Characterization and Esterification of Hemicelluloses from Rye Straw

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Hemicelluloses were extracted with 10% KOH/0.5% $Na_2B_4O_7 \cdot 10H_2O$ from delignified rye straw. Esterification of the hemicelluloses with various acyl chlorides was performed in a homogeneous *N*,*N*-dimethylformamide and lithium chloride system using 4-(dimethylamino)pyridine catalyst and triethylamine as a neutralizer. The degree of substitution was controlled between 0.37 and 1.65. Under an optimum condition (sample 14, molar ratio 3:1), >90% of the free hydroxyl groups in native hemicelluloses were stearoylated at 75 °C for 40 min. Meanwhile, the products were characterized by FT-IR and GPC techniques as well as their solubilities. The molecular mass measurements (31400−123300 g mol^{-1}) showed only a minimal degradation of the macromolecular hemicelluloses during rapid reactions at 48−75 °C for 20−40 min.

Keywords: *Rye straw; extraction; hemicelluloses; esterification; homogeneous system*

INTRODUCTION

Rye straw is a major agricultural residue with a worldwide annual yield of ∼40−50 million tons (Ghaly and Ergudenler, 1994). This straw and other agricultural byproducts are abundant renewable resources for animal feed, bioconversion to sugars, and paper-making, especially in countries where wood is limited such as China, India, and Malaysia (Gatewood et al., 1998). These byproducts are not used as industrial raw materials on a significant scale as most of the straw is discarded as a waste in developed countries (Montane et al., 1998).

Hemicelluloses are present in amounts equal to cellulose but are synthesized by a different path than cellulose (Gabrielii and Gatenholm, 1998). Hemicelluloses are polymers that can be extracted from plant cell walls by alkali. Most hemicelluloses are water soluble after alkaline extraction. Isolation is a two-stage process, involving alkaline hydrolysis of any ester groups followed by extraction into aqueous media (Doner and Hicks, 1997). Hemicelluloses are associated with lignin, mainly by covalent bonds (Sun et al., 1998). Hydroxycinnamic acids, particularly ferulic and *p*-coumaric acids, occur widely in cell walls of graminaceous plants such as rye straw with *p*-coumaric acid esterified to lignin or hemicelluloses and ferulic acid identified as linked to lignin through ether bonds and to hemicelluloses through ester bonds (Sun et al., 2000). From such associations, hemicelluloses can be freed during alkaline extraction. Polyphenolics such as lignin can also form alkali-resistant linkages with the hemicelluloses. Thus, hemicellulosic preparations probably contain some residual lignin.

The principal constituents of rye straw are cellulose (35−38%) and hemicelluloses (30−37%). The latter are L-arabino-D-xylans with various degrees of branching. The main polysaccharide chain consists of D-xylopyranose (Xyl*p*) units linked glycosidically by β (1→4) bonds. Side chains consist of L-arabinofuranosyl (Ara*f*) units linked by α (1→3) bonds. The uronic acid, mainly 4-*O*-methyl-D-glucuronic acid (MeGlcA), is bound to D-xylosyl units of the main chain by α (1→2) bonds (Sun et al., 1999). The hemicelluloses also contain small amounts of glucosyl and galactosyl units. Some trace amounts of rhamnose and mannose units were found in the neutral fractions.

Recent research on the technological applications of natural hemicelluloses has been receiving considerable attention because these compounds are characterized by a high hydrolytic stability and easy biodegradability. Examples of potential future applications of hemicelluloses are as food additives, thickeners, emulsifiers, gelling agents, adhesives, and adsorbents (Gabrielii and Gatenholm, 1998). However, due to their hydrophilic nature, hemicelluloses blended with hydrophobic plastics have poor mechanical properties. The hydrophilicity of hemicelluloses results in their inability to form a continuous phase with the synthetic polymer. These shortcomings can be overcome by etherification or esterification of the hydroxyl groups and cross-linking. Hence, we report optimized conditions for preparing esterified hemicelluloses in a homogeneous solution of *N*,*N*-dimethylformamide (DMF)/lithium chloride (LiCl). The modified hemicelluloses are expected to exhibit increased hydrophobic character due to the incorporation of long alkyl groups. Products are characterized by yield of esterified hemicelluloses, degree of substitution, FT-IR spectroscopy, molecular size, and solubility.

