LXXV. THE DETERMINATION OF PENTOSANS IN THE ANALYSIS OF WOODS

I. THE GRAVIMETRIC DETERMINATION OF FURFURALDEHYDE

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THE determination of pentosans in plant materials has long been a subject of controversy. These bodies are estimated indirectly from the amount of furfuraldehyde obtained by distilling a known weight of the parent plant material with 12 % HCl under standard conditions. If the furfuraldehyde is to be determined gravimetrically much will depend on the choice of a precipitant. In recent years there has been a tendency to discontinue the use of phloroglucinol for this purpose and to use in its stead thiobarbituric acid as originally suggested by Dox & Plaisance [1916] or, alternatively, diphenylthiobarbituric acid as recently suggested by Tischtschenko & Koschkin [1934]. The use of thiobarbituric acid has been stated to overcome all the objections raised against phloroglucinol. For instance, Dox & Plaisance [1916] have shown that the condensation product formed with furfuraldehyde is of constant composition. No solubility corrections are considered to be necessary, and above all, the presence of hydroxymethylfurfuraldehyde in the hydrochloric acid distillate is stated not to interfere with the estimation of furfuraldehyde, since the condensation product 5-(hydroxymethyl)-furfurylidene malonylthiocarbamide is soluble under normal experimental conditions. By some workers the condensation product of furfuraldehyde and thiobarbituric acid is considered to be easily separable from the hydrochloric acid system by filtration.

Thiobarbituric acid has not been used to any great extent in analytical work connected exclusively with wood and the authors have therefore deemed it desirable to examine critically several aspects of the determination of furfuraldehyde by means of this reagent so that it may be compared in efficacy with phloroglucinol. For the present the general question of the expression of the results of furfuraldehyde determinations in terms of pentosans, uronic acids etc. has been left aside as this raises issues which had best be dealt with in a subsequent communication.

EXPERIMENTAL

It is axiomatic that, in furfuraldehyde determinations, the conditions of the initial distillation with 12 % HCl should be rigidly standardized. So far as wood chemistry is concerned this has been realized for many years [Schorger, 1926, p. 534], but the point has recently been re-emphasized by Angell *et al.* [1936]. The method of distillation used here was essentially that recommended by Schorger [1926, p. 534 *et seq.*], except that the distillate was passed through a vertical, coiled condenser.

Estimation of pure furfuraldehyde

A sample of furfuraldehyde (B.D.H. preparation) was purified first by distillation under atmospheric pressure and, immediately before use, by redistillation *in vacuo*, generous head and tail fractions being discarded. The clear, colourless liquid had B.P. 72.5° at 39 mm. and refractive index 1.5245 at 23°. A weighed quantity of the pure substance was dissolved in 12% HCl and made up to a known volume with the acid. Aliquots of the solution were made up to 360 ml. with 12% HCl and the furfuraldehyde was estimated by precipitation (1) with 40 ml. of phloroglucinol (AnalaR) solution according to the method of Schorger [1926, p. 535], and (2) with twice the theoretical quantity of thiobarbituric acid (supplied by B.D.H.) dissolved in warm 12% HCl (Table I).

Table I. *Direct estimation of pure furfuraldehyde*

Reagent	Phloroglucinol				Thiobarbituric acid							
	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Furfurald. taken, g.	0.0544	0.0544	0.04974	0.04974	0.04974	0.04974	0.05124	0.05124	0.1066	0.1066	0.1066	0.1066
Wt. of ppt., g.	0.1015	0.1030	0.0921	0.0922	0.1201	0.1187	0.1228	0.1221	0.2582	0.2565	0.2577	0.2561
Furfurald. recovered, g.	0.0554	0.0562	0.0505	0.0506	0.0519	0.0514	0.0531	0.0528	0.1116	0.1109	0.1114	0.1108
% recovery	101.8	103.3	101.5	101.6	104.3	103.1	103.6	103.0	104.7	104.0	104.4	103.9

For comparative purposes aliquots of pure furfuraldehyde were diluted to 100 ml. with 12% HCl and, after distillation according to the procedure outlined above, estimated by means of both phloroglucinol and thiobarbituric acid (Table II).

