

Isolation and Characterization of Polysaccharides from Abaca Fiber

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Cellulose and xylan were found to be the major polysaccharide constituents in abaca fiber. Both hemicelluloses I and II were enriched in xylose, together with arabinose and glucose as the other major sugar constituents. These data implied that hemicelluloses I and II are probably composed of arabinoxylan, glucoxylan, and/or xylan, which corresponded with the studies by FT-IR spectroscopy. Arabinose and galactose were higher in all fractions of hemicelluloses I than in those of hemicelluloses II, whereas xylose and mannose were higher in all fractions of hemicelluloses II than in those of hemicelluloses I, suggesting that the dilute alkali pretreatments mainly solubilize the more branched hemicelluloses. The results obtained also suggested that dilute alkali pretreatments favored removal of small molecular chains of hemicelluloses I ($M_w = 75\,000\text{--}130\,000$) as compared to the hemicelluloses II, which had a higher degree of polymerization with molecular average weights between 123 000 and 227 000. Further studies showed that lignins, rich in syringyl units, are tightly associated with hemicelluloses in abaca fiber cell walls.

Keywords: *Abaca fiber; hemicelluloses; celluloses; lignin; alkali pretreatment; sugars; uronic acids; molecular weight; phenolic acids and aldehydes; FT-IR spectroscopy*

INTRODUCTION

Abaca (*Musa textilis* Nee.) fiber, also known as Manila hemp, is an excellent raw material for the manufacture of specialty papers, such as tea bag papers, meat casings, vacuum bags, and wrapping papers since its long fiber length, high strength, and fineness make it a superior material for the production of thin, lightweight papers of high porosity and excellent tear, burst, and tensile strengths (Peralta, 1996; Maddern and French, 1995).

The mature wall of abaca fiber cells consists of cellulose (~60%), hemicelluloses (~21%), pectic substances (~1.0%), and lignin (12–16%). The pectic material is particularly associated with the middle lamellae, and lignin is deposited increasingly with age (Sun et al., 1998a). This naturally high content of cellulose can be exploited for the manufacture cellulose-rich fibers.

The roles of the hemicellulose components in fiber structure are less clear. They do not appear to be absolutely required for the formation of a well-defined secondary wall, as they are absent in cotton fibers. This is probably a consequence of the fact that bast and hard fibers have a different structural role from the seed fibers of cotton (McDougall, 1993). However, the hemicelluloses contribute significantly to fiber properties such as water absorbency, swelling, elasticity, and (wet) strength. Understanding the composition, structure, and location of these polysaccharides, therefore, is important to help explain fiber properties and thus to control fiber quality during processing (Hazendonk et al., 1996).

The hemicelluloses from bast fibers, such as flax, have been extensively studied (Pallesen, 1996; Hazendonk et al., 1996; McDougall, 1993; Gorshkova et al., 1996; Stewart and Morrison, 1995; Stewart et al., 1995).

However, the composition and structure of the hemicelluloses from abaca fiber have not been studied in any depth. McDougall (1993) showed that the flax hemicelluloses contain a β -(1 \rightarrow 4)-linked glucomannan and found evidence for the presence of xylan and some xyloglucan. He also indicated that the hemicelluloses in flax are present near the surface of the fiber.

Alkaline impregnation affects swelling and the formation of a certain tunnel network in the cell walls, facilitating the removal of reaction products from the lignocellulosic matrix (Groot et al., 1994). As part of a continuing study of polysaccharides from abaca fiber, we have now examined the hemicelluloses both solubilized during the alkali pretreatments and extracted from the pretreated and delignified residues. Their chemical compositions, associated lignin composition, and molecular weights are reported.

MATERIALS AND METHODS

Material. Abaca fiber was kindly obtained from the Radcliffe Mill, England. The fibers were cut into 1–2 cm lengths, air-dried, and ground to pass through a 0.7 mm screen. The ground fiber was then stored at 5 °C until used.

Alkali Pretreatments and Isolation of Solubilized and Residual Hemicelluloses. Alkali pretreatments (10 g of fiber/600 mL of alkaline extractants) were performed using sodium hydroxide concentrations of 1, 2.5, and 5% (w/v) solutions, temperatures of 25, 35, and 50 °C, and pretreatment times of 0.5, 2.5, and 5 h under continuous agitation conditions (Table 1 and Figure 1). The alkali soluble hemicelluloses I were recovered by precipitation of the neutralized hydrolysate in 4 volumes of ethanol. Remaining hemicelluloses II were extracted with 17.5% NaOH at 20 °C for 2 h from the pretreated and delignified residues and were isolated as above. The crude hemicellulosic fractions were washed with 70% ethanol and air-dried. The weight of the residue that remained after the 17.5% NaOH extraction, corrected for ash content, was considered to be predominantly cellulose (Figure 1).