MATERIALS AND METHODS

Materials. Rye straw was provided by Compak Co. (Gainsborough, U.K.). The composition (% w/w, dry basis) of the straw is 37.9% cellulose, 36.9% hemicelluloses, 17.6% lignin, 3.3% protein, 3.0% ash, and 2.0% wax. The straw was cut into 1−2 cm lengths by hand, ground to pass a 0.7 mm screen, and stored at 5 °C. 4-(Dimethylamino)pyridine (DMAP) and triethylamine (TEA) were of reagent grade. DMF was dried according to conventional methods. Anhydrous LiCl was obtained by drying at 130 °C for 2 h. Other reagent chemicals

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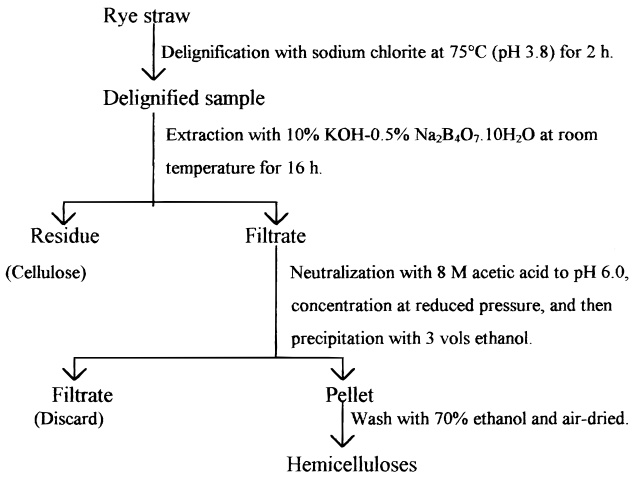

Figure 1. Scheme for extraction of hemicelluloses from rye straw.

such as acetyl chloride (AC), propionyl chloride (PC), *n*-octanoyl chloride (OC), phthaloyl dichloride (PDC), decanoyl chloride (DC), lauroyl chloride (LC), palmitoyl chloride (PAC), stearoyl chloride (SC), and oleoyl chloride (OLC) were purchased from Aldrich Chemical Co. (Gillingham, U.K.).

Isolation and Characterization of Hemicelluloses. Isolation of hemicelluloses from rye straw is shown in Figure 1. Ground straw was first delignified with sodium chlorite in acetic solution (pH 3.8, adjusted by 10% acetic acid solution) at 75 °C for 2 h. Hemicelluloses were extracted from the delignified residue with 10% KOH/0.5% $Na_2B_4O_7 \cdot 10H_2O$ at room temperature for 16 h with a liquor ratio from 1:20. The solubilized hemicelluloses were isolated by precipitation of the neutralized extract (pH 6.0) by 3 volumes of 95% ethanol. After filtration, the pellets of the hemicelluloses were washed with 70% ethanol and air-dried.

The neutral sugar composition of the isolated hemicelluloses was determined by hydrolysis and gas chromatography (GC) analysis of their alditol acetates (Blakeney et al., 1983). Methods of uronic acid analysis, determination of phenolic acids and aldehydes in nitrobenzene oxidation mixtures with high-performance liquid chromatography (HPLC), and measurement of the native hemicellulosic molecular weight have been described in previous papers (Lawther et al., 1995; Sun et al., 1995, 1996).

FT-IR spectra were obtained on an FT-IR (Nicolet 750) spectrophotometer using a KBr disk containing 1% finely ground samples. The solution-state ^{13}C NMR spectrum was obtained on a Bruker 250 AC spectrometer operating in the FT mode at 62.4 MHz under total proton decoupled conditions. It is recorded at 25 °C from 150 mg of sample dissolved in 1.0 mL of D_2O after 10000 scans. A 60° pulse flipping angle, a 3.9 μs pulse width, and an 0.85 s acquisition time were used.

