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Dialkylaminoethyl xylans: polysaccharide ethers with pH-sensitive solubility

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Summary

The reaction of glucuronoxylan from birch wood with 2-chloro-N,N-dimethylethyl-, 2-chloro-N,N-diethylethyl- and 2-chloro-N,N-diisopropylethylamine hydrochloride in 1,2-dimethoxyethane as slurry medium was investigated. The degree of substitution (DS, up to 1.54) of the products could be controlled by adjusting the molar ratio of biopolymer to reagent and depends on the reagent used. The structure of the novel xylan derivatives was confirmed by means of DEPT(135) NMR spectroscopy. The solubility of the polymers with different alkyl moieties possesses a pH value-dependency as studied by turbidity measurements.

Introduction

The hemicellulose xylan is an immense, today largely unused, renewable resource of biopolymers. The structure of xylan may be rather complex and depends on the natural source, which is used for isolation of the biopolymer. The polymer backbone consists of xylose that is decorated with various other sugars [1]. Xylans are usually divided into six main groups: homoxylan, glucuronoxylan, (arabino)glucuronoxylan, arabinoxylans, (glucurono)arabinoxylan and heteroxylan, which have a more complex structure [2]. More than 90% of the hemicellulose component in hardwood and herbal plants represents 4-*O*-methyl-D-glucurono-D-xylan [3]. Therefore, in our investigations xylan from birch wood was studied possessing a single side chain of 4-*O*-methyl-α-D-glucuronic acid attached at position 2 of the β-(1→4) linked xylopyranose backbone. Thus, the polymer contains carboxylic acid groups and offers the possibility to obtain amphoteric products by reacting with 2-chloro-N,N-dialkylethylamine hydrochloride. Although the reaction of the polyglucans cellulose and starch with these reagents is known, yielding cationic products useful, e.g., as chromatographic materials in protein separation or for immobilizing enzymes [4,5], no information about the reactivity of xylan were published up to now. To synthesize the cellulose and starch derivatives a mixture of 1,2-dimethoxyethane and water as slurry medium is used as described in the patent literature [6], on one hand. On the other, various papers describe the introduction of cationic moieties into xylan by reaction of the biopolymer with 1-chloro-2-hydroxypropyltrimethylammonium chloride or the corresponding epoxide

[7-10]. In the present paper, we studied the reaction of 4-*O*-methyl-D-glucurono-D-xylan with 2-chloro-N,N-dimethylethyl-, 2-chloro-N,N-diethylethyl- and 2-chloro-N,N-diisopropylethylamine hydrochloride. The products were characterized regarding structure and some properties.

Experimental

Materials

Xylan from birch wood was purchased from Roth (Karlsruhe, Germany) and was bleached with ClO_2. 1,2-Dimethoxyethan (DME), 2-chloro-N,N-dimethylethyl-, 2-chloro-N,N-diethylethyl- and 2-chloro-N,N-diisopropylethylamine hydrochloride were purchased from Merck (Darmstadt, Germany).

Measurements

The DEPT(135) spectra were recorded with a Bruker AVANCE 400 NMR spectrometer at 60°C in DMSO-d_6.

Turbidity measurements were carried out with a Turbiquant®3000 IR from Merck, which was calibrated with an AMCO Clear®calibration standard kit.

Elemental analysis (EA) was carried out by means of a Vario EL III (Elementar Analysensyteme Hanau, Germany).

The degree of substitution (DS) of the xylan derivatives was calculated from the ratio of nitrogen- to carbon content according to the equation:

$DS_N = (60 \cdot \% N)/(14 \cdot \% C - X \cdot \% N)$, with $X = 96$ for N,N-diisopropylaminoethyl (DIAE) xylan, $X = 72$ for N,N-diethylaminoethyl (DEAE) xylan, and $X = 48$ for N,N-dimethylaminoethyl (DMAE) xylan. From the chloride content, the DS was calculated according $DS_{Cl} = (60 \cdot \% N)/(35{,}45 \cdot \% C - X \cdot \% N)$ and the chloride ratio according to $I (\%) = DS_{Cl}/DS_N \cdot 100$.

