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Carbohydrate Stabilization in Wood by Quinones and Oxygen

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Summary

Spruce meal, impregnated with magnesium sulfate to suppress the depolymerization of the carbohydrates by oxygen, was treated with 1 M sodium hydroxide at 100°C in the presence of anthraquinone (AQ) or anthraquinone-2-sulfonic acid (AMS). A decreased loss of carbohydrates obtained in the presence of oxygen is related to an increased conversion of the reducing sugar end groups to aldonic acid end groups. Larger effects of oxygen were obtained with AMS compared to AQ.

Introduction

LÖWENDAHL and SAMUELSON (1978) found that addition of anthraquinone (AQ) to wood meal led to a decreased loss of carbohydrates during treatment in 1 M sodium hydroxide at 80°C and that reducing sugar end groups were oxidized to aldonic acid end groups with high stability in alkaline medium. Although the addition of AQ on a molar basis was approximately six times the number of reducing sugar end groups, 40% of the reducing hexose end groups remained after treatment for 2 hours. The results are consistent with the observation that a major proportion of AQ is reduced in reactions with soluble products such as 4-deoxy-2,3-diuloses (SAMUELSON, SJÖBERG 1978). An attempt was therefore made to increase the conversion of reducing sugar end groups to aldonic acid end groups by treating the wood with either AQ or anthraquinone-2-sulfonic acid (AMS) in the presence of oxygen.

Experimental

Wood meal (0.13-0.36 mm) from Scandinavian spruce (*Picea abies*, Karst) corresponding to 30 g dry wood was mixed with 80 ml magnesium sulfate solution in a steel autoclave (1500 ml). The addition corresponded to 0.25% Mg on wood. Sodium hydroxide solution was added so that the total liquor volume was 210 ml and the alkali concentration was 1.00 mol per liter after precipitation of magnesium hydroxide. The autoclaves were closed and the air displaced by nitrogen or oxygen of atmospheric pressure. The autoclaves were rotated in a preheated polyglycol bath at 100°C.

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Reducing sugar end groups were determined as alditols after borohydride reduction and aldonic acids determined in the unreduced samples (LÖWENDAHL, SAMUELSON 1978).

In experiments with birch xylan (Betula verrucosa) 8 g were treated with 800 ml 0.5 M NaOH at 100°C. The hydrolysis was made with 0.125 M sulfuric acid for 10 hr at 100°C.

All analytical results and additions refer to 100 g dry xylan or extract-free wood meal.

Results and discussion

No determination of the formation of aldonic acid end groups in xylan during treatment with alkali in the presence of quinone compounds have been published. To elucidate the origin of the aldonic acids formed during the treatments of wood meal some results with xylan are, therefore, given in Table 1. Like treatment in the absence of quinone additives (not shown) the treatment under nitrogen in the presence of AMS gave rise to a very low proportion of 3-deoxypentonic acid end groups. This is explained by a strongly retarded endwise degradation after the loss of the reducing 1,4-linked xylose end group as 4-deoxy-2,3-pentodiulose and the formation of a more stable 1,2-linked reducing galacturonic acid end group (JOHANSSON, SAMUELSON 1977). The reaction path leading to 3-deoxypentonic acid groups should become less important in an oxygen atmosphere and as expected only traces were formed.

TABLE 1

Carboxylic acid end groups in birch xylan after treatment with 0.5 M NaOH, for 90 min at 100°C under nitrogen or oxygen with addition of 2.4 mmol of AMS

Acids	mmol per 100 g xylan	
	N_2	O_2
3-Deoxy-erythro-pentonic	0.013	< 0.002
3-Deoxy-threo-pentonic	0.031	0.02
Xylonic	0.12	0.81
Lyxonic	0.24	3.0
Threonic	0.051	0.89
Erythronic	0.010	0.19
Glyceric	0.76	5.2

An appreciable number of aldonic acid end groups was produced by oxidation with AMS under nitrogen. When oxygen was present their number was much larger than that of the added moles of AMS. The larger proportion of lyxonic compared to xylonic acid suggests that the pentonic acid end groups are at least in part formed by benzilic acid rearrangement of threo-pentosulose groups produced by oxidation of the reducing end group (KOLMODIN, SAMUELSON 1971). Consecutive reactions can explain the fragmentation to threonic, erythronic and glyceric acid end groups. It should be pointed out that a small proportion of glyceric acid is obtained also from xylan which has not been subjected to any intentional oxidation. The large proportion reported in the table shows, however, that glyceric acid belongs to the most abundant aldonic acid end groups formed during alkali treatment in the presence of AMS both under nitrogen and under oxygen.

The experiments with wood meal were made with spruce. Mannose derived from glucomannan was the predominant reducing hexose end group. The total number of reducing hexose end groups determined as glucitol plus mannitol was 480 μmol per 100 g. In addition 280 μmol of xylose end groups were present. Table 2 shows that only 230 μmol of hexose end groups and 100 μmol of pentose end groups remained per 100 g treated wood meal in the blank treated with 1 M sodium hydroxide at 100°C under nitrogen without quinone and magnesium additions. The formation of deoxyaldonic and aldonic acid end groups was small. The severe loss of pentose end groups can mainly be ascribed to the rapid cleavage of the 1,4-glycosidic bond between the xylose end group and the galacturonic acid unit in the xylan. The liberated reducing galacturonic acid end group is in consecutive reactions converted to end groups which are decomposed during acid hydrolysis and therefore not determined by the applied techniques (JOHANSSON, SAMUELSON 1977). A large proportion of the glucomannan is decomposed by stepwise alkaline degradation from the reducing end (peeling) even under mild conditions. The low number of reducing hexose end groups and acid end groups derived from these indicates that, in a large proportion of the glucomannan molecules, the peeling proceeded so far that the whole molecules were converted to soluble products.

