Studies of the Lauroylation of Wheat Straw Hemicelluloses under Heating

JUN-LI REN,[†] FENG XU,[‡] RUN-CANG SUN,*,[†,‡] BAI PENG,[§] AND JIN-XIA SUN[§]

State Key Laboratory of Pulp and Paper Engineering, South China University of Technology,
Guangzhou, China, Institute of Biomass Chemistry and Utilization, Beijing Forestry University,
Beijing, China, and College of Forestry, The North-Western University of Agricultural and Forestry
Sciences and Technology, Yangling, China

Lauroylation of wheat straw hemicelluloses in the *N,N*-dimethylformamide/lithium chloride system under microwave irradiation was studied. The parameters optimized included lauroyl chloride concentration as the molar ratio of xylose unit in hemicelluloses/lauroyl chloride (1:1–1:4), 4-dimethylaminopyridine concentration (2–10%), reaction time (1–8 min), molar ratio of xylose unit in hemicelluloses/triethylamine (1:2), and reaction temperature (78 °C). The reaction efficiency was measured by the yield and degree of substitution (DS). Under an optimum reaction condition (molar ratio of xylose unit in hemicelluloses/lauroyl chloride 1:3, molar ratio of xylose unit in hemicelluloses/triethylamine 1:2, 5% 4-dimethylaminopyridine, 78 °C, 5 min), a DS of 1.63 was obtained. Changes in the structure of hemicelluloses were verified by FT-IR and ^{1}H and ^{13}C NMR spectroscopy. The results showed that the lauroylation occurred preferentially at the C-3 position of the xylose unit in hemicelluloses. The behavior of the lauroylated hemicelluloses was monitored by means of thermogravimetric (TG) and differential thermogravimetric (DTG) analysis. It was found that the product with low DS had a lower thermal stability than the native hemicelluloses, whereas the lauroylated polymers with high DS showed a higher thermal stability than the unmodified hemicelluloses.

KEYWORDS: Hemicelluloses; microwave; lauroylation; ^{13}C NMR; thermal stability

INTRODUCTION

Nowadays, we are confronted with a number of environmental problems such as pollution and decreasing natural resources. As petroleum reserves will be exhausted within half a century, it will become more and more expensive to produce petroleum-based polymers. Moreover, domestic wastes such as plastic packing materials are increasing daily (*1*). Development will certainly pave the way for new materials created from renewable resources, providing these alternative materials have equivalent properties and can be produced easily enough to make them economically competitive with traditional plastics (*2*).

Hemicelluloses are the second most abundant plant biopolymers on earth. They are heteropolysaccharides present in large quantities in wood and annual plants, such as cereal straws and grasses, where they are interconnected together with cellulose and lignin in the cell wall (*2, 3*). The major hemicelluloses in the cell walls of cereal straws are arabinoxylans or arabino-4-*O*-methylglucuronoxylans, which constitute up to 38% of the dry wheat straw (*3*). They have a backbone of β-(1 → 4)-D-xylopyranose residues, which can be substituted in C-2 and/or C-3 by short and flexible side chains of L-arabinofuranose and D-glucuronic acid (or its 4-*O*-methyl derives) residues in a single unit (*4*). Hemicelluloses have a lower degree of polymerization of 80–200 than cellulose. For example, wheat straw hemicelluloses, L-arabino (4-*O*-methyl-D-glucurono) xylans have been reported to have an approximate degree of polymerization (DP) of 217, equivalent to a molecular mass of 28600 g/mol (*5*). The hydrophilic nature of hemicelluloses is a major constraint that seriously limits the development of hemicellulosic polymer-based materials. Chemical modification, such as esterification with long-chain fatty acids, is known to produce thermoplastic and waterproof materials (*6*). However, reactions on hemicelluloses to prepare highly substituted derivatives are not easy, mainly because of the almost impossible proposition of dissolving granular hemicelluloses in a suitable medium without significant degradation (*7*). Studies in our group have recently reported the use of organic solvents to achieve first hemicellulose solubilization after swelling with water and then modification (*8*). A series of systematically hydrophobized hemicellulosic derivatives have been prepared by acylation of the polysaccharide with the appropriate acid chlorides (C_3–C_{18}). In this case, acyl chlorides react with hemicelluloses more readily than acids and anhydrides. However, liberated hydrochloride hydrolyzes the polymers, which need to be removed or neutralized by alkali. The main aim in our group is to produce biodegradable thermoplastic materials to replace the non-biodegradable plastics used in the plastics industry. Modification of the

* Address correspondence to this author (e-mail bcs00a@bangor.ac.uk).
† South China University of Technology.
‡ Beijing Forestry University.
§ College of Forestry, The North-Western University of Agricultural and Forestry Sciences and Technology, Yangling, China.

Table 1. Yield[a] of Lauroylated Wheat Straw Hemicelluloses Obtained by Microwave Irradiation and the Degree of Substitution (DS)

lauroylation conditions					lauroylated hemicelluloses		
molar ratio (X:LC)[b]	irradiation time (min)	temp (°C)	catalyst (% dried hemicelluloses)	molar ratio (X:TEA)[c]	sample	yield (%)	DS
1:2	1	78	5% DMPA[d]	1:2	1	55.2	0.78
1:2	2	78	5% DMAP	1:2	2	61.9	0.96
1:2	3	78	5% DMAP	1:2	3	70.6	1.20
1:2	4	78	5% DMAP	1:2	4	77.5	1.39
1:2	5	78	5% DMAP	1:2	5	81.3	1.49
1:2	8	78	5% DMAP	1:2	6	81.5	1.50
1:1	5	78	5% DMAP	1:2	7	55.0	0.77
1:2.5	5	78	5% DMAP	1:2	8	83.7	1.56
1:3	5	78	5% DMAP	1:2	9	86.5	1.63
1:3.5	5	78	5% DMAP	1:2	10	86.8	1.64
1:4	5	78	5% DMAP	1:2	11	86.8	1.64
1:2	5	78	2% DMAP	1:2	12	75.8	1.34
1:2	5	78	4% DMAP	1:2	13	78.1	1.40
1:2	5	78	6% DMAP	1:2	14	82.0	1.51
1:2	5	78	8% DMAP	1:2	15	82.2	1.51
1:2	5	78	210% DMAP	1:2	16	81.3	1.49
1:2	5	78	5% pyridine	1:2	17	59.8	0.90
1:2	5	78	5% pyridine	1:0	18	58.1	0.86
1:2	5	78	5% MPI[e]	1:2	19	59.7	0.90
1:2	5	78	5% MPO[f]	1:2	20	60.3	0.92

