Esterification of Wheat Straw Hemicelluloses in the *N,N*-Dimethylformamide/Lithium Chloride Homogeneous System

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ABSTRACT: The esterified hemicelluloses were prepared under homogeneous reaction conditions in the system *N,N* -dimethylformamide/lithium chloride by reacting the native hemicelluloses with various acyl chlorides (C_3—C_{18}) in the presence of 4-dimethylaminopyridine as a catalyst and triethylamine as a base within 30 min at 70–75°C. The products obtained were characterized by means of Fourier transform IR chromatography, gel permeation chromatography, thermal analysis, and solubility. The degree of substitution of esterified hemicelluloses was controlled between 0.38 and 1.75 as a function of experimental conditions. Under an optimum reaction condition xylose unit/acyl chloride (molar ratio 1 : 3, tetraethylammonium % 160, 75°C, 30 min), about 95% hydroxyl groups in native hemicelluloses were esterified. The molecular weight measurements showed a minimal degradation and hydrolysis of the products. The thermal stability of the products was also increased by modification. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2301–2311, 1999

Key words: esterification of hemicelluloses; homogeneous solution; hemicellulose solvent

INTRODUCTION

Hemicelluloses comprise roughly one-fourth to one-third of most plant materials, and this amount will vary according to the particular plant species. For examples, annual plants and woods contain about 25–35% hemicelluloses.[1] The predominating constituents of wheat straw are cellulose (~38%) and hemicelluloses (~32%).[2] The latter are commonly removed from plant materials by extraction with dilute alkali and are isolated by neutralization of the alkaline extracts and by alcohol precipitation. Hemicelluloses, isolated from wheat straw, are D-xylans [usually bearing side chains of other sugars, such as 4-*O*-methyl-α-D-glucopyranosyluronic acid (MelcA) and L-arabinose], which consist of about 200 β-xylopyranose residues linked together by 1,4-glycosidic bonds.[3] The hemicelluloses are, in general, contaminated to a small extent by neutral polysaccharides containing glucose and galactose units. Some trace amounts of rhamnose and mannose are also found in the neutral fractions.[4]

The preparation and properties of new polymers from hemicelluloses should thus be an important part of any research program aimed at utilizing annually renewable, agriculturally derived polymers as extenders and replacements for polymers prepared from petrochemicals. However, the hemicelluloses with one or two free hydroxyl groups are hydrophilic, and synthetic polymers are usually hydrophobic. This results in significantly different solubility characteristics of

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the hemicelluloses, i.e., solubility in aqueous alkali but insolubility in virtually all organic solvents. Furthermore, due to their different chemical and molecular structure—i.e., branched, amorphous, composed of several different types of monosaccharides (heteropolysaccharides), and consisting of different types of functional groups (i.e., OH groups, acetoxy groups, carboxyl groups, methoxyl groups, etc.)—hemicelluloses represent a different type of polysaccharide that behaves differently with cellulose and starch, which reduce their use in industrial applications. These shortcomings can be overcome by their modification, such as by partial hydrolysis, oxidation, reduction, etherification or esterification of the hydroxyl groups, and crosslinking. Up to now, cellulose and starch have been the main starting materials for the bulk production of modified polysaccharides, and their derivatives have found use in the industrial production of food, textiles, paper, and cosmetics, while analogous polymerizations with hemicelluloses as the substrates have received comparatively little attention. The reason for this is presumed due to the different behaviors of the hemicelluloses during modification than cellulose and/or starch derivatives. O'Malley and Marchessault[5] prepared and characterized graft copolymers of aspenwood 4-*O*-methylglucuronoxylan by allowing the fully methylated polysaccharide to react with either living polystyrene or living poly(2-vinylpyridine). Church[6] reported the preparation of aspenwood 4-*O*-methylglucuronoxylan graft copolymers by the ammonium persulfate-sodium thiosulfate-initiated reaction with sodium acrylate. Fanta et al.[1] and El-Shinnawy and El-Kalyoubi[7] independently investigated the graft copolymerization of acrylonitrile onto hemicelluloses using ceric ammonium nitrate as an initiator and stated that the graft yield depends on the monomer and initiator concentration as well as reaction time and temperature. Fan and Fen[8] illustrated that carboxymethyl-modified hemicelluloses can be used as a new antitumor drug in which the modified hemicelluloses augment cellular immunity by enhancing the number and activity of immunocytes. However, due to the hydrophilic nature in xylan, a number of hemicellulose derivatives were currently prepared under heterogeneous conditions in our previous studies. Aside from the inherently unfavorable reaction kinetics, some problems such as poor uniformity of substitution, low yields, and extensive by-product formation arise during the heterogeneous solutions (unpublished data). Based on the procedures of derivatization of cellulose in lithium chloride (LiCl) and *N,N*-dimethylacetamide (DMA) solutions, proposed by McCormick and co-workers,[9,10] we investigated to find suitable reaction media to perform derivation reactions in homogeneous phase, in which the substitutions along the hemicellulose backbone can be achieved with satisfactory yields and with little depolymerization of the hemicellulose chains. Strongly polar aprotic solvents such as *N,N*-dimethylformamide (DMF) were found to be able to prevent the aggregation of flexible hemicellulose chains, promoting the interactions between substrate and reagents in our recent studies. Esterification of the hydroxyl groups of hemicelluloses with acyl chloride to increase hydrophobicity is one approach toward increasing the water resistance of hemicelluloses. Derivatization of hemicellulose hydroxyl groups may also reduce the tendency of hemicelluloses to form strong hydrogen-bonded networks and increase film flexibility.

In this work, we report optimized synthetic conditions for preparing esterified hemicelluloses in homogeneous solutions of DMF/(LiCl). The products are characterized by yield of esterification, degree of substitution (DS), Fourier transform IR (FTIR) spectroscopy, molecular size, solubility, and thermal analysis.

