On Anhydrosugars, Part II.
The Action of Superheated Water on Anhydrosugars.

By

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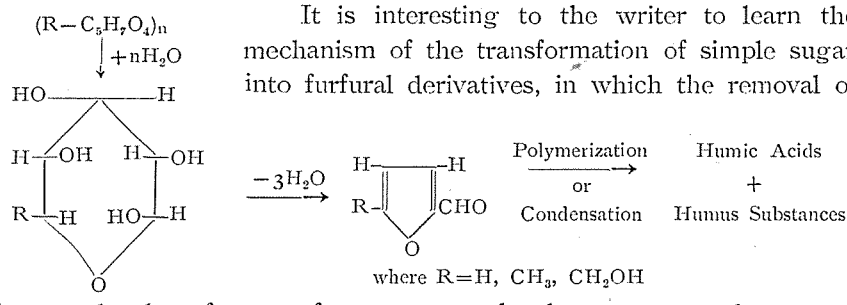
In the article entitled "On the Action of Superheated Water upon Sugars," Prof. Komatsu[1] and the present writer put forward a theory, based on their experimental results, as to the formation of humus and humic acid in nature. In that theory, cellulose and other polysaccharides which occur in plant tissues are regarded as playing an important part in the humification of vegetable substances; they are first hydrolysed into simple sugars and then pass, by splitting of three molecules of water, into furfural derivatives which are then in turn polymerised into humus substances, as illustrated by the following schemes:



It is interesting to the writer to learn the mechanism of the transformation of simple sugar into furfural derivatives, in which the removal of three molecules of water from sugar molecule may proceed at once, or in a step reaction as in the following schemes:—

1. $C_6H_{12}O_6 = C_6H_6O_3 + 3H_2O$
2. $\begin{cases} C_6H_{12}O_6 = C_6H_{10}O_5 + H_2O \\ C_6H_{10}O_5 = C_6H_6O_3 + 2H_2O \end{cases}$

It is, however, natural to consider an anhydrosugar, which is regarded as being formed from hexoses by the loss of one molecule

1. S. Komatsu & C. Tanaka: Sexagint. Prof. Y. Osaka. Univ. Kyoto, Japan, 1 (1926); C. Tanaka: ibid. 13.

of water, as an intermediate reaction product in the huminication of sugars, and in consequence the present study dealing with several anhydrosugars of glucose & fructose origins, whose structures are shown in the table given below, has been undertaken.

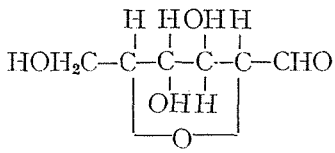
Reference to the literature shows that laevulosane[1], *α*-glucosane[2] and laevane[3], which easily reduce Fehling's solution, are hydrolysed by dilute mineral acids into hexose, while laevoglucosane[4] and hetero-laevulosane[5], which do not reduce Fehling's solution, are converted by the action of strong mineral acids into the hexose. Chitose[6] which has a hydrofurfural ring in its molecule, reduces Fehling's solution, is transformed easily by the action of dilute oxalic acid under pressure at 130° into hydroxymethyl furfural, laevulinic acid and formic acid.

The chemical behaviour of these anhydrosugars towards the action of superheated water, which may be similar in its nature to that toward the mineral acids, may offer some explanation of the formation of humus from sugars. In the present experiments, anhydrosugars were heated in a sealed tube with water at 100°, 120° and 150° respectively, and the chemical changes which occur in the sugars were measured, by physical and chemical means, from time to time; the results are tabulated as follows:

