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Xylan derivatives and their application potential – Mini-review of own results

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ABSTRACT

The chemical modification of xylan is a promising path to new biopolymer ethers and esters with specific properties depending on the functional groups, the degree of substitution, and the substitution pattern. The reaction of 4-O-methylglucuronoxylan (GX) from birch with sodium monochloroacetate and 2,3-epoxypropyltrimethylammonium chloride in aqueous sodium hydroxide/slurry medium is described. The influence of the conditions of activation on product structure and properties are discussed in some detail. Methylation of GX was investigated under completely heterogeneous conditions or starting with dissolved polymer using methyl halides as reagents in the presence of NaOH. An activation of the biopolymer has been carried out before the reaction to enhance the accessibility of the reagents. Furthermore, novel xylan esters were efficiently synthesized by conversion of the hemicellulose with furan- and pyroglutamic acid as well as ibuprofen and N,N′-carbonyldiimidazole as activating agent under homogeneous conditions in dimethyl sulfoxide. This conditions are also appropriate to synthesize novel xylan ester containing xylan-4-[N,N,N-trimethylammonium]butyrate chloride moieties. Homogeneous syntheses of xylan sulfates could be carried out in a *N*,*N*-dimethylformamide (DMF)/LiCl as solvent applying sulfur trioxide complexes with DMF or pyridine. Advanced analytical techniques including NMR spectroscopy, HPLC, scanning electron microscopy, rheology, measurements of turbidity and surface tension allow description of structure–property-relationships; selected results will be briefly discussed. Xylan esters may form spherical nanoparticles of a size down to 60 nm and a narrow particle size distribution applying a simple dialysis process and may be used for drug delivery applications. For cationic xylan derivatives a wide range of applications as paper strength additives, flocculation aids, and antimicrobial agents are proposed.

1. Introduction

The hemicellulose xylan is one of the most abundant biopolymers present in hard wood and perennial plants such as grasses, cereals, and herbs. The most prevalently studied xylans are composed of a backbone of β-(1 → 4)-linked anhydroxylose units (AXU) (Cunha & Gandini, 2010; Ebringerová, 2005; Ebringerová & Heinze, 2000; Spiridon & Popa, 2008). Recently, xylan derivatives gain increasing importance as new biopolymeric based materials and functional polymers (Heinze, Koschella, & Ebringerova, 2004; Söderqvist Lindblad & Albertsson, 2004). Due to the functional properties of natural xylans various application fields are considered, e.g., xylans have gained increasing interest due to their potential as wound dressings (Lloyd, Kennedy, Methacanon, Paterson, & Knill, 1998) or pharmaceutical auxiliaries (Miraftab, Qiao, Kennedy, Anand, & Groocock, 2003). Xylans of higher molar mass from plantain interact with the complement system (Samuelsen et al., 1999), and glucuronoxylans from *Rudbeckia fulgida* are immunomodulating (Bukovský, Kardosová, Koscova, & Kostálová, 1998). Xylooligosaccharides are of interest due to their health benefits as prebiotics on the intestinal and their food flavour modifying characteristics (Crittenden & Playne, 1996; Gullón et al., 2010; Moure, Gullón, Dominguez, & Parajo, 2006) and acidic oligosaccharides containing uronic substituents possess their antimicrobial properties (Christakopoulos et al., 2003).

The application potential of biopolymers can be significantly enhanced by chemical derivatization. Xylan derivatives with non-ionic functions (e.g. pyroglutamate, furoate and ibuprofen esters of xylan as well as xylan propionates and hexanoates) could be synthesized by the reaction of the biopolymer with the activated carboxylic acid using N,N′-carbonyldiimidazol or with the acid anhydrides in the presence of methanesulfonic acid (Belmokaddem, Pinel, Huber, Petit-Conil, & Perez, 2011; Daus & Heinze, 2010; Heinze, Petzold, & Hornig, 2007; Heinze

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Table 1
Overview of xylans used (Daus et al., 2011; Petzold et al., 2006a, 2006b; Schwikal et al., 2006; Vega et al., 2012).

Source	Carbohydrate composition [%][a]							Mw [g/mol]
	Xyl	Ara	Rha	Glc	4MGA	GAUA	GLUA	
Birch	93.9	3.6	2.5	–	9.7	13 000		
Birch	73.0	10.1	4.2	–	2.9	4.1	0.7	10,700
Beech	87.2	2.6	–	7.0	1.7			1900

[a] Xyl xylose, Ara arabinose, Rha rhamnose, Glc Glucose, 4MGA 4-O-methylglucuronic acid, GAUA galacturonic acid, GLUA glucuronic acid.

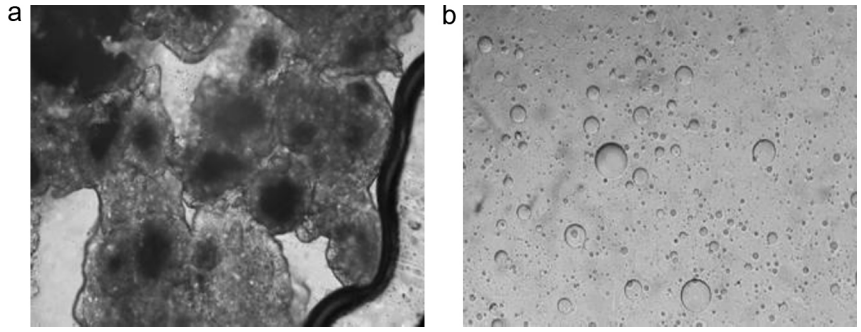

Fig. 1. Polarization microscopic illustration of xylan after activation (1 g xylan in 5 ml 25% NaOH and 7 ml 2-propanol): (a) xylan in 2-propanol followed by addition of aqueous NaOH, (b) xylan dissolved in 25% aqueous NaOH followed by addition of 2-propanol.

