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Comparative study of hemicelluloses released during two-stage treatments with acidic organosolv and alkaline peroxide from *Caligonum monogoliacum* and *Tamarix* spp

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Abstract

Two-stage treatments of *Caligonum monogoliacum* and *Tamarix* spp. with acidic organosolv and alkaline peroxide were performed. Pre-treatment with ethanol–H_2O (60/40, v/v) under acid catalyst (0.2 N HCl) at 70 °C for 4 h released 18.7 and 17.8% hemicelluloses from dewaxed *C. monogoliacum* and *Tamarix* spp., respectively, Sequential treatment with 2% H_2O_2 at pH 11.5 for 16 h at 45 °C solubilized 26.2 and 26.5% hemicelluloses from pre-treated *C. monogoliacum* and *Tamarix spp.,* respectively. Cellulose predominated in the insoluble residues, accounting for 36.7–37.8% of dry materials. It was found that the two alkaline peroxide soluble hemicellulosic preparations contained a much higher amount of xylose (74.1–77.3%) but lower in glucose (7.4–18.6%), galactose (3.0–8.3%), rhamnose (2.3–2.9%), mannose (0.8–2.7%), and arabinose (1.3–1.4%) than those of the two acidic organosolv soluble hemicellulosic fractions in which xylose (31.8–50.8%), glucose (21.4–30.3%), galactose (7.6–24.1%), and rhamnose (5.7–10.1%) were the major sugar components. The content of uronic acids was slightly higher in the two alkaline peroxide soluble hemicellulosic preparations (7.5–8.3%) than the two acidic organosolv soluble hemicellulosic fractions (5.0–6.5%). Furthermore, the studies showed that the two alkaline peroxide soluble hemicellulosic preparations were more linear and acidic, and had a large molecular mass ($\bar{M}_w$, 27,220–31,410 g mol^{-1}) than the two acidic organosolv soluble hemicellulosic fractions ($\bar{M}_w$, 13,820–18,380 g mol^{-1}). Lignin content and its composition associated in the four isolated hemicelluloses were determined by alkaline nitrobenzene oxidation and monitored with HPLC. No significant differences in lignin content (5.94–9.82%) and its composition were found. Further comparative study of the four hemicellulosic preparations and two cellulosic fractions was carried by both degraded methods such as acid hydrolysis and thermal analysis and non-degradation techniques such as FT-IR and ^{13}C-NMR spectroscopy.

Keywords: Hemicelluloses; *Caligonum monogoliacum*; *Tamarix* spp.; Acidic organosolv; Alkaline peroxide

1. Introduction

During the last years, considerable interest has been directed to hemicellulosic polymer because of the variety of its possible pharmaceutical, biotechnological, and industrial applications [1–3]. Promising results were obtained in the field of papermaking, baking, and food additives. More importantly, the modification or derivatization of these molecules creates novel opportunities to maximally exploit the various valuable properties of hemicelluloses for industrial applications [4]. Hemicelluloses are the second most abundant biopolymer in the cell wall of woody tissues of higher plants, such as hardwoods, softwoods, grasses, and straws, where they exit in many different compositions and structures [5]. In terrestrial plants, xylans, one of the most common hemicelluloses, have a variety of side chains attached to the linear β-(1,4)-D-xylopyranan backbone. They include mainly single α-L-arabinofuranosyl and α-D-

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glucopyranosyl uronic acid or its 4-*O*-methyl ether units. In addition, rhamnose, xylose, galactose, glucose, and a variety of di- and trimetric side chains, next to acetyl groups and phenolic acids, like ferulic and *p*-coumaric acids, have been identified [6].

Caligonum monogoliacum and *Tamarix* spp. are the two main shrubs and have been planted in the desert region of China since the 1960s to prevent wind erosion and control desertification [7]. These shrubs not only has great importance for reforestation of deserts and dry steppes, they also provide wood, fuel, fodder, etc [8]. Studies on the utilization of these shrubs have shown the potential of this lignocellulosic raw material for a variety of applications. Particularly, hemicelluloses comprised over 40% of the cell walls of *Caligonum monogoliacum* and *Tamarix* spp. [9]. The preparation and properties of new polymers from hemicelluloses should thus be an important part of any research program aimed at utilizing renewable polymers as extenders and replacements for polymers prepared from petrochemicals.

Extraction of the hemicelluloses from the cell wall matrix of wood and straws, is restricted by the present lignin network as well as ester and ether lignin–carbohydrate linkages. Additionally, extensive hydrogen bonding between the individual polysaccharide components may impede their isolation. For the isolation of hemicelluloses from woods and annual plants, various multi- and two-step extraction procedures have been proposed. In the case of woods, delignification with acidic sodium chlorite is usually used before the alkaline extraction of hemicelluloses [4]. More recently, environmental concerns have heightened interest in chlorine-free extraction sequence. Alkaline peroxide process is of particular interest and has been successfully applied in the delignification and isolation of hemicelluloses from agricultural residues such as cereal straws [10,11]. A considerable extraction of hemicelluloses could be also achieved using aqueous organic solvents under acidic or alkaline conditions. This process allows to fractionate the lignocellulosic materials into three major components by separation of residue from black liquor: cellulosic fibre, hemicelluloses, and lignin [12,13]. In this study, the hemicellulosic preparations from *C. monogoliacum* and *Tamarix spp*. were isolated by sequential treatments with ethanol–H_2O (60/40,v/v) under acid catalyst (0.2 N HCl) at 70 °C for 4 h and with 2% H_2O_2 at pH 11.5 for 16 h, respectively. The chemical composition and physico-chemical properties of acidic organosolv soluble and alkaline peroxide soluble hemicelluloses were comparatively studied by both degraded methods such as acid hydrolysis and thermal analysis and non-degradation techniques such as Fourier transform infrared (FT-IR) and carbon-13 magnetic resonance (^{13}C-NMR) spectroscopy as well as gel permeation chromatography (GPC), and the results are reported.

