered off and the solution was then treated with dilute acetic acid. This precipitated the aniline derivative of the acid. Theurer makes no mention of a heavy curdy precipitate which comes down instantly when the cold solution is treated with aniline. Furthermore it is possible by using less aniline and not heating so long to avoid the formation of more than a trace of oxanilide, with a correspondingly increased yield of the aniline derivative; while, if the heating is too long the product will be entirely oxanilide, and no solid can be precipitated with dilute acetic acid.

Four g. of crystalline acid were dried in the hot closet and then dissolved in 25 cc. of alcohol. 1.5 cc. of aniline in 5 cc. of alcohol were added. Instantly the mixture became solid with the curdy white precipitate of the aniline salt. After warming a few minutes on the steam bath the entire precipitate had disappeared and a trace of oxanilide formed. This was filtered off (0.1 g.) and the filtrate immediately treated with water and a little dilute acetic acid. A yellowish precipitate came down slowly (2.5 g.). As in the case of the *p*-toluidine compounds, the products will be discussed separately as Ppt. A (the aniline salt of xanthogallic acid) and Ppt. B, melting at 145° .

Precipitate A.—This substance is much less stable than the corresponding *p*-toluidine compound. It was obtained in better condition by using a more dilute solution than that just described (0.4 g. in 15 cc. alcohol). The material was washed once with alcohol, in which it was very soluble, and dried on a tile. It consisted of clean, white crystals, which, however, became orange on standing overnight in a stoppered tube and in two days had entirely changed to a brown transparent gum. This gum dissolved in alcohol, showing that no oxanilide was formed in the decomposition. No solid was obtained on dilution of the alcoholic solution.

Ppt. A melts about 70°. It is somewhat soluble in alcohol, readily in ether, insoluble in water. With warm water it is decomposed.

With aniline in alcohol, Ppt. A gives oxanilide, melting at 248°. With *p*-toluidine, it gives oxalyl-*p*-toluidide, melting at 262–263°.

Precipitate B.—The purest sample of Ppt. B melted after recrystallization from acetic acid at 148–149°, with evolution of gas. Theurer gives no melting point for his product.

With aniline in alcohol, Ppt. B gives oxanilide. On dilution of the solution a very sticky product is obtained, which gives no crystalline product with semicarbazide hydrochloride. With *p*-toluidine, Ppt. B gives the mixed oxalyl-anilide-*p*-toluidide, melting at 206°.

With dimethylaniline in alcohol no crystalline product was obtained. With *o*-phenylene diamine a dark amorphous precipitate came out on standing.

Molecular-weight determinations on Ppt. B could not be made in benzene or in nitrobenzene, owing to the very slight solubility. A determination was made in glacial acetic acid, the results proving similar to those with the *p*-toluidine derivative.

Analyses were made on material which had been twice recrystallized from dilute alcohol and dried for a week over sulfuric acid. It melted at 148–149°. The nitrogen determinations were made by the closed tube method and were undoubtedly too high.

0.1793 g. gave 0.2253 g. AgBr; 0.1846 g. gave 0.2314 g. AgBr. 0.1773 g. gave 0.0346 g. H₂O, 0.1920 g. CO₂; 0.1677 g. gave 0.0311 g. H₂O, 0.1816 g. CO₂. 0.3184 g. gave 10.6 cc. nitrogen, 22°, 772 mm.; 0.2880 g. gave 9.8 cc., 19°, 780 mm.

0.2047 g. in 22.05 g. acetic acid gave lowering 0.102°; 0.2891 g. gave 0.147°.

	Theory.			Found.	
	C ₁₅ H ₇ Br ₁₁ O ₈ (NH ₂ C ₆ H ₅) ₈	C ₈ H ₁₀ O ₂ Br ₈ .NH ₂ C ₆ H ₅	C ₈ H ₁₀ O ₂ Br ₈ NC ₆ H ₅ .1½H ₂ O	Theurer.	Thomas.
C.....	40.0	29.86	29.20	39.70	29.54, 29.54
H.....	3.15	1.81	2.21	2.97	2.18, 2.07
Br.....	44.4	54.30	53.10	43.96	53.49, 53.35
N.....	5.67	3.17	3.10	...	3.86, 4.00
M. wt.....	...	442	453	...	355, 348

Xanthotonic Acid.

This acid is merely mentioned by Theurer, who found it difficult to obtain in the pure condition, and who therefore analyzed the barium salt.

