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Characterization of hemicelluloses obtained by classical and ultrasonically assisted extractions from wheat straw

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Abstract

The extractability of the wheat straw hemicelluloses was investigated using extraction method with and without application of ultrasonic irradiation in 0.5 M KOH aqueous solution. The isolated eight hemicellulosic preparations were comparatively characterised by yield, composition, structural and molecular properties, and thermal stability. The results showed that ultrasonically assisted extraction in a period of 20–35 min produced a slightly higher yield of hemicelluloses and lignin than those of the classical alkali procedure by 0.8–1.8% of the original hemicelluloses and 0.6–5.3% of the original lignin, respectively. The hemicelluloses, obtained by ultrasound-assisted extraction, seemed more linear and less acidic than that of the hemicelluloses extracted by alkali in the absence of ultrasonic irradiation. In addition, the hemicellulosic preparations obtained by ultrasound-assisted extractions showed a relatively lower content of associated lignin, but a higher molecular weight and a slightly higher thermal stability in comparison with the hemicelluloses isolated by alkali without ultrasonic irradiation. However, there were no significant differences between the primary structural features of the hemicellulosic preparations obtained by extraction in 0.5 M KOH solution with and without application of ultrasound.

Keywords: Wheat straw; Hemicelluloses; Ultrasound; Alkali; Lignin

1. Introduction

Agricultural residues, such as wheat straw essentially consisted of three different polymer entities, linear and crystalline polysaccharides (cellulose), branched non-cellulosic and non-crystalline heteropolysaccharides (hemicelluloses), and branched (non-crystalline) lignin (Glasser, Kaar, Jain, & Sealey, 2000). The hemicelluloses comprise roughly one-fourth to one-third of most plant materials. On a dry weight basis, wheat straw contains approximately 35–38% hemicelluloses. They are heterogeneous fractions and classically defined as the alkali-soluble material remaining after removal of the pectic substances (Sun, Lawther, & Banks, 1995). Arabino (glucurono) xylan types containing single side chains of 2-*O*-linked α-D-glucopyranosyl uronic acid unit and/or its 4-*O*-methyl derivatives and 3-linked α-L-arabinofuranosyl units are typical of hemicelluloses from cereal straws. Interestingly, the variability in sugar constituents, glycosidic linkages and structure of glycosyl side chains, as well as two reactive hydroxyl groups at the xylose repeating unit of the main chain offer various possibilities for regioselective chemical and enzymatic modifications. This creates novel opportunities to exploit the various valuable properties of hemicelluloses for previously unconceived applications (Ebringerova & Heinze, 2000).

Recently, some important applications for hemicelluloses, such as xylans have been discovered. The highly branched heteroxylan from corn hulls, a by-product of starch production, is used as a new food gum (Hromadkova & Ebringerova, 1995; Saulnier, Chanliaud, Thibault, Despre, & Messager, 1998). The beneficial effect of some xylans in papermaking was confirmed in the case of ramie hemicelluloses that might be used as a beater additive (Bhaduri, Ghosh, & Deb Sarkar, 1995). In addition, xylans from cereals contribute to the effects of dietary fibre upon some biochemical and physiological processes in human and animal organisms by lowering of blood cholesterol and decrease of post-prandial glucose and insulin responses (Asp, Bjorck, & Nyman, 1993; Baghurst, Baghurst, & Record, 1996; Chesson, 1995). Moreover, some of the xylan-rich hemicelluloses isolated from agricultural

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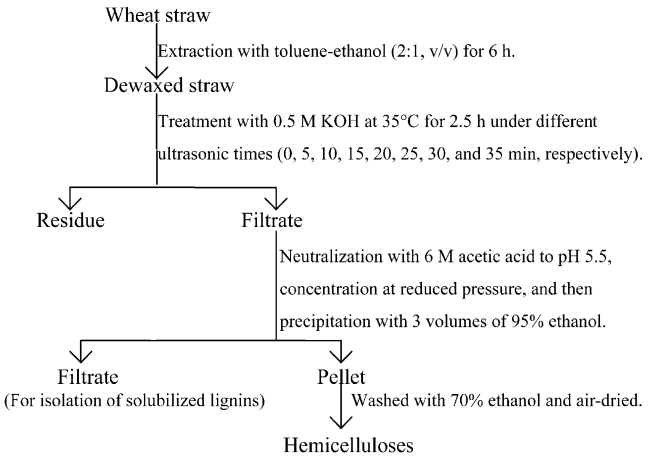

Fig. 1. Scheme for extraction of hemicelluloses from wheat straw.

residues, such as corn stalks, wheat straw, bamboo leaves, etc. (Whistler, Bushway, Singh, & Nakahara, 1976) and the 4-*O*-methylglucuronoxylan from Japanese beechwood (Hashi & Takeshita, 1979) have been reported to inhibit the growth rate of sarcoma-180 and other tumours. Carboxymethylated xylan-rich wood hemicelluloses (Fan & Feng, 1987) has been found to activate T-lymphocytes and immunocytes and claimed as a new Chinese anti-tumour drug (Ebringerova & Heinze, 2000).

