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Separation of polymeric galactoglucomannans from hot-water extract of spruce wood

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HIGHLIGHTS

- We separated and purified high-Mw GGMs from a hot-water extract of spruce wood.
- Two separation techniques were evaluated and compared.
- Precipitation in ethanol separates exclusively pure polymeric hemicelluloses.
- Membrane filtration separates fractions rich in poly-, oligo- and monosaccharides.
- An economical purification solution might be achieved by combining both techniques.

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ABSTRACT

Two methods for separation of polymeric galactoglucomannans (GGMs) from a hot-water extract of spruce wood, i.e., membrane filtration and precipitation in ethanol–water, were compared. Filtration through a series of membranes with different pore sizes separated GGMs of different molar masses, from polymers to oligomers. Only polysaccharides were precipitated in ethanol–water. With the optimal water content of 5–15%, the precipitated amount was about 6% on wood basis. The average molar mass of the precipitated polysaccharides was 10–12 kDa with a molar mass range of 4–20 kDa. GGMs comprised about 80% of the precipitated hemicelluloses. Other precipitated polysaccharides were mainly arabinoglucuronoxylans and pectins (rhamnogalacturonans). Analysis of a lignin-free, ethanol-precipitated GGM preparation by ^{13}C NMR spectroscopy verified that it was structurally almost identical with a GGM-rich ethanol precipitate obtained from spruce wood by extraction at much milder conditions, 90 °C for 60 min.

1. Introduction

Galactoglucomannans (GGMs) have attracted growing interest in recent years because of their potential applications in many different areas. GGMs are the dominating hemicelluloses in spruce and other conifer wood, amounting to approximately 14–20% of the wood (Willför et al., 2005). GGMs are heteropolysaccharides, i.e., non-cellulosic polysaccharides. GGMs in wood have been reported to have an approximate degree of polymerisation of 100–150, corresponding to a molar mass of 16–24 kDa (Timell, 1967). The backbone of GGMs consists of β-(1 → 4)-D-Man$p$ and β-(1 → 4)-D-Glc$p$ units at a ratio of approximately 10:1.9–2.6, with side units of α-(1 → 6)-D-Gal$p$ on about every tenth mannopyranosyl unit (Timell, 1967). The mannopyranosyl units are acetylated at C-2 or C-3 with a degree of acetylation of about 0.5 in spruce wood (Capek et al., 2002) and 0.28–0.37 for GGMs dissolved in spruce TMP waters (Hannuksela and Hervé du Penhoat, 2004). GGMs are located primarily in the secondary cell wall layer of softwood fibres (Meier, 1985). GGMs have been extensively studied for over 50 years, initially mainly because of their importance in pulping and papermaking. More recently, research has been more focused on extraction of GGMs from wood and novel applications, as part of biorefinery concepts.

GGMs have potential to become high added-value products with various applications in food, health, papermaking, textile and cosmetic industries (Ebringerová et al., 2005; Mikkonen et al., 2012; Willför et al., 2008). Different applications request GGMs in different forms, e.g. different molar masses.

GGMs can be separated from thermomechanical pulp waters (Willför et al., 2003a, 2003b) and also directly from wood. GGM extraction from softwoods has been studied for years, such as from pine (Casebier et al., 1969). Extraction of GGMs from spruce wood has been studied by water at temperatures below 100 °C (Örså et al., 1997), by microwave heat-fractionation (Lundqvist et al., 2003), by alkaline extraction (Capek et al., 2000) and by pressurised hot-water extraction (Leppänen et al., 2010, 2011; Song et al., 2008, 2011a, 2011b, 2012).

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Pressurised hot-water extraction of spruce wood at different conditions with plain water has been studied previously (Song et al., 2008). GGMs, which still contain a major part of their acetyl groups, were extracted from ground spruce wood in yields of 80–90%, corresponding to 13–15% on dry wood basis. Such high GGM yields were obtained at temperatures of 170 °C with an extraction time of 60 min. However, higher temperatures and longer extraction times led to a lower pH level, causing deacetylation and partly hydrolytic cleavage of GGMs, and consequently, decreasing the solubility of GGM and its yield, and lower the molar mass of extracted GGMs.

GGMs with high molar mass have been separated from water extracts and TMP water before by different filtration techniques (Krawczyk and Jönsson, 2011; Manasrah et al., 2012; Persson and Jönsson, 2010) and ethanol precipitation (Pranovich et al., 2010; Willför et al., 2003b; Xu et al., 2008). The present study aimed at finding optimal conditions for separation of hemicelluloses, and especially of high-molar-mass GGMs, from extracts obtained by hot-water extraction of spruce wood. Two separation methods, membrane filtration and precipitation in ethanol, were evaluated and compared. The tests were made on a hot-water extract of ground spruce wood obtained by ASE extraction at 170 °C for 20 min, which in previous studies (Pranovich et al., 2010; Song et al., 2008) has been found to give a high yield of high-molar-mass GGMs.

2. Methods

2.1. Spruce wood material

A 15-m long healthy spruce tree (*