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Synthesis and characterization of methyl xylan

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ABSTRACT

The synthesis of methyl xylan using methyl chloride and methyl iodide as etherifying agent under varying reaction conditions was studied. The reaction of xylan with an excess of methyl chloride under pressure in the presence of 40% aqueous NaOH led to a methyl xylan with a degree of substitution (DS) of 0.94. The conversion of xylan with methyl iodide yielded DS values of about 0.5 independent of the molar ratio of methyl iodide to anhydroxylose unit homogeneously in 25% aqueous NaOH or after addition of acetone leading to a heterogeneous slurry. The DS and the distribution of the substituents were determined by means of one and two-dimensional NMR spectroscopy.

1. Introduction

The hemicellulose xylan is most abundant in hardwoods and other plants such as grasses, cereals, and herbs. The biopolymer backbone comprises mainly of β-1 → 4-linked xylose units (Ebringerova & Heinze, 2000). Recently, xylans as one of the most important renewable resources gain increasing importance as basis for new biopolymeric materials and functional polymers accessible by chemical modification reactions (Heinze, Koschella, & Ebringerova, 2004; Lindblad & Albertsson, 2004). Due to the functional properties of xylans various application fields are considered to be of interest. Important possible applications of xylan and its derivatives are drug carrier, wound dressing materials, or additives in papermaking (Ebringerova, 2006). A problem that limits the use of xylans is their usually bad solubility in water or aqueous systems at neutral pH value. To get soluble polysaccharide derivatives, etherification in particular methylation, hydroxyalkylation, and carboxymethylation of the hydroxyl groups is a suitable path (Petzold, Schwikal, Günther and Heinze, 2006).

Etherification of hemicelluloses was performed under heterogeneous and homogeneous conditions as reviewed by Lindblad and Albertsson (2004). In particular methylation seems to be an appropriate functionalization to get water-soluble products. Up to now, the methylation of xylan was used both to analyze the non-reducing end groups and to get information about the branching of hemicelluloses already in the 1960s (Lindblad & Albertsson, 2004; Zinbo & Timell, 1965). For methylation of xylan, the methylsulfinyl anion (Na dimsyl) in dimethyl sulfoxide (DMSO) as reaction medium, introduced for linkage analysis by Hakomori (1964), was widely used (Aspinall, 1982; Fang, Fowler, Tomkinson, & Hill, 2001; Han & Swan, 1968; Shimizu, 1976). This method substituted the dimethyl sulfate procedure, which led to partially methylated products (Kislitsyn, Ishcherikov & Il'ina, 1970; deBelder, Lindberg, & Theander, 1962; Croon and Timell; 1960; Heuser & Ruppel, 1922). An efficient methylation method for carbohydrates was introduced about 20 years ago using methyl iodide, DMSO, and powdered NaOH (Ciucanu & Kerek, 1984).

The present paper deals with investigations of the methylation of xylan using methyl halides as etherification agent in the presence of NaOH in order to get water-soluble products. The main focus of the studies was the detailed structure characterization regarding the degree of substitution (DS) and the substitution pattern by means of one and two-dimensional NMR spectroscopic techniques.

2. Experimental part

2.1. Materials

Birch xylan was purchased from Roth (Karlsruhe, Germany). For bleaching, 15 g ClO_2 in water (20–25% w/v) was added to a suspension of 500 g xylan in 1500 ml water at pH 5 (controlled by sulphuric acid). After 3 h at 70 °C, the suspension was divided into two batches (1000 g). Every batch was put into a beaker (5000 ml volume) and diluted with 400 ml water. The xylan was precipitated in 3.6 l methanol, 3 times washed with methanol and diethyl ether,

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and air dried. Then, xylan was washed 3 times with 80% (v/v) methanol and 2 times with pure methanol, and dried in vacuum at 30 °C. It had a water content of about 6%. Dimethyl sulfoxide (DMSO) over molecular sieve and *N,N*-dimethyl formamide (DMF) over molecular sieve were obtained from FLUKA. Methyl chloride and dimethyl ether were taken from compressed gas cylinder (GHC Gerling, Holz & Co. Handels GmbH, Hamburg, Germany). Methyl iodide was obtained from ACROS and acetyl chloride was obtained from MERCK. Ethanol, methanol, 2-propanol, acetone, and acetic acid were reagent grade chemicals.

