Derivatization and Characterization of Xylan from Oat Spelts

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Summary: Xylan is the predominant hemicellulose component in the residues of annual plants, e.g., in oat spelts xylan amounts to 35–40% of the total mass. For our investigation xylan was separated through alkaline extraction of oat spelts. Our aim was to synthesize water-soluble hemicellulose derivatives from oat spelts xylan preferably under heterogeneous conditions. Esterification was used for derivatization. The synthesises were optimised by variation of the temperature, reaction time and the molar ratios to achieve complete solubility, with good reproducibility and in good yields. Other modification possibilities and application areas of xylan from oat spelts could be proved.

Keywords: esterification; gels; hemicellulose; oat spelts; xylan

Introduction

Hemicellulose is one of the key structural ingredients of the wooden cell-wall, besides cellulose and lignin. In general, a group of polysaccharides with different composition is termed as hemicellulose which is found in vegetable fibres and in cell-walls of grass and corn. Hemicellulose monomer units can be divided into hexoses and pentoses, and include mainly galactose, glucose, mannose (hexoses), and arabinose and xylose (pentoses). Hemicelluloses with hexoses as monomer units occur mainly in softwoods, wheat and barley. Those with pentoses as monomer units occur in hardwoods, rye and oat. However different hemicelluloses do not only differ in the monomer units. Structural differences also occur in branching as side groups or side chains in position C-2 and C-3 (Figure 1)[1]. The degree of polymerisation (DP) of hemicelluloses is lower than the DP of cellulose.

Xylan is a predominant hemicellulose component found in plants and in some algae. Xylan represents about 10–15% in softwoods, about 10–35% in hardwoods and about 35–40% of the total mass in the residues of annual plants, such as oat spelts.

The structure of xylan is more complex than that of cellulose, and has been summarized in several reviews on hemicelluloses in wood[2,3], grass[4] and cereals[5,6]. A proposal for the structure of hemicellulose in annual plants is shown in Figure 1[4]. The monomer units are linked together by β-(1 → 4) glycosidic bonds. Typical examples of side chains or groups in xylan are arabinofuranose, xylopyranose, rhamnose, glucuronic acid and acetyl groups.

Oat spelts are residues of oat flakes production. They contain high amounts of xylan and have a relatively low lignin content. Hence this raw material is an interesting source for the isolation of xylan. Some aspects about the structure of xylan from oat spelts were discussed by Saake et al.[7].

In recent years there has been a growing interest in the application of xylan as a natural polymer with promising properties. The gel- and film-forming properties of

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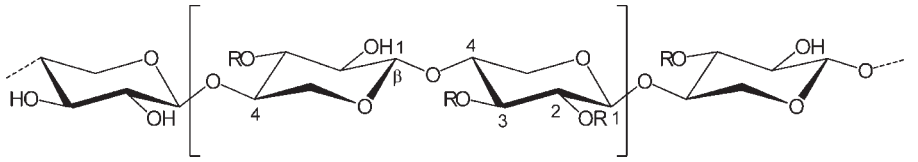

Figure 1.
Structure of a xylan from annual plant.

xylans were investigated by several studies. The nature of oxidative cross-linking of arabinoxylan were shown[8]. The film-forming properties were examined at various mixtures of the hemicellulose and chitosan[9,10]. Stable films could also formed by addition of various plasticizer to a arabinoxylan solution[11].

Thermoplastic xylan derivatives can be obtained by reaction of xylan with polypropylene oxide[12]. The obtained hydroxypropyl xylan (HPX) is a low molecular mass, branched, water-soluble polysaccharide with low intrinsic viscosity and thermoplasticity. Following peracetylation of HPX in formamide solution, acetoxypropyl xylan is formed that is also thermoplastic but no longer water soluble.

The formation of polymer blends between xylan esters and cellulose esters are described by Buchanan et al.[13]. In this study the arabinoxylan was treated with C2–C4 aliphatic anhydride using methanesulfonic acid as a catalyst or trifluoroacetic anhydride as a promoter rapidly and conveniently provided the corresponding arabinoxylan esters. The arabinoxylan esters are soluble in a range of solvents and can tolerate significant amounts of water as a co-solvent. Optically clear films of arabinoxylan acetate and cellulose acetate were prepared by forming films from common solvents.

Some biological and physiological effects of xylans are presented by Ebringerova & Hromadkova[14]. A review is presented on the isolation of xylans from wood and annual plants as well as on the elucidation of structure of these polysaccharides and especially on alkylation, acylation and degradation of these polymers[15]. In a further review the naturally occurring xylan structures, isolation procedures and properties are shown[16]. The chemical modification of hemicellulose with succinic anhydride using N-bromosuccinimde as a catalyst and N,N-dimethylacetamide/lithium chloride system as solvent were studied by Sun et al.[17]. The degree of substitution of succinylated hemicelluloses ranged between 0.19 and 1.39.