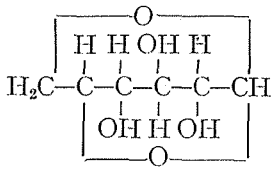
Constitution of Anhydro-sugars

A. Anhydro-glucose

I. Chitose

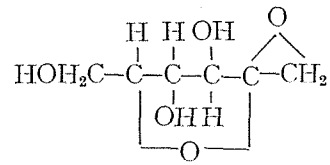


II. Laevoglucosane

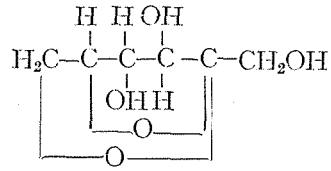


B. Anhydro-fructose

I. Laevane

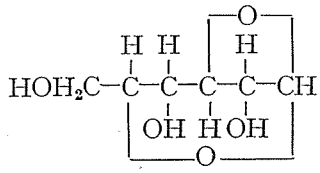


II. Hetero-laevulosane

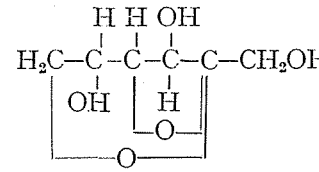


1. Gelis: A. ch. (3), **57** (1859), 234; Pictet. A. & Reilly: Hel., **4** (1921), 613.
2. Pictet. A. & Castan: Hel., **3** (1920), 645.
3. Schlubach. H. & Elsner. H.: Ber. D. Chem. Ges., **61** (1928), 2362.
4. Pictet. A. & Sarasin: Hel., **1** (1918), 87.
5. Pictet. A. & Chavan: Hel., **9** (1926), 809.
6. Mendendrop: C., 1919, **2**, 844.

III. *α*-Glucosane



III. Laevulosane



I. Chitose

Reaction Temp.	Reaction Times	Colour of Solution	As Hydroxy-methyl-furfural	Humus substance	Rotation $[\alpha]_D$	pH-Value	Reducing power. Percentage of Glucose
0	0	uncoloured	0	0	+22°.4	5.36	57.5%
100°	2 hrs.	light yellow	6.4%	0	+30°.6	3.46	59.3 „
„	2 „	light brown	16.4 „	0	+16°.0	2.94	62.1 „
„	12 „	brown	20.0 „	0	+ 9°.0	2.53	62.3 „
„	24 „	dark brown	26.9 „	0.8%	0	2.18	75.2 „
120°	2 „	brown	32.6 „	0 „	+13°.5	3.10	62.3 „
„	6 „	dark brown	39.7 „	1.5 „	+ 3°.5	2.40	68.7 „
„	12 „	„	47.8 „	5.1 „	0	2.34	69.7 „
„	24 „	„	57.9 „	11.0 „	0	2.93	61.2 „
150°	0.5 hrs.	dark brown	31.1 „	0.3 „	+14°.0	3.12	67.9 „
„	2 „	„	37.9 „	2.1 „	+ 3°.0	2.37	69.0 „
„	6 „	brown	40.5 „	10.1 „	0	2.37	63.9 „
„	12 „	„	34.4 „	14.7 „	0	2.75	53.5 „

II. Laevoglucosane

Reaction Temp.	Reaction Time	Colour of solution	As Hydroxy-methyl-furfural	Humus substance	Rotation $[\alpha]_D$	pH-Value	Reducing power as Glucose
0	0	uncoloured	0	0	−66.°3	5.31	0
120°	2 hrs.	„	0	0	−66.°3	5.16	0
„	6 „	„	0	0	−66.°3	4.78	0
„	12 „	„	0	0	−66.°3	4.27	0
„	24 „	„	0	0	−64.°0	3.64	trace
150°	2 „	„	0	0	−65.°0	4.44	„
„	6 „	slightly yellow	0	0	−59.°0	4.19	5.41%
„	12 „	„	0	0	−42.°0	3.60	19.1 „
„	24 „	yellow	trace	0	− 4.°0	3.12	51.3 „

III. α-Glucosane

Reaction Temp.	Reaction Time	Colour of solution	As Hydoxy-methyl furfural %	Humus substance %	Rotation $[\alpha]_D$	pH-Value	Reducing power Percentage of Glucose
0	0	uncoloured	0	0	+50°.5	5.28	46.8%
100°	2 hrs.	„	0	0	+50°.5	4.28	50.7 „
„	6 „	„	0	0	+51°.0	4.12	54.8 „
„	12 „	„	0.5%	0	+51°.0	3.64	60.0 „
„	24 „	slightly yellow	1.8 „	0	+51°.5	3.43	63.4 „
120°	2 hrs.	very slightly yellow	0	0	+51°.0	3.78	59.2 „
„	6 „	slightly yellow	0.8 „	0		3.26	63.4 „
„	12 „	yellow	3.0 „	0		2.51	73.3 „
„	24 „	brown	3.5 „	0		2.10	78.0 „
150°	0.5 „	uncoloured	1.2 „	0		3.38	59.2 „
„	2 „	yellow	2.2 „	0		2.95	64.4 „
„	6 „	brown	4.0 „	0		2.42	79.3 „
„	12 „	dark brown	6.9 „	trace		2.10	87.4 „

