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The Phloroglucinol Furfural Reaction

Eleanor Frances Chase

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THE PHLOROGLUCINOL FURFURAL REACTION

Eleanor Frances Chase

Thesis submitted for
the degree of
Master of Science

MASSACHUSETTS AGRICULTURAL COLLEGE

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PURPOSE OF THE INVESTIGATION

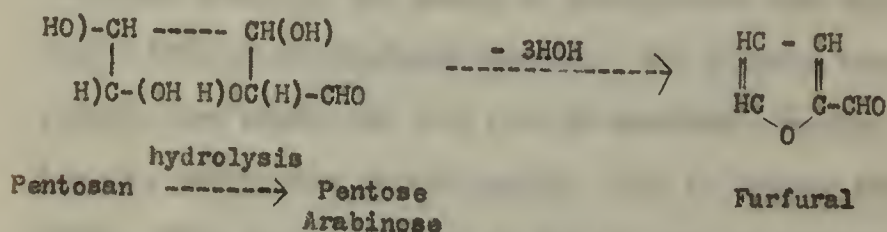
The purpose of this investigation was to form various derivatives of phloroglucinol and to treat these with furfural in hydrochloric acid solution to see if, in this manner, a clearer understanding of the nature of the reaction between furfural and phloroglucinol might not be ascertained.

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REVIEW OF LITERATURE

The method of determining pentoses and pentosans by means of phloroglucinol given in the Methods of Analysis of the Association of Official Agricultural Chemists, is decidedly empirical and little is known of the exact nature of the reaction.

The method is a modification of that proposed by Counciler and perfected by Kröber in 1900 (1). It is based upon the fact that pentoses and pentosan materials on boiling with strong hydrochloric acid yield furfuraldehyde in sufficient amount to be estimated quantitatively. The reactions involved may be represented as follows:



The furfuraldehyde is precipitated from a hydrochloric acid solution by phloroglucinol.

The method of procedure is as follows (2): "Place a quantity of the material, 2 to 5 grams, chosen so that the weight of phloroglucinol obtained shall not exceed 0.300 gram,

(1) J. Landw. 48, 357, 1900.

(2) Official and Tentative Methods of Analysis of the A.O.A.C., p. 96.

in a 300 cc. distillation flask, together with 100 cc. of 12 per cent hydrochloric acid (sp. gr. 1.06) and several pieces of recently heated pumice stone. Place the flask on a wire gauze, connect with a condenser, and heat, rather gently at first, and regulate so as to distil over 30 cc. in about 10 minutes, the distillate passing through a small filter paper. Replace the 30 cc. distilled by a like quantity of the dilute acid, added by means of a separatory funnel in such a manner as to wash down the particles adhering to the sides of the flask, and continue the process until the distillate amounts to 360 cc. To the total distillate add gradually a quantity of phloroglucin dissolved in 12 per cent hydrochloric acid and stir thoroughly the resulting mixture. The amount of phloroglucin used should be about double that of the furfural expected. The solution turns first yellow, then green, and very soon an amorphous greenish precipitate appears, which grows darker rapidly, till it becomes finally almost black. Make the solution up to 400 cc. with 12 per cent hydrochloric acid and allow to stand overnight.

Filter the amorphous black precipitate in a tared Gooch crucible having an asbestos mat, wash carefully with 150 cc. of water in such a way that the water is not entirely removed from the crucible until the very last, then dry for 4 hours at the temperature of boiling water, cool and weigh in a weighing bottle; the increase in weight being reckoned as furfural phloroglucid. To

calculate the furfural, pentose, or pentosan from the phloroglucid, use the following formulas given by Kröber:

(1) For a weight of phloroglucid, designated by "a" in the following formulas, under 0.03 gram,

$$\begin{aligned}\text{Furfural} &= (a + 0.0052) \times 0.5170 \\ \text{Pentoses} &= (a + 0.0052) \times 1.0170 \\ \text{Pentosans} &= (a + 0.0052) \times 0.8949\end{aligned}$$

In the above and also in the following formulas, the factor 0.0052 represents the weight of phloroglucid which remains dissolved in the 400 cc. of acid solution.

(2) For a weight of phloroglucid "a" between 0.03 and 0.300 gram, use Kröber's table XXX, Table 2, or the following formulas:

$$\begin{aligned}\text{Furfural} &= (a + 0.0052) \times 0.5185 \\ \text{Pentoses} &= (a + 0.0052) \times 1.0075 \\ \text{Pentosans} &= (a + 0.0052) \times 0.8866\end{aligned}$$

(3) For a weight of phloroglucid "a" over 0.300 gram,

$$\begin{aligned}\text{Furfural} &= (a + 0.0052) \times 0.5180 \\ \text{Pentoses} &= (a + 0.0052) \times 1.0026 \\ \text{Pentosans} &= (a + 0.0052) \times 0.8824\end{aligned}$$

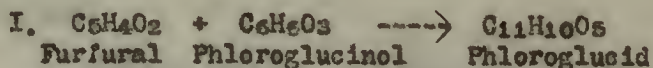
The furfural-phloroglucid formed is an amorphous black precipitate which is insoluble in ordinary reagents, so that a molecular weight determination by ordinary methods cannot be accomplished. It is hygroscopic and, upon exposure to air and light, undergoes oxidation.

Counciler (1) who first used phloroglucinol, attempted to explain the reaction as well as that between pyrogallol and furfural. (2)

(1) Chem. Zeit. 18, 966, 1894.

(2) Hötter, Chem. Zeitung, 17, 1743, 1893.

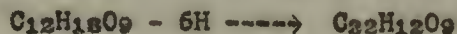
He expected the action of both pyrogallol and phloroglucinol with furfural to be like the general reaction between phenols and aldehydes, namely a condensation of one molecule of each without loss of water, as in I, and a second condensation of two molecules of the product with loss of one molecule of water, as in II.



However, Hötter by a combustion analysis of the precipitates from pyrogallol and furfural obtained results which did not agree with the theoretical figures based on a reaction analogous to that above.

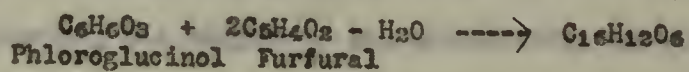
	<u>Hötter's Results</u>	<u>Theoretical</u>
C.	62.19 62.11	61.97
H.	2.92 2.62	4.23

Counciler expected to find a figure for the condensation product of phloroglucinol and furfural which would correspond to that of Baeyer, (1) who found in an analogous case that from one to six atoms of hydrogen are lost through oxidation. The loss of six atoms of hydrogen would give a compound of the formula $\text{C}_{22}\text{H}_{12}\text{O}_9$ which would have a percentage composition: C. 62.86, H. 2.86.



(1) Ber. 8, 525, 1872.

His analyses were made with copper oxide in a current of oxygen. The results agreed with neither formula, $C_{22}H_{18}O_6$, nor $C_{22}H_{12}O_6$, but more nearly with $C_{16}H_{12}O_6$ which would result from the reaction of one molecule of phloroglucinol and two molecules of furfural, with the loss of one molecule of water.



Coumcler obtained:

	<u>A. Without excess Phloroglucinol</u>	<u>B. With large excess Phloroglucinol</u>	<u>Theoretical $C_{16}H_{12}O_6$</u>
C.	63.86	62.85	64.00
	63.76	63.13	
	63.91	63.29	
	63.54		
	63.63		
H.	4.19	3.92	4.00
	3.99	3.94	
	3.87	3.98	
	4.03		
	3.56		

Welbel and Zeisel (1) sum up the furfural phloroglucinol reaction as follows:

1. In the presence of 12 per cent hydrochloric acid, phloroglucinol is condensed with furfural, somewhat easily in the cold, and still more easily in the warm, to a dark colored insoluble product.
2. The condensation does not follow the other well known rules for the reactions between aldehydes and phenols.
3. After standing a long time, in hydrochloric acid solution, furfural and phloroglucinol react in the proportion of three molecules of furfural to one molecule of phloroglucinol. By

(1) Zeit. Angew. Chemie, 1895, p. 678.

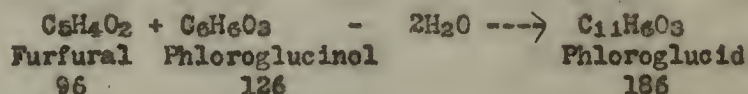
varying the proportion of the reacting substances the proportion present in the precipitate remains constant.

