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# Carbohydrate Stabilization with Anthraquinone During Alkaline Pulping

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Summary. Treatment of wood meal with aqueous alkali in the presence of anthraquinone at 80°C leads to a conversion of reducing hexose end groups in the polysaccharides to mannonic and gluconic acid end groups. Xylose end groups are oxidized to xylonic and lyxonic acid groups. This leads to a stabilization of the polysaccharides against endwise alkaline degradation.

## Introduction

Previous investigations showed that anthraquinone (AQ) promotes the formation of aldonic acid end groups in the polysaccharides both during soda cooking (LÖWENDAHL, SAMUELSON 1978) and kraft cooking (LÖWENDAHL, SAMUELSON 1977). This reaction leads to a stabilization against endwise alkaline degradation (peeling). Model experiments (CARLSON, SAMUELSON in press) showed that at 170°C pure cotton cellulose is stabilized effectively against consecutive peeling following the hydrolytic cleavage of the cellulose molecules while the stabilization of hydrocellulose is very slight at 170°C and fairly modest at 80-100°C. The extremely rapid alkaline peeling at 170°C starting at the reducing glucose end groups in the hydrocellulose and the low solubility of AQ at 80-100°C explain the results obtained with hydrocellulose.

Glucomannan in softwood contains reducing mannose end groups (PAL, SAMUELSON 1976) which are subjected to a rapid peeling during an early stage of the heating period in alkaline cooking. To elucidate the possibilities to increase the yield of pulp by suppressing the alkaline peeling a study was made of the effect of AQ on alkaline treatment of wood meal at 80°C.

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## Experimental

Wood meal (20 g) prepared from Scots pine with a particle size of 0.13-0.36 mm was treated for 1 or 2 hours with 140 ml 1 M NaOH at 80°C in rotating autoclaves with a volume of 1500 ml. Experiments were made with (1% on dry wood) and without addition of AQ. In some of the experiments the air present in the autoclave was displaced by nitrogen. After the treatment the autoclaves were cooled under tap water. The meal was washed with water, 1% acetic acid and finally with water again.

Three of the samples were subjected to acid hydrolysis with hydrochloric acid. The non-volatile monocarboxylic hydroxy acids were separated as a group and analyzed for aldonic and deoxyaldonic acids by a combination of anion exchange chromatography (LÖWENDAHL, SAMUELSON 1977) and gas chromatography (PETERSSON 1976). The reducing sugar end groups in the same samples were determined by partition chromatography of the alditols present in the hydrolysate after reduction of the wood meal with borohydride and acid hydrolysis of the reduced wood meal (PÄÄRT, SAMUELSON 1970).

## Results and discussion

The effect of AQ on the yield after treatment of wood meal from pine in 1 M sodium hydroxide at 80°C is shown in Table 1. It is seen that an addition of 1% AQ calculated on the weight of the dry wood led to a significantly enhanced yield when the alkaline treatment was made in both the presence and in the absence of air. Determinations of the mannose formed by acid hydrolysis of the treated wood meals showed that the increased yield was in part due to a stabilization of glucomannan. Xylose determinations indicated that the effect of AQ on the yield of xylan was less important. Under the applied conditions the presence of air led to a decrease in yield both ih the experiments with AQ and in the blanks.

TABLE 1

Yields (%) and sugars in hydrolyzates (% of treated meal) after treatment of wood meal with sodium hydroxide for 1 or 2 hours in the presence of air or nitrogen

| | Yield after | | Mannose | | Xylose | |
|---|---|---|---|---|---|---|
| | 1 h | 2 h | 1 h | 2 h | 1 h | 2 h |
| Air, no addition | 88.2 | 84.7 | | | | |
| Air, 1% AQ | 90.0 | 87.1 | | | | |
| $N_2$, no addition | 89.0 | 86.3 | 10.3 | 9.1 | 4.8 | 4.8 |
| $N_2$, 1% AQ | 91.5 | 88.6 | 11.6 | 11.6 | 4.9 | 5.4 |

Determinations of the aldonic and deoxyaldonic acid end groups as well as the reducing sugar end groups (as alditols) were made for the wood meals treated under nitrogen in the presence of AQ for one and two hours and in a blank treated with alkali for one hour without any additive. Table 2 shows that the number of polysaccharide molecules with a 3-deoxyaldonic ("metasaccharinic") acid end group was small compared to the number of reducing sugar end groups. Hence, the β-hydroxy elimination of OH-3 in the reducing sugar moieties was of little importance. This holds true both for xylose end groups which give rise to 3-deoxypentonic acids and for hexose end groups which give the diastereomeric 3-deoxyhexonic acids. As expected the number of these groups increased with an increasing time of reaction. 2-C-methylglyceric acid is an important end group formed during alkali treatment of hydrocellulose at 95°C (JOHANSSON, SAMUELSON 1978) and during the kraft cook (LÖWENDAHL, SAMUELSON 1977) but the formation of this acid was not detected in these experiments.