2.2. Measurements

FTIR spectra were recorded on a Nicolet Avatar 370 DTGS spectrometer with the KBr-technique. NMR spectra were acquired on a Bruker AVANCE 250 and AVANCE 400 spectrometer (BRUKER, Rheinstetten, Germany). The surface tension of the solutions (1%) was measured with a tensiometer K 100 (KRÜSS, Hamburg, Germany).

2.3. Methods

2.3.1. Methylation

2.3.1.1. Methyl chloride. Xylan (10 g, 75.7 mmol) was suspended in 30 ml H_2O in a stainless steel autoclave and 40.0 g NaOH in 30 ml water were added resulting in a 40% (w/v) NaOH solution. The xylan dissolved to a viscose solution. After addition of the methyl chloride (71.4 g, 1.43 mol), the reaction was performed at room temperature under pressure of 5 bar. The mixture was heated for 3 h at 78 °C leading to a pressure of 12 bar. After cooling and decompression, the polymer was precipitated in ethanol (500 ml), washed two times with 80% ethanol (500 ml), with a mixture of ethanol/acetone (1:1, v/v, 500 ml), and with acetone (500 ml). The product was dried in vacuum at 60 °C. Yield: 6.71 g (61%). DS 0.94 (**1**).

2.3.1.2. Methyl iodide. Procedure (*a*)*:* Xylan (5 g, 37.8 mmol) was dissolved in 25 ml of 25% aqueous NaOH (6.25 g, 156.6 mmol). The solution was stirred 1 h at room temperature. After addition of methyl iodide (see Table 1), the reaction mixture was stirred for 5 h at room temperature. Ethanol was added (20 mol/mol methyl iodide) and kept overnight at room temperature. The polymer was precipitated in ethanol (250 ml) and neutralized with 50% acetic acid. The product was washed three times with 80% methanol (150 ml), two times with ethanol (150 ml), and dried in vacuum at 60 °C. Yield: 85–99%. Results see Table 1.

Procedure (*b*)*:* Before addition of methyl iodide to the xylan solution prepared as described above (procedure a), acetone was added (35 ml). The resulting mixture was vigorously stirred for 30 min at 30 °C leading to a heterogeneous system. Reaction- and work-up procedure were carried out as described above (a). Yield: 85–99%. For results see Table 2.

2.3.2. Peracetylation

For peracetylation, the methyl xylan derivatives (0.3 g) were suspended in 12 ml DMF and 2 ml of acetyl chloride were added. The mixture was stirred overnight at 80 °C. After cooling to room temperature, the polymer was precipitated in ethanol, neutralized with $NaHCO_3$, washed four times with ethanol, and dried in vacuum at 60 °C.

3. Results and discussion

The xylan used for the methylation studies was a commercially available 4-*O*-methylglucuronoxylan (MGX) from birch showing a yellow to brownish colour after bleaching with ClO_2. ClO_2 was selective for lignin residues and MGX was stable under the conditions that could be applied for bleaching. It possessed a molecular mass of 13,500 g/mol (degree of polymerization, DP 102) and a xylose content of 93.9% (related to the total sugar content) containing 9.7% uronic acid units (4-*O*-methylglucuronic acid, 4-MGA) based on the air dried sample.

The methylation of MGX **1** was performed with methyl chloride or methyl iodide in the presence of aqueous NaOH in order to check the accessible DS values (Scheme 1). To determine both the DS and the substitution pattern by means of ^{1}H NMR spectroscopy (including line fitting analyses), the methyl xylans obtained were peracetylated in DMF.

The methylation with a high excess of methyl chloride (19 mol/mol anhydroxylose unit, AXU) was carried out under pressure (12 bar) in the presence of 40% aqueous NaOH. Surprisingly, only partially methylated xylan ether (DS 0.94, **2**) was obtained under these drastic conditions. The reaction with 5 mol methyl chloride per mole AXU in dimethyl ether as slurry medium in the presence of 50% aqueous NaOH led to a DS of 0.27 (**3**) only.

The conversion of MGX **1** with methyl iodide in the presence of 25% aqueous NaOH for 5 h at room temperature yielded methyl xylans with DS of about 0.5 (**4**–**8**) independent of the molar ratio (Table 1). At a molar ratio of 1.0:4.0 (AXU:methyl iodide), a product with a higher DS of 0.76 (**9**) resulted. In a mixture of 25% aqueous NaOH and acetone as slurry medium (Table 2), the reaction with methyl iodide led to DS values of 0.41–0.51 (**10**–**15**) independent of the molar ratio too, i.e., there is no change of DS; the differences are in the margin of error.

The structure of methyl xylans were studied by means of one- and two-dimensional NMR spectroscopic techniques. Table 3 gives

Table 1
Degree of substitution (DS) and water-solubility of methyl xylan prepared homogeneously by reaction of the xylan **1** with methyl iodide in the presence of 25% aqueous NaOH (5 h at room temperature)

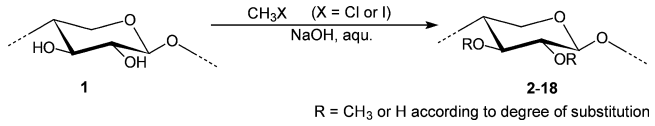
Molar ratio	No.	DS[a]	DS[b]	H_2O-solubility
AXU:CH_3I				
1.0:0.5	**4**	0.47	0.45	Yes, at 90 °C
1.0:1.0	**5**	0.51	0.51	Yes, at room temperature
1.0:1.5	**6**	0.46	0.46	Yes, at 60 °C
1.0:2.0	**7**	0.55	0.36	Yes, at 60 °C
1.0:3.0	**8**	0.48	0.49	Yes, at 60 °C
1.0:4.0	**9**	0.76	0.57	Yes, at 60 °C

[a] Determined by means of ^{1}H NMR spectroscopy after peracetylation and line form analysis of the H-1 signal.
[b] Determined by means of ^{1}H NMR spectroscopy after peracetylation and calculation of the signals of the acetyl group, all carbohydrate signals (5.5–2.8 ppm) and the methyl protons.

Table 2
Degree of substitution (DS) and water-solubility of methyl xylan prepared heterogeneously by reaction of the xylan **1** with methyl iodide in acetone/25% aqueous NaOH (5 h at room temperature)

Molar ratio	No.	DS[a]	DS[b]	H_2O-solubility
AXU:CH_3I				
1.0:0.5	**10**	0.41	0.48	Partially, at 90 °C
1.0:1.0	**11**	0.46	0.73	Partially, at 90 °C
1.0:1.5	**12**	0.47	0.47	Partially, at 90 °C
1.0:2.0	**13**	0.47	0.38	Yes, at 90 °C
1.0:3.0	**14**	0.51	0.52	Yes, at 90 °C
1.0:4.0	**15**	0.46	0.52	Yes, at 90 °C

[a] Determined by means of ^{1}H NMR spectroscopy after peracetylation and line form analysis of the H-1 signal.
[b] Determined by means of ^{1}H NMR spectroscopy after peracetylation and calculation of the signals of the acetyl group, all carbohydrate signals (5.5–2.8 ppm) and the methyl protons.



Scheme 1. Methylation of an idealized xylan with a methyl halide in the presence of NaOH.

an overview about the main repeating units, which could be detected by NMR investigations of methyl xylan **5** (DS 0.51). By means of HSQC-TOCSY NMR technique, the ^{1}H NMR signals were assigned to the main repeating units of the methylated xylan. Using ^{1}H,^{1}H COSY NMR spectroscopy, it was possible to assign the signals of the protons to the position within the repeating unit (Fig. 1). However, not all substructures could be clearly identified by the NMR spectroscopic experiments. About ten signals were detected with the typical shift of C1 in the HSQC spectrum, which appeared from the different substructures of the methylated xylan (comparable to a copolymer) and indicate the broad variety of the differently substituted xylose repeating units (methyl, 4-MGA, sugar moieties) within the polymer chains depending on the substitution pattern, the linkage of the different repeating units, and on other monosaccharides beside xyloses (4-MGA, arabinose, rhamnose) that appeared in this particular type of xylan.

Table 3
^{1}H and ^{13}C NMR data of the main repeating units of the methyl xylan **5** in D_2O depending on the functionalization pattern

Repeating unit[a]	H/C Chemical shift (ppm) of position					
	1	2	3	4	5a	5b
X_{int}	4.73	3.57	3.83	4.06	3.65	4.38
	102.0	73.2	74.2	76.9		63.3
*X*2	4.80	3.33	3.87	4.06	3.65	4.38
	101.8	82.6	73.4	76.7		63.2
*X*23	4.83	3.41	3.68	4.14		4.36
	101.7	81.8	82.5	75.4		63
4-MGA	5.54	3.85	4.06	3.58		4.76
	98.2	71.5	72.6	82.2		71.2

[a] X_{int} internal nonsubstituted anhydroxylose, *X*2 2-mono-*O*-methyl anhydroxylose, *X*23 2,3-di-*O*-methyl anhydroxylose, 4-MGA 4-*O*-methylglucuronic acid.

The signals of the anomeric protons were identified in the region of 5.54-4.73 ppm (Fig. 1). The anomeric proton (H-1β) was detected at 4.73 ppm for the main structure of the non-substituted anhydroxylose unit (internal, end groups not evaluated, X). Based on the cross-peaks, the signals for H-2 (3.57 ppm), H-3 (3.83 ppm), H-4 (4.06 ppm), H-5a (3.65 ppm), and H-5b (4.38 ppm) could be assigned.

As a consequence of methylation, the signals were shifted to higher field. The signal for the H-2 was detected at 3.33 ppm in case of methylated position 2. According to the cross-peaks, no methylation of position 3 (H-3, 3.87 ppm) was found for this repeating unit (X2). The other signals of this repeating unit are summarized in Table 3. For a methylation in postion 3, the H-3 signal was found at 3.68 ppm. The signal at 3.41 ppm detected for H-2 proofed clearly that a di-etherified anhydroxylose unit occured. This finding regarding the chemical shift was in contrast to other methyl polysaccharides. In own studies with regioselectively functionalized cellulose, the H-2 (methylated position 2) was shifted to higher field in the case of a methylation in position 3 (Koschella, Fenn, Illy, & Heinze, 2006). In case of a 3-mono-*O*-methylated

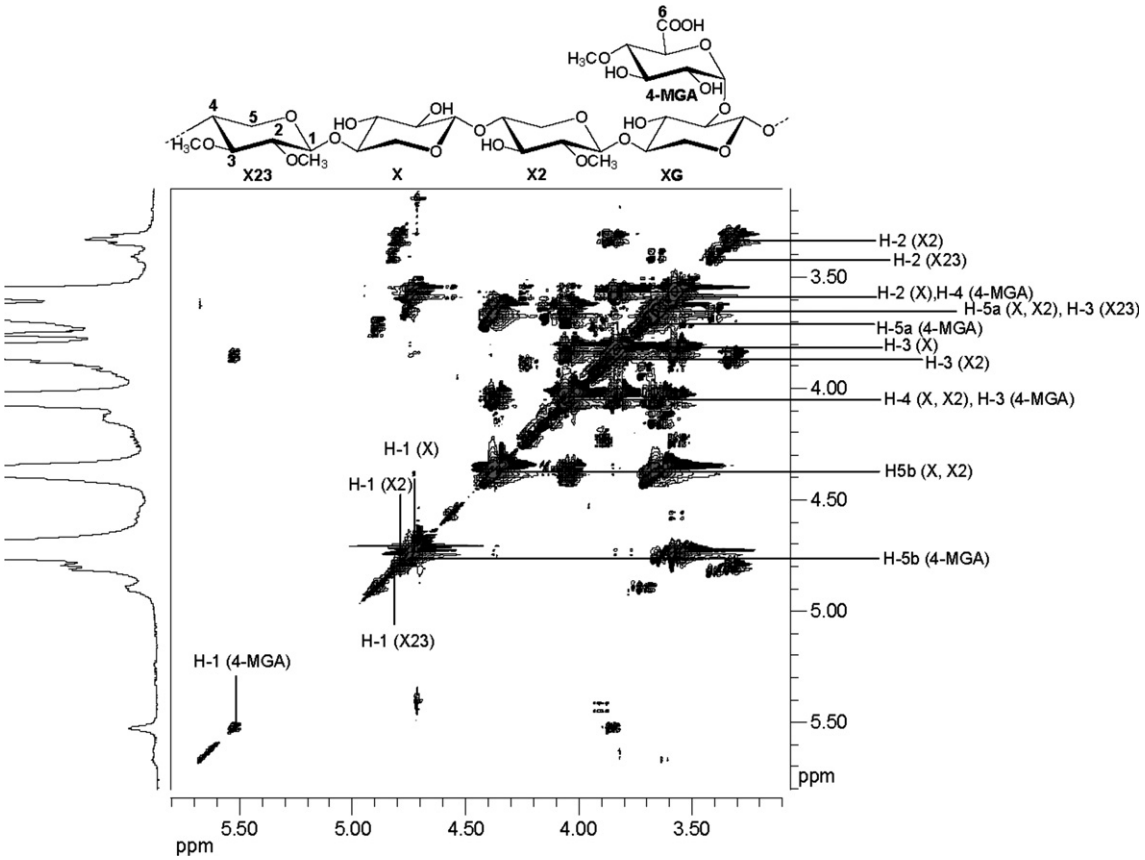


Fig. 1. ^{1}H,^{1}H COSY NMR spectrum of methyl xylan **5** (degree of substitution, DS 0.51) in D_2O.

anhydroxylose unit, the H-3 signal was detected at 3.72 ppm but no clear identification of the H-2 signal for non-methylated position 2 was possible. Signals at 4.73 ppm (H-1), 4.23 ppm (H-5b), 3.92 ppm (H-4) and 3.59 ppm (H-5) were assigned to the same unit. A repeating unit with cross-peaks of very low intensity starting at 4.91 ppm (H-1) followed by 3.71 ppm (H-2) and 3.88 ppm (H-3) was identified as anhydroxylose unit linked with α-4-MGA in position 2. However, the signal at 4.91 ppm arose from two different protons. Additionally, by evaluation of the cross-peaks in different two-dimensional NMR spectra of the methyl xylan **5**, the signals of 4-MGA were detected (Table 3). This assignment was difficult because no carbonyl signal was found in ^{13}C NMR spectra of methyl xylan **5** measured in D_2O at 30 °C and even at 55 °C (Fig. 2c). A signal at 97.9 ppm was ascertained that is typical for the α-linked C-1 of 4-MGA (Kováč, Alföldi, Kočiš, Petráková, & Hirsch, 1982; Teleman, Lundqvist, Tjerneld, Stalbrand, & Dahlman, 2000; Teleman, Tenkanen, Jacobs, & Dahlman, 2002). ^{13}C NMR spectrum of **5** in DMSO at room temperature indicates the carbonyl signal at 172.0 ppm (Fig. 2a). At 55 °C (Fig. 2b), the signal could not be detected because of the relaxation time (T_1) of the carbonyl carbon at this temperature was too long to reach a nearly complete relaxation within the given relaxation delay. According to the assignment of the ^{1}H signals (Table 3), the main part of 4-MGA is not methylated in positions 2 and 3. Very small signals for H-1 appeared at 5.67 ppm that showed a cross-peak to H-2 (3.61 ppm) indicating a methylation of the 4-MGA at position 2. An additional proof for this substitution pattern was obtained by means of HSQC-DEPT and HSQC-TOCSY experiments, which allows relating the signals of the carbon atoms (Table 3).

The peaks of the methyl substituent were found at 59.5–60.3 ppm in the ^{13}C NMR spectra (see Fig. 2). The splitting of the peaks was caused by the distribution of the various substituted units methylated at different positions along the polymer chains.

The DS values of the methyl xylans were estimated after peracetylation by means of ^{1}H NMR spectroscopy using following equation:

$$\mathrm{DS} = 2 - \frac{\frac{1}{3} I_{\mathrm{Ac}}}{I_{\mathrm{H-1}}}.$$

I_{Ac} peak area of the signals of the methyl protons of the acetyl group

$I_{\mathrm{H-1}}$ peak area of the signals of H-1

The DS of the methyl xylan was calculated from the ratio of the integral of H-1 signal of the AXU and the integral of the methyl protons of the acetyl group (~ 1.9 ppm). To calculate the methyl DS, the DS (ester) was subtracted from 2. This is possible due to the complete esterification of the methyl xylans that was demonstrated by FT-IR spectroscopy by the absence of any OH band. The integral of H-1 signal was acquired after line form analysis of the peaks in the range of 4.9–4.5 ppm. It was necessary to clearly assign H-1 signal that was possible by means of two-dimensional NMR techniques. The mistake emerging from the loss of the H-1 of the MGA in this region is very low (within the margin of error). Similar DS values for acetate and consequently for methyl were obtained by integration of the signals assigned to acetyl groups and of all carbohydrate signals (5.5–2.8 ppm) including the signals for methyl groups. By using the different methods to calculate the DS values, the influence

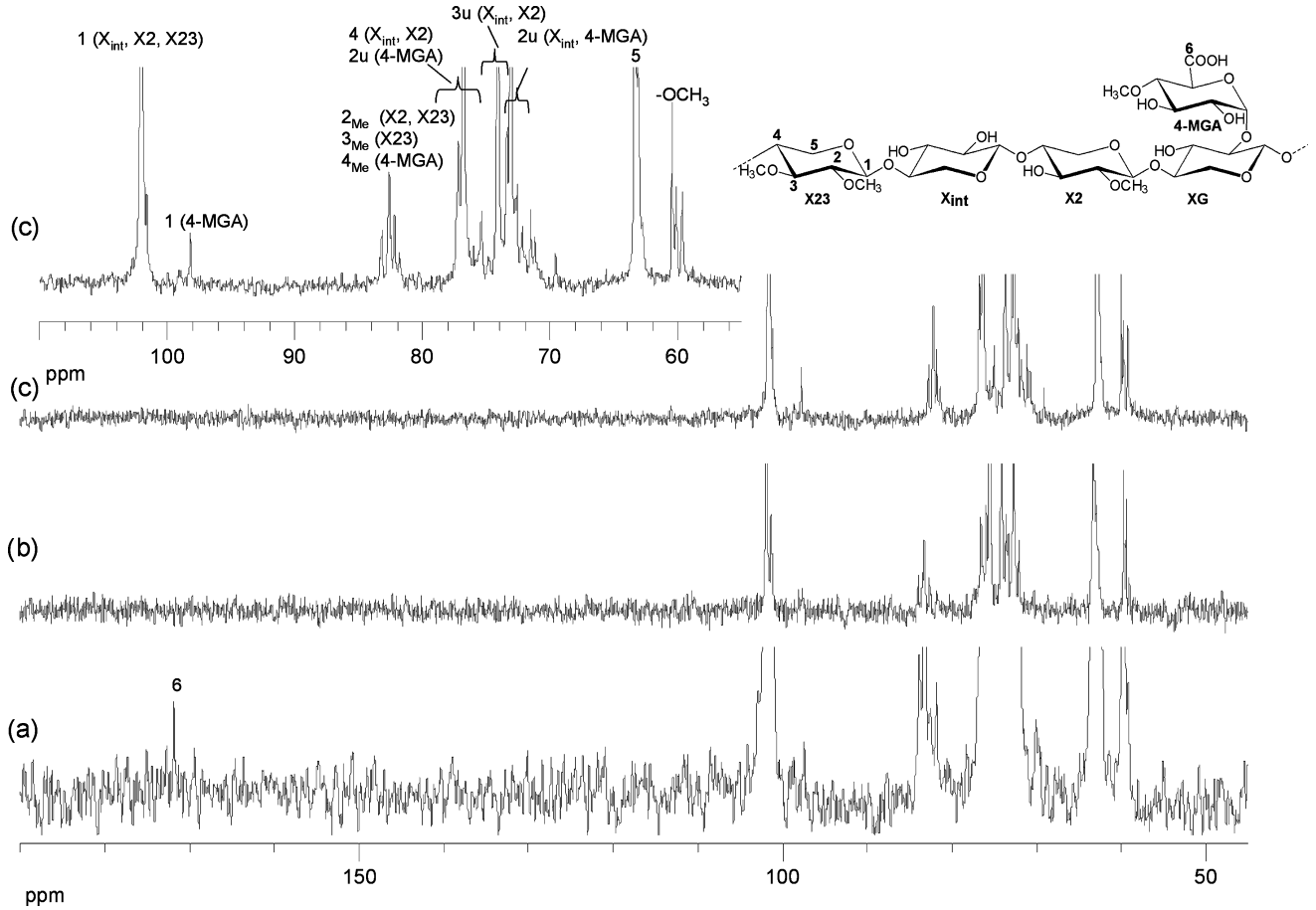


Fig. 2. ^{13}C NMR spectra of methyl xylan **5** (degree of substitution, DS 0.51) in (a) dimethyl sulfoxide-d_6 (DMSO-d_6) at 24 °C, (b) in DMSO-d_6 at 55 °C, and (c) in D_2O at 55 °C.

of remaining water was excluded, which signals were found in the same region like the proton signals of the AXU.

In Fig. 3, $^1H,^1H$ COSY NMR spectra of the peracetylated methyl xylan **5** (DS 0.51) acquired in DMSO-d_6 (a) or in $CDCl_3$ (b) were compared. The signals of the protons H-2 and H-3 (acetylated positions) were detected at 4.9 ppm (H-3) and 4.5 ppm (H-2) recording the spectrum in DMSO-d_6. The signals of H-2 and H-3 of the methylated position 2 and 3 could be identified in the region between 2.8 and 3.3 ppm. In Fig. 3 (b), the $^1H,^1H$ COSY NMR spectrum of peracetylated **5** in $CDCl_3$ indicated that the signals of H-1, H-2 and H-3 (in case of peracetylation of these positions) were also detected in the range of 4.5–4.9 ppm, however, differently influenced by the solvent compared to DMSO-d_6. The H-1 signal was detected at 4.5 ppm and the peak of H-2 was identified at 4.7 ppm. The signals of H-2 and H-3 (methylated positions) were located approximately in the region of 2.9 ppm and 3.2 ppm. Consequently, it was necessary to use two-dimensional methods to analyse the copolymer structure of these biopolymer derivatives by NMR spectroscopy.

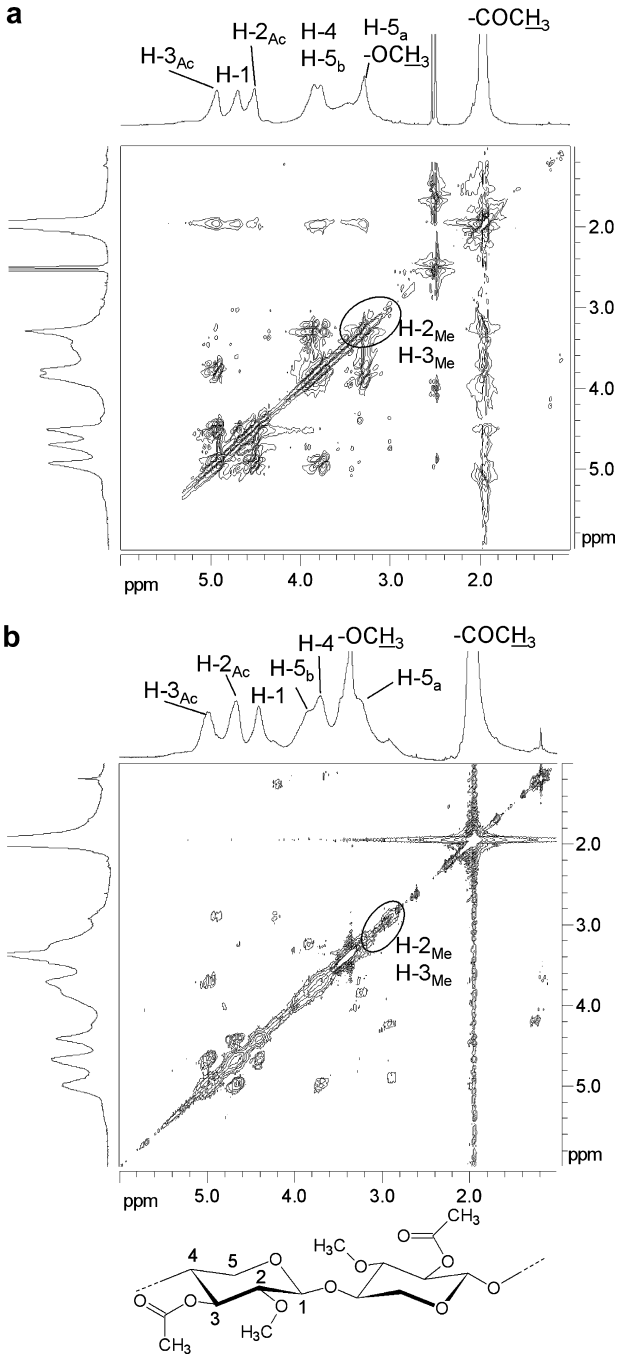


Fig. 3. $^1H,^1H$ COSY NMR spectra of peracetylated methyl xylan **5** recorded in DMSO-d_6 (a) or in $CDCl_3$ (b), (degree of substitution, DS 0.51, Ac means acetylated and Me means methylated according to the distribution of the functional groups).

Methyl xylan **2** was partially soluble in water at room temperature. By heating up to 90 °C, it became completely soluble and did not precipitate by cooling. A 5% aqueous solution of **2** possessed a low shear viscosity (1–5 mPas) even at a low shear rate (measured with a Rheostress 150 rheometer, HAAKE, Karlsruhe, Germany). Regarding this very low viscosity, the products were not of interest as viscosity modifiers as compared, e.g., to methyl celluloses. In preliminary experiments, the surface tension of a 1% aqueous solution of **2** was studied. It was found that a decrease to 40.4 mN/m compared to pure water (72.7 mN/m) appeared. It became obvious that the samples possess a certain amphiphilicity. Further studies will be carried out to investigate the structure formation of the methyl xylans in water.

Methyl xylans **4**–**9** were water-soluble. Sample **5** was soluble at room temperature while **4** and **6**–**9** dissolve at 60–90 °C. They do not precipitate after cooling. The methyl xylans (**13**–**15**) synthesized in the acetone/aqueous NaOH slurry showed water-solubility only at high temperature independent of the DS. The differences in the solubility of the methyl xylans depended on the substitution pattern within the AXU and also along the polymer chain that is controlled by the condition of methylation (homogeneous versus heterogeneous path).

The solubility of **5** at room temperature could not be satisfactory explained with the present results. The better water-solubility of the samples **7**–**9** than **4** suggested a more even distribution of the substituents by higher molar ratio during the methylation. In case of the heterogeneous methylation, the samples synthesized with a higher molar ratio (**13**–**15**) seemed to have also a more even distribution of the substituents than those synthesized with a lower content of reagent (**10**–**12**).

4. Conclusions

The methylation of 4-*O*-methylglucuronoxylan was investigated under homogeneous or heterogeneous conditions using methyl chloride or methyl iodide as reagents in the presence of aqueous NaOH. The maximum degree of methylation achieved was 0.94 using methyl chloride in the presence of 40% aqueous NaOH while the other samples synthesized with methyl iodide, 25% aqueous NaOH with/without acetone had a DS of about 0.5. It should be emphasized that the determination of both the degree of substitution and the functionalization pattern could be carried out efficiently by means of one- and two-dimensional NMR spectroscopic techniques directly applying the methyl xylan or after peracetylation of the remaining OH groups. The methyl xylans were water-soluble beginning at room temperature up to 90 °C depending on the substitution pattern within the AGU and along the chain, which were controlled by the methylation conditions forming solutions of very low viscosity even at a rather high polymer concentration of 5%. Further investigations should include the determination of the distribution of the functional groups along the polymer chain in order to get comprehensive structure-property-relationships.

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