EXPERIMENTAL

Materials

Wheat straw was obtained from the Silsoe Research Institute (Silsoe, Bedfordshire) and was ground in a Christie laboratory mill to pass a 0.7 mm size screen. The ground straw was dried in a cabinet oven with air circulation for 16 h at 60°C and then stored at 5°C until used. DMF solvent was dried prior to use according to conventional methods. Anhydrous LiCl was dried at 130°C for 2 h before use. Other reagent grade chemicals such as propionyl chloride (PC), butyryl chloride (BC), hexanoyl chloride (HC), *n*-octanoyl chloride (OC), decanoyl chloride (DC), lauroyl chloride (LC), palmitoyl chloride (PAC), stearoyl chloride (SC), oleoyl chloride (OLC), 4-dimethylaminopyridine (DMAP), and triethylamine (TEA) were purchased from Aldrich Chemical Company (England).

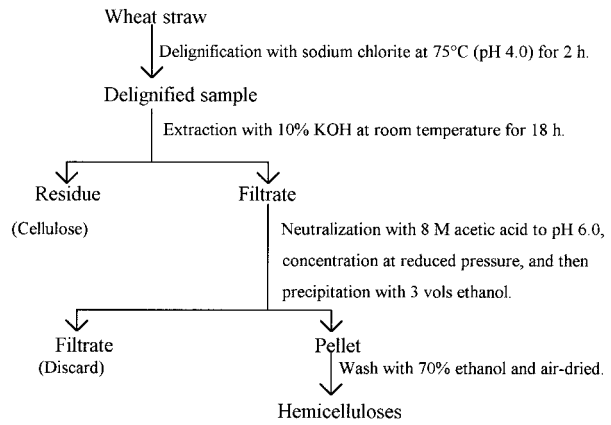


Figure 1 Scheme for extraction of hemicelluloses from wheat straw.

Isolation and Characterization of the Native Hemicelluloses

Wheat straw hemicelluloses were isolated after removal of lignin by the method described previously.[2,11,12] The straw was first delignified with sodium chlorite in acetic solution (pH 4.0, adjusted by 10% acetic acid) at 75°C for 2 h. The hemicelluloses were then obtained from the holocellulose by extraction with 10% potassium hydroxide for 18 h at room temperature with a liquor ratio of 1:20. The hemicelluloses were recovered by precipitation of the neutralized hydrolysate in 3 volumes of 95% ethanol. After filtration, the pellets of the hemicelluloses were washed with 70% ethanol and then air dried (Fig. 1).

Hemicelluloses were analyzed for neutral sugars and uronic acids after hydrolyzing 10 mg samples for 2 h at 120°C in 7 mL of 2.0*M* trifluoroacetic acid (sealed vials). Samples were evaporated to dryness and the sugars were then converted to their alditol acetates. The sugar derivatives in dichloromethane were analyzed by gas chromatography, and the relative percentages were calculated.[13] Alkaline nitrobenzene oxidation of residual lignin from hemicellulosic preparations was performed at 170 C for 3 h. The lignin content in hemicelluloses was calculated by 2.40 multiplying the yield of phenolics, obtained by nitrobenzene oxidation.[14] Methods of uronic acid analysis, determination of phenolic acids, and aldehydes in nitrobenzene oxidation mixtures with high performance liquid chromatography, and measurement of the native hemicellulosic molecular weights have been described in previous papers.[2,12]

FTIR spectra were obtained on an FTIR (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 200 mg of sample dissolved in 1.0 mL D_2O after 10,000 scans. A 60° pulse flipping angle, a 3.9 μs pulse width and 0.85 s acquisition time were used.

Esterification of Hemicelluloses

The amount of 0.6 g hemicelluloses (0.008 mol of hydroxyl functionality) in 30 mL distilled water were heated to 80°C under stirring until completely dissolved (approximately 5 min). Then 30 mL DMF was added and the reaction was stirred for another 5 min. The water was removed from the swollen gel by repeated distillation under reduced pressure at 50°C. To this mixture, 0.15 g LiCl, 0.10 g DMAP, and corresponding amounts of various acyl chlorides (PC, BC, HC, OC, DC, LC, SC, and OLC, Table I) with required amounts of TEA (% of the native hemicelluloses, w/w) in 15 mL DMF were gradually added over a time period of 10 min, while stirring the reaction mixture at 70 or 75°C. The resulting reaction mixtures were continued stirring for a total period of 15, 20, 25, and 30 min at 70 or 75°C, respectively. After being cooled to room temperature, the homogeneous reaction mixture was slowly poured into 120 mL of 95% ethanol with stirring. The white product that separated from the solution was filtered off and collected. The filtrate was washed thoroughly with 95% ethanol and acetone. The product was first air dried for 24 h and then further dried in an oven at 55°C for another 24 h.

Characterization of the Esterified Hemicelluloses

The yield percentages were calculated based on the assumption that all of the hemicelluloses were converted to diesterified hemicelluloses (Scheme 1). In the case the yield percentage and the DS would be 100% and 2.0, respectively. The unreacted acyl chloride in a mixture of reaction was separated from the product by dissolving in 95% ethanol and acetone. If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would be 54.1% for propionylation, 48.8% for butyrylation, 40.2% for hexanoylation, 34.4% for octanoylation, 29.9% for decanoylation, 26.6% for lauroylation, 21.7% for