et al., 2004). For ionic functions, esterification of xylan, e.g., to xylan 4-[N,N,N-trimethylammonium]butyrates and maleates were developed using comparable conditions described above (Peng, Ren, & Sun, 2010; Vega, Petzold-Welcke, Fardim, & Heinze, 2012). The introduction of sulphuric acid half ester groups led to ionic esters (Daus et al., 2011; Simkovic, Gedeon, Uhliarikova, Mendichi, & Kirschnerova, 2011). Etherification using slurry processes were described in the literature for preparation of cationic xylans and anionic carboxymethyl xylan (Bigand et al., 2011; Heinze et al., 2004; Petzold, Schwikal, & Heinze, 2006a; Petzold, Schwikal, Günther, & Heinze, 2006b; Schwikal & Heinze, 2007; Schwikal, Heinze, Ebringerová, & Petzold, 2006). Recently, amphoteric xylan-type hemicelluloses having carboxymethyl- and quaternary ammonium groups prepared under microwave irradiation were described recently (Peng, Ren, Zhong, & Sun, 2012). The present article summarizes own results regarding etherification and esterification of 4-O-methylglucuronoxylan (GX) of different sources, especially from birch and beech, in detail (Table 1). The structure characterization and some property–structure relationships are described as well. Moreover, the application potential of the products is briefly discussed.

2. Ionic xylan derivatives

Anionic xylan derivatives based on GX, which was obtained from birch, can be obtained by the introduction of carboxylmethyl (CM) moieties. In addition, cationic xylan derivatives from birch wood GX are accessible by the functionalization with hydroxypropyltrimethylammonium (HPMA) groups (Scheme 1). In any case, an activation of the xylan is necessary to enhance the accessibility of the functional groups for the reagents. The activation could be carried out heterogeneously or starting from the dissolved polymer (Fig. 1, Petzold et al., 2006a; Schwikal et al., 2006). The heterogeneous activation starts with a stirred suspension of the xylan in the slurry medium, which is usually an alcohol or 1,2-dimethoxyethane (DME). The addition of aqueous NaOH leads to the activation of the xylan, however to an aggregated system (Fig. 1a). Otherwise, xylan could be dissolved in aqueous NaOH and precipitated by addition of 2-propanol yielding a uniform suspension and the activated xylan (Fig. 1b).

For the preparation of the anionic CM xylan (CMX), the biopolymer was mixed with 2-propanol followed by the addition of aqueous NaOH (heterogeneous activation). For the conversion (usually for 5 h at 55 °C), different molar ratios of sodium monochloroacetate (SMCA) to repeating unit were applied (Table 2). A different activation consists in the dissolution of xylan in 25% aqueous NaOH solution followed by addition of 2-propanol (homogeneous activation). Subsequently, SMCA was added and the reaction proceeds at 65 °C for 70 min (Table 2, Petzold et al., 2006a).

In both cases, the DS increases with increasing molar ratio of SMCA per anhydroxylose unit (AXU). By increasing the molar ratio from 1.0 mol SMCA per mol AXU to 10 mol SMCA/mol AXU, the DS increases from 0.39 to 1.09 in case of the complete heterogeneous carboxymethylation (heterogeneous activation). Surprisingly, no reaction occurred at a molar ratio of SMCA/AXU of 0.5 mol/mol. Starting with the dissolved polymer (procedure (ii) homogeneous activation, Table 2), the DS of the CMX obtained is in the range from 0.24 to 1.22 using molar ratio from 0.5 to 4.0 mol SMCA per

Table 2
Degree of substitution (DS) and substitution pattern of carboxymethyl xylan (CMX) obtained by the carboxymethylation of xylan (from birch, 5 g) with sodium monochloroacetate (SMCA) by (i) after heterogeneous activation (see text, carboxymethylation was carried out at 55 °C for 5 h) and (ii) after homogeneous activation (reaction was carried out at 65 °C for 70 min, adopted from Petzold et al., 2006a).

Molar ratio	Activation procedure	NaOH aq. [%]	DS (^{1}H NMR)		
AXU:SMCA:NaOH			At O-2	At O-3	Σ
1.0:0.5:0.5	(i)	15	–	–	–
1.0:1.0:1.0	(i)	15	0.29	0.10	0.39
1.0:1.5:1.5	(ii)	15	0.19	0.04	0.23
1.0:2.0:2.0	(i)	15	0.52	0.39	0.91
1.0:3.0:3.0	(i)	15	0.55	0.49	1.04
1.0:10.0:10.0	(i)	15	0.60	0.49	1.09
1.0:0.5:4.1	(ii)	25	0.20	0.04	0.24
1.0:1.0:4.1	(ii)	25	0.32	0.17	0.49
1.0:1.5:4.1	(ii)	25	0.39	0.13	0.52
1.0:2.0:4.1	(ii)	25	0.45	0.23	0.68
1.0:3.0:4.1	(ii)	25	0.57	0.49	1.06
1.0:4.0:4.1	(ii)	25	0.60	0.62	1.22