IV. Hetero-laevulosane

Reaction Temp.	R action Time	Colour of solution	As Hydroxy methyl-furfural	Humus substance	Rotation $[\alpha]_D$	pH-Value	Reducing power as Fructose
0	0	uncoloured	0	0	—65°.3	6.69	0
100°	2 hrs.	„	0	0	—65°.3	6.39	0
„	6 „	„	0	0	—65°.3	5.93	0
„	12 „	„	0	0	—65°.3	5.66	0
„	24 „	slightly yellow	0	0	—	5.31	0
120°	2 hrs.	slightly yellow	0	0	—65°.3	5.76	0
„	6 „	yellow	0	0	—65°.3	5.31	0
„	12 „	„	0	0	—	4.85	0
„	24 „	„	0	0	—	4.62	0
150°	0.5 „	slightly yellow	0	0	—65°.0	5.23	0
„	2 „	yellow	0	0	—	4.82	0
„	6 „	brown	0	0	—	4.46	0
„	12 „	„	0	0	—	4.16	trace

V. Laevulosane

Reaction Temp.	Reaction Time	Colour of solution	As Hydroxy methyl-furfural	Humus substance	Rotation $[\alpha]_D$	pH-Value	Reducing power Percentage of Fructose
o	o	uncoloured	o	o	+18.°o	5.26	45.1%
100°	2 hrs.	„	o	o	−11.°o	4.21	58.5 „
„	6 „	„	o	o	−40.°o	4.09	77.8 „
„	12 „	„	o	o	−50.°o	3.88	85.2 „
„	24 „	slightly yellow	o	o	−60.°o	3.69	88.2 „
120°	2 hrs.	slightly yellow	0.6%	o	−58.°o	3.53	63.0 „
„	6 „	slightly brown	3.9 „	o	—	3.04	63.0 „
„	12 „	brown	7.5 „	o	—	2.53	61.7 „
„	24 „	dark	13.1 „	1.1%	—	2.34	60.4 „
150°	0.5 hrs.	yellow	2.5 „	o	40.°o	3.36	82.3 „
„	2 „	brown (cloudy)	8.9 „	1.1%	—	3.07	81.2 „
„	6 „	dark brown (cloudy)	16.8 „	2.3 „	—	2.51	76.2 „
„	12 „	dark brown (cloudy)	23.6 „	3.6 „	—	2.34	73.9 „

VI. Laevane

Reaction Temp.	Reaction Time	Colour of solution	As Hydroxy methyl-furfural %	Humus substance	Rotation $[\alpha]_D$	pH-Value	Reducing power Percentage of Glucose
o	o	uncoloured	o	o	−11.°o	7.00	9.9%
100°	2 hrs.	„	o	o	−14.°5	5.54	14.0 „
„	6 „	slightly yellow	o	o	−20.°o	5.18	20.7 „
„	12 „	yellow	o	o	−23.°o	4.70	24.3 „
„	24 „	yellow	o	o	−26.°o	4.35	28.5 „
120°	2 hrs.	yellow	o	o		5.15	
„	6 „	yellowish brown	o	o		4.29	
„	12 „	brown	0.6%	o		3.52	
„	24 „	dark brown	3.0 „	0.6%		3.19	
150°	0.5 hrs.	slightly yellow	o	o		4.19	
„	2.0 „	yellowish brown	2.2 „	o		3.48	
„	6.0 „	brown	6.3 „	0.5%		3.25	
„	12.0 „	dark brown	—	—		3.01	

Laevulosane, as will be seen in the above table, begins to be hydrolysed by superheated water already at 100°, and the reaction proceeds with the progress of time, as is indicated by the increase in reducing power, the decrease in rotatory power, and also by the colour change of the solution. And the formation of hydroxymethyl furfural as well as of the humus substance increases in proportion to the rise of reaction temperature and the lapse of reaction time, while the pH-value of the solution decreases inversely. The same phenomena are also observed with α-glucosane and laevane.

The ease by which laevulosane, α-glucosane and laevane were hydrolysed into hexoses by the action of superheated water at 100°, should be ascribed to the presence of an ethylen oxide or a propylen oxide linking in their molecules. Laevoglucosane, however, which is assumed to possess a 1–6 oxide linking in its molecules is so stable that the rupture of an amylene oxide linking does not take place at 120°, and by heating at 150° for 24 hours, about 50% of laevoglucosane was transformed into glucose. Heterolaevulosane which is more stable than laevoglucosane, begins to hydrolyse at the end of 24 hours when heated at 150°.