4. If one uses one part of furfural to 1.25 to 3 parts of phloroglucinol figured as water-free, and if 12 per cent HCl is used as a condensation medium, and if the certain fixed conditions are observed, the weights of the precipitates obtained are sufficiently proportional to consider the reaction as a basis for the quantitative determination of furfural.

5. The condensation products of phloroglucinol and furfural contain chlorine. In cold water they give up one part of their chlorine as hydrochloric acid, while another part remains in the compound.

6. Counselor's figures are not correct because of the presence of di-resorcin, and because of oxidation of the condensation product by drying in the air.

Kröber (1) believed that two molecules of water were lost in the reaction, as follows:



He based his assumption upon the fact that he found that 0.1 gm. furfural gave 0.1926 gms. of phloroglucid, thus making 96 parts (the molecular weight of furfural) yield 184.89 parts of phloroglucid. If the reaction proceeded as above the molecular weight of the phloroglucid would be 186, which number agrees closely with the 184.89 calculated from his experiments.

(1) J. Landw, 48, 377, 1900.

In order to establish more fully whether only one condensation product was formed, or whether more than one could be formed, Kröber varied his reacting quantities of furfural and phloroglucinol:

1 & 2. To 0.0516 gms. furfural, he added 0.035 gms. phloroglucinol (one-half the quantity calculated to be necessary to react according to his equation, as above).

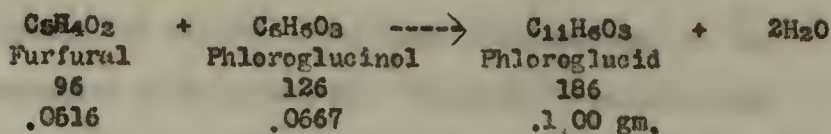
3 & 4. To 0.0516 gms. furfural he added 0.07 gms. phloroglucinol (equal to 0.0678 gms. pure phloroglucinol which is the exact quantity necessary to react with 0.0516 gms. furfural).

5 & 6. To 0.0516 gms. furfural he added 0.140 gms. phloroglucinol (twice the quantity of phloroglucinol necessary to react with furfural).

Results:

	Furfural sol. 1.032 gms. per 1000 cc.	Phloroglucinol sol. .7 gms. per 1000 cc.	Phloroglucinol + .0052 gms.
1.	50 cc. = .0516 gm.	50 cc. .0350 gm.	.0470 gms. .0522
2.	50 cc. = .0516	50 cc. .0350	.0466 .0518
3.	50 cc. = .0516	100 cc. .0700	.0933 .0985
4.	50 cc. = .0516	100 cc. .0700	.0936 .0988
5.	50 cc. = .0516	200 cc. .1400	.0936 .0988
6.	50 cc. = .0516	200 cc. .1400	.0937 .0989

From above equation of Kröber the following data result:



From the figures (p. 7) he assumes that only one condensation product is formed. Experiments 3 and 4, in which the proportion was 1 mol. furfural to 1 mol. phloroglucinol, gave the same results as experiments 5 and 6, in which 1 mol. of furfural to 2 mols. of phloroglucinol, were used. Experiments 1 and 2, in which less (1/2 mol.) quantities of phloroglucinol were used to 1 mol. furfural gave also no other condensation product, except a possible combination of 2 mols. furfural with 1 mol. phloroglucinol; though once the appearance of free furfural in the filtrate, as well as the slight quantity of phloroglucid obtained, argued against this.

Kröber also claimed that in experiments 1 and 2 the quantity of phloroglucid obtained from the phloroglucinol added agrees with the equation. That is, phloroglucinol : phloroglucid = 126 : 186.

$$\begin{aligned}
 \frac{.035}{x} &= \frac{126}{186} \\
 x &= .0516
 \end{aligned}$$

Therefore, the theoretical amount of phloroglucid obtained from .035 gm. phloroglucinol is .0516. As explained on next page, there remains in solution .0052 gm. phloroglucid. Subtracting this from .0516 gm. there is obtained .0464 gm. which represents the amount of phloroglucid which should actually be obtained from .035 gm. phloroglucinol. The amount found in experiments 1 and 2 was .0468 which agrees closely.

Kröber and Rimbach and Tollens (1) published another paper giving the results of further investigations on the "Determination of Pentosans and Pentoses by means of the Hydrochloric Acid Distillation and Precipitation of Furfural with Phloroglucinol." As to the treatment and properties of the phloroglucid; they washed the phloroglucid in a weighed Gooch crucible with 150 cc. of water in such a way that the precipitate was never free of the mother liquor until the very end, when it was sucked dry and the crucible was allowed to stand in a drying closet at 97-98° for four hours. The crucible was then cooled in a covered weighing bottle in a sulphuric acid desiccator, the weighing bottle and contents thus being weighed without being opened. In this way the addition of moisture by the hygroscopic phloroglucid was avoided.

Kröber also found that four hours drying was sufficient and that by standing in an open crucible or in the light an increase in weight was noted.

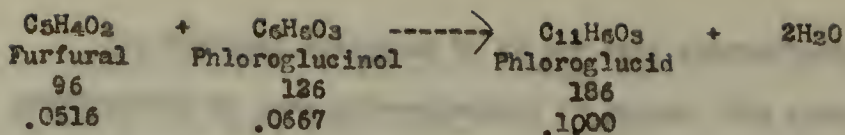
Weight of phloroglucid:

After 4 hrs. drying,	.1764
After 12 more hrs. drying in desiccator,	.1764
After 5 more hrs. drying,	.1764
After 3 more hrs. standing in light,	.1926
After 5 1/2 more hrs. drying,	.1791

After 20 to 24 hours, the results as Welbel and Zeisel believed, showed oxidation.

From the results of experiments 3, 4, 5 and 6, cited on page 7 Kröber concluded that the reaction proceeds according to the equation:

(1) Zeit. Angew. Chemie, 15, 477, 1902.



In these cases .0516 gms. furfural and .0667 gms. phloroglucinol yielded from .0985 to .0988 gms. phloroglucid. The theoretical amount of phloroglucid according to the above equation should be .1000 g. With the addition of the .0052 gms. phloroglucid, which represents the amount of phloroglucid remaining in solution;⁺ the results, in numbers 3 and 4 (p. 7) where sufficient phloroglucinol was used, and in numbers 5 and 6, where an excess of phloroglucinol was used, agree with theory. There is, however, a slight loss (1.000 - .0988 = .0012 gms.) which is probably due to the fact that the phloroglucid formula is perhaps not simply C₁₁H₁₀O₃ as given above, but is more complex due to polymerization with the loss of water. The results in numbers 1 and 2 are approximately one-half those in 3 and 4.

In the same year Jäger and Unger (2) published results which they obtained by using various pentoses and pentosans and analysing the resulting phloroglucids by combustion. The furfural-yielding substances used were: furfural, which was previously fractionated, pure arabinose, mucin from flaxseed, pine wood shavings, and a mixture of black and white pepper. Their method of procedure differed in a few respects from that proposed by Kröber.

⁺(The derivation of the addition figure .0052, representing the phloroglucid held in solution, was made on empirical and mathematical grounds from determinations of the phloroglucid, obtained from varying quantities of furfural and phloroglucinol, with a comparison of the amounts of phloroglucid held in solution when the volumes of the liquids remained constant. (See J. Landw. 48, pp. 372, 376, 1900))

2. Ber. 35, 4440 (December) 1902.

The furfural dissolved in 12 per cent hydrochloric acid was precipitated by pure phloroglucinol in excess, the precipitates filtered off after no more furfural was observed in the supernatant liquids, and washed with cold water until the washings gave no more chloride reaction. Then the products were dried at 105° and analyzed.

Furfural-yielding substances	C per cent	H per cent
1. Furfural,	64.28	3.98
2. Arabinose,	61.57	4.45
3. Mucin from flaxseed,	62.98	4.65
4. Pine wood shavings,	62.16	4.42
5. Black and white pepper,	60.45	4.54

They thus obtained a marked dissimilarity of composition of the various precipitates.

The results obtained from pure furfural indicate that the reaction proceeds according to the equation:



	C. per cent	H. per cent
Theoretical, $C_{11}H_8O_4$,	64.70	3.95
Found in "1"	64.28	3.98

They think that these differences from Kröber's theoretical C. 70.94, H. 3.26 results, may be due to the fact that they worked with larger quantities.