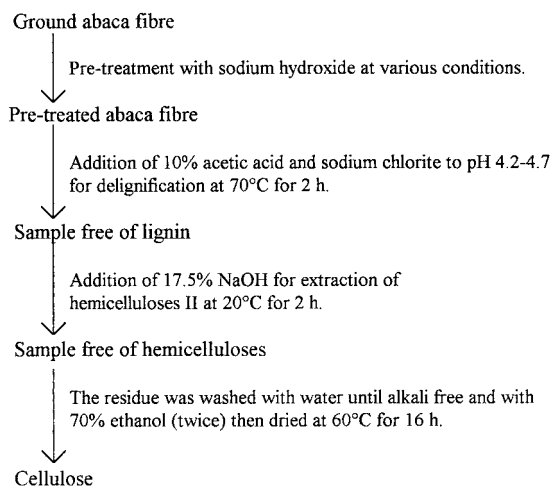
Partial Characterization of Hemicelluloses and Cellulose. The neutral sugar composition of the isolated hemi-

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Table 1. Yields (Percent, w/w) of Hemicelluloses and Cellulose Extracted from Abaca Fiber

alkali pretreatment conditions	fraction	yield		
		hemi-celluloses I ^a	hemi-celluloses II ^b	cellulose ^c
5% NaOH, 25 °C, 0.5 h	1	15.2	5.6	62.7
1% NaOH, 25 °C, 5 h	2	9.2	11.6	62.0
5% NaOH, 25 °C, 5 h	3	15.7	5.1	62.8
1% NaOH, 50 °C, 0.5 h	4	9.2	11.6	62.8
5% NaOH, 50 °C, 0.5 h	5	16.7	4.1	61.9
1% NaOH, 50 °C, 5 h	6	15.4	5.4	63.3
5% NaOH, 50 °C, 5 h	7	19.5	1.4	61.3
2.5% NaOH, 35 °C, 2.5 h	8	14.5	6.3	63.2

^a Yield of hemicelluloses I represents the dissolved hemicelluloses during the various alkali pretreatment processes (10 g of abaca fiber/600 mL of alkaline extractant). ^b Yield of hemicelluloses II represents the hemicelluloses extracted with 17.5% NaOH at 20 °C for 2 h (2.6 g of residue/100 mL of alkali extractant) from the alkali pretreated and delignified abaca fiber residues. ^c Yield of cellulose represents the residues after extraction with 17.5% NaOH at 20 °C for 2 h from the alkali pretreated and delignified abaca fiber samples.

**Figure 1.** Scheme for extraction of residual hemicelluloses from alkali pretreated abaca fiber.

celluloses was determined by GC analysis of their alditol acetates (Blakeney et al., 1983). Alkaline nitrobenzene oxidation of the lignin associated in the hemicelluloses I, and of the residual lignin bound in hemicelluloses II and cellulose, was performed at 170 °C for 3 h. Methods of uronic acid analysis and determination of phenolic acids and aldehydes in nitrobenzene oxidation mixtures with HPLC have been described in previous papers (Lawther et al., 1995; Sun et al., 1996). FT-IR spectra were obtained on an FT-IR spectrophotometer (Nicolet, 750) using a KBr disk containing 1% finely ground samples.

The molecular-average weights of hemicelluloses I and II were determined by gel permeation chromatography on a PL Aquagel-OH 50 column. The samples were dissolved with 0.02 M NaCl in 0.005 M sodium phosphate buffer, pH 7.5, at a sample concentration of 0.1%, and 200 μ L of this solution was injected. The columns were operated at 40 °C, and eluted with 0.02 M NaCl in 0.005 M sodium phosphate buffer, pH 7.5, at a flow rate of 0.3 mL min⁻¹. The column was calibrated with PL pullulan polysaccharide.

RESULTS AND DISCUSSION

Yield of Hemicelluloses and Cellulose. The yields of the hemicelluloses and cellulose, isolated from abaca fiber, are shown in Table 1. All values are calculated on the basis of the mass of untreated starting material. These results showed that abaca fibers contain \approx 21%

Table 2. Composition of Neutral Sugars (Relative Percent Hemicellulosic Sample, w/w) and Content of Uronic Acids (Percent Hemicellulosic Sample, w/w) in the Fractions of Hemicelluloses I Isolated from the Hydrolysates of Alkali Pretreatments of Abaca Fiber

hemicellulosic fraction	neutral sugar composition						uronic acids
	Rha	Ara	Xyl	Man	Glc	Gal	
1	0.55	6.41	75.93	0.37	14.53	2.17	13.06
2	0.61	10.30	61.70	0.40	21.91	5.11	9.70
3	0.48	6.68	77.39	0.29	11.95	3.08	11.44
4	0.82	8.88	46.30	0.59	38.17	4.83	6.02
5	0.60	6.57	67.38	0.40	21.23	3.82	6.82
6	0.64	11.83	50.49	0.60	30.03	6.43	8.56
7	0.42	7.48	72.72	0.26	15.03	4.02	8.33
8	0.58	7.67	74.12	0.42	13.12	4.16	10.58

