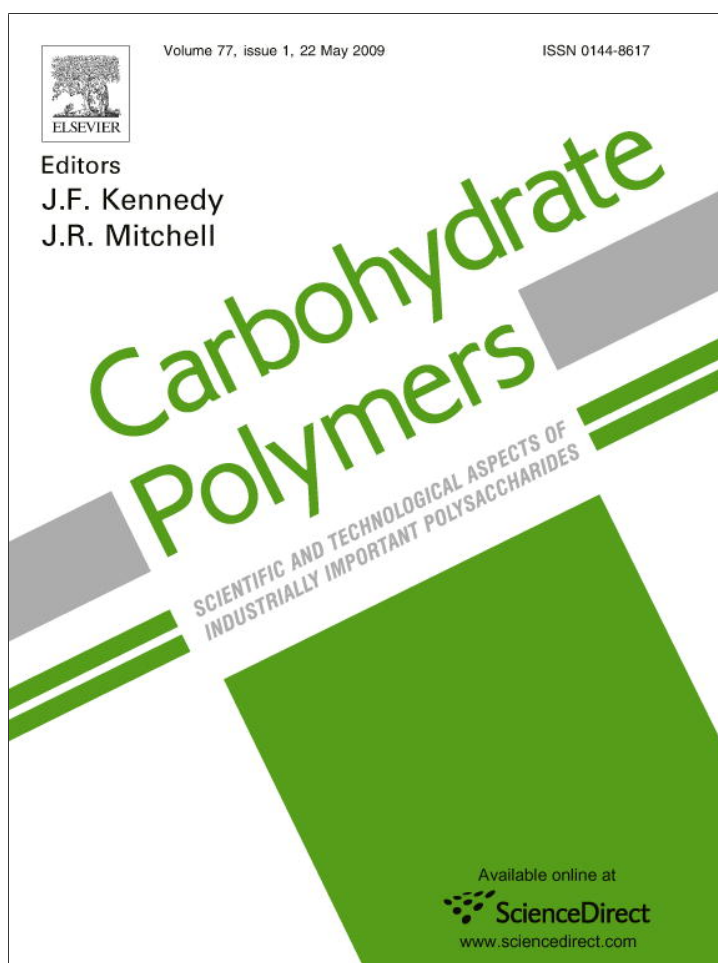


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## Carbohydrate Polymers

journal homepage: [www.elsevier.com/locate/carbpol](http://www.elsevier.com/locate/carbpol)Ethylation of arabinoxylan from Ispaghula (*Plantago ovata*) seed huskShazia Saghir<sup>a,c</sup>, Mohammad Saeed Iqbal<sup>b</sup>, Andreas Koschella<sup>c</sup>, Thomas Heinze<sup>c,\*</sup><sup>a</sup> Department of Chemistry, University of Sargodha, Sargodha 40100, Pakistan<sup>b</sup> Department of Chemistry, GC University, Lahore 54000, Pakistan<sup>c</sup> Centre of Excellence for Polysaccharide Research, Friedrich Schiller University of Jena, Humboldtstrasse 10, D-07743 Jena, Germany

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## ABSTRACT

The ethylation of arabinoxylan, isolated from Ispaghula seed husk by alkali extraction, was carried out heterogeneously with ethyl iodide in the presence of aqueous sodium hydroxide (25%). The reaction parameters were varied in terms of molar ratio anhydrosugar unit:reagent, slurry medium, and temperature. In order to determine the total degree of substitution of ethyl groups ( $DS_{Et}$ ),  $^1H$  NMR spectroscopic investigations of ethyl arabinoxylans (EAX) after peracetylation with acetyl chloride in *N,N*-dimethyl formamide were carried out. Structural elucidation of the peracetylated EAX was conducted by means of  $^1H$ ,  $^1H$  COSY- and HSQC-DEPT NMR experiments.  $DS$  values for EAX as high as 0.61 were achieved. Samples were soluble in dimethyl sulfoxide at 80 °C. The intrinsic viscosity  $[\eta]$  of EAX samples depends on reaction conditions applied. The highest  $[\eta]$  obtained was 518 mL/g for a sample synthesized at 40 °C in methanol as slurry medium using a molar ratio arabinoxylan:ethyl iodide of 1:18.

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## 1. Introduction

Xylans are the most common hemicelluloses and they are considered to be the second most abundant biopolymer in the plant kingdom. These biopolymers are not only present in wood but also in various other plants such as grasses, cereals, and herbs (Stephen, 1983). Heteroxylans of higher plants possess  $\beta$ -(1→4) linked Xylp units as the backbone, usually substituted with sugar units and *O*-acetyl groups (Ebringerova & Heinze, 2000).