2. Experimental

2.1. Materials

C. monogoliacum and *Tamarix* spp., 6 years old, were harvested in the July of 1999, in the desert region of Gansu Province, China. It was dried in sunlight and then chipped into small pieces. The chips were then ground to pass a 1.0 mm size screen. After being further dried at 60 °C for 16 h, the powder was dewaxed with toluene–ethanol (2:1, v/v) in a Soxhlet for 6 h, respectively. The dewaxed sample was dried in a cabinet oven with air circulation at 60 °C for 16 h and then kept at 5 °C before treatment. All weights and calculations were made on an oven-dried (60 °C, 16 h) basis.

2.2. Two-stage extraction

The dewaxed *C. monogoliacum* and *Tamarix* spp. were sequentially extracted with ethanol–H_2O under acidic condition and hydrogen peroxide under alkaline condition as described previously [9] and their extraction scheme is shown in Fig. 1. In organosolv pre-treatment, the extractive free powder (9.75 g) was treated with ethanol–H_2O (195 ml, 60/40, v/v) under acid catalyst (0.2 N HCl) at 70 °C for 4 h. The solubilized polymers were separated from the insoluble residue by filtration with a nylon cloth. The residue was subsequently washed with ethanol and distilled water, and then oven dried at 60 °C for 16 h. Ethanol in the combined supernatant was removed with a rotary vacuum evaporator at 40 °C. Then the supernatant was neutralized to pH 5.5 with 1 M NaOH, concentrated on a rotary evaporator under reduced pressure to about 100 ml, and then mixed with 3 volumes of 95% ethanol (12 h, 25 °C) for isolation of hemicelluloses. The isolated hemicellulosic preparations were washed with 70% ethanol at room temperature and dried in air. The alkaline peroxide soluble hemicellulosic fractions were isolated from the above residues by post-treatment with 2% H_2O_2 (residue:extractant, 1:25) at pH 11.5 for 16 h at 45 °C as the method mentioned above. No further adjustments in pH were made during the course of the post-treatment. Under these conditions, the reaction pH remained nearly constant for two hours before slowly rising to a final value of ca 12.8. Note that the hemicelluloses solubilized during the pre-treatment of *C. monogoliacum* with ethanol–H_2O and post-treatment with alkaline peroxide were labeled as hemicellulosic fractions 1 (F_1) and 2 (F_2), and the hemicelluloses solubilized during the corresponding pre- and post-treatments of *Tamarix* spp. were named as the hemicellulosic fractions 3 (F_3) and 4 (F_4), respectively. The two residues of *C. monogoliacum* and *Tamarix* spp. were considered to be crude cellulose fractions 5 (F_5) and 6 (F_6), respectively.

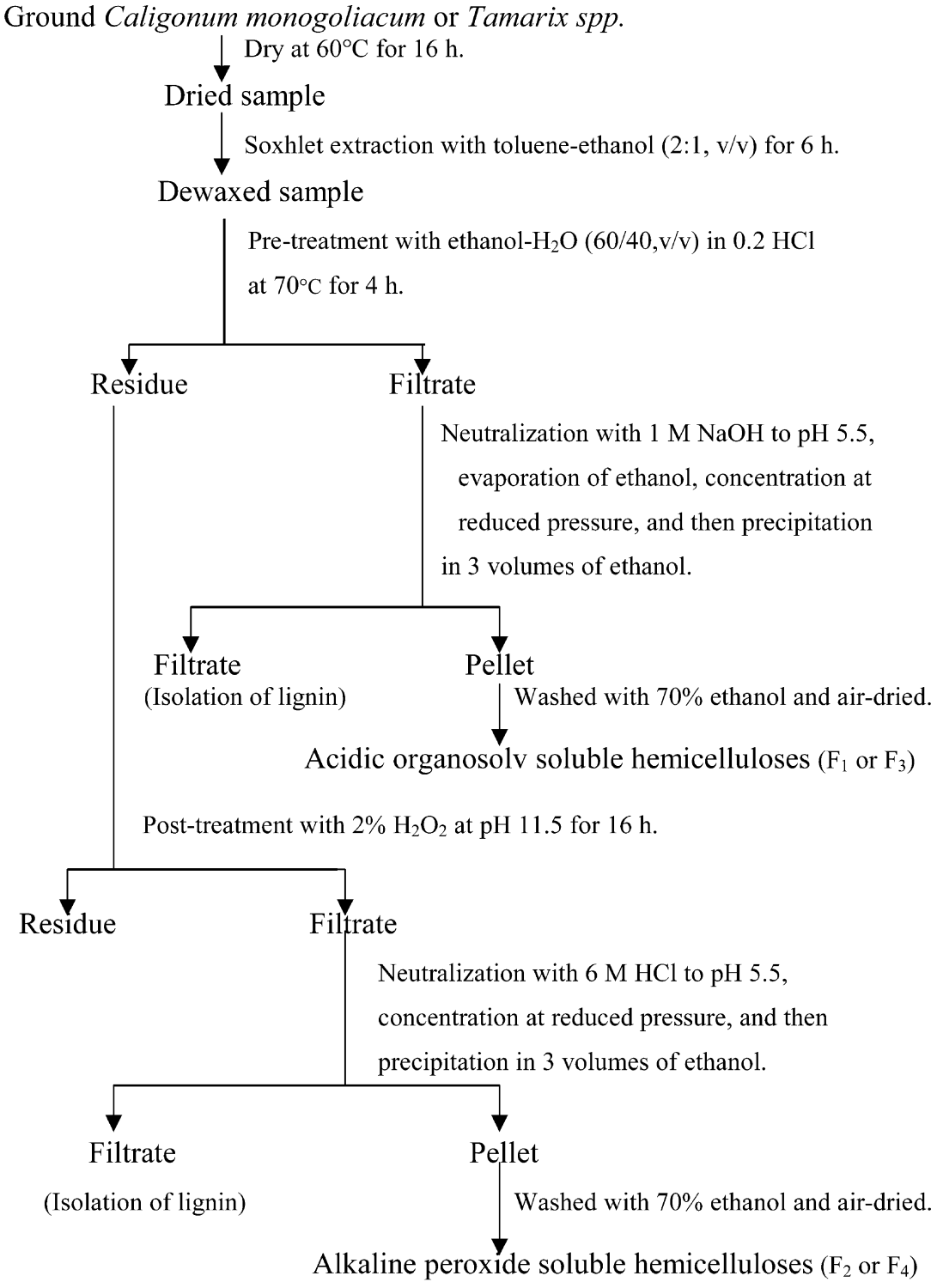

Fig. 1. Scheme for isolation of hemicellulosic preparations from dewaxed *Caligonum monogoliacum* or *Tamarix* spp.