In January, 1903, Tollens (1) published an article replying to that of Jäger and Unger, saying that the latter had obtained varying results, because from the pentosans used, they had produced other substances than furfural, in the hydrochloric acid

1. Ber. 36, 1903.

distillation, and these were capable of being precipitated with phloroglucinol and were thus weighed as furfural phloroglucid.

He also stated that their procedure varied from that of Kröber's, which would cause their results to be different.

He claimed, too, that the composition of the precipitate was not important to the exactness of the method, if the same procedure was used in every case, since corresponding amounts of precipitate would be obtained from corresponding amounts of pentosan material.

A year later Goodwin and Tollens (1) published an article on the composition of the phloroglucid. They acknowledged the percentage composition obtained by Jäger and Unger, viz., C. 64.28 and H. 3.98, and also the formulas suggested by Welbel and Zeisel, and Jäger and Unger, as differing from that suggested by Kröber, viz., $C_{11}H_8O_3$.

With view to clearing up this uncertainty, Goodwin precipitated the usual phloroglucid from 2000 cc. of a solution of .761 gms. furfural in hydrochloric acid (1.06 sp. gr.) with 1 gm. phloroglucinol, and filtered it on a hardened filter, washed it and dried it in the air, and then as the pentosan method prescribed, dried it at 97 - 98° for four hours, and analyzed it.

In the analysis, addition of moisture from the air by the hygroscopic precipitate was avoided as much as possible, the dried substance being kept in a porcelain boat in a closed weighing bottle in a sulphuric acid desiccator.

1. Ber. 37, 315, 1904.

The results were:

		C. per cent	H. per cent
		63.94	4.06
		63.92	3.97
		63.33	3.99
Counciler,	$C_{16}H_{12}O_6$	64.00	4.03
Jäger and Unger,	$C_{11}H_8O_4$	64.70	3.92
Kröber,	$C_{11}H_8O_3$	70.94	3.26

Goodwin's results conform more closely to the formulas of Counciler, and Jäger and Unger, than to that of Kröber, but there is still a small deficit of carbon.

According to Welbel and Zeisel the weight increases by oxidation through long drying, and this is not disproven by the work of Kröber.

Goodwin, in order to prove this point, kept a crucible with phloroglucid which had been dried previously at 98° for four hours, still at this temperature for eight hours, and then let it cool for a longer period in the desiccator, before weighing. The following weights for the crucible and its contents are given:

After 1 hour drying,	22.3816
2 " "	22.3818
3 " "	22.3828
5 " "	22.3822
8 " "	22.3838

The product dried in this manner gave, on analysis, C. per cent 62.76, H. per cent 3.90, showing a slight loss in carbon over that in the phloreoglucid dried only four hours.

Another dried sample was placed in a boat and further dried at a higher temperature, $140 - 145^{\circ}$, in an air current, and the excess air conducted over baryta water.

Weight of boat + phloroglucid, 20.2442 g.
 Weight after 2 hours, 20.2400
 Weight after 4 1/2 hours, 20.2402

This sample contained only C. per cent, 61.44, H. per cent, 3.04.
 In the baryta water there was a precipitate of barium carbonate.
 Thus at 140 - 145° there is oxidation with partial loss of carbon,
 and one may assume that substances richer in oxygen than $C_{11}H_8O_4$
 have been formed as follows:

	C. per cent	H. per cent
$C_{11}H_8O_5$,	60.55	2.75
$C_{22}H_{12}O_9$,	62.86	2.86

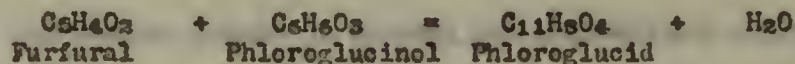
A weight increase was not encountered here because a part of the carbon was volatilized as carbon dioxide.

The oxidation at 100° is very slight, for the new, as well as the previously dried substances, were further dried in an air current at 105° for 3 1/2 hours, the baryta water showing only a slight turbidity, and the resulting phloroglucid giving an analysis: C. per cent, 64.41, H. per cent, 4.25.

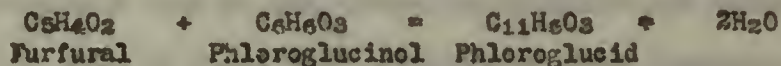
Goodwin then dried the phloroglucid in a current of hydrogen at 103°. These products gave figures which agree closely to the formula $C_{11}H_8O_4$.

	C. per cent	H. per cent
Found after 2 1/2 hrs. drying,	65.12	4.25
3 1/2 " " "	64.48	4.07
	64.41	4.25
Theoretical $C_{11}H_8O_4$,	64.70	3.92

The formula $C_{11}H_8O_4$ gives rise to the following equation:



This differs from that of Kröber and Tollens which was based on the quantity of phloroglucid obtained by means of a weighed quantity of furfural:



It is possible that some of the actual furfural might have gone over into other soluble matter so that a smaller weight of phloroglucid resulted. Goodwin and Tollens were not able to separate from the precipitation medium any such product, however, nor could they find any formic acid. It is possible that the furfural of Kröber and of Rimbach, who found the same result as Kröber, contained in spite of the greatest care of purification, a small impurity; or that the phloroglucinol had increased its weight through addition of moisture.

Tollens claims that it is unnecessary for the estimation of the pentosans to know the composition of the precipitate, for the quantity of phloroglucid which results from arabinose, xylose, and pentosans, has been determined from numerous experiments so that the formula or percentage composition is unimportant.

For the purposes of the method, viz., the determination of the amount of furfural obtained from 1.0 g. of substance, on distillation with hydrochloric acid, it is immaterial whether the composition of the phloroglucid precipitate is $C_{11}H_8O_4$ or $C_{11}H_8O_3$ for; if the first is the correct formula, the amount of phloroglucid

obtained represents .094 gm. furfural or 9.5 per cent, whereas if the second formula is correct, the phloroglucid represents .103 gm. furfural or 10.3 per cent, and these differences are within the limits of experimental error.

Goodwin and Tollens by boiling 5 gms. of the furfural phloroglucid with 30 gms. potassium hydroxide and water for 1/4 to 1/2 hour at about 230°, obtained by ether extraction a small amount of crystalline phloroglucinol which melted at 213 - 215°, and which gave the characteristic color reactions with ferric chloride, and with aniline nitrate and potassium nitrite, thus showing the hydrolysis of the phloroglucid into phloroglucinol.

Votocek and Potmesil, (1) used excess furfural to determine phloroglucinol quantitatively. The carbon content of their product, dried in hydrogen, was somewhat less than that of Goodwin and Tollens. Moreover, the composition of the dried product did not remain constant but decreased noticeably in carbon content when kept for a long time in a desiccator.

The phloroglucid obtained from 1.0 gm. phloroglucinol and 3.0 gm. furfural and also from 1.0 gm. phloroglucinol and excess (10 gm.) of furfural was dried in hydrogen at 105° with the following results:

1. Ber. 49, 1184, 1916.

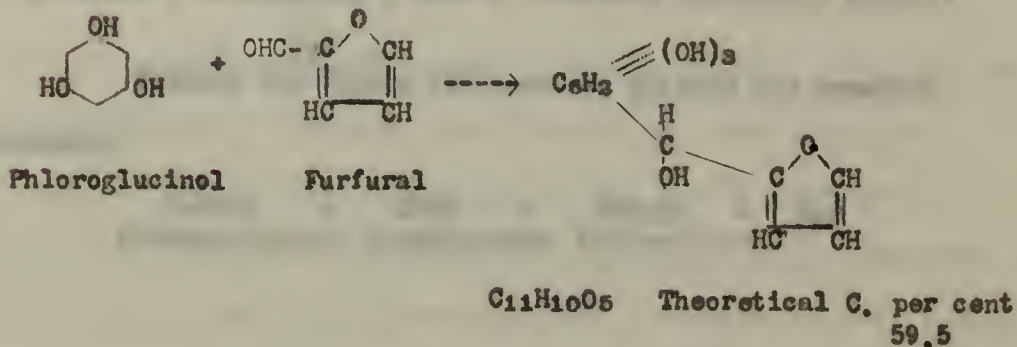
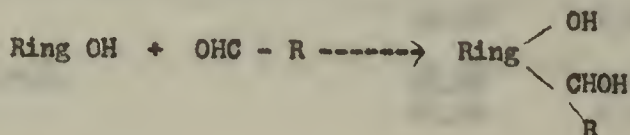
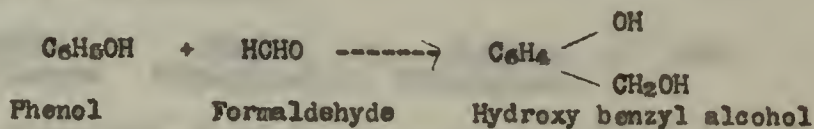
1 g. : 3.0

1.0 g. : 10 g.