hemicelluloses and 61.3–63.3% cellulose. As can be seen in Table 1, \sim 44.2–93.8% of the total hemicelluloses and \sim 17.0–30.9% of the total lignin (data not shown) were dissolved under the given alkaline pretreatment conditions. This high solubility of hemicelluloses was probably due to cleavage of the ester bonds between hydroxycinnamic acids and hemicelluloses or lignin by alkali. Increasing sodium hydroxide concentration, extraction time, and temperature produced high yields of solubilized hemicelluloses and lignin during the alkali pretreatment processes. Increasing alkali concentration from 1 to 5% (25 °C, 0.5 h) produced a corresponding increasing solubilization of hemicelluloses from 9.2 to 15.2%. Increases of alkali pretreatment times from 0.5 to 5 h (1% NaOH, 50 °C) and temperatures from 25 to 50 °C (1% NaOH, 5 h) resulted in both significant yields of dissolved hemicelluloses from 9.2 to 15.4%, while pretreatment at a relatively high concentration of alkali (5% NaOH, 25 °C) produced only a small increase of hemicelluloses with an increase of pretreatment time from 0.5 to 5 h. This result indicated that in the initial stage of alkali pretreatment of abaca fiber at a relatively high concentration of alkali (5% NaOH), hemicelluloses are probably deacetylated and a considerable amount of hemicelluloses is dissolved, along with a small amount of lignin. During the next pretreatment stage, most of the lignin polymer and a small amount of the remaining hemicelluloses are dissolved or degraded, which resulted in only a slight increase in dissolved hemicelluloses but a significant yield of solubilized lignin. A much lower yield of hemicelluloses II obtained in fraction 7 (1.4%) is undoubtedly due to a fraction of hemicelluloses (19.5%) being extracted during the 5% NaOH pretreatment at 50 °C for 5 h.

Content of Neutral Sugars and Uronic Acids.

The data on sugar and uronic acid composition of hemicelluloses I and II are summarized in Tables 2 and 3, respectively. Xylose was the major sugar in all of the hemicelluloses, comprising \sim 46–82% of the total sugars. Arabinose and glucose appeared as the other major sugar constituents. Galactose, rhamnose, and mannose were observed as minor constituents. The content of arabinose and galactose was higher in all of the hemicelluloses I, obtained from the pretreatment hydrolysates, than in the hemicelluloses II, isolated with 17.5% NaOH from the alkali-pretreated and delignified residues, whereas the relative amount of xylose and mannose in the hemicelluloses II was higher than in the hemicelluloses I. This phenomenon provides evidence that in abaca fiber cell walls arabinose and galactose, probably as a side chain in hemicelluloses and pectic substances, are easily released, whereas the xylose and mannose in the main chain of hemicelluloses are

Table 3. Composition of Neutral Sugars (Relative Percent Hemicellulosic Sample, w/w) and Content of Uronic Acids (Percent Hemicellulosic Sample, w/w) in the Fractions of Hemicelluloses II Extracted with 17.5% NaOH at 20 °C for 2 h from the Alkali Pretreated and Delignified Abaca Fiber Residues

hemicellulosic fraction	neutral sugar composition						uronic acids
	Rha	Ara	Xyl	Man	Glc	Gal	
1	0.52	5.40	75.64	2.72	13.67	2.12	10.21
2	0.76	5.56	77.03	2.52	11.08	2.25	10.43
3	0.68	5.05	73.69	3.75	14.61	2.24	7.76
4	0.75	4.39	82.10	1.98	8.29	2.48	9.81
5	0.64	4.88	77.22	3.37	11.86	1.98	8.29
6	0.88	3.21	78.29	2.87	12.52	2.23	6.27
7	0.86	3.99	69.28	3.70	20.47	1.85	6.07
8	0.50	4.21	76.02	2.46	14.62	2.14	9.84

Table 4. Composition of Neutral Sugars (Relative Percent Cellulosic Sample, w/w) in the Isolated Cellulose Fractions

cellulose fraction	Rha	Ara	Xyl	Man	Glc	Gal
1	ND ^a	0.36	2.40	1.16	96.06	tr ^b
2	tr	0.37	2.39	1.18	96.04	tr
3	tr	0.33	2.23	1.01	96.43	tr
4	tr	0.37	2.36	1.02	96.22	tr
5	ND	0.20	1.98	0.80	97.00	tr
6	tr	0.18	1.89	0.78	97.10	tr
7	ND	0.10	1.75	0.10	98.00	tr
8	ND	0.16	2.06	0.56	97.20	tr

^a ND, not detectable. ^b tr, trace.