Isolation of hemicelluloses actually involves alkaline hydrolysis of ester linkages to liberate them from the lignocellulosic matrix followed by extraction into aqueous media. For the isolation of xylan from hardwoods, a combination of alkaline extraction and steam treatment (Ishihara, Nojiri, Hayashi, & Shimizu, 1996; Kosikova & Ebringerova, 1991) have been proved to be successful method for fractionation of the lignified plant biomass into cellulose, hemicelluloses, and lignin. In comparison, the extractability of hemicelluloses from annual plants is easier than that of wood xylans due to the lower amounts and different structure of lignin. It can be affected by the alkali type and conditions (Lawther, Sun, & Banks, 1996) and improved by a multistep mechanical–chemical treatment (Ebringerova & Hromadkova, 1999). The mechanical and chemical effects of ultrasonication on the cell wall material during alkaline extraction of corn cob hemicelluloses was shown to be very effective. Higher yields of xylan and separation of the water-soluble, biological active component can be achieved at lower temperatures and shorter extraction times (Ebringerova & Hromadkova, 1997; Hromadkova, Kovacikova, & Ebringerova, 1999).

Recently, applications of ultrasound techniques in laboratory and food industry cause more and more attentions, to depolymerise macromolecules, make emulsions, disrupt biological cells, and deflocculate droplets (Lii, Chen, Yeh, & Lai, 1999), particularly, to extract low molecular substances from plant raw materials (Mason, Paniwnyk, & Lorimer, 1996). For example, ultrasonication has been reported to improve significantly the apple pectin technology (Panchev, Kirtchev, & Kratchanov, 1994) and increase the extractability of the non-cellulosic polysaccharides from corn hulls (Hromadkova, Ebringerova, Kovacikova, Machova, & Kacurakova, 1996). Additionally, the ultrasonically assisted extraction of oil, tea, and the seeds of dill and fennel has been discussed in detail (Vinatoru et al., 1997). However, More modern techniques like the use of ultrasound are not yet in common usage and also not widely explored, particularly, the use of ultrasound for direct extraction of hemicelluloses from straw and wood has not been reported. The purpose of the present work is to study the influence of ultrasonic irradiation time on the hemicellulosic yield and components in alkaline media from wheat straw, and the structural, molecular, and thermal properties of the isolated hemicellulosic preparations are comparatively discussed.

2. Experimental

2.1. Materials

Wheat straw (*Variety Riband*) was kindly supplied by B Lloyd Co., Llangefni. The composition (%, w/w) of the straw is cellulose 38.8%, hemicelluloses 39.5%, lignin 17.1%, ash 1.8%, and wax 2.2% on a dry weight basis. After being dried at 60 °C in an oven for 16 h, the straw was ground to pass through a 0.7 mm screen and stored at 5 °C until use.

2.2. Ultrasound-assisted extraction and isolation of hemicelluloses

Prior to ultrasonication, the dried powder was first extracted with toluene–ethanol (2:1, v/v) in a Soxhlet extractor for 6 h. To 9.78 g dewaxed sample in a 500 ml beaker, 300 ml 0.5 M KOH aqueous solution was added. The irradiation was carried using the Sonic system SOMERSET (England, 20 kHz) provided with a horn at sonic power of 100 W and sonication time for 0, 5, 10, 15, 20, 25, 30, and 35 min in 0.5 M KOH aqueous solution, respectively. The mixture was then successively treated with the remaining 0.5 M KOH aqueous solution at 35 °C for a total period of 2.5 h, respectively, under continuous agitation. After filtration on a nylon cloth, the hemicelluloses were isolated from the hydrolysates by precipitation of the neutralised hydrolysate (pH 5.5 adjusted with 6 M acetic acid) with three volumes of 95% ethanol. After filtration, pellets rich in the hemicelluloses were washed with 70% ethanol and air-dried. The residues rich in cellulose were washed with water and ethanol, then dried at 60 °C for 16 h. The scheme for ultrasonically assisted extraction of hemicelluloses from wheat straw is illustrated in Fig. 1. All experiments were performed at least in duplicate. Yields of the hemicelluloses

Table 1
The yield of residue, hemicelluloses and lignin (% dry matter) obtained with or without ultrasonic-assisted alkaline extraction of wheat straw in 0.5 M KOH at 35 °C for 2.5 h under different ultrasonic times

	Ultrasonic time (min)							
	0	5	10	15	20	25	30	35
Hemicelluloses	24.8	24.9	24.8	24.8	25.1	25.1	25.4	25.5
Lignin	7.5	7.5	7.5	7.6	7.6	7.8	8.0	8.4
Residue	65.7	65.5	65.5	65.4	65.0	64.8	64.5	64.1

and lignin are given on a dry weight basis related to the wheat straw.

