

# Constitution of Polysaccharides, I. Xylan and Its Acetyl Derivatives, I.

By

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## *I. Xylan.*

The xylan used in the present investigation was obtained from wheat straws and corn cobs grown in Kyoto, by following generally the method of Allen and Tollens.<sup>1</sup>

150 grm. air dried wheat-straws were treated in the cold for twenty-four hours with ammonia water (120 c.c. of conc. ammonia in 850 c.c. water); the ammoniacal solution is then removed by decantation and by pressing. The material after washing with water, was immersed in 300 c.c. of 7 % sodium hydroxide solution for forty-eight hours. The extract was separated from insoluble matter by filtration through a silk cloth. To the clear brown-coloured solution, an equal volume of 98 % alcohol was added with constant stirring to precipitate the xylan; the mother liquor was siphoned off and the precipitate washed with dilute alcohol and dissolved again in 7 % sodium hydroxide solution and reprecipitated with alcohol. The precipitate separated from the mother liquor, was treated with dilute hydrochloric acid and dilute alcohol until all hydrochloric acid was removed, washed with ether three times and dried on paraffin and sulphuric acid in vacuo. The yield was 25 grm. (16.7 %).

Xylan thus prepared is a light-yellow amorphous powder, easily soluble in alkaline solution and showed the specific rotation  $[\alpha]_D = -78^\circ$

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Lieb. Ann. d. Chem., **260**, 290 (1890).

in 2.5 % sodium hydroxide solution, but is insoluble in water and alcohol. Analysis of the substance gave the following results:

- I. 0.3155 gm. substance gave 0.5204 gm. CO<sub>2</sub>,  
0.1643 gm. H<sub>2</sub>O and 0.0025 gm. ash.
- II. 0.1355 gm. substance gave 0.2213 gm. CO<sub>2</sub>,  
0.0817 gm. H<sub>2</sub>O and 0.0011 gm. ash.

	Calc. for C <sub>6</sub> H <sub>8</sub> O <sub>4</sub>	Found. (ash-free)	
		I	II
Carbon	45.43	45.35	45.01
Hydrogen	6.16	5.83	6.81
Ash	—	0.79	0.79

On heating xylan with water at 120–130° for three hours in a sealed tube, no change could be observed, however, at 145° for three hours it yields a trace of xylose by hydrolysis. The hydrolysis of xylan was also in a slight degree observed when heated with phosphoric acid at 145° for three hours. On the other hand, 0.496 gm. of the xylan upon heating with 1.5% hydrochloric acid on a water-bath for two hours, is quickly hydrolysed to laevo-xylose, indicating by Fehling's solution 0.2418 gm. xylose (48.6%) present in the reaction product. In another experiment, 10.4468 gm. of the xylan heated with 4% sulphuric acid on a water bath for two hours, yielded 62.3% xylose and 3% fuming acid<sup>1</sup> which separated and was confirmed by its analysis:

0.0986 gm. substance gave 0.2091 gm. CO<sub>2</sub>, 0.0611 gm. H<sub>2</sub>O and 0.003 gm. ash.

	Found. (ash-free)
Carbon	59.64
Hydrogen	7.09
Ash	3.13

3.8 grams of the laevo-xylose (36.38%) were isolated in a pure crystalline state from the above reaction product, with 1.955 gm. xylose remaining in the solution.

Xylan prepared from corn cobs by the same treatment as shown in the above case, is a slight yellow-coloured amorphous powder and showed the specific rotation  $[\alpha]_D = -80^\circ$  in 2.5% sodium hydroxide solution.

<sup>1</sup> S. Odén, *Die Huminsäuren*, 1919, s. 100.

It gave the following analytical results :

C 45.22 %, H 5.88 % and ash 1.28 %.

It is a noteworthy fact that xylan prepared from corn cobs hardly yields an acetyl derivative by the action of acetic anhydride and acetyl chloride with or without catalytic agents, whereas xylan from wheat straws yields easily acetyl compounds.

## 2. *Acetyl Xylans.*

As we saw in an acetylation of polysaccharides such as starch and cellulose<sup>1</sup>, the velocity of the acetylation of xylan was observed to be greatly influenced by the presence of a catalytic agent.

### Monoacetyl Xylan.<sup>2</sup>

A mixture of 2 gm. of the wheat xylan 25 gm. acetyl chloride was heated in a pressure bottle on a water bath; all of the mass passed into a light brown solution in five minutes. On adding 70 c.c. absolute alcohol to the solution, a white voluminous substance was precipitated which separated from the mother liquor by filtration, dried on air. To purify, the product was dissolved in chloroform, filtered, and the filtrate poured into 50 c.c. petroleum ether to precipitate the acetyl compound, which after being separated from the solution was dried in vacuo. The yield was 1 gm. (40%).

It is a light yellow amorphous powder and is soluble in chloroform and an alkaline solution but insoluble in ether and alcohol.