Esterification of Hemicelluloses. Hemicelluloses (0.6 g, 0.009 mol of hydroxyl functionality) in 30 mL of distilled water were heated to 80 °C under stirring until dissolved (~5 min). Then a 30 mL volume of DMF was added, and the mixture was stirred for another 5 min. Water was removed from the swollen gel by distillation under reduced pressure at 50 °C. To this mixture were added dropwise 0.15 g of LiCl, 0.10 g of DMAP, and corresponding amounts (molar ratio 1:1 to 1:3) of various acyl chlorides (AC, PC, OC, DC, LC, PAC, SC, and OLC; Table 1) and phthaloyl dichloride (PDC) together with required amounts of TEA (110−215 wt % of the native hemicelluloses), previously dissolved in 15 mL of DMF, and the homogeneous reaction mixture was stirred for a total period of 20, 30, 35, and 40 min at temperatures of 48, 65, and 75 °C, respectively. The reaction was stopped by cooling the reaction mixture with water. After being cooled to room temperature, the homogeneous reaction mixture was slowly poured into 120 mL of 95% ethanol with stirring. Organic solvents were removed by dissolution in ethanol. The white product that separated from the solution was filtered off and collected. The product was washed thoroughly with 95% ethanol and acetone, air-dried for 24 h, and further dried in an oven at 55 °C for another 24 h.

Table 1. Yield[a] of Esterified Hemicellulose and Degree of Substitution (DS)

esterification conditions				esterified hemicelluloses		
molar ratio[b]	temp (°C)	time (min)	TEA[c] (%)	sample	yield (%)	DS
1:2 (X, AC)	48	20	140	1	71.1	0.52
1:2 (X, PC)	65	20	140	2	62.6	0.37
1:2 (X, OC)	65	20	120	3	44.7	0.37
1:2 (X, OC)	75	35	180	4	62.2	0.92
1:1 (X, PDC)	75	30	235	5	81.7	1.26
1:2 (X, DC)	65	30	150	6	44.6	0.42
1:3 (X, DC)	75	40	180	7	70.2	1.15
1:2 (X, LC)	75	30	150	8	41.2	0.40
1:3 (X,,LC)	75	40	220	9	78.2	1.38
1:2 (X, PAC)	75	30	150	10	34.9	0.34
1:3 (X, PAC)	75	40	220	11	81.8	1.48
1:2 (X, SC)	75	30	110	12	38.7	0.47
1:3 (X, SC)	75	35	180	13	76.8	1.47
1:3 (X, SC)	75	40	240	14	87.8	1.65
1:2 (X, OLC)	75	30	110	15	36.3	0.41
1:3 (X, OLC)	75	40	180	16	74.6	1.28

[a] Based on the assumption that all of the hemicelluloses are converted to di-esterified hemicellulose (yield, 100%; DS, 2.0). If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would be 61.0% for acetylation, 54.1% for propionylation, 34.4% for octanoylation, 50.3% for phthaloylation, 29.9% for decanoylation, 26.6% for lauroylation, 21.7% for palmitoylation, 19.8% for stearoylation, and 20.0% for oleoylation, respectively. [b] Molar ratio represents the moles of xylose (X) in hemicelluloses per mole of acetyl chloride (AC), propionyl chloride (PC), *n*-octanoyl chloride (OC), phthaloyl dichloride (PDC), decanoyl chloride (DC), lauroyl chloride (LC), palmitoyl chloride (PAC), stearoyl chloride (SC), and oleoyl chloride (OLC), respectively. [c] TEA (%) represents the weight percentage of hemicelluloses (w/w).

Characterization of the Esterified Hemicelluloses. The yield percentages were calculated on the basis of the assumption that the hemicellulose was converted to di-esterified hemicelluloses. Hence, the yield percentage and degree of substitution (DS) would be 100% and 2.0, respectively. The unreacted acyl chloride in the reaction mixture was separated from the product by dissolution in 95% ethanol and acetone. If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would be 61.0% for acetylation, 54.1% for propionylation, 34.4% for octanoylation, 50.3% for phthaloylation, 29.9% for decanoylation, 26.6% for lauroylation, 21.7% for palmitoylation, 19.8% for stearoylation, and 20.0% for oleoylation, respectively.

The average molecular weights of esterified hemicelluloses were determined by gel permeation chromatography (GPC) on a PLgel 5μ Mixed-D column. The samples were dissolved in pyridine/LiCl (0.1%, w/w) at a concentration of 0.1%, and 200 μL of sample solution was injected. The column was operated at 80 °C and eluted with pyridine/LiCl at a flow rate of 1 mL min^{-1}. The column was calibrated using PL pullulan polysaccharide standards. The solubility of the esterified hemicelluloses was measured at 3.0% concentration in different organic solvents.