The synthesis of hemicellulose ether was described by Fang et al.[18]. The ether was prepared by methylation with methyl iodide using sodium hydride as a catalyst reacted in dimethyl sulfoxide.

A detailed report is given on the extraction of xylanes, their chemical modification and the applicability by Ebringerova[19]. A further review summarizes the chemical functionalization of xylan by Heinze at al.[20].

Despite the large number of promising applications xylan is not yet available in quantities large enough for industrial processing.

In general the derivatization of xylan can be carried out in homogenous or heterogeneous ways. The homogenous way contains the derivatization after dissolution in a suitable solvent. On the other side the reaction occurs in slurry without dissolution of the polymer in a heterogeneous synthesis. The preferred method of the polysaccharide derivatization in industry is the heterogeneous way.

The focus of our study was the derivatization of oat spelts xylan by esterification and etherification under nearly industrially heterogeneous conditions. In this work the results regarding the formation of xylan esters with adjustable DS values, good water solubility as well as film forming properties are presented.

Experimental

Material

Xylan was isolated by alkaline extraction of oat spelts and obtained from Wolff Cellulosics GmbH & Co. KG. An explicit description of the procedure used will be given in the paper of Puls et al. in this issue. For comparative study the commercial oat spelts xylan and birch wood xylan were obtained from Fluka. The reactants for the modification of xylans and the solvents used for product purification were obtained from Aldrich.

Measurements

^{13}C-NMR Spectroscopy

The ^{13}C-NMR spectra were recorded by means of a Varian UNITY 400 NMR spectrophotometer at a frequency of 100.58 MHz. High-resolution solid-state spectra were obtained with the cross-polarization/magic angle spinning (CP/MAS) method at spinning frequencies at 5–6 kHz. The contact time was 1–2 ms and the repetition time of the experiments was 3 s. For the ^{13}C-CP/MAS NMR measurements, the samples which were wetted with lye were mechanically squeezed. About 0.1 cm^3 of the xylan was filled into a sample rotor. Depending on the sample and the specific goal, the measuring time ranged from 1 to 15 h.

FT Raman Spectroscopy

FT Raman spectra of all cellulosic samples were acquired using a Bruker RFS 100 spectrometer with a liquid-nitrogen cooled Ge diode as detector. A cw-Nd:YAG-laser operating with an exciting line of $\lambda_{Nd:YAG} = 1064$ nm and maximum power of 1500 mW was applied as a light source for the excitation of Raman scattering. The spectra were recorded over the range of 3400–100 cm^{-1} using an operating spectral resolution of 4 cm^{-1}. The powders were analysed in small metallic discs which were placed across the normal sample holders. 180° backscattering geometry was applied. The spectra were averaged over 400 scans using 300–500 mW laser power output. The measurements were repeated three times for each sample under the same conditions. Then these three spectra were normalized and an average spectrum was calculated yielding the resulting spectrum for each of the samples.

Rheology

A Bohlin controlled-stress rheometer (CS 10; Bohlin, Cirencester, UK) with air bearing was applied to perform measurements of viscosity as a function of shear rate and small-amplitude dynamic oscillatory measurements. The xylan paste was filled into the preheated cone-plate system (temperature 25 °C, cone angle 4°, plate diameter 40 mm) taking care to avoid air bubbles. A thin layer of light silicone oil was added around the measuring system to prevent evaporate loss. To remove ''memory'' of the loading history, all samples were initially sheared at a shear rate of 10 s^{-1} for 60 s. The shear rate ranged from 1 to 50 s^{-1}. The frequency sweeps with autostrain of 0.01 was measured in the range 0.01–10 Hz.

X-ray

The scattering curves of the xylan samples were measured stepwise in the 2 Θ-region between 4° and 104° by a Siemens-diffractometer D5000 (Siemens, Munich, Germany). Monochromatic (Ge monochromator) Cu-Ka-radiation (40 kV, 30 mA) was used.

Molar Mass Distribution

The weight-average molar mass (Mw) and the molar mass distribution were determined by HPSEC-MALLS. The HPSEC system consisted 600MS pump module, autoinjector, column compartment and MALLS detector Dawn-F-DSP laser photometer (Wyatt Technolgy, Santa Barbara, CA, USA). The sample was dissolved as 0.5% (w/w) in dimethyl sulfoxide at 95 °C for the weight-average molar mass and molar mass distribution. Each sample was measured with the GPC system. Elution of the sample was carried out with DMSO and 0.9 M $NaNO_3$ solution. The molar mass

distribution was calculated through calibration with pullulan standards.

