XLVIII. THE PRODUCTION OF ω -HYDROXY-S-METHYLFURFURALDEHYDE FROM CARBOHYDRATES AND ITS INFLUENCE ON THE ESTIMATION OF PENTOSANS AND METHYLPENTOSANS.

BY MARY CUNNINGHAM AND CHARLES DORÉE.

(From the Chemistry Department, Borough Polytechnic Institute, S.E.)

(Received July 13th, 1914.)

In the method for the estimation of pentosans devised by Kröber and now extensively in use, the substance is boiled with a 12 per cent. solution of hydrochloric acid. The conditions are regulated so that 30 cc. are distilled over every fifteen minutes, 30 cc. of fresh acid being then added to the contents of the flask. The furfuraldehyde contained in the distillate is precipitated by the addition of phloroglucinol, and from the weight of the greenish black precipitate obtained the amount of furfuraldehyde, and consequently of pentosan present, may be calculated with the help of tables given by Kröber [1901]. In the case of methylpentosans, methylfurfuraldehyde is obtained which gives a red precipitate with phloroglucinol. This, unlike the black compound given by furfuraldehyde, is easily soluble in alcohol and on this difference Ellet and Tollens [1905] have based a method for the separation of the two phloroglucides and the consequent estimation of pentosan and methylpentosan groupings.

The phloroglucinol method has long been recognised as a "conventional" one in that (i) a definite procedure of working must be followed, (ii) the relation of the phloroglucide formed to pentosan present is empirical, (iii) other substances may be present in the distillates which also give a precipitate with phloroglucinol.

The difficulty last mentioned was investigated by Unger [1902], who noticed that various pure substances, and also natural products which contained no pentosan groupings, such as dextrose and starch, yielded, on

distillation with hydrochloric acid, volatile substances which could be precipitated with phloroglucinol. Tollens [1902] determined the percentage of "pentosan" given in this way by substances expected to contain very few or no pentosan groupings as follows:

Per cent.			Per cent.		
Cane sugar	..	1.2	Filter paper	..	1.5
Potato starch	..	0.8	Cotton wool	..	1.6

Grund [1902] also in an investigation of the content of "combined pentoses" in various animal tissues obtained an orange red precipitate from hexoses and from glycogen, and remarks that "apparently with hexoses in addition to furfuraldehyde, another and, till now, unknown body is formed." The complications brought about by the presence of these unknown substances are mentioned in many researches dealing with technical applications of the phloroglucinol method. Reed and Schubert [1914] for example, criticising methods in use for the testing of tanning materials, mention that the red phloroglucide precipitate indicating methylfurfuraldehyde given by various substances which are capable of yielding rhamnose on hydrolysis, such as xanthorhamnin, hesperidin, etc., is not absolutely reliable as a test for these, since dextrose gives a very similar, brown coloured precipitate.

A series of experiments described below has led us to the conclusion that, in the majority of cases, the substance giving this brown precipitate and the superficial reactions of methylfurfuraldehyde is ω -hydroxy-*s*-methylfurfuraldehyde, and that it is a constant product of the action of dilute hydrochloric acid on hexoses and on polyoses, such as starch and cellulose, which are capable of yielding hexoses on hydrolysis.

METHOD OF EXPERIMENT.

The Kröber method prescribes that the distillation is finished when a drop of the liquid gives no red colour when brought on to aniline acetate paper. As methylfurfuraldehyde does not give this reaction, a solution of phloroglucinol in hydrochloric acid is used when methylpentosans are to be estimated. A solution of aniline in alcohol is also a very sensitive reagent for the detection of furfuraldehyde and its derivatives, and in some estimations we made use of it. We found however that the rose colour given by aniline-alcohol persisted in portions of the distillate long after the aniline acetate paper had ceased to indicate the presence of furfuraldehyde. As is well known in the case of vegetable tissues which contain a considerable proportion of pentosan groupings, the formation and elimination of the furfuraldehyde

are comparatively rapid, *e.g.* with 2 grams of jute (which yielded 9 per cent. of furfuraldehyde) 210 cc. of distillate were sufficient. After this stage no colour with aniline acetate could be obtained. A further 950 cc. however were distilled over before the colouration with aniline-alcohol had ceased to be given.