RESULTS AND DISCUSSION

Characterization of the Isolated Hemicelluloses. On the basis of the dry weight of rye straw, treatment of the holocellulose with 10% KOH/0.5% $Na_2B_4O_7 \cdot 10H_2O$ at room temperature for 16 h yielded 30.8% hemicelluloses. The neutral sugar composition showed that xylose is a predominant component sugar, which comprised 78.3% of the relative total sugars. Arabinose (12.4%) appeared as the second major sugar component. Glucose (5.9%) and galactose (2.5%) appeared in small

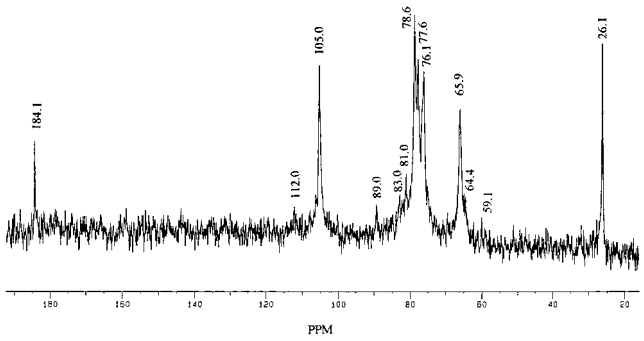

Figure 2. ^{13}C NMR spectrum (in D_2O) of native hemicelluloses extracted with 10% KOH/0.5% $Na_2B_4O_7 \cdot 10H_2O$ at 25 °C for 16 h from delignified rye straw.

amounts. Rhamnose (0.6%) and mannose (0.4%) were present as minor sugar constituents. The uronic acids, mainly MeGlcA, were present in a noticeable amount (5.0%). GPC showed that the native hemicelluloses had a weight-average molecular mass of 28460 g mol^{-1} with a polydispersity of 2.2.

The ^{13}C NMR spectrum of the native hemicelluloses is shown in Figure 2. The spectrum was interpreted on the basis of reported data for arabinoxylan, glucuronoxylan, and L-arabino-(4-*O*-methyl-D-glucurono)-D-xylan, as well as for the wheat straw hemicelluloses extracted before delignification (Kato et al., 1987; Focher et al., 1989; Ebringerova et al., 1992; Imamura et al., 1994; Sun et al., 1996). The main 1,4-linked β-D-Xyl*p* units are characterized by the signals at 105.0, 78.6, 77.6, 76.1, and 65.9 ppm, which, respectively, are attributed to C-1, C-4, C-3, C-2, and C-5 of the β-D-Xyl*p* units. The signals at 112.0, 89.0, 83.0, 81.0, and 64.4 ppm correspond to C-1, C-4, C-2, C-3, and C-5 of α-L-Ara*f* residues, respectively. A very weak signal at 59.1 ppm originates from C-4 of the 4-*O*-methoxyl group of the glucuronic acid unit in the xylan. The strong signal at 26.1 ppm related to $-CH_3$ in MeGlcA or in $Ar-COCH_3$, resulting from the associated lignins. The signal at 184.1 ppm originates from the carboxylic group of MeGlcA.

Rye straw was delignified with sodium chlorite under the acidic condition. The hemicelluloses were obtained by extraction of the residues with 10% KOH/0.5% $Na_2B_4O_7 \cdot 10H_2O$. The hemicelluloses obtained contained 2.6% residual lignin. To identify the composition of the associated lignin, alkaline nitrobenzene oxidation of the isolated hemicelluloses was performed at 170 °C for 3 h. The results revealed that vanillin (0.37% w/w), vanillic acid (0.19%), and syringaldehyde (0.15%) constituted ~70% of the total phenolic acids and aldehydes in the oxidation mixture. Small amounts of ferulic acid (0.081%), *p*-hydroxybenzaldehyde (0.077%), *p*-hydroxybenzoic acid (0.052%), syringic acid (0.045%), acetosyringone (0.021%), acetovanillone (0.018%), and *p*-coumaric acid (0.013%) were also identified in the nitrobenzene oxidation products. This relatively high amount of vanillin and vanillic acid indicated that the lignins in the cell walls of rye straw are linked to hemicelluloses mainly via guaiacyl units. The occurrence of small amounts of ferulic and *p*-coumaric acids in the oxidation mixture indicated that hydroxycinnamic acids are closely associated with hemicelluloses and lignin in the cell walls of rye straw.