Preparation of N,N-dialkylaminoethyl xylan, typical procedure

For a typical synthesis, 5 g (0.038 mol AXU) of xylan (**1**) suspended in 17.5 ml H_2O was heated under reflux for 15 min. The mixture was cooled to room temperature and a solution of 9.09 g (0.227 mol) NaOH in 10 ml water was added. After 30 min at room temperature, 82.5 ml DME were added to the dissolved xylan, yielding a heterogeneous mixture. 19.53 g (0.114 mol) 2-chloro-N,N-diethylethylamine hydrochloride was added and the mixture was allowed to react for 24 h under stirring at room temperature. After decantation of DME and neutralization with 1 N HCl, the polymer was dialyzed against water and lyophilized, product **5** was obtained.

Yield: 6.06 g (49.9%); calculated according to: $\text{Yield} = m/m_{theor} \cdot 100$; $m_{theor} = M \text{ (g/mol)} \cdot 0{,}038 \text{ mol}$; $M = 132 \text{ (g/mol)} + DS \cdot (I/100 \cdot 136.45 \text{ g/mol} + (1 - I/100) \cdot 100 \text{ g/mol}) - DS$.

EA: C = 45.53%; H = 9.34%; N = 5.67%; Cl = 13.86%

$DS_N = 1.48$

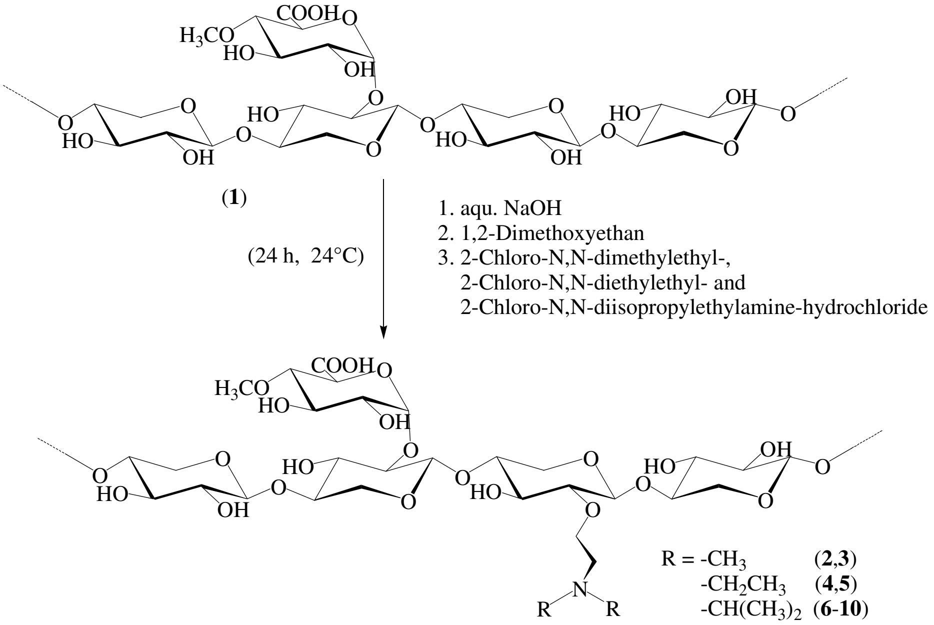
DEPT(135) NMR (D_2O): δ (ppm) = 104.1 (C-1), 103.1 (C1'), 83.9 (C-2s), 77.8-73.9 (C4, C3, C2u), 68.3-46.9 (C5 and CH_2-groups of the substituent), 10.7 (CH_3-groups of the substituent)

Results and discussion

The xylan used in our studies was isolated from birch wood. Sugar analysis revealed xylose as the main neutral sugar component (93.9%) and the presence of low amounts of arabinose (3.6%) and rhamnose (2.5%), originating very probably from co-extracted, contaminating polysaccharides. The xylan contains also 9.7% uronic acid and 1.48% ash based on the air dried substance. These data indicate that the xylan is a 4-*O*-methylglucuronoxylan. These findings are supported by the FT-IR spectrum (not shown) possessing a spectral pattern typical for this xylan type [11].