2.3. Characterization of the isolated hemicelluloses

The neutral sugar composition of the isolated hemicelluloses was determined by gas chromatography (GC) analysis of the corresponding alditol acetates, following hydrolysis of each samples with 2 M trifluoroacetic acid for 2 h at 120 °C (Blakeney, Harris, Henry, & Stone, 1983). The uronic acid content was assayed colorimetrically using the 3-phenylphenol reagent according to the procedure outlined by Blumenkrantz and Asboe-Hanson (1973). Methods for the determination of phenolic acids and aldehydes in nitrobenzene oxidation mixtures of lignins associated in the isolated hemicelluloses with high performance liquid chromatography (HPLC), measurement of the molecular weights, and thermal analysis have been described in a previous paper (Sun, Fang, Goodwin, Lawther, & Bolton, 1998). The lignin content in hemicellulosic preparations was calculated multiplying the yield of phenolics obtained from alkaline nitrobenzene oxidation by 1.9 (Sun, Tomkinson, Ma, & Liang, 2000).

FT-IR spectra were obtained on an FT-IR spectrophotometer using a KBr disc containing 1% finely ground samples. Solution-state ^{13}C NMR spectrum was obtained on a Bruker MSI-300 spectrometer operating in the FT mode at 74.5 MHz under total proton decoupled conditions. Spectrum was recorded at 25 °C from 125 mg of sample dissolved in 1.0 ml D_2O following 20,000 scans. A 60° pulse flipping angle, a 3.9 μs pulse width and 0.85 s acquisition time were used.

3. Results and discussion

3.1. Yield of hemicelluloses

The aim of the present study was to investigate the extractability of the hemicellulosic components and their structural changes from wheat straw by the classical (alkali extraction) and ultrasound-assisted extraction methods. For this purpose, the extraction with 0.5 M aqueous KOH solution was performed with and without ultrasound-assisted conditions. The yield of the isolated hemicelluloses and lignin are given in Table 1. As can be seen, the application of ultrasonic irradiation for 20–35 min during the extraction of hemicelluloses with 0.5 M KOH solution resulted in a slight increase in the yield of hemicelluloses and lignin in comparison with the classical extraction method. Obviously, treatment with sonication time for 20, 25, 30, and 35 min solubilised 0.8, 0.8, 1.5, and 1.8% higher of the original hemicelluloses, and 0.6, 1.8, 2.9, and 5.3% higher of the original lignin, respectively, in comparison with the control experiment. This slightly higher efficiency of the ultrasound-assisted extractions can be explained by the mechanical action of the ultrasound on the cell walls resulting in an increased accessibility and extractability of the hemicellulosic and lignin components (Hromadkova et al., 1999). However, the differences between ultrasound mediated and the control extraction were found to be negligible, when the sonication time was carried out for 5–15 min. To enhance this effect, strong sonication conditions, such as increase of sonic power or further extension of ultrasonic irradiation time are needed.

3.2. Neutral sugar composition and content of uronic acids

The neutral sugar composition and the content of uronic acid of the eight hemicellulosic preparations obtained by the classical and ultrasound-assisted extraction procedures are listed in Table 2. Evidently, xylose was the dominant sugar component (62.9–69.3%) and increased with extended

Table 2
The content of neutral sugars (relative % hemicellulosic sample, w/w) and uronic acids (% hemicellulosic sample, w/w) in isolated hemicellulosic preparations obtained at different ultrasonic times from wheat straw

Neutral sugars/Uronic acids	Ultrasonic time (min)							
	0	5	10	15	20	25	30	35
Rhamnose	0.41	0.42	0.44	0.42	0.49	0.52	0.67	0.63
Arabinose	13.78	12.89	13.50	12.85	12.22	12.10	12.98	12.84
Xylose	62.94	67.62	67.22	67.89	68.61	68.88	69.25	69.22
Mannose	0.37	0.56	0.42	0.42	0.33	0.33	0.26	0.29
Glucose	17.81	15.20	15.00	14.80	14.54	14.30	14.07	14.06
Galactose	4.72	3.41	3.10	3.56	3.80	3.71	2.72	2.93
Uronic acids	7.03	6.32	6.02	6.13	5.86	5.87	5.62	5.78

