Structure of Eucalyptus Xylans and its Effects on Kraft Pulp Retention

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Abstract

The 4-*O*-methylglucuronoxylans were isolated *Eucalyptus grandis* and *Eucalyptus urograndis* wood by extraction of peracetic acid delignified holocellulose with KOH 24%. The 4-*O*-methylglucuronoxylans content was 14.6% in *Eucalytpus grandis* wood and 17.1% in *Eucalyptus urograndis*. The backbone of these xylans consist of (1→4)-linked β-D-xylopyranosyl units and short side chains of (1→2)-linked 4-*O*-methylglucuronic acids residues (MeGlcA) in a 2.80:10 and 1.90:10 molar ratio in *E. grandis* and *E. urograndis*, respectively, as determined by ^{1}HNMR. Size-exclusion chromatography (SEC) revealed a weigh-average molecular (M_w) of about 28.4 kDa (*P=1.14*) in glucuroxylans of *Eucalytpus grandis* and 26.6 kDa (*P=1.16*) in *Eucalytpus urograndis*. Woods were kraft pulped to similar residual lignin content (kappa number 16) and showed high retention of xylans, 54% and 48,5% for *Eucalyptus grandis* and *urograndis*, respectively. The different xylan retention is associated to differences in degree of branching for MeGlcA of the *Eucalyptus grandis* xylans, that higher than in *Eucalyptus urograndis*. The substitution degree of uronic acids, including MeGlcA and HexA, in the xylans isolated from pulps were 1.07 groups per 10 xyloses units (*E. grandis*) and 0.86 group per 10 xyloses units (*E. urograndis*). The pulp xylans from *E. grandis* showed 0.71 HexA and 0.36 MeGlcA groups per 10 xyloses units, while in *E. urograndis* was 0.36 HexA and 0.50 MeGlcA unit. A significant fraction of these units persist in xylan till the end of pulping and, probably, may contribute to retard the sequential elimination of reducing end groups (peeling) in xylan. During the pulping, the M_w of *E. grandis* and *E. urograndis* xylans is reduced to 20.9 and 19.9 kDa, respectively.

Keywords: 4-*O*-methylglucuronoxylans, *Eucalyptus*, Kraft Pulp.

Introduction

The growing interest in eucalyptus wood has stimulated studies on the structural features of its main constituents and its behavior in the kraft pulping process. Some relevant eucalyptus wood chemistry traits are the content and nature of hemicelluloses. The importance of hemicelluloses for pulp properties have traditionally been interpreted as a contribution to the swelling tendency of the fiber, which facilitates the beating action and gives wet flexibility to fibers during paper formation, and/or a direct strengthening effect of the fiber/fiber bond.

O-Acetyl-4-*O*-methylglucuronoxylans is the dominant component of the hemicelluloses fraction of angiosperm woody biomass, typically comprising 20–35% of the dry wood weight. The backbone of this polymer consists of β-(1→4)-linked xylopyranosyl units with 4-*O*-methyl-α-**D**-glucuronic acid (MeGlcA) attached at the O-2 in xylopyranosyl residues and with *O*-acetyl groups at position C-2 and/or C-3. Their chemical composition has in the past been largely elucidated for various wood species [1–4].

During kraft cooking, lignin, a large portion of the hemicelluloses, and a small portion of the cellulose, are dissolved in the cooking liquor. Although some of the dissolved hemicelluloses, particularly xylan, can be redeposited onto the fiber surface, a large part of the hemicelluloses remain dissolved [5].

The solubility, adsorption behavior and strength of hemicellulose polymers are influenced to various degrees by the neutral monosaccharide and uronic acid residues they contain, as well as their molar mass [6]. Therefore, information concerning the quantity of the hemicelluloses together with their molecular properties (e.g., compositon, frequency of side groups and molar mass parameters) is required in order to understand the fators responsible for their precipitation onto fiber surfaces. This study investigated the importance of the structure of xylan of the *Eucalyptus grandis and Eucalyptus urograndis* kraft in the xylan stability and its retention in fibers, thus affecting the kraft pulping yield.

Experimental

Materials

Industrial eucalyptus wood chips derived from 6- to 8-year-old trees were obtained from different pulp mill sites. Carbohydrates, uronic acids, and acetyl groups in wood were measured according to Kaar *et al*. [7], Scott [8], and Solar *et al*. [9], respectively.

Isolation of 4-*O*-Methylglucuronoxylans of Wood Sawdust

The extractives-free sawdust was delignified with 10% peracetic acid at pH 3.5 and the resulting holocellulose was extracted using 24% KOH [10]. The hemicelluloses were precipitated from the extract after addition of excess ethanol and acidification with formic acid. The xylans were isolated by centrifugation, washed with dry methanol, and dried under vacuum with P_2O_5.

Kraft Pulping Experiments

The screened wood chips (250 g) were cooked under the following conditions: 170ºC maximum temperature, 60 min to temperature, 90 min at temperature, 25% sulfidity, 4:1 (L/kg) liquor–wood ratio, and active alkali dose to achieve kappa number 16.

