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A COMPARISON OF BARBITURIC ACID, THIOBARBITURIC ACID AND MALONYLGUANIDINE AS QUANTITATIVE PRECIPITANTS FOR FURFURAL.

ARTHUR W. DOX AND G. P. PLAISANCE.

All of the methods for the quantitative determination of pentoses and pentosans in agricultural products are based upon the conversion of pentose into furfural by distillation with a mineral acid, preferably hydrochloric, and subsequent estimation of furfural in the distillate by means of a suitable reagent. Günther, Chalmot and Tollens¹ titrated the furfural with phenylhydrazine, using aniline acetate paper as an indicator. Stone² made use of the same reaction, but used Fehling's solution to determine the excess of phenylhydrazine. Later, Flint and Tollens³ showed that this titration method was not accurate, on account of the levulinic acid resulting from the decomposition of hexoses, as well as the instability of the standard phenylhydrazine acetate reagent used. Jolles⁴ titrated the furfural with potassium bisulphite and iodine. In the absence of other reducing substances, the furfural could be determined directly with Fehling's solution. Günther and Tollens⁵ precipitated the furfural as hydrofurfuralimide by means of ammonia, while Chalmot and Tollens⁶ used phenylhydrazine and weighed the resulting hydrazone. In both cases the condensation product was somewhat soluble.

Councilor⁷ was the first to use phloroglucinol for the quantitative determination of furfural. This method was later studied and perfected by Tollens and his co-workers. The phloroglucinol method, although known to be faulty in several respects, is the one in general use today, having been adopted as provisional by the Association of Official Agricultural Chemists.⁸ It is strictly empirical, since the nature of the reaction and the constitution of the condensation product have not been determined. Kröber⁹ compiled a table in which the weight of furfuralphloroglucide obtained is interpreted in terms of furfural, xylose, arabinose or pentose. This table is purely empirical, being based on trial distillations and precipitations of the furfural or the particular pentose employed, and not upon the

molecular weight of the condensation product. Furthermore, this method calls for solubility corrections. Kröber assumes that two molecules of water are split out in the reaction between furfural and phloroglucinal. Goodwin and Tollens¹⁰ claim that only one molecule of water is liberated at ordinary temperature, but if the reaction is carried out at a temperature of 80° three molecules are liberated. A slight variation in the conditions may, therefore, affect the result considerably. Kröber noted the fact also that when the phloroglucide is allowed to stand in the air for a time, it takes up moisture which cannot be expelled by subsequent drying. From this brief survey of the literature, it is obvious that the phloroglucinol method in common use is not altogether satisfactory.

Other reagents also have been tried with varying success. Kerp and Unger¹¹ used semioxamizine as a precipitant for furfural, but obtained results that were too low. Conrad and Reinbach¹² found that furfural and barbituric acid condensed in the presence of dilute hydrochloric acid. Subsequently, Unger and Jäger¹³ applied this reaction to the quantitative determination of furfural. They found that six to eight times as much barbituric acid as the theory required was needed to give the calculated value for furfural. The condensation product had the advantage of being only very slightly soluble in hydrochloric acid (1.22 mgm. per 100 cc.). They claim that barbituric acid does not precipitate the furfural derivatives of hexose origin and that these merely tend to color the solution yellow. The reaction is a very simple one, consisting in the condensation of one molecule of furfural and one molecule of barbituric acid, through the aldehyde group of the former and the methylene group of the latter, with the splitting out of one molecule of water. The product was found to contain 13.75 per cent nitrogen, which is in close agreement with the calculated value of 13.63 per cent. When prepared from the furfural distillate from natural sources, the product was found to contain 13.96 per cent nitrogen.

Fromherz¹⁴ used barbituric acid as a precipitant for methylfurfural, and found the condensation product to be not appreciably soluble. Fallada, Stein and Ravinka¹⁵ found that barbituric acid and phloroglucinol gave very nearly the same results when pure xylose and arabinose were distilled and precipitated. On the other hand, when sucrose was added to the pentose, the

results were very much higher when phloroglucinol was used as a precipitant than when barbituric acid was employed, the latter giving normal values. This substantiates the statements of other workers who found that hydroxymethylfurfural was not precipitated by barbituric acid.