Ispaghula (*Plantago ovata*) is an indigenous product of south Asia. The seed husk is a rich source of arabinoxylan (AX) and is used as traditional herbal remedies as well as in modern medicines (Cummings & Stephen, 1980).

Modification of hemicelluloses is an innovative field of research (Heinze, Koschella, & Ebringerova, 2004; Lindblad & Albertsson, 2005). It is a useful path to tailor the properties of the biopolymer as desired for specific applications. Only few studies have been carried out on the ethylation of xylan. Up to now, ethyl xylan has been synthesized in an autoclave with excess of ethyl chloride in the presence of aqueous NaOH (50%) (Glasser, Jain, & Sjostedt, 1995; Koz'mina et al., 1965). However, the chemical modification of AX to get novel products is not thoroughly investigated. Carboxymethylation of AX from Ispaghula had been studied to get water soluble

anionic polyelectrolytes (Saghir, Iqbal, Hussain, Koschella, & Heinze, 2008).

This paper describes the ethylation of arabinoxylan isolated from Ispaghula seed husk with ethyl iodide in the presence of NaOH applying acetone, methanol or ethanol as slurry medium. The structure of the polymers was characterized by NMR spectroscopy.

## 2. Experimental part

## 2.1. Materials

Arabinoxylan **1** was isolated from Ispaghula seed husk by alkali extraction as described elsewhere (Saghir et al., 2008). Ethyl iodide was obtained from ALFA Aesar (Karlsruhe, Germany), acetyl chloride from MERCK (Darmstadt, Germany), *N,N*-dimethyl formamide (DMF) from ACROS Organics (Geel, Belgium), sodium hydroxide from Riedel-de Haën (Seelze, Germany) and sodium hydrogen carbonate ( $NaHCO_3$ ) was obtained from T.J. Baker (Deventer, the Netherlands). Ethanol, methanol and acetone are reagent grade chemicals.

## 2.2. Measurements

FTIR spectra were recorded on a Nicolet AVATAR 370 DTGS spectrometer using the KBr-technique.

1D- and 2D-NMR spectra were measured on a Bruker AVANCE 400 NMR spectrometer (400 MHz, Rheinstetten, Germany) with

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Bruker standard pulse programs and processed with MestReC software package as well as XWINNMR.  $^1\text{H}$  NMR (in  $\text{D}_2\text{O}$ ) and selective TOCSY (in  $\text{DMSO}-d_6$ ) NMR spectra of EAX **2** were taken at 400 MHz spectral frequency and 70 °C temperature.

$^1\text{H}$ ,  $^1\text{H}$  COSY and HSQC–DEPT experiments for peracetylated EAX **2** were performed at 50 °C temperature in  $\text{CDCl}_3$  solvent with number of scans (NS) of 96. The spectrometer frequency for F2 and F1 was 400 MHz in  $^1\text{H}$ ,  $^1\text{H}$  COSY experiment whereas in case of HSQC–DEPT experiment spectrometer frequency for F2 was 400 MHz and for F1 100 MHz. The solvent signal was used for the calibration of the chemical shift values. For the determination of the degree of substitution of ethyl groups ( $\text{DS}_{\text{Et}}$ ), peracetylated ethyl arabinoxylan derivatives were dissolved in  $\text{CDCl}_3$  and  $^1\text{H}$  NMR spectra were measured at 50 °C. The  $\text{DS}_{\text{Et}}$  was calculated according to Eq. (1).

$$\text{DS}_{\text{Et}} = 2 - \left( \frac{9}{\frac{I_{\text{AXU}}}{I_{\text{AC}}} + 2} \right) \quad (1)$$

$I_{\text{AC}}$ : peak area of the signals of the methyl protons of the acetyl group in the range from 1.7 to 2.4 ppm;  $I_{\text{AXU}}$ : peak area for 5 H of anhydrosugar unit and 2 H of ethyl  $\text{CH}_2\text{-DS}_{\text{Et}}$  in the range from 3.1 to 5.5 ppm.

The intrinsic viscosities  $[\eta]$  were determined with an automatic viscometer (Lauda PVS 1/2) equipped with a dilution Ubbelohde viscometer (capillary No. 1c, Schott Instruments, Mainz, Germany) in a thermostated water bath (Lauda E 200, Lauda-Königshofen, Germany) at 20 °C. An automatic burette (Metrohm Dosimat 765, Filderstadt, Germany) was used to dilute the solutions automatically. An initial sample concentration of 6.3 mg/mL in aqueous NaOH (2.45%, w/v) was chosen for the experiments. To determine the  $[\eta]$  values, the extrapolation of reduced viscosity to zero concentration was performed in a concentration range up to 4 mg/mL in order to minimize the influence of intermolecular interactions (Mutalik et al., 2006). The  $[\eta]$  values were obtained by linear regression.