[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 26.6% for lauroylation with a DS value of 0.0. [b] Molar ratio of X:LC represents the moles of xylose units in hemicelluloses/moles of lauroyl chloride (LC). [c] Molar ratio of X:TEA represents the moles of xylose units in hemicelluloses/moles of triethylamine (TEA). [d] 4-Dimethylaminopyridine. [e] *N*-Methyl pyrrolidine. [f] *N*-Methylpyrrolidinone.
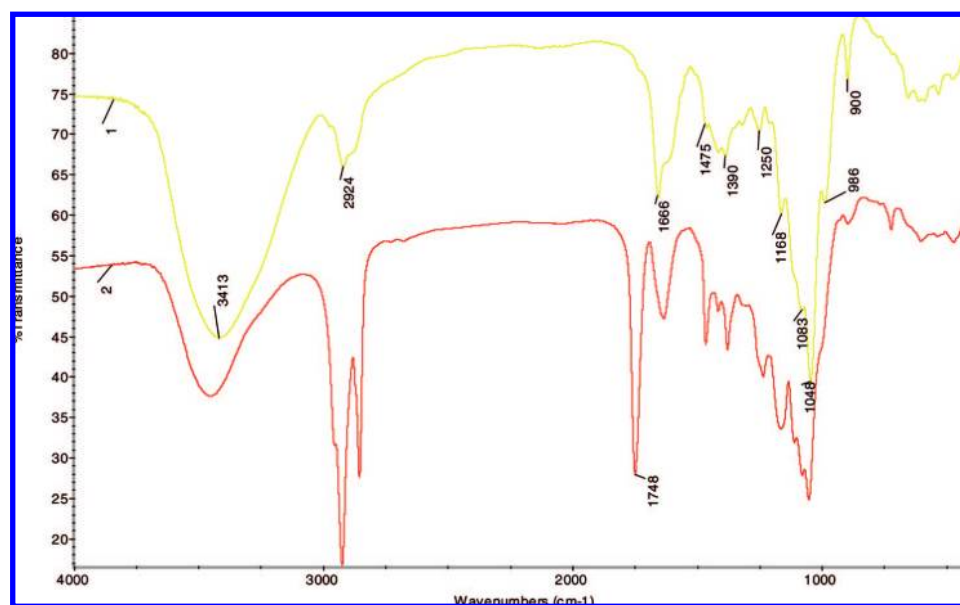

Figure 1. FT-IR spectra of native wheat straw hemicelluloses (spectrum 1) and lauroylated hemicellulosic sample 2 (spectrum 2) prepared under microwave irradiation at 78 °C for 2 min.

abundant hydroxyl groups of straw hemicelluloses to form esters afforded a material that can be processed and shaped like traditional plastic products. The water resistance of such polymer esters is greatly improved over that of the unmodified hemicelluloses (*3*).

Recently, microwave heating, as an alternative to conventional heating technique, has been proved to be more rapid and efficient. Considerable efforts have been devoted to investigate the microwave-assisted reaction in the synthesis and modification of polymer materials (*9, 10*). Especially in the modification of natural polymers, a number of different polysaccharide derivatives, such as ester-cellulose (*11*) and starch acetates (*12*), have been synthesized with the aid of microwaves. It has been shown that through esterification of carboxylic acids and transesterification of methyl and ethyl esters with different

alcohols high yields (90–97%) are obtained for a short period of time (up to 10 min) under simplified process conditions (*13*). To scale up this process, microwave heating was chosen in this study, because it gives fast, uniform heating and enhanced reaction times (*14*). The aim of this research is to study the influence of the conditions under which the reaction takes place (reaction time, temperature, molar proportion of the initial lauroyl chloride, and quantity of the catalyst) on the degree of esterification of the products obtained.