Solubility

The solubility of the xylan derivatives was characterized by preparation of aqueous solutions (2%, w/w) and stirring for 18 h at room temperature. The solution turbidity was measured with a nephelometer 2100AN (Hach, Loveland, Colorado, USA). The calibration of the instrument was carried out with a formazin standard.

SEM

The xylan paste was characterized with SEM by a JSM 6330 F (Joel, Japan) with an accelerating voltage 0.5 ... 30 kV. Alto 2500 (Oxford Instruments, UK) was used as cryo transfer system. The paste was frozen as a drop in liquid nitrogen and subsequently broken at −160 °C. After the break the temperature of the sample was adjusted to −95 °C. At this temperature the polymer structure became visible by sublimation of water with a rate of 10 nm/s.

Derivatization

Succinylation of xylan

The synthesis was carried out according to Sun et al.[17] 3.3 g (0.025 mol) xylan was suspended in 29.5 g aqueous NaOH solution of 5% (w/w) at 80 °C for 1 h. Subsequently the sample was stirred for 18 h at room temperature (25 °C). Then the pH value of the xylan suspension was adjusted at 8.9 by addition of diluted hydrochloric acid and was adjusted at 28 ± 0.5 °C. This was followed by the addition of 1 g (0.01 mol) of succinic acid anhydride under stirring. The pH value was maintained between 8.5 and 9.0 by addition of a NaOH solution of 5% (w/w). After a period of 2 h the product was precipitated in 200 mL ethanol, filtered and washed with a mixture of 600 mL ethanol /water (90/10 v/v). Afterwards, the product was consecutively washed with pure ethanol and acetone. Finally, the product was dried at 50 °C and 75 mbar. The degree of substitution (DS) was determined by means of ^{13}C NMR. ^{13}C CP/MAS NMR: δ (ppm) = 31 (CH_2), 37 (CH_2), 62 (C_5-sub), 64 (C_5), 73 (C_2), 75 (C_3), 77 (C_4), 103 (C_1), 181 (O=C-O_{Ester}), 184 (COOH)

Acetylation of Xylan

3.3 g (0.025 mol) xylan was placed in 50 mL acetic acid and stirred for 18 h. 4.5 mL (0.075 mol) acetic acid anhydride and sulphuric acid were added as catalyst. The mixture was stirred at room temperature. The product was obtained by precipitation into 250 mL ethanol/water (50/50 v/v). The pH was adjusted to 8.5 with NaOH. The acetylated xylan was washed three times with 200 mL ethanol and dried at 40 °C and 75 mbar. ^{13}C NMR (DMSO-d_6): δ (ppm) = 20 (CH_3), 62 ($C_{5\text{-sub}}$), 63 (C_5), 73–78 (C_2, C_3, C_4), 99 ($C_{1\text{-sub}}$), 103 (C_1), 169 (O=C-O_{Ester})

Sulfation of Xylan

Variant I: 3.3 g (0.025 mol) of xylan was dissolved in dried dimethyl sulfoxide at 80 °C and then stirred at room temperature for 18 h. Subsequently, 7.28 g (0.075 mol) amidosulfuric acid was added batchwise. The reaction mixture was stirred at 80 °C for 3 h. After cooling to room temperature the polymer was isolated by precipitation into a solution of NaOH in ethanol (9 g solved in 300 mL) and washed with 300 mL ethanol/water (90/10, v/v). Afterwards, the polymer was dispersed in 400 mL ethanol/water (90/10, v/v) (pH = 11.3) and the pH adjusted to 8.1 with hydrochloric acid/ethanol (50/50, v/v). Finally the product was washed with methanol / water (90/10, v/v) and 2-propanol and dried in vacuum (75 mbar) at 40 °C.

Variant II: The synthesis was accomplished according to Wagenknecht et al.[21]. 3.3 g (0.025 mol) xylan was added into 110 mL of dried dimethyl formamide (DMF). The sample was heated at 80 °C for 2 h along with stirring. After cooling at room temperature the sample was stirred for further 18 h. The reagent mixture was prepared in a separate closed flask under cooling. 9.5 ml of acetic acid anhydride (4 mol per mol AGU) was added to 25 mL