Elemental analysis was carried out on a CHNS analyzer Vario EL III (Elementaranalysensysteme, Hanau, Germany). The halogen content was determined after combustion and titration according to Schöniger's method (Schöniger, 1956).

### 2.3. Methods

#### 2.3.1. Isolation of arabinoxylan from Ispaghula seed husk

Isolation of arabinoxylan from Ispaghula seed husk was carried out by soaking the seed husk with water, extraction with aqueous sodium hydroxide and coagulation with acetic acid as described elsewhere (Saghir et al., 2008).

#### 2.3.2. Ethylation of arabinoxylan

In a typical procedure, 2.5 g (18.9 mmol) of arabinoxylan was suspended in 180 mL of methanol. The reaction mixture was vigorously stirred at room temperature for 1 h after addition of 15.15 mL of aqueous NaOH solution (25%, w/v, 94.5 mmol). 7.75 mL of ethyl iodide (94.5 mmol, 5 mol/mol anhydrosugar unit, ASU) was added and the temperature of the reaction bath was raised to 40 °C. The etherification was performed for 5 h. The polymer precipitated after addition of 110 mL of ethanol (20 mol/mol of ethyl iodide). After standing overnight, the product was neutralized with aqueous 50% acetic acid, collected, washed three times with 80% methanol (100 mL), two times with ethanol (100 mL), and dried in vacuum at 60 °C.

Yield: 2.45 g, 87% based on arabinoxylan (sample **9**).

$\text{DS}_{\text{Et}}$ : 0.61 (obtained by  $^1\text{H}$  NMR spectroscopy after peracetylation).

IR (KBr) of EAX: 3423 ( $\nu$  OH), 2924 ( $\nu$  CH), 1625 (absorbed  $\text{H}_2\text{O}$ ), 1417 ( $\delta$   $\text{CH}_2$ ), 1377 ( $\delta$  CH), 1321, 1248, 1162 ( $\delta$  C–O–C), 1043 ( $\delta$  C–O), 896 ( $\delta$  C–O), 607, 532 (polymer backbone)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (in  $\text{D}_2\text{O}$ ) of EAX:  $\delta$  1.58 ( $\text{CH}_3$  of ethyl group), 3.64–4.90 (H-2, H-3, H-4, H-5), 5.37–5.66 (H-1).

#### 2.3.3. Peracetylation

In a typical conversion, 0.3 g ethyl arabinoxylan was suspended in 12 mL DMF and 2 mL of acetyl chloride was added. The mixture was stirred for 16 h at 80 °C. After cooling down to room temperature, precipitation was carried out in ethanol, followed by neutralization with 2% aqueous  $\text{NaHCO}_3$ , and washing four times with ethanol. The peracetylated ethyl arabinoxylan was dried in vacuum at 60 °C.

IR (KBr) of peracetylated EAX: Peak at  $3423 \text{ cm}^{-1}$  ( $\nu$  OH) disappeared and a new peak at  $1747 \text{ cm}^{-1}$  ( $\delta$  C=O) appeared.