Table II. *Estimation of pure furfuraldehyde after distillation with 12% HCl*

Phloroglucinol method								
Furfurald. taken, g.	0.1141	0.1141	0.1141	0.1141	0.02508	0.02508	0.05047	0.05047
Wt. of ppt., g.	0.2014	0.2030	0.2015	0.2045	0.0416	0.0417	0.0907	0.0902
Wt. furfurald. recovered, g.	0.1072	0.1080	0.1073	0.1088	0.0243	0.0244	0.0498	0.0495
% recovery	93.96	94.65	94.03	95.37	96.9	97.3	98.7	98.1
Thiobarbituric acid method								
Furfurald. taken, g.	0.1066	0.1066	0.1066	0.1066	0.1066	0.0861	0.0861	0.0861
Wt. of ppt., g.	0.2514	0.2508	0.2503	0.2521	0.1964	0.1968	0.1954	0.1954
Wt. of furfurald. recovered, g.	0.1087	0.1084	0.1082	0.1090	0.08496	0.08511	0.08433	0.08433
% recovery		102.4	101.7	101.5	102.6	98.7	98.9	98.0

In every case furfuraldehydophloroglucide could be collected readily in a Gooch crucible with asbestos mat but this was not the case with furfurylidene-malonylthiocarbamide. Owing to the extreme slowness with which this latter substance could be separated by filtration at the pump it was found expedient to use alundum crucibles (porosity RA 360) for this operation. Even then, collection was a much slower operation than in the case of the phloroglucide precipitates. Washing of the furfurylidene-malonylthiocarbamide was difficult.

In some cases after washing the precipitate with 500 ml. of water the filtrate was still acid to litmus although it gave no precipitate with silver nitrate. A neutral filtrate was obtained only by finally washing with a small quantity of water at 40–50°. This latter practice is not recommended, however, since although the condensation product is insoluble in cold water it is slightly soluble in hot water. Moreover it is also slightly soluble in cold 12% HCl. In these and subsequent experiments furfuraldehydophloroglucide was converted to furfuraldehyde by means of Kröber's [1900] tables and the weight of furfurylidene-

malonylthiocarbamide was similarly converted by multiplying by the factor 0.4324.

The results in Table II indicate that a certain amount of furfuraldehyde was lost during the distillation. The results obtained with both reagents vary considerably among themselves, however, and this is attributed to the fact that precipitation was allowed to take place in beakers covered only by clock glasses. In all subsequent work greater consistency was attained by allowing precipitation to take place in stoppered Erlenmeyer flasks. Consideration of the results obtained by using phloroglucinol as precipitant in Tables II, VI and IX suggests that the loss of furfuraldehyde during one distillation is of the order of 1.6%. Angell *et al.* [1936] estimate this loss at about 1%.

Purification of thiobarbituric acid

Up to this stage the thiobarbituric acid as supplied by Messrs B.D.H. was used without further purification since it conformed to the requirements of Dox & Plaisance [1916]. In view however of the high results recorded in Tables I and II and the fact that the reagent developed an unpleasant odour on standing in a sealed container, it was purified as required by dissolving in dilute aqueous sodium hydroxide, filtering and acidifying with dilute hydrochloric acid. After standing at 10° for several hours, pure thiobarbituric acid settled out in crystalline form. After filtration, washing with water and drying at 105° the reagent was odourless and almost colourless. It was used in this form in all subsequent experiments.

The results in Table III amply demonstrate the advisability of using thiobarbituric acid in pure form.

Table III. *Estimation of pure furfuraldehyde (after distillation with 12% HCl) by means of purified thiobarbituric acid*

Furfurald. taken g.	Wt. of ppt., g.	Fur- furald. recovered g.	% recovery	Fur- furfurald. taken g.	Wt. of ppt., g.	Fur- furfurald. recovered g.	% recovery
0.0868	0.2001	0.0865	99.7	0.1226	0.2828	0.1223	99.8
0.0868	0.2022	0.0874	101.0	0.1226	0.2833	0.1225	99.9
0.0868	0.2002	0.0866	99.7	0.1226	0.2841	0.1230	100.3
0.0868	0.2030	0.0878	101.5	0.1226	0.2826	0.1222	99.7
0.09584	0.2226	0.0963	100.4	0.05047	0.1184	0.05130	101.5
0.09584	0.2219	0.0960	100.1	0.05047	0.1166	0.05043	99.93
0.09584	0.2223	0.0961	100.3	0.0945	0.2187	0.0946	100.1
				0.0945	0.2206	0.0954	100.9
				0.0945	0.2205	0.0953	100.8
				0.0945	0.2210	0.0956	101.1

