# Constitution of Polysaccharides, II : Constitution of Xylan

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# Constitution of Polysaccharides, II. Constitution of Xylan.

By

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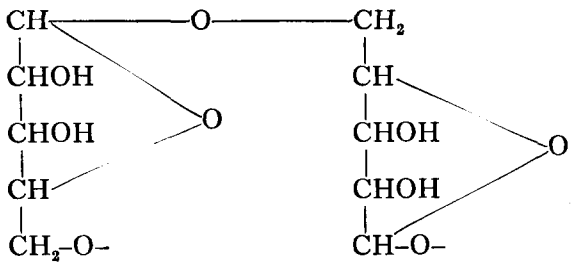
In the previous article on this subject, S. Komatsu and K. Kashima[1] proposed the constitutional formula (I) for xylan prepared from wheat straw, based on acetylation, yielding mono- and di- acetyl compounds. With regard to the exact position of the two free hydroxyl groups in the constituent pentose, study of the chemical dynamics of the hydrolysis of xylan and its acetyl derivatives seems to afford no evidence, and remained to be solved.



(I)

Among many devices, the investigations of the methylated sugars proposed by J. C. Irvine and W. N. Haworth[2] has been recognised by chemists as bringing the most satisfactory results in this problem.

The present study was, therefore, concerned with the preparation of methyloxylan, its hydrolysis and the oxidation of the cleavage product.

## 1. XYLAN.

Xylan was prepared from two sources, one wheat straw, and the other rice straw, both grown in Kyoto. The procedure used in the

1 These memoirs, **5**. 313 (1922).

2 J. Chem. Soc., 109, 1321 (1916); **115**, 593, 809 (1919).

preparation was the same as that described in the previous article,[1] and the yield of the crude xylan was 14% in the former and 19% in the latter. When calculated on samples, purified by repeating the precipitation and treatment with hydrochloric acid, the yield was reduced to 6.6% and 8.2% respectively. 210 grm. of air dried wheat straw yielded, by Salkowski's[1] method, 4 grm. pure xylan. The purified samples, on analysis, gave ,the following results, calculated as ash free substance.

1. Xylan from wheat straw :

| | | | |
|---|---|---|---|
| | C=45.00 | H=6.33 | Ash=0.66 |
| | 45.14 | 6.16 | 0.84 |
| | 45.40 | 6.00 | 0.76 |
| | 45.30 | 6.21 | 0.86 |
| | 45.34 | 6.21 | 0.75 |
| mean | 45.23 | 6.18 | 0.77 |

2. Xylan from rice straw :

| | | | |
|---|---|---|---|
| | C=44.78 | H=6.10 | Ash=1.45 |
| | 45.26 | 6.03 | 1.68 |
| | 45.06 | 6.11 | 1.48 |
| mean | 45.03 | 6.08 | 1.54 |

3. Xylan from wheat straw by Salkowski's method.

| | | |
|---|---|---|
| C=45.53 | H=6.01 | Aas=4.60 |
| 45.66 | 5.20 | 5.03 |

The specific rotatory power of xylan from rice straw in 2.5% caustic soda solution, showed $[\alpha]_D^{20}=\frac{-4\times 100}{0.046\times 100}=-14.°49$.

## 2. DIMETHYL ETHER OF XYLAN.

Methylation of Xylan by the method of Pudie and Irvine,[2] with the silver oxide-methyl iodide reaction, was tried but with no result. While the authors were engaged in the methylation, E. Heuser and W. Ruppel's article[3] " Über Methyläther des Xylans " appeared. The

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1 Zs. Physiol. Chem., **34**, 162 (1901).
2 J. Chem. Soc., **83**, 1021 (1903); **85**, 1049 (1904)
3 Ber. D. Chem. Ges., **55**, 2084 (1922).

method used in the preparation of methyloxylan was similar to their processes, somewhat different in details.

10 grm. xylan from wheat straw were treated with 150 c.c. 30% sodium hydroxide solution and 100 grm. dimethylsulphate, and the methyloxylan deposited on heating with some water, was separated by filtration from the mother liquor. The crude product was washed with hot water to remove some inorganic substance admixed, and dried in a dessiccator ; it was 6.5 grm. 35 grm. of xylan from rice straw, in the same way, yielded 32.5 grm. crude methylated compound which consisted of partly and fully methylated derivatives as descrived by Heuser and Ruppel. It was, therefore, soon methylated completely by treatment with silver oxide and methyl iodide in the following manner : 1 grm. raw methyloxylan, 6 grm. silver oxide and 20 grm. methyl iodide were heated in a sealed tube at 100° for 3 days, and the product, separated from silver salt, on distilling off the volatile substance, gave a syrup. It was extracted with chloroform in Soxlet's apparatus, and on the solvent being evaporated there remained a light brown syrup, which after drying for 3 weeks in vacuo at 80°, became solid softening at 50-60°.

It gave, on analysis, the following results :

C=52.61 ; 52.31 ; H=7.70 ; 7.37 ; $CH_3O$=35.77 ; 36.19., theory requires C=52.47 ; H=7.56 ; $CH_3O$=38.76 for $C_5H_6O_2(OCH_3)_2$.