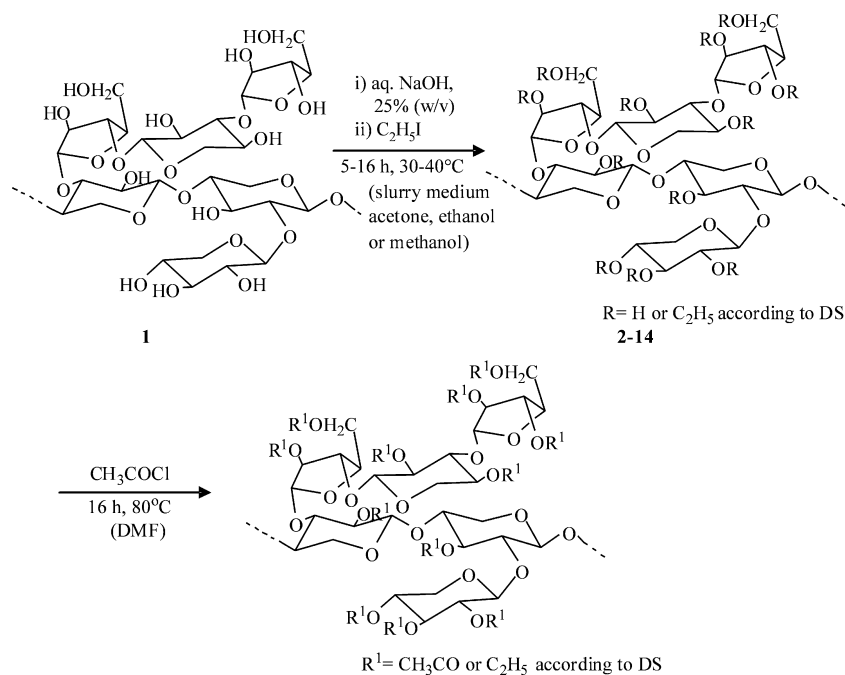
### 3. Results and discussion

The extraction of arabinoxylan **1** from Ispaghula seed husk and its characterization is described elsewhere (Saghir et al., 2008). It contains 72.5% Xylp, 21.8% Araf, 2.3% Rhap, and 1.4% uronic acids. Ethylation of **1** was carried out heterogeneously with ethyl iodide in the presence of aqueous NaOH solution at 30 °C and 40 °C. Acetone, methanol or ethanol was used as slurry medium. The degree of substitution of ethyl groups ( $\text{DS}_{\text{Et}}$ ) was determined by means of  $^1\text{H}$  NMR spectroscopy after peracetylation of the sample with acetyl chloride in DMF at 80 °C (Scheme 1).

Ethylation was carried out applying different molar ratios of ethyl iodide to anhydrosugar unit (Table 1). The increase of the molar ratio of ethyl iodide:anhydrosugar unit up to 5 mol reagent/mol ASU results in an increase of the  $\text{DS}_{\text{Et}}$  value (**7**,  $\text{DS}_{\text{Et}}$  0.13; **9**,  $\text{DS}_{\text{Et}}$  0.61 in methanol). Surprisingly, further increase of molar ratio leads to products with decreased  $\text{DS}_{\text{Et}}$  (**9**,  $\text{DS}_{\text{Et}}$  0.61; **10**,  $\text{DS}_{\text{Et}}$  0.53; **11**,  $\text{DS}_{\text{Et}}$  0.47). It must be considered that by increasing the molar ratio also the amount of water in the reaction medium is increased that may lead to a less activation of the polymer.

A  $\text{DS}_{\text{Et}}$  of 0.48 was obtained without slurry medium, i.e., conversion of **1** in aqueous NaOH with ethyl iodide (sample **6**). Methanol, ethanol or acetone was used as slurry medium. The reaction was completely heterogeneous and results in comparatively easy work up when methanol or ethanol was used as slurry medium. Methanol was found to be an appropriate slurry medium as the highest  $\text{DS}_{\text{Et}}$  value obtained (**9**,  $\text{DS}_{\text{Et}}$  0.61 in methanol; **12**, 0.41 in ethanol; **5**, 0.36 in acetone). However, in case of acetone as slurry medium, a hard lump formed after over night treatment with ethanol during workup to destroy the excess of ethyl iodide, which was disintegrated into small particles before neutralization and further washing with ethanol to remove trapped impurities. The temperature was maintained at 30 or 40 °C. A reaction at 40 °C was found to be more effective leading to a product of slightly higher  $\text{DS}_{\text{Et}}$  (**4**, 0.30 at 30 °C; **5**, 0.36 at 40 °C). EAX **9** with the highest  $\text{DS}_{\text{Et}}$  0.61 was obtained at 40 °C using methanol as slurry medium applying a molar ratio of ASU:EI:NaOH of 1:5:5. Most of the reactions were carried out for 5 h. A reaction over 16 h was carried out but there was no significant difference of DS (**12**, 0.41 for 5 h; **14**, 0.44 for 16 h) which means that the reaction was almost finished after 5 h.

The ethyl arabinoxylans (samples **2–14**) swell in water at room temperature and formed a viscous milky suspension at high temperature. These samples were insoluble in DMSO at room temperature but dissolve upon stirring at 80 °C. Samples **2–14** are also soluble in 2.45% (w/v) aqueous NaOH solution. The  $^1\text{H}$  NMR- and  $^{13}\text{C}$  NMR spectra of sample **2** were not well resolved due to the highly viscous solution in  $\text{DMSO}-d_6$  even at low concentration and hence it was difficult to interpret these. In particular, the proton signals belonging to the polymer backbone and those of the ethyl group could not be unscrambled. Thus, the  $^1\text{H}$  NMR signals were assigned applying the selective total correlation spectroscopy



**Scheme 1.** Conversion of arabinoxylan **1** with ethyl iodide and sodium hydroxide under heterogeneous reaction conditions and subsequent peracetylation. Structure characterization of arabinoxylan **1** from Ispaghula seed husk is described elsewhere (Fischer et al., 2004; Saghir et al., 2008).

**Table 1**

Conditions for and results of the reaction of arabinoxylan with ethyl iodide in the presence of sodium hydroxide in different slurry media (reaction time 5 h).