MATERIALS AND METHODS

Materials and Reagents. Wheat straw hemicelluloses were isolated after removal of lignin according to the method described previously
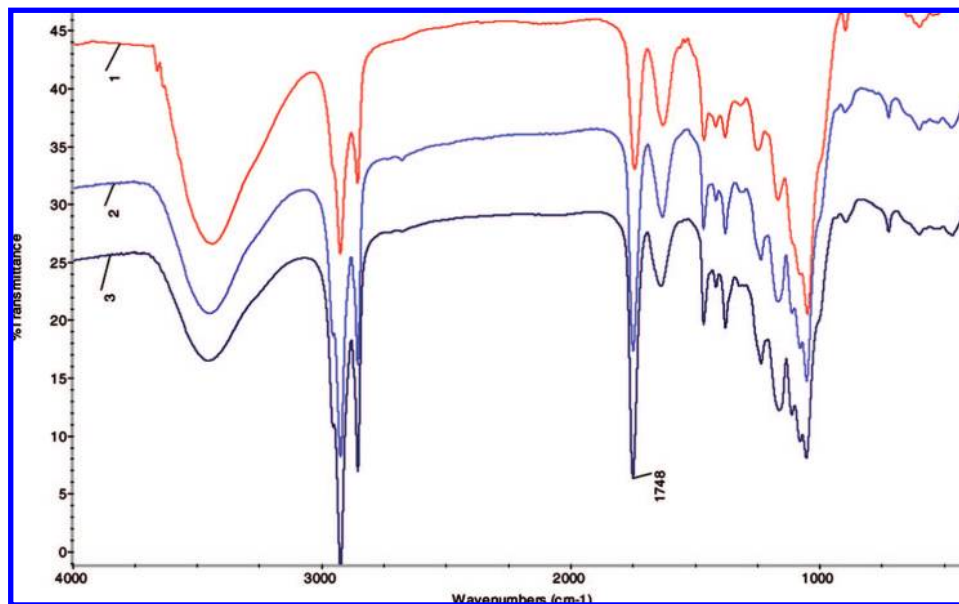
Figure 2. FT-IR spectra of lauroylated hemicelluloses prepared under microwave irradiation at 78 °C for 1 min (spectrum 1, sample 1), 3 min (spectrum 2, sample 3), and 4 min (spectrum 3, sample 4).
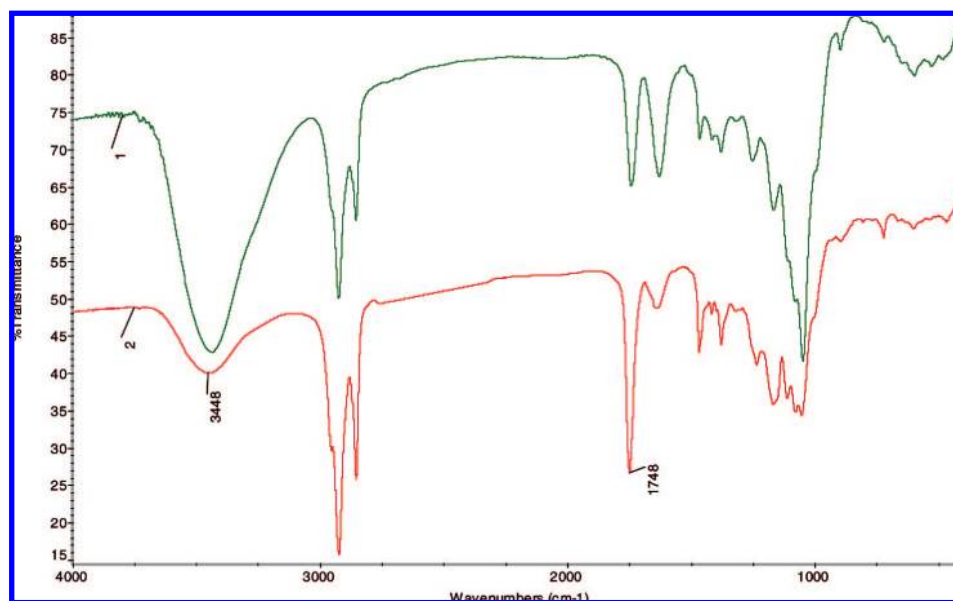

Figure 3. FT-IR spectra of lauroylated hemicellulosic samples prepared under microwave irradiation at 78 °C for 5 min with a molar ratio (X:LC) of 1:1 (spectrum 1, sample 7) or 1:3 (spectrum 2, sample 9).

(*5*). The sugar analysis of the hemicelluloses isolated showed that xylose presented as a predominant sugar component, comprising 76.3% of the total sugars. Arabinose (9.2%) appeared as the second major sugar constituent. The uronic acids, mainly 4-*O*-methyl-α-D-glucuronic acid (5.3%) and glucose (4.8%), were present in noticeable amounts. Galactose (2.2%) and rhamnose (1.4%) were observed as minor constituents. Lauroyl chloride (LC), 4-dimethylaminopyridine (DMAP), *N*-methylpyrrolidine (MPI), *N*-methylpyrrolidinone (MPO), *N,N*-dimethylformamide (DMF), triethylamine (TEA), pyridine, and lithium chloride (LiCl) were purchased from Aldrich-Sigma Chemical Co. (Beijing, China).

Lauroylation of Hemicelluloses. Hemicelluloses powder (0.66 g, 0.01 mol of hydroxyl functionality in hemicelluloses) in 10 mL of distilled water was heated to 78 °C under stirring until completely dissolved. Twenty milliliters of DMF was added, and the reaction mixture 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 were added 0.10 g of LiCl, 15 mL of DMF, different quantities of the catalyst (1–10% DMAP, pyridine, MPI, or MPO per weight of hemicelluloses), and various molar ratios [xylose (X) unit in

hemicelluloses/LC)] of X/LC 1:1, 1:2, 1:2.5, 1:3, 1:3.5, and 1:4. The samples were put into the microwave oven at a controlled temperature of 78 °C and were processed at 300 W for different periods of time (1, 2, 3, 4, 5, and 8 min). The obtained product was cooled and then slowly poured into 120 mL of ethanol with stirring. The white product that separated from the solution was filtered off and collected. The filtrate was washed thoroughly with ethanol and acetone to eliminate any color impurities such as unreacted lauroyl chloride and byproduct. The product was first air-dried for 24 h and then further dried in a forced-air oven overnight at 50 °C.