The specific rotatory power of the substance in chloroform solution, $[\alpha]_D^{20} = +\frac{37' \times 10}{0.2025 \times 60} = +30°.45$, showed an opposite sign to that acetyl derivatives of xylan.

### 3. HYDROLYSIS OF DIMETHYL XYLAN.

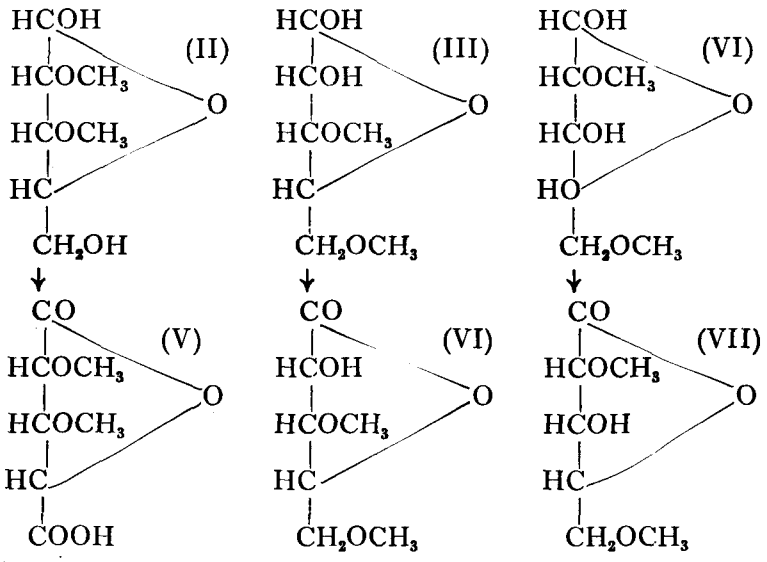
2 grm. dimethyl ether of rice xylan were heated in 200 c.c. 5% HCl solution (sp. gr. 1.024) at 100° for 4 hours. When hydrolysis was complete, the acid solution was neutralized by treating with freshly precipitated silver carbonate, filtered, and heated at 50° with some charcoal and again filtered.

To remove trace of silver salt in the solution, it was treated with

sulphuretted hydrogen, and filtered, and the filtrate was evaporated to syurp at 40° under reduced pressure. The remaining syrup consisted of dimethyl xylose, which reduced the Fehling solution, but not potassium permanganate solution. It was soon subjested to oxidation without isolating the sugar in the pure state.

## 4. OXIDATION OF DIMETHYL XYLOSE.

Three constitutional formulae of the butylene oxide type are possible for dimethyl xylose, the cleavage product from the hydrolysis of dimethyl xylan :




| $C_7H_{10}O_6$ | $C_7H_{12}O_6$ |
|---|---|
| C=44.2 | C=47.8 |
| H= 5.3 | H= 6.8 |
| $CH_3O$=32.6 | $CH_3O$=35.3 |

The two free hydroxyl groups in these formulae must have been presisely those groups concerned in the coupling of the pentose in the original xylan, since all the hydroxyl groups exposed in xylan are protected by a methyl group in dimethyl derivative.

Methyl xylose, thus formed, when oxidized carefully with nitric acid as in the cases of methyl hexoses observed by Haworth[1], should be transformed into a methylated sugar acid as shown in the scheme. Of these possible formulae, (III) and (IV) can easily be excluded by finding the proof for the presence of a free primary alcohol group in the isolated pentose.

Granting formula (II) for the methyl xylose, a lactonic acid having the molecular formula $C_7H_{10}O_6$ (V) and containg two methoxy groups, should result from its oxidation.

The syrup obtained by hydrolysis of methyloxylan, was oxidized with 20 c.c. nitric acid (D=1.2) following precisely Haworth's direction[2]. The reaction temperature was maintained at 80° for a few minutes, and thereafter at 65° for 3½ hours. The acidic solution was treated with alcohol and then ether and afterwards evaporatad under reduced pressure, to remove completely nitric acid, and finally a pale bluish white syrup was obtained which was dried at 80° under reduced pressure for many weeks. The yield of the oxidation product was 0.8 grm. It gave, on analysis, the following results :

C=45.06 ; H=5.49 ; $CH_3O$=28.23.

(Theory requires C=44.2 ; H=5.3 ; $CH_3O$=32.6 for $C_5H_4O_4(OCH_3)_2$).

The results agree with the theoretical value for optically active dimethoxy glutaric acid (V). The specific rotatory power of the acid in alcohol solution showed $[\alpha]_D=\frac{+1.82\times 100}{0.0137\times 100}=+132°$.

Admitting that the fully methylated xylan gives, when hydrolysed with dilute acid, methylated simple sugar, in which the linkings are preserved exactly as in the parent polysaccharide, and traceing it back reaction by reaction, the authors are led to conclusion that the constitu-

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[1] Loc. cit.

[2] J. Chem. Soc., **115**, 815 (1919).

tional formula for xylan is as represented in formula(I).

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