Table I The Yield[a] of Esterified Hemicelluloses and DS

	Esterification Conditions			Esterified Hemicelluloses		
Molar Ratio[b]	Temperature (°C)	Time (min)	TEA (%)[c]	Sample	Yield (%)	DS
1 : 2 (X : PC)	75	15	28	1	70.3	0.70
1 : 3 (X : PC)	75	15	170	2	86.5	1.41
1 : 3 (X : PC)	75	15	360	3	91.0	1.60
1 : 3 (X : BC)	75	20	360	4	89.4	1.59
1 : 2 (X : HC)	70	20	360	5	74.3	1.14
1 : 2 (X : OC)	70	20	170	6	55.3	0.64
1 : 2 (X : OC)	70	20	180	7	64.1	0.91
1 : 2 (X : OC)	70	20	254	8	73.9	1.20
1 : 2 (X : DC)	70	20	110	9	63.4	0.95
1 : 2 (X : DC)	70	20	145	10	66.9	1.05
1 : 2 (X : LC)	70	30	145	11	61.6	0.95
1 : 2 (X : PAC)	75	30	116	12	64.4	1.09
1 : 1 (X : SC)	75	20	68	13	35.1	0.38
1 : 1.5 (X : SC)	75	25	83	14	44.0	0.60
1 : 1.5 (X : SC)	75	30	95	15	50.3	0.76
1 : 2 (X : SC)	75	25	118	16	55.0	0.88
1 : 3 (X : SC)	75	30	160	17	90.1	1.75
1 : 3 (X : OLC)	75	30	160	18	75.8	1.40

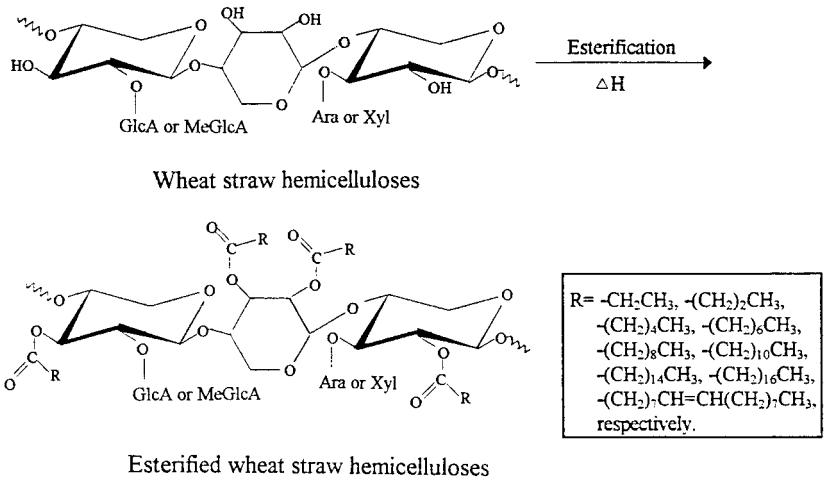
[a] Based on assumption that all of the hemicelluloses are converted to diesterified hemicelluloses (yield, 100%; DS, 2.0). If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would be 54.1% for propionylation, 48.8% for butyrylation, 40.2% for hexanoylation, 34.4% for octanoylation, 29.9% for decanoylation, 26.6% for lauroylation, 21.7% for palmitoylation, 19.8% for stearoylation, and 20.0% for oleoylation with a DS value of 0.0, respectively.

[b] Molar ratio represents the mol of xylose units in hemicelluloses/mol of PC, BC, HC, OC, DC, LC, PAC, SC, and OLC, respectively.

[c] TEA (%) represents the weight percentage of hemicelluloses (w/w).

palmitoylation, 19.8% for stearoylation, and 20.0% for oleoylation with a degree of substitution 0.0, respectively. The solubility was measured at 5% concentration in different organic solvents.

The molecular-average weights of the esterified hemicellulosic preparations were determined by gel permeation chromatography (GPC) on a PLgel 5μ Mixed-D column. The samples were dis-



Scheme 1 Esterification of wheat straw hemicelluloses.

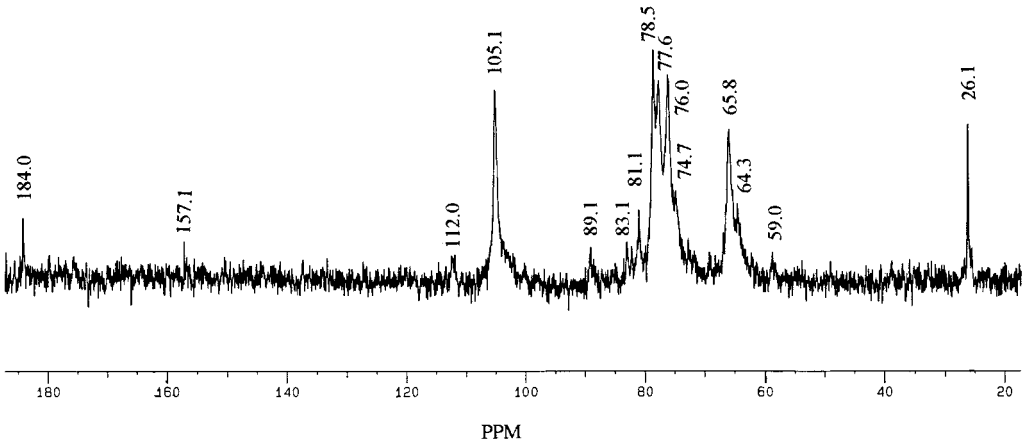


Figure 2 ^{13}C-NMR spectrum (in D_2O) of native hemicelluloses extracted with 10% KOH at 25°C for 28 h from delignified wheat straw.

solved in pyridine/LiCl (0.1%, w/w) at a concentration of 0.1%, and a 200 μL sample in solution was injected. The column was operated at 80°C and eluted with pyridine at a flow rate of 1 mL min^{-1}. The column was calibrated using PL pullulan polysaccharide standards.

Thermogravimetric analysis of the esterified hemicellulosic preparations was performed with a Simultaneous Thermal Analyser (STA 625). This apparatus provides for a continuous measurement of sample weight at a range of temperatures between ambient and 600°C. Samples of approximately 10 mg weight were heated in a platinum crucible to 600°C at a heating rate of 10°C min^{-1}. Provision was made for electronic differentiation of the weight signal to give the rate of weight loss. Air was used as the purge gas, and a positive pressure was maintained through the weighing chamber.