Analysis of the Esterified Hemicelluloses. The degree of substitution represents the average number of esterified hydroxyl groups in one xylose structural unit of hemicelluloses. Because each repeating unit contains two hydroxyl groups, the theoretical maximum DS is 2. In this study, the DS of hydroxyl groups of the products obtained was determined on the basis of the yield of the product. The yield of percentages was calculated on the basis of the 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 26.6% for lauroylation with a DS value of 0.0 (*5*). The unreacted
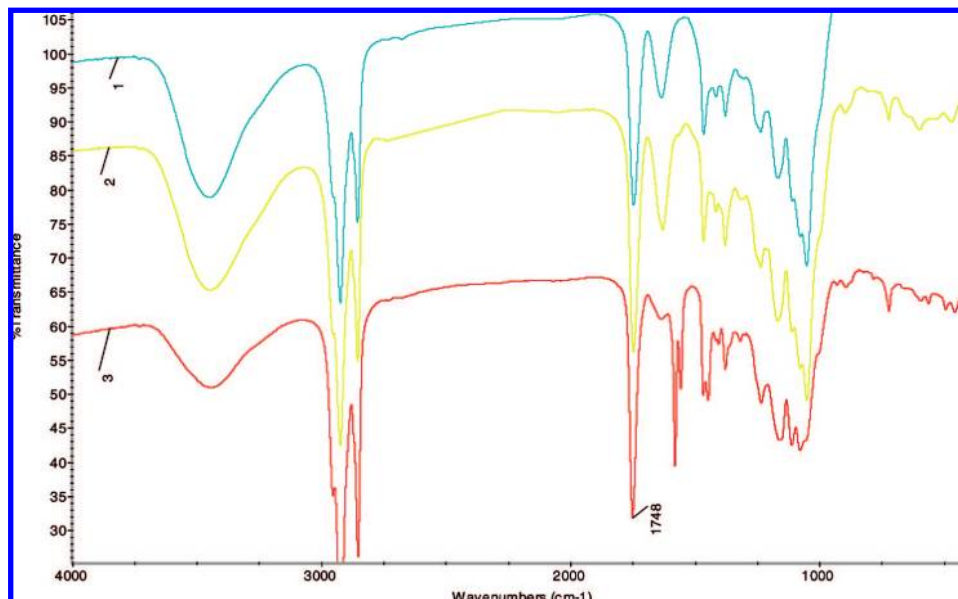
Figure 4. FT-IR spectra of lauroylated hemicellulosic samples prepared under microwave irradiation at 78 °C for 5 min with 2% DMAP (spectrum 1, sample 12), 4% DMAP (spectrum 2, sample 13), or 6% DMAP (spectrum 3, sample 14) as a catalyst.
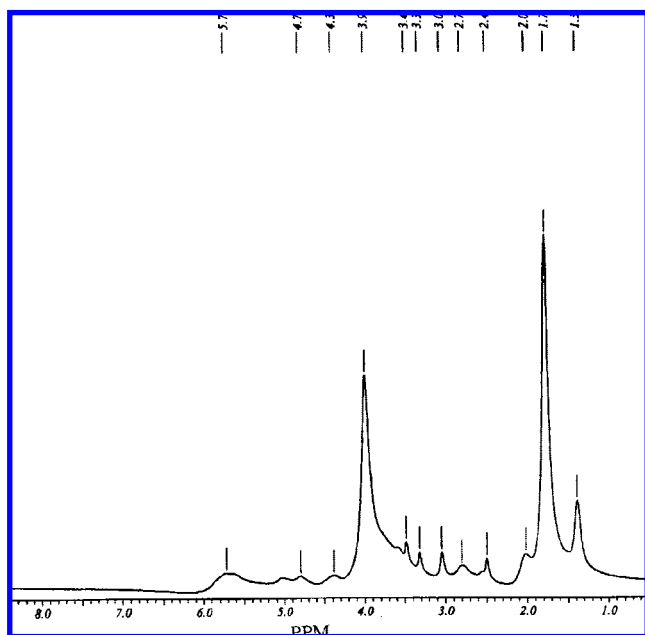

Figure 5. ^{1}H NMR spectrum of lauroylated hemicellulosic sample 1.

lauroyl chloride and catalyst together with DMF solvent in the mixture of reactions were removed from the product by dissolution in 95% ethanol and acetone.

The chemical structure of the lauroylated hemicelluloses was evaluated by FT-IR abd ^{1}H and ^{13}C NMR spectroscopy. The FT-IR spectra were recorded from a KBr disk containing 1% finely ground samples on a Nicolet 750 FT-IR spectrophotometer in the range 4000–400 cm^{-1}. The solution-state ^{1}H and ^{13}C NMR spectra were obtained on a Bruker MSL300 spectrometer operating in the FT mode at 74.5 MHz. The unmodified hemicellulosic sample (80 mg) was dissolved in 1 mL of D$_2$O, and the esterified product (20 mg for ^{1}H and 80 mg for ^{13}C) was dissolved in 1 mL of DMSO-d_6. The ^{13}C NMR spectra were recorded at 25 °C after 30000 scans. A 60° pulse flipping angle, a 3.9 μs pulse width, a 0.85 s acquisition time, and 1.2 s relaxation delay time were used.

Thermal analysis of the esterified hemicelluloses was performed using thermogravimetric (TG) and differential thermogravimetric (DTG) analysis on a simultaneous thermal analyzer (SDT Q600, TA Instrument, Selb, Germany). The apparatus was continually flushed with

nitrogen. The product was weighed between 9 and 11 mg and heated from room temperature to 600 °C at a rate of 10 °C per minute.

RESULTS AND DISCUSSION

Yield and Degree of Substitution. Microwave heating of a polar solvent differs little in comparison to conventional heating. It is possible that the reaction is accelerated under microwave conditions mainly due to the speed with which a mixture can be heated and the high temperatures easily obtainable in vessels (*15*). DMF is a good solvent for the reactions in microwave because it absorbs microwave radiation very well and heats rapidly. In this study, we synthesized lauroyl esters of hemi-celluloses with various DS values. For this purpose, we used the LiCl/DMF system as a solvent, lauroyl chloride as an acylating agent, DMAP as a catalyst, TEA as a base, and microwaves as an activator. In comparison, another three tertiary amine catalysts, pyridine, MPI, and MPO, were also investi-gated. Furthermore, to investigate the effect of microwave energy on the DS of lauroylation, different reaction times, molar ratios of xylose units in hemicelluloses/lauroyl chloride, and amounts of DMAP were examined. The results are given in **Table 1**. At 78 °C, the yield and DS increased quickly at the beginning of the reaction as shown by a DS value of 0.78 at 1 min. After that, the DS increased smoothly from 0.78 to 1.49 with the increment of reaction time from 1 to 5 min. This indicated that the hemicelluloses, swollen by water, make the reactive chemical sites more accessible and, therefore, enhance the reaction rate. In other words, it was obvious that lauroylation of hemicelluloses went along easily with increasing reaction time up to 5 min. However, a longer reaction time of 8 min was unfavorable, because it resulted in a product with a deep color, which is probably due to the degradation of the products. For this reason, in the following study we chose to use a reaction time of 5 min at 300 W.