Table 3
The content (% hemicellulosic sample, w/w) of phenolic acids and aldehydes, determined by HPLC, from nitrobenzene oxidation of the associated lignin in isolated hemicellulosic preparations obtained at different ultrasonic times from wheat straw

Phenolic acids and aldehydes	Ultrasonic time (min)							
	0	5	10	15	20	25	30	35
p-Hydroxybenzoic acid	0.18	0.14	0.14	0.14	0.12	0.11	0.10	0.088
p-Hydroxybenzaldehyde	0.15	0.14	0.13	0.13	0.13	0.13	0.11	0.082
Vanillic acid	0.042	0.040	0.038	0.043	0.030	0.028	0.026	0.025
Syringic acid	0.17	0.17	0.16	0.15	0.15	0.15	0.15	0.15
Vanillin	1.67	1.48	1.46	1.48	1.40	1.49	1.17	1.18
Syringaldehyde	0.91	0.86	0.88	0.85	0.83	0.85	0.64	0.70
p-Coumaric acid	0.15	0.12	0.11	0.10	0.093	0.090	0.084	0.078
Ferulic acid	0.10	0.092	0.10	0.10	0.094	0.090	0.068	0.062
Total	3.37	3.04	3.02	3.08	2.85	2.94	2.35	2.37
Lignin content (%)	6.40	5.78	5.74	5.85	5.41	5.59	4.47	4.50

sonication time. Glucose and arabinose appeared as the second and third major sugars, comprising 14.1–17.8 and 12.1–13.8% of the total sugars, respectively. Uronic acids (mainly glucuronic acid or its 4-*O*-methyl derivative, 5.6–7.0%) and galactose (2.7–4.7%) were identified as noticeable amounts, and rhamnose (0.41–0.67%) and mannose (0.26–0.56%) were observed as minor constituents. An increase in sonication time, in general, resulted in an increase of xylose from 62.9 to 69.3%, but decreases of arabinose from 13.8 to 12.10%, glucose from 17.8 to 14.1%, galactose from 4.7 to 2.7%, and uronic acids from 7.0 to 5.6%, respectively. This increase in xylose content and substantial decreases in arabinose, glucose, galactose, and uronic acids with the increase of ultrasonic irradiation duration provided evidence that in the wheat straw cell walls, arabinose, glucose, galactose, and uronic acids are probably present in the side chains of hemicelluloses and easily released at a short period of sonication time, whereas xylose in the main chain of hemicelluloses is favourably extracted at a relatively longer sonication duration. The lower the arabinose content, indicating a lower degree of branching of the xylan chains, the lower the solubility of the polymers (Hromadkova et al., 1999). The results indicated that the xylans were the main hemicellulosic components in the cell walls of wheat straw. In other words, the hemicelluloses, obtained by ultrasound-assisted extraction, seemed more linear and less acidic than that of the hemicelluloses extracted by alkali in the absence of ultrasonic irradiation. Probably, due to the above mentioned sonication effects, the lower substituted xylans from the less accessible regions of the cell walls were also degraded and solubilised. This confirmed again the significance of cell wall disruption during sonication. Similar results have been reported by Ebringerova, Hromadkova, Alfoldi, and Hribalova (1998) during the extraction of xylan from ultrasound-treated corn cobs.

3.3. Content of associated lignin and its phenolic composition

Based on the study of homolytic scission of interunitary bonds in lignin induced by ultrasonic irradiation of MWL dissolved in dimethylsulphoxide, Yoshioka, Seino, Tabata, and Takai (2000) stated that the alkyl phenyl ether bonds, –CH–*O*-phenyl, known as interunitary bonds in lignins were homolytically cleaved by ultrasonic irradiation. To verify the effect of ultrasonic treatment on the linkages between lignin and hemicelluloses, the phenolic acids and aldehydes, released from the eight hemicellulosic preparations by alkaline nitrobenzene oxidation of the associated lignin, were determined by HPLC, and the results are given in Table 3. As expected, compared to the lignin content (6.4%) in the hemicelluloses isolated with 0.5 M KOH solution without ultrasonic irradiation, extractions with ultrasonic assistance solubilised the hemicelluloses having a relatively lower content of associated lignin (4.5–5.9%). This is particularly true for the hemicellulosic fractions obtained during a longer irradiation period of 30 and 35 min, indicating that ultrasound-assisted extraction had a positive affect on the cleavage of α-ether bonds between lignin and hemicelluloses from wheat straw. The observed beneficial sonication effect on the extractability of the hemicelluloses can be explained by both the mechanical disruption of the cell walls and breaking of α-benzyl ether linkages between lignin and polysaccharides, enhanced in the extension of irradiation time. As a result, the accessibility, solubility, and diffusion of the dissolved molecules from the cell walls increased (Ebringerova et al., 1998).