The barbituric acid method possesses, therefore, certain advantages over the phloroglucinol method, in that the reaction is more specific and a definite condensation product is formed. The precipitate, however, is sufficiently soluble to render a solubility correction necessary. Then again, a large excess of the reagent appears to be necessary, indicating that possibly an occlusion of the precipitant leads to a compensation of errors.

The possibility of obtaining better results by using some derivative of barbituric acid will be discussed in the experimental part of this paper.

EXPERIMENTAL.

Barbituric acid ordinarily is prepared by the condensation of urea with the sodium salt of malonic ester. The corresponding thio derivative was prepared by Michael¹⁶ ¹⁷ and by Gabriel and Colmann¹⁸ by condensing thiourea with sodium malonic ester, and the imino derivative was prepared by Michael¹⁷ and by Traube¹⁹ from guanidine and malonic ester. These two derivatives are analogus in many respects to barbituric acid. It remained to be determined whether they would react in a similar manner with furfural, and possibly give a more complete precipitation.

The barbituric acid used in this work was a Kahlbaum preparation, which we purified further by recrystallization from water. Analysis showed it to contain 21.80 per cent nitrogen; theory 21.87 per cent.

Our first preparation of thiobarbituric acid was made according to the method of Gabriel and Colmann. Two and three-tenths gms. of sodium was dissolved in 50 cc. absolute alcohol, and 16 gms. malonic ester added, then 7.6 gms. dry thiourea, previously dissolved in absolute alcohol. The mixture was heated on a water bath under a reflux condenser for ten hours. The white pasty mass which resulted was then treated with 80 cc. water and 7.6 cc. hydrochloric acid and gently warmed until it had dissolved. Upon standing, thiobarbituric acid crystal-

lized out. The yield was about 30 per cent of the theory. In preparing a further quantity of thiobarbituric acid we found that a much better yield was obtained when less solvent was used and the mixture heated for 15 hours in a sealed tube at 105°, with twice the theoretical amount of sodium, as recommended by Fischer and Dilthey²⁰ in their preparation of methyl-ethyl and dimethylthiobarbituric acid. The product, after acidifying with hydrochloric acid, was a slightly yellowish crystalline powder containing 19.61 per cent nitrogen, whereas the theory calls for 19.45 per cent. The yield in this case was 45 per cent of the theory.

Malonylguanidine was made according to Traube from free guanidine and malonic ester. The condensation took place readily and gave an excellent yield. The product was used directly without further purification. It contained 32.07 per cent nitrogen; theory, 33.06 per cent.

Parallel determinations were now conducted, using barbituric acid, thiobarbituric acid and malonylguanidine as precipitants for furfural. For this work a stock solution of pure, freshly distilled furfural of exactly 1 per cent strength was prepared, and a 5 cc. aliquot taken for each determination. The furfural was diluted with 12 per cent hydrochloric acid and solutions of the different precipitants in 12 per cent hydrochloric acid added, the total volume of the reaction mixture being 400 cc. The conditions were, therefore, similar to those obtaining in pentosan determinations. Unless otherwise indicated, a slight excess of the precipitant was employed, the reaction carried out at room temperature, and the precipitate allowed to stand over night before filtering on Gooch crucibles and drying to constant weight at 100°. The analytical results are set forth in the following tables:

TABLE I.
 BARBITURIC ACID.

FURFURAL TAKEN GMS.	WT. OF PRECIPITATE GMS.	FURFURAL CALCULATED GMS.	ERROR MGMS.	FURFURAL RECOVERED PER CENT
.0583	.1180	.0550	— 3.3	94.3
.0583	.1180	.0550	— 3.3	94.3
.0583	.1171	.0546	— 3.7	93.6
.0583	.1174	.0547	— 3.6	93.8
.0583	.0976	.0455*	—12.8	78.0
.0583	.1194	.0556**	— 2.7	95.4
.0583	.1238	.0580***	— 0.3	99.5

*Precipitated with a little more than the theoretical amount of barbituric acid.

**Precipitated with 4 times the theoretical amount of barbituric acid.

***Precipitated with 16 times the theoretical amount of barbituric acid.

From the above table it is at once apparent that the results with barbituric acid are uniformly low. The last three determinations show the effect of increasing amounts of the precipitant. With barbituric acid and furfural in molecular proportions of sixteen to one, the result is nearly quantitative. This observation is in accord with statement of Unger and Jäger that eight times the theoretical amount of barbituric acid is necessary for complete recovery of the furfural.