	C. per cent	H. per cent	C. per cent	H. per cent
Immediately after drying,	63.46	4.27	63.77	4.06
After 4 days in desiccator,	62.24	4.16		
" 7 " more "	61.97	4.01		
" 19 " " "	61.37	4.25		

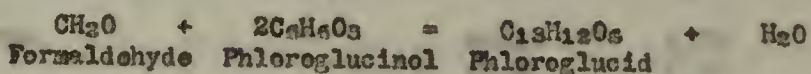
A similar immediate composition was shown also from 1 gm. phloroglucinol with a large excess of furfural (10 gms.) in the presence of hydrochloric acid: C. per cent 63.77, H. per cent 4.06.

According to these analyses the reaction does not seem to take place as the general action of aldehydes and phenols as is represented by the reaction between formaldehyde and phenol.



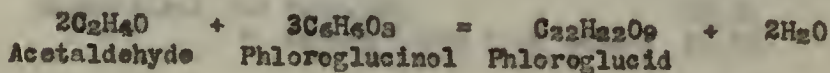
The study of the reaction between formaldehyde and phloroglucinol does not give much aid to the problem.

Counciler (1) studied the reaction of phloroglucinol with formaldehyde, acetaldehyde, propionaldehyde, etc., but his conclusions do not throw much light on the furfural-phloroglucinol problem. He decided that the reaction, in the case of formaldehyde, took place as follows:



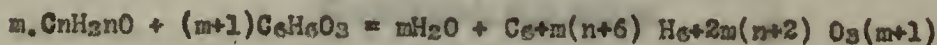
Theoretical, $\text{C}_{13}\text{H}_{12}\text{O}_6$,	C. per cent	H. per cent
	59.09	4.55
Found,	59.07	4.37
	59.09	4.50
	59.17	4.42

In the case of acetaldehyde:

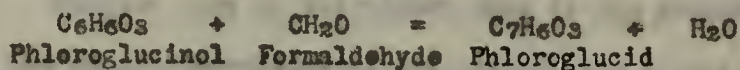


Theoretical, $\text{C}_{22}\text{H}_{22}\text{O}_9$,	C. per cent	H. per cent
	61.40	5.12
Found,	61.62	4.83
	61.41	5.16

or generally:



Tollens and Clowes (2) however, believe the reaction proceeds:



1. Chem. Zeit. 20, II, 599, 1896.
2. Ber. 32, 2841, 1899.

They found that 30 parts of formaldehyde yielded 135 to 136 parts of phloroglucid, whereas 138 parts would be yielded theoretically. Their analyses were as follows:

	C. per cent	H. per cent	H ₂ O per cent
Theoretical for C ₇ H ₆ O ₃ .1/7H ₂ O,	59.73	4.51	1.83
Found,	59.83 59.57	4.75 4.26	1.73

They believe that these numbers differ from Counciler's because they precipitated their product at 70 - 80°, while Counciler prepared his in the cold, and because the C₁₃H₁₂O₆ obtained by Counciler is the same as C₇H₆O₃ with 3 per cent H₂O.

	C. per cent	H ₁ per cent
Theoretical for C ₁₃ H ₁₂ O ₆ ,	59.09	4.55
" " C ₇ H ₆ O ₃ (with 2.9% water)	59.15	4.26
Found by Counciler,	59.11	4.43

Evidently then, the reaction between formaldehyde and phloroglucinol is no more clear cut than that between furfural and phloroglucinol.

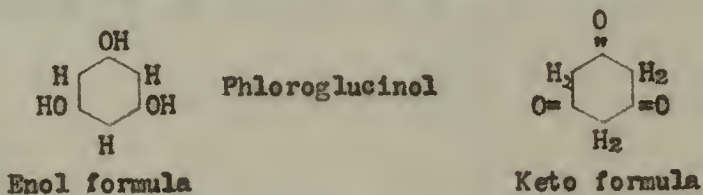
Theoretical Discussion

The problem which still presents itself is, just how does the reaction take place between furfural and phloroglucinol?

Tollens (see p. 12) claims that if the procedure is always the same, a knowledge of the composition is not necessary for the exactness of the determination. He also claims in a later article (see p. 15) that either of the formulas C₁₁H₈O₄, or C₁₁H₆O₃ for furfural phloroglucid, agree within limits of experimental error, with results obtained by actual determination.

This may be true, but a knowledge of the exact nature of the phloroglucinol-furfural reaction should help in the estimation of pentoses and methyl pentoses as they occur in nature, and should show more conclusively that a quantitative relationship of furfural to furfural-phloroglucida does exist. Furthermore, to attack the problem from a different angle, that is to study the reaction of derivatives of phloroglucinol with furfural rather than to try to ascertain the composition of the precipitates formed, might help to throw light upon the problem. Again, it was thought that a derivative of phloroglucinol might yield a phloroglucida soluble in some ordinary reagent, permitting the determination of its molecular weight and a more definite knowledge of the entire reaction.

Now we know that phloroglucinol, symmetrical tri-hydroxy benzene, is capable of tautomerism.



We do not know in which way it reacts with furfural.

It seems reasonable to accept the analyses of Goodwin and Tollens, and Votocek and Potmesil, as being fairly correct as their conditions were against oxidation or addition of moisture. The average C. per cent 64.67 (Goodwin and Tollens) and 63.61 (Votocek and Potmesil) agree within the limits of experimental error, with either Councler or Tollens and Goodwin.

I. Phloroglucinol in Enol Form

				C. %	P : F - H ₂ O	Ratio
1a	Phloroglucinol 1 mol.	+ Furfural 1 mol.	----> Phloroglucid "A ₁ "	59.46	1 : 1 - 0	
1b	Phloroglucid "A ₁ " 1 mol.	+ Phloroglucinol 1 mol.	-H ₂ O-> Phloroglucid "B ₁ "	61.97	2 : 2 - 1	
1c	Phloroglucid "B" 1 mol.	--	-H ₂ O-> Phloroglucid "C ₁ "	64.70	2 : 2 - 2	
2a	Phloroglucinol 1 mol.	+ Furfural 2 mols.	----> Phloroglucid "A ₂ "	60.39	1 : 2 - 0	
2b	Phloroglucid "A ₂ " 1 mol.	--	=H ₂ O-> Phloroglucid "B ₂ "	64.00	1 : 2 - 1	
3a	Phloroglucinol 1 mol.	+ Furfural 3 mols.	----> Phloroglucid "A ₃ "	60.86	1 : 3 - 0	
3b	Phloroglucid "A ₃ " 1 mol.	--	-H ₂ O-> Phloroglucid "B ₃ "	68.69	1 : 3 - 1	

II. Phloroglucinol in Keto Form

				C. %	P : F - H ₂ O	Ratio
1a	Phloroglucinol 1 mol.	+ Furfural 1 mol.	----> Phloroglucid "A ₁ "	59.46	1 : 1 - 0	
1b	Phloroglucid "A ₁ " 1 mol.	--	-H ₂ O-> Phloroglucid "B ₁ "	64.70	1 : 1 - 1	
or	Phloroglucinol 1 mol.	+ Furfural 1 mol.	-H ₂ O-> Phloroglucid "B ₁ "	64.70	1 : 1 - 1	
1c	Phloroglucid "A ₁ " 1 mol.	+ Phloroglucinol 1 mol.	-H ₂ O-> Phloroglucid "C ₁ "	61.97	2 : 2 - 1	
2a	Phloroglucinol 1 mol.	+ Furfural 2 mols.	----> Phloroglucid "A ₂ "	60.39	1 : 2 - 0	

+ The ratio P:F-H₂O refers to the ratio of the number of molecules of phloroglucinol reacting with the number of molecules of furfural minus the number of molecules of water lost in the reaction.

