

Alkali Treatment of Xylotriose and Birch Xylan in the Presence of Anthraquinone

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It was shown in our recent investigation¹ that addition of anthraquinone (AQ) in kraft pulping of birch wood results in some differences in the proportions of carboxylic acids derived from polysaccharides. In this study, xylotriose and birch xylan have been employed as model substances to elucidate the effect of AQ on carbohydrate reactions during alkaline pulping of hardwood.

Experimental. Materials. Xylotriose was prepared from esparto grass xylan in connection with a previous work in this laboratory.² Birch xylan was isolated and purified from acetone-extracted birch wood meal as described elsewhere.³

Experiments and analytical methods. Xylotriose (40 mg) or birch xylan (300 mg) were treated under nitrogen atmosphere with 0.5 M sodium hydroxide solution at 140 °C for 2 h. The amounts of NaOH solution and AQ were 30 ml and 10 mg for xylotriose, and 60 ml and 30 mg for xylan, respectively. Reference samples were prepared under identical conditions without AQ. Nonvolatile carboxylic acids were trimethylsilylated as their ammonium salts and analysed by GLC-MS using the same apparatus and technique as described previously.⁴ Identification of 2-C-methyltetronic acids was based on the published mass spectrum.⁵ The other carboxylic acids were identified previously.¹

Results and Discussion. Reactions of xylotriose. Degradation of xylotriose gave rise to 16 hydroxy monocarboxylic acids (Table 1), most of which have been identified earlier by Malinen and Sjöström.² The reaction routes for the formation of the main degradation products were recently¹ discussed and will not be repeated here in detail.

In agreement with earlier results from pulping experiments of birch wood,¹ one of the most striking effects of AQ was the decreased proportion of 2-hydroxybutanoic acid. As expected,¹ the formation of xyloisosaccharinic and lactic acids was also slightly depressed. Oxidation of glyceraldehyde by AQ to glyceric acid competes with β -hydroxy elimination and partially explains the decreased proportion of lactic acid.⁶

AQ markedly accelerated the formation of 3-deoxytetronic acid, which is in accordance with the previous conclusion¹ that this acid mainly originates from xylan analogously with the formation of 3-deoxypentonic acids from hexosans. It should be noted, that 3-deoxytetronic acid can be formed also *via* aldol condensation of glycolaldehyde formed in various fragmentation reactions.⁶ In the presence of AQ glycolaldehyde is, however, mainly oxidized to glycolic acid.

The formation of 3,4-dideoxypentonic (2,5-dihydroxypentanoic) acid from xylotriose most likely follows a reaction path analogous to that responsible for the formation of 3,4-dideoxyhexonic acid from cellobiose,⁶ cellulose,⁷ and mannan.⁸ Reduction of 4-deoxy-2,3-pentodiulose followed by β -hydroxy elimination at C-3 gives rise to 3,4-dideoxypentosulose, from which 3,4-dideoxypentonic acid is formed by benzilic acid rearrangement. The proportion of this acid was higher in the presence of AQ, which indicates that anthrahydroquinone (reduction product of AQ) can reduce intermediates formed by alkaline peeling (*cf.* Ref. 7).

Both diastereomers of 2-C-methyltetronic acid (xylosaccharinic acid) were formed in small amounts in the absence and presence of AQ. In separate experiments it was observed that these acids are formed from D-xylose under similar conditions with about 1 % yield, which shows that they are most probably formed from a xylose unit liberated after complete peeling. These acids have previously been identified after calcium hydroxide treatment of xylose,⁹ fructose,⁹ and sorbose.¹⁰ According to Kiprianov *et al.*¹¹ the hydroxy acid fraction of birch kraft black liquor also contains xylosaccharinic acid at about 0.2 %, and more recently, small peaks at the retention time of 2-C-methylthreonic acid have been detected

Table 1. Yields of nonvolatile carboxylic acids from treatment of xylotriose with 0.5 M NaOH at 140 °C with and without addition of AQ. Weights (mg) refer to 1 g of charged xylotriose.

Carboxylic acid	AQ absent	AQ present
Monocarboxylic acids		
Lactic	158	106
Glycolic	49	83
2-Hydroxybutanoic	158	65
3-Hydroxypropanoic	10	23
2-C-Methylglyceric	5	3
Glyceric	4	15
3-Deoxytetronic	35	84
3,4-Dideoxypentonic	4	6
Threonic	2	4
2-C-Methylthreonic	2	1
2-C-Methylerythronic	2	1
Xyloisosaccharinic	236	188
3-Deoxy- <i>erythro</i> -pentonic	24	20
3-Deoxy- <i>threo</i> -pentonic	70	67
Xylonic	— ^a	3
Lyxonic	+ ^b	6
Dicarboxylic acids		
Oxalic	5	2
Succinic	4	3
C-Methyltartronic	2	3
Tartronic	+	2
Malic	2	1
Unidentified	17	8
Total amount, mg	789	694

^a None detected. ^b Traces.

during gas-chromatographic analysis of birch kraft black liquors.¹ The results with xylotriose give more support to the presence of small amounts of 2-C-methyltetronic acids in hardwood black liquors.

2-C-Methylglyceric acid has been found in birch kraft black liquors,¹ but has not been previously identified after alkaline treatment of xylan or xylo-oligosaccharides. The small amount suggests that its formation is mostly *via* a xylose unit liberated after complete peeling. The results with xylotriose combined with those with cellulose,⁷ amylose,¹² mannan,¹³ and pectic substances¹⁴ indicate that all polysaccharides present in wood are responsible for the formation of 2-C-methylglyceric acid during alkaline pulping of wood.

Some dicarboxylic acids were also formed from xylotriose in the absence and presence of AQ. Separate experiments carried out with xylose indicated that they can be formed from a xylose unit liberated after complete peeling.

Reactions of birch xylan. As in the experiments with xylotriose, addition of AQ markedly depressed the formation of 2-hydroxybutanoic acid, but here the amount of xyloisosaccharinic acid was also clearly decreased (Table 2). Analogously, increased amounts were observed for glycolic and 3-deoxytetronic acids. Very small amounts of 3,4-dideoxypentonic and 2-C-methylaldonic acids were also formed from xylan.

Rhamnose moieties present in birch xylan give rise to diastereomeric 3,6-dideoxyhexonic acids.³ Here their formation was decreased in the presence of AQ, although they have been found to occur in equal amounts in birch kraft and kraft-AQ black liquors.¹ A number of

Table 2. Yields of nonvolatile carboxylic acids from treatment of birch xylan with 0.5 M NaOH at 140 °C with and without addition of AQ. Weights (mg) refer to 1 g of charged xylan.

Carboxylic acid	AQ absent	AQ present
Lactic	63	35
Glycolic	20	33
2-Hydroxybutanoic	143	41
3-Hydroxypropanoic	3	8
2-C-Methylglyceric	3	1
Glyceric	— ^a	6
3-Deoxytetronic	6	19
2-Deoxytetronic	+ ^b	—
3,4-Dideoxypentonic	2	1
2-C-Methylthreonic	+	1
Xyloisosaccharinic	131	55
3-Deoxy-erythro-pentonic	3	2
3-Deoxy-threo-pentonic	9	5
3,6-Dideoxy-ribo-hexonic	2	1
3,6-Dideoxy-arabino-hexonic	5	3
Total amount, mg	390	211

^a None detected. ^b Traces.

dicarboxylic acids were also formed, but they are not dealt with in this connection because of the strong evidence¹⁵ that they are formed from 4-*O*-methylglucuronic acid groups.

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