prevented from extraction prior to delignification. These different sugar ratios between the hemicelluloses I and II suggested that the alkali-extracted hemicelluloses I and II may have different structures. Similar results have been reported on polysaccharides in developing flax plants by Gorshkova et al. (1996). The authors reported that xyloglucan constituted the major portion of hemicelluloses in leaves and the growing tip, whereas xylan was the main polysaccharides in fibrous tissues. Further studies showed that the xylans contain (1→4)-β-D-xylosyl units branched exclusively at the xylosyl O-2 with (4-O-methyl)glucosyluronic acid and (galacto)glucomannans (Gorshkova et al., 1996). Our research also confirmed earlier studies reported by McDougall (1993), who found that extraction of the flax with aqueous 24% potassium hydroxide produced the hemicellulosic fraction, which was enriched in xylose and, to a lesser extent, glucose- and galactose-containing polysaccharides. Further extraction of the fiber residue with aqueous 18% potassium hydroxide supplemented with 4% of boric acid removed a hemicellulosic fraction, which was enriched in mannose-containing polysaccha-

rides. Obviously, a much lower content of mannose in all of the hemicellulosic fractions, obtained from abaca fiber in our studies, was probably due to the lack of added boric acid during the alkali extraction processes since extraction of plant material with alkaline boric acid is known to favor the removal of mannose-containing polysaccharides (McDougall, 1993). Uronic acid values averaged ~6–13% in hemicelluloses I and II, which was higher than observed in hemicelluloses extracted from wood or straw samples. These findings are consistent with those of an early study reporting that 4-O-methylglucuronoxylan is the principal noncellulosic polysaccharide of xylem-enriched flax straw (Geerdes and Smith, 1955).

Successive treatment of crude cellulose with 72% H₂SO₄ (2 h, 20 °C) and 3% H₂SO₄ (6 h, 100 °C) produced a neutral sugar composition of glucose, 96.04–98.00%, xylose, 1.75–2.40%, mannose, 0.1–1.18%, and arabinose, 0.1–0.37%, together with trace amounts of galactose and rhamnose (Table 4). The resistance to further extraction with 17.5% NaOH suggested that the hemicelluloses are very strongly associated to the surface of celluloses.

Composition of Phenolic Acids and Aldehydes.

To verify the presence of associated lignin, nitrobenzene oxidation of isolated hemicelluloses I and II as well as cellulose was performed at 170 °C for 3 h. This method provides an estimate of the total amount of lignin and an indication of the composition of phenolic units. In this case, the three constitutive monomeric lignin units *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) are oxidized into corresponding benzaldehydes: *p*-hydroxybenzaldehyde, vanillin, and syringaldehyde (Billa et al., 1996). *p*-Coumaric and ferulic acids in the particular case of the Gramineae are also oxidized to *p*-hydroxybenzaldehyde and vanillin, respectively, and therefore interfere with the analysis. However, at the temperatures of oxidation as low as 120 and 160 °C, these acids are only partially oxidized into the corresponding benzaldehyde, as demonstrated by Iiyama and Lam (1990). The predominant product (Table 5) was identified to be syringaldehyde, which ranged between 67.7 and 73.9% of the total phenolic monomers. Small amounts of *p*-hydroxybenzaldehyde and vanillin, and traces of *p*-hydroxybenzoic acid, vanillic acid, syringic acid, *p*-coumaric acid, and ferulic acid, were also found to be present in the nitrobenzene oxidation mixtures. No significant difference in the phenolic molar ratios was found among the eight isolated hemicellulose I fractions. These higher amounts of syringaldehyde suggested that the majority of the hemicelluloses are linked to lignin

Table 5. Content (Percent Hemicellulosic Sample, w/w) of Residual Lignin and Yield (Percent Hemicellulosic Sample, w/w) of Phenolic Acids and Aldehydes from Alkaline Nitrobenzene Oxidation of Associated Lignin in the Fractions of Hemicelluloses I Isolated from the Hydrolysates of Alkali Pretreatments of Abaca Fiber

phenolic acid or aldehyde	hemicellulosic fraction							
	1	2	3	4	5	6	7	8
<i>p</i> -hydroxybenzoic acid	0.0058	0.014	0.016	0.012	0.012	0.0029	0.0029	0.0058
<i>p</i> -hydroxybenzaldehyde	0.21	0.23	0.13	0.23	0.13	0.087	0.050	0.14
vanillic acid	0.013	0.026	0.019	0.021	0.010	0.010	0.011	0.021
syringic acid	0.064	0.091	0.073	0.091	0.068	0.041	0.046	0.073
vanillin	0.16	0.21	0.17	0.23	0.16	0.12	0.095	0.14
syringaldehyde	1.11	1.33	1.18	1.43	1.16	0.76	0.64	0.84
<i>p</i> -coumaric acid	0.010	0.011	0.0083	0.0086	0.0033	0.0017	0.0016	0.0017
ferulic acid	0.024	0.023	0.012	0.067	0.029	0.034	0.024	0.019
total	1.60	1.94	1.61	2.09	1.57	1.06	0.87	1.24
lignin content	5.94	7.20	5.97	7.75	5.82	3.93	3.23	4.60