A number of experiments on these lines was therefore carried out on cellulose and other carbohydrates (see Table III). In each case the aniline-alcohol reaction was obtained during a more or less prolonged period of distillation. In some instances the aniline acetate test for furfuraldehyde could not be observed, in others it was possible to separate the distillate into (*a*) a portion giving the reaction with aniline acetate and containing furfuraldehyde, and (*b*) a portion reacting only with aniline-alcohol.

This second portion in every case gave several of the tests prescribed as characteristic of methylfurfuraldehyde, including the absorption spectrum test devised by Oshima and Tollens [1901] for the detection of this aldehyde in the presence of furfuraldehyde, and a brown precipitate with phloroglucinol soluble in alcohol. Seeing however that pentoses (I) and methylpentoses (II) readily yield furfuraldehyde (IV) and methylfurfuraldehyde (V) respectively, it seemed more probable that hexoses (III) would yield ω -hydroxy-methylfurfuraldehyde (VI) thus :

van Ekenstein and Blanksma [1910] have already shown that this substance is formed by the action of dilute oxalic acid, under pressure, on hexoses, and they have proved that many of the colour tests given by the hexoses are due to the formation of ω -hydroxymethylfurfuraldehyde and not to furfuraldehyde as previously supposed. We therefore made a careful comparative examination of the hydrochloric acid distillates obtained from dextrose, starch, cellulose and lignocellulose and satisfied ourselves that these contained besides furfuraldehyde small quantities of ω -hydroxymethylfurfuraldehyde. This derivative is attacked by dilute acids, being converted into laevulic and formic acids thus :

so that no very large proportion of the theoretical yield could be expected. A recent note of E. Fischer [1914] shows, however, that if the action of the acid be controlled and stopped before this secondary decomposition has begun, comparatively large yields of ω -chloromethylfurfuraldehyde may be obtained.

PROPERTIES AND REACTIONS OF FURFURALDEHYDE AND ITS DERIVATIVES.

For purposes of comparison methylfurfuraldehyde was prepared from rhamnose [Fromherz, 1906] and ω -hydroxymethylfurfuraldehyde both by the action of oxalic acid on cane sugar [Kiermayer, 1895] and from the chloro-derivative obtained from laevulose by Fenton's reaction. Our observations made from distillates from about 0.2 gram of each aldehyde are given in the following table.

TABLE I.

Reactions of furfuraldehyde and its derivatives.

			Furfuraldehyde	Methyl- furfuraldehyde	ω -Hydroxymethyl- furfuraldehyde
1.	Aniline acetate		pink	yellow	pink
2.	Aniline-alcohol		bright red	yellow-red	bright red
3.	Phloroglucinol-ppt.		black	red	red-brown
4.	„ -filtrate		green	red-brown	orange-red
5.	Absorption spectrum of (4)		none	band in blue green	band in blue green
6.	α -Naphthol + H_2SO_4 *		grey red greenish	colourless scarlet greenish	violet crimson emerald green
7.	Thymol in alcohol + H_2SO_4		red, violet above	red-pink, yellow above	scarlet with violet above
8.	Barbituric acid		yellow ppt.	yellow ppt.	No ppt.

* Colours given in order from the top.

The second portion of the distillates from all the substances mentioned in Table IV gave reactions indistinguishable from those shown by ω -hydroxymethylfurfuraldehyde. The Maquenne test for methylfurfuraldehyde was obtained only with rhamnose. In order further to confirm the presence of the hydroxyaldehyde 64 grams of viscose silk were boiled under a reflux for 2 hours with 600 cc. of the hydrochloric acid. The filtered liquid was neutralised and extracted with ether. From the extract a brown oil giving the reactions of furfuraldehyde was obtained. The extracted water solution was distilled in a current of steam and gave a distillate which answered all the tests for ω -hydroxymethylfurfuraldehyde. This observation is in keeping with the fact that this substance is not extracted by cold ether from aqueous solution.