Yield and Degree of Substitution. Because unreacted acyl chloride had been removed from the isolated products, the DS values of the modified hemicelluloses were determined from the yield percentage of esterified hemicelluloses on the basis of a theoretical value of two acyl units per xylose unit. The yield percentage and the degree of substitution (DS) are summarized in Table 1. Clearly, the yield and DS of the products depended on the molar ratio of reactant agents, reaction duration, amounts of TEA, and temperature used. Increases in molar ratio of DC/X from 2:1 (sample 6) to 3:1 (sample 7), reaction duration from 30 to 40 min, TEA concentration from 150 to 180%, and temperature from 65 to 75 °C resulted in a significant yield increase from 44.6 to 70.2% and a DS value increase from 0.42 to 1.15. Similar observations were found between samples 3 and 4, 8 and 9, 10 and 11, 12 and 13, and 15 and 16. These increases in yield and DS by increment of the reactant concentration could be interpreted in terms of greater availability of acyl chloride molecules in the proximity of the hemicellulosic molecules at higher concentration of the esterifying agent (Khalil et al., 1995). This observed phenomenon was consistent with the study on acetylation of maize starch by Khalil et al. (1995). Table 1 also shows that the yield and DS increased with the increase of TEA concentration and reaction duration. For example, increments of TEA concentration from 180 to 240% and reaction duration from 35 to 40 min between samples 13 and 14 resulted in growth of yield and DS from 76.8 to 87.8% and from 1.47 to 1.65, respectively. The highest yield (87.8%) and DS (1.65) were obtained using 3 M stearoyl chloride/xylose in hemicelluloses ratio, 240% TEA concentration, and 40 min time of reaction at 75 °C (sample 14).

The esterification of hemicelluloses was performed in a homogeneous DMF/LiCl system, using acyl chloride to exchange hemicellulose O−H protons. Many of the problems encountered during the esterification of hemicelluloses can be greatly reduced or eliminated by the use of homogeneous organic solutions. We found that first dissolution of native hemicelluloses in water and then treatment in a dipolar aprotic solvent such as the DMF/LiCl system can lead to a highly swollen gel suspension of the polymer and activate the polymers. Owing to their property of forming hydrogen bonds, strongly polar aprotic solvents are able to prevent the aggregation of flexible hemicellulose chains, promoting the interactions between substrate and reagents (Focher et al., 1989). Another obvious advantage of this solvent system for the preparation of hemicellulose derivatives lies in the ability to conduct a variety of organic reactions, producing a high degree of substitution under mild conditions and increasing the efficiency of such reactions in homogeneous solutions. A further advantage of the homogeneous reaction system is the extremely high swelling degree of the polymer because hemicelluloses in the lithium salt form can be activated in the same manner (Vogt et al., 1996). Additionally, DMF/LiCl acted as the solvent for the esterified hemicelluloses, which would ensure not only high substitution but also more uniform substitution due to greater accessibility of the reagent (McCormick and Callais, 1987). Furthermore, the lower reagent quantities required and a rapid reaction process were two other significant advantages for the esterification of hemicelluloses in the homogeneous DMF/LiCl system. All in all, the homogeneous esterification of hemicelluloses dissolved in DMF/LiCl represents a suitable, rapid, and effective method for the preparation of esterified hemicelluloses. The degree of substitution can be simply controlled by the molar ratio of acyl chloride/xylose unit

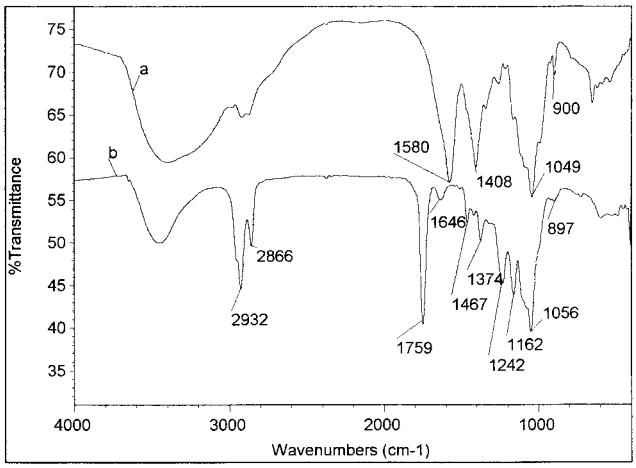

Figure 3. FT-IR spectra of native hemicelluloses (a) and octanoylated hemicelluloses (b, sample 3).

in hemicelluloses. Such a conclusion has been already drawn for cellulose derivatives prepared in an *N*,*N*-dimethylacetamide/LiCl solvent system (McCormick and Callais, 1987; Rahn et al., 1996).