2.3. Physico-chemical and thermal analysis

The neutral sugar composition of the isolated hemicelluloses was determined by gas chromatography (GC) analysis of their alditol acetates [14]. The hemicelluloses were hydrolyzed with 2 M trifluoroacetic acid at 120 °C for 2 h and the resulting monosaccharides reduced and acetylated. The residual samples were treated with 72% (w/w) sulphuric acid for 45 min at 25 °C prior to hydrolyses with 1 M sulphuric acid for 2.5 h at 100 °C. Alkaline nitrobenzene oxidation of associated lignin from the solubilized hemicellulosic preparations was

performed at 170 °C for 2.5 h. The lignin content in hemicellulosic preparations was calculated multiplying by 2.6, the yield of phenolics obtained by nitrobenzene oxidation [10]. Total uronic acid content was determined colorometrically by the method of Blumenkrantz and Asboe-Hansen [15]. Method for measurement of the hemicellulosic molecular weights has been described in a previous paper [16].

The FT-IR spectra were recorded from KBr pellets containing 1% finely ground samples on a Nicolet-510 FT-IR spectrophotometer. The 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. It was recorded at 25 °C from 150 mg of sample dissolved in 1.0 mL D_2O after 15,000 scans. A 60° pulse flipping angle, a 3.9 μs pulse width and 0.85 s acquisition time were used.

Thermal analysis of the hemicellulosic preparations was performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (NETZSCH STA-409). The apparatus was continually flushed with nitrogen. The sample weighed between 8 and 12 mg. Each sample was heated from room temperature to 600 °C at a rate of 10 °C per minute.

3. Results and discussion

3.1. Yield of hemicelluloses

Organosolv pulping has proved to be a promising process to achieve complete-utilization of lignocellulosics without impact to environment [17,18]. In this case a mixture of organic solvent and water is used as cooking liquor. The solvent primarily acts on the promotion of vegetal tissue impregnation and the solubilization of the lignin fragments so produced [19]. Wood materials can be fractionated to pulp, lignin, degraded hemicelluloses, which makes it easy to utilize them for more valuable products. The pulp can be used for either paper or cellulose derivatives. The lignin can be converted to valuable products such as activated carbon and adhensives [20]. From the degraded hemicelluloses, sweetening materials, food additives, and polymers can be producted [18]. During organosolv acid delignification, lignin is dissolved by acid-catalyzed cleavage of such bonds as α-aryl ether and arylglycerol-β-aryl ether in the lignin macromolecule [21], which results in release or degradation of hemicelluloses. However, the cleavage of β-aryl ether bonds occurs at a lower extent [22,23]. In the present study, pre-treatment of dewaxed *C. monogoliacum* and *Tamarix* spp. with ethanol–H_2O (60/40, v/v) under acid catalyst (0.2 N HCl) at 70 °C for 4 h resulted in 28.8% and 31.2% of the original lignin removal, and 41.7% and 40.2% of the original hemicelluloses release, respectively (Table 1) [9]. This high solubility of hemicelluloses was probably that the hemicelluloses are present mainly on outer fibre surface, from where they dissolve easily in the organosolv pre-treatment. In contrast, cellulose is located in the inner parts of the fibres and therefore are not easily dissolved. Furthermore, cellulose has partly crystal structure which reduces its solubility [24].

As mentioned above, hydrogen peroxide as chlorine-free bleaching agents have become increasingly important in the today's bleaching technology as the pulp and paper industry is moving toward minimization of environmental impact. In fact, hydrogen peroxide in alkaline condition reacts also as a delignifying agent to remove lignin and solubilize hemicelluloses from lignocellulosic raw materials. In this case, dissociated hydrogen peroxide, i.e. hydroperoxide anion (HOO^-), reacts with lignins in woods mainly as a nucleophile although it also acts as an oxidant. The hydroperoxide anion attacks carbonyls conjugated with aromatic rings in the residual lignin, such as α-carbonyl in β-*O*-4 type substructures, rather than oxidatively degrades the lignin directly [25,26]. Thus, the degraded or solubilized lignins and hemicelluloses during the alkaline peroxide treatment under mild conditions are both theoretically interesting for their structural studies and commercially interesting for industrial applications. In this study, 2% H_2O_2 at pH 11.5 for 16 h was used for a sequential

Table 1
The yield of hemicelluloses (% dry matter) solubilized during two-stage treatments of dewaxed *C. monogoliacum* and *Tamarix* spp. with ethanol–H_2O (60/40,v/v) under acid catalyst (0.2 N HCl) at 70 °C for 4 h and with 2% H_2O_2 at pH 11.5 for 16 h

Yield	*Caligonum monogoliacum*	*Tamarix* spp.
Total solubilized hemicellulosesin two-stage treatments	44.9	44.3
Solubilized hemicelluloses in pre-treatment[a]	18.7	17.8
Solubilized lignin in pre-treatment[a]	3.9	5.3
Solubilized hemicelluloses in post-treatment[b]	26.2	26.5
Solubilized lignin in post-treatment[b]	8.3	9.5
Residue (Crude cellulose)	37.8	36.7

[a] Represent for the hemicellulosic and lignin fractions obtained by pre-treatment of dewaxed *C. monogoliacum* and *Tamarix* spp. with ethanol–H_2O (60/40,v/v) under acid catalyst (0.2 N HCl) at 70 °C for 4 h.