DMF. Subsequently 3.3 mL of chlorosulfuric acid was added drop wise into the reagent flask along with stirring and cooling. Then the mixture was stirred for a further 15 min. After adding the reagents to the xylan sample, the mixture was heated to 50 °C and stirred for 6 h. The polymer was precipitated in 500 mL of a 3% sodium acetate solution in ethanol. After filtration the polymer was washed three times with 300 mL ethanol. The cleavage of the acetyl groups was achieved with 50 mL of an alkaline solution (2 g sodium hydroxide, 4 g water filled up to 50 mL with ethanol) by stirring for 12 h. The pH was adjusted to 8.0 with acetic acid/ethanol (50/50, v/v). Finally the product was washed again with ethanol and dried at 40 °C under vacuum. The DS was calculated by means of sulfur content determined by elemental analysis, ^{13}C NMR (D_2O-d_6): δ (ppm) = 62 ($C_{5\text{-sub}}$), 63 (C_5), 73–75 (C_2, C_3, C_4), 78 ($C_{3\text{-sub}}$), 80 ($C_{2\text{-sub}}$), 101 ($C_{1\text{-sub}}$), 103 (C_1)

Xylan Paste

The modification to xylan paste was carried out according to a patented procedure[22]. A dispersion of 35.25 g (0.267 mol) xylan in 311.7 g sodium hydroxide solution (5%, w/w) was prepared and stirred for 1 h at 80 °C. Subsequently 5.7 g H_2O_2 (35%) was added to the solution heated and stirred for 2 h. Further 4.3 g H_2O_2 (35%) was added to the solution and stirred for 1 h. The product was precipitated by adjusting the pH to 8 with acetic acid / water (50/50, v/v). The pH value was decreased to about 4.5 with aqueous citric acid. The product was separated by centrifugation for 45 min at 15000 rpm. The liquid was decanted and a further centrifugation for 30 min at 15000 rpm was followed. The dry content of the resulting xylan paste was 22.7%.

Results and Discussion

Characterization of Xylan from Oat Spelts

The natural polymers cellulose, lignin and hemicellulose could be detected in the untreated oat spelts by micro Raman spectroscopy (Figure 2), a rapid method determining the constituents of the spelts.

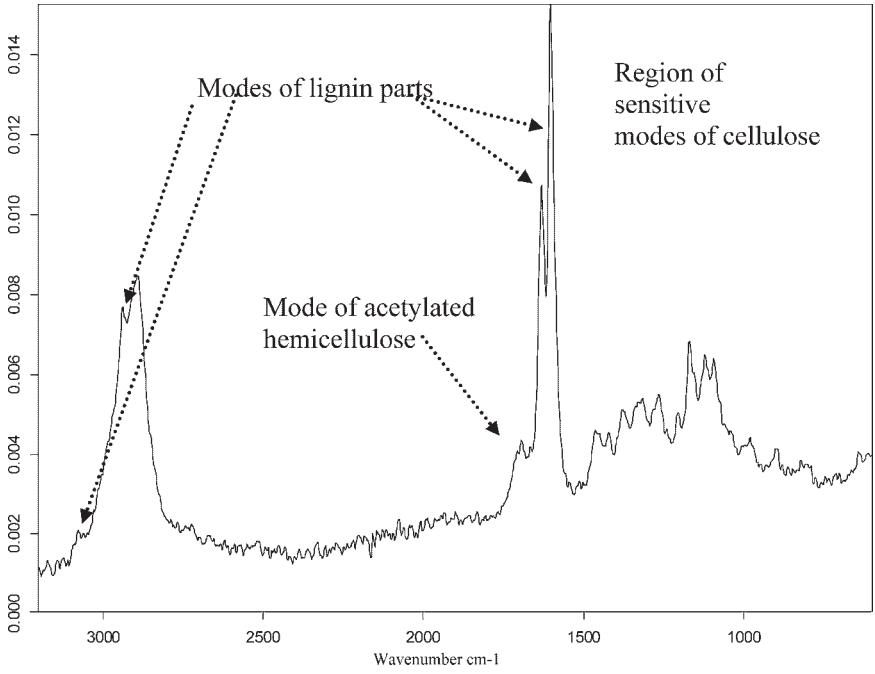

Figure 2.
FT-Raman spectrum of the untreated oat spelts.

The FT Raman spectrum of the oat spelts has to be considered as a superposition of the vibrational spectra of all cell wall components. Thus, the vibrational modes of cellulose, hemicelluloses and lignin are observed, as presented in Figure 2. The peak near 1700 cm^{-1} in the spectra is suggested acetyl groups, that are side groups in xylans. By the alkaline extraction, however, the acetyl groups would be separated from the isolated xylan used for synthesis.