When hemicelluloses were reacted with lauroyl chloride at different molar ratios of X/LC 1:1, 1:2, 1:2.5, 1:3, 1:3.5, and 1:4 using 2 mol of TEA per mole of xylose in hemicelluloses as a base scavenger and 5% DMAP as a catalyst at 78 °C, we obtained DS in the range of 0.77–1.64. Obviously, increasing the molar ratio of X/LC from 1:1 to 1:3 (with 5% DMAP at 78 °C for 5 min) resulted in a significant increment of lauroylation
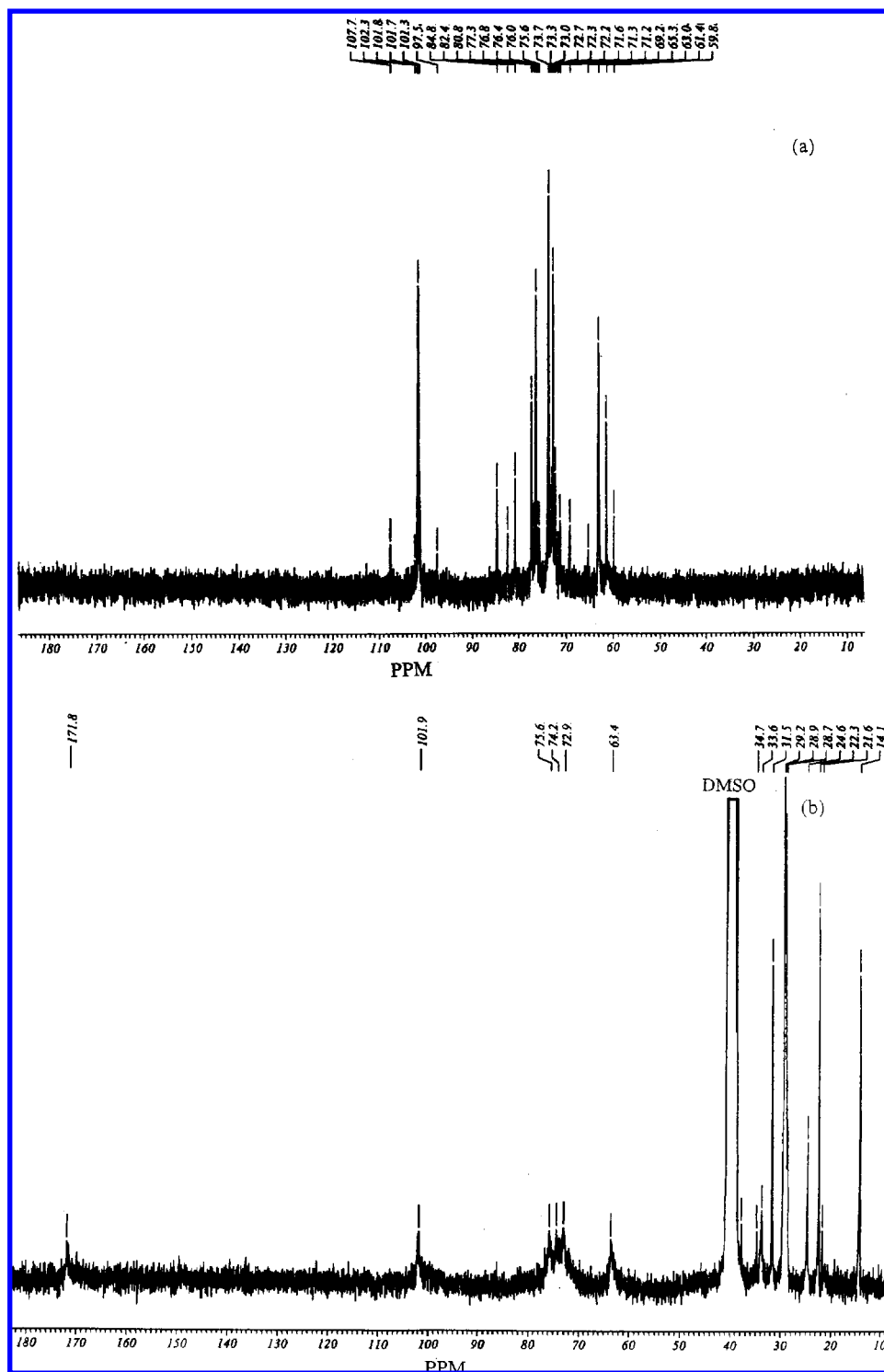
Lauroylation of Wheat Straw Hemicelluloses

J. Agric. Food Chem., Vol. 56, No. 4, 2008 **1255**

Figure 6. ^{13}C NMR spectra of the native wheat straw hemicelluloses in D_2O (**a**) and lauroylated hemicellulosic sample 1 in DMSO-d_6 (**b**).

reaction efficiency as shown by both a yield increase from 55.0 to 86.5% and a DS increase from 0.77 to 1.63, respectively. It can be seen from the results in **Table 1** that lauroyl chloride should be employed in large excess to give high DS and optimum yield of the hemicellulosic ester. This could be interpreted in terms of greater availability of lauroyl chloride molecules in the proximity of the hemicellulosic molecules at higher concentration of the esterifying agent (*16*). On the other hand, further increase in the molar ratio of X/LC to 1:4 did not obviously influence the DS, suggesting that a sufficient time may not have been given for large extents of lauroylation at the higher lauroyl chloride concentrations.

It is evident that as the catalyst of DMAP is increased from 2 to 4, 5, and 6% the DS value increased from 1.34 to 1.40, 1.49, and 1.51, respectively. The data in **Table 1** also revealed that the DS did not increase above 0.2 with an increase of DMAP from 5 to 6%, and there was no further increase in DS from 6 to 8%. In contrast, an excess amount of DMAP (10%) resulted in a slight decrease of the DS. Thus, we concluded that 5% DMAP was the optimum amount.