TABLE II.
 THIOBARBITURIC ACID.

FURFURAL TAKEN GMS.	WT. OF PRECIPITATE GMS.	FURFURAL CALCULATED GMS.	ERROR MGMS.	FURFURAL RECOVERED PER CENT
.0583	.1351	.0584	+ 0.1	100.2
.0583	.1360	.0588	+ 0.5	100.8
.0583	.1372	.0593	+ 1.0	101.7
.0583	.1367	.0591	+ 0.8	101.4
.0583	.1361	.0588	+ 0.5	100.8
.0583	.1368	.0591	+ 0.8	101.4
.0583	.1271	.0550*	— 3.3	94.3
.0583	.1294	.0559*	— 2.4	95.9

*Precipitated at 60°.

With thiobarbituric acid, as shown in the above table, the precipitation is quantitative without using a large excess of the reagent. The results tend even to run just a trifle over the

theory. The last two determinations above show that the reaction should not be allowed to occur at a high temperature since this leads to results that are too low.

TABLE III.
MALONYLGUANIDINE.

FURFURAL TAKEN GMS.	WT. OF PRECIPITATE GMS.	FURFURAL CALCULATED GMS.	ERROR MGMS.	FURFURAL RECOVERED PER CENT
.0583	.0649	.0305	-27.8	52.3
.0583	.0640	.0300	-28.3	51.5

The condensation of furfural with malonylguanidine is not quantitative. The yield in the two determinations quoted above was only a little more than half the theory, hence under these conditions malonylguanidine is not applicable for the quantitative determination of furfural.

Having shown that thiobarbituric acid in moderate excess gives quantitative results under the conditions of the above experiments, whereas barbituric acid under the same conditions gives less than 95 per cent of the theoretical yield, it remains to compare these two reagents as regards their sensitiveness to smaller amounts of furfural. In the determinations recorded in table IV, four times the theoretical amount of barbituric acid was used.

TABLE IV.
BARBITURIC ACID.

FURFURAL TAKEN GMS.	WT. OF PRECIPITATE GMS.	FURFURAL CALCULATED GMS.	ERROR MGMS.	FURFURAL RECOVERED PER CENT
.0117	none	none	no ppt.	none
.0117	.0061	.0028	- 8.9	26.5
.0233	.0225	.0105	-12.8	45.6
.0233	.0334	.0156	- 7.7	67.0
.0350	.0475	.0221	-12.9	63.1
.0350	.0640	.0298	- 5.2	85.1

It is obvious therefore, that the barbituric acid method is inapplicable to the determination of small quantities of furfural.

In table V, varying amounts of furfural are treated with varying amounts of thiobarbituric acid.

TABLE V.
THIOBARBITURIC ACID.

FURFURAL TAKEN GMS.	THIOBARBITURIC ACID TAKEN GMS.	WT. OF PRECIPITATE GMS.	FURFURAL CALCULATED GMS.	ERROR MGMS.	FURFURAL RECOVERED PER CENT
.0592	.18	.1369	.0592	0.0	100.0
.0592	.18	.1398	.0603	+1.1	101.8
.0592	.18	.1370	.0592	0.0	100.0
.0592	.18	.1400	.0605	+1.3	102.3
.0592	.12	.1390	.0601	+0.9	101.6
.0592	.12	.1400	.0605	+1.3	102.3
.0592	.20	.1372	.0593	+0.1	100.2
.0360	.11	.0835	.0361	+0.1	100.3
.0360	.11	.0852	.0369	+0.9	102.5
.0244	.08	.0568	.0247	+0.3	101.2
.0244	.08	.0560	.0243	-0.1	99.6
.0244	.06	.0556	.0240	-0.4	98.3
.0244	.16	.0573	.0248	+0.4	101.6
.0119	.04	.0277	.0120	+0.1	100.8
.0119	.04	.0275	.0119	0.0	100.0
.0119	.03	.0261	.0113	-0.6	95.0
.0119	.08	.0278	.0120	+0.1	100.8

Here again, the results are just a trifle in excess of the theory. Even so small an amount of furfural as 12 mgms. gave practically a quantitative yield, and variations in the amount of precipitant were of very little influence.

Analysis of the condensation products showed the percentage of nitrogen to be in close agreement with the values calculated from the formulas.