It is important to note that the major products, obtained from the alkaline nitrobenzene oxidation of the associated lignin in the isolated eight hemicellulosic fractions, were identified to be vanillin and syringaldehyde, which together represented for 75.5–79.6% of the total phenolic acids and aldehydes. Moreover, as can be seen in Table 3, a much higher content of vanillin than syringaldehyde in all the hemicellulosic fractions implied that the hemicelluloses in the cell walls of wheat straw are linked to lignin mainly by guaiacyl units. A noticeable amount of *p*-hydroxybenzoic acid, *p*-hydroxybenaldehyde and syringic acid were also found to be present in the nitrobenzene oxidation products.

Table 4
Weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights and polydispersity ($\bar{M}_w/\bar{M}_n$), determined by GPC, of isolated hemicellulosic preparations obtained at different ultrasonic times from wheat straw

	Ultrasonic time (min)							
	0	5	10	15	20	25	30	35
$\bar{M}_w$	10,730	16,800	18,400	22,320	22,380	19,890	19,620	19,060
$\bar{M}_n$	3790	5100	4570	5390	4530	4680	4510	4510
$\bar{M}_w/\bar{M}_n$	2.83	3.29	4.03	4.14	4.94	4.25	4.35	4.23

p-Coumaric acid, ferulic acid, and vanillic acid were detected to be present in trace amounts. No significant differences in the phenolic molar ratios were found among the eight solubilised hemicellulosic preparations.

3.4. Molecular mass

The molecular weight parameters of the isolated hemicellulosic fractions were assessed using gel permeation chromatography (GPC) in aqueous medium, and the weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights and the polydispersity ($\bar{M}_w/\bar{M}_n$) of the their preparations are illustrated in Table 4. Evidently, all the seven hemicellulosic fraction obtained by ultrasound-assisted extraction showed a higher molecular weight $\bar{M}_w$ between 16,800 and 22,380 g mol^{-1} and a relatively higher degree of polydispersity ($\bar{M}_w/\bar{M}_n$, 3.3–4.9) than that of the hemicellulosic fraction isolated without ultrasonic irradiation ($\bar{M}_w$, 10,730 g mol^{-1}; $\bar{M}_w/\bar{M}_n$, 2.8). This suggested that the extractions with 0.5 M KOH solution without application of ultrasound led to solubilisation of the small molecular size of hemicelluloses, and the ultrasound-assisted extractions with 0.5 M KOH solution under the conditions used did not result in any significant degradation of the macromolecular structure of hemicelluloses. On the other hand, Table 4 showed that the ultrasonic treatment with an increase in irradiation time from 5 to 20 min under the alkaline condition used (0.5 M KOH, 35 °C, 2.5 h) resulted in a growth of $\bar{M}_w$ from 16,800 to 22,380 g mol^{-1}, indicating that increasing irradiation time from 5 to 20 min at least in part, enhanced dissolution of large molecular size hemicelluloses during the alkaline extraction of the straw. In contrast, as the irradiation time was further increased from 20 to 25, to 30, and to 35 min, the $\bar{M}_w$ decreased slightly from 22,380 to 19,890, to 19,620, and to 19,060 g mol^{-1}, respectively, implying that a noticeable degradation occurred during the irradiation time over 20 min. The results, in general, indicated that ultrasound-assisted extraction under the alkaline condition given resulted in a significant increase of the relative molar mass averages of the hemicelluloses from wheat straw. These data were consistent with the studies on the ultrasonic treatment of corn cob and corn hull xylans in water and aqueous NaOH solutions (Ebringerova & Hromadkova, 1997). The authors stated that a significant decrease of