Thus, these anhydrosugars by the action of superheated water, are first hydrolysed into some hexoses which then yield some acidic substances and hydroxymethyl furfural, and the latter is on the one hand resolved into organic acids, and on the other polymerized into humus substance, though there is some difference in the hydrolytic velocity of the anhydrosugars owing to the difference in the chemical constitution of their molecules. However, it must be born in mind that the pH value of the original sugar solution will play an important rôle in the rate of hydrolysis, since the reaction of superheated water with anhydrosugar is regarded as an example of homogeneous catalysis performed in a closed vessel.

Chitose, however, shows quite different behaviour towards superheated water, and is easily converted into hydroxymethyl furfural which in turn polymerizes into humus substance; the yield of hydroxymethyl furfural and humus substance 24 hours after the start of the reaction is 27% and 0.8% respectively, and 57.9% and 11% at 100° and 120° respectively, At a high temperature, hydroxymethyl furfural tends to polymerize into the humus substance, and the reaction product at 150° for 12 hours, was composed of 34.4% of hydroxymethyl furfural, and 14.7% of humus substances.

The transformation of laevoglucosane, laevulosane and chitose into acidic and humus substances was investigated quantitatively under the same conditions and the results are summarized in Table III.

Table III

Anhydro-sugar	Reaction Temp.	Reaction Time	Formic Acid	Levulinic Acid	Hydroxy-methyl Furfural	Humus Subst.	Humic Acid	Unchanged sugar	Hexose
Laevoglu-cosane (15 gm.)	155°—160°	22. h.	0.30gm.	0.45 gm.	2.5 gm.	2.8 gm.	0.1 gm.	0.6 gm.	Glucose. 5.4 gm.
			2.0%	3.0 „	16.7 „	18.7 „	0.7 %	4.0 „	36.7 „
Laevulo-sane (18 gm.)	152—155°	3.5 h.	0.37gm.	0.55 gm.	3.1 gm.	2.6 gm.		0.9 gm.	Fructose 5.8 gm.
			2.1%	3.1 „	17.2 „	14.4 „		5.0 %	32.0 „
Chitose (24 gm.)	150—153°	3.5 h.	12. gm.	0.9 gm.	3.7 gm.	11.5gm	0.6 gm.	1.6 gm.	—
			5.0%	3.8 „	15.4 „	47.9 „	2.5 „	6.7 „	—

The humus obtained from the anhydrosugars, as will be seen in Table IV, is similar in composition to those obtained from glucose, fructose and hydroxymethyl furfural by the same treatment.

Table IV

Anhydrosugar	Humus Substances		Humic Acid	
	C%	H%	C%	H%
Chitose	66.68	4.60	61.10	4.60
Laevo -glucosane	67.25	4.59		
Laevulosane	66.15	4.63		
Glucose	65.83	4.55	61.80	4.23
Fructose	65.70	4.35	62.26	4.47
Hydroxymethyl Furfural	66.77	4.58	62.42	4.61

The anhydrosugars may thus be classified according to their behaviour towards superheated water into two groups; the first group is that to which belong laevoglucosane, α-glucosane, laevulosane, heterolaevulosane and laevane, and they hydrolyse into hexose; and chitose, which is converted with loss of a water molecule by the action of superheated water into hydroxymethyl furfural belongs to the other one.

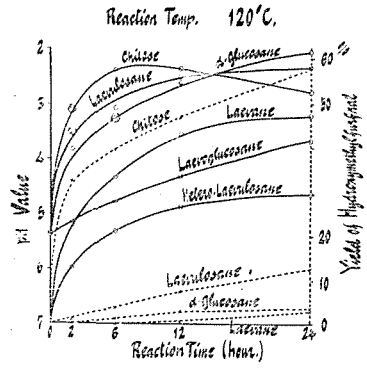
Although there exists a distinction in the primary phase of the reaction of these two groups of anhydrosugars with the superheated water, the formation of hydroxymethyl furfural seems to occur when the pH-value of all the sugar solutions has reached 3. 5-3. The formation of furfural derivative, which is detected by the colour test, as is illustrated in Fig. 1, happens with a 2 % solution of glucose and fructose, investigated under the same conditions as the anhydrosugars, at pH 3–3.5 as shown in the following table.