In the present work it has been prepared in three ways, from xanthogallol and sodium hydroxide, xanthogallic acid and sodium hydroxide, and xanthogallic acid and alcoholic potassium hydroxide.

When xanthogallol was used, other products were obtained, the amount depending upon the concentration. With strong caustic a white precipitate formed together with a colorless oil. On acidification a small amount of xanthotonic acid could be extracted with ether. With more dilute alkali the yield of acid was increased and that of the other products diminished. When 4 g. xanthogallol suspended in 25 cc. of water were treated with 10% sodium hydroxide a powdery precipitate slowly formed, together with a colorless oil. The solid (1.5 g.), melting at 134-136°, was the hexabromodihydrobenzene described by Theurer as melting at 139°. On acidification of the mother liquor and extraction with ether only a trace of xanthotonic acid was obtained.

With greater dilution the yield of acid was greatly increased.

According to the second method, xanthogallic acid was substituted for the xanthogallol. This gave a cleaner product, as no hexabromodihydrobenzene was formed and only a little oil. The best method was to leave the acid standing with dilute alkali until the sodium salt which formed had entirely dissolved, then to extract once with ether to remove oily impurities, then to acidify with dilute sulfuric acid and extract three times with ether. On evaporation of the combined ether extracts an oily residue was left which solidified on scratching. Crystallization could be hastened by adding benzene or ligroin. 10 g. of xanthogallic acid gave 4.9 g. of xanthotonic acid, and in another case 5 g. gave 2.7 g. 15 g. of xanthogallol gave 4.2 g. of the acid, first converting it to xanthogallic acid and then treating with alkali.

The third method of preparation, from xanthogallic acid and alcoholic potassium hydroxide, was not used because, while a fairly good yield of the acid is obtained and the reaction goes much more rapidly than in aqueous solution, the product is contaminated with considerable brown oil.

The acid crystallizes from ether-ligroin in shining white needles which melt at 79-80°. Dried, they become opaque and melt at 110-115°. Theurer gives the melting point of the acid he obtained as 124° and says that it gradually decomposed.

The acid is very soluble in water, in ether, and in alcohol, difficultly in benzene, and still more so in ligroin.

With sodium hydroxide solution it dissolved giving no hexabromodihydrobenzene. All the acid disappeared, the product being an oil which

could be extracted from the alkaline solution with ether. The solution gave a strong test for bromide.

An aqueous solution of xanthotonic acid gives a very characteristic color reaction with ferric chloride. There is an instant purple-red coloration, changing in a few minutes through blood-red to yellow.

The acid rapidly decolorizes permanganate, but no solid product can be found. With silver nitrate the acid gives a yellow precipitate of the silver salt, partly soluble in nitric acid and blackening on standing. The acid dissolves at once in strong nitric acid with slight evolution of gas. It is almost entirely undissolved by strong sulfuric acid. It apparently reacts with acetic anhydride, but not as smoothly as does xanthogallic acid. No product could be isolated but unchanged acid. In one small test a trace of oxanilide was obtained from the acid and aniline in alcoholic solution, but this could not be repeated. With phenylhydrazine the acid gives a dirty yellow turbidity but no hydrazone. With *o*-phenylene diamine it gives a yellow precipitate, which decomposes on warming the solution.

Lederer¹ made various iodo-acetones from acetone-dicarboxylic acid by the action of iodine, using various agents to catch the hydriodic acid formed. For instance, sodium carbonate gave symmetrical di- and tetra-iodoacetone, iodic acid gave periodoacetone, and mercuric oxide gave tetra-, while potassium bromate gave penta-iodoacetone. The xanthotonic acid gave no product which could be recognized as a mixed bromo-iodo-acetone. A strong iodoform odor developed and iodoform was isolated from the solution after standing some time.

A sample of good shiny crystals of the acid was dried rapidly on a tile, then weighed on a watch glass and dried to constant weight over sulfuric acid. After five days it was heated for five hours at 60–75° without further loss.

1.8005 g. lost 0.1023 g. = 5.68%. Theory $C_8H_5Br_3O_4 \cdot H_2O = 4.68\%$; $2H_2O = 8.93\%$.

It was hoped to determine the basicity of xanthotonic acid by titration with alkali but no sharp end point could be obtained. This is not surprising since experiment showed that the acid is decomposed by alkali.

Xanthotonic acid was dried to constant weight in a desiccator and analyzed for bromine, carbon and hydrogen. Molecular-weight determinations were made in nitrobenzene, in which the acid is not very readily soluble.