The ^{13}C-CP/MAS NMR spectra show the significance of optimized bleaching and working up conditions (Figure 3). Peaks of impurities were detected in the range of 25 ppm and 180 ppm (sample PST1). The commercial Fluka sample also showed such small peaks in the NMR spectrum. A possible impurity in the samples could be sodium acetate. The peaks in the Fluka spectrum disappeared after bleaching and washing again. The extraction of xylan can be accomplished without impurities, if the processing conditions are optimized (sample PST3) then a bright and pure xylan was obtained. Overall, the peaks of C-atoms in the monomer unit can access well. The peaks of C-2, C-3 and C-4 were at 76 ppm. Two separate peaks can be observed: for C-5 at 63 ppm, and for C-1 at 101 ppm.

For the isolated oat spelts xylan an average molecular mass (M_w) of 79200 g/mol was determined. This value can be considered as relatively high in comparison with other isolated hemicelluloses.

Besides the molecular mass the crystallinity of the polymer is important for the reactivity. The crystallinity can be determined by x-ray methods[23]. The crystallinity of the oat spelts xylan (sample PST1) was relatively low in comparison to the Fluka sample. The diffractograms did not show any discrete Bragg reflexes for the PST1 sample (Figure 4) indicating that the sample was amorphous. The Fluka sample revealed the typical scatter graph of a partly crystalline polymer sample with discrete Bragg reflexes at 2θ angles 10.9°, 12.4° and 19.0°.

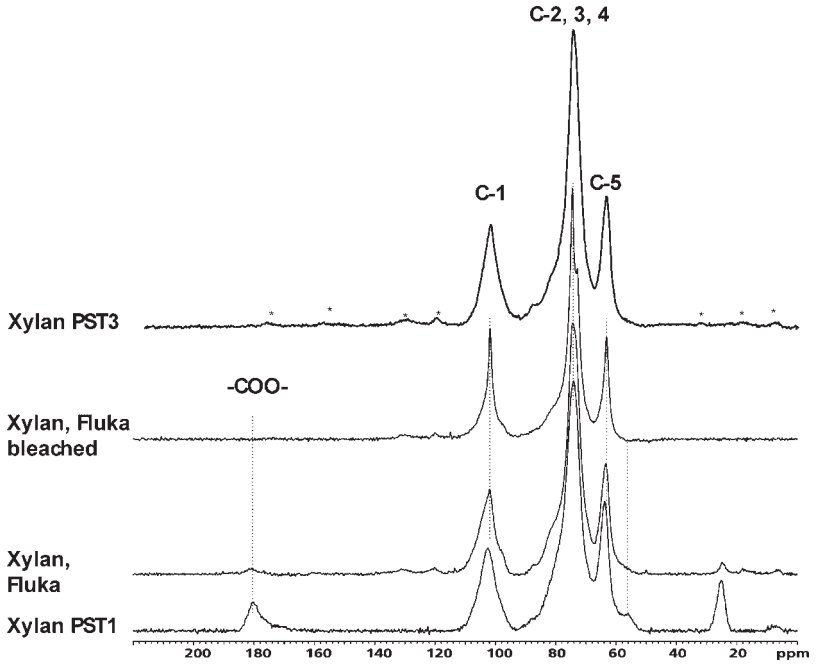

Figure 3.
^{13}C-CP/MAS NMR spectra of different xylan samples; *rotation side bands.

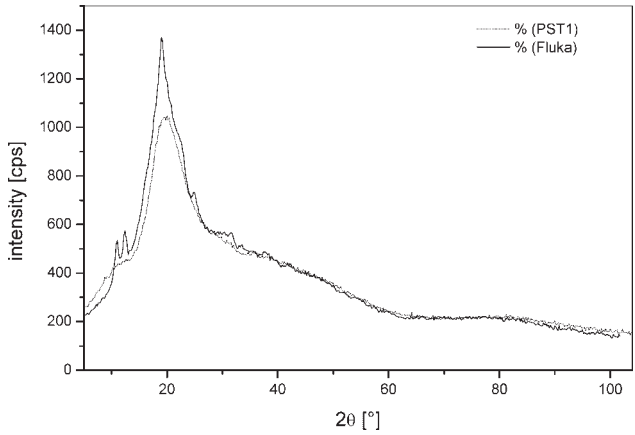

Figure 4.
Comparison of the crystallinity of commercial xylan and isolated xylan from oat spelts.

Derivatization

The aim of this part of our research was to investigate the accessibility of xylan derivatives and the conditions of their formation. For this purpose heterogeneous synthesises should be used. Cationic xylans, ethers and esters of xylan have the largest potential for industrial application. Both organic and inorganic esters of xylan were synthesized and their properties investigated. The results of etherification and cationization are presented in a separate paper.