Structural studies on native rye straw hemicelluloses showed that these hemicelluloses are essentially (1→4) β-D-xylan with L-Ara*f* and MeGlcA groups as side chains (Sun et al., 2000). The molar ratios of xylose/arabinose/MeGlcA in native hemicelluloses, isolated with 10% KOH/0.5% $Na_2B_4O_7 \cdot 10H_2O$ at room temperature for 16 h from the delignified rye straw holocellulose in this study, are approximately 85:12:3. For every 7 D-Xyl*p* residues in the main chain, there is 1 L-Ara*f* group as a side chain, and for every 28 such D-Xyl*p* residues, there is 1 MeGlcA unit as a side chain. On the basis of this branched structure of hemicellulose, for every 28 D-Xyl*p* residues in the backbone, there are 5 side chains attached at C-2 or C-3 of xylose in the main chain, which, however, needs to be confirmed by methylation analysis of the hemicelluloses. This implied that for every 28 D-Xyl*p* residues in the hemicelluloses only 51 hydroxyl groups are free, allowing a maximum DS of 1.82. Sample 14 (Table 1) gave a maximum yield of 87.8%, and the highest DS value of 1.65 suggested that >90% of the free hydroxyl groups in native hemicelluloses were stearoylated under the reaction condition used. It is likely that for complete substitution (DS, 1.82), a higher proportion of acyl chloride or a longer reaction time is needed.

The esterifying reaction mechanism involved an attack of the acyl carbon center by a nucleophile such as DMAP and neutralization of hydrochloric acid by TEA. In general, DMAP, a widely used versatile hypernucleophilic acylation catalyst, is 10^4 times more active than pyridine during the esterification process. Similarly, TEA is more efficient than pyridine as an acid acceptor and stabilizes the reaction pH between 5.5 and 6.0. This lessens the possibility of acid-catalyzed degradation of the hemicelluloses.

FT-IR Spectra. The FT-IR spectra of native hemicelluloses (spectrum a) and octanoylated hemicelluloses (spectrum b, sample 3) are given in Figure 3. The absorbances at 1580, 1408, 1049, and 900 cm^{-1} seen in spectrum a are associated with native hemicelluloses. A sharp band at 900 cm^{-1} is characteristic of β-glucosidic linkages between the sugars units (Gupta et al., 1987). This confirmed that the xylose residues forming the backbone of the macromolecule are linked by β form

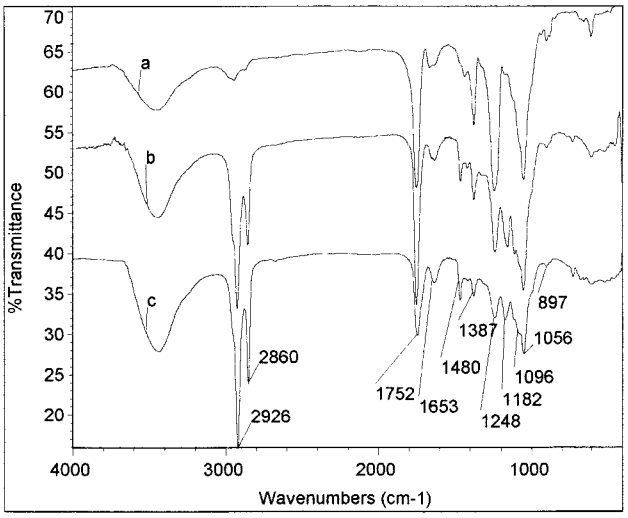

Figure 4. FT-IR spectra of acetylated hemicelluloses (a, sample 1), decanoylated hemicelluloses (b, sample 6), and oleoylated hemicelluloses (c, sample 15).