II. Phloroglucinol in Keto Form (Con't.)

				C. %	Ratio P : F - H ₂ O
2b	Phloroglucinol "A ₃ " 1 mol.		-H ₂ O→	Phloroglucinol "B ₂ " C ₁₆ H ₁₂ O ₆	64.00 1 : 2 - 1
2c	Phloroglucinol "A ₂ " 1 mol.		-H ₂ O→	Phloroglucinol "B ₂ " C ₁₆ H ₁₂ O ₆	64.00 1 : 2 - 1
2d	Phloroglucinol "B ₂ " 1 mol.		-H ₂ O→	Phloroglucinol "C ₂ " C ₁₆ H ₁₀ O ₆	67.63 1 : 2 - 2
or	Phloroglucinol 1 mol.	+ Furfural 2 mols.	-2H ₂ O→	Phloroglucinol "C ₂ " C ₁₆ H ₁₀ O ₆	67.63 1 : 2 - 2
2e	Phloroglucinol "A ₂ " 1 mol.	+ Phloroglucinol "A ₂ " 1 mol.	-H ₂ O→	Phloroglucinol "D ₂ " C ₃₂ H ₂₆ O ₁₃	62.13 2 : 4 - 1
2f	Phloroglucinol "A ₂ " 1 mol.	+ Phloroglucinol "A ₂ " 1 mol.	-2H ₂ O→	Phloroglucinol "E ₂ " C ₃₂ H ₂₆ O ₁₂	64.00 2 : 4 - 2
3a	Phloroglucinol 1 mol.	+ Furfural 3 mols.	----	Phloroglucinol "A ₃ " C ₂₁ H ₁₈ O ₉	60.86 1 : 3 - 0
3b	Phloroglucinol "A ₃ " 1 mol.		-H ₂ O→	Phloroglucinol "B ₃ " C ₂₁ H ₁₆ O ₈	68.69 1 : 3 - 1
3c	Phloroglucinol "B ₃ " 1 mol.		-H ₂ O→	Phloroglucinol "C ₃ " C ₂₁ H ₁₄ O ₇	66.66 1 : 3 - 2
3d	Phloroglucinol "C ₃ " 1 mol.		-H ₂ O→	Phloroglucinol "D ₃ " C ₂₁ H ₁₂ O ₆	70.00 1 : 3 - 3
or	Phloroglucinol 1 mol.	+ Furfural 3 mols.	-3H ₂ O→	Phloroglucinol "D ₃ " C ₂₁ H ₁₂ O ₆	70.00 1 : 3 - 3
3e	Phloroglucinol "A ₃ " 1 mol.		-H ₂ O→	Phloroglucinol "B ₃ " C ₂₁ H ₁₆ O ₈	68.69 1 : 3 - 1
3f	Phloroglucinol "B ₃ " 1 mol.		-H ₂ O→	Phloroglucinol "C ₃ " C ₂₁ H ₁₄ O ₇	66.66 1 : 3 - 2
3g	Phloroglucinol "A ₃ " 2 mols.		-H ₂ O→	Phloroglucinol "E ₃ " C ₄₂ H ₃₅ O ₁₇	62.14 2 : 6 - 1
3h	Phloroglucinol "A ₃ " 2 mols.		-2H ₂ O→	Phloroglucinol "F ₃ " C ₄₂ H ₃₅ O ₁₆	63.54 2 : 6 - 2

II. Phloroglucinol in Keto Form (Con't.)

			C. %	P : F - H ₂ O	Ratio
3i	Phloroglucinol "A ₃ " 2 mols.	Phloroglucinol "G ₃ "	C ₄₂ H ₃₁ O ₁₅	65.03	2 : 6 - 3
3j	Phloroglucinol "A ₃ " 3 mols.	Phloroglucinol "H ₃ "	C ₆₃ H ₅₃ O ₂₆	61.71	3 : 9 - 1
3k	Phloroglucinol "A ₃ " 3 mols.	Phloroglucinol "J ₃ "	C ₆₈ H ₅₁ O ₂₈	62.63	3 : 9 - 2
3l	Phloroglucinol "A ₃ " 3 mols.	Phloroglucinol "K ₃ "	C ₆₈ H ₄₉ O ₂₄	63.49	3 : 9 - 3

III. Phloroglucinol in the Enol Form as a Phloroglucinol Ether.

1a	Phloroglucinol 2 mols.	+ Furfural 1 mol.	Phloroglucinol "A ₁ "	C ₁₇ H ₁₄ O ₇	61.82	2 : 1 - 1
1b	Phloroglucinol 1 mol.		Phloroglucinol "B ₁ "	C ₁₇ H ₁₂ O ₆	65.00	2 : 1 - 2
1c	Phloroglucinol 1 mol.		Phloroglucinol "C ₁ "	C ₁₇ H ₁₀ O ₅	69.39	2 : 1 - 3
1d	Phloroglucinol 2 mols.		Phloroglucinol "D ₁ "	C ₃₄ H ₂₆ O ₁₃	63.56	4 : 2 - 3
2a	Phloroglucinol 2 mols.	+ Furfural 2 mols.	Phloroglucinol "A ₂ "	C ₂₂ H ₁₆ O ₉	61.97	2 : 2 - 1
2b	Phloroglucinol 1 mol.		Phloroglucinol "B ₂ " ⁺	C ₂₂ H ₁₆ O ₈	64.70	2 : 2 - 2
2c	Phloroglucinol 1 mol.		Phloroglucinol "C ₂ "	C ₂₂ H ₁₄ O ₇	67.77	2 : 2 - 3

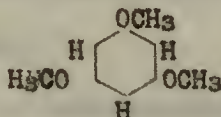
+ III, "B₂" is identical with I, "B₂".

The following is a summary of the possibilities offered:

No.	Formula	C, %	P : F - H ₂ O	=	P : F - H ₂ O	Proposed by
I 1c	C ₂₂ H ₁₆ O ₈	64.70	2 : 2 - 2	=	1 : 1 - 1	Goodwin and Tollens
I 2b	C ₁₆ H ₁₂ O ₆	64.00	1 : 2 - 1	=	1 : 2 - 1	Counciler
II 1b	C ₁₁ H ₈ O ₄	64.70	1 : 1 - 1	=	1 : 1 - 1	Goodwin and Tollens
II 2b	C ₁₆ H ₁₂ O ₆	64.00	1 : 2 - 1	=	1 : 2 - 1	Counciler
II 2c	C ₁₆ H ₁₂ O ₆	64.00	1 : 2 - 1	=	1 : 2 - 1	Counciler
II 2f	C ₃₂ H ₂₄ O ₁₂	64.00	2 : 4 - 2	=	1 : 2 - 1	Counciler
II 3h	C ₄₂ H ₃₀ O ₁₆	63.56	2 : 6 - 2	=	-	-
II 3i	C ₄₂ H ₃₁ O ₈	65.03	2 : 6 - 3	=	-	-
III 1b	C ₁₇ H ₁₂ O ₈	65.00	2 : 1 - 2	=	-	-
III 1d	C ₃₄ H ₂₆ O ₁₃	63.56	4 : 2 - 3	=	-	-
III 2b	C ₂₂ H ₁₆ O ₈	64.70	2 : 2 - 2	=	1 : 1 - 1	Goodwin and Tollens

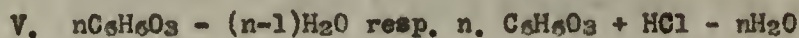
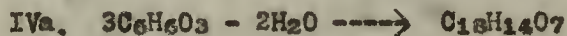
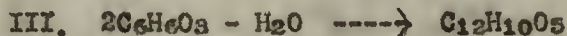
Thus in the enol form we limit the possibilities (I 1c) to a simple condensation of 2 mols. phloroglucinol + 2 mols. furfural - 2 mols. water agreeing with Goodwin and Tollens; or (I 2b) to a condensation of one mol, phloroglucinol + 2 mols furfural - one mol. water, agreeing to Counciler's formula; or (III 1b) to a more complicated reaction of phloroglucinol condensing with itself to form an ether as well as with the aldehyde group of the furfural. In the keto form the limits are not so narrow.

Before we discuss the possibilities of the reaction we should try to establish whether the phloroglucinol acts in the keto or enol form. If, for instance, it reacts in the keto form, the tri-methyl ether of phloroglucinol should not react, for this can exist only in the enol form.