RESULTS AND DISCUSSION

Structural Characterization of the Isolated Native Hemicelluloses

The yield of hemicelluloses was found to be 32.6% of the dry wheat straw. The sugar analysis showed that xylose was present as a predominant sugar component, comprising 81.4% of the total sugars. Arabinose (10.1%) appeared as the second major sugar constituent. Glucose (4.6%), galactose (3.0%), and rhamnose (1.0%) were observed as minor constituents. The uronic acids, mainly MelcA, were present in a noticeable amount (5.2%). The results obtained by GPC analysis showed that the native hemicelluloses had a weight-average molecular weight of 28, 600 g mol^{-1} with a polydispersity of 6.0, corresponding to a degree of polymerization of 190. Further studies by nitrobenzene oxidation showed that the isolated native hemicelluloses contained approximately 1.0% residual lignin. The main product in the oxidation mixture was identified to be vanillin (0.18% of hemicelluloses, w/w), which comprised about 40% of the total phenolic monomers. Small amounts of *p*-coumaric acid (0.055%), syringic acid (0.054%), vanillic acid (0.051%), *p*-hydroxybenzaldehyde (0.044%), syringaldehyde (0.032%), and ferulic acid (0.025%), and traces of protocatechuic acid (0.0087%), gallic acid (0.0066%), and *p*-hydroxybenzoic acid (0.0054%), were also found to be present in the nitrobenzene oxidation products. This relatively higher amount of vanillin suggested that the majority of the lignins in the wheat straw cell walls are linked to hemicelluloses via guaiacyl units.

To confirm the structural features of the native hemicelluloses, the isolated hemicelluloses were analyzed by ^{13}C-NMR spectroscopy in D_2O (Fig. 2). This allows elucidation of the polymer backbone and can also be employed to evaluate the type of side chains branching along the backbone.[15,16] The spectrum was interpreted on the basis of reported data for structurally defined arabinoxylan type, glucoronoxylan type, and L-arabino-(4-*O*-methyl-D-glucurono)-D-xylan, as well as those of wheat straw hemicelluloses extracted before delignification.[12,15,17–19] The main 1,4-linked β-D-Xylp units are obviously characterized by the signals at 105.1, 78.5, 77.6, 76.0, and 65.8

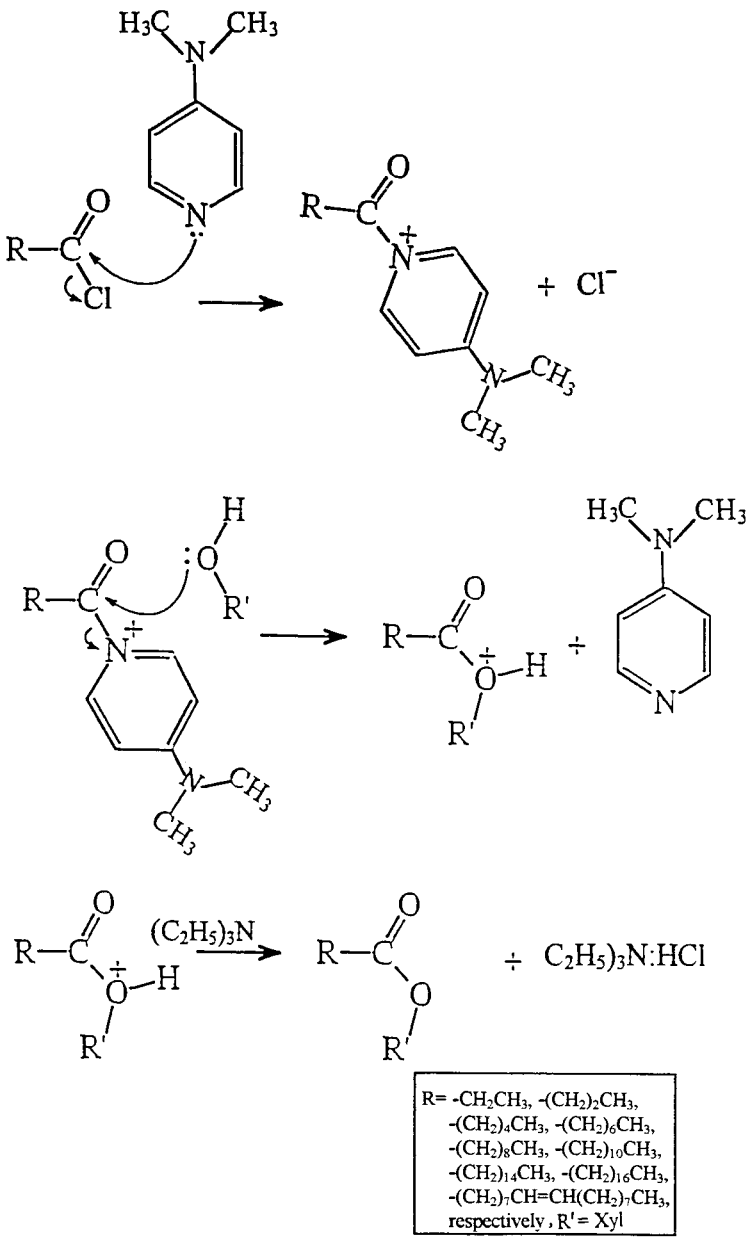
ppm, which respectively attributes to C-1, C-4, C-3, C-2, and C-5 of the β-D-Xylp units. The signals at 112.0, 89.1, 83.1, 81.1, and 64.3 ppm correspond to C-1, C-4, C-2, C-3, and C-5 of α-L-Araf residues, respectively. Signals at 74.7 and 73.1 ppm (data not shown) correspond to C-2 and C-5 in 1,2,4-linked β-D-Xylp units, respectively. The signal at 59.0 ppm originates from the 4-*O*-methoxyl group of glucuronic acid residue in the xylan. This very weak signal is in accord with the low uronic acid content. The signal at 26.1 ppm relates to —CH_3 in MelcA or in Ar—$COCH_3$, resulting from the associated lignins. The signal at 184.0 ppm originates the carboxylic group in salts of MelcA. These signals with further methylation analysis clearly show that α-(1 → 2)-linked MeGlcA unit and α-(1→3)-linked L-Araf and D-Xylp units represent the main side chains of the xylan backbone.[12]