Isolation of Pulp Xylans

The xylans were extracted from pulps by 10% KOH solution as described elsewhere [11]. The solution was acidified to pH 3.5 with formic acid and an excess of ethanol was added. The xylans were recovered by centrifugation, washed with dry methanol, and dried under vacuum.

Analysis by NMR and SEC

^{1}H and ^{13}C NMR spectra, 2D ^{1}H-^{1}H TOCSY contour map and analysis by SEC were realized according to procedures described elsewhere [12].

Results and Discussion

Xylans Wood

The 4-*O*-methylglucuronoxylans content was 14.6% in *Eucalytpus grandis* wood and 17.1% in *Eucalyptus urograndis*. The 4-*O*-methylglucuronoxylans were isolated of *Eucalyptus grandis* and *Eucalyptus urograndis* wood by extraction of peracetic acid delignified holocellulose with KOH 24%. Extraction yields were in the range of 80% for two woods, indicating efficient removal of these hemicelluloses from the holocellulose fraction.

The ^{1}H NMR spectra of xylans was used as structural reporter signals and for obtaining quantitative data. The anomeric proton resonances of MeGlcA and Xyl are well separated from each other and were used for determination of the carbohydrate composition. The xylans of the *E. grandis* e *urograndis* containing 2.8 and 2.0 4-*O*-methylglucuronic acid substituent for approximately every 10 D-xylose residues, respectively.

Table 1- Relative amounts of MeGlcA, MeGlcA substituted at *O*-2 and Xyl in xylans extracted from *Eucalyptus grandis* and *Eucalyptus urograndis* wood

Sample	MeGlcA/10 Xyl (mol/mol)	MeGlcA substituted at *O*-2/ 10 Xyl (mol/mol)	MeGlcA substituted at *O*-2/Total MeGlcA (mol %)
E. grandis	2.8	0.64	23%
E. urograndis	1.9	0.19	10%

Unlike other hardwoods species studied so far, the NMR analyses revealed that xylans from the different eucalyptus wood species have MeGlcA substituted in *O*-2 (Table 1). These types of *O*-2 linkages in MeGlcA have been found for *E. globulus* by other authors [10]. The *O*-2 linkage likely occurs between xylans and other cellwall polysaccharides such as ramnoarabinogalactans and glucans. This feature could explain why *E. globulus* retains more xylans during kraft pulping than birch, which does not contain *O*-2-substituted MeGlcA [3].

The average molar-mass values were determined by SEC for xylans (Table 2). The average molar-mass values determined here correspond to DP-values of approximately 175 and 164 for the *E. grandis* and *E. urograndis*, respectively.

Table 2- The weight and number-average molar mass values (*Mw* and *Mn*) and the polydispersity indices (*Mw/Mn*) of the xylans wood investigated here

Sample (wood)	*Mw*	*Mn*	Polidispersity (*Mw/Mn*)
E. grandis	28405	24917	1,14

E. urograndis	26525	22866	1,16

Xylans Pulp

The xylans content of the *E. grandis* and *urograndis* pulps (kappa number 16) are 11.7 and 14.6% and yields of extraction, with solution of KOH 10%, were 51 and 52% for *Eucalyptus grandis* and *Eucalyptus urograndis*, respectively.

Considering the original value present in the wood, xylan retention in pulps were 54 and 48.5% for *E. grandis* and *urograndis*, respectively. The difference in retention level was probably due the difference between degree of 4-*O*-methylglucuronoxylan substitution with MeGlcA and molecular weight of xylans wood.

The degree of 4-*O*-methylglucuronoxylan substitution with MeGlcA affects stability across kraft pulping. This result is intriguing because a high degree of substitution with MeGlcA should increase xylan's solubility in alkali and removal during pulping. On the other hand, the fact that MeGlcA is partially O-2 substituted may retard the peeling reaction of xylan chains. In this study, the highest degree of substitution for uronic acids in *E. grandis* xylans contributed to a greater degree of retention of xylan in the pulp.

Significant quantities of uronic acids were retained in the glucuronoxylans extracted from pulp. In addition to the regular MeGlcA and HexA, *O*-2-substituted MeGlcA were also found in the pulp (Table 3).

Table 3- Molar ratios of MeGlcA, *O*-2-substituted MeGlcA, and HexA/10 xyloses in kappa 17 pulp as measured by ^{1}H NMR

Sample	MeGlcA	MeGlcA substituted at *O*-2	HexA	Uronic Acids Total
E. grandis	0.30	0.06	0.71	1.07
E. urograndis	0.46	0.04	0.36	0.85

Additionally, the amount of uronic acids, expressed as a percentage by pulp mass, was calculated (Table 4). With these results and with the content of 4-*O*-methylglucuronic acids present in wood, met the remaining acid content in pulp after kraft cooking (Table 5).