[b] Represent for the hemicellulosic and lignin fractions obtained in the post-treatment with 2% H_2O_2 at pH 11.5 for 16 h.

treatment of the organosolv treated *C. monogoliacum* and *Tamarix* spp. The results showed that the post-treatment dissolved 26.2% and 26.5% of hemicelluloses (% dry starting material) from *C. monogoliacum* and *Tamarix* spp., respectively. Meanwhile, the post-treatment dissolved 10.6% and 12.1% lignin (% dry starting material), corresponding to dissolution of 55.5% and 59.0% of the original lignin, respectively. Taking together, the two-stage treatments yielded 44.9% and 44.3% polysaccharides solubilized from *C. monogoliacum* and *Tamarix* spp., respectively. A higher yield of both lignin and hemicelluloses solubilized during the post-treatment than the pre-treatment revealed that the alkaline peroxide post-treatment under the condition used significantly cleaved the ether linkages between lignin and hemicelluloses from the cell walls of *C. monogoliacum* and *Tamarix* spp.

3.2. Sugar composition

Table 2 gives the neutral sugar composition and content of uronic acids in the solubilized hemicellulosic preparations and crude cellulose. Obviously, the organosolv soluble hemicelluloses F_1 contained xylose, galactose, and glucose as the major neutral sugars. Rhamnose, mannose, and arabinose were present in relatively small amounts (a total of 22.8%). Similarly, the F_3 fraction contained more than 50% xylose, and the next most abundant sugar being glucose, accounting for 30.3%. Galactose (7.6%), Rhamnose (5.7%), Arabinose (2.8%), and mannose (2.7%) were identified in minor quantities. The dominance of xylose and a noticeable amount of glucose in this fraction might characterize it as an glucoxylan, or as a mixture of xylan and glucan, having the minor sugars probably as side-chain components. The sequential treatment performed revealed a meaningful increase in the xylose content for the hemicelluloses (F_2 and F_4), which are more strongly associated to the cellulose. Xylose was the predominant component for the two hemicellulosic fractions solubilized during the alkaline peroxide post-treatment, and glucose was the second major one in the fraction (F_4) obtained from *Tamarix* spp. Most of the xylose residues probably originated from the backbone of a xylan. The presence of a noticeable amount of glucose residues in F_4 fraction indicated that glucan was also a part of the hemicelluloses in the cell walls of *Tamarix* spp. These results implied that the hemicelluloses solubilized by alkaline peroxide were less branched than those solubilized by acidic organic solvent and more strongly associated with cellulose microfibrils. Unfortunately, based on the sugar composition alone it is difficult to draw conclusions on the branching patterns of the hemicelluloses from *C. monogoliacum* and *Tamarix* spp. Similar to xylose, the content of uronic acids in the hemicellulosic preparations solubilized by alkaline peroxide were relatively higher than those in the hemicellulosic preparations solubilized by organic solvent.

Table 2
The content of neutral sugars (relative% hemicelluloses, w/w) and uronic acids (% hemicelluloses, w/w) in isolated hemicellulosic fractions and residues obtained by the pre-treatment of dewaxed *C. monogoliacum* and *tamarix* spp. with ethanol–H_2O (60/40,v/v) under acid catalyst (0.2 N HCl) at 70 °C for 4 h and with 2% H_2O_2 at pH 11.5 for 16 h

Sugars (%)	Hemicellulosic and residual fractions					
	F_1[a]	F_2[a]	F_3[b]	F_4[b]	F_5[c]	F_6[c]
Rhamnose	10.1	2.9	5.7	2.3	ND[d]	ND
Arabinose	4.5	1.4	2.8	1.3	0.2	0.5
Xylose	31.8	77.3	50.8	74.1	15.0	16.7
Mannose	8.2	2.7	2.7	0.8	Tr[e]	Tr
Glucose	21.4	7.4	30.3	18.6	84.9	82.7
Galactose	24.1	8.3	7.6	3.0	Tr	Tr
Uronic acids	5.0	7.5	6.5	8.3	Tr	Tr

[a] Fractions 1 (F_1) and 2 (F_2) represent the hemicellulosic fractions extracted sequentially with ethanol–H_2O (60/40, v/v) under acid catalyst (0.2 N HCl) at 70 °C for 4 h and 2% H_2O_2 at pH 11.5 for 16 h at 45 °C from dewaxed *C. mongoliacum*.

[b] Fractions 3 (F_3) and 4 (F_4) represent the hemicellulosic fractions extracted sequentially with ethanol–H_2O (60/40, v/v) under acid catalyst (0.2 N HCl) at 70 °C for 4 h and 2% H_2O_2 at pH 11.5 for 16 h at 45 °C from dewaxed *Tamarix* spp.

[c] Fractions 5 and 6 represent the two-stage treated residues of *C. monogoliacum* and *Tamarix* spp., respectively.

[d] ND = not detected.

[e] Tr = trace.

Analysis of the two residue fractions showed that the two sequential treatments used to extract the dewaxed *C. monogoliacum* and *Tamarix* spp. were not able to solubilize all hemicellulosic substances. About 62–63% of the dewaxed *C. monogoliacum* and *Tamarix* spp. were extracted leaving the residues, which consisted of about 83–85% of cellulose and about 15–17% of (much less branched) hemicelluloses, xylans. The hemicelluloses which remains in the residue verified again that the xylans are tightly bound to the cell wall component, cellulose.

3.3. Content of lignin

It is commonly assumed that lignin is tightly linked to polysaccharides in the cell walls of plants by various linkage types, such as ether linkage of the hydroxyl group at the α-position of the lignin side chain with alcoholic hydroxyl of sugar residue [27], ester linkage of the alcohol OH of lignin with the carboxylic group of uronic acid [28], ester linkage of the carboxylic group of the cinnamic acid unit in lignin with the alcoholic OH of polysaccharides [29], and glycoside linkage with the primary alcoholic OH at the γ-position of the phenylpropane unit [30]. To verify the contaminated lignin in the hemicellulosic preparations and the residual lignin associated in the residues, the four hemicellulosic frac-