THE COMPOSITION OF THE PRECIPITATES GIVEN BY PHLOROGLUCINOL WITH
FURFURALDEHYDE AND ITS DERIVATIVES.

Kröber [1901] stated that the phloroglucide was formed by the condensation of one molecule of furfuraldehyde and one molecule of the phenol with elimination of two molecules of water thus :

and that the composition of the precipitate (C = 71.0 ; H = 3.2 per cent.) was independent of the conditions of precipitation. Tollens and Goodwin [1904] showed that the compound is considerably oxidised on drying in the air, but that preparations dried in hydrogen gave figures agreeing exactly with those required by the equation :

Assuming that a similar reaction takes place with the derivatives we have the following theoretical values :

TABLE II.

	Phloroglucide of :	Formula	requires
(I)	Furfuraldehyde	$\text{C}_{11}\text{H}_8\text{O}_4$	C = 64.7 ; H = 4.0
(II)	Methylfurfuraldehyde .. .	$\text{C}_{12}\text{H}_{10}\text{O}_4$	C = 66.0 ; H = 4.6
(III)	Hydroxymethylfurfuraldehyde .. .	$\text{C}_{12}\text{H}_{10}\text{O}_5$	C = 61.5 ; H = 4.2

The alcohol soluble part of a phloroglucide which we obtained from dextrose, after drying as far as possible with exclusion of air, gave results agreeing to some extent with the composition of the hydroxymethyl derivative :

0.1260 ; 0.2856 CO_2 ; 0.0550 H_2O .

Found C = 61.8 ; H = 4.3 per cent. •

The formula $\text{C}_{12}\text{H}_{10}\text{O}_5$ gives the factor 0.54 for conversion of the weight of phloroglucide to weight of hydroxymethylfurfuraldehyde. In calculating Table III, the factor 0.6 was employed.

QUANTITATIVE EXPERIMENTS.

In order to ascertain whether the constant formation of hydroxymethylfurfuraldehyde involves any error in the estimation of furfuraldehyde by the phloroglucinol method, and to obtain an idea of the amount produced, the experiments summarised in the table below were made. The precipitate given by that portion of the distillate which reacted to aniline acetate, if it could be collected separately, or if not, the portion of the total precipitate

insoluble in alcohol, was calculated as furfuraldehyde. The soluble portion was calculated as ω -hydroxymethylfurfuraldehyde (factor 0.6). A comparative value only can, however, be attached to these latter numbers. For the purification of the celluloses employed see Dorée [1913].

TABLE III.

No. Substance	Weight (anhydrous)	Distillate cc.*	Weight of phloro- glucide	Weight soluble in alcohol	Furfur- aldehyde per cent.	ω -hydroxy- methyl- furfur- aldehyde per cent.	Remarks
1. Rhamnose	0.424	760	0.2630	all	—	—	Ppt. red and consists of methylfurfural phloroglucide
2. Dextrose	2.123	610	0.0565	0.0550	0.18	1.6	No aniline acetate reaction; ppt. brown
3. Laevulose	3.770	240	0.0843	0.0712	0.20	1.1	After 60 cc. no aniline acetate reaction; ppt. red
4. Starch (potato)	3.774	680	0.0981	0.0902	0.15	1.4	After 250 cc. no aniline acetate reaction; ppt. red
5. Cellulose (cotton wool)	2.021	(a) 100 (b) 600	0.0073 0.0344	none 0.0115	0.20 (0.67)	0.34	Ppt. black Ppt. red
6. Cellulose (filter paper)	5.090	(a) 250 (b) 1080	0.0296 0.0580	— —	0.35 —	— 0.69	
7. Cellulose (No. 5 mercerised)	1.662	1025	0.0227	all	0.00	1.0	
8. Cellulose (structureless from the xanthate)	2.142	(a) 200 (b) 300	0.0358 0.0317	— —	1.04 —	— 0.9	After 180 cc. no aniline acetate reaction
9. Cellulose „	4.753	1560	0.2466	0.1862	0.76	2.4	
10. Oxycellulose (from No. 7 by ozone)	2.00	660	0.0550	0.0193	1.11	0.66	After 300 cc. no aniline acetate reaction
11. Lignocellulose (Jute)	1.869	(a) 210 (b) 950	0.3291 0.0357	0.0010 0.0127	9.4 —	— 0.90	Part soluble was red
12. Lignocellulose (Beech Wood)	2.600	(a) 400 (b) 660	0.6909 0.0148	— —	12.68 —	— 0.50	

