

Short communication

Isolation and structural characterization of hemicelluloses
from palm of *Phoenix dactylifera* L.Abdelkader Bendahou^a, Alain Dufresne^b, Hamid Kaddami^a, Youssef Habibi^{b,*}^a *Laboratoire de Chimie Bioorganique et Macromoléculaire, Faculté des Sciences et Techniques (Université Cadi Ayyad),
B.P. 549 Marrakech, Maroc, France*^b *Ecole Française de Papeterie et des Industries Graphiques (EFG-IPG), BP 65, 38402 St-Martin d'Hères Cedex, France*

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Abstract

Hemicellulose-type polysaccharides were isolated from the leaflets and the rachis of palm of *Phoenix dactylifera* L. by alkaline extraction and fractionated by precipitation. The structural investigations were achieved by sugar analysis and NMR spectroscopy. Three fractions were obtained and purified from leaflets as well as from rachis. From leaflets, the water soluble fractions were assumed to be arabinoglucuronoxylans, with 4-*O*- α -D-glucopyranosyluronic acid groups linked at C-2 and arabinofuranosyl at C-3. The water non-soluble fraction from leaflets and all fractions extracted from rachis were assumed to be (1 \rightarrow 4)-linked β -D-xylan with a 4-*O*-methyl- α -D-glucopyranosyluronic acid group attached at C-2. The sugar composition and the ¹H and ¹³C NMR spectra showed that their chemical structures were very similar, but with different proportions of 4-*O*-Me-D-GlcA.

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1. Introduction

The date palm (*Phoenix dactylifera* L.) is a tropical and subtropical tree that belongs to the plamae (*Arecaceae*) family and plays an essential ecological role in Arabian countries. It is extremely useful in controlling desertification by creating a microclimate which prevents long-term degradation of ecologically weak environments. On the other hand fruits exploitation of date palm trees represents an important economical support for indigenous populations (Goaman, Dunkley, & King, 1993). Actually, the mean yield of date production is important as it varies between 18 and 50 kg of dates per tree.

Considering the food importance of the date fruit, numerous studies have been engaged on the characterization of its chemical composition particularly, polysaccharides identification of different parts of date. Ishrud,

Zahid, Ahmad, and Pan (2001), Ishrud, Zahid, Zhou, and Pan (2001), Ishrud, Sun, Xiao, Ashour, and Pan (2002) have isolated and studied polysaccharides from seed of date. They characterized galactomannan-type polysaccharides, heteroxylan, and glucomannan. From pulp fruit, Haq and Gomes (1977) have isolated a xylan and Ishrud et al. (2002) have purified a linear glucan which shows mixing linkages, (1 \rightarrow 3)- and (1 \rightarrow 4)-. More recently, Ishrud, Zgheel, Kermagi, Flefla, and Elmabruk (2004), Ishrud and Kennedy (2005) reported that this glucan was found to exhibit potent antitumor activity.

Xylans represent the most abundant hemicellulose-type polysaccharides constituent in the plant kingdom. They are known to display several structural varieties in terrestrial plants and, even in different plant tissues within one plant. Previous studies have shown that plant xylans form a family of polysaccharides which consist of a backbone of β -(1 \rightarrow 4)-D-xylopyranose residues which can be substituted in C-2 and/or C-3 by short and flexible side chains. Depending on their origin, i.e., *Gramineae* (grasses and

* Corresponding author. Fax: +33476826933.

E-mail address: Youssef.Habibi@efpg.inpg.fr (Y. Habibi).

cereals), *Gymnosperms* (softwoods) or *Angiosperms* (hardwoods), these chains are mainly constituted of units of α -D-glucuronic acid, or 4-*O*-methyl- α -D-glucuronic acid and occasional units of α -L-arabinofuranose, α -D-xylopyranose or α -D-galactopyranose. Among the common side groups are acetyl groups, phenolic acids, ferulic, and coumaric acids (Stephen, 1983; Whistler & Chen, 1991).