Reaction Temperature	Reaction Time	Glucose		Fructose	
		pH-Value	Hydroxymethyl-furfural-Test	pH-Value	Hydroxymethyl-furfural-Test
0	0	6.05	−	5.90	−
100°	2 hrs.	5.82	−	4.22	−
„	6 „	5.44	−	3.65	−
„	12 „	4.63	−	3.08	+
„	24 „	3.87	−	2.44	+
120°	2 „	4.13	−	3.20	+
„	6 „	3.20	+	2.40	+
„	12 „	2.50	+	1.93	+
„	24 „	2.14	+	1.69	+
150°	0.5 hrs.	3.97	−	3.28	+
„	2.0 „	3.45	+	2.47	+
„	6.0 „	2.73	+	1.93	+
„	12.0 „	2.00	+	1.48	+

The fact that both hexoses and anhydrosugars yield the furfural derivative at the pH value (3.5–3) of the solution indicates that these sugars of different constitutions are converted first into the same intermediate substance in the course of their transformation into hydroxymethyl furfural.

The conversion of chitose into hydroxymethyl furfural will take place directly by the elimination of two molecules of water, while laevulosane and α-glucosane after hydrolysis will

Fig. 1



change into the dehydration product, and the reaction product from the anhydrosugars by hydrolysis was assumed to possess a chemical structure similar to that of chitose.

Such an assumption of the occurrence of a chitose-like substance as an intermediate reaction product in the transformation of the sugars into hydroxymethyl furfural will be supported by the study of the heat of combustion and of the ultra-violet ray absorption spectrum of sugars and furfural derivatives.

The heat toning during the formation of hydroxymethyl furfural from glucose and xylose is represented, by the aid of the thermal data of these compounds, by the following equations respectively :

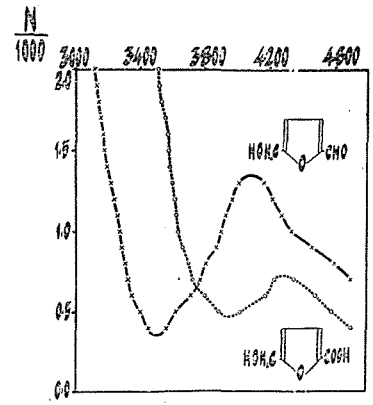
Glucose = Hydroxymethyl furfural + $3H_2O$ + 2.9 K

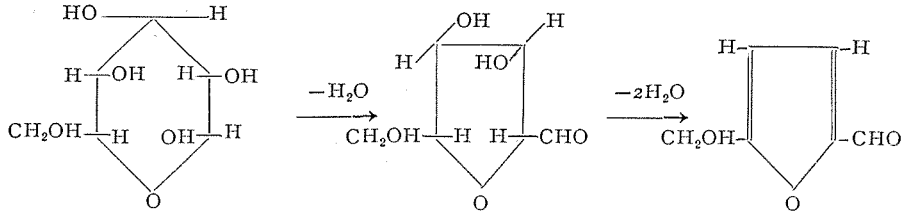
Xylose = Furfural + $3H_2O$ + 3.9 K

The equations indicate that the reaction is accompanied by the evolution of heat of 3–4 K, and therefore, the true nature of these reactions will be explained reasonably by taking into consideration the occurrence of an anhydrosugar having such a structure as chitose, as an intermediate reaction product which would be derived from hexoses or pentoses with evolution of heat.

The absorption spectrum of hydroxymethyl furfural when examined in a $\frac{1}{1000}$ mol. aqueous solution of various thicknesses, shows an absorption curve with a band at 3500 frequency, as illustrated in Fig. 2, and the curve closely resembles in form that of chitose, except that the former is more hyperchromatic, and the similarity of the spectra of these compounds is certainly due to an analogy which exists in their chemical constitution. The chemical mechanism of the formation of hydroxymethyl furfural from hexoses, therefore, may be interpreted in the following manner : hexoses are transformed, by losing one molecule of water, into a chitose-like substance which at pH 3.5–3 of the solution is further converted into hydroxymethyl furfural by the splitting of two molecules of water :