* (a) represents portion of distillate reacting to aniline acetate, (b) is the portion subsequently obtained active to the aniline-alcohol reagent.

DISCUSSION OF THE RESULTS.

(1) These results show that the condensation which produces furfuraldehyde takes place rapidly and is almost completed before the hydroxymethyl derivative begins to distil over. In experiments 5 and 11 for example the

phloroglucides obtained from the first portion of the distillates were practically insoluble in alcohol, consisting entirely of the furfuraldehyde compound. The aniline acetate paper test therefore determines the separation of the two aldehydes and practically no error is made in pentosan estimations if this indicator is used. The possible error is further minimised in the case of bodies such as jute and beech wood which contain a large proportion of pentosan constituent, for the results show that these typical substances give the smallest yields of hydroxymethylfurfuraldehyde (Nos. 11 and 12).

(2) The hydroxylaldehyde is produced at a very slow rate. Its total amount is small, varying between 1 and 2 per cent. in the case of the hexoses and those celluloses which contain little or no pentosan. The probable reason for this is the ready hydrolysis of the hydroxymethylfurfuraldehyde to formic and laevulic acids already mentioned. This property no doubt explains the observations of Fraps [1901]. He found that if the distillates obtained from a number of natural products, food-stuffs, etc. were distilled again a considerable loss of "furfural" was shown. With pure furfuraldehyde this did not occur. The reduction in the amount of pentosan constituent varied from 7 per cent. in the case of oak wood to 22.6 in the case of bran. He considered that this portion could not be regarded as true pentosan, and, in the absence of further knowledge, designated it as the "furaloid" constituent. In all probability however the "furaloid" is a hexose-yielding constituent which gives hydroxymethylfurfuraldehyde and this on a second distillation is largely decomposed.

(3) The constant presence of ω -hydroxymethylfurfuraldehyde in the distillates from cellulose and starch renders determinations of methylpentosan, previously made, open to considerable suspicion. In the only method available, that of Ellet and Tollens [1905], the alcohol-soluble portion of the phloroglucide is calculated as methylpentosan. The work of Fromherz [1906] is interesting in this respect. In order to carry out an examination of the variation in the pentosan and methylpentosan constituents of wood under various alkaline and hydrolytic treatments and anticipating the presence of unknown substances likely to give a precipitate with phloroglucinol he used the method of precipitation with barbituric acid, first suggested by Unger [1902], as a check on the results. Fromherz worked out the application of this reagent to the estimation of methylfurfuraldehyde, finding that combination took place according to the equation:

Some of his results with phloroglucinol are as follows:

TABLE IV.

	Furfuraldehyde per cent.	Methyl- furfuraldehyde per cent.
Wood (extracted with alcohol-ether) ..	12.68	0.43
„ (6 times treated + NaOH) ..	2.29	0.50
„ (9 times „ „) ..	2.27	0.50

It will be observed that while the pentose constituent represented by the furfuraldehyde obtained is rapidly dissolved by treatment with sodium hydroxide, the methylpentosan remains unchanged in amount. This in itself is exceedingly improbable, but it will further be noticed that the amount of “methylfurfuraldehyde” obtained agrees closely with the amount obtained by ourselves from purified beech wood and shown to consist in all probability of ω -hydroxymethylfurfuraldehyde derived from the cellulose. Unfortunately the barbituric acid method does not permit of a separate estimation of the methylfurfuraldehyde, but calculating by an indirect method Fromherz found that the total of the furfuraldehydes given by phloroglucinol was always higher than that given by barbituric acid, the figures in one case for example being 2.78 and 1.92 per cent. respectively. In a series of experiments we found that in the dilutions commonly obtained in the distillates, ω -hydroxymethylfurfuraldehyde did not give a precipitate at all with barbituric acid. This observation would seem to confirm our view that it is not a case of methyl- but of hydroxymethyl-furfuraldehyde of quite different origin.