Preparation of N,N-dialkylaminoethyl xylans

To synthesize the N,N-dialkylaminoethyl xylans, a convenient heterogeneous procedure was used applying a mixture of aqueous NaOH and 1,2-dimethoxyethane as reaction medium (Scheme 1). Prior the reaction, the xylan was refluxed in water and dissolved in aqueous NaOH. The amount of aqueous NaOH was adjusted to a molar ratio of NaOH to reagent of 2:1. Subsequently, to the dissolved xylan, 1,2-dimethoxyethane (DME) was added, yielding a heterogeneous reaction medium. As reagents, 2-chloro-N,N-dialkylethylammine hydrochlorides, with methyl, ethyl and diisopropyl moieties as alkyl substituents were used.



1. aqu. NaOH
2. 1,2-Dimethoxyethan
3. 2-Chloro-N,N-dimethylethyl-,
   2-Chloro-N,N-diethylethyl- and
   2-Chloro-N,N-diisopropylethylamine-hydrochloride

R = $-CH_3$ (**2**,**3**)
$-CH_2CH_3$ (**4**,**5**)
$-CH(CH_3)_2$ (**6**-**10**)

Scheme 1. Reaction scheme for the preparation of N,N-dimethylaminoethyl (DMAE)- (**2**,**3**), N,N-diethylaminoethyl (DEAE)- (**4**,**5**) and N,N-diisopropylaminoethyl (DIAE) xylan (**6**-**10**) in aqueous NaOH and 1,2-dimethoxyethane.

The synthesis procedure applied yields highly functionalized products with an amphotheric character. Depending on the molar ratio of AXU to 2-chloro-N,N-dimethylethyl-, 2-chloro-N,N-diethylethyl- or to 2-chloro-N,N-diisopropylethylamine hydrochloride, different values of the degree of substitution (DS) are obtained (Table 1).

At a molar ratio of 1:1 (AXU to reagent) low DS of 0.19 (**2**) was obtained using the 2-chloro-N,N-diethylethylamine hydrochloride. 2-chloro-N,N-diisopropylethylamine hydrochloride gives a product with a DS of 0.33 (**6**) under comparable conditions, while the highest DS of 0.44 (**4**) was obtained with 2-chloro-N,N-diethylethylamine hydrochloride. An increased molar ratio of 1:3 (AXU to reagent) does not yield products of higher DS in case of N,N-dimethylaminoethyl (DMAE) xylan (0.18, **3**). On the contrary, N,N-diethylaminoethyl (DEAE) xylan and N,N-diisopropylaminoethyl (DIAE) xylan of significantly higher DS values of 1.48 (**5**) and 1.25 (**9**) were accessible by increasing the molar ratio. The functional groups appear partly as ammonium functions, indicated by the chloride content given in Table 1 as well.

The results correspond with the known difference in reactivity, which is influenced by the alkyl substituent bound at the nitrogen atom. On one hand, the reagent containing bulky substituents is more stable against hydrolysis. On the other, the sterical demand reduces the reactivity. Furthermore, the reactive species is assumed to be the corresponding aziridine, which may be formed in aqueous NaOH by the nucleophilic attack of the nitrogen at the chloromethylene group of the 2-chloro-N,N-dialkylethylamine hydrochloride. The formation of the aziridine depends also on the alkyl substituents of the amine. In addition, a direct reaction at the electrophlilic C-atom may occur. Consequently, a detailed understanding of the reactivity needs further studies.

Table 1. Degree of substitution (DS) and solubility of the N,N-dimethylaminoethyl (DMAE)-, N,N-diethylaminoethyl (DEAE)- and N,N-diisopropylaminoethyl (DIAE) xylan depending on the molar ratio of reagent to anhydroxylose unit (AXU).