However, tri-methyl ether of phloroglucinol was made and it was found to react readily with furfural. This, therefore, would seem to exclude the keto form.

(Note) - Annalen, 276-330, 1893, Hesse found tri-methyl ether with 1.18 sp. gr. HCl in closed flask at 140° was changed to phloroglucinol which was quickly changed to secondary products. He believed they were formed thus.



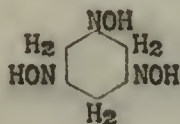
The tri-methyl ether used in the present investigation stood one week in 8.5 per cent hydrochloric acid solution, containing 20 per cent alcohol, and it did not hydrolyze. No purple color was obtained with ferric chloride after standing two weeks with hydrochloric acid of sp. gr. 1.06. Nor would it dissolve in water. Also no change

in the methyl ether occurred when it was heated with hydrochloric acid, 1.18 sp. gr., to 140° in an open flask.

Again tri-bromo phloroglucinol tri-methyl ether was not changed at all by the action of furfural in hydrochloric acid, 1.06 sp. gr., and was recovered after the attempted reaction. If, under the conditions existing, the tri-methyl ether is hydrolyzed to phloroglucinol it would seem that the bromo derivative should also have been hydrolyzed.

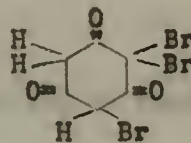
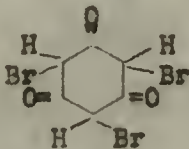
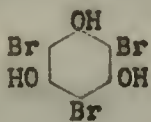
The tri-oxime of phloroglucinol, which can result only from the keto form, was prepared and the action of it upon furfural was studied. No reaction occurred although several attempts were made.

If the phloroglucinol reacts in the



keto form with furfural then this tri-oxime should also react as in it the CH₂ groups remain.

Tri-bromo phloroglucinol, which must have the constitution of one of the following formulas, was prepared, but showed no reaction with furfural.



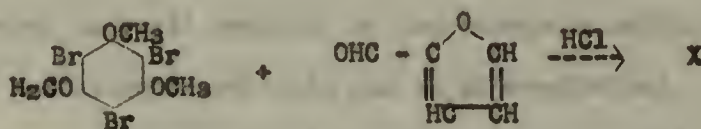
Tri-bromo phloroglucinol

(No references in literature to other bromo-phloroglucinols were found.)

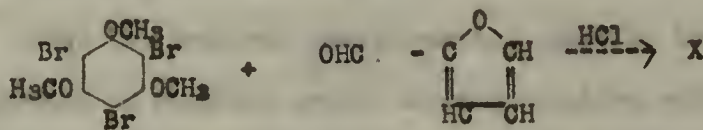
The fact that the tri-methyl ether of phloroglucinol reacts with furfural indicates that the reaction with furfural takes place with the enol form of phloroglucinol, and that the reactive group of phloroglucinol is one or more of the CH groups unless a methoxy group is capable of condensing with the furfural. An attempt was, therefore, made to produce tri-bromo phloroglucinol tri-methyl ether to see if it reacted with the furfural. This compound should not react if the OCH₃

group is not active in the reaction since the hydrogens in the ring have all been replaced by bromine.

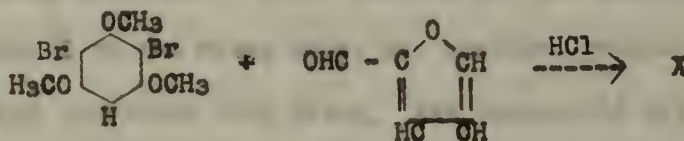
Tri-bromo phloroglucinol tri-methyl ether was accordingly made, and was found to have no reaction with furfural. Also di-bromo phloroglucinol tri-methyl ether was isolated, and found to have no reaction with furfural. Mono-bromo phloroglucinol tri-methyl ether also gave a negative reaction.



Tri-bromo phloroglucinol tri-methyl ether + furfural \rightarrow no reaction.



Di-bromo phloroglucinol tri-methyl ether + furfural \rightarrow no reaction.



Mono-bromo phloroglucinol tri-methyl ether + furfural \rightarrow no reaction.

If the reaction takes place as one mol. phloroglucinol to two mols. furfural minus one mol. water, mono-bromo phloroglucinol tri-methyl ether should have reacted and the di-bromo and tri-bromo phloroglucinol tri-methyl ethers should not have reacted. Since the mono-bromo, di-bromo and the tri-bromo phloroglucinol tri-methyl ethers do not react the -OCH₃ group is not capable of condensing with the aldehyde. Also possibilities which III offer, of two mols. phloroglucinol condensing through OH groups to form an ether must be excluded since there are no hydroxyl groups free to react.

EXPERIMENTAL PART

Review of Experimental Literature.Preparation of tri-methyl ether of phloroglucinol,

C₆H₃(OCH₃)₃. The tri-methyl ether of phloroglucinol has been prepared by different methods with varying success.

Beilstein (1) gives the following: Tri-methyl ether is prepared in small quantity by the energetic action of methyl alcohol and hydrochloric acid gas on phloroglucinol. It forms very long prisms from petroleum ether, easily soluble in water, ether and benzene, which melt at 52°.

Will (2) prepared the tri-methyl ether by treating phloroglucinol in absolute methyl alcohol solution with hydrochloric acid gas until saturated, and then fully methylated with methyl iodide and potassium hydroxide. After driving off the methyl iodide and methyl alcohol on the steam bath, the reaction product was made alkaline and distilled with steam. The semi-solid oil was crystallized from alcohol and then precipitated with water, yielding colorless crystals which melted at 52.5°.

	C. per cent	H. per cent
Theoretical, C ₆ H ₃ (OCH ₃) ₃	64.29	7.14
Found,	64.45	7.31

Mannich (3) obtained tri-methyl ether of phloroglucinol in 55 to 65 per cent of theory by heating phloroglucinol in absolute methyl alcohol and concentrated sulphuric acid, and then methylating with 40 per cent potassium hydroxide and dimethyl sulphate.

1. Beil., II, 614.
2. Ber., 21, 603, 1888.
3. Chemisches Zentralblatt (2) 1387, 1904.

Tutin and Caten (1) attempted to prepare the tri-methyl ether of phloroglucinol by methylation with di-methyl sulphate and potassium hydroxide, but they were not successful. They, therefore, used the method of Will, but used di-methyl sulphate instead of methyl iodide and obtained a satisfactory yield.

Mauthner (2) in preparing tri-methyl ether of phloroglucinol, saturated an absolute methyl alcohol solution with anhydrous hydrochloric acid gas and dissolved the product in 10 per cent sodium hydroxide, and fully methylated with di-methyl sulphate.

Freudenberg (3) describes this process more completely. He dissolved 10 gms. anhydrous phloroglucinol in 100 cc. methyl alcohol and upon cooling saturated with anhydrous hydrochloric acid, and then concentrated to a thick syrup. This was dissolved in 40 cc. di-methyl sulphate, and 120 cc. 7.5 N potassium hydroxide added in portions so that the temperature remained between 60° to 70°. It was then heated for ten minutes at 90° and the product distilled with steam. He obtained 10.7 gms. pure product equal to an 80 per cent yield.

Preparation of mono-bromo phloroglucinol-tri-methyl ether,
 $C_6H_2(OCH_3)_3Br$. According to Beilstein (4) this product is prepared by the distillation of benzoyl bromo-phloroglucinol tri-methyl ether. It forms needles from strong alcohol, m.p. 96 to 97°.

Hesse (5) formed mono-bromo phloroglucinol tri-methyl ether by heating one molecule tri-methyl ether of phloroglucinol in chloroform solution with two molecules bromine at suitable temperature.

1. J. Chem. Soc. 97, 2064, 1910.
2. J. pr. (2) 87, 408, 1913.
3. Ber. 53, 1425, 1920.
4. Weil. II, 1920.
5. Annalen, 276-330, 1893.

Hydrobromic acid was given off. The solution was concentrated and the residue recrystallized from hot alcohol. Small colorless needles were formed which melted at 97° .