TABLE VI.
ANALYSIS OF CONDENSATION PRODUCTS.

	NITROGEN		SULPHUR	
	FOUND	CALCULATED	FOUND	CALCULATED
Furfuralmalonylurea	13.60	13.65
Furfuralmalonylthiourea	12.44	12.61	14.93	14.41
Furfuralmalonylguanidine ...	15.61	16.01

The furfuralmalonylurea is a bright lemon yellow, somewhat granular precipitate which settles readily. Furfuralmalonylthiourea is also a brilliant lemon yellow precipitate but very flocculent and voluminous. No difficulty was experienced in filtering and washing it, although the filtration was somewhat

slow. It was practically insoluble in cold dilute mineral acids and only slightly soluble in hot acids. It was practically insoluble in alcohol, ether, petroleum ether, methyl alcohol, acetic acid, benzene, carbon disulphide and turpentine. In ammonia, pyridine and caustic alkalies it dissolves with ease, giving at first a greenish blue solution which gradually loses its color. From the alkaline solution it can be recovered by neutralizing with acid. The filtrates from both the furfuralmalonylurea and the furfuralmalonylthiourea had a very slight tinge of yellow. Furfuralmalonylguanidine, on the other hand, is a very dark green, flocculent precipitate, appreciably soluble in hydrochloric acid. The filtrate is an intense greenish brown.

It was early noted that unless the thiobarbituric acid was carefully purified, the precipitation of furfural was not complete, only 90 or 95 per cent of the latter being recovered, and the filtrate possessed a red color or sometimes a green color. In one set of determinations the difficulty was traced with reasonable certainty to the presence of cyanacetic ester in the malonic ester from which the thiobarbituric acid was made. In preparing malonic ester from chloracetic acid in the usual way, some cyanacetic ester is apt to remain unless precautions are taken to carry the saponification to completion. This is difficult to separate from the malonic ester because the boiling points of the two substances lie only a few degrees apart. The cyanacetic ester in all probability reacts with the thiourea, forming a dicyanacetylthiourea. On fractional crystallization of one of the impure preparations of thiobarbituric acid, white needle-shaped crystals were obtained, which on analysis yielded 26.66 per cent nitrogen; calculated for dicyandiacylthiourea, 26.65 per cent nitrogen. These crystals when dissolved in 12 per cent hydrochloric acid gave an intensely green precipitate with furfural, just as did the thiobarbituric acid before purification. For the preparation of thiobarbituric acid it is, therefore, recommended that the malonic ester be subjected to a repetition of the simultaneous saponification and esterification before condensation with thiourea, and that the thiobarbituric acid be purified by one or two crystallizations of its sodium salt.

DISCUSSION.

Our experiments, quoted above, show that thiobarbituric acid condenses readily with furfural in the presence of 12 per cent hydrochloric acid. The reaction is quantitative, giving a volum-

inous precipitate which can be filtered, dried and weighed. As a precipitant for furfural, thiobarbituric acid is superior to phloroglucinol, in that no correction for solubility of the product is necessary. It is also preferable to barbituric acid for the reason that the reaction is quantitative with as small amounts of furfural as 12 mgms. and a large excess of the precipitant is not necessary, thus avoiding possible errors due to inclusion. Unlike the phloroglucinol product, the resulting furfuralmalonylthiourea is a definite substance resulting from the condensation of one molecule of furfural with one molecule of thiobarbituric acid by the elimination of one molecule of water, and a definite chemical formula can be assigned to it. It has a further advantage in that the percentages of nitrogen and sulphur, which agree with those calculated from the formula, can be determined by analysis and used as a positive means of identification of the product to distinguish it from, or detect the presence of, similar products which might result in case homologues of furfural were present. For example, if a mixture of furfural and methylfurfural were precipitated, the determinations of nitrogen and sulphur on the product should enable us to compute the relative amounts of these two aldehydes, and therefore the relative amounts of pentosans and methylpentosans in the original sample. At present the only means of estimating separately the furfural and methylfurfural present in a mixture such as is frequently met with in analysis, is the supposed differential solubility of their phloroglucides in alcohol, and this admittedly is unreliable.

It is suggested that thiobarbituric acid, which is not difficult to prepare in a pure state, may be found useful in the analysis of agricultural products, in place of phloroglucinol or barbituric acid, for the determination of pentoses and pentosans.

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