Yield Percentage and Degree of Substitution

The homogeneous esterification of hemicelluloses in the DMF/LiCl system represents a suitable and effective method for the chemical modification of hemicelluloses, especially esterification. The degree of substitution can be simply controlled by the molar ratio of xylose unit in hemicelluloses/acyl chloride. The DMF/LiCl system acts as a solvent for both the starting hemicelluloses and the final products, and the reactions could be conducted within a short period of time. The yield percentage and degree of substitution are given in Table I. Due to the lack of associated unreacted acyl chloride in isolated products, the DS values of the hemicellulose derivatives were determined from the yield percentage of esterified hemicelluloses on the assumption of each xylose in xylan containing two free hydroxyl groups. As can be seen in Table I, the yield percentage and DS varied from 35.1 to 91.0% and 0.38 to 1.75, respectively. Lowest yield (35.1%) and DS (0.38) were obtained from sample 13 when the low molar ratio (1:1) and low concentration of TEA (68%) were used. This indicated that if the esterification reaction did not proceed to give a high degree of substitution, mostly unreacted or lightly esterified hemicelluloses were obtained. On the other hand, five samples (2, 3, 4, 17, and 18) with a reactant molar ratio of 1:3 and TEA concentration of 160–360% gave products with higher yields between 75.8 and 91.0%, corresponding to DS values between 1.40 and 1.75. Increasing molar ratios from 1:1 to 1:3 and TEA concentrations from 68 to 160% (samples 13–17) resulted in a significant increment of esterification reaction efficiency as shown by both yield from 35.1 to 90.1% and DS value from 0.38 to 1.75, respectively. This 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.[20] It is probably that the hemicellulose hydroxyls are immobile and their reaction will therefore rely on the availability of the acyl chloride molecules in the vicinity of hydroxyl groups.

In the present work, we studied the esterification reaction of hemicelluloses in a new nonaqueous swollen system, using acyl to exchange hemicellulose O—H protons. Obviously, a progressive increase of product yield and DS was observed on increasing the molar ratio (acyl chloride/anhydroxylose unit) up to 3.0 and TEA concentration up to 160%. The highest DS value (1.75) was obtained using 3.0 molar stearoyl chloride per molar anhydroxylose ratio, 160% TEA, and 30 min reaction time (sample 17). These data showed that a high rate of proton exchange between acyl and hydroxyl groups of hemicellulose chains occurred under the conditions given. The 160% TEA and 30 min was sufficient to obtain the high yield and DS. In comparison with the esterification of hemicelluloses in the heterogeneous phase, lower reagent quantities and much shorter reaction time were required. The same advantage was observed with respect to the sulfopropylation of cellulose and starch carried out in a mixture of alkaline organic solvent, which required high temperature.[15] It was found that first dissolution of native hemicelluloses in water and then treatment in a dipolar-aprotic solvent like DMF with LiCl resulted in a high swollen gel suspension of the polymer. Owing to their property of forming hydrogen bonds, strong polar aprotic solvents are able to prevent the aggregation of flexible hemicellulose chains, promoting the interactions between substances and the reagents.[15] Furthermore, the hemicelluloses in the lithium salt form can be further activated. This brought about an extremely high degree of swelling, and therefore enhanced the esterification not only by high substitution but also by more uniform substitution due to greater accessibility of the reagent.[21] These features assure uniform substitution and lessen the chance of degradation of the hemicellulose backbone by acid hydrolysis.

In a previous study, we showed that the hemicelluloses, extracted with 0.5*M* NaOH at 30°C for



Scheme 2 Mechanism of esterification of wheat straw hemicelluloses.

2 h from lignified wheat straw, were a (1 → 4)-linked β-D-xylan with D-glucopyranosyluronic acid (or MelcA) group attached at position 2, and L-arabinofuranosyl and D-xylopyranosyl groups attached at position 3. For every 26 D-xylopyranosyl residues in the main chain, there is one uronic acid. For 13 such D-xylopyranosyl residues, there is one L-arabinofuranosyl group, and for 18 such D-xylopyranosyl residues, there is one D-xylopyranosyl group. Based on this branched structure, for every 20 D-xylopyranosyl residues in the main chain, there are three side chains attached at C-2 or C-3 of xylose in the main chain, and therefore there are only 37 free hydroxyl groups that can be esterified, and this can account for a maximum yield value less than 100%, 94%, and a maximum DS value less than 2.0, 1.85. The highest DS value was obtained from sample 17, in which the DS was 1.75, corresponding that approximately 95% of the free hydroxyl groups in native hemicelluloses were stearoylated under the conditions given. One possible reason for this lack of complete reaction is presumed due to the relatively high molecular weight of the hemicellulose sub-

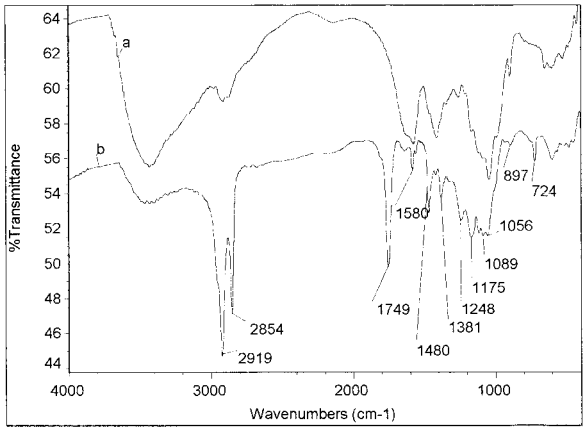


Figure 3 FTIR spectra of native hemicelluloses (spectrum a) and palmitoylated hemicelluloses (spectrum b).

strate, which is not significantly degraded by the DMF/LiCl solvent during a very short period of 30 min. A second explanation for incomplete reaction is probably due to the high viscosity of the reaction medium, leading to diffusion-controlled kinetics.[9] In order to gain a complete substitution (DS, 1.85), addition of more mol of acyl chloride per mol of free OH groups or prolonging reaction duration is needed.