Organic Xylan Esters

Recent studies on the modification of hemicellulose have demonstrated that these polymers can be modified by means of esterification reactions to obtain conventional thermoplastics[24]. The formation of xylan succinates could increase the hydrophilicity of the hemicellulose. The derivatization of miscellaneous polysaccharides with succinic acid anhydride has been studied extensively under varying reaction conditions[25–28]. Such succinates offer a number of advantageous properties, such as high viscosity, high thickening power, low gelatinization temperature and good filming-forming properties. If the synthesis is carried out in aqueous alkaline solution, a DS value of only 0.2 can be achieved[17]. An increase of the amount of succinic acid anhydride does not lead to higher DS values. The extension of the reaction time or an increase of the reaction temperature yield give lower DS values due to hydrolysis of the anhydride. The solubility in water of the xylan succinates was determined. When the insoluble xylan fraction in the aqueous alkaline solution was separated before the start of the reaction, a xylan succinate with clear water solubility was obtained as can be seen on the turbidity values (Table 1).

Xylan acetate was synthesized according a method of cellulose derivatization as described above (Table 2). The DS values were determined by ^{13}C-NMR and ^{13}C-CP/MAS NMR spectroscopy. The obtained DS values agreed with each other (Figure 5). The distribution of the acetate groups

Table 1.
Reaction conditions and results of the synthesis of xylan succinates.

Sample	Reaction temperature [°C]	Reaction time [h]	n_{SA}/n_{xylan} [mol]	DS	Turbidity [NTU]
XS1	28	2	0.4	0.19	577
XS2	28	3	1.0	0.22	26

Table 2.
Reaction conditions and results of the synthesis of xylan acetates.

Sample	Reaction time [h]	$n_{Ac2O}/n_{xylan\text{-}AGU}$ [mol]	DS
XA1	8	3	0.85
XA2	24	3	1.17

within the monomer unit was similar, as shown by the ^{13}C-NMR spectra ($DS_{C\text{-}2} = 0.5$, $DS_{C\text{-}3} = 0.6$). The xylan acetates showed good solubility in dimethyl sulfoxide and in a mixture of methylene chloride/methanol (90/10, v/v).

Inorganic Esters

Xylan sulfates can be attractive to the pharmaceutical industry as raw materials for high-value products. Studies have been carried out to determine the anticoagulant effects of xylan sulfates in comparison with heparin[29–31]. The antithrombine effect of xylan sulfates was described in further research[32,33]. In addition, the inhibiting effect of several polysaccharide sulfates on tumour cell attack have been proven[34]. However, such applications require a certain quality standard for the product to be developed, e. g., purity, regioselectivity and especially for polymers, homogenous distribution of the functional group between and along the polymer chains. Hence the xylan sulfates were synthesized by homogenous and quasihomogenous routes[35]. As is known from homogenous synthesis, the reaction occurs after dissolution of the polymer. The quasihomogenous synthesis is characterized by dissolution of the polymer during the reaction. The reaction of xylan with amidosulfuric acid after dissolution in DMSO was used as a homogenous method for preparing xylan sulfate (variant I in the experimental section). The acetosulfation of polysaccharides can be considered as a quasihomogenous synthesis (variant II). At first a mixed

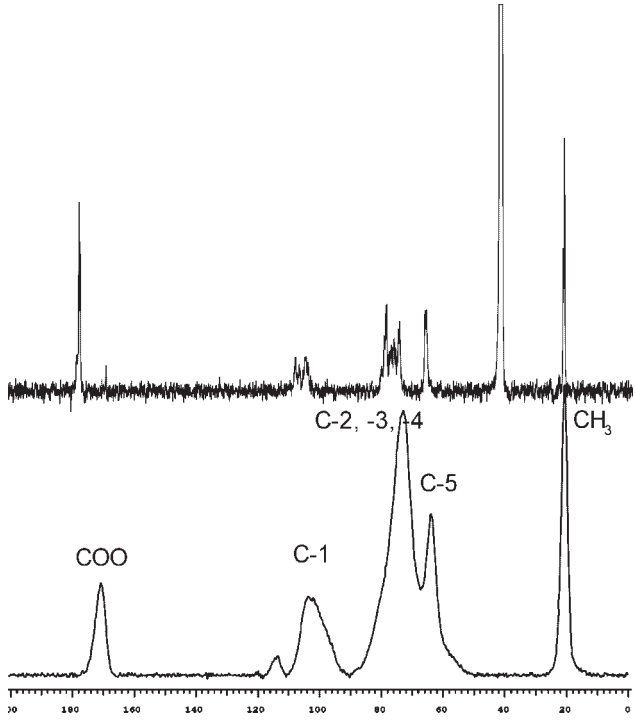

Figure 5.
^{13}C-NMR (upper) and ^{13}C-CP/MAS NMR (below) spectra of xylan acetate (XA2).

Table 3.
Reaction conditions and results of the synthesis of xylan sulfates.