The reaction of lauroylation is generally carried out in the presence of a base such as TEA along with the catalyst (*5*). To compare the effects of various catalysts on the esterification of hemicelluloses, three other tertiary amine catalysts have been

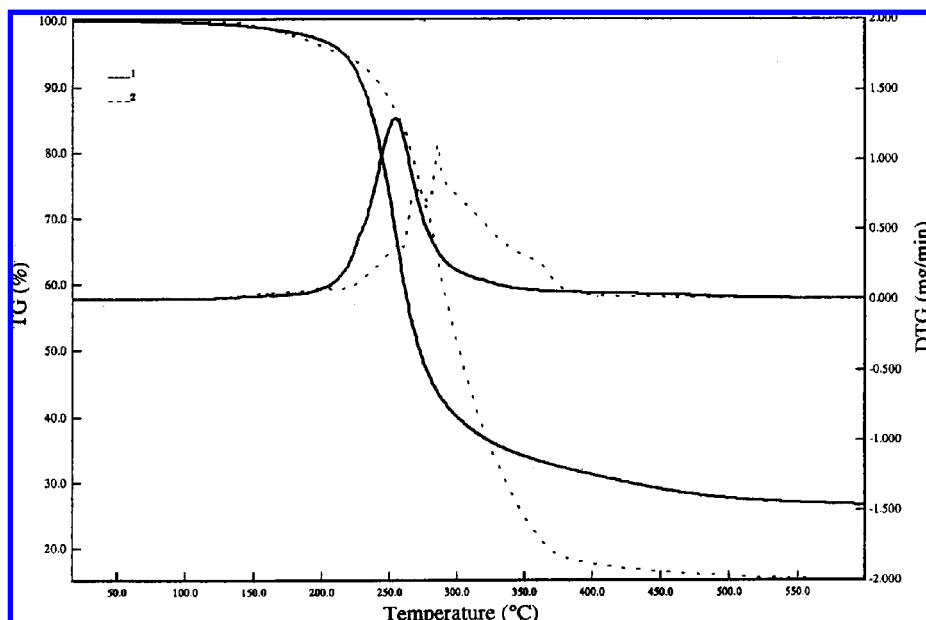**1256** *J. Agric. Food Chem.,* Vol. 56, No. 4, 2008

Ren et al.

Figure 7. Thermograms of lauroylated hemicellulose samples 1 (spectrum 1) and 8 (spectrum 2).

examined. As can be seen in **Table 1**, addition of 5% pyridine, MPI, and MPO to the reaction system (molar ratio of X/LC 1:2, molar ratio of X/TEA 1:2) at 78 °C for 5 min resulted in yield and DS values of 59.8% and 0.90, 59.7% and 0.90, and 60.3% and 0.92, respectively, whereas using an equal amount of DMAP led to a yield and DS of 81.3% and 1.49, respectively. This indicated that DMAP is a much better catalyst than pyridine, MPI, and MPO. In general, pyridine catalyst esterification is a standard method for the modification of hydroxyl compounds and other acylable substances. The mechanism involves nucleophilic catalysts with the intermediate formation of the acylpyridinium ion. More interestingly, DMAP has been found to be an effective catalyst for some synthetic acylations, having a specific catalytic activity about 10^4 time greater than that of the pyridine, but it is very expensive and not commercially available (*17*).

FT-IR Spectra. A comparison of the FT-IR spectra of native hemicelluloses (**Figure 1**, spectrum 1) and lauroylated hemicellulosic sample 2 (spectrum 2) prepared under microwave irradiation at 78 °C for 2 min clearly shows the relative efficiency of acylation. For unmodified hemicelluloses, the absorptions at 1666, 1476, 1390, 1250, 1168, 1083, 1048, and 900 cm^{-1} seen in spectrum 1 are indicative of the native hemicelluloses. A sharp band at 900 cm^{-1} is assigned to β-glucosidic linkages between the sugar units, indicating that the xylose residues forming the backbone of the macromolecule are linked by β-form bonds. The prominent absorption at 1048 cm^{-1} originates from C—O contributions in glycosidic linkages. The intense band at 1666 cm^{-1} is due to the absorbed water. A strong broad band belonging to hydrogen-bonded hydroxyls occurs at 3413 cm^{-1} and the symmetric C—H vibration band at 2924 cm^{-1} (*8*). For the lauroylated hemicelluloses, a decrease in the intensity of the characteristic band for hydroxyl groups and a shift from 3413 to 3479 cm^{-1} (data not shown) due to the consequent loss of the hydrogen bonding as normally occurred in hemicelluloses were observed. This decrease in intensity gives the concomitant appearance of a band at 1748 cm^{-1} characteristic of carbonyl ester groups. A band at 1158 cm^{-1} (data not shown) characteristic of a C—O—C ester stretching vibration was also observed in spectrum 2 obtained for the hemicellulosic esters. The presence of the aliphatic fatty chains of lauroyl ester was also readily detected by the

absorbance observed at 2924 and 2853 cm^{-1} corresponding to the symmetric and asymmetric C—H stretching and the occurrence of a small sharp peak at 710 (data not shown) characteristic for at least four linearly connected CH_2 groups (*18*). It is clearly shown that the disappearance of peaks at 1800 cm^{-1} in spectrum 2 indicated that the product is free of the unreacted lauroyl chloride.

Figure 2 illustrates FT-IR spectra of lauroylated hemicelluloses prepared under microwave irradiation at 78 °C for 1 min (spectrum 1, sample 1), 3 min (spectrum 2, sample 3), and 4 min (spectrum 3, sample 4). In comparison, the spectra showed an increase in the intensity of the band at 1748 cm^{-1} characteristic of C=O ester with an increment of microwave irradiation time from 1 to 3 and 4 min, corresponding to the increase of DS values from 0.78 (spectrum 1) to 1.20 (spectrum 2) and 1.39 (spectrum 3) and a decrease in the intensity of band at 3479 cm^{-1}. Similarly, the effect of molar ratio of X:LC, quantity of DAMP, and various catalysts on the DS was also investigated by the peak intensity of lauroylated hemicellulosic samples. As shown in **Figures 3, 4** an increase in the molar ratio of X:LC from 1:1 to 1:3 or of the amount of DMAP from 2 to 6% resulted in an increase in the intensity of the ester peak at 1748 cm^{-1} but a decrease in OH stretching, indicating a rise of lauroylation, which corresponded to the increasing data of DS in **Table 1**.