The reaction mechanism involves an attacking of the acyl carbon center by a nucleophile such as DMAP and a removal of hydrochloric acid by TEA (Scheme 2).[9,22] It was found that DMAP, a widely used versatile hypernucleophilic acylation catalyst, was 10^4 times more active than pyridine during the esterification, and TEA, used as a base, has a more significant efficiency than the pyridine. Addition of TEA can counteract the hydrochloric acid by forming amine salt. Furthermore, DMF forms strong hydrogen bonds with hydroxyl groups of hemicelluloses, changing to some extent the original pattern of intra- and intermolecular hydrogen bonds within and between the hemicellulose chains. Meanwhile, the proton acceptor properties of DMF increase the nucleophilicity of hydroxyl groups—hence the reactivity toward various electrophilic agents.[15]

FTIR Spectra

A comparison of FTIR spectra of native hemicelluloses with that of palmitoylated hemicelluloses (sample 12) are given in Figure 3. The absorbancies at 1640, 1580, 1418, 1346, 1260, 1176, 1090, 1048, and 897 cm^{-1} seen in the spectrum (a) are associated with native hemicelluloses. A sharp band at 897 cm^{-1} is characteristic of β-glucosidic linkages between the sugars units.[23] This confirmed that the xylose residues forming the backbone of the macromolecule are linked by β-form bonds. Clearly, all these original bands for native hemicelluloses decreased significantly in the esterified products. Meanwhile, the esterification reactions were monitored by observing in the FTIR spectra a reduction in the acyl chloride carbonyl absorbance at 1802 cm^{-1} and the appearance of an ester carbonyl absorbance at 1749 cm^{-1}. The spectrum of palmitoylated hemicelluloses (b) provides evidence of palmitoylation by showing the presence of two important ester bands at 1749 (C═O ester) and —C—O— stretching band at 1248 cm^{-1}.[24] The appearances of other three prominent bands at 1480, 1381, and 1175 cm^{-1} in spectrum b are attributed to the CH_2 bending, C—H bending, and C—C stretching, respectively, in palmitoylated hemicelluloses. Two increasing peaks at 2854 and 2919 cm^{-1} in spectrum b indicates methyl and methylene C—H stretching in palmitoylated hemicelluloses. A small peak at 3400 cm^{-1} in spectrum b represents the unexchanged hydroxyl. The absorption at 1580 cm^{-1} in both spectra is principally associated with the C═O stretch of carboxylic anion (salt) for MelcA in native hemicelluloses and products. The band at 1052 cm^{-1} may be assigned to C—O stretching. The disappearance of peaks at 1802 cm^{-1} in spectrum b indicated that the products are free of the unreacted acyl chloride.

Figure 4 shows the FTIR spectra of propiony-

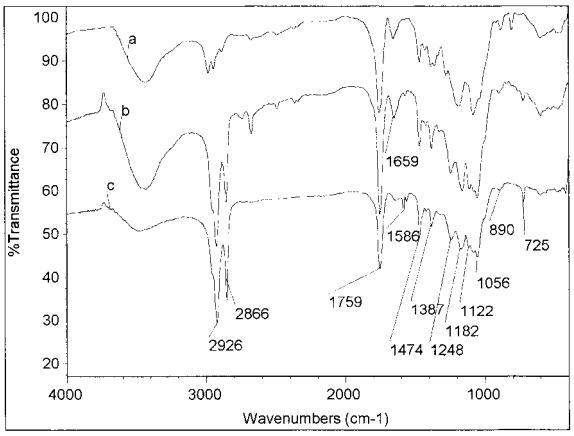


Figure 4 FTIR spectra of propionylated hemicelluloses (spectrum a, sample 2), decanoylated hemicelluloses (spectrum b, sample 9), and stearoylated hemicelluloses (spectrum c, sample 17).

Table II 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 Preparations

	Esterified Hemicellulosic Preparations[a]											
	1	3	4	5	6	8	9	10	11	12	17	18
$\bar{M}_w$	33800	42400	48300	48100	42600	57800	56500	58100	60900	78200	94800	95600
$\bar{M}_n$	31300	40000	46000	45400	39400	54500	51800	54800	54900	69800	82400	86900
$\bar{M}_w/\bar{M}_n$	1.08	1.06	1.05	1.06	1.08	1.06	1.09	1.06	1.11	1.12	1.15	1.10

[a] Corresponding to sample no. in Table I.

lated hemicelluloses (sample 2, spectrum a), decanoylated hemicelluloses (sample 9, spectrum b), and stearoylated hemicelluloses (sample 17, spectrum c). The similar spectral profiles indicate the similar structures of the esterified hemicelluloses. However, on a close comparison between the spectra, some small differences are observed. In cases of a comparatively low DS values (spectrum b, sample 9, DS = 0.95; spectrum a, sample 2, DS = 1.41), the signal for ester band at 1759 cm^{-1} appears slightly stronger than or as strong as the band at 1056 cm^{-1} for the C—O stretching, while in the case of a comparatively higher DS value in sample 17 (spectrum c, DS = 1.75) the signal for ester band appears much stronger than that of the signal for C—O stretching. In addition, Figure 4 also showed that the absorbance for the unexchanged hydroxyl band at 3400 cm^{-1} decreased dramatically from spectrum b to a and to c as the increment of DS went from 0.95 to 1.41 and to 1.75, respectively.