0.3186 g. in 22.02 g. $C_6H_5NO_2$ gave lowering 0.223°; 0.2457 g. in 21.15 g. gave 0.178°.

0.2087 g. gave 0.3222 g. AgBr; 0.1774 g. gave 0.2747 g. AgBr; 0.1660 g. gave 0.2544 g. AgBr. 0.2005 g. gave 0.0159 g. H_2O , 0.1200 g. CO_2 ; 0.1825 g. gave 0.0146 g. H_2O , 0.1110 g. CO_2 .

¹ Ger. Pat. 95,440, Friedlaender, "Fortschritte der Teerfarbenfabrikation," 1897–1900, p. 711.

	Theory.		Found.
	$C_8H_4Br_2O_4$.	$C_8H_2Br_4O_4$.	
C.....	22.06	16.35	16.32, 16.58
H.....	1.47	0.82	0.89, 0.90
Br.....	58.81	65.39	65.68, 65.90, 65.40
M. wt.....	272	367	459, 461

Xanthotonic Acid—Barium Salt.

Theurer emphasizes the difficulty of getting the free acid pure, and accordingly he made and analyzed the barium salt. The salt was prepared according to his directions, but seemed to be much less stable than he describes it and gave no concordant results when an analysis was attempted.

Pentabromoacetone.

When xanthotonic acid is treated with bromine water it reacts in the cold, the bromine water is decolorized, and a white precipitate of pentabromoacetone forms. From the solution oxalic acid can be obtained by evaporation. In one case 4.9 g. of crude acid gave 5 g. of crude pentabromoacetone.

The preparation was simplified by working from the crude xanthogallolic acid without isolating the xanthotonic acid. 15 g. of crude xanthogallolic acid were suspended in water and treated with sodium hydroxide, the total volume amounting to several liters. When all the solid had dissolved, it was acidified with dilute sulfuric acid and treated directly with bromine water, and left standing overnight. The crude pentabromoacetone weighed 12 g. One recrystallization from alcohol gave a good product.

In one preparation rough quantitative results were obtained. One g. of good xanthotonic acid gave 0.55 g. of pentabromoacetone and 0.25 g. of hydrated oxalic acid. 0.37 g. of the latter might be expected if one molecule was formed from one of the acid.

Pentabromoacetone is also obtained from xanthogallolic acid by heating with bromine water.

In order to prove the identity of the acetone it was also prepared from acetone-dicarboxylic acid, according to the directions of Lederer,¹ by treating a dilute solution of the latter with bromine water.

Our purest pentabromoacetone melted at 79–80° (uncorr.). This is several degrees higher than the values given by previous workers.² The melting point falls quite rapidly to about 72–74° if the material is kept.

The acetone was further identified as follows: It reacted with alcoholic ammonia, giving a crystalline precipitate of dibromoacetamide, melting at 156°. With sodium carbonate it gave dibromoacetic acid (m. p. 40°)

¹ Ger. Pat. 98,009, Friedlaender, "Fortschritte der Teerfarbenfabrikation," 1897–1901, p. 711.

² Jackson and Beggs, THIS JOURNAL, 38, 677 (1916).

and bromoform. With sodium hydroxide the action was more rapid, but the bromoform was further decomposed into carbon dioxide and hydrobromic acid. The bromoform was identified by its odor, boiling point (147–148°, given 151°), and by conversion into tetrabromomethane (m. p. 92°) with bromine and potassium hydroxide in the sunlight.

Chlorotribromoacetone, $\text{CHBr}_2\cdot\text{CO}\cdot\text{CHBrCl}\cdot 4\text{H}_2\text{O}$.

Chlorotribromoacetone was prepared in two ways, by the action of chlorine water on xanthotonic acid, and by the action of hydrochloric acid and potassium chlorate on the same substance. The latter method was suggested by the work of Levy and Jedlicka,¹ who obtained from chloroanilic acid with hydrochloric acid and potassium chlorate oxalic acid and symmetrical tetrachloroacetone hydrate, while chlorine and iodine gave pentachloroacetone.

An aqueous solution of xanthotonic acid was treated with chlorine water. It became milky at once, but no precipitate formed even on long standing. On extraction of the solution an oily substance was obtained, which crystallized on the addition of a very little water. From the mother liquor oxalic acid was obtained by evaporation.