tions and two crude cellulose samples were oxidized by alkaline nitrobenzene. This method provided an estimate of the amount of associated lignin and an indication of its composition. Results concerning the characterization of lignin bound to hemicelluloses and cellulose are given in Table 3. The data showed that the six polysaccharide preparations contained relatively low amounts of associated lignins, ranging between 5.64% in F_6 and 9.82% in F_4. This relatively lower content of bound lignin in the acidic organosolv and alkaline peroxide soluble hemicelluloses and the residues suggested that the α-benzyl ether linkages between lignin and hemicelluloses were substantially cleaved during the two-stage treatments under the conditions given. On the other hand, this measurable amount of residual lignin in the two-stage treated residues also implied that the polysaccharides in the cell walls of *C. monogoliacum* and *Tamarix* spp. are tightly associated with lignin. Our previous studies by ^{13}C-NMR spectroscopy confirmed that the hydroxyl groups of sugar residue in the hemicelluloses are mainly linked at the C-α position of the side chain of phenylpropane units in the lignin molecules [9]. The major products, obtained from the alkaline nitrobenzene oxidation, were identified to be vanillin and syringaldehyde, which together represented for 57.2–71.1% of the total phenolic acids and aldehydes. A noticeable amount of *p*-hydroxybenzoic acid, vanillic acid, syringic acid, and *p*-coumaric acid were also found to be present in the nitrobenzene oxidation products. *p*-Hydroxybenaldehyde, acetovanillin, acetosyringone, and ferulic acid were detected to be present in trace amounts.

3.4. Molecular mass

The four hemicellulosic fractions were further characterized by the determination of their molecular mass, and their weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights and polydispersity ($\bar{M}_w/\bar{M}_n$) are given in Table 4. Clearly, the hemicellulosic fractions F_2 and F_4, solubilized during the alkaline peroxide post-treatment, showed a much higher degree of polymerization with $\bar{M}_w$ values between 27,220 and 31,410 g mol^{-1} than those of the hemicellulosic preparations F_1 ($\bar{M}_w$, 18,380 g mol^{-1}) and F_3 ($\bar{M}_w$, 13,820 g mol^{-1}), released during the acidic organosolv pre-treatment. Additionally, the analysis showed that the two polymeric hemicelluloses, released during the acidic organosolv pre-treatment, gave more narrow molar mass distribution, corresponding to polydispersity indexes of 1.26 for F_1 and 1.06 for F_3 as compared to those of the alkaline peroxide soluble hemicellulosic products F_2 and F_4 having polydispersity indexes of 1.45 and 1.46, respectively. In other words, the molecular weight distribution of the two alkaline peroxide soluble hemicellulosic fractions was broader, and the average molecular weight was higher than the two acidic organosolv soluble hemicelluloses. This implied that the pre-treatment with ethanol–H_2O under the condition given favoured solubilization of the small molecular size of hemicelluloses, while the post-treatment with alkaline peroxide under the condition used did not significantly degraded the macromolecular structure of the hemicelluloses.

3.5. FT-IR spectra

The analysis of FT-IR data showed that all the four hemicellulosic preparations clearly illustrated the typical signal pattern for hemicellulosic moiety, and had a specific band maximum in the 1200–1000 cm^{-1} region shown in Fig. 2. This region is dominated by ring vibrations overlapped with stretching vibrations of (C–OH) side groups and the (C–O–C) glycosidic bond

Table 3
The yield (% sample, w/w) of phenolic acids and aldehydes from alkaline nitrobenzene oxidation of lignins in isolated hemicellulosic fractions and residues

Phenolic acids and aldehydes	Hemicellulosic and residual fractions[a]					
	F_1	F_2	F_3	F_4	F_5	F_6
p-Hydroxybenzoic acid	0.57	0.41	0.17	0.24	0.25	0.15
p-Hydroxybenzaldehyde	0.11	0.08	0.07	0.15	0.05	0.08
Vanillic acid	0.11	0.13	0.08	0.19	0.18	0.07
Syringic acid	0.14	0.17	0.15	0.25	0.23	0.12
Vanillin	1.15	1.19	0.80	1.24	1.01	0.64
Syringaldehyde	0.71	0.90	0.80	1.34	1.08	0.70
Acetovanillin	0.08	0.07	0.06	0.10	0.06	0.14
p-Coumaric acid	0.14	0.13	0.06	0.07	0.05	0.10
Acetosyringone	0.09	0.06	0.07	0.09	0.09	0.10
Ferulic acid	0.07	0.13	0.05	0.06	0.07	0.04
Total	3.17	3.27	2.25	3.73	3.07	2.14
Content of lignin	8.34	8.61	5.94	9.82	8.08	5.64

[a] Corresponding to hemicellulosic and residual fractions in Table 2.

Table 4
Weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights and polydispersity ($\bar{M}_w/\bar{M}_n$) of the hemicellulosic fractions isolated sequentially with ethanol–H_2O (60/40, v/v) at 70 °C for 4 h and 2% H_2O_2 at pH 11.5 for 16 h at 45 °C from dewaxed *C. mongoliacum* and *Tamarix* Spp

	Hemicellulosic fractions[a]			
	F_1	F_2	F_3	F_4
$\bar{M}_w$	18,380	27,220	13,820	31,410
$\bar{M}_n$	14,530	18,730	13,050	21,450
$\bar{M}_w/\bar{M}_n$	1.26	1.45	1.06	1.46

[a] Corresponding to hemicellulosic fractions in Table 2.