Neutral homoxylans contained only xylose residues. These xyloses can be either linear such as the (1 \rightarrow 4)- α -D-xylan of guar seed husk, tobacco stalk and esparto grass, or branched such as the xylans of groundnut seed endosperm and those of the angiosperm. Neutral heteroxylans or arabinoxylans contained either single α -L-arabinofuranose residues which are usually attached by (1 \rightarrow 3) linkages. However, in the more substituted arabinoxylans, such as those from cereal endosperms, double branching (1 \rightarrow 3) and (1 \rightarrow 2) on xylose units are observed. In general, most of the acidic xylans from different plant sources contained only 4-*O*-methyl- α -D-glucuronic acid (Ebringerova & Heinze, 2000).

In this work, we investigated the isolation and structural characterization of the hemicellulose-type polysaccharides from leaflets and rachis of *P. dactylifera* palm. Actually, each year after the fruit harvesting, the upkeep of the date palm trees results in the production of a huge renewable amount of palms. These renewable resources are essentially used as biofuel for domestic purposes and also to build shelters (Barreveld, 1993). To our knowledge no studies have been done on the characterization of polysaccharides from leaflets and rachis of *P. dactylifera* palm. A better understanding of their chemical composition could allow opening new opportunities for both food and non-food applications of this abundant renewable resource.

2. Experimental

2.1. Analytical methods

Sugars composition was determined by high performance anion exchange chromatography (HPAEC) using fucose as the internal standard. Non-cellulosic fractions were hydrolyzed for 1 h at 100 °C in 1 M H₂SO₄. Cellulosic fractions were prehydrolyzed for 2 h at 30 °C in 6 M H₂SO₄, before adjusting the acid concentration to 1 M for further hydrolysis, for 2 h at 100 °C. After hydrolysis, the samples were diluted 2-fold, filtered and injected on to a CarboPac PA1 anion-exchange column (4 \times 250 mm, Dionex). Neutral sugars were separated in 5 mM NaOH for 12 min and a further 7 min with a linear gradient up to 100 mM NaOH. Acidic sugars were separated using a linear gradient of NaOAc (0–300 mM) in 100 mM NaOH for 30 min. The flow rate was 1 mL/min and detection was performed by pulsed amperometry (PAD 2, Dionex). A post-column addition of 300 mM NaOH at a flow rate of 0.7 mL/min was used. Calibration was performed with

standard solutions of arabinose, glucose, xylose, glucuronic, and galacturonic acids.

The LPSF-2 and LPSF-4 samples were methylated twice by the Hakomori procedure, as described by Jansson, Kenne, Liedgren, Lindberg, and Lonngren (1976). The partially methylated carbohydrates were then converted into their alditol acetates by successive treatments with NaBH₄ and pyridine-Ac₂O and analyzed on a fused-silica widebore column (30 m 0.53 mm) half bonded with SP-2380. Peak identification was based on retention times using partially methylated alditol acetates standard and confirmed by GLC by using a SP-2380 capillary column (0.32 mm) coupled with a Nermag R1010C mass spectrometer. Peak areas were corrected by using the molar response factors according to Sweet, Shapiro, and Albersheim (1975).

The ash content, which corresponded to minerals content, was measured after heating overnight the specimens at 600 °C. The percentage of protein was computed and applying a factor of 6.25 to the percentage of nitrogen. The lignin analysis was achieved according to the TAPPI standard T222-03-75.

2.2. Preparation of defatted residues (DR)

Fats, waxes, and oils were removed from leaflets and rachis powder by refluxing in a Soxhlet apparatus during 24 h with 38:62 toluene–EtOH.