The condensation products obtained from the acid distillates of pure sugars

Small samples of pure glucose, sucrose and mannose were separately distilled with 12% HCl in the usual way, and in each case the addition of thiobarbituric acid to the distillate produced a golden yellow coloration which deepened to amber. The only sugar the distillate from which gave a slight precipitate with the reagent was mannose but only when 0.5 g. or more of the sugar was used. The presence of hydroxymethylfurfuraldehyde was confirmed in each case by the resorcinol and aniline acetate tests. It was established that the acid distillate from 0.5 g. mannose also gave a slight precipitate with phloroglucinol.

*Estimation of the furfuraldehyde obtained on distilling various woods with
12% HCl*

(a) *Hardwoods.* Weighed samples of the hardwoods mentioned in Table IV were distilled with 12 % HCl under the usual conditions and the furfuraldehyde was estimated by each of the two reagents. 1 g. (air-dry) samples were used in

Table IV. *Yields of furfuraldehyde from three hardwoods on distillation with
12% HCl*

Reagent	Beech (<i>Fagus sylvatica</i> L.)				Jarrah (<i>Eucalyptus marginata</i> Sm.)				Oak sapwood (<i>Quercus</i> sp.)			
	Phloroglucinol		Thiobarbituric acid		Phloroglucinol		Thiobarbituric acid		Phloroglucinol		Thiobarbituric acid	
Oven-dry wt. of wood, g.	0.8977		0.4489		0.8847		0.4424		0.8884		0.4442	
Oven-dry wt. of ppt., g.	0.2355	0.2332	0.1447	0.1450	0.1286	0.1300	0.0799	0.0810	0.2224	0.2247	0.1392	0.1393
Furfurald. as % of oven-dry wood	13.90	13.77	13.94	13.96	7.85	7.93	7.83	7.91	13.28	13.43	13.55	13.55
Mean % yield of furfurald.	13.84		13.95		7.89		7.87		13.36		13.55	

conjunction with phloroglucinol, and 0.5 g. samples with thiobarbituric acid because of the comparative bulkiness of the furfurylidenemalonylthiocarbamide precipitate. The latter was flocculent and of yellow colour in each case.

(b) *Softwoods.* In the course of the estimation of furfuraldehyde obtained by distilling weighed samples of softwoods with 12 % HCl several important features, which do not appear to have been recorded previously, were brought to light. When phloroglucinol was added to the distillates obtained from the woods mentioned in Table V the precipitates were all normal in appearance but the

Table V. *Yields of furfuraldehyde from four softwoods on distillation
with 12% HCl*

Reagent	Sitka spruce (<i>Picea sitchensis</i> Carr.)				Douglas fir (<i>Pseudotsuga taxifolia</i> Brit.)			
	Phloroglucinol		Thiobarbituric acid		Phloroglucinol		Thiobarbituric acid	
	1.8114		0.9057		1.8114		0.9057	
	Oven-dry wt. of wood, g.	0.1656	0.1633	0.0700	0.0696	0.1760	0.1717	0.0915
Oven-dry wt. of ppt., g.	4.89	4.83	3.34 _p	3.32 _p	5.19	5.07	4.38 _p	4.15 _p
Apparent furfurald. as % of oven-dry wood								
Mean % yield of apparent furfurald.	4.86		3.33		5.13		4.27	
Reagent	African pencil cedar (<i>Juniperus procera</i> Hochst.)				Cypress pine (<i>Callitris robusta</i> R.Br.)			
	Phloroglucinol		Thiobarbituric acid		Phloroglucinol		Thiobarbituric acid	
	0.7112		0.7112		0.8813		0.4407	
	Oven-dry wt. of wood, g.	0.0898	0.0900	0.1123	—	0.1650	0.1635	0.0913
Oven-dry wt. of ppt., g.	6.93	6.94	6.83 _p	—	10.0	9.9	8.96	8.96
Apparent furfurald. as % of oven-dry wood								
Mean % yield of apparent furfurald.	6.94		6.83		9.95		8.96	

supernatant liquors were much darker in colour than those obtained with either pure furfuraldehyde or the hardwoods examined. The precipitates formed in the distillates from Sitka spruce, Douglas fir and African pencil cedar on the addition of thiobarbituric acid were of a coarse granular texture in contrast to

the flocculent precipitates formed in the distillates from pure furfuraldehyde and the hardwoods examined. The supernatant liquors were of a dark amber colour. The precipitate formed in the distillate of Cypress pine was an exception, however, since it was of the flocculent type.