^{1}H and ^{13}C NMR Spectra. The ^{1}H NMR spectrum of lauroylated hemicellulosic sample 1 (**Figure 5**) allows two distinct zones to be distinguished, between 3 and 5 ppm for the protons of anhydrosugar units and between 0.5 and 2.5 ppm for aliphatic chains. The integration ratio also permits the calculation of the DS (*19*). The signal at 1.3 ppm relates to the three protons for the terminal methyl group of the acyl chain (ending CH_3, t, 3 H). A sharp peak at 1.7 ppm arises from the methylene groups in the acyl chain [$(CH_2)_8$, m, 16 H], whereas at a chemical shift of 2.4 ppm, the signal of the two protons of the α-methylene group (CH_2 in α position of carboxylic function, t, 2 H) (*6, 18*) was observed. Additionally, the ^{1}H NMR spectrum of the lauroylated hemicelluloses revealed the presence of the protons of the anhydrosugars in hemicelluloses between 3.0 and 5.7 ppm, which were found in the NMR spectrum of the esterified hemicelluloses as well.

Lauroylation of Wheat Straw Hemicelluloses

J. Agric. Food Chem., Vol. 56, No. 4, 2008 **1257**

The lauroylation reaction of hemicelluloses was also monitored by ^{13}C NMR spectroscopy. **Figure 6** illustrates ^{13}C NMR spectra of the native wheat straw hemicelluloses in D_2O (**a**) and lauroylated hemicellulosic sample 1 in DMSO-d_6 (**b**). The ^{13}C NMR spectrum of the native hemicelluloses (**Figure 6a**) showed five major signals at 102.3, 75.6, 73.7, 73.0, and 63.0 ppm, which are attributed to C-1, C-4, C-3, C-2, and C-5 of the β-D-Xyl residues, respectively (*20*). The presence of arabinose was detected by the presence of characteristic signals at 107.7 (C-1), 84.8 (C-4), 80.8 (C-2), 76.0 (C-3), and 61.4 (C-5) ppm in the ^{13}C NMR spectrum. The ^{13}C NMR measurements confirmed that the monomeric side chains of the L-arabinofuranosyl residues are linked to C-3 of backbone xylan. The two signals observed at 82.4 and 59.8 ppm arise from C-4 and the methoxyl group of a 4-*O*-methyl-D-glucuronic acid residue in the xylan attached at the C-2 position. This revealed that the wheat straw hemicelluloses are composed mainly of L-arabino-(4-*O*-methyl-D-glucurono)-D-xylan (*4*).

Evidently, as compared to the spectrum of unmodified hemicelluloses in **Figure 6a**, the strong signals assigned to methyl and methylene groups in the spectrum of lauroylated hemicellulosic sample 1 between 14.1 and 34.7 ppm and the carbonyl group in esters at 171.8 ppm revealed the presence of lauroyl groups and the occurrence of lauroylation in sample 1. In the region of aliphatic chains, the peak at 14.1 ppm represents the methyl end of the chain, whereas the other peaks between 21.6 and 34.7 ppm are characterized by the methylene units successively farther from the methyl group (*21*). Interestingly, the spectrum was very similar in the carbohydrate region (60–110 ppm) as compared to spectrum **a** of the native hemicelluloses, namely, C-1 (101.9 ppm), C-4 (75.6 ppm), C-3 (74.2 ppm), C-2 (72.9 ppm), and C-5 (63.4 ppm) of xylan, indicating that the structure of the hemicellulosic polymers did not significantly degrade in the conditions of microwave irradiation given. In comparison, a decrease in the intensity of the signal at carbon C-3 of the anhydroxylose unit in the spectrum of lauroylated hemicellulosic sample 1 (**Figure 6**) verified that the substitution mainly occurred at the C-3 hydroxyl group.

Thermal Analysis. The results obtained from the typical thermogravimetry and differential thermogravimetric curves of the lauroylated hemicellulose samples 1 (spectrum 1) and 8 (spectrum 2) are given in **Figure 7**. The TG of the native hemicelluloses shows a two-step weight loss curve (curve not shown). The first one occurs between 70 and 150 °C and corresponds to the loss of water naturally trapped into the hemicellulose structure. This water represents about 6% of hemicelluloses initial weight. This phenomenon disappeared for the hemicellulose esters due to the more hydrophobic lauroyl chains in the product. In addition, as can be observed, the native hemicelluloses and the lauroylated polymer samples 1 (spectrum 1) and 8 (spectrum 2) started to decompose at 208, 203, and 218 °C, and their maximum rate of weight loss occurred at 258, 251, and 293 °C, respectively. This indicated that the native hemicelluloses were more stable than the lauroylated polymer sample 1 (DS, 0.78) but less stable than the hemicellulose ester sample 8 (DS, 1.56). In other words, the thermal stability of the unmodified hemicelluloses was higher than that of the lauroylated hemicellulosic polymers with a low DS, but lower than that of the hemicellulosic esters with a higher DS, and their thermal stability increased with an increment of the DS. This lower thermal stability of the lauroylated polymers with low DS was probably due to the disintegration of the intramolecular interactions such as hydrogen bonds between the polymer chains under microwave heating. In the DTG curves, the exothermic peaks of the native hemicelluloses (curve not shown) and the esterified hemicellulosic samples 1 and 8 occurred around 265, 255, and 290 °C, respectively, indicating again that the thermal stability of the lauroylated hemicelluloses increased with an increment of the DS. The reason for this higher thermal stability of the lauroylated hemicellulosic polymers with a higher DS value is presumed to be due to the increment of molar mass of the polymer esters.