(4) Experiments do not throw any light on the remarkable fact that the ketoses give comparatively large yields of hydroxymethylfurfuraldehyde by the action of acids, while the aldoses give little or none. Some of these values calculated as the hydroxy-derivative are given in the following table :

TABLE V.

Yield of ω -hydroxymethylfurfuraldehyde per cent.

	HBr in chloroform solution ¹	Aqueous oxalic acid ²	40 % aqueous HCl (sp. g. 1.21) ³	Aqueous HCl (sp. g. 1.06) ³
Dextrose ..	2	1	1	1.6
Laevulose ..	15	20 to 25	—	1.1
Cane Sugar	6	—	15 to 20	—
Cellulose ..	20	—	5	0.6

¹ Cross and Bevan.

² van Ekenstein and Blanksma.

³ Dorée and Cunningham.

Although by the action of 40 per cent. aqueous hydrochloric acid cellulose is converted quantitatively into dextrose [Willstätter, 1913], yet with an ethereal solution of the acid it gives a high yield of ω -chloromethylfurfuraldehyde. It has been argued from this that cellulose must have a structure similar to that of laevulose and probably therefore contains a carbonyl grouping in the complex. But on theoretical grounds it seems to us that under anhydrous conditions the transition of laevulose to hydroxymethylfurfuraldehyde is far more likely to take place if the sugar functions in the γ -oxide form (II), and if this is so the cellulose formula (I) given by Green [1906], modified to show a connection between the unit groupings, explains very simply the conversion of cellulose, through laevulose, to ω -hydroxymethylfurfuraldehyde.

I. Cellulose formula (Green) modified for an aggregate of groupings.

II. Laevulose; γ -oxide formula.

SUMMARY.

(1) ω -Hydroxymethylfurfuraldehyde is formed by the action of dilute hydrochloric acid on hexoses, starch and the celluloses. Its amount varies from one to two per cent.

(2) Owing to its slow formation it does not interfere with the accuracy of pentosan estimations made by the Kröber phloroglucinol method, if aniline acetate is used as the indicator.

(3) Its occurrence, however, renders previously made estimations of methylpentosan of doubtful value.

(4) It is probably the unknown substance giving a precipitate with phloroglucinol referred to by previous workers, and its presence explains many of their observations.

REFERENCES.

- Dorée (1913), *J. Chem. Soc.* **103**, 1347.
van Ekenstein and Blanksma (1910), *Ber.* **43**, 2355.
Ellet and Tollens (1905), *J. Landwirth.* **53**, 13.
Fischer (1914), *Ber.* **47**, 973.
Fraps (1901), *Amer. Chem. J.* **25**, 201.
Fromherz (1906), *Zeitsch. physiol. Chem.* **50**, 217, 241.
Green (1906), *J. Chem. Soc.* **89**, 811.
Grund (1902), *Zeitsch. physiol. Chem.* **35**, 120.
Kiermayer (1895), *Chem. Zeit.* **19**, 1003.
Kröber (1901), *J. Landwirth.* **49**, 7.
Oshima and Tollens (1901), *Ber.* **34**, 1425.
Reed and Schubert (1914), *J. Amer. Leather Chem. Assoc.* **9**, 131.
Tollens (1902), *Zeitsch. angew. Chem.* **477**, 408.
—— and Goodwin (1904), *Ber.* **37**, 315.
Unger (1902), *Ber.* **35**, 4440.
Willstätter (1913), *Ber.* **46**, 2401.