As found by BASTA and SAMUELSON (1979) addition of magnesium salt has a very slight effect on the yield in experiments under nitrogen while in those with oxygen present, the oxidative attack on the carbohydrates is retarded. The experiments with AQ and AMS under oxygen were therefore made with wood meal impregnated with magnesium sulfate. The same impregnated wood meal was used in the experiments under nitrogen with the quinone additives.

TABLE 2

Alditols and aldonic acids derived from end groups and yields after treatment of wood meal with 1 M NaOH for 90 min at 100°C

	No addn N_2	1.2 mmol AQ N_2	1.2 mmol AQ O_2	1.2 mmol AMS N_2	1.2 mmol AMS O_2
Pentitols [a], µmol	100	40	<10	30	<10
Glucitol, µmol	104	38	20	28	14
Mannitol, µmol	126	57	30	50	60
Gluconic, µmol	1	29	57	32	40
Mannonic, µmol	4	25	196	20	247
Allonic, µmol	0	0	5	0	6
Ribonic, µmol	0	0	5	0	10
Arabinonic, µmol	4	8	34	11	15
Xylonic, µmol	3	10	14	12	13
Lyxonic, µmol	3	5	46	32	67
Erythronic, µmol	9	7	76	26	177
Threonic, µmol	1	3	32	14	42
Glyceric, µmol	12 [b]	38	71	124	246
Total yield, %	82.3	81.4	85.5	82.3	86.4
Lignin yield, %	23.5	22.1	22.7	23.3	23.0
Carbohydr. yield, %	58.8	59.3	62.8	59.0	63.4

a) Mainly xylitol

b) In addition 3-deoxy-ribo-hexonic, 3-deoxy-arabino-hexonic (together 28 µmol) and the two diastereomeric 3-deoxypentonic acids (together 12 µmol) were produced. Oxygen suppressed their formation

Like the previously reported treatment with a fourfold amount of AQ at 80°C the addition of either AQ or AMS in the experiments carried out under nitrogen led to a predominant loss of reducing sugar end groups. Aldonic acid end groups were produced in much larger amounts than in the blank without quinone additive. The number of hexonic, arabinonic and erythronic acid groups produced exclusively or predominantly from reducing hexose groups was much smaller than the loss of these sugar end groups. A loss of an appreciable proportion of the glucomannan molecules, consistent with the low carbohydrate yield explains these observations.

Both the total loss of reducing sugar end groups and the formation of aldonic acid groups was more prominent with AMS than with AQ although as indicated by the lignin yields the reoxidation of the hydroquinone form in reactions with lignin must be more important with AQ. The number of reducing pentose end groups was somewhat lower after treatment with AMS than with AQ while lyxonic, threonic and glyceric acid end groups in the xylan were much more abundant when AMS was used. Evidently, AMS led to a rapid oxidation of the terminal xylose group while when AQ was used a major proportion of these groups was lost by peeling.

In the experiment with AMS the presence of oxygen led to an increased number of mannose end groups and to so many aldonic acid end groups that the total number of end groups in the potentially reducing end was larger than that in the untreated wood meal. Evidently, the carbohydrates suffered a depolymerization despite addition of magnesium salt as protector. With AQ oxygen led to a decreased number of reducing sugar end groups and a large increase in the number of all types of aldonic acid end groups. The results permit the conclusion that the oxidative depolymerization of the carbohydrates was less severe with AQ than with AMS.

It is noteworthy that with either AQ or AMS the presence of oxygen led to a strikingly enhanced carbohydrate yield. The effect was larger for AMS than for AQ although consecutive peeling, following the depolymerization, must be more severe in the experiments with AMS. A pretreatment of the wood at about 100°C with an alkaline solution of AMS with continuous oxidation of the hydroquinone form by oxygen will obviously lead to an effective stabilization of the carbohydrates provided that direct contact of oxygen and peroxide formed during the oxidation with the wood can be avoided.

The experiments with xylan and AMS indicated that the formation of aldonic acid groups via threo-pentosulose end groups is an important reaction path. This is true also for the xylan reaction in the wood meal in the presence of AMS under either nitrogen or oxygen and of AQ under oxygen. In the absence of oxygen some other reaction path seems to be more important when AQ is present. The high gluconic acid: mannonic acid ratio strongly indicates that the corresponding reaction path via arabino-hexosulose is of little importance in the experiments with AQ and AMS when oxygen is absent, while the product composition indicates that this is a very important reaction path when oxygen is present. The importance of the reaction path via aldosuloses in experiments under oxygen was confirmed by the aldonic acid end groups formed during treatment with the methylester of anthraquinone-1-acetic acid under otherwise identical conditions. [Gluconic (51), mannonic (227), allonic (19), ribonic (11), arabinonic (38), xylonic (20), lyxonic (31) and glyceric acid (61) μmol/100 g].

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