Molar ratio ASU:EI:NaOH <sup>a</sup>	Slurry medium	Time (h)	Temperature (°C)	Product			
				No.	Yield (%)	DS <sup>b</sup>	[ $\eta$ ] (mL/g) <sup>c</sup>
1:3:4.1	Acetone	5	30	<b>2</b>	n.d. <sup>d</sup>	0.25	321
1:4:8	Acetone	5	30	<b>3</b>	99	0.37	318
1:5:5	Acetone	5	30	<b>4</b>	n.d. <sup>d</sup>	0.3	258
1:5:5	Acetone	5	40	<b>5</b>	99	0.36	244
1:10:10	None	5	30	<b>6</b>	n.d. <sup>d</sup>	0.48	271
1:2:4	Methanol	5	40	<b>7</b>	87	0.13	365
1:3:4.1	Methanol	5	30	<b>8</b>	91	0.36	376
1:5:5	Methanol	5	40	<b>9</b>	87	0.61	368
1:9:9	Methanol	5	40	<b>10</b>	87	0.53	432
1:18:18	Methanol	5	40	<b>11</b>	89	0.47	518
1:5:5	Ethanol	5	40	<b>12</b>	n.d. <sup>d</sup>	0.41	297
1:5:5 <sup>e</sup>	Ethanol	5	40	<b>13</b>	90	0.4	366
1:5:5 <sup>f</sup>	Ethanol	16	40	<b>14</b>	100	0.44	262

<sup>a</sup> Molar ratio anhydrosugar unit: ethyl iodide:aqueous NaOH (25%).

<sup>b</sup> Degree of substitution determined by means of <sup>1</sup>H NMR spectroscopy after peracetylation.

<sup>c</sup> Intrinsic viscosity determined by viscometry and linear regression.

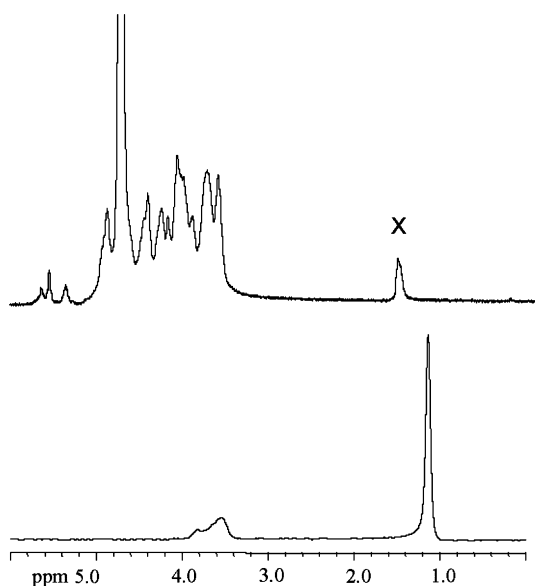
<sup>d</sup> Not determined (n.d.).

<sup>e</sup> Aqueous NaOH (15%).

<sup>f</sup> Reaction time 16 h.

(TOCSY) technique that allows the transfer of magnetization of a selectively excited proton signal to other protons, belonging to the same spin system (system of at least two sorts of magnetically nonequivalent protons connected by scalar coupling). The <sup>1</sup>H NMR for EAX **2** was recorded in D<sub>2</sub>O and signal for CH<sub>3</sub> protons appeared at 1.58 ppm whereas for TOCSY experiment, spectrum was recorded in DMSO-*d*<sub>6</sub> and CH<sub>3</sub> proton signals were detected at 1.135 ppm. This CH<sub>3</sub> proton signal was selectively excited with the mixing time of 60 ms (Fig. 1). That was sufficient to transfer magnetization over three bonds. A group of two very broad and not resolved signals appeared in the range from 3.5 to 3.8 ppm, which were assumed as the NMR signals caused by a number of slightly different ethyl groups chemically bonded to various sites of a polymer, namely at different positions within the repeating unit and at different sugars.

The products **2–14** were peracetylated in order to achieve solubility in CDCl<sub>3</sub>, to minimize the intra- and intermolecular interactions and to introduce a probe for the DS<sub>Et</sub> calculation. The typical procedure applying acetic anhydride and pyridine yields crosslinked and hence insoluble products due to the presence of a low amount of carboxylic acid groups in the starting polymer **1**. Alternatively, the peracetylation of ethyl arabinoxylans was carried out with acetyl chloride heterogeneously in DMF. The mixture was stirred for 16 h at 80 °C according to a procedure successfully applied for methylated birchwood xylan (Petzold, Günther, Kötteritzsch, & Heinze, 2008). The peracetylation as a prerequisite of the exact DS<sub>Et</sub> determination by means of <sup>1</sup>H NMR spectroscopy was confirmed by the absence of the OH band at ~3480 cm<sup>-1</sup> and appearance of new band at ~1748 cm<sup>-1</sup> for  $\nu$ (C=O) of the acetyl group in the FTIR spectrum.