Preparation of di-bromo phloroglucinol tri-methyl ether,
 $C_6H(OCH_3)_3Br_2$. In Beilstein (1) there is no method of preparation given, simply a statement of properties, namely crystallizes from alcohol in leaflets, m.p. 136° . Di-bromo phloroglucinol tri-methyl ether was obtained by Hesse (2) by treating the chloroform solution of hydrocoton (tri-methyl ether of phloroglucinol) with bromine until no more absorption was obtained. The solution was distilled and the crystalline residue purified through crystallization from alcohol. White leaves which melted at 133° were obtained. An analysis gave:

	Br per cent
Theoretical, $C_6H_{10}BrO_3$,	49.08
Found,	49.29

Preparation of tri-bromo phloroglucinol tri-methyl ether,
 $C_6(OCH_3)_3Br_3$. (3) Phloroglucinol tri-methyl ether was treated with excess bromine. Long needles from alcohol, m.p. 145° , were produced.

Will (4) heated tri-methyl ether of phloroglucinol with excess bromine and obtained long colorless needles which melted at 145° , and gave for analysis:

	Br. per cent
Theoretical, $C_6(OCH_3)_3Br_3$,	59.26
Found,	59.15

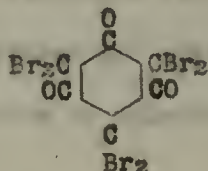
1. Beil. II, 1020.
2. Annalen 276, 330, 1893.
3. Beil. II, 1020.
4. Ber. 21, 603, 1868.

Preparation of tri-bromo phloroglucinol (1) $C_6Br_3(OH)_3$.

Tri-bromo phloroglucinol, $C_6Br_3(OH)_3 + 3H_2O$ is obtained by treating phloroglucinol with bromine water, or better, by dropping bromine into an acetic acid solution of phloroglucinol. Prismatic crystals are formed which melt at 149 to 151°.

Zincke and Kegel (2) in a research on the action of bromine on phloroglucinol prepared the tri-bromo phloroglucinol by the treatment of phloroglucinol with excess bromine in glacial acetic acid. This product was freed from water of crystallization by drying at 100°. No carbon dioxide was noticed on addition of sodium carbonate to the solution, but the solution was colored yellow and became darker in the light. The water free product melted at 152 to 153° with slow heating, but melted at a lower temperature if heated quickly.

Preparation of hexa-bromo phloroglucinol (3),



This compound crystallizes from carbon disulphide and ligroine in large needles, m.p. 146 to 147°. They are easily soluble in ether, hot acetic acid, chloroform and benzene. It decomposes in the light to octo-bromo acetyl acetone. By heating in water or treatment with zinc chloride, tri-bromo phloroglucinol results.

Zincke and Kegel (2) also prepared this compound by the action of bromine on phloroglucinol in water solution. They were able to form it only in water solution as the chloroform or glacial

1. Beil. II, 1020.
2. Ber. 23, 1730, 1890.
3. Beil. I, 1026.

acetic acid solution gave only the tri-bromo phloroglucinol.

Their product, recrystallized from carbon disulphide and ligroine, melted at 146 to 147°, and gave on analysis:

	C. per cent	H. per cent	Br per cent
Theoretical, $C_6H_3Br_3O_3$,	12.00	0.00	80.00
Found,	12.12	.07	80.64-80.40

The compound was found to decompose in the light assuming a red color and eliminating bromine which could be detected by the use of starch potassium iodide paper.

Preparation of phloroglucinol tri-oxime, $C_6H_3(NO_2)_3$.

Adolf Baeyer (1) prepared phloroglucinol tri-oxime by adding to one part of crystalline phloroglucinol in 45 parts of water, 1.5 parts or 3 molecules of hydroxyl amine hydrochloride and 1.5 parts potassium carbonate. The liquid was allowed to stand in a stoppered flask in the dark at 0° until the tri-oxime separated out as a pure brown flakey precipitate which was filtered off after standing about 12 hours. It was washed until it was free of chlorine, dried in vacuum and gave the following analysis:

	C. per cent	H per cent	N per cent
Theoretical, $C_6H_3N_3O_3$,	42.10	5.2	24.5
Found,	42.51	5.1	24.8

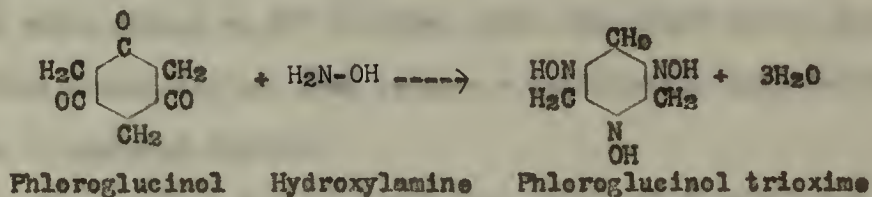
The product was a sandy crystalline powder which was very insoluble in water, and alcohol, and somewhat soluble in chloroform and acetone.

By evaporation of the acetone solution it appeared as colorless globules. It became black at 140° and at 155° exploded quite violently

1. Ber. 19, 159, 1886.

with a red flame. A wet pine shaving was colored yellow-red with hydrochloric acid and alcohol. It dissolved in alkali without color, but was not again precipitated by acid. It dissolved easily in hydrochloric acid with a colorless solution which changed on standing or warming to a dark brown color.

Baeyer believed the tri-exime to be formed:



EXPERIMENTAL PROCEDURE

Preparation of tri-methyl ether of phloroglucinol.

- Five grams anhydrous phloroglucinol were placed in 50 cc. absolute methyl alcohol, and anhydrous hydrochloric acid gas, generated by the action of concentrated sulphuric acid on rock salt, and washed and dried by passing through concentrated sulphuric acid, was passed into the solution until an increase of 24 gms. was observed. One-half of the resulting liquid (33 cc.) was freed from hydrochloric acid gas by evaporation on the steam bath and potassium carbonate was added until the liquid was neutral. Water was added to dissolve the inorganic salt and the heavy oil was then separated from the saline solution by means of a separating funnel. The oil was then dissolved in absolute methyl alcohol yielding a fluorescent solution.

A solution of 5.5 cc of 20 per cent potassium hydroxide (1.1 g.) was then added together with 3 gms. of methyl iodide, and warmed on a water bath to 33 to 35°, with a return condenser for 36 hours, and then allowed to stand two days. One hundred cc. of 10 per cent potassium hydroxide were then added and the product distilled with steam. A small amount of white crystals were obtained which melted at 47° (melting point tri-methyl ether, pure, 52°). This method did not seem to give a sufficiently satisfactory yield to be employed further.

2. A second lot was tried after the method of Mannich (1), 8 gms. water-free phloroglucinol were dissolved in 20 gms. methyl alcohol and 8 gms. concentrated sulphuric acid added. This was allowed to stand with a return condenser for five hours, after which 25 cc. water were added, and the alcohol expelled by distillation. The residue was extracted three times with ether. After evaporation of the ether the product was treated alternately with 400 cc. 10 per cent sodium hydroxide and 24 gms. di-methyl sulphate at 60° for half an hour, the alkali always being kept in excess. The product was distilled with steam but the yield was very small, only about one-half gram being obtained.

3. A third lot was tried with the use of di-methyl sulphate after methylating with anhydrous hydrochloric acid. Ten grams of dried phloroglucinol were dissolved in 100 cc. absolute methyl alcohol and anhydrous hydrochloric acid was passed into the solution until an increase of 55 gms. was observed, which was after 18 hours. The methyl alcohol was then distilled off under reduced pressure until a temperature of 75° was reached. To neutralize the acid 27 cc. of a 10 per

cent sodium hydroxide was required, and in the course of an hour 39 gms. of di-methyl sulphate and 345 cc. of sodium hydroxide were added alternately, the alkali always being kept in excess. During this addition the temperature was kept between 60 to 65°, and afterward heated to 90° for ten minutes. The product was then distilled with steam, a white crystalline substance coming over. This was filtered off, dissolved in ether, dried, and allowed to crystallize. Large white crystals were formed which melted between 51.5 to 52°. The yield was 60 per cent of theory. They contained no water of crystallization and gave an average molecular weight of 165.

Molecular weight $C_6H_3(OCH_3)_3$, Theoretical, 168.09

Found, 163.1
161.8
170.3

Average 165.00

An analysis yielded the following results:

	C. per cent	H. per cent
Theoretical, $C_6H_3(OCH_3)_3$,	64.28	7.14
Found,	64.71	7.35
	64.54	7.47

No violet color was obtained with ferric chloride.