Molecular Weight

In order to illustrate the extent of degradation that occurred during the reaction in the DMF/LiCl system, the molecular weights of esterified hemicelluloses were determined by GPC, and their values are presented in Table II. As compared to the theoretical molecular weights, which were based on the molecular weight of the starting hemicelluloses (M_w, 28,600 g mol^{-1}) and the DS, all of the molecular weights obtained were lower than the expected values. It was found that the esterified hemicellulosic preparations 5–11 were within 8% below the expected values, while the samples 1–4 and 12–18 within 12% lower the calculated values. The results indicated that a little degradation occurred during the reaction to produce esterified hemicelluloses at 70–75°C for a short period of 30 min, and the extent of degradation is proportional to the reaction temperature used. The elution profiles of lauroylated hemicelluloses (sample 11) is shown in Figure 5. The molecular weight distribution ranged between 29,500 and 125,000 g mol^{-1} with a major peak at 63,200 g mol^{-1}.

Solubility

Introduction of hydrophobic acyl groups in the molecular structure of hemicelluloses would be expected to alter the solubility properties. Such alteration would rely essentially on the degree of substitution and the nature of hemicelluloses. It is therefore the solubility of the polymers that was investigated using only sample 16 as a sample in different organic solvents. The sample showed a good solubility in pyridine at 80°C, and was partially soluble in dimethylsulfoxide (DMSO), tetrahydrofuran (THF), toluene, chloroform, and dichloromethane. Interestingly, the esterified hemicelluloses are considerably more hydropho-

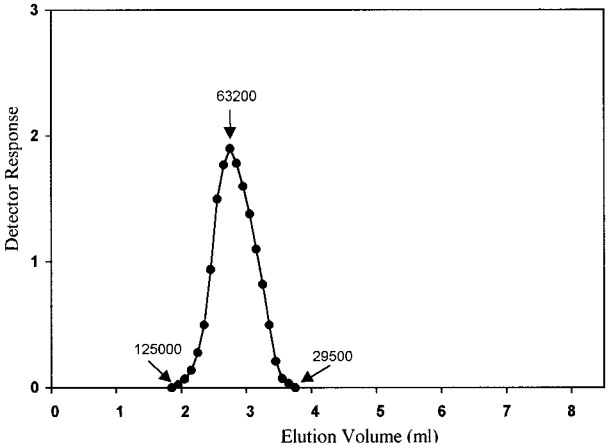


Figure 5 GPC molecular weight distribution of lauroylated hemicelluloses (sample 11).

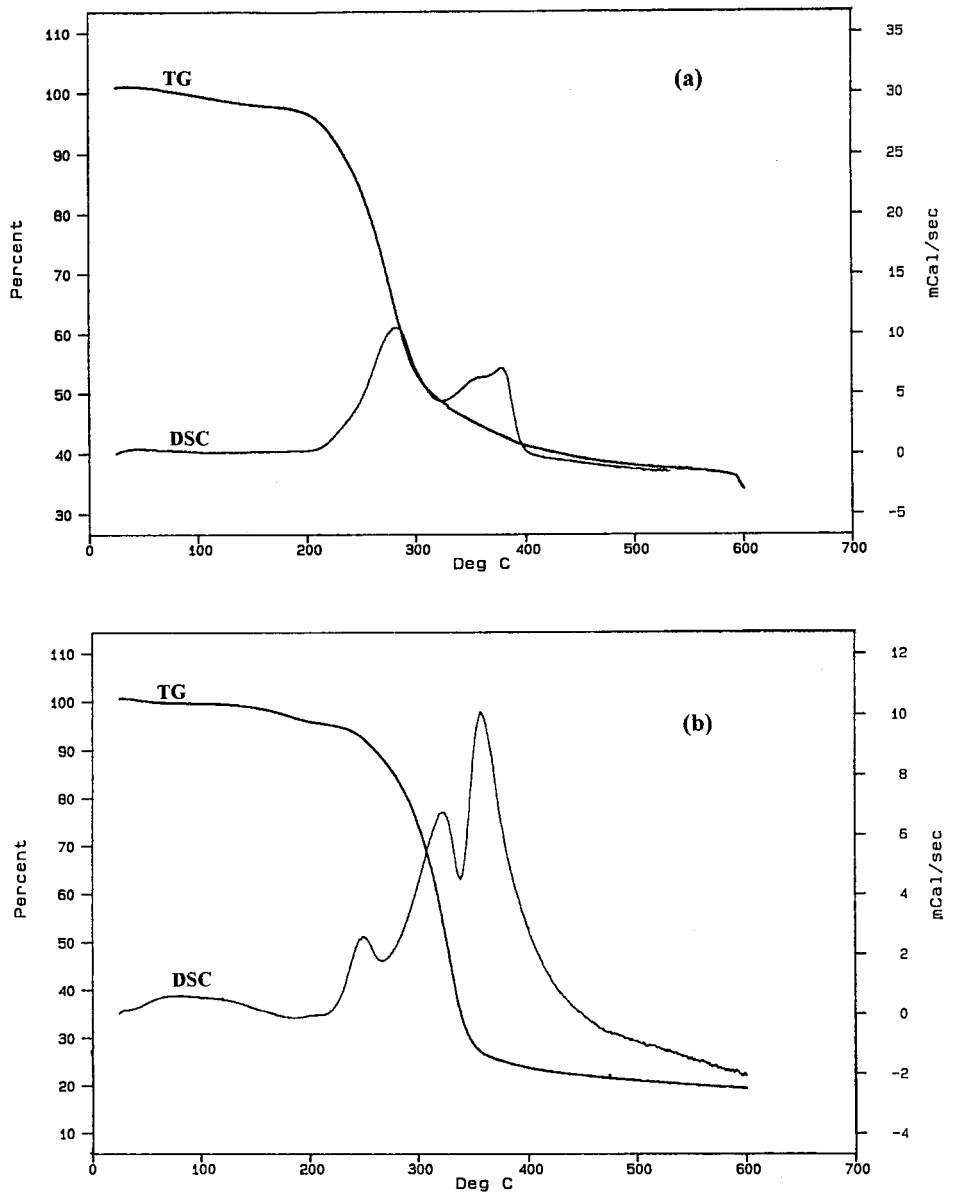


Figure 6 Thermogram of native hemicellulose (a) and octanoylated hemicelluloses (b, sample 8).

bic than the nature hemicelluloses. Presence of acyl groups in the hemicellulosic molecules may open the structure of hemicelluloses. This together with the physical changes in the hemicellulosic structure and molecular degradation occurring during esterification would act in favor of solubility. This increasing hydrophobic capacity would lead to potential use of esterified hemicelluloses in the production of plastic, especially biodegradable and/or environmentally degradable plastics, resins, films, and coatings in the food industry. Another potential utilization of the hemicellulosic derivatives produced by the process of present study is in pharmaceuticals.