0.3162 gm. of the acetyl compound were digested with 74.28 c.c.  $\frac{N}{2}$  H<sub>2</sub>SO<sub>4</sub> for ten hours, filtered and washed with water. The filtrate and washing made up 100 c.c. with water. For the neutralization of 10 c.c. of the solution requires of 7 c.c.  $\frac{N}{2}$  NaOH.; whence acetyl value 25.48; theory requires 24.72%.

For the preparation of monoacetyl xylan, the following method is very convenient and affords a fruitful result, and was formerly employed in the preparation of acetyl cellulose by W. L. Barnett.<sup>3</sup>

10 gm. xylan suspended in a mixture of 60 gm. glacial acetic acid and 85 gm. acetic anhydride, were mixed with 40 gm. of 2.45%

<sup>1</sup> J. Böeseken, J. C. van den Berg, & A. H. Kerstjens, *Rec. trav. chim.*, **35**, 320 (1916).

<sup>2</sup> R. Bader, *J. Chem. Soc.*, **70**, 1, 335 (1896).

<sup>3</sup> *J. Soc. Chem. Indust.*, **40**, 8 (1921).

chlorine containing glacial acetic acid and 18.8 grm. of 4.66% sulphur dioxide containing glacial acetic acid. The mixture was shaken for 30 minutes and the xylan passed into solution with a slight evolution of heat. The solution was poured into cold water and the precipitate purified was dried in vacuo. The yield was 9 grm. (70%).

On analysis, it gave the following results:

- I. 0.1252 grm. substance gave 0.2187 grm. CO<sub>2</sub>, 0.0679 grm. H<sub>2</sub>O and 0.0008 grm. ash.
- II. 0.0719 grm. substance gave 0.0923 grm. BaSO<sub>4</sub> on hydrolysis by the method of Herzig.

	Calc. for C <sub>5</sub> H <sub>7</sub> O <sub>4</sub> (CH <sub>3</sub> CO)	Found (ash-free)	
		I	II
Carbon	48.26	47.95	—
Hydrogen	5.79	6.06	—
Acetyl	24.72	—	23.64
Ash	—	0.64	—

0.2186 grm. of the substance dissolved in chloroform to make up 10 c.c.  $\alpha_D^{21} = -4^\circ.25'$  in one dm. tube; whence  $[\alpha]_D^{21} = -202^\circ.6'$ .

The molecular weight of the substance was determined in the chloroform solution by the ebullioscopic method:

Solvent	Substance.	$\Delta$	Mol. wt.	
			Found.	Calc. for (C <sub>7</sub> H <sub>10</sub> O <sub>5</sub> ) <sub>2</sub>
31.6543 grm.	0.0580 grm.	0.02°	337.5	
„	0.2761 grm.	0.09°	357.0	
		Mean	347.2	348

#### *Diacetyl Xylan.*<sup>1</sup>

In the course of the acetylation of xylan with acetyl chloride, when pyridine was used as catalyser, diacetyl xylan was formed. 3.5 grm. xylan, 70 grm. acetyl chloride and 3 grm. pyridine in 15 c.c. glacial acetic acid were heated on a water bath for five minutes. The light-brown-coloured solution thus obtained, was poured into 100 c.c. absolute alcohol. The precipitate was washed with alcohol and dried in air and dissolved in chloroform and reprecipitated with petroleum

<sup>1</sup> R. Bader, J. Chem. Soc., 70, 1335 (1896)

ether; the same process was twice repeated and then the substance dried in vacuo.

The yield was 2 gm. (35 %).

On analysis, it gave the following results :

0.1881 gm. substance gave 0.3413 gm. CO<sub>2</sub>, 0.0946 gm. H<sub>2</sub>O and 0.0007 gm. ash.

	Calc. for C <sub>5</sub> H <sub>6</sub> O <sub>4</sub> (CH <sub>3</sub> CO) <sub>2</sub>	Found (ash-free)
Carbon	49.97	49.68
Hydrogen	5.56	5.60
Ash	—	0.37

0.1986 gm. substance gave 0.2075 gm. BaSO<sub>4</sub> on hydrolysis; whence acetyl value 38.57% theory requires 39.79%.

This compound was obtained from xylan and acetic anhydride and an excess of chlorine and sulphur dioxide used as a catalyser. The mixture 10 gm. xylan in 55 gm. glacial acetic acid, 100 gm. of 2.45% chlorine-glacial acetic acid and 50 gm. of 4.66% sulphur dioxide-glacial acetic acid, shaken in a bottle for 30 minutes; all passed into solution which was then poured into water. The acetyl compound separated from the solution, dissolved in chloroform and reprecipitated by adding petroleum ether. The yield was 9 gm. (55%).

I. 0.1681 gm. substance gave 0.3042 gm. CO<sub>2</sub>, 0.0905 gm. H<sub>2</sub>O and 0.0007 gm. ash.

II. 0.1970 gm. substance gave 0.2196 gm. BaSO<sub>4</sub> on hydrolysis by the method of Herzig.

	Calc. for C <sub>5</sub> H <sub>6</sub> O <sub>4</sub> (CH <sub>3</sub> CO) <sub>2</sub>	Found (ash-free)	
		I	II
Carbon	49.97	49.58	—
Hydrogen	5.56	5.97	—
Acetyl	39.79	—	41.06
Ash	—	0.42	—

It was also prepared from xylan by the action of acetic anhydride and zinc chloride; 2 gm. xylan mixed with 15 gm. acetic anhydride and 2 gm. zinc chloride, and heated on water bath for five minutes. The reaction product was poured into water and the precipitated diacetyl xylan was purified with chloroform and petroleum ether as usual. The yield was 1.7 gm. (52%).