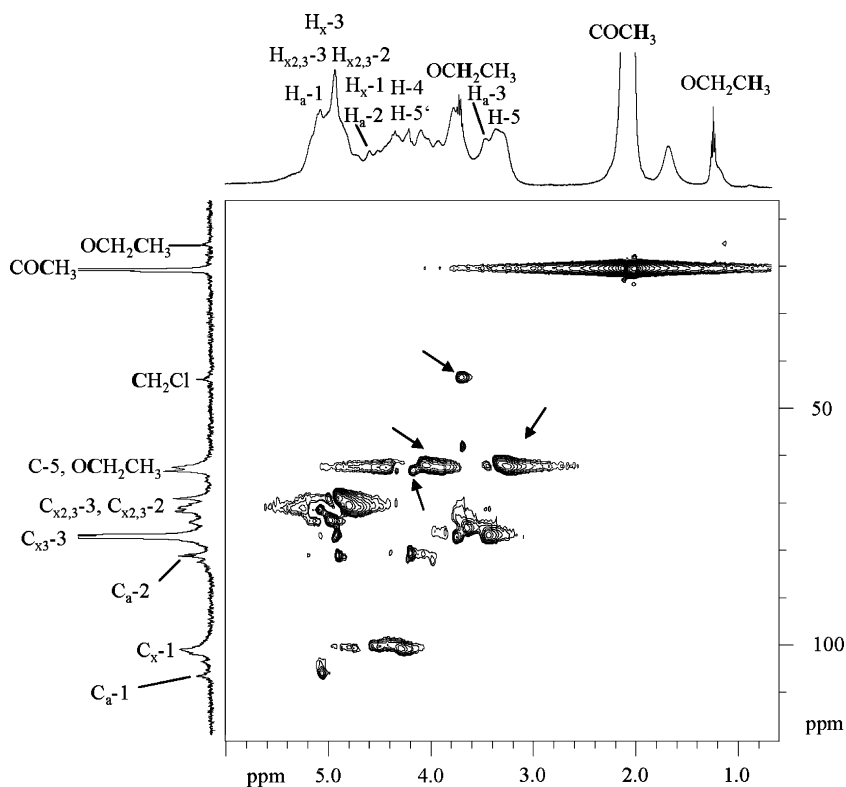
**Fig. 1.**  $^1\text{H}$  NMR- (top, recorded in  $\text{D}_2\text{O}$ ) and selective TOCSY NMR spectrum (x: excitation at 1.58 ppm, mixing time 60 ms, recorded in dimethyl sulfoxide- $d_6$ ) of ethyl arabinoxytan **2** (degree of substitution of ethyl groups 0.25).

$\text{DS}_{\text{Et}}$  values of ethyl arabinoxytan after peracetylation were calculated according to Eq. (1) considering five protons of the anhydrosugar unit and two protons of the  $\text{CH}_2$  group of the ethyl ether in the range from 3.2 to 5.2 ppm as well as the methyl group of the acetyl moiety between 1.4 and 2.4 ppm.

The peracetylated sample **2** was subsequently examined by means of 1D- and 2D-NMR spectroscopy for detailed structure characterization. The signal assignment was supported by previ-