Fig 2

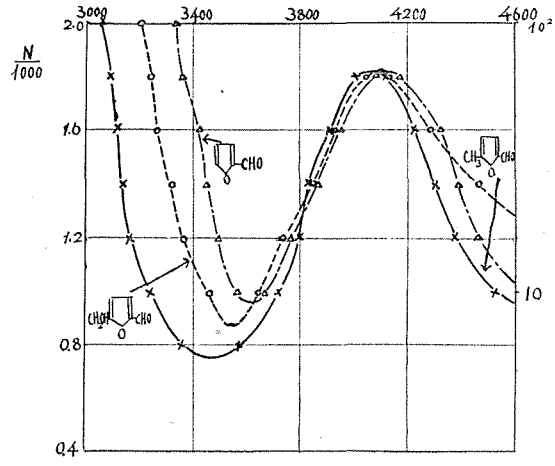


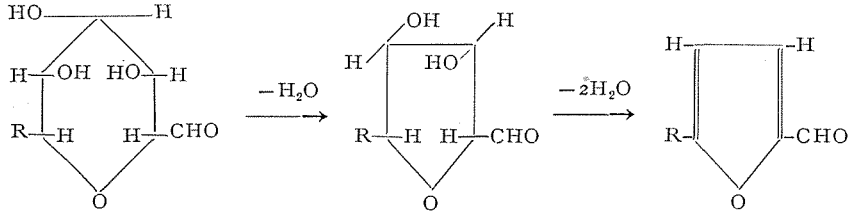


The conversion of methyl pentose and pentose by the action of superheated water into methyl furfural and furfural respectively, may be explained analogously by assuming a chitose-like anhydrosugar as an intermediate compound.

The facts that the amount of heat evolved in the formation of methyl furfural from methyl pentose and of furfural from pentoses is almost the same as that evolved in the formation of hydroxymethyl furfural from hexoses, and that the ultra-violet ray absorption curves of these furfural derivatives closely resemble each other in form as shown in Fig. 3, are in favour of the writer's view that a chitose-like substance should be assumed as an intermediate substance in the transformation of sugars into furfural derivatives, as is illustrated by the following schemes:

Fig. 3



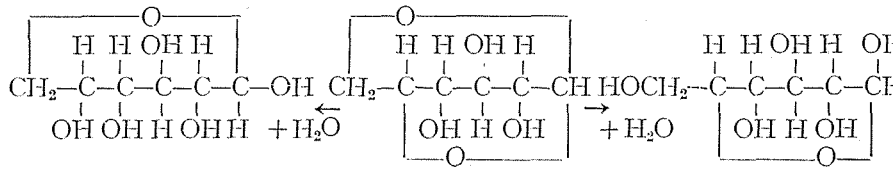


where R=H, CH_3, CH_2OH

The ease by which fructose is converted into hydroxymethyl furfural may be explained by assuming that this sugar is more easily transformed into the intermediate substance than other hexoses, while

α-glucosane shows greater velocity in the transformation than laevoglucosane owing to the ease with which the former is converted into hexose.

The hydrolysis of anhydrosugars which will result from the addition of one mol. of water to the sugars, would theoretically occur in two ways by the opening of any one of the two oxide linkings in their molecules, and one anhydrosugar yields two isomeric hexoses according to the mode of addition of the water molecule:



γ-glucose Laevoglucosane *α*-glucose

In order to obtain a more definite knowledge of the hydrolysis of anhydrosugars, 15 gms. of laevoglucosane dissolved in 150 c.c. of distilled water were heated in an autoclave at a temperature of 155–160° for 22 hours, and it was observed that the sugar was converted by rupture of the 1–6 oxide linking into the normal glucose. Laevulosane by the same treatment was hydrolysed by rupture of the 2–4 oxide ring into fructose.

When the anhydrosugars, except chitose, are subjected to the action of superheated water, they are converted reversibly by the rupture of the glucoside linking in their molecules into the hexoses from which they are derived.

It is a noteworthy fact that laevoglucosane, on being treated with conc. hydrochloric acid at 0°C was observed by Pringsheim[1] to change into *γ*-glucose, which contains a 1–6 oxide linking in its molecule. The intra-molecular transformation of hexoses in an alkaline solution, which was observed by Lobry de Bruyn and Ekenstein[2] and explained by the hypothesis of Nef[3], will suggest the possibility of the rupture of the 1–5 oxide linking instead of the 1–6 oxide ring of laevoglucosane or laevulosane, and success in such a task would open up a new path in the field of sugar chemistry; this will be reported on in the near future from our laboratory.

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1. Pringsheim. H. & Kolodny. S.: Ber. D. Chem. Ges., **59** (1926), 1135.
2. Lobry de Bruyn & Ekenstein: Rec. trav. Chim., **14** (1895), 203; **15** (1896), 93.
3. Nef: Ann., **335** (1904), 329; **357** (1907), 294; **376** (1910), 1.

Experimental Part.

1. Furfural.

Purified commercial furfural shows the constants: B.p.$=71°/31$ mm., $d_{25}^{25}=1.1534$, $n_D^{25}=1.5181$. The heat of combustion for 1 gm. of this substance is observed to be 5816 cal. from which its molecular heat of combustion is calculated to be 558.3 K. The absorption spectrum of the substance, examined in a $\frac{1}{1000}$ mol. aqueous solution, shows a selective absorption band at 3600 frequency.