Table 6. Content (Percent Hemicellulosic Sample, w/w) of Residual Lignin and Yield (Percent Hemicellulosic Sample, w/w) of Phenolic Acids and Aldehydes from Alkaline Nitrobenzene Oxidation of Residual Lignin in the Fractions of Hemicelluloses II Extracted with 17.5% NaOH at 20 °C for 2 h from Alkali Pretreated and Delignified Abaca Fiber Residues

phenolic acid or aldehyde	hemicellulosic fraction							
	1	2	3	4	5	6	7	8
<i>p</i> -hydroxybenzoic acid	ND	ND	ND	ND	ND	0.0029	ND	ND
<i>p</i> -hydroxybenzaldehyde	0.016	0.019	0.0077	0.0097	0.077	0.0082	0.071	0.0041
vanillic acid	0.018	0.018	0.010	0.0077	0.012	0.0090	0.026	0.0026
syringic acid	0.0046	0.0023	0.0046	0.0034	0.0046	0.0023	0.0046	0.0034
vanillin	0.014	0.012	0.012	0.010	0.0086	0.0079	0.0072	0.0058
syringaldehyde	0.016	0.012	0.020	0.016	0.02	0.012	0.016	0.012
total	0.069	0.063	0.054	0.047	0.055	0.042	0.038	0.028
lignin content	0.26	0.23	0.20	0.17	0.20	0.16	0.14	0.10

^a ND, not detectable.**Table 7. Content (Percent Cellulosic Sample, w/w) of Residual Lignin and Yield (Percent Cellulosic Sample, w/w) of Phenolic Acids and Aldehydes from Alkaline Nitrobenzene Oxidation of Residual Lignin in the Cellulose Fractions Obtained from Alkali Pretreated and Delignified Abaca Fiber Residues**

phenolic acid or aldehyde	cellulose fraction							
	1	2	3	4	5	6	7	8
<i>p</i> -hydroxybenzoic acid	0.012 ^a	0.012	ND	ND	ND	0.0058	0.0014	0.0058
<i>p</i> -hydroxybenzaldehyde	0.012	0.012	0.012	0.014	0.011	0.0071	0.0087	0.0087
vanillic acid	0.0065	0.0077	0.0065	0.0077	0.0077	0.0026	0.0046	0.0044
syringic acid	ND	0.0023	ND	ND	0.0023	ND	ND	ND
vanillin	0.0043	0.0058	0.0050	0.0057	0.0043	0.0014	0.0043	0.0043
syringaldehyde	0.029	0.031	0.035	0.037	0.027	0.012	0.020	0.020
<i>p</i> -coumaric acid	0.0030	0.0016	0.0033	0.0043	0.0033	0.0008	0.0017	0.0008
total	0.067	0.072	0.062	0.069	0.056	0.031	0.041	0.044
lignin content	0.25	0.27	0.23	0.26	0.21	0.12	0.15	0.16

^a ND, not detectable.

via syringyl units, which is consistent with our previous studies on abaca fiber lignins (Sun et al., 1998b).

The occurrence of *p*-coumaric and ferulic acids has been reported in the products of nitrobenzene oxidation of grasses, such as rice callus tissue culture (Uchiyama et al., 1983), wheat straw (Sun et al., 1995; Scalbert et al., 1986), and oil palm fibers (Sun et al., 1998c). The recovery yields of ferulic and *p*-coumaric acids, detected in the products of the alkaline nitrobenzene oxidation, decreased with increase in temperature and reaction time for both wheat straw internodes and leaves. Ferulic acid was not detected among the oxidation products after 4 h at 170 °C or after 2 h at 180 °C, and the molar content in ferulic acid corresponded to an equivalent molar increase in vanillin (Billa et al., 1996). These results suggested that large amounts of ferulic acids were quantitatively oxidized to vanillin by nitrobenzene under the reaction conditions given in our studies (170 °C, 3 h) as shown by a small amount of ferulic acid in the nitrobenzene oxidation mixtures. Similarly, most of the *p*-coumaric acids appeared to be quantitatively oxidized to *p*-hydroxybenzaldehyde under the conditions of the alkaline nitrobenzene oxidation as shown by the trace of *p*-coumaric acid in the nitrobenzene oxidation products. Further studies showed that *p*-coumaric acids were linked to lignin by ester bonds, whereas the ferulic acids are linked to lignin by ether bonds (Sun et al., 1998b).