The phloroglucide precipitates were readily collected by the normal procedure, but all attempts to collect the furfurylidenemalonylthiocarbamide precipitates quantitatively from Sitka spruce, Douglas fir and African pencil cedar, on either Gooch or alundum crucibles, proved fruitless. At a certain stage in the washing with water the precipitates became peptized and part of them passed into the filtrate as a yellow colloidal solution from which the disperse phase was precipitated on coming into contact with hydrochloric acid. Increasing amounts of the precipitates were dispersed if washing were continued. It was observed that a hydrochloric acid solution of 5-(hydroxymethyl)-furfurylidenemalonylthiocarbamide derived from the acid distillate from 0.5 g. of pure mannose showed no signs of turbidity on excessive dilution with water, so that the phenomenon mentioned above can only be ascribed to the peptization of the true furfuraldehyde condensation product. The precipitate obtained from Cypress pine filtered slowly but it was not observed to peptize on continued washing with cold water. The results for the four softwood species examined are recorded in Table V, the letter "p" being used to designate precipitates which became peptized during washing.

In view of the difficulties experienced in connexion with filtration it is obvious that, with the exception of the results for Cypress pine, little reliance can be placed on the results obtained by using thiobarbituric acid as a precipitant for furfuraldehyde in the presence of hydroxymethylfurfuraldehyde (Table V). It would appear that, in the circumstances, the error introduced by the presence of this latter substance can only be overcome by submitting the original acid distillate to a second distillation as recommended by Antoniani [1928] and others. This view is confirmed by the results of the following experiments.

Estimation of furfuraldehyde in the redistilled acid distillates from three softwoods

Since redistillation of the first distillate must inevitably involve a loss of furfuraldehyde the following experiments were carried out with pure furfuraldehyde in order to assess this loss. Aliquots were distilled with 12% HCl in the usual way and estimations were made on a portion of each distillate by means of both precipitants. Similar estimations were made on another portion of each distillate after redistillation (Table VI).

Table VI. *The effect of two distillations with 12% HCl on the estimation of pure furfuraldehyde*

Reagent	After one distillation				After two distillations			
	Phloroglucinol		Thiobarbituric acid		Phloroglucinol		Thiobarbituric acid	
Wt. of furfurald. taken, g.	0.0573	0.0573	0.0573	0.0573	0.0573	0.0573	0.0573	0.0573
Wt. of ppt., g.	0.1032	0.1033	Filtration too tedious to be completed in 1 day		0.0974	0.0980	0.1310*	0.1312*
Wt. of furfurald. recovered, g.	0.0563	0.0564			0.0533	0.0536	0.0566	0.0567
% recovery	98.3	98.5	—	—	93.0	93.5	98.8	98.9
Mean % recovery	98.4				93.3		98.9	

* Volume of wash water restricted to 150 ml.

It will be observed (Table VI) that approximately 5.15% of the furfuraldehyde estimated by means of phloroglucinol after one distillation is lost during the second distillation. Antoniani [1928] assessed this loss at 7%. Strictly comparable figures are not available for the thiobarbituric acid method of estimation from Table VI alone, but reference to Table III enables us to assess the apparent loss of furfuraldehyde during the second distillation at approximately 1%. Since the washing of the precipitates (Table VI) was admittedly inadequate this figure of 1% is of little significance.

The yield of furfuraldehyde from each of three of the above-mentioned softwoods was now estimated after redistilling portions of the original acid distillates. In order to allow for losses of furfuraldehyde the results obtained by the phloroglucinol method were multiplied by 100/94.9 and those obtained by the thiobarbituric acid method were multiplied by 100/99 (Table VII). In the latter

Table VII. *Yields of furfuraldehyde from three softwoods after two distillations with 12% HCl*