Sample	Sulfation method	$n_{sulfate\ reagens}/n_{xylan\text{-}AGU}$ [mol]	Sulfur content [%]	DS	Turbidity [NTU]
XSUL1	quasihomogenous	2/1	17.0	1.54	22
XSUL2	homogenous	1/1	11.0	0.70	182
XSUL3	quasihomogenous	1/1	11.7	0.77	62
XSUL4	homogenous	3/1	19.1	1.97	19
XSUL5	quasihomogenous	1/1	9.7	0.58	-

ester of acetate and sulfate is formed. Usually the mixed ester is soluble in an aprotic polar solvent like DMF.

In principle, every DS value can be adjusted with both variants of synthesis (Table 3). But the results of the turbidity measurement show that a clear water solubility of the xylan sulfates could not be achieved in the case of high DS values. The residual turbidity of the aqueous solution of xylan sulfate is probably generated by branching of the remaining side groups. The results also suggest that the chain degradation during the reaction is higher in the quasihomogenous synthesis than in the homogenous one. This observation could be explained by the strong acidity resulting from the presence of the chlorosulfuric acid in the quasihomogenous method.

The dissolution of the nearly completely substituted xylan sulfates was sufficient enough and could be investigated by standard ^{13}C-NMR spectroscopy as shown in Figure 6. Both at room temperature and at 70 °C the signal-to-noise ratio was low in the spectra. However the chemical shift as can be seen resulted from the substitution. The peaks of C-2 and C-3 with the half-ester group were found at 80 and 78 ppm. As a result of the substitution at the C-2 position the peak at C-1 position was shifted from 103 to 101 ppm. Furthermore, it can be shown that the distribution of the half-ester group is similar in C-2 and C-3 position.

The FT Raman spectra of xylan sulfates in comparison with the raw xylan are given in Figure 7. The assigned vibrations of the sulfate group are at 1070 cm^{-1} (ν_{as}), 980 cm^{-1} (ν_s), 620 cm^{-1} (δ_s), 450 cm^{-1} (δ_{as}). The intensity of these vibrations increases with increasing DS of xylan sulfate. Determination of the DS values with FT Raman spectroscopy can be achieved by calibration with differently substituted xylan sulfates.

Xylan Paste

According to the procedure described in the experimental section, a xylan derivative was obtained with pasty consistency. The

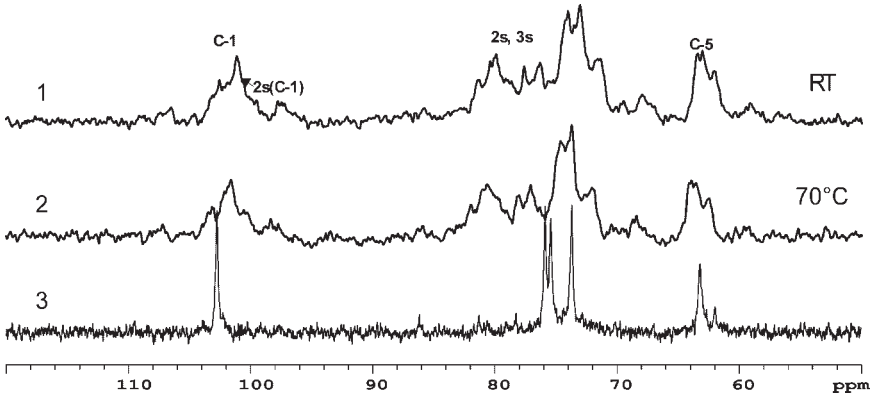

Figure 6.
Comparison of ^{13}C-NMR spectra of pure xylan (3) and of xylan sulfate (DS = 1.97) at room temperature (1) and at 70 °C (2).

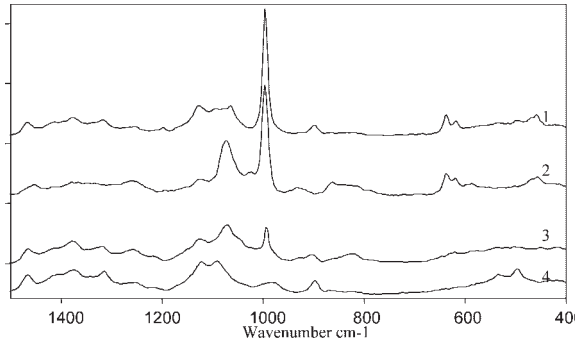

Figure 7.
Comparison of Raman spectra of xylan sulfate with different DS values; 1 - DS = 1.54, 2 - DS = 1.97, 3 - DS = 0.57, 4 - pure xylan.

water content of the paste can be varied in a wide range. The paste is formed although the oat spelts contain practically no ferula acid or other cross-linking substances.