Due to the hemicellulose–lignin complex in the cell walls of abaca fiber, the lignin content in the hemicelluloses I (3.2–7.8%, Table 5), extracted directly from the lignified fibers, was 23–46 times that of the hemicelluloses II (0.10–0.26%, Table 6), extracted from the alkali-pretreated and delignified residue. Syringalde-

hyde and vanillin were the major components of the phenolic monomers in the mixtures of nitrobenzene oxidation of residual lignin from isolated hemicelluloses II. The absence of *p*-coumaric acid and ferulic acid in the nitrobenzene oxidation products indicated that a majority of these compounds are linked to lignin in abaca fiber cell walls, or they are oxidized into *p*-hydroxybenzaldehyde and vanillin, respectively under the nitrobenzene oxidation condition given (170 °C, 3 h).

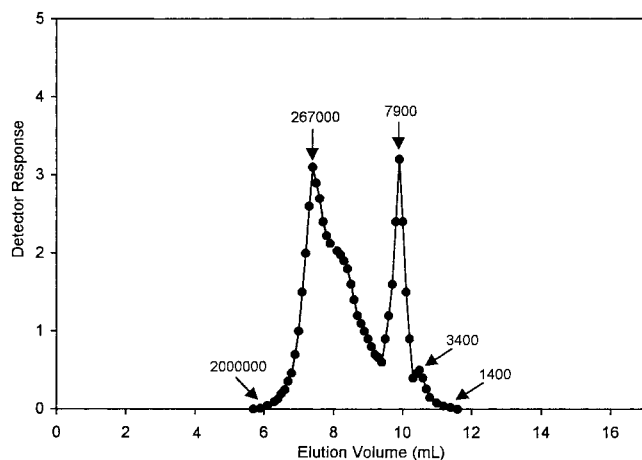
The yield of phenolic acids and aldehydes obtained in the products of alkaline nitrobenzene oxidation of residual lignin from the isolated cellulose is summarized in Table 7. The major compound remaining was found to be syringaldehyde. The low content of associated lignin in cellulose preparations, ranging between 0.12 and 0.27%, indicated a preparation relatively free of lignin.

Molecular Weight Distribution. The weight-average (\bar{M}_w) and number-average (\bar{M}_n) molecular weights as well as the polydispersity (\bar{M}_w/\bar{M}_n) of the hemicelluloses I and II are reported in Table 8. In general, the fractions of hemicelluloses II, isolated with 17.5% NaOH at 20 °C for 2 h from alkali-pretreated and delignified fiber residues, showed a higher degree of polymerization with molecular-average weights between 123 000 and 227 000 than the hemicelluloses I, obtained from the hydrolysates of 1–5% NaOH pretreatments, as shown by the molecular-average weights from 75 000 to 130 000. This suggested that the first alkali pretreatment produced a dissolution of low molecular weight polysaccharides, and the second strong alkali extraction (17.5% NaOH) did not cause a significant degradation of the

Table 8. Weight-Average (\bar{M}_w) and Number-Average (\bar{M}_n) Molecular Weights and the Polydispersity (\bar{M}_w/\bar{M}_n) of the Isolated Fractions of Hemicelluloses I and II

hemicellulosic fraction	\bar{M}_w		\bar{M}_n		\bar{M}_w/\bar{M}_n	
	I ^a	II ^b	I	II	I	II
1	88480	178310	10320	21530	8.57	8.28
2	99570	226990	11060	28830	9.00	7.87
3	94140	159250	11790	24970	8.00	6.38
4	74770	178900	11980	21300	6.24	8.40
5	112970	161500	13150	14720	8.59	10.98
6	12960	184080	16210	19780	8.00	9.30
7	126280	123040	13270	12660	9.51	9.72
8	118830	151780	15300	16440	7.77	9.23

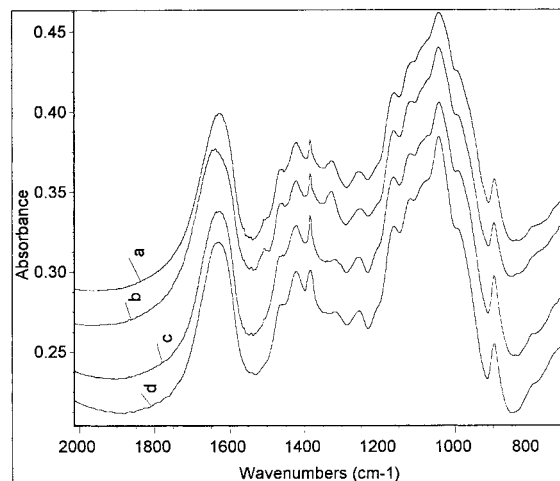
^a Hemicelluloses I isolated from the hydrolysates of various alkali pretreatments of abaca fiber. ^b Hemicelluloses II extracted with 17.5% NaOH at 20 °C for 2 h from the alkali pretreated and delignified abaca fiber residues.

**Figure 2.** GPC molecular weight distribution of hemicelluloses I isolated from the hydrolysate of 1% NaOH pretreatment (50 °C, 5 h).

hemicelluloses and, therefore, resulted in dissolution of large molecular size hemicelluloses from abaca fiber.