TABLE 2

Carboxylic acids and alditols derived from end groups in wood meal treated with sodium hydroxide for 1 and 2 hours under nitrogen

| Acids and alditols | μmol per 100 g of treated wood meal<br>No addition<br>1 hour | Addition of 1% AQ<br>1 hour | <br>2 hours |
|---|---|---|---|
| 3-Deoxy-*ribo*-hexonic | 9 | 6 | 9 |
| 3-Deoxy-*arabino*-hexonic | 7 | 4 | 8 |
| 3-Deoxy-*erythro*-pentonic | 6 | 7 | 9 |
| 3-Deoxy-*threo*-pentonic | 10 | 6 | 11 |
| Gluconic | 14 | 28 | 71 |
| Mannonic | 7 | 26 | 62 |
| Arabinonic | 6 | 8 | 12 |
| Xylonic | 7 | 12 | 19 |
| Lyxonic | 1 | 8 | 15 |
| Erythronic | 21 | 23 | 22 |
| Threonic | 7 | 8 | 9 |
| Xylitol | 47 | 36 | 22 |
| Lyxitol | 31 | 13 | 8 |
| Mannitol | 202 | 170 | 120 |
| Glucitol | 136 | 109 | 90 |

In contrast to the deoxy acids formed in the absence of oxidants most aldonic acid groups are formed exclusively after an oxidation of the terminal reducing sugar end group. The tetronic acid groups may be obtained by fragmentations and rearrangements even in the absence of added oxidants (JOHANSSON, SAMUELSON 1978). Their formation was hardly affected by the AQ addition nor by the time of reaction while the number of pentonic and hexonic acid end groups was much higher after the alkali treatment in the presence of AQ than in the blank.

Interestingly, the number of hexonic acid groups after treatment in the presence of AQ for two hours was more than twice the number formed after one hour. It has previously been demonstrated in model experiments that the oxidation of dissolved peeling products such as 4-deoxy-2,3-diulose consumed a larger proportion of the additive than that responsible for the formation of aldonic acid end groups. On the other hand the reduced form of the additive (AHQ) formed in these reactions is reoxidized by the reaction with lignin (LÖWENDAHL, SAMUELSON 1978; BASTA, SAMUELSON 1978; FLEMING et al. 1978). Since the additive is mainly present in the reduced form after one hour we conclude that it is reoxidized already at 80°C and that regenerated AQ is mainly responsible for the formation of aldonic acid end groups during the time interval between one and two hours.

The gluconic and mannonic acid end groups must be mainly formed in glucomannan but a small proportion must be derived from the cellulose. Arabinonic acid end groups, formed by fragmentation of the terminal reducing glucose moiety in cellulose is the predominant aldonic acid group after alkaline oxidation of cellulose under conditions prevailing during the ageing of alkali cellulose (SAMUELSON, THEDE 1969). The low proportion of arabinonic acid shows that the fragmentation of the terminal reducing moiety in glucomannan and cellulose is of little importance under the applied conditions. The arabinonic acid end groups which are linked by 1,3-glycosidic bonds are more unstable during alkali cooking than hexonic acid end groups. It is therefore of practical interest that the proportion of arabinonic acid end groups in the wood meal treated in the presence of AQ was small compared to the number of hexonic acid end groups.

The formation of hexonic acid groups by oxidation in the presence of AQ is reflected also in a lower number of reducing hexose end groups (determined as glucitol and mannitol) in the wood meal treated in the presence of the additive than in the blank. The rapid reaction on prolonged treatment is confirmed by the large decrease in the number of reducing hexose end groups when the duration of the treatment was increased from one to two hours.

The presence of xylonic and lyxonic acids shows that xylose end groups in the xylan were converted to these end groups. The number of these groups was higher after alkali treatment in the presence of AQ than in the blank and increased markedly with increasing reaction time. As expected the number of reducing xylose, lyxose and xylulose end groups determined as xylitol and lyxitol (arabinitol) was correspondingly lower than in the blank.

In agreement with results obtained previously a small but significant proportion of pentonic and hexonic acid end groups was formed also in the blank without addition of AQ.

As expected the most abundant acids present in the hydrolyzates were 2-O-(4-O-methyl-α-D-glucopyranosyluronic acid)-D-xylose, 4-O--methylglucuronic and galacturonic acid. The total amount of 4-O--methylglucuronic acid including that determined as the biouronic acid was approximately 1% by weight in the alkali treated samples investigated. Similarly, the proportion of galacturonic (0.3%) and glucuronic (0.04%) acid was unaffected by the presence of AQ and by the change in the time of the treatment.

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