vibration [31]. In particular, the band at 1055 cm^{-1} is dominated by glycosidic linkage ν (C–O–C) contribution. In the carbonyl stretching region, in addition to a strong signal due to the absorbed water (1626 cm^{-1}), a small band at 1745 cm^{-1} in the two spectra (a and c) of acidic organosolv soluble hemicellulosic fractions are originated from the acetyl and uronic ester groups of the hemicelluloses or from the ester linkage of carboxylic group of the ferulic acid, while the absence of this signal in the spectra (b and d) of alkaline peroxide soluble hemicellulsic preparations indicated that the alkaline peroxide post-treatment under the condition used completely cleaved this ester bond from the hemicelluloses. As expected, the absence of a signal at 1720 cm^{-1} for carbonyl stretching in all the four spectra implied that both pre- and post-treatments under the conditions given did not significantly attack or oxidise the glycosidic linkages and hydroxyl groups of hemicelluloses. The fact that the glycosidic linkages and hydroxyl groups of hemicelluloses remained unattached during the two-stage treatments revealed a great difference in reaction rates between glycosidic and phenolic structures. Our previous studies showed that both of the lignins, solubilized during the alkaline peroxide post-treatment from *C. monogoliacum* and *Tamarix* spp., were significantly oxidized as shown by a noticeable band at 1720 cm^{-1} for carboxylic groups [9]. The absence of this band in all the spectra of hemicelluloses implied that lignin can compete with the hemicelluloses for alkaline peroxide and thus exhibit a protective effect from the oxidation of hemicelluloses. Similar results have been reported from the degradation of model compounds for cellulose and lignocellulosic pulp during ozonation in aqueous solution. The authors [32] stated that the degradation of phenolic structure in the lignin was very rapid, while the degradation of the carbohydrates part was slower. This implied that lignin provides some protection for the hemicelluloses in lignin-containing *C. monogoliacum* and *Tamarix* spp. against attack by alkaline peroxide. Similar to ozone–lignin reaction, the total oxidation rates of the lignin and polysaccharide moieties are strongly dependent on the ratio between the reaction rates of the hydroxyl radicals formed with lignin and polysaccharides, respectively. This ratio was found to be about 5 [33]. More hydroxyl radicals are formed via ozone or peroxide-lignin reactions than via the ozone or peroxide-polysaccharide reaction [32].

Fig. 3 illustrates the FT-IR spectra of two residues (crude cellulose) obtained by sequential treatments from dewaxed *C. monogoliacum* (spectrum a) and *Tamarix* spp. (spectrum b). The absence of a absorption band at

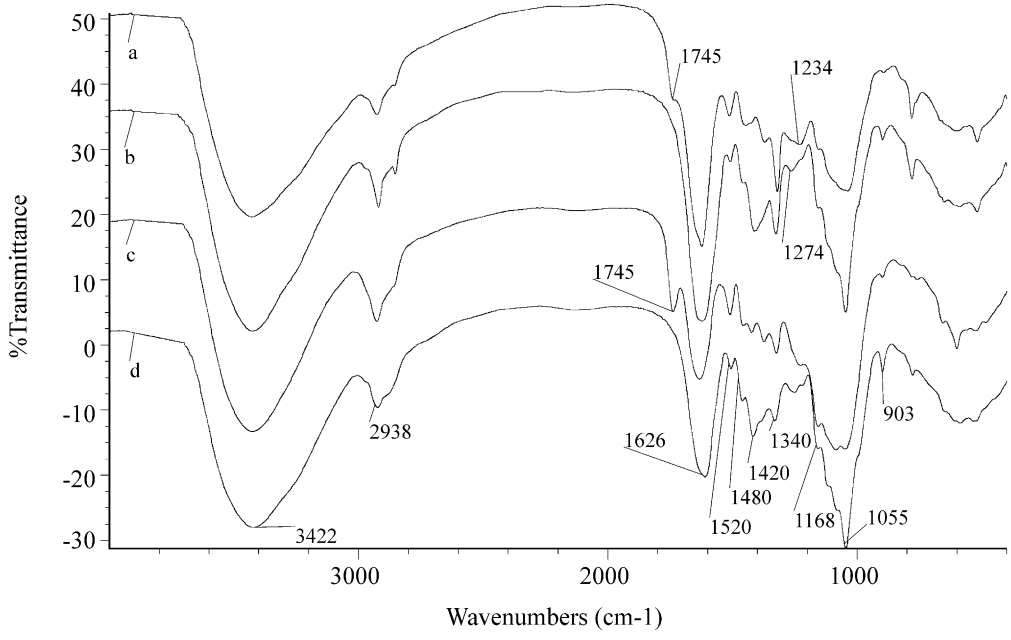

Fig. 2. FT-IR spectra of hemicellulosic preparations F_1 (spectrum a), F_2 (spectrum b), F_3 (spectrum c), and F_4 (spectrum d).

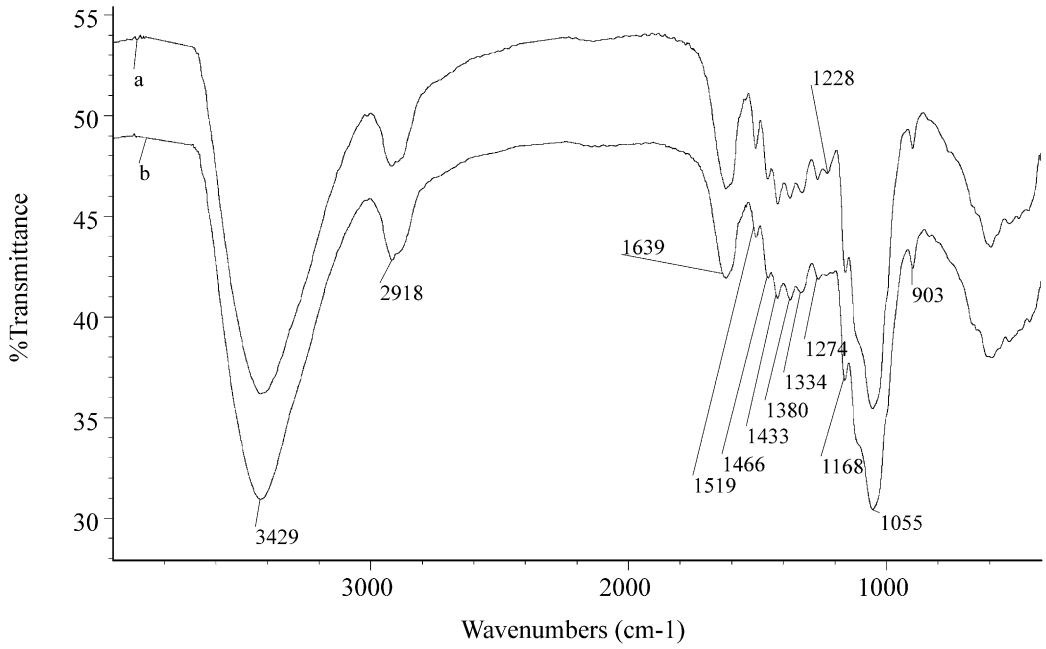

Fig. 3. FT-IR Spectra of ethanol–H_2O and sequentially alkaline peroxide treated residues of *C. mongoliacum* (spectrum a) and *Tamarix* spp. (spectrum b).