2. Hydroxymethyl furfural.

This substance was obtained by heating a 25 % cane sugar solution in an autoclave at 153–157° for 3.5 hours, and was purified by fractional distillation under reduced pressure; B.p.$=126°/2.5$ mm., $d_{25}^{25}=1.2620$, $n_D^{25}=1.5533$. The heat of combustion for 1 gm.$=5320$ cal., and its molecular heat of combustion$=670.3$ K. Hydroxymethyl furfural in a $\frac{1}{1000}$ mol. aqueous solution shows a selective absorption band having its head at 3550 frequency.

3. Methyl furfural.

Methyl furfural was prepared by digestion of rhamnose with 12% hydrochloric acid; B.p.$=89$–$90°/26$ mm, $d_{25}^{25}=1.1902$, $n_D^{25}=1.5073$. This substance in its $\frac{1}{1000}$ mol. aqueous solution shows a selective absorption band having a head at 3500 frequency.

4. Hydroxymethyl pyromucic acid.

This substance, which was prepared by oxidizing hydroxymethyl furfural with moist silver oxide, following the method of Fenton and Gostling[1], melts at 163°. It shows in a $\frac{1}{1000}$ mol. alcohol solution a selective absorption band at 3900-4000 frequency, as will be seen in Fig. 2.

I. Action of Superheated Water on Sugars.

In the experiments, each 25 c.c. of 2% sugar solution contained in a glass stoppered bottle which was previously washed with steam in order to remove completely any alkaline substance which might be

1. Fenton & Gostling: J. Chem. Soc., **75** (1899), 429.

generated from the glass wall, was heated in a water bath at 100°, and in an oil bath at 120° for 2, 6, 12 and 24 hours in one series of experiments and in an other at 150° for 0.5, 2, 6 and 12 hours respectively.

After the solution has been heated for the required time, for each 5 c.c. of the solution the pH-value was estimated by the electric method, the hydroxymethyl furfural content by means of phloroglucine solution, and the reducing power with Fehling's solution; the rotatory power and humus content were also estimated and the experimental results are shown in the Table I.

(1) Laevoglucosane.

15 gms. of laevoglucosane (M.p.=178°) was dissolved in 150 c.c. of distilled water and heated in an autoclave at a temperature of 155–160° for 22 hours. There was formed a black humus substance which was separated from an acidic solution by means of filtration and washed with hot water, and 11.5 gms. of a humus substance were obtained and were analysed with the following results:

	Sample	CO_2	H_2O	C%	H%
1.	0.1116 gm.	0.2744 gm.	0.0458 gm.	67.05	4.56
2.	0.1128 gm.	0.2790 gm.	0.0470 gm.	67.45	4.63

The brown filtrate separated from the humus substance, which had an acidic and bitter taste was subjected to distillation under reduced pressure to drive off some volatile substances.

1. Formic Acid.

The quantity of the acidic matter in the distillate was determined by means of the standard alkaline solution, and then it was neutralized with calium carbonate, and evaporated to a syrup under reduced pressure, from which by addition of 94% alcohol, white crystals were precipitated, weighing 0.42 gm. The chemical and physical properties of the substance agree with those of calcium formate, and to confirm this, the lead salt was analysed:

		Pb%	
Sample	$PbSO_4$	Found.	Calc. for $C_2H_2O_4Pb$
0.2573 gm.	0.2647 gm.	70.27	69.72

2. Hydroxymethyl furfural.

The non-volatile part was treated many times with ether to extract an acidic and a neutral substance, and the ethereal solution was neut-

ralized with a sodium bicarbonate solution. After the neutral ethereal solution had been dried with anhydrous sodium sulphate, the ether was removed by distillation, and 2.5 gm. of oily substance was obtained which was purified by distillation under 4 mm. pressure.

	Fraction	Yield	Remark
1.	—— 136°	trace.	Slightly yellow.
2.	136 — 137°	1.7 gm.	,,
3.	Residue.	0.6 gm.	Reddish brown oil, solidifying on cooling.

Fraction (2), $n_D^{25}=1.5560$, $d_{25}^{25}=1.2623$, agrees in its properties with hydroxymethyl furfural.

Sample	CO_2	H_2O	C%	H%
0.1238 gm.	0.2580 gm.	0.0546 gm.	56.84	4.94
Calc. for $C_6H_6O_3$			57.12	4.79

3. Laevulinic Acid.

On acidifying the sodium salt solution with dilute sulphuric acid, a brownish black substance was precipitated, which was filtered and washed with water; the yield was 0.1 gm. The filtrate was treated with ether to extract a non-volatile acid weighing 0.45 gm. which was purified by fractional distillation under 6 mm. pressure.