It was thought that a comparison between the reaction of this tri-methyl ether of phloroglucinol with furfural, and phloroglucinol with furfural might be of value.

Since the tri-methyl ether of phloroglucinol is not soluble in hydrochloric acid, sp. gr. 1.06, alcohol had to be added. Therefore the same amount of alcohol was added to the hydrochloric acid solutions

of phloroglucinol that was added to the hydrochloric acid solutions of the tri-methyl ether of phloroglucinol.

Comparative determinations were conducted according to the official method. The furfural used was commercial and was not purified since a comparison of results was all that was sought. The phloroglucinol, however, was pure, water-free, and gave no test for di-resorcin. The precipitated phloroglucids were filtered into Gooch crucibles after having stood over night, washed in the prescribed manner, dried at 97° for four hours, and weighed in weighing bottles. Hydrochloric acid, 1.06 sp. gr. or 12 per cent, was used in the following experiments:

I.	Phloroglucinol	added to	Furfural	Weights
	.1 gm. in 10 cc. HCl		.05 gm. in 15 cc HCl + 375 cc. HCl	.0474 .0396
II.	Furfural	added to	Phloroglucinol	
	.05 gm. in 15 cc. HCl		.1 gm. in 300 cc. HCl + 84 cc. alcohol	.0546 .0528
IIIa.	Furfural	added to	Phloroglucinol tri-methyl ether	
	.05 gm. in 15 cc. HCl		.0962 gm. in 300 cc. HCl + 84 cc. alcohol	.0448 .0482
IIIb.	As in IIIa with .05 gm. more furfural added.			.0835 .0843
IV.	Furfural	added to	Phloroglucinol	
	.0504 gm. in 15 cc. + 375 cc. HCl		.1 gm. in 332 cc. HCl + 68 cc. alcohol	.0393 .0398 .0436 .0411

Bromination of Phloroglucinol Tri-methyl Ether,

Tri-bromo phloroglucinol tri-methyl ether was prepared by adding 7 cc. bromine slowly to 1.3 gms. phloroglucinol tri-methyl ether. Hydrobromic acid was given off, and after the excess bromine had disappeared the white solid remaining was recrystallized from hot alcohol. A heavy mass of white silky needle-like crystals was precipitated upon cooling. These when filtered from the alcohol and dried gave a melting point of 143° and the following molecular weight.

Theoretical, $C_6(OCH_3)_3Br_3$, 403.2

Found, 400.7

This product dissolved in alcohol and hydrochloric acid, 1.06 sp. gr., gave no reaction with furfural.

Di-bromo phloroglucinol tri-methyl ether. An attempt to prepare this compound in chloroform solution according to Hesse, (p. 31) by adding bromine until no more absorption took place, was unsuccessful as the tri-bromo phloroglucinol tri-methyl ether alone resulted. Alcohol was, therefore, used as a solution medium and bromine was added until a faint brown color was observed which disappeared upon stirring. Di-bromo phloroglucinol tri-methyl ether was precipitated upon evaporating the alcohol slowly in the cold. When purified from hot alcohol, square plate crystals were formed which melted at 132° . (Hesse found 133°). This product dissolved in alcohol and hydrochloric acid, 1.06 sp. gr., gave no reaction with furfural.

Mono-bromo phloroglucinol tri-methyl ether was prepared by dissolving 1 gm. phloroglucinol tri-methyl ether in chloroform and adding bromine (.9 cc.) until the brown color caused by the addition of the bromine was slow to disappear. By evaporating the chloroform and dissolving the residue in hot alcohol oblong crystals appeared which melted at 96° . This agrees with the recorded melting point, 97° . This compound could not be made to react with furfural when dissolved in hydrochloric acid, 1.06 sp. gr., and alcohol.

Bromination of Phloroglucinol.

Tri-bromo phloroglucinol. Five tenths of a gram of phloroglucinol was treated with .6 cc. bromine in glacial acetic acid. Upon slow evaporation of the acetic in the cold and dark, prismatic crystals settled out which when purified and freed of the water of crystallization melted at 150° . (Recorded m.p. $149-151^{\circ}$.) No reaction took place between this compound and furfural.

Preparation of phloroglucinol tri-oxime. The tri-oxime of phloroglucinol was prepared according to Baeyer's method, 1.0 gm. phloroglucinol being used. There was a brown powder which separated out at 0° in the dark after two days. This was filtered off and washed with water and dried. Upon heating in the open it exploded. More of the product separated out on standing at room temperature. This was darker but exploded upon heating. These properties agree with those described for the tri-oxime. With this compound furfural did not react, (p. 27). A check was made on the constitution of the tri-methyl ether of phloroglucinol, as an ether of the enol form, by attempting the preparation of an oxime.

The ether did not react at all with hydroxyl amine. Therefore the tri-methyl ether is an enol derivative and does not undergo rearrangement.

Reaction of phloroglucinol with furfural in alcohol solution and without hydrochloric acid. It was found that in alcohol solution and without the presence of acid, phloroglucinol and furfural react slowly after three or four days, forming a thick jelly. This would indicate the colloidal nature of the phloroglucid ordinarily obtained as an amorphous black precipitate on following the official methods. The same jelly formation was obtained, under like conditions from the tri-methyl ether after standing two weeks.

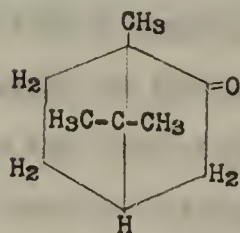
Reaction of other substances with furfural. In addition to pyrogallol which is known to react with furfural (p. 3) the following substances were tried with the results listed below:

<u>Substance</u>	<u>Formula</u>	<u>Reaction</u>
Pyrogallol	$C_6H_3(OH)_3$ 1,2,3	+
Resorcinol	$C_6H_4(OH)_2$ 1,3	+ (phloroglucid soluble in alcohol)
Phenol	C_6H_5OH	-
Hydroquinone	$C_6H_4(OH)_2$ 1,4	-
Malonic acid ⁺	$\begin{array}{c} \text{COOH} \\ \\ \text{CH}_2 \\ \\ \text{COOH} \end{array}$	-
ortho-Cresol	$C_6H_4 \begin{array}{l} \text{CH}_3 \\ \text{OH} \end{array} \quad 1,2$	-

(+ This seems strange because barbituric acid, malonyl urea, will react (Conrad and Rimbach, Ber. 34, 1339, 1901; Jäger and Unger Ber. 36, 1222) as well as thio-barbituric acid (Dox and Plaessance, J. Am. Chem. Soc., 28, 2156, 1916).)

meta-Cresol	C_6H_4 $\begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{OH} \end{array}$	1, 3	-
para-Cresol	C_6H_4 $\begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{OH} \end{array}$	1, 4	-
Thymol	C_6H_3 $\begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{OH} \\ \diagdown \text{C}_6\text{H}_7 \end{array}$	1, 3, 4	-
Anisole	$\text{C}_6\text{H}_5\text{-O-CH}_3$		-
Aceto acetic ester	$\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$		-

Camphor



CONCLUSIONS

(1) The fact that the tri-methyl ether of phloroglucinol reacts with furfural leads to the view that the ordinary furfural phloroglucinol reaction takes place with the enol form of phloroglucinolas in I, 1c or I, 2b, (p. 25). The phloroglucid precipitates obtained in the tri-methyl ether experiments (p. 37) indicate that this reaction is similar to the ordinary furfural phloroglucinol reaction in the resulting product and in the nature of the reaction.

(2) The fact that no reaction takes place between the tri-oxime of phloroglucinol and furfural indicates that furfural does not react with the keto form of phloroglucinol.

(3) The fact that the tri-bromo derivative of the tri-methyl ether does not react with furfural, taken together with conclusions 1, means that the meth-oxy groups (OCH₃) do not have anything to do in this particular reaction. The reaction of the tri-methyl ether of phloroglucinol and of phloroglucinol itself, with furfural must, therefore, be concerned with the CH groups.

(4) The fact that both pyrogallol and resorcinol as well as phloroglucinol react with furfural supports conclusion 1, that the reaction takes place with the enol form of phloroglucinol.

(5) The formation of a colloidal gel when phloroglucinol and furfural react in alcohol solution, in absence of hydrochloric acid, suggests that the amorphous phloroglucid precipitates, as obtained by the official methods, may be colloidal.

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