Xanthotonic acid (0.2 g.) was dissolved in as little water as possible, treated with 1 cc. of hydrochloric acid, and then with 0.1 g. of powdered potassium chlorate in small amounts. The action was very slow but after several hours flaky white crystals of the chlorotribromoacetone hydrate formed.

The hydrate as obtained from the aqueous solution melted at 61–63°. Recrystallized from dilute alcohol it melted at 64–65°, but most of the material was lost. On standing in the air, or very rapidly in a desiccator over sulfuric acid, the substance lost water changing to a colorless liquid, which again crystallized on the addition of a little water.

With sodium hydroxide the compound gave no odor of bromoform. With alcoholic ammonia the substance entirely decomposed, without the formation of any bromoform or chlorobromoform or any dibromoacetamide.

With zinc and sulfuric acid (1.0 g. of hydrate was heated with a return condenser on the steam bath for 1½ hours with 20 cc. of water, 8 g. of 50% sulfuric acid, and 3 g. of granulated zinc) acetone was obtained. Five cc. of the liquid were distilled off and gave good tests for acetone. It was identified by preparing indigo with *o*-nitrobenzaldehyde, and dibenzylidene acetone with benzaldehyde.

It was found impossible to carry out the analyses on anhydrous material. On drying in a desiccator there was a steady loss in weight due to volatilization. The loss in eighteen hours was 18.08%, partly due to this cause. Analyses were accordingly made on hydrated material. The

¹ *Ann.*, 249, 87 (1888).

material was weighed as rapidly as possible after removing from the water, but even so the last samples were decidedly greasy. The carbon and hydrogen results given below were obtained on a different preparation from the halogen results.

0.3444 g. gave 0.5580 g. mixed Ag salt, loss 0.1075 g. = 0.4539 g. AgBr; 0.4070 g. gave 0.6019 g. Ag salt, loss 0.1151 g. = 0.4870 g. AgBr. 0.3146 g. gave 0.0626 g. H₂O, 0.1011 g. CO₂.

	Theory. CHBr ₂ .CO.CHBr ₂ .Cl.4H ₂ O.	Found.
C.....	8.98	8.76
H.....	2.49	2.23
Br.....	59.86	56.09, 50.81
Cl.....	8.73	7.48, 6.99
H ₂ O.....	17.95	18.08

Tetrabromoacetone, CHBr₂.CO.CHBr₂.4H₂O.

A substance which we suppose to be symmetrical tetrabromoacetone was obtained in one case when xanthotonic acid was treated with bromine water. After the precipitate of pentabromoacetone was filtered off the solution was extracted with ether and crystals were obtained from this extract by evaporation.

The same product was obtained by treating the acid (0.2 g.) dissolved in 2 cc. of water with 1.5 cc. of hydrobromic acid, and adding 0.1 g. of powdered potassium chlorate in very small portions. After fifteen minutes the solution contained considerable precipitate, which was filtered off and washed with water.

The crystals obtained in the first case melted at 56–58°, those in the second at 58–60°. On standing in the air, or more rapidly over sulfuric acid, they liquefied. If a little water was added they solidified again. This behavior indicates a hydrated acetone.

With sodium hydroxide the crystals gave no bromoform, and no bromoform or dibromoacetamide with alcoholic ammonia.

This compound has never been described and no analyses were made. The formula chosen is based on its similarity in preparation and properties to the chlorine derivative just described.

Hexabromodihydrobenzene.

According to Theurer, xanthogallol suspended in water and treated with sodium hydroxide gives a white precipitate mixed with drops of oil. This can be filtered off and a further amount obtained by extraction with ether. On acidification and extraction Theurer obtained an oily acid which he could purify only by conversion to the barium salt. This is xanthotonic acid.

Various experiments were made to determine the conditions most favorable for a large yield of the benzene compound. Previous experiments in the preparation of the acid showed that with sufficient dilution the amount

of the benzene compound could be greatly diminished. With increasing concentration the yield of acid—and also of oil—decreased, but the crude product was very brown and contained considerable inorganic matter if 25% alkali was used. Heat could be applied, but this gave the same result.