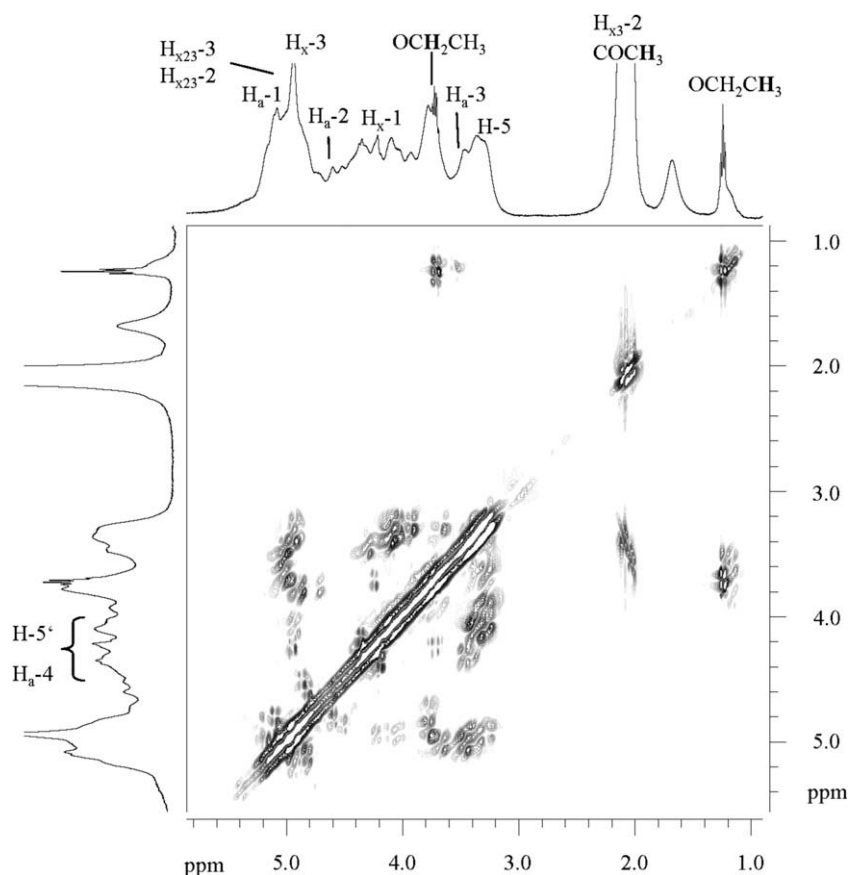
ously published reports (Teleman, Lundqvist, Tjerneld, Ståbrand, & Dahlman, 2000; Teleman, Tenkanen, Jacobs, & Dahlman, 2002). The signal observed at approximately 2.1 ppm in the  $^1\text{H}$  NMR spectrum indicates that the polymer is acetylated, which was also confirmed by  $^{13}\text{C}$  NMR spectroscopy showing signals at 20.5 ppm ( $-\text{CH}_3$ ) and two signals at 170.5 and 169.8 ppm ( $\text{C}=\text{O}$ ). The small signal at 15.5 ppm was attributed to the  $\text{CH}_3$  group of the ethyl ether bonded to the polymer. The  $\text{CH}_3$  group of the ethyl ether appeared at 1.2 ppm in  $^1\text{H}$  NMR spectrum. The methyl groups of the acetates ( $\delta$  2.1/21.0 ppm) and ethyl ethers ( $\delta$  1.2/15.5 ppm) were detected in the HSQC-DEPT experiment (Fig. 2). In addition, cross peaks corresponding to different methylene groups of the ethyl ether appeared in the spectrum. The reason for these signals may be either due to ethylation at the anhydroxylose unit and at the arabinose moieties or due to adjacent chiral carbon atoms. The methylene groups corresponding to  $\text{CH}_2$  of the ethyl ether and the chlorodeoxy group were assigned in Figs. 2 and 3. However, it could not be distinguished whether the C-5/H-5 signal belongs to AraF or Xylp. Cross peaks at 3.55/66.2 and 3.65/66.2 ppm were assigned to  $\text{CH}_2$  of EAX whereas, the cross peak at 3.72/58.3 ppm is assigned to ethanol, which seems to be trapped in the polymer structure. In some cases, even volatile solvents, e.g., diethyl ether may remain in the polymer even after drying in vacuum at room temperature. It was found in previous studies that traces of diethyl ether are removed from cellulose trifluoroacetate in vacuum at  $150^\circ\text{C}$  (Liebert, Schnabelrauch, Klemm, & Erler, 1994). We did not apply such high temperatures in order to prevent decomposition of the polymer. According to the  $^1\text{H}$ ,  $^1\text{H}$  COSY experiment (Fig. 3) the found multiplicity of cross peaks at 1.15–1.25/3.51–3.72 ppm, corresponding to the protons of the ethyl groups indicate their various positions in the sugar units of AX.

Surprisingly a broad signal appeared at 43.9 ppm in  $^{13}\text{C}$  NMR spectrum. By HSQC-DEPT experiment this peak was identified as

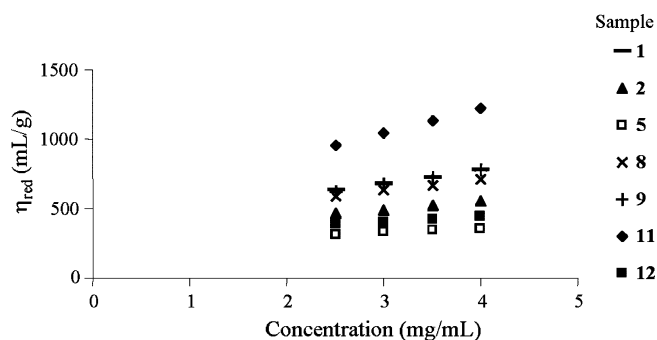


**Fig. 2.** The HSQC-DEPT NMR spectrum of peracetylated ethyl arabinoxytan **2** (degree of substitution of ethyl groups 0.25) recorded in  $\text{CDCl}_3$ . x: xylose moiety; a: arabinose moiety; x2,3: xylose moiety in polymer bearing acetyl groups at position 2 and 3; x3: xylose moiety bearing acetyl groups at position 3.