Table 4- Quantification of uronic acids of the pulp xylans for ^{1}H NMR (%, g/100g pulp)

Sample	MeGlcA	MeGlcA substituted at *O*-2	HexA	Uronic Acids Total
E. grandis	0.50	0.10	0.98	1.58
E. urograndis	0.97	0.08	0.63	1.68

Table 5- Uronic acid content retained in kraft pulp of eucalyptus (%, g uronic acids of the pulp/ 100g uronic acids wood)

Sample	MeGlcA	MeGlcA substituted at *O*-2	HexA	Uronic Acids Total

E. grandis	8.52	1.70	16.67	26.89
E. urograndis	13.40	1.16	8.66	23.22

For the analysis of Table 5, we can see that the whole uronic acid initially present in the wood, on average, 25.1 % remains in pulps: 11.0 % in the form of 4-*O*-methylglucuronic acids, 1.4 % as 4-*O*-methylglucuronic acids substituted at *O*-2 and 12.7 % are converted to hexenuronic acids. According MAILEN (2006) [13] the maximum amount of hexenuronic acids which can be found in non-bleached pulps corresponds at 50% 4-*O*-methylglucuronic acids of the wood.

The difference in average molar-mass values of xylans *E. grandis* and *urograndis* wood also explains retention level of xylans in Kraft pulp. *Eucalyptus grandis* xylans also showed average molecular weight (M_w) higher than that of *E. urograndis* xylans, 28.4 against 26.5 kDa, respectively, contributing to retard the removal of xylan from fibres.

For the 4-*O*-methylglucuronoxylans isolated from kraft pulps were observed bimodal curves, in SEC analysis, which were found two main fractions of polysaccharides, hemicelluloses containing an average molar mass greater than 20000 $g.mol^{-1}$ and another of less than 10.000 $g.mol^{-1}$ (Figure 1). The presence of xylans fraction of low molecular weight may be related to the breakdown of the ramifications of these hemicelluloses during kraft pulping. The M_w value obtained here for *E. grandis* was 20224 $g.mol^{-1}$ (66% of xylans with M_w 24300 $g.mol^{-1}$ and 34% with M_w 7541 $g.mol^{-1}$) and for *E. urograndis* was 29960 $g.mol^{-1}$ (76% of xylans with M_w 24228 $g.mol^{-1}$ and 24% with M_w 6443 $g.mol^{-1}$). LISBOA *et al.* (2005) [14] found average molecular weight of 25500 $gmol^{-1}$ for the pulp glucuronoxylans *E. globulus* (Kappa number 13). Moreover, PINTO *et al.* (2005) [15] reported molecular weight of 16000 $g.mol^{-1}$ and 14000 $g.mol^{-1}$ for xylans isolated from *E. globulus* and *urograndis* pulps (kappa number 18.6), respectively.

When compared to the 4-*O*-methylglucuronoxylans wood, it was found that there was a reduction of 29 and 25% for pulp xylans *E. grandis* and *urograndis*, respectively.

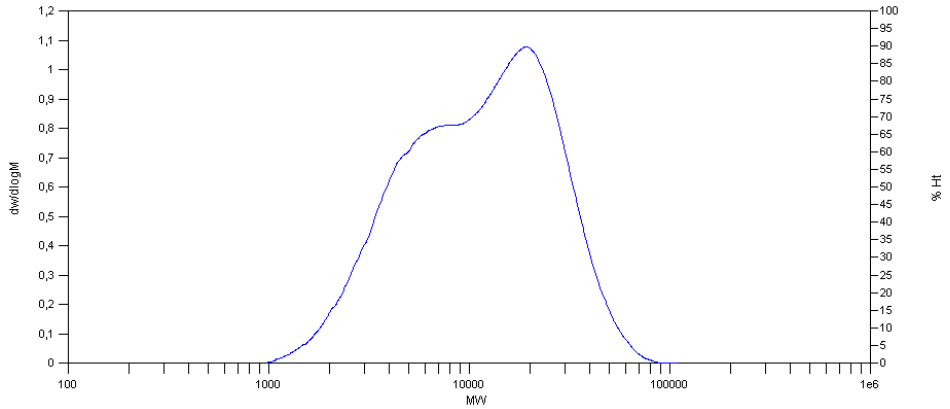

Figure 1– SEC elution curve of *E. grandis* xylan.

Conclusions

The 4-O-methyglucuronoxylans of *E. grandis* and *E. urograndis* presented similar structural compositions but the proportion of each component varied significantly among them. After Kraft cooking, xylan retention in pulps were 54.0 for *E. grandis* and 48.5% for *E. urograndis*. The difference in retention level was probably due the difference between degree of 4-*O*-methylglucuronoxylan substitution with MeGlcA and molecular weight of xylans wood: the xylans of the *E. grandis* e *urograndis* containing 2.8 and 2.0 4-*O*-methylglucuronic acid substituent for approximately every 10 D-xylose residues, respectively. Additionaly, the average molar-mass values determined here correspond to DP-values of approximately 175 for the *E. grandis* xylans and 164 for *E. urograndis* xylans.

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