2.3. Isolation of polysaccharides

Polysaccharides were sequentially extracted from LDR and RDR by water (2 \times 2 h at 100 °C) and aqueous solution of calcium chelator agent 0.5% EDTA (2 \times 2 h at 100 °C). The residues of leaflets and rachis were treated by chlorite solution at 70 °C to remove residual proteins and lignin. Finally, hemicellulose-type polysaccharides were extracted by alkaline treatments. The residues were extracted by 2% NaOH aqueous solution (2 \times 2 h at 80 °C). The different alkaline extracts were neutralized by acetic acid solution 20% at pH 5–6 and precipitated with EtOH (4 volumes) resulting in LSF-2 from leaflets and RSF-2 from rachis. The 2% NaOH residues were treated by a 4% NaOH aqueous solution (2 \times 2 h at 80 °C) and the extracts were neutralized by acetic acid solution at pH 5–6. The precipitates formed were recovered by centrifugation to give LIF-4 from leaflets and RIF-4 from rachis. The supernatants were finally precipitated with EtOH (4 volumes) resulting LSF-4 and RSF-2 from leaflets and rachis, respectively.

2.4. Purification of polysaccharides

The water soluble fractions (LSF-2, LSF-4, RSF-2, and RSF-4) were purified by size-exclusion chromatography on a polyacrylamide Biogel P6 column (4–100 cm) column, eluted at 80 mL/h flow rate with 0.05 M NaNO₃ solution,

and at room temperature. The column effluent was monitored using a refractive index detector. The salts were removed by dialysis and the solution was freeze-dried, to give the purified fractions LPSF-2, LPSF-4, RPSF-2, and RPSF-4.

The water insoluble fractions (LIF-4 and RIF-4) were purified by precipitation with Fehling solution according to Jones and Stoodley (1965). The samples were dissolved in 0.5 M NaOH solution and the Fehling solution was added to this solution until precipitation of the copper complex. After 4 h the precipitate is collected by centrifugation, washed with water, and decomposed by maceration for 1 min with ethanol containing 5% (v/v) of hydrochloric acid, washed exhaustively with water and freeze-dried.

2.5. Determination of molecular weights

Solutions were prepared by dissolution of soluble fractions in water, at a concentration of 2 g/L, filtrated through 0.2 µm Sartorius filters and injected through Shodex OHpak SB 804 HQ and SB 805 HQ columns, on an Alliance GPCV 2000 (from Waters). The eluant was 0.1 M NaNO₃. Solutions were then analyzed using two on line detectors: a differential refractometer, and a multi-angle laser light scattering DSP-F (Wyatt Technology, USA) at 25 °C.

2.6. NMR spectroscopy

¹³C NMR experiments were obtained with a Bruker Avance 500 spectrometer (operating frequency of 125 MHz). Samples of water soluble fractions were recorded as solution in D₂O at 333 K in 5 mm o.d. tube (internal acetone ¹³C (CH₃) at 31.5 ppm relative to Me₄Si). Samples of water insoluble fractions were examined in DMSO-*d*₆ at 333 K in 5 mm o.d. tube. NMR experiments were recorded in quantitative ¹³C NMR conditions using the Invgate Bruker sequence, with 90° pulse length (6.5 µs), relaxation delay of 2 s, 8000 data points, 0.54 s acquisition time, and 30,000 scans.

3. Results and discussion

3.1. Preliminary study

In the whole *P. dactylifera* palm, the amount of leaflets is (46.6%) and rachis is (53.4%) on a dry weight basis. The constituents and chemical composition of the leaflets and rachis of *P. dactylifera* palm are given in Table 1. For leaflets, important amounts of lignin (27 wt%), as well as minerals (6.5 wt%) are observed. The protein content is low (2 wt%), and the main constituents are polysaccharides (59.5 wt%), including cellulose (33.5 wt%). However, in the case of rachis, we can observe a lower lignin content (14 wt%) and higher amount of protein (6 wt%). The major components are

Table 1

Chemical composition of leaflets and rachis of *Phoenix dactylifera* palm

Constituent	Leaflets ^a	Rachis ^a
Ash	6.5	2.5
Fat and wax	3	4
Lignin	27	14
Protein (<i>N</i> × 6.25)	2	6
Cellulose	33.5	44
Other polysaccharides	26	28

^a As % of dry matter.

the polysaccharides and cellulose is majority with 44 wt% of the whole rachis.

3.2. Extraction and purification of hemicellulose polysaccharides

The dry matter of leaflets and rachis was refluxed in a toluene–EtOH (38–62) mixture to remove fats and waxes in order to prepare the leaflets defatted residue (LDR) and rachis defatted residue (RDR). The sugar compositions of these residues are reported in Table 2. The high content of glucose and xylose (35.6%) suggested the presence of an important amount of cellulose and xylan type polymers in the cell wall.

LDR and RDR were depectined sequentially by water and aqueous solution of calcium chelator agent (disodium EDTA) at 80 °C and sodium chlorite treatment was performed to remove residual proteins and lignins. The hemicellulose polysaccharides were extracted from depectined and bleached residues of LDR and RDR by sequential extractions with alkaline solutions as given in experimental section.

The extractions were performed at 80 °C with 2% and 4% alkaline solutions for LDR and RDR, respectively, and all extracts were acidified (pH 5–6). In the case of leaflets and rachis, the precipitate was formed from 4% extract that was recovered by centrifugation to give the crude water insoluble fraction labeled LIF-4 and RIF-4 for leaflets and rachis, respectively. From 2% extracts no insoluble fractions could be recovered. For each extract (2% and 4%), the resulting supernatant was precipitated with EtOH (4 volumes) to give crude water soluble fractions LSF-2 and LSF-4 from leaflets, RSF-2 and RSF-4 from rachis.

To eliminate the extracted oligosaccharides, the soluble fractions LSF-2, LSF-4, RSF-2, and RSF-4 were purified by size-exclusion chromatography to give LPSF-2, LPSF-4, RPSF-2, and RPSF-4, respectively. The water insoluble fractions LIF-4 and RIF-4 were purified by copper precipitation according to Jones and Stoodley (Jones & Stoodley, 1965) to give purified insoluble fractions LPIF-4 and RPIF-4, respectively.

The relative amounts of extracted polymers and their sugar composition are also reported in Table 2. These results indicated that all extracts accounted for 10.5% and 17.7% of dry matter of leaflets and rachis, respectively. On the other hand, the largest extract was solubilized by

Table 2
Yield and sugar composition of defatted residues and hemicelluloses fractions from leaflets and rachis of *Phoenix dactylifera* palm

Fraction	Yield ^a	Sugar composition ^b (% wt/wt)					\bar{M}_w ($\times 10^3$) (g mol ⁻¹)
		Uronic acid	Arabinose	Xylose	Galactose	Glucose	
LDR	97	10	12	24	2	51	–
LSF-2	6.2	11	21	56	8	3	–
LSF-4	2.5	11	11	73.3	3	1	–
LIF-4	1.8	5	2.2	90	1	1.7	–
LPSF-2	–	16	11	68.2	1.6	2	16.5
LPSF-4	–	17	6.3	75	1	0.3	21
LPIF-4	–	6.3	0	93.1	0	0.5	–
RDR	96	9.7	5	25	2	58	–
RSF-2	11.7	13	5	77	3	2	–
RSF-4	3.9	10	4.2	80	3	1	–
RIF-4	2.1	6	1.3	90	0	1	–
RPSF-2	–	20	0.7	78	1	0	33
RPSF-4	–	20.5	0.5	79.2	0	0	44
RPIF-4	–	6.5	0.3	92	0	1	–

^a As % of dry matter.

^b Expressed in relative weight percentages.

2% NaOH solution for both the leaflets (LSF-2) and the rachis (RSF-2). The fractions solubilized by 4% NaOH solution, including water non-soluble polysaccharides, corresponded to only 4.3 wt% and 6 wt% of dry matter of leaflets and rachis, respectively.

From the monosaccharide compositions, it can be clearly concluded that all fractions are xylane-type polysaccharides. Indeed the major monosaccharide in both soluble and insoluble fractions extracted from leaflets and rachis is xylose. The water soluble fractions extracted from leaflets contain arabinose and uronic acid. This result suggested that the hemicelluloses from the palm leaflets are mainly composed of arabinoglucuronoxylan. The molar ratio of xylose, arabinose, and glucuronic acid, respectively, was approximately 6:1:1 and 12:1:2 for LPSF-2 and LPSF-4, respectively. However, the water insoluble fraction (LPIF-4) contained only the xylose and uronic acid suggesting that it is glucuronoxylan with the molar ratio Xyl to UA of 20:1.

All fractions extracted from rachis belong to glucuronoxylan as indicated by sugar analysis. The fractions contain high amount of uronic acid in both soluble and insoluble fractions with different molar ratio. Indeed, the molar ratio of Xyl/UA is 6:1 for water soluble fractions (RPSF-2 and RPSF-4) and 19:1 for the water insoluble fraction (RPIF-4).

These results indicated that water soluble hemicelluloses are more highly branched than water insoluble hemicelluloses. This observation agrees very well with previous reports: the lower the arabinose or uronic acid content indicating a lower degree of branching of the xylan chains, the lower the solubility of the polymer.

The average molecular weight of soluble fractions extracted from leaflets and rachis are reported in the Table 2. The average molecular weight of fractions extracted from leaflets varied from 16,500 g/mol for LPSF-2 to 21,000 g/mol for LPSF-4 which correspond to degree of polymerization values of approximately 110 and 140 for LPSF-2 and

LPSF-4, respectively. The weight-average molecular weight of soluble fractions extracted from rachis is somewhat higher than the ones of fractions isolated from leaflets. They ranged between from 33,000 g/mol for RPSF-2 and 44,000 g/mol for RPSF-4 which correspond to DP-values of 220 and 290 for RPSF-2 and RPSF-4, respectively. These values corroborated the weight-average molecular weight reported earlier for xylans extracted from plants holocellulose with aqueous alkaline solutions (Ebringerova & Heinze, 2000).

The results of methylation analysis of LPSF-2 and LPSF-4 indicated that the monomeric side chains of the L-arabinofuranosyl residues are linked to C-3 of xylan backbone which consisted of (1 → 4) linked xylopyranose. Indeed, the results showed the presence, in addition to 2,3-di-O-methyl-xylitol, of O-2 and O-3 substituted xylose confirmed by the presence of 3-O-methyl-xylitol and 2-O-methyl-xylitol. The presence of 2,3,4-tri-O-methyl-arabinitol in approximately the same amount than the 2-O-methyl-xylitol confirmed that the arabinose units are linked to position O-3 of the xylan backbone. Furthermore, we noticed the poor yields of 3-O-methyl-xylitol due to incomplete hydrolysis of the 4-O-Me-GlcpA-(1 → 2)-Xylp linkage. This problem can be solved by the reduction of acid group, but this alternative was abandoned considering that structural analyses were carried out by NMR.

3.3. NMR characterization of extracted polysaccharides

The structure of all fractions isolated from leaflets and rachis of *P. dactylifera* palm were also investigated by NMR spectroscopy. The ¹³C NMR spectra of water soluble fractions were recorded in D₂O and those of water insoluble fractions were recorded in DMSO-*d*₆.

The ¹³C NMR spectra of fractions isolated from leaflets (LPSF-2, LPSF-4, and LPIF-4) are given in Fig. 1. The ¹³C NMR spectrum of LPSF-2 showed five major signals corresponding to (1 → 4) linked β-D-Xyl residues. Other

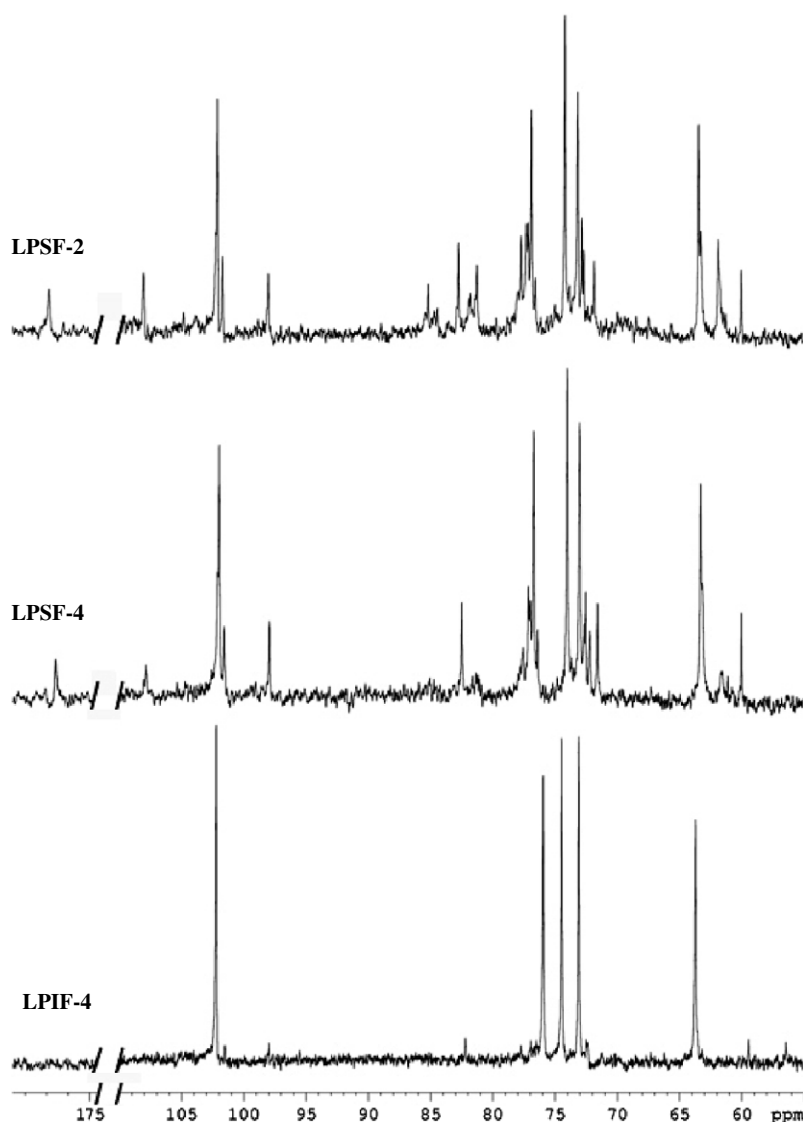


Fig. 1. ^{13}C NMR spectra of xylan fractions isolated from leaflets of *Phoenix dactylifera* L. palm.

less intense signals observed are characteristic of a 4-*O*-methyl- α -D-glucuronic acid residue and β -D-Xyl units substituted with 4-*O*-methyl- α -D-GlcA in O-2. The presence of arabinose was also confirmed by the presence in the ^{13}C NMR spectrum of characteristic signals at 108.05 (C-1), 81.28 (C-2), 77.71 (C-3), 85.20 (C-4), and 61.88 (C-5) ppm. 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 spectra of LPSF-4 showed similar configurations with a difference in the intensity of characteristic signals of arabinose and demonstrated that LPSF-4 is also assumed to be an arabinoglucuronoxylan.

In the case of fraction LPIF-4, we notice the absence of characteristic signals of arabinose demonstrated that LPIF-4 is glucuronoxylan.

The average integration of all signals for the different sugar residues, in ^{13}C NMR quantitative spectrum, revealed a respective molar ratio of xylose, arabinose

to 4-*O*-methyl- α -D-glucuronic acid of 6:1:1 for LPSF-2, 12:1:2 for LPSF-4 and 22:0:1 for LPIF-4. These results corroborated sugar and methylation analysis.

In the same way, the ^{13}C NMR spectra of fractions extracted from leaflets (LPSF-2, LPSF-4, and LPIF-4) are given in Fig. 2. The ^{13}C NMR spectra of all fractions are similar with a discrepancy in the signals intensity. They present the simplicity of the structure as revealed by five major signals corresponding to (1 \rightarrow 4) linked β -D-Xyl residues and other multiples less intense signals characteristic of 4-*O*-methyl- α -D-glucuronic acid residue and β -D-Xyl units substituted with 4-*O*-methyl- α -D-GlcA in O-2.

In ^{13}C NMR quantitative spectrum, the average integration of all signals for the different sugar residues, demonstrated that respective molar ratio of xylose to 4-*O*-methyl- α -D-glucuronic acid is of 6:1 for LPSF-2, 6:1 for LPSF-4, and 22:1 for LPIF-4 which corroborated sugar analysis.

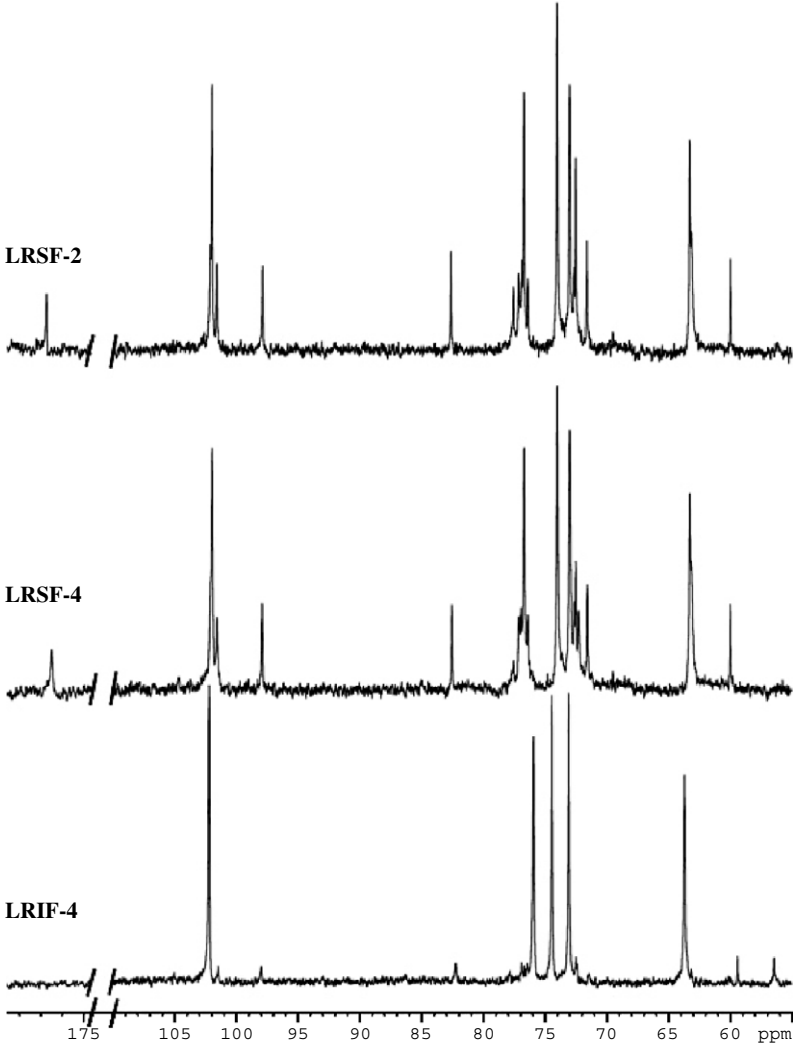


Fig. 2. ¹³C NMR spectra of xylan fractions isolated from rachis of *Phoenix dactylifera* L. palm.

Table 3

Carbon-13 chemical shift data^a (333 K) for related residues of LPSF-2, LPSF-4, and LPIF-4 fractions from *Phoenix dactylifera* palm leaflets

Glycosyl residues	Assignment					
	1	2	3	4	5	6
<i>LPSF-2</i>						
→4)-β-D-Xylp-(1→	102.12	73.16	74.20	76.90	63.46	–
→2,4)-β-D-Xylp-(1→	101.69	77.30	71.84	75.75	62.19	–
→3,4)-β-D-Xylp-(1→	102.32	72.07	76.60	76.20	63.50	–
α-L-Araf-(→	108.05	81.28	77.71	85.20	61.88	–
4-O-Me-α-D-GlcpA-(→	98.02	72.68	77.14	82.76	72.84	176.96/OCH ₃ : 60.03
<i>LPSF-4</i>						
→4)-β-D-Xylp-(1→	102.17	73.21	74.22	76.91	63.49	–
→2,4)-β-D-Xylp-(1→	101.77	77.34	71.80	75.80	62.10	–
→3,4)-β-D-Xylp-(1→	102.20	72.21	76.61	na	na	–
α-L-Araf-(→	108.07	81.35	77.76	85.26	61.80	–
4-O-Me-α-D-GlcpA-(→	98.13	72.63	77.18	82.70	72.87	177.01/OCH ₃ : 60.01
<i>LPIF-4</i>						
→4)-β-D-Xylp-(1→	102.30	73.45	74.45	77.15	63.74	–
→2,4)-β-D-Xylp-(1→	98.77	77.41	72.12	75.95	62.39	–
4-O-Me-α-D-GlcpA-(→	98.77	72.95	77.44	83.01	73.15	177.16/OCH ₃ : 60.23

^a In ppm relative to the signal of internal acetone in deuterium oxide or DMSO at 31.5 ppm.

Table 4

Carbon-13 chemical shift data^a (333 K) for related residues of RPSF-2, RPSF-4, and RPIF-4 fractions from *Phoenix dactylifera* palm rachis

Glycosyl residues	Assignment					
	1	2	3	4	5	6
RPSF-2						
→4)-β-D-Xylp-(1→	102.15	73.19	74.20	76.90	63.47	–
→2,4)-β-D-Xylp-(1→	101.75	77.31	71.81	75.95	62.39	–
4-O-Me-α-D-GlcpA-(→	98.04	72.74	77.74	82.80	73.15	176.54/OCH ₃ : 60.16
RPSF-4						
→4)-β-D-Xylp-(1→	102.16	73.45	74.21	77.05	63.48	–
→2,4)-β-D-Xylp-(1→	101.77	77.32	72.12	75.95	61.90	–
4-O-Me-α-D-GlcpA-(→	98.10	72.95	77.75	82.74	73.15	176.67/OCH ₃ : 60.20
RPIF-4						
→4)-β-D-Xylp-(1→	102.27	73.30	74.55	76.02	63.88	–
→2,4)-β-D-Xylp-(1→	101.95	77.50	72.24	75.95	62.39	–
4-O-Me-α-D-GlcpA-(→	98.30	72.95	77.73	83.04	73.33	177.16/OCH ₃ : 60.21

^a In ppm relative to the signal of internal acetone in deuterium oxide or DMSO at 31.5 ppm.

The NMR data for all fractions are reported in Tables 3 and 4 and are in good agreement with the structures of xylans substituted by arabinose (Izydorczyk & Biliaderis, 1995; Subba Rao & Muralikrishna, 2004) and (4-O-methyl-α-D-glucurono)-β-D-xylans already described in a number of plants (Vignon & Gey, 1998; Dinand & Vignon, 2001; Habibi, Mahrouz, & Vignon, 2002; Habibi, Mahrouz, & Vignon, 2003).

4. Conclusion

The hemicellulose-type polysaccharides were extracted from leaflets and rachis of *P. dactylifera* palm. The sugar analysis and NMR measurements show that they belong to the xylans family. The water soluble fractions isolated from leaflets are arabinoglucuronoxylans which are mono-substituted at C-3 with arabinose while the water non-soluble fraction is 4-O-methyl-glucuronoxylans. However, both water soluble and water non-soluble polysaccharides extracted from rachis are 4-O-methyl-glucuronoxylans. The molar ratios of arabinose and/or 4-O-methyl-glucuronic acid of all xylans fractions extracted from leaflets and rachis of *P. dactylifera* palm correspond to those usually found in the plants.

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