0.1388 grm. substance gave 0.2526 grm. CO<sub>2</sub>, 0.0701 grm. H<sub>2</sub>O and 0.0005 grm. ash.

	Calc. for C <sub>5</sub> H <sub>6</sub> O <sub>4</sub> (C <sub>2</sub> H <sub>3</sub> O) <sub>2</sub>	Found (ash-free)
Carbon	49.97	49.97
Hydrogen	5.56	5.63
Ash	—	0.36

The same diacetyl compound is obtained when monoacetyl xylan is treated with acetic anhydride in the presence of chlorine and sulphur dioxide.

Diacetyl xylan is a light yellow amorphous powder, and is soluble in chloroform but insoluble in ether and alcohol. The specific rotation of the compound in chloroform solution was observed and the following result was obtained:

0.2170 grm. substance dissolved in chloroform make up to 10 c.c. gave  $\alpha_D^{20.5} = -2^{\circ}57'$  in 1 dm. tube; whence  $[\alpha]_D^{20.5} = -135^{\circ}9'$ .

The substance standing in contact with sodium hydroxide solution passed gradually into solution.

### 3. *Hydrolysis of Xylan and Acetyl Xylans.*

Certain quantities of xylan and acetyl compounds were mixed with  $\frac{N}{5}$  C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>H solution, and the mixture kept in a boiling water bath, and the quantity of reducing substance formed by the hydrolysis was determined by the aid of Fehling's solution. The constant of the reaction velocity was calculated by the formula of a monomolecular reaction as in the case of the hydrolysis of polysaccharides by E. Hildt.<sup>1</sup>

#### I. Xylan from wheat-straw.

Substance (in grm.)	T (minute)	Cu <sub>2</sub> O (grm.)	x (grm. xylose)	$K = \frac{2.3}{1} \log \frac{a}{a-x}$
0.1378	20	0.1116	0.0521	0.024
0.1361	40	0.1262	0.0594	0.014
0.1267	60	0.1344	0.0636	0.012
0.1221	80	0.1560	0.0747	0.012
0.1303	100	0.1680	0.0810	0.010
				Mean 0.014

<sup>1</sup> C. R., **170**, 1505 (1920).

II. Monoacetyl xylan.

Substance (in gramm.)	T (minute)	Cu <sub>2</sub> O (gramm.)	x (gramm. xylose)	$K = \frac{2.3}{T} \log \frac{a}{a-x}$
0.1905	90	0.0284	0.0126	0.0008
0.1446	180	0.0576	0.0261	0.0011
0.1442	270	0.0838	0.0384	0.0011
0.1238	360	0.1010	0.0468	0.0013
0.1208	450	0.1000	0.0464	0.0011
Mean				0.0011

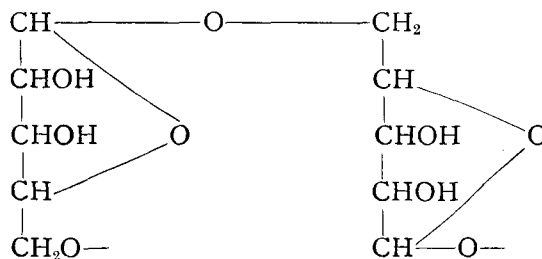
III. Diacetyl xylan.

Substance (in gramm.)	T (minute)	Cu <sub>2</sub> O (gramm.)	x (gramm. xylose)	$K = \frac{2.3}{T} \log \frac{a}{a-x}$
0.1269	90	—	—	—
0.1358	180	0.0064	0.0028	0.00012
0.1238	300	0.0140	0.0062	0.00017
0.1216	425	0.0240	0.0106	0.00027
0.1386	530	0.0550	0.0249	0.00037

From the experimental data, we have learned that the time in which 18% of mono- and diacetyl xylans have been hydrolysed, requires 18 and 530 minutes respectively, whereas the same quantity of xylan can be hydrolysed in a few minutes. The discrepancy in the constants of reaction velocity of diacetyl xylan calculated and observed, may be explained by assuming that autocatalysis takes place during the hydrolysis.

4. *Constitution.*

Xylan is a non-reducing polysaccharide which yields laevo-xylose on hydrolysis with mineral acids such as hydrochloric and sulphuric acids. Consequently, it is regarded as a polyose in which a reducing group of one xylose molecule is jointed with the hydroxyl group of another molecule as indicated below :



The above formula contains two free hydroxyl groups which indicate xylan by the acetylation yields monoacetyl and diacetyl compounds.

The exact constitution of xylan, however, is still a matter of doubt and will be studied and reported in a future article.

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