The elution profiles for a fraction of hemicelluloses I, isolated from the hydrolysate of 1% NaOH pretreatment at 50 °C for 5 h, showed two major peaks (Figure 2). A large peak I eluted in the volume (7.4 mL) and had a molecular weight equal to 267 000. The second peak showed a molecular weight value around 7900. The low molecular weight (3400) eluted at a small peak III was probably due to the degradative fragmentation of hemicelluloses during the 1% NaOH pretreatment process. As can be seen from the diagram, the distribution had a large fraction of high molecular weight polymers and a small fraction of low molecular weight polymers.

FT-IR Spectra. Figure 3 shows the four FT-IR spectra of hemicellulosic fractions, two from hemicelluloses I (a, b) and two from hemicelluloses II (c, d). The spectral profiles and relative intensities of the bands between a and b or between c and d were rather similar, indicating similar structures of the hemicelluloses. The absorption at 1640 cm^{-1} is principally associated with the C=O stretch of carboxylic anions (salt) for uronic acids in hemicelluloses (Stewart et al., 1995). The prominent band at 1044 cm^{-1} is attributed to the C—OH bending in hemicelluloses. The sharp band at 895 cm^{-1} , which corresponds to the glycosidic C₁—H deformation with ring vibration contribution and OH bending, is characteristic of β -glycosidic linkages between the sugar units (Gupa et al., 1987). A low-intensity band at 1166 cm^{-1} represents the C—O, C—O—C stretching and C—OH bending. The very low intensity band at 997 cm^{-1}

**Figure 3.** FT-IR spectra of hemicelluloses: (a) hemicelluloses I, extracted with 5% NaOH at 50 °C for 5 h during the alkali pretreatment; (b) hemicelluloses I, extracted with 2.5% NaOH at 35 °C for 2.5 h during the alkali pretreatment. (c) hemicelluloses II, extracted with 17.5% NaOH at 20 °C for 2 h from 5% NaOH (50 °C, 5 h) pretreated and delignified fiber residues; (d) hemicelluloses II, extracted with 17.5% NaOH at 20 °C for 2 h from 2.5% NaOH (35 °C, 2.5 h) pretreated and delignified abaca fiber residues.

corresponds to C—O stretching in C—O—C linkages. Bands between 1125 and 1000 cm^{-1} are typical of xylans. The small band at 1125 cm^{-1} corresponds to the C—O and C—C stretching in xylans. The bands at 1254, 1384, 1524, and 1471 cm^{-1} represent C—H bending, CH₂ and OH bending, CH and OH bending, and CH₂ bending, respectively (Kacurakova et al., 1994). The occurrence of small bands at 1512 and 1329 cm^{-1} in spectra a and b (extracted with 5% NaOH at 50 °C for 5 h and with 2.5% NaOH at 35 °C for 2.5 h, respectively, during the alkali pretreatments) is due to the presence of small amounts of associated lignin in the hemicelluloses I. The band at 1512 cm^{-1} indicates the aromatic skeleton vibrations in lignin. The syringyl ring breathing with CO stretching appears at 1329 cm^{-1} . The near absence of these two bands in spectra c and d, extracted with 17.5% NaOH at 20 °C for 2 h from alkali-pretreated and delignified fiber residues, indicates a relative lack of associated lignin in the samples, which corresponds to the results obtained by alkali nitrobenzene oxidation.

In short, pretreatments of abaca fiber with aqueous 1–5% (w/v) sodium hydroxide produced the hemicelluloses I, which contained 3.2–7.8% lignin and had a degree of polymerization giving molecular-average weights between 75 000 and 130 000. Further extraction of the alkali-pretreated and delignified fiber residues with 17.5% NaOH removed the hemicelluloses II, which are relatively free of bound lignin and had a higher degree of polymerization with molecular-average weights between 123 000 and 227 000. Syringaldehyde was found to be a predominant phenolic monomer in all of the alkaline nitrobenzene oxidation products from associated lignin in both hemicelluloses I and hemicelluloses II as well as cellulose, indicating that lignin is associated to hemicelluloses mainly via syringyl units. Both of the hemicelluloses I and II were enriched in xylose and, to a lesser extent, glucose-, arabinose-, and galactose-containing polysaccharides. The contents of arabinose and galactose were higher in all of the hemicelluloses I than in the hemicelluloses II, whereas the amounts of xylose and mannose in the hemicellu-

loses II were higher than in the hemicelluloses I. The results obtained also showed that both of the isolated hemicelluloses I and II contained higher amounts of uronic acids (6–13%) as compared to the hemicelluloses extracted from wood or straw materials.