bonds. The absorption at 1580 cm^{-1} is principally associated with the C═O stretch of carboxylic anion (salt) for MelcA in native hemicelluloses. The high intensity at 1408 cm^{-1} implies the CH and OH bending in native hemicelluloses. A strong absorption band at 1056 cm^{-1}, largely due to the stretching of a C−O bond (Kacurakova et al., 1994), is present in the spectra of both native and esterified hemicelluloses, and its intensity was negligibly affected by octanoylation, whereas other bands for native hemicelluloses decreased significantly in the octanoylated products. The spectrum of octanoylated hemicelluloses (spectrum b) shows three important ester bands at 1759 (C═O ester), 1242 (−C−O− stretching), and 1162 cm^{-1} (C−O−C vibration) (Saikia et al., 1995). Two other prominent bands at 1467 and 1374 cm^{-1} in spectrum b are attributed to CH_2 and C−H bending, respectively, in octanoylated hemicelluloses. Two increasing peaks at 2866 and 2932 cm^{-1} in spectrum b indicate the methyl and methylene C−H stretching in octanoylated hemicelluloses. Esterification is also evident from the decrease of the hydroxyl absorption at 3400 cm^{-1} in spectrum b. The lack of peak at 1802 cm^{-1} in spectrum b indicates that the products are free of unreacted acyl chloride.

The evolution of the FT-IR spectra of acetylated hemicelluloses (sample 1, spectrum a), decanoylated hemicelluloses (sample 6, spectrum b), and oleoylated hemicelluloses (sample 15, spectrum c) with variation of the acyl group is shown in Figure 4. These spectra are characterized by the presence of three important bands: a C═O (in ester) stretching band at 1752 cm^{-1}, a C−H deformation band at 1387 cm^{-1}, and a C−O stretching band at 1248 cm^{-1}. The lack of a peak at 1802 cm^{-1} in the spectra indicates that the esterified hemicellulosic preparations are free of unreacted acyl chloride. Figure 5 shows the FT-IR spectra of native hemicelluloses (spectrum a) and phthaloylated hemicelluloses (spectrum b, sample 5). The formation of aromatic ester reactions was confirmed by the appearance of an ester carbonyl absorbance at 1740 cm^{-1}, and the purity of the product was shown by the absence of phthaloyl dichloride, by the lack of phthaloyl chloride absorbance at 1802 cm^{-1}, and by the disappearance of the carboxylic group absorbance at 1700 cm^{-1}. This complete aromatic esterification by the phthaloyl dichloride was largely due to the versatile hypernucleophilic

Table 2. Weight-Average ($\bar{M}_w$) and Number-Average ($\bar{M}_n$) Molecular Weights and Polydispersity ($\bar{M}_w/\bar{M}_n$) of the Esterified Hemicellulosic Fractions

	esterified hemicellulosic preparations[a]												
	1	2	3	4	5	6	7	8	9	10	12	13	15
$\bar{M}_w$	31600	31400	34900	51600	43300	36400	62800	38100	77800	39800	49200	99400	46300
$\bar{M}_n$	30400	29300	33200	46100	39400	35600	54600	34000	67100	35200	42800	77700	38600
$\bar{M}_w/\bar{M}_n$	1.04	1.07	1.05	1.12	1.10	1.08	1.15	1.12	1.16	1.13	1.15	1.28	1.20

[a] Corresponding to sample number in Table 1.

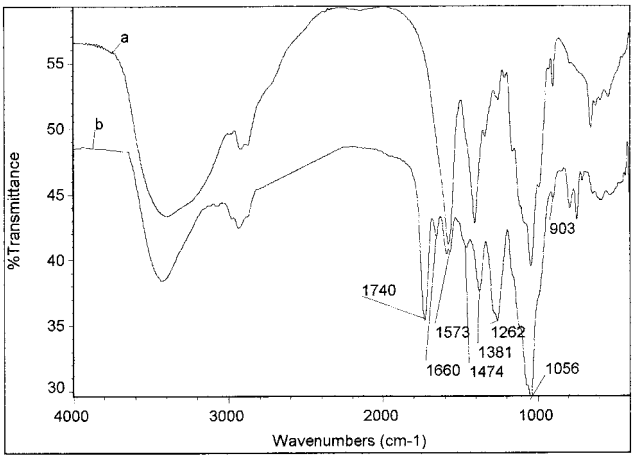

Figure 5. FT-IR spectra of native rye straw hemicelluloses (a) and phthaloylated hemicelluloses (b, sample 5).