Thermal Property

The results obtained from the typical thermogravimetry (TG) and differential scanning calorimetry (DSC) curves for the native hemicelluloses (a) and octanoylated hemicelluloses (b) are given in Figure 6. The TG curves were used to determine the weight loss of a material as the material is heated, cooled, or held isothermally,

whereas the DSC curves showed how exothermic or endothermic the reactions were. The two-step nature of the thermogravimetric curves and the dual peak characteristics of the DSC curves showed that the native hemicelluloses had two distinct reaction zones, while the octanoylated hemicelluloses had three distinct reaction zones. This indicated the different thermal degradation characteristics between the nature and esterified hemicelluloses. The thermogravimetric analysis of native hemicelluloses showed that approximately 40 and 20% of the weight are lost at temperatures of 280 and 370°C, respectively [Fig. 6(a)], whereas the thermogram of octanoylated hemicelluloses [Fig. 6(b)] exhibited three thermal decompositions at temperatures of 260, 330, and 370°C, which represented about 6, 40, and 30% of the total weight loss, respectively. Both samples began to degrade at temperature around 220°C. The native hemicelluloses were totally consumed at temperature 400°C, whereas the esterified sample was totally consumed when the temperature reached to over 500°C, suggesting that the degradation rate of the former was faster than that of the latter at the temperature ranges. Furthermore, in the curve of octanoylated hemicelluloses, the main two peaks shifted toward higher temperature between 280 and 500°C, indicating an increase of the thermal stability of the products.

In short, a wide range of esterified hemicelluloses have been prepared in homogeneous DMF/LiCl solution, which represents a suitable, effective, and rapid method for the preparation of esterified hemicelluloses with a significant exchange of the free hydroxyl groups in native hemicelluloses. The DMF/LiCl acted as the solvent for the derivatives and ensured uniform substitution by great accessibility of the reagent. Additionally, reactions to esterified hemicelluloses can be controlled with high accuracy by adjusting the concentration of TEA and the molar ratio of reagent and hydroxyl functionality. The reaction conditions were optimized to give high degrees of substitution under mild reaction conditions with a short period of reaction time. Under an optimum reaction condition (molar ratio 1:3, TEA% 160, 75°C, 30 min), a high DS value of 1.75 was obtained, in which about 95% of the free hydroxyl groups in native hemicelluloses were esterified. The results obtained by GPC analysis showed that no significant degradation occurred during the reaction. It was also found that the thermal stability of the product is increased by chemical modification.

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REFERENCES

1. Fanta, G. F.; Burr, R. C.; Doane, W. M. J Appl Polym Sci 1982, 27, 4239.
2. Lawther, J. M.; Sun, R. C.; Banks, W. B. J Agric Food Chem 1995, 43, 667.
3. Cai, Z. S.; Paszner, L. Holzforschung 1988, 42, 11.
4. Kohn, R.; Hromadkova, Z.; Ebringerova, A. Collection Czechoslovak Chem Commun 1986, 51, 2250.
5. O'Malley, J. J.; Marchessault, R. H. J Polym Sci C 1968, 24, 179.
6. Church, J. A. J. Polym. Sci. A-1, 5, 3183 (1967).
7. El-Shinnawy, N. A.; El-Kalyoubi, S. F. J Appl Polym Sci 1988, 30**,** 2171.
8. Fan, X. R.; Fen, Z. H. Acta Pharmacol Sinica 1987, 8, 169.
9. McCormick, C. L.; Callais, P. A. Polymer 1987, 28, 2317.
10. McCormick, C. L.; Callais, P. A.; Hutchinson, B. H. Macromolecules 1985, 18, 2394.
11. Sun, R. C.; Lawther, J. M.; Banks, W. B. Ind Crops Prod 1995, 4.
12. Sun, R. C.; Lawther, J. M.; Banks, W. B. Carbohydr Polym 1996, 29, 325.
13. Blakeney, A. B.; Harris, P. J.; Henry, R. J.; Stone, B. A. Carbohydr Res 1983, 113, 291.
14. Sun., R. C.; Fang, J. M.; Rowlands, P.; Bolton, J. J Agric Food Chem 1998, 46, 2804.
15. Focher, B.; Marzetti, A.; Naggi, A.; Torri, G. Makromol Chem 1989, 190, 129.
16. Williams, D. L.; Pretus, H. A.; McNamee, R. B.; Jones, E. L.; Ensley, H. E.; Browder, I. W. Carbohydr Res 1992, 235, 247.
17. Kato, A.; Azuma, J.; Koshijima, T. Agric Biol Chem 1987, 51, 1691.
18. Ebringerova, A.; Hromadkova, Z.; Alfoldi, J.; Berth, G. Carbohydr Polym 1992, 19, 99.
19. Imamura, T.; Watanabe, T.; Kuwahara, M.; Koshijima, T. Phytochemistry 1994, 37, 1165.
20. Khalil, M. I.; Hashem, A.; Hebeish, A. Starch/Stärke 1995, 47, 394.
21. Vogt, S.; Klemm, D.; Heine, T. Polym Bull 1996, 36, 549.
22. Williamson, S. L.; McCormick , C. L. J Macromol Sci 1998, A35, 1915.
23. Gupta, S.; Madan, R. N.; Bansal, M. C. Tappi J 1987, 70, 113.
24. Yang, C. Q.; Wang, X. Textile Res J 1996,66, 595.