Reagent		Product			
R[a)]	Molar ratio[b)]	No.	DS_N	Cl^- form [%][c)]	NTU[d)]
CH_3	1:1	**2**	0.19	37.6	-[e)]
CH_3	1:3	**3**	0.18	29.7	-
CH_2CH_3	1:1	**4**	0.42	61.5	-
CH_2CH_3	1:3	**5**	1.48	90.6	76
$CH(CH_3)_2$	1:1	**6**	0.33	60.7	65
$CH(CH_3)_2$	1:1,5	**7**	0.51	86.9	79
$CH(CH_3)_2$	1:2	**8**	0.91	92.7	34
$CH(CH_3)_2$	1:3	**9**	1.25	82.2	48
$CH(CH_3)_2$	1:5	**10**	1.54	70.7	15

[a)] Reagent with $ClCH_2CH_2N^+(R)_2HCl^-$

[b)] AXU:$ClCH_2CH_2N^+(R)_2HCl^-$

[c)] Determined from $DS_{Cl}/DS_N \cdot 100$ and indicates the amount of ammonium moieties

[d)] Nephelometric turbidity units (NTU) of a 1% aqueous solution at pH = 7

[e)] Turbidity out of range (>11000 NTU)

Structural characterization

DEPT(135) spectra of DIAE xylan dissolved in D_2O proof the structure of the biopolymer derivatives (Figure 1). As known, peaks of the CH_2 groups at positions 5, 6 and 7 show negative intensities and can easily be distinguished from the CH moieties. The signals of the DIAE function appear at 46.7 (7) and 68.4 ppm (6) for sample **10** (71% ammonium form calculated form the chloride content). Depending on the ratio of the amine/ammonium form, a shift of the peaks of carbon neighboring to the nitrogen is observed. Thus, the peak of carbon 7 shifts to 47.1 ppm for sample **8** (92.7% ammonium form) and to 45.4 ppm for sample **6** (60.7% ammonium form). The peak of the carbon 8 also shifts depending on amine/ammonium form of the samples; from 54.4 ppm (**10**), via 55.9 (**8**) to 49.8 ppm (**6**).

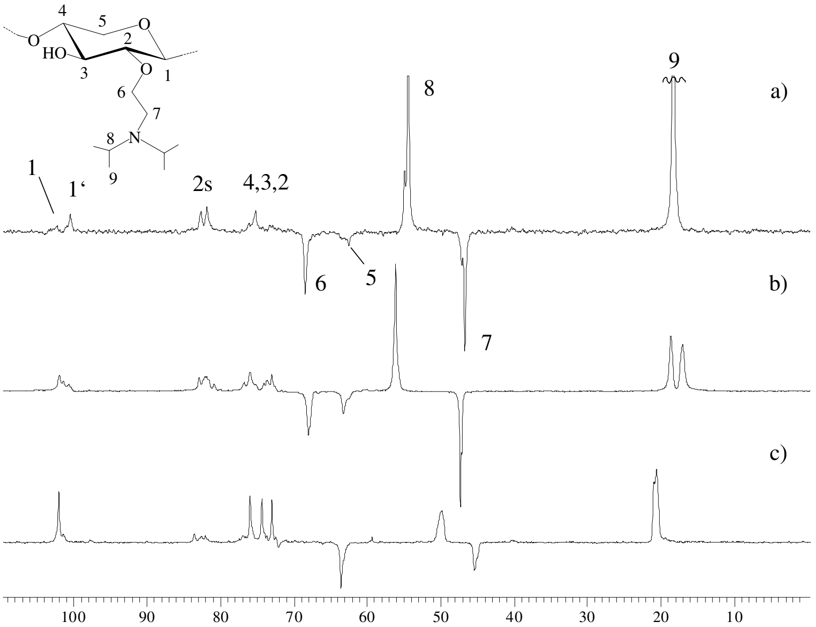


Figure 1. DEPT(135) NMR spectra of N,N-diisopropylaminoethyl (DIAE) xylan with different degree of substitution (DS) in D_2O, a) DS = 1.54 (**10**), b) DS = 0.91 (**8**), c) DS = 0.33 (**6**) s means substituted, ' means influenced by substitution at position 2.