In short, lauroylated hemicelluloses with DS values of 0.77–1.64 were prepared quickly and efficiently by microwave heating of wheat straw hemicelluloses with lauroyl chloride. It was found that microwave irradiation improved the speed of this homogeneous reaction remarkably and made reaction processing smoother. The lauroylation for a short period of time (5 min) at relatively low temperature (78 °C) was achieved. A DS of 1.63 was obtained when hemicelluloses in DMF/LiCl reacted with 3 mol of lauroyl chloride in the presence of 2 mol of TEA and 5% DMAP. The DS of hemicellulosic esters significantly increased with an increase in the dose of lauroyl chloride applied. Because they are more hydrophobic, these modified hemicellulosic polymers may be used as biodegradable materials to replace petrochemical commodity plastics and have potential applications such as food packages and plastic films. Certainly, much more work is needed on the effects of substituent distribution on the properties of the modified polymers such as molecular weight distribution and viscosity.

LITERATURE CITED

(1) Satge, C.; Granet, R.; Verneuil, B.; Branland, P.; Ktausz, P. Synthesis and properties of biodegradable plastic films obtained by microwave-assisted cellulose acylation in homogeneous phase. *C. R. Chim.* **2004**, *7*, 135–142.

(2) Hoije, A.; Grondahl, M.; Tommeraas, K.; Gatenholm, P. Isolation and characterization of physicochemical and material properties of arabinoxylans from barley husks. *Carbohydr. Polym.* **2005**, *61*, 266–275.

(3) Sun, R. C.; Sun, X. F.; Tomkinson, J. Hemicelluloses and their derivatives. *Hemicelluloses: Science and Technology*; ACS Symposium Series 864; American Chemical Society: Washington, DC, 2003; pp 1−23.

(4) Sun, R. C.; Lawther, J. M.; Banks, W. B. Fractional and structural characterization of wheat straw hemicelluloses. *Carbohydr. Polym.* **1996**, *29*, 325–331.

(5) Fang, J. M.; Sun, R. C.; Fowler, P.; Tomkinson, J.; Hill, C. A. S. Esterification of wheat straw hemicelluloses in the *N,N*-dimethylformamide/lithium chloride homogeneous system. *J. Appl. Polym. Sci.* **1999**, *74*, 2301–2311.

(6) Kapusniak, J.; Siemion, P. Thermal reactions of starch with long-chain unsaturated fatty acids. Part 2. Linoleic acid. *J. Food Eng.* **2007**, *78*, 323–332.

(7) Sagar, A. D.; Merill, E. W. Properties of fatty-acid esters of starch. *J. Appl. Polym. Sci.* **1995**, *58*, 1647–1656.

(8) Sun, X. F.; Sun, R. C.; Sun, J. X. Oleoylation of sugarcane bagasse hemicelluloses using *N*-bromosuccinimide as a catalyst. *J. Sci. Food Agric.* **2004**, *84*, 800–810.

(9) Lewandowicz, G.; Fornal, J.; Walkowski, A.; Maczynski, M.; Urbaniak, G.; Szymanska, G. Starch esters obtained by microwave radiation-structure and functionality. *Ind. Crops Prod.* **2000**, *11*, 249–257.

(10) Liu, L.; Li, Y. P.; Li, Y.; Fang, Y. E. Rapid N-phthaloylation of chitosan by microwave irradiation. *Carbohydr. Polym.* **2004**, *57*, 97–100.

(11) Satge, C.; Verneuil, B.; Branland, P.; Granet, R.; Krausz, P.; Rozier, J.; Petit, C. Rapid homogeneous esterification of cellulose induced by microwave irradiation. *Carbohydr. Poly.* **2002**, *49*, 373–376.

(12) Koroskynyi, B.; McCarthy, S. P. Microwave-assisted solvent-free or aqueous-based synthesis of biodegradable polymers. *J. Polym. Environ.* **2002**, *10*, 93–104.

(13) Loupy, A.; Petit, A.; Ramdani, M.; Yvanaeff, C.; Majdoub, M.; Labiad, B.; Villemin, D. The synthesis of esters under microwave irradiation using dry-media conditions. *Can. J. Chem.* **1993**, *71*, 90–95.

(14) Shogren, R. L.; Biswas, A. Preparation of water-soluble and water-swellable starch acetates using microwave heating. *Carbohydr. Polym.* **2006**, *64*, 16–21.

(15) Biswas, A.; Shogren, R. L.; Kim, S.; Willett, J. L. Rapid preparation of starch maleate half-esters. *Carbohydr. Polym.* **2006**, *64*, 484–487.

(16) Khalil, M. I.; Hashem, A.; Hebeish, A. Preparation and characterization of starch acetate. *Starch/Staerke* **1995**, *47*, 394–398.

(17) Connors, K. A.; Albert, K. S. Determination of hydroxyl compounds by 4-dimethylaminopyridine-catalyzed acetylation. *J. Pharm. Sci.* **1973**, *62*, 845–846.

(18) Joly, N.; Martin, P.; Lienard, L.; Rutot, D.; Stassin, F.; Granet, R.; Krausz, P.; Cavrot, J. P. Effect of degree of substitution on the mechanical and thermomechanical properties of lauroyl cellulose ester films. *e-Polym.* **2006**, *70*, 1–9.

(19) Ruiz, G.; Gloaguen, V.; Granet, R.; Roy, A.; Mouradi-Givernaud, A.; Louvet, F.; Kranusz, P. Hydrophobic plastics films synthesis by means of agaroid acylation with lauroyl chloride in the *N*,*N*-dimethylacetamide homogeneous system. *J. Appl. Phycol.* **2007**, *19*, 1–3.

(20) Imamura, T.; Watanabe, T.; Kuwahara, M.; Koshijima, T. Esters linkages between lignin and glucuronic acid in lignin-carbohydrate complexes from *Fagus crenana*. *Phytochemistry* **1994**, *37*, 1165–1173.

(21) Musser, B. J.; Kipatrick, P. K. Molecular characterization of wax isolated from a variety of crude oils. *Energy Fuels* **1998**, *12*, 109–114.