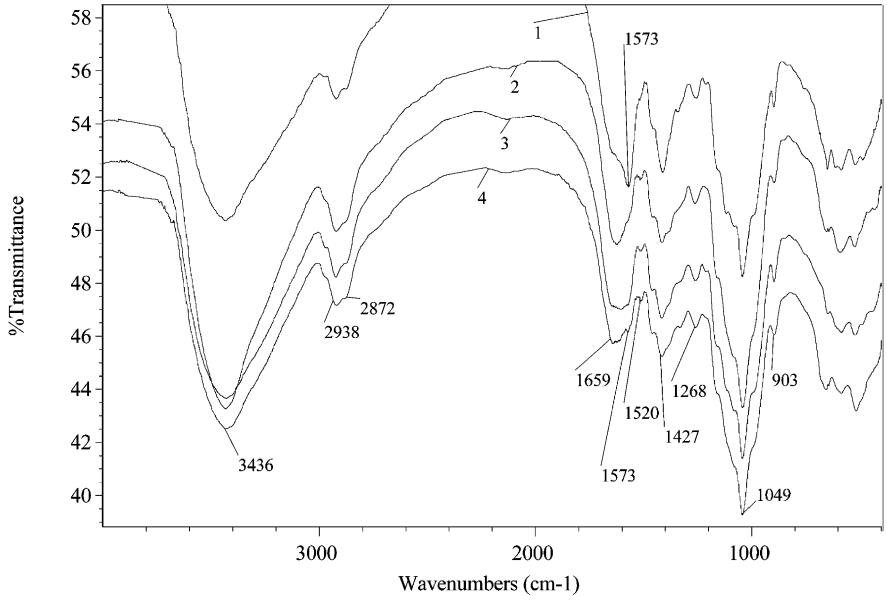

Fig. 2. FT-IR spectra of wheat straw hemicellulosic preparations obtained by extraction with 0.5 M KOH aqueous solution (35 °C, 2.5 h) without ultrasonic-assistance (spectrum 1) and with ultrasonic irradiation for 5 (spectrum 2), 10 (spectrum 3), and 15 min (spectrum 4).

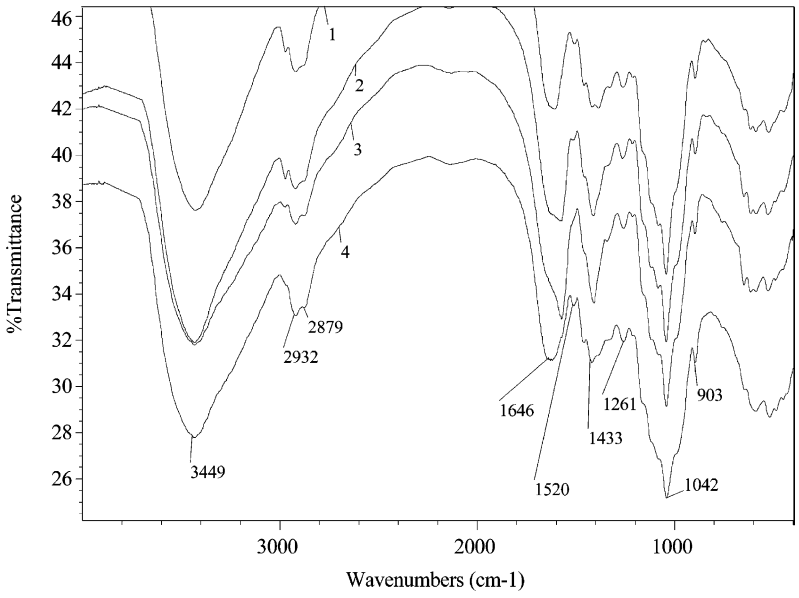

Fig. 3. FT-IR spectra of wheat straw hemicellulosic preparations obtained by extraction with 0.5 M KOH aqueous solution (35 °C, 2.5 h) under ultrasonic irradiation for 20 (spectrum 1), 25 (spectrum 2), 30 (spectrum 3), and 35 min (spectrum 4).

the molar mass averages only after sonication at the highest temperature and/or in presence of the stronger alkali.

3.5. FT-IR spectra

To verify the absence of oxidation reactions in hemicellulosic samples, FT-IR spectroscopy was used. The IR spectra of the four hemicellulosic preparations obtained by treatment with 0.5 M KOH solution (35 °C, 2.5 h) without ultrasonic irradiation (spectrum 1) and with ultrasonic-assistance for 5 (spectrum 2), 10 (spectrum 3), and 15 min (spectrum 4) are illustrated in Fig. 2. Clearly, the four hemicellulosic preparations showed the typical signal pattern expected for a hemicellulosic moiety and their IR spectra without relevant differences with and without ultrasonic treatment. In particular, all the spectra are dominant by signals in the region 3600–2800 cm^{-1} due to stretching vibrations of CH and OH and by signals in the C–O stretching region (1200–950 cm^{-1}). A sharp band at 1049 cm^{-1} in the four spectra is originated from typical of xylans, indicating a dominant xylan of the isolated hemicelluloses, which corresponded to the results obtained by sugar analysis. In the anomeric region (950–700 cm^{-1}), a small sharp band at 903 cm^{-1} is indicative of typical for β-anomers that indicated the presence of dominant β-glycosidic linkages between the sugar units in all the hemicellulosic fractions. In the carbonyl stretching region, the bands between 1659 and 1573 cm^{-1} are due to the absorbed water (Sun et al., 2000). The disappearance of signal at 1745 cm^{-1} in all the spectra revealed that the alkaline extraction with or without ultrasonic irradiation under the conditions used completely saponified the ester bonds, such as acetyl and uronic ester groups from the hemicelluloses. More importantly, the absence of a signal at 1720 cm^{-1} for carbonyl stretching in all the four spectra revealed that ultrasound-assisted extraction under the conditions given did not significantly attack or oxidise the glycosidic linkages and hydroxyl groups of hemicelluloses. Similar phenomenon was also observed in other four hemicellulosic fractions obtained by a longer ultrasound-assisted extraction (20–35 min; Fig. 3). The presence of xylan-rich hemicelluloses in the extracts of 0.5 M KOH solution with ultrasonic irradiation for 20–35 min was evidenced also by their FT-IR spectral pattern in the 800–1700 cm^{-1} region. An intense band at 1646 cm^{-1} is related to the absorbed water. The prominent absorption at 1042 cm^{-1} is originated from the glycosidic linkage ν (C–O–C) contributions in xylans.