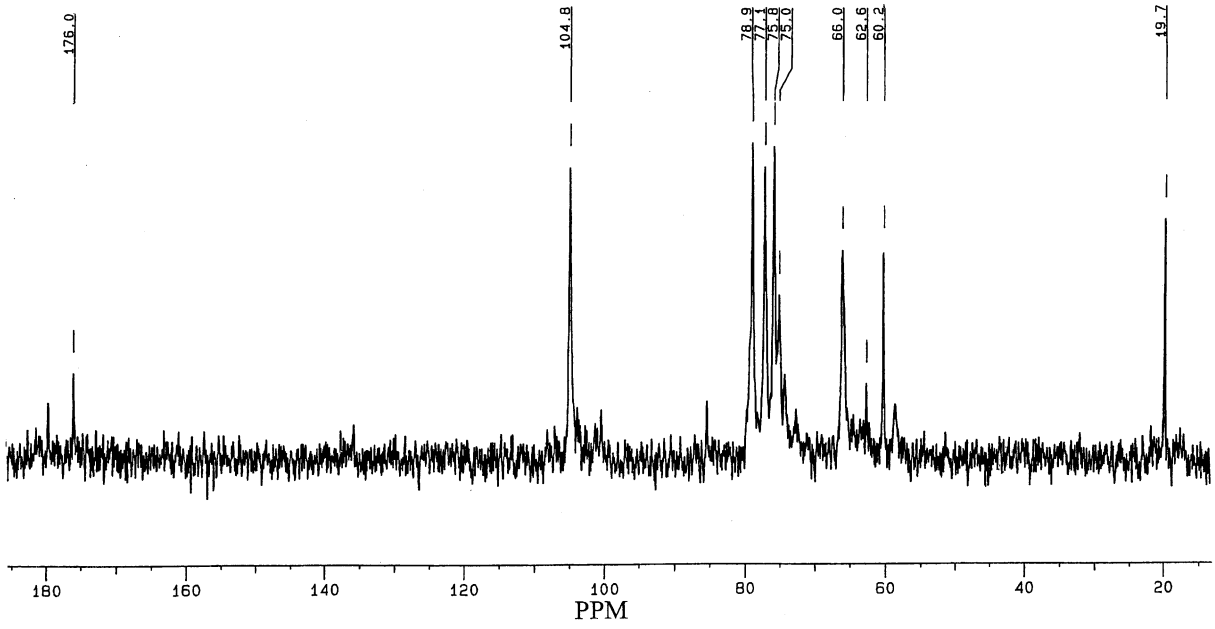

Fig. 4. ^{13}C-NMR spectrum of hemicellulosic fraction F_4 extracted with 2% H_2O_2 at 45 °C for 16 h at pH 11.5 from the pre-treated *Tamarix* spp.

1720 cm^{-1} for carbonyl or carboxyl groups indicated once again that lignin also exhibited a protective effect on the oxidation of cellulose during the alkaline peroxide post-treatment. An intense band at 1639 cm^{-1} is assignated to the absorbed water. The prominent absorption at 1055 cm^{-1} is attributed to the C–O, C–C stretching, C–OH bending or glycosidic linkage ν (C–O–C) contribution. The small sharp band at 903 cm^{-1} is indicative of β-glycosidic linkage between glucose units in cellulose [31].

3.6. ^{13}C-NMR spectrum

The alkaline peroxide soluble hemicellulosic fraction (F_4) obtained from *Tamarix spp.* gave well-reserved the ^{13}C-NMR spectrum (Fig. 4), whose interpretation was made on the basis of chemical results and earlier reports for structurally-defined arabinoxylan-type, glucuronoxylan-type, and L-arabino-(4-*O*-methyl-D-glucurono)-D-xylan polysaccharides [34-36]. The main 1,4-linked β-D-Xylp units are obviously characterized by five strong signals at

104.8, 78.9, 77.1, 75.8, and 66.0 ppm, which are assigned respectively to C-1, C-4, C-3, C-2, and C-5 positions of the β-D-Xylp units. A intensive signal at 60.2 ppm originates from the 4-*O*-methoxyl group of glucuronic acid residue in the xylan. The carbonyl resonances from uronic acids may contribute to a signal at 176.0 ppm which indicates C-6 in methyl uronates. The C-1 and C-4 of the 4-*O*-methylglucuronic acid residue in the hemicelluloses give signals at 100.2 and 85.1 ppm (data not shown), respectively. The methyl group appears with a relative strong signal at 19.7 ppm. The data supported a xylan structure substituted with 4-*O*-methyl-α-D-Glc*p*A groups. In addition, two intense signals at 75.0 and 62.6 ppm correspond to C-5 and C-6 of D-Glc*p*