**Fig. 3.**  $^1\text{H}$ ,  $^1\text{H}$  COSY NMR spectrum of peracetylated ethyl arabinoxyylan, **2** (degree of substitution of ethyl groups 0.25) recorded in  $\text{CDCl}_3$ . x: xylose moiety; a: arabinose moiety; x2,3: xylose moiety in polymer bearing acetyl groups at position 2 and 3; x3: xylose moiety bearing acetyl groups at position 3.



**Fig. 4.** Correlation between reduced viscosity  $\eta_{\text{red}}$  and concentration of arabinoxyylan before and after conversion with ethyl iodide and sodium hydroxide in different slurry media (measured by capillary viscometry in 2.45% (w/v) aqueous NaOH).

$\text{CH}_2$  group leading to a cross peak with the proton signal at 3.7 ppm. It was assumed that this signal is caused by a chlorodeoxy moiety, which is formed by a Vilsmeier–Haack-type reaction at the primary carbon atom (position 5) of arabinofuranosyl moiety in the presence of acyl chlorides and DMF (Heinze, Liebert, & Koschella, 2006). This finding was underpinned by the determination of 2% chlorine in ethyl arabinoxyylan **12** after peracetylation.

The intrinsic viscosity  $[\eta]$  reflects the behavior of the macromolecules in the corresponding solvent, what affects the size (hydrodynamic volume occupied by a macromolecule), which depends not only on the molar mass but also on the type of the substituent (might be ionic or non-ionic) as well as on the distribution of the substituents. Due to the very low amount of uronic acids, the polyelectrolyte effect of the carboxylate groups should be negligible.

The intrinsic viscosity of the arabinoxyylan **1** and ethyl arabinoxylylans (**2–14**) was determined by capillary viscometry in 2.45% (w/v) aqueous NaOH at 20 °C (Table 1, Fig. 4). The intrinsic viscosities were measured in a concentration range up to 4 mg/mL. A value of  $[\eta] = 386 \text{ mL/g}$  was determined for sample **1**. It was found that value of intrinsic viscosity of EAX prepared in acetone as slurry medium decreased with increasing  $\text{DS}_{\text{Et}}$  (**2**,  $\text{DS}_{\text{Et}}$  0.25,  $[\eta]$  321 mL/g; **4**,  $\text{DS}_{\text{Et}}$  0.30,  $[\eta]$  258 mL/g; **5**,  $\text{DS}_{\text{Et}}$  0.36,  $[\eta]$  244 mL/g). The intrinsic viscosity of the samples depends also on the reaction path, i.e. the product structure is influenced by the slurry medium applied during the preparation. Sample **5** synthesized in the presence of acetone as slurry medium possesses a  $[\eta]$  of 244 mL/g while sample **8** (methanol slurry medium) shows a value of  $[\eta]$  376 mL/g with comparable  $\text{DS}_{\text{Et}}$  of 0.36. In methanol, at 40 °C, increase in molar ratio of ethyl iodide and aqueous NaOH to ASU results increase in  $[\eta]$  values (**7**, 365 mL/g; **9**, 368 mL/g; **10**, 432 mL/g; **11**, 518 mL/g) Not only polymer degradation but also aggregation effects must also be taken into account (e.g. samples **10** and **11**). It is known that an increasing rigidity affects the ability of the chain to form a random coil and leads to an increased intrinsic viscosity. However, changes in the chemical structure of the polymer also affect the interactions of the polymer segments with the solvent that are hardly to separate (Kulicke & Clasen, 2004).

#### 4. Conclusion

Arabinoxyylan from Ispaghula seed husk has been converted with ethyl iodide in the presence of NaOH to get non-ionic ethyl arabinoxylylans (EAX). The degree of substitution of ethyl groups ( $\text{DS}_{\text{Et}}$ ) can be determined by  $^1\text{H}$  NMR spectroscopic investigations

after peracetylation of ethyl EAX. Peracetylation of ethyl arabinoxylan with acetyl chloride in *N,N*-dimethyl formamide results in the partial formation of chlorodeoxy groups at the arabinofuranosyl moieties in polymer chain. Alternative peracetylation procedures must be developed in order to prevent undesired side reactions like crosslinking or chlorination. The intrinsic viscosity of the polymers is somehow influenced by the reaction parameters (slurry medium, reagent amounts) and also by the structure of the polymers in solution, which is hard to elucidate.

Further research will include investigations about the thermogravimetric analysis, biological activity and rheological characteristics of EAX.

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