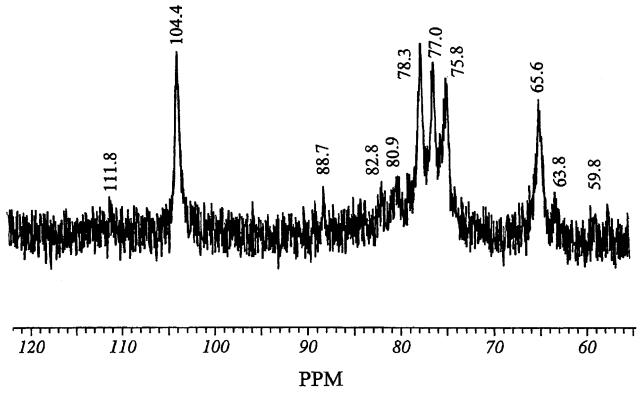

Fig. 4. ^{13}C NMR spectra (in D_2O) of the hemicellulosic preparation obtained by extraction with 0.5 M KOH aqueous solution (35 °C, 2.5 h) under ultrasonic irradiation for 35 min.

3.6. ^{13}C NMR spectrum

The structural features of the hemicellulosic fractions isolated by the classical and ultrasound-assisted extractions

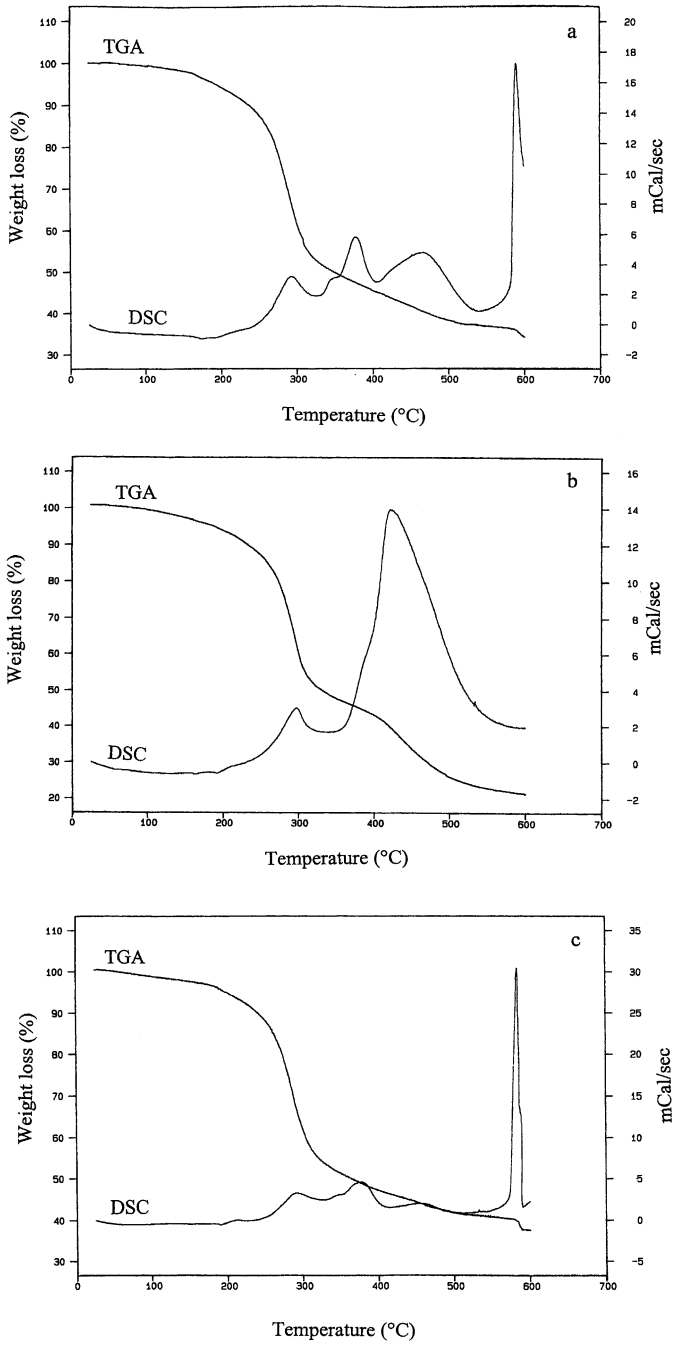

Fig. 5. TGA/DSC curves of hemicellulosic preparations obtained by extraction with 0.5 M KOH aqueous solution (35 °C, 2.5 h) without ultrasonic-assistance (a) and with ultrasonic irradiation for 10 (b), and 25 min (c).

were comparatively investigated using the ^{13}-NMR spectra (Fig. 4). Most of the major resonances were assigned in a previous paper (Sun, Lawther, & Banks, 1996) by references to data in literature (Ebringerova, Hromadkova, Alfodi, & Berth, 1992; Gabrielii, Gatenholm, Glasser, Jain, & Kenne, 2000; Imamura, Watanabe, Kuwahara, & Koshijima, 1994). The main features of the spectra are almost identical, indicating a similar structure of the hemicelluloses. The main 1,4-linked β-D-Xylp units are obviously characterised by five strong signals at 104.4, 78.3, 77.0, 75.8, and 65.6 ppm, which are assigned, respectively, to C-1, C-4, C-3, C-2, and C-5 positions of the β-D-Xylp units. The resonance of C-4 and the methoxyl group of the methylated glucuronic acid residue in the xylan was seen at 59.8 ppm, although its intensity is much lower when compared to those of the signals for β-D-Xylp units. The signals at 111.8, 88.7, 82.8, 80.9, and 63.8 ppm relate to C-1, C-4, C-2, C-3, and C-5 of α-L-Arabinofuranosyl residues linked to β-D-xylans, respectively. Such groups of arabinose signals are typical of

arabinoxylan isolated from cereal straws (Sun et al., 1996). These results suggested that the main structural feature of the hemicelluloses were not significantly affected by the ultrasound during the alkaline extraction under the sonication conditions given. This is in a good agreement with the study of the effects of ultrasonication on the corn cob xylan (Hromadkova et al., 1999).

3.7. Thermal analysis