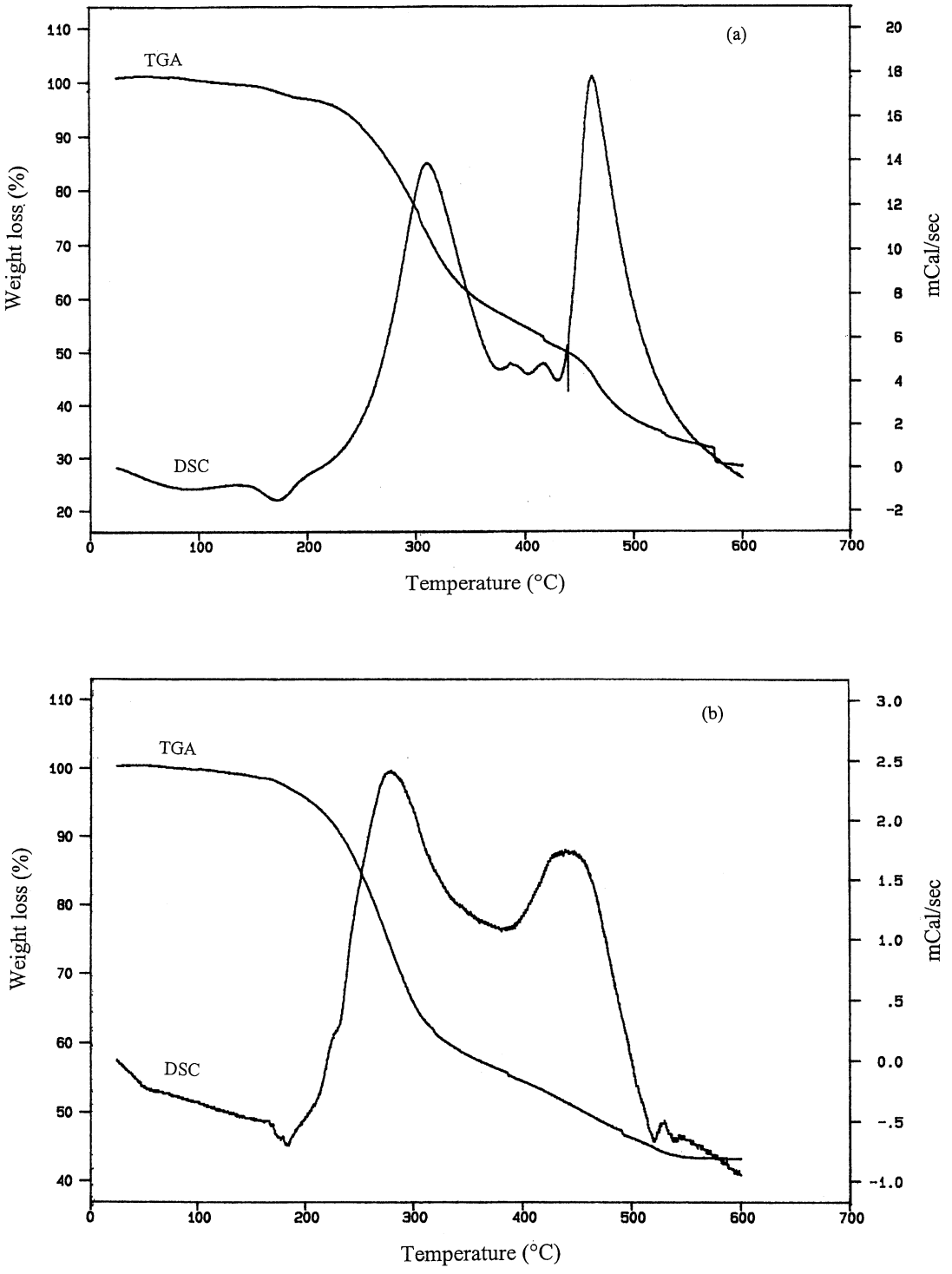

Fig. 5. Thermogram of hemicellulosic fractions F_1 (a) and F_2 (b) obtained from dewaxed *C. monogoliacum*.

units, indicating a noticeable amount of D-glucan. It is therefore very likely that the major component of the hemicellulosic fraction F_4 was an acidic xylan and it was contaminated with a noticeable amount of glucan. This finding is of significance in the understanding of the structure of the primary plant cell wall from *Tamarix* spp. in which 4-*O*-methylglucuronoxylan is a major component.

3.7. Thermal analysis

Hemicelluloses represent thermally labile cell wall components of higher plants [3]. In this study, the thermal properties of the four hemicellulosic preparations were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results showed that all of the hemicelluloses began to decompose at 170–176 °C, and most hemicelluloses observed showed their maximum rate of weight loss between 230 °C and 340 °C. Fig. 5 illustrates the thermograms of the acidic organosolv soluble hemicellulosic preparation F_1 (Fig. 5a) and alkaline peroxide soluble hemicellulosic fraction F_2 (Fig. 5b) from dewaxed *C. monogoliacum*. At 10% weight loss the degradation temperature was observed at 250 °C for preparation F_1 and 235 °C for preparation F_2. In contrast, when weight loss arrived at 50%, the temperature raised to 446 °C for F_1 fraction and 457 °C for F_2 fraction. Continuously, at 60% weight loss the decomposition temperature occurred at 488 °C for F_1 fraction and over 600 °C for F_2 fraction. This phenomenon suggested that, in general, the alkaline peroxide soluble hemicelluloses had a slightly higher thermal stability than that of the acidic organosolv soluble hemicelluloses, and the thermal stability of the hemicelluloses increased with an increasing molecular weight.

In comparison with cellulose having a narrow temperature range, the hemicelluloses decomposed at relatively higher temperatures and in a broader temperature interval. However, the degradation of hemicelluloses in insert atmosphere included dehydration and condensation reactions. The glass transition temperature T_g of the hemicelluloses was observed at 171 °C for F_1 and 178 °C for F_2 fraction, respectively. Similar temperature range of 167–180 °C has been reported from wood xylans [37].

The above results showed that sequential treatments with ethanol–H_2O (60/40, v/v) under acid catalyst (0.2 N HCl) at 70 °C for 4 h and with 2% H_2O_2 at pH 11.5 for 16 h together yielded 44.9% hemicelluloses from *C. monogoliacum* and 44.3% from *Tamarix* spp., respectively. FT-IR and ^{13}C-NMR spectroscopies confirmed the results obtained by chemical methods, and showed that the alkaline peroxide post-treatment under the condition given did not result in a significant oxidation of the hemicellulosic and cellulosic polymers. It is very likely that lignin can compete with the hemicelluloses and cellulose for alkaline peroxide and thus exhibit a protective effect from the oxidation of hemicelluloses and cellulose. Further study of the alkaline peroxide soluble hemicellulosic fraction from *Tamarix* spp. by ^{13}C-NMR spectroscopy found that the preparation is composed mainly of a 4-*O*-methylglucuronoxylan together with a noticeable amount of glucan. The thermal stability of the hemicelluloses was found to increase slightly with increasing molecular weight.

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