The methyl groups of the isopropyl residues were determinate at 18.3 ppm. The peaks of the AXU appear at 102.2 for carbon 1 for an unmodified position 2 and at 100.4 ppm for carbon 1' where the position 2 is modified. The remaining carbons of the AXU can assigned as following; the signal for a substituted position 2 shifted to 82.6 ppm, for an unsubstituted position 2, the signal can be identified at 73.0 ppm. In case of the highly substituted sample **10**, two peaks can be observed at ~83 ppm indicating a substitution at both positions 2 and 3. The interactions of differently substituted AXUs may lead to signal splitting that is observed for samples with low DS (Figure 1, b and c). The area of the peak of 2s increases comparing with the peak of carbon 5 with increasing DS, as can be clearly seen in Figure 1. The signals of position 3 and 4 can be detected at 74.1 and 75.7 ppm. At 62.5 ppm, the negative signal for the CH_2-group of C5 can be identified.

Solubility in water at different pH

The novel xylan derivatives are soluble in water depending on both the DS and type of alkyl chain (see Table 1). The pH value of the dissolved samples was adjusted to 7 and the turbidity of the resulting systems was measured. A solution, showing a nephelometric turbidity unit (NTU) of 100, is considered to be optically clear (observed by naked eye). Summarizing the results, the DIAE xylan samples in the DS range from 0.33 (**6**) to 1.54 (**10**) are soluble. The solubility for the DEAE xylan depends on DS. The lower substituted sample with a DS of 0.42 (**4**) is insoluble, while the sample with a DS of 1.48 (**5**) is soluble. The DMAE xylan (**2**, **3**) are completely insoluble.

Nephelometric turbidity units (NTU) of the samples were determined. The polymers were put in water containing a known amount of HCl or NaOH. After stirring for 24 h, the values of pH and NTU were measured (Figure 2). The turbid samples are stable for one week and then flocculation starts.

A DIAE xylan sample with a low DS of 0.33 (**6**) is soluble independent of the pH value. Samples with higher DS (**7-10**) show certain turbidity. It is obvious that the NTU increases with increasing DS, while the pH value, where turbidity starts, decreases with increasing DS.

In the case of DMAE xylans (DS 0.19, **2**, DS 0.18, **3**) and DEAE xylan (DS 0.42, **4**), no solubility was observed with changing the pH value. Higher substituted DEAE xylan (DS 1.48, **5**) is water soluble and dos not show turbidity over the whole pH range from 2 to 12.

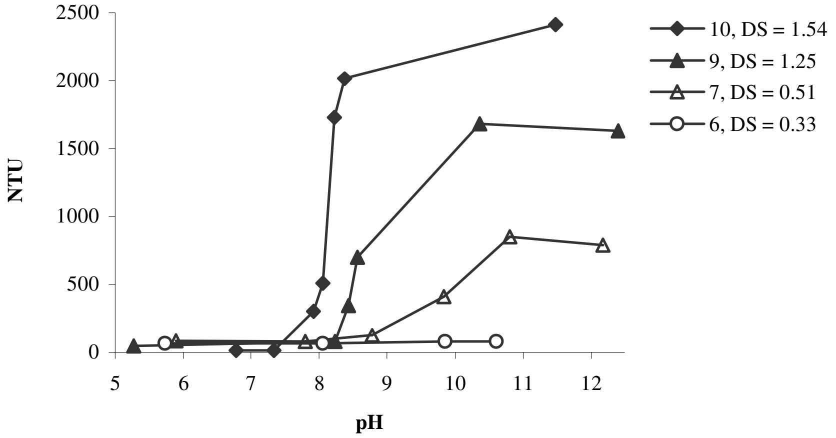


Figure 2. Nephelometric turbidity units (NTU) of a 1% (w/w) aqueous dipersion of N,N-diisopropylaminoethyl (DIAE) xylan dependent on the degree of substitution (DS) and pH.

Conclusion

Various dialkylamino derivatives could be prepared from xylan by a simple heterogeneous synthesis path. Maximum DS values (up to 1.54) were achieved in the case of the DIAE xylan. Due to the present uronic acid and amine residues, the derivatives are amphoteric and pH sensitive. They show differences in water solubility depending on the pH value, DS and type of the alkyl chains.

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