The method finally used in the preparation of material for analysis was to suspend the xanthogallol (6 g.) in water (125 cc.) and add 25% sodium hydroxide (20 cc.). The xanthogallol began to disappear at once, giving a milky solution in which an apparently clean white precipitate slowly formed. This, however, became oily if it was filtered. Instead, the solution was extracted four times with ether (after standing twenty minutes). The extracts left an orange oil. With absolute alcohol this partly dissolved and the undissolved part gradually changed to a clean white crystalline solid. From a total of 16 g. of xanthogallol about 2 g. crude hexabromodihydrobenzene were obtained. The crude product was recrystallized three times from boiling absolute alcohol, in which it was difficultly soluble, melting successively at 134–136°, 136–136.5° and 136.5–137°. About 0.9 g. of material was left after the last recrystallization. Theurer gives the melting point as 139°.

The mother liquors after extraction with ether were acidified with sulfuric acid and extracted once with ether to remove xanthotonic acid. Only a few tenths of a gram were obtained. Oxalic acid was found in the mother liquors after this extraction. In one case the sulfuric acid solution from 6 g. of xanthogallol was evaporated to a small volume over the free flame. The solution was then extracted with ether, on the evaporation of which there remained about 0.2 to 0.25 g. of oxalic acid, melting at 99–100°. It gave the usual qualitative tests for oxalic acid.

In another case the mother liquors from 16 g. of xanthogallol were combined, treated with calcium carbonate, the precipitate filtered off and washed with dilute hydrochloric acid. The hydrochloric acid solution was then extracted with ether, and the residue on evaporation of the ether consisted of oxalic acid.

That the oxalic acid is not to be considered as a product of the decomposition of xanthotonic acid rather than of xanthogallol is shown by the following results:

0.5 g. of acid melting at 79–80° was dissolved in 10 cc. of water and treated with 2 cc. of sodium hydroxide and left standing five hours. It was very dark in color and had the sharp odor characteristic of alkaline solutions of xanthogallol. Extraction with ether removed nothing. On acidification with dilute sulfuric acid and extraction with ether a very oily black residue was obtained, from which no solid could be isolated. The sulfuric acid after extraction gave only a trace of possible calcium oxalate.

Two other experiments of the same kind gave similar results.

Hexabromodihydrobenzene is rather more soluble in glacial acetic acid than in most solvents, but even in this molecular weight determinations could not be made. It is difficultly soluble in absolute alcohol, hot and cold, in benzene, nitrobenzene and aniline. It dissolves readily in ethylene bromide, in which the molecular weight was determined.

0.3090 g. in 42.56 g. $C_2H_4Br_2$ gave lowering 0.166° ; 0.5236 g. gave 0.282° .
 0.1661 g. gave 0.0073 g. H_2O , 0.0802 g. CO_2 ; 0.1685 g. gave 0.0077 g. H_2O , 0.0813 g. CO_2 . 0.1562 g. gave 0.3215 g. AgBr; 0.1542 g. gave 0.3170 g. AgBr.

	Theory. $C_6H_2Br_6$.	Found.	
		Theurer.	Thomas.
C.....	13.00	13.26, 13.09, 13.14	13.17, 13.16
H.....	0.36	0.79, 0.50, 0.50	0.49, 0.51
Br.....	86.63	86.8, 86.72, 86.41	87.50, 87.60
M. wt.	554	514, 516

Summary.

I. It has been shown that the hitherto accepted formula for xanthogallol is inconsistent with its molecular weight and with the fact that it contains no hydrogen.

II. A new cyclic formula has been suggested based essentially upon several series of reactions leading to oxalic acid and brominated acetones. This formula also permits a simple interpretation of the reaction by which xanthogallol is formed from pyrogallol.

III. The genetic relationships studied in these reactions serve to establish the constitution of nearly twenty other substances closely allied to xanthogallol.

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[CONTRIBUTION FROM CHEMISTRY SECTION, IOWA STATE COLLEGE.]

SYNTHESIS OF A NAPHTHOTETRAZINE FROM DIETHYL SUCCINYL SUCCINATE AND DICYANODIAMIDE.

By ARTHUR W. DOX.

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On account of the ease with which dicyanodiamide can be prepared in quantity and at very small cost from the crude calcium cyanamide of commerce, this substance is beginning to find numerous applications in organic syntheses. Among other properties, the amidine structure of dicyanodiamide has been taken advantage of for the preparation of certain nitrogen heterocycles. For example, by condensation with such substances as α -ketone acid esters, various pyrimidine derivatives are obtained. Thus, dicyanodiamide condenses with malonic ester derivatives¹ and with acetoacetic ester² to form substituted pyrimidines. It is not

¹ German Patent 165,223 (1905).

² Söll and Stutzer, *Ber.*, 42, 4534 (1910).