	Fraction	Yield	Remarks
1.	—— 125°	trace.	Colourless.
2.	125 — 126°	0.3 gm.	Slightly yellow.
3.	Residue.	0.1 gm.	Black oil.

Fraction (2), $n_D^{25}=1.4549$, gave the reactions of laevulinic acid and was analysed with the following results:

Sample	CO_2	H_2O	C%	H%
0.1174 gm.	0.2220 gm.	0.0729 gm.	51.56	6.95
Calc. for $C_5H_8O_3$			51.69	6.95

4. Unchanged sugar.

The syrup, separated from the ether soluble substances, was extracted with hot acetone. When the acetone was removed by distillation under diminished pressure, 0.6 gm. of reddish brown coloured syrup was obtained, which crystallized on standing. By recrystallization from hot absolute alcohol, it was obtained as white prisms melting at 178°, and the chemical and physical properties were coincident with those of laevoglucosane.

5. Glucose.

The acetone insoluble substance was dissolved in water and neutralized with some silver carbonate, and hydrogen sulphide gas was passed over it to remove the silver salt. The filtrate free from silver salt and the excess of hydrogen sulphide, was evaporated to a syrup under reduced pressure. From 5.4 gms. of the syrup, by addition of absolute alcohol, white crystals were precipitated, which were purified by crystallization from hot alcohol, M.p.$=147^{\circ}$. The sugar is fermented by yeast and reduces Fehling's solution, its specific rotation in aqueous solution being

$$[\alpha]_D^{14}=\frac{+1.35-0.01}{2.504\times 1}\times 100=+54.3^{\circ};\ 7 \text{ minutes after solution}$$

$$[\alpha]_D^{13}=\frac{+1.32-0.01}{2.504\times 1}\times 100=+52.3^{\circ}\ 24 \text{ hours} \quad ,, \quad ,,$$

The analytical results were:

	Sample	CO_2	H_2O	C%	H%
1.	0.1092 gm.	0.1602 gm.	0.0686 gm.	40.01	6.98
2.	0.1084 gm.	0.1586 gm.	0.0664 gm.	39.90	6.86
	Calc. for $C_6H_{12}O_6$			40.00	6.60

The osazone of this substance melts at 211°. All of these chemical and physical properties agree with those of glucose.

From the filtrate separated from glucose, alcohol was removed and it was diluted to 10 c.c. with water; 1 gm. of yeast was added and the mixture was left at ordinary temperature (25°C). All the sugars in the solution was fermented, so that it was impossible to isolate any trace of γ-glucose which was supposed to be formed from laevoglucosane and to occur with ordinary glucose in the solution.

(2) Laevulosane.

18 gms. of laevulosane were heated with 180 c.c. of distilled water at $150-153^{\circ}$ for 3.5 hours, and the reaction products were treated in the same way as in the case of laevoglucosane. Fructose was actually obtained from laevulosane, as we had expected, weighing 5.8 gms, and also 0.37 gm. of formic acid, 0.55 gm. of laevulinic acid, 3.1 gms. of hydroxymethyl furfural, and 2.6 gms. of humus substance were isolated together with 0.9 gm. of unchanged sugar. The analysis of the humus substance was as follow:

	Sample	CO_2	H_2O	C%	H%
1.	0.1022 gm.	0.2480 gm.	0.0412 gm.	66.18	4 47
2.	0.1042 gm.	0.2526 gm.	0.0450 gm.	66.11	4.79
			Mean	66.15	4.63

(3) Chitose.

24 gms. of chitose were heated with 175 c.c. of distilled water at 150–153° for 3 5 hours, and the treatment of the reaction products was the same as in the case of laevoglucosane. No fermentable hexose could be detected in the reaction products, which consisted of 1.2 gms. of formic acid, 0.9 gm. of laevulinic acid, 3.7 gms. of hydroxymethyl furfural, 11.5 gms. of humus substance, 0.6 gm. of humic acids and 1.6 gms. of unchanged chitose. The humus substance and humic acids were analysed with the following results:

Humic acids	CO_2	H_2O	C%	H%
0.0881 gm.	0.1792 gm.	0.0370 gm.	61.10	4.60
Humus subst.	CO_2	H_2O	C%	H%
1. 0.1185 gm.	0.2871 gm.	0.0489 gm.	66.79	4.58
2. 0.0998 gm.	0.2436 gm.	0.0414 gm.	66.60	4.61

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