Reagent	Sitka spruce				Douglas fir				African pencil cedar			
	Phloro-glucinol		Thiobarbituric acid		Phloro-glucinol		Thiobarbituric acid		Phloro-glucinol		Thiobarbituric acid	
Oven-dry wt. of sample, g.	0.9057	0.9057	0.9057	0.9057	0.9057	0.9057	0.9057	0.9057	0.7112	0.7112	0.7112	0.7112
Wt. of ppt., g.	0.0534	0.0542	0.0753	0.0736 _p	0.0548	0.0552	0.0720 _p	0.0665 _p	0.0779	0.0798	0.1123 _p	0.1153
Vol. of wash water, ml.	150.0	150.0	135.0	170.0	150.0	150.0	160.0	230.0	150.0	150.0	150.0	150.0
Furfurald. as % of oven-dry wood (A)	3.36	3.40	3.58	3.51	3.44	3.46	3.48	3.18	6.08	6.18	6.83	7.00
*Total furfurald. as % of oven-dry wood	3.54	3.58	3.62	3.55	3.62	3.65	3.51	3.21	6.41	6.51	6.90	7.07
Mean % total furfurald.	3.56		3.59		3.64		3.36		6.46		6.99	

* By phloroglucinol method total furfuraldehyde = $A \times 100/94.9$.
 By thiobarbituric acid method total furfuraldehyde = $A \times 100/99$.
 "p" designates precipitates which became peptized.

method the volume of wash water was carefully controlled. It was observed that, after the second distillation, the precipitate formed on adding thiobarbituric acid was of the normal, flocculent type. Nevertheless the liability to become peptized was not entirely eliminated.

Diphenylthiobarbituric acid as a precipitant for furfuraldehyde

The following experiments were carried out in order to test the conclusion of Tishchtschenko & Koschkin [1934] concerning the suitability of diphenylthiobarbituric acid as a precipitant for furfuraldehyde. A sample of the reagent, prepared by the method recommended by the above authors, was obtained from Messrs B.D.H. and purified by crystallization from benzene. The purified compound sublimed on heating to 204–205° and condensed in the form of long, silky needles. This latter form showed signs of decomposition at 241° and melted with complete decomposition at 251°. The substance dissolved readily in 4% aqueous ammonium acetate to form a colourless solution.

Estimation of pure furfuraldehyde. Aliquots of a hydrochloric acid solution of pure furfuraldehyde were distilled with 12% HCl according to standard procedure and the furfuraldehyde in the distillates was precipitated by adding 2.5 times the theoretical quantity of freshly purified reagent dissolved in 4% aqueous ammonium acetate. The precipitate in each case filtered readily and was collected in an alundum crucible (R.A. 360). It was then washed with

50 ml. of a boiling, weakly acid 4% solution of ammonium acetate, followed by 20 ml. of cold water, and dried at 105° according to the directions given by Tischtschenko & Koschkin [1934]. The results are recorded in Table VIII.

Table VIII. *Estimation of pure furfuraldehyde after distillation with 12% HCl by means of diphenylthiobarbituric acid*

	(1)	(2)
Wt. of furfurald. taken, g.	0.02508	0.02508
Wt. of ppt., g.	0.1081	0.1082
Calculated wt. of ppt., g.		0.1213

After completing the determinations (Table VIII), the precipitates were each treated with a further 50 ml. of the hot ammonium acetate solution, followed by cold water, and then dried and weighed. This resulted in a loss of 5.1 mg. from the first precipitate and 5.6 mg. from the second. The low results in Table VIII suggest either that the condensation product formed between furfuraldehyde and diphenylthiobarbituric acid is soluble in hot aqueous ammonium acetate or that the constitution assigned to it by the above authors is incorrect. Confirmation of these suggestions is forthcoming from the results in Tables IX and X despite the fact that here the condensation product formed with diphenylthiobarbituric acid was washed with cold ammonium acetate solution followed by cold water.

Table IX. *Comparative efficacies of phloroglucinol, thiobarbituric and diphenylthiobarbituric acids as precipitants for pure furfuraldehyde after distillation with 12% HCl*

Reagent	Phloroglucinol		Thiobarbituric acid		Diphenylthiobarbituric acid	
	0.05047	0.05047	0.05047	0.05047	0.05047	0.05047
Wt. of furfurald. taken, g.						
Wt. of ppt., g.	0.0907	0.0902	0.1184	0.1166	0.2208	0.2146
Furfurald. recovered, g.	0.0498	0.0495	0.05125	0.05043	0.0458	0.0446
% recovery	98.67	98.08	101.5	99.93	90.75	88.37
Mean % recovery		98.38		100.7		89.56