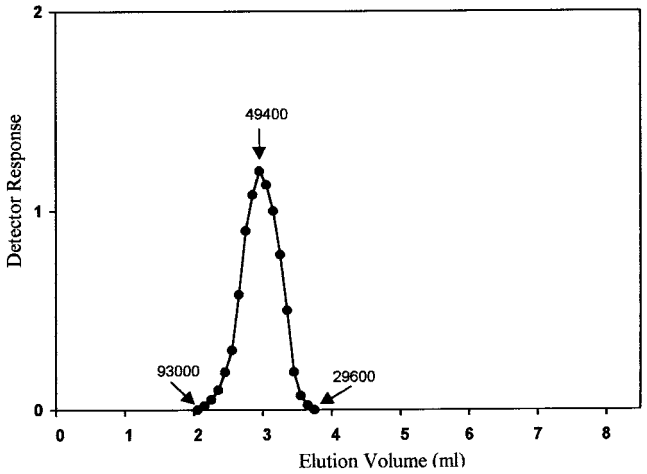

Figure 6. GPC molecular weight distribution of stearoylated hemicelluloses (sample 12).

acylation catalyst, DMAP, and the strong neutralizer, TEA, used in the homogeneous reaction. Signals at 1381 and 1262 cm^{-1} indicate the C−H deformation and C−O stretching, respectively. Aromatic skeleton vibrations are assigned at 1598 and 1474 cm^{-1} (Scalbert et al., 1986).

Molecular Weight. The molecular weights of selected hemicellulosic derivatives were determined to illustrate whether degradation occurred during the reaction in DMF/LiCl system. The weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights and polydispersity ($\bar{M}_w/\bar{M}_n$) of the esterified hemicelluloses were computed from their chromatograms, and the results are given in Table 2. The theoretical molecular masses were based on the molecular weight of the starting native hemicelluloses ($\bar{M}_w$= 28460 g mol^{-1}) and the value of DS. The data showed that the molecular weights of esterified hemicellulosic preparations were slightly lower than the calculated values by 8−13%. This indicated that only a minimal degradation occurred during the reaction conditions used. The GPC molecular weight distribution of stearoylated hemicelluloses (sample 12) is illustrated in Figure 6. The elution profile of the esterified hemicelluloses showed a narrow polymolecularity, ranging from 29600 to 93000 g mol^{-1} with a main peak at 49400 g mol^{-1}.

Solubility. Introduction of hydrophobic acyl or aromatic groups in the molecular structure of hemicelluloses would be expected to alter their solubility properties. Such alteration would rely essentially on the degree of substitution (Rahn et al., 1996; Lepeniotis and Feuer, 1997). The primary studies showed that all of the samples, esterified with various acyl chlorides and aromatic acyl chloride within in the DS range, are soluble in dimethyl sulfoxide (DMSO) at 25 °C and in pyridine at 80 °C. In addition, the samples of low DS such as sample 10 are also partially soluble in chloroform, dichloromethane, toluene, and tetrahydrofuran (THF) at room temperature. Variation in solubility of trimethylsilylated polysaccharides has been reported by Rahn et al. (1996). They found that samples of low DS are soluble in DMSO and *N*,*N*-dimethylacetamide (DMA), those of medium DS in tetrahydrofuran, and samples of high DS in hexane or CCl_4 only. The results obtained in our experiments also showed that the esterified hemicelluloses can form the films and membranes from the solution by casting and evaporating of the solvent. This work, however, needs further examination.

Overall, esterification of the free hydroxyl groups from hemicelluloses in the homogeneous DMF/LiCl system using DMAP as a catalyst and TEA as a base represents a suitable, rapid, and effective method for the esterification of rye straw hemicelluloses. The degree of substitution can be simply controlled by the molar ratio of acyl chloride/xylose unit and by adjusting the TEA concentration, reaction time, and temperature. Under the strongest reaction conditions examined (molar ratio 3:1, 240% TEA, 75 °C, 40 min), >90% of the hydroxyl groups of the rye straw hemicelluloses were stearoylated. Thus, both the procedure and the rye straw hemicelluloses are satisfactory for producing hemicellulose esters.

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