The thermal properties of the eight hemicellulosic preparations were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). In particular, TGA is one of the most convenient techniques used to determine general degradation characteristics and activation energies of materials under pyrolysis and combustion. This analysis includes a precise study of weight loss during programmed exposure to temperature (Becall, 1969). Fig. 5 gives the thermograms of the hemicellulosic preparations obtained by 0.5 M KOH solution without ultrasonic irradiation (Fig. 5a) and with ultrasound-assisted extraction for 10 (Fig. 5b) and 25 min (Fig. 5c) from wheat straw. As can be seen from Fig. 5, the three hemicellulosic preparations began to decompose at 157, 164, and 186 °C, respectively, and their maximum rate of weight loss occurred between 250 and 320 °C. At 10% weight loss, the degradation temperature was observed at 228 °C for the preparation obtained without ultrasonic irradiation, and 243 and 250 °C for the preparations obtained by irradiation time for 10 and 25 min, respectively. Similarly, when weight loss arrived at 50%, the temperature raised to 340 °C for the hemicellulosic preparation obtained in the absence of ultrasonic treatment, and 343 and 364 °C for the hemicellulosic fractions obtained by sonication time for 10 and 25 min, respectively. This result suggested that the hemicellulosic preparations obtained by the assistance of ultrasonic irradiation had a slightly higher thermal stability than that of the hemicellulosic obtained by alkali without ultrasonic assistance, and their thermal stability corresponded to the increasing molecular weight (Table 4).

The above results demonstrated that the efficiency of the ultrasound-assisted extraction procedures of hemicelluloses from wheat straw exceeded that of the classical extractions. A slightly higher yield of hemicelluloses and lignin can be achieved by using ultrasonic irradiation for 20–35 min. In addition, the hemicellulosic preparations obtained by ultrasound-assisted extractions showed a relatively lower content of associated lignin, but a higher molecular mass and a slightly higher thermal stability in comparison with the hemicelluloses isolated by alkali without ultrasonic irradiation. Therefore, the application of ultrasound treatment during the preparation of hemicelluloses and lignin from agricultural residues and wood samples might result in a better exploitation of the raw material.

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