Table X. *Estimation of furfuraldehyde in the acid distillate from Jarrah wood by means of diphenylthiobarbituric acid (cf. Table IV)*

Oven-dry wt. of wood sample, g.	0.4424	0.4424
Wt. of ppt. (P), g.	0.1547	0.1529
Wt. of furfurald., g. = $P \times (96/464)$	0.0320	0.0316
Furfurald. as % of oven-dry wood	7.23	7.14
Mean % furfurald.		7.19

DISCUSSION OF RESULTS

In view of the widespread belief concerning the suitability of thiobarbituric acid as a precipitant for furfuraldehyde many of the foregoing results were unexpected. Since however we have no reason to doubt their accuracy it is patent that the claims advanced for the superiority of thiobarbituric acid over phloroglucinol for the estimation of furfuraldehyde obtained by the acid distillation of woods are premature and unfounded. It is a matter for comment that, even when dealing with pure furfuraldehyde, Dox & Plaisance [1916] and several subsequent investigators, including the authors (Tables II and III),

record recoveries of more than 100% on treating the acid distillate with thiobarbituric acid, although it is obvious from Tables I and II that a certain amount of furfuraldehyde must be lost either during the distillation itself or subsequently. Even when highly purified thiobarbituric acid is used (Table III) it has been shown that it is extremely difficult to wash the furfuraldehyde condensation product entirely free from the excess of reagent. In fact it would appear that sorption of part of the reagent by the condensation product is a factor to be reckoned with. This, coupled with the observation that the condensation product is slightly soluble in 12% HCl, introduces the possibility that recoveries of furfuraldehyde which approximate to 100% by the thiobarbituric acid method may be to some extent fortuitous and due to a compensation of errors of sorption and solubility.

It is clear that sorption is probably also involved in the estimation of furfuraldehyde by the phloroglucinol method since, in the absence of distillation, recoveries amount to over 100% (Table I). Nevertheless, it is claimed that, under rigidly standardized conditions, this method is capable of yielding reasonably satisfactory results. Perhaps the chief advantage of the method is that the phloroglucide can be collected and washed with comparative ease.

It has been amply demonstrated in previous work that the inaccuracy introduced by the presence of hydroxymethylfurfuraldehyde in the acid distillates is of prime importance in connexion with the determination of the furfuraldehyde yields from woods. Schorger [1926, p. 533] has stated that under the standard conditions of distillation the formation of hydroxymethylfurfuraldehyde is not of great importance. On the other hand Gierisch [1925], in supporting the view of Erdmann [1910] that at 160° pure hydroxymethylfurfuraldehyde is decomposed into formaldehyde, states that, when formed from carbohydrates, hydroxymethylfurfuraldehyde does not decompose in this way. Both beech and spruce woods gave rise to sufficient hydroxymethylfurfuraldehyde during distillation with hydrochloric acid to render the results obtained for furfuraldehyde by means of phloroglucinol substantially higher than those obtained by means of barbituric acid. It is obvious, however, that, for the hardwoods, including beech, dealt with in the present investigation (Table IV), if hydroxymethylfurfuraldehyde were formed it was without influence on the furfuraldehyde determination since the results obtained by the phloroglucinol and thiobarbituric acid methods were in close agreement. The flocculent nature of the furfurylidenemalonylthiocarbamide precipitate and the pale lemon yellow colour of the supernatant liquor obtained from the hardwoods strongly suggested the absence of hydroxymethylfurfuraldehyde from the distillates.

It is remarkable that with three of the softwoods examined (Table V) the precipitate formed on adding thiobarbituric acid to the distillate assumed a granular, instead of the normal flocculent form obtained with pure furfuraldehyde, and this was associated with a dark amber colour in the supernatant liquor. In contrast to the other softwoods Cypress pine gave the normal type of precipitate and supernatant liquor. The colours of the respective supernatant liquors, coupled with the results in Table V, strongly suggest that hydroxymethylfurfuraldehyde was present in appreciable quantities in the distillates from Sitka spruce, Douglas fir and African pencil cedar, but not in the distillate from Cypress pine. The first three species are known to contain mannan [Schorger, 1926, pp. 164, 165, 354; Nowotowna, 1936] from which hydroxymethylfurfuraldehyde could readily be derived. Unfortunately, sufficient evidence is not available to indicate why the granular type of precipitate obtained from the softwoods referred to became peptized during washing. At first sight it appears