The structure of the paste was investigated by different SEM techniques. Figure 8 shows a scanning electron micrograph after a cryo break and sublimation of water (Figure 8 left). The breaking area in the lower part of the picture shows a reticular structure. On the surface (upper part) particles are shown which are embedded in a film forming matrix. No particles could be detected below the break on the surface. Below the surface freezing artefacts in the form of separation effects appear inside the drop. Such artefacts are generated by separation of the liquid parts from the xylan paste. The liquid parts, especially water, have pushed the polymer forward up to forming a wall. Finally the walls are situated ahead of the freezing front (zone). The structure has widely disappeared in the walls. Crystalline water is located between the walls (dark areas).

In Figure 8 (right) the xylan paste was diluted with water and subsequently dried on the sample carrier. Larger particles (about 5 μm) ,visible in this picture, are again embedded in a film forming matrix.

The flow behaviour of a xylan paste from oat spelts and from birch wood is shown in Figure 9 (left). The xylan paste from oat spelts offers a much higher viscosity than the paste from birch wood. The dry content was 23%. Xylan pastes with considerably

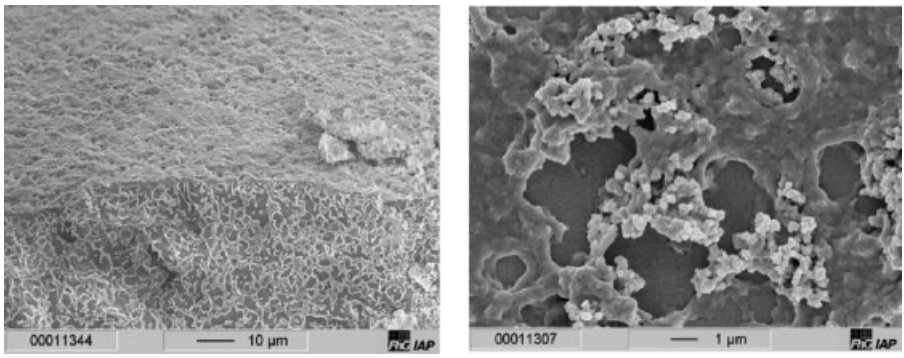

Figure 8.
Scanning electron micrograph (SEM) of the xylan paste after rupture and sublimation of water (left), and after dilution with water and subsequently drying (right).

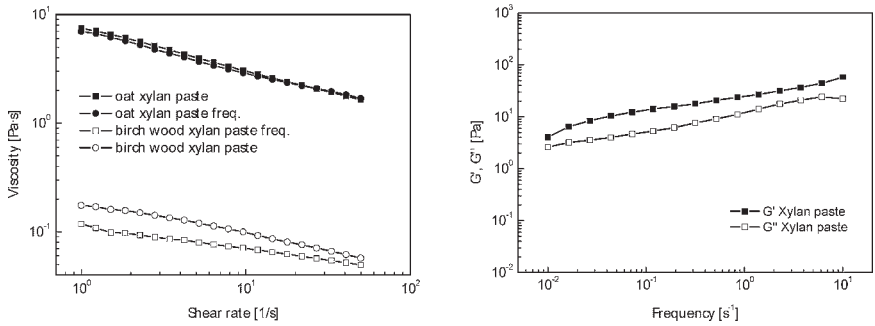

Figure 9.
Flow behaviour of xylan paste from oat spelts and birch wood (dry content: 23%) as a function of the shear rate (left) and frequency sweep testing of the oat spelts xylan paste.

higher viscosities can be obtained if the dry content of the paste is increased. The DP of the commercial birch wood xylan is obviously much lower than that of the oat spelts xylan. The flow curve of the birch wood xylan used in our investigation is also remarkable, with the primary viscosity disappearing after shear stress. The structure of the paste, based on adhesive force between the particles and surrounding polymer solution is apparently partly irreversibly destroyed through the mechanical stress. Frequency sweep testing of the paste produced higher G′ values than G″ values. The xylan paste of the oat spelts shows typical gel-like behaviour.

Conclusion

Oat spelts are an attractive raw material for the isolation of xylan. They are obtainable in large amounts at oat mills at a moderate price. The isolated xylan exhibits interesting characteristics, e.g. relatively high molar mass, high purity, amorphous structure and film-forming properties. It could be shown that the derivatization of xylan from oat spelts is possible under heterogenous conditions which are preferred in industry polysaccharide derivatization. Most of the synthesises are succeeded with good yields and adjustable DS. The xylan derivatives show interesting and versatile properties. A xylan with a pasty structure could be prepared for alternative applications.

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