LITERATURE CITED

- Billa, E.; Tollier, M. T.; Monties, B. Characterization of the monomeric composition of in situ wheat straw lignins by alkaline nitrobenzene oxidation: Effect of temperature and reaction time. *J. Sci. Food Agric.* **1996**, *72*, 250–256.
- Blakeney, A. B.; Harris, P. J.; Henry, R. J.; Stone, B. A. A simple and rapid preparation of alditol acetates for monosaccharide analysis. *Carbohydr. Res.* **1983**, *113*, 291–299.
- Geerdes, J. D.; Smith, F. The constitution of the hemicellulose of the straw of flax (*Linum usitatissimum* Sp.). II. Hydrolysis of the methylated hemicellulose. *J. Am. Chem. Soc.* **1955**, *77*, 3572–3576.
- Gorshkova, T. A.; Wyatt, S. E.; Salnikov, V. V.; Gibeaut, D. M.; Ibragimov, M. R.; Lozovaya, V. V.; Carpita, N. C. Cell-wall polysaccharides of developing flax plants. *Plant Physiol.* **1996**, *110*, 721–729.
- Groot, B. D.; Dam, J. E. G. V.; Zwan, R. P. V. D.; Riet, K. V. Simplified kinetic modeling of alkaline delignification of hemp woody core. *Holzforchung* **1994**, *48*, 207–214.
- Gupta, S.; Madan, R. N.; Bansal, M. C. Chemical composition of *Pinus caribaea* hemicellulose. *Tappi J.* **1987**, *70*, 113–114.
- Hazendonk, J. M. V.; Reinerink, E. J. M.; Waard, P. D.; Dam, J. E. G. V. Structural analysis of acetylated hemicellulose polysaccharides from fibre flax (*Linum usitatissimum* L.). *Carbohydr. Res.* **1996**, *291*, 141–154.
- Iiyama, K.; Lam, T. B. Lignin in wheat internodes. Part 1: The reactivities of lignin units during alkaline nitrobenzene oxidation. *J. Sci. Food Agric.* **1990**, *51*, 481–491.
- Kacurakova, M.; Ebringerova, A.; Hirsch, J.; Hromadkova, Z. Infrared study of arabinoxylans. *J. Sci. Food Agric.* **1994**, *66*, 423–427.
- Lawther, J. M.; Sun, R.-C.; Banks, W. B. Extraction, fractionation, and characterization of structural polysaccharides from wheat straw. *J. Agric. Food Chem.* **1995**, *43*, 667–675.
- Maddern, K. N.; French, J. The potential application of nonwood fibres in papermaking: an Australian perspective. *Appita* **1995**, *48*, 191–196.
- McDougall, G. J. Isolation and partial characterization of the noncellulosic polysaccharides of flax fibre. *Carbohydr. Res.* **1993**, *241*, 227–236.
- Pallesen, B. E. The quality of combine-harvested fibre flax for industrial purpose depends on the degree of retting. *Ind. Crops Prod.* **1996**, *5*, 65–78.
- Peralta, A. G. Pulp produced from decorticated abaca fibre. *Tappi J.* **1996**, *79*, 263–266.
- Scalbert, A.; Monties, B.; Guittet, E.; Lallemand, J. Y. Comparison of wheat straw lignin preparations I. Chemical and spectroscopic characterizations. *Holzforchung* **1986**, *40*, 119–129.
- Stewart, D.; Morrison, I. M. Delignification and bleaching of non-tree fibres with peroxy monosulphate. II. Flax and forage rape. *Cellulose Chem. Technol.* **1995**, *29*, 17–27.
- Stewart, D.; McDougall, G. J.; Baty, A. Fourier transform infrared microspectroscopy of anatomically different cells of flax (*Linum usitatissimum*) stems during development. *J. Agric. Food Chem.* **1995**, *43*, 1853–1858.
- Sun, R.-C.; Lawther, J. M.; Banks, W. B. Influence of alkaline pre-treatments on the cell wall components of wheat straw. *Ind. Crops Prod.* **1995**, *4*, 127–145.
- Sun, R.-C.; Lawther, J. M.; Banks, W. B. Fractional and structural characterization of wheat straw hemicelluloses. *Carbohydr. Polym.* **1996**, *29*, 325–331.
- Sun, R. C.; Goodwin, A.; Lawther, J. M. Fractional and structural characterization of water soluble polysaccharides and pectic substances from abaca fibre. *Carbohydr. Polym.* **1998a**, in press.
- Sun, R. C.; Goodwin, A.; Lawther, J. M. Physicochemical and structural characterization of alkali lignins from abaca fibre. *Wood Chem. Technol.* **1998b**, in press.
- Sun, R. C.; Mott, L.; Bolton, J. Isolation and fractional characterization of ball milled and enzyme lignins from oil palm trunk. *J. Agric. Food Chem.* **1998c**, *46*, 718–723.
- Uchiyama, T.; Sato, J.; Ogasawara, N. Lignification and qualitative changes of phenolic compounds in rice callus. *Agric. Biol. Chem.* **1983**, *47*, 1–10.

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