that peptization might have been aided by hydroxymethylfurfuraldehyde or its condensation product with thiobarbituric acid, but it is clear from the data in Table VII that redistillation of the original acid distillate, which is reputed to decompose hydroxymethylfurfuraldehyde, does not eliminate the difficulty. Kline & Acree [1932] have referred to this phenomenon and have suggested washing the precipitate with hydrochloric acid, but the authors are satisfied that the tendency towards peptization is not entirely eliminated by this expedient. It is conceivable that, where peptization of the precipitate occurs, the causal agent may be a minor wood component, such as an oil, which is volatile under the conditions of the acid distillation. This possibility could readily be tested by carrying out furfuraldehyde estimations on specific woods before and after extraction with neutral solvents such as alcohol : benzene, ether etc.

From the foregoing considerations it must be concluded that no entirely satisfactory method of estimating gravimetrically the furfuraldehyde yields from woods has yet been discovered but, since a choice of precipitant must be made, phloroglucinol is still to be preferred to thiobarbituric acid for reasons which have been given. In all cases in which hydroxymethylfurfuraldehyde is likely to be produced the first distillate should be redistilled before attempting to precipitate the furfuraldehyde as phloroglucide, due allowance being made for the losses incurred during the second distillation. An arbitrary factor for correcting the result obtained after the second distillation obviously cannot be given as this is likely to vary somewhat among different investigators. For the present it is suggested that each investigator should determine his own factor experimentally.

At this stage the authors are not in a position to make more than a passing comment on the work of Angell *et al.* [1936] in which the validity of Kröber's tables [1900] as a means of converting the weight of phloroglucide to xylan, araban etc. is questioned. It is observed, however, that the weights of phloroglucide obtained by the above authors from the acid distillates of a series of samples of xylose are in all but one case identical with the corresponding data given in Kröber's tables, whereas in the case of arabinose there is no agreement between the weights of phloroglucide obtained and the corresponding data in Kröber's tables. Work is at present in progress in which the findings of Angell *et al.* [1936] will be examined.

It is conceded that the principal objection to the use of phloroglucinol still remains in the fact that the condensation product formed with furfuraldehyde may not be of constant composition. It is therefore to be hoped that an alternative precipitant with which this objection is not associated will ultimately be found. The authors are prompted to suggest in this connexion that further investigation of the possibilities of diphenylthiobarbituric acid should be made. The indications are that the condensation product formed between this substance and furfuraldehyde may be of constant composition and it can readily be separated from the mother-liquors by filtration. A satisfactory method of washing the precipitate however remains to be found.

SUMMARY

1. A critical study has been made of the gravimetric estimation of furfuraldehyde by means of thiobarbituric acid and this substance is compared in efficacy with phloroglucinol as a precipitant for general use in the analysis of woods.

2. Whereas furfuraldehydephloroglucide can be collected and washed with comparative ease this is not the case with furfurylidenemalonylthiocarbamide.

3. It is suggested that the uniformly high results obtained in furfuraldehyde estimations by means of thiobarbituric acid may be due to some extent to a compensation of errors of sorption of reagent by the furfuraldehyde condensation product and the slight solubility of the latter in 12% HCl.

4. Distillation of certain hardwoods and at least one softwood with 12% HCl under standard conditions gives rise to little or no hydroxymethylfurfuraldehyde so that the substitution of thiobarbituric acid for phloroglucinol as a precipitant for furfuraldehyde conveys no special advantage in such cases.

5. Certain softwoods have been shown to yield appreciable quantities of hydroxymethylfurfuraldehyde on distillation with 12% HCl and in such cases the furfurylidenemalonylthiocarbamide precipitate assumes a granular, in contrast to the normal flocculent, form.

6. In its granular form furfurylidenemalonylthiocarbamide is readily peptized during washing with cold water and cannot be collected quantitatively by the ordinary filtration procedure.

7. The difficulties mentioned in 2, 3 and 6 above provide strong objections to the adoption of thiobarbituric acid as a general precipitant for furfuraldehyde in the analysis of woods.

8. It is suggested that further research may prove the suitability of diphenylthiobarbituric acid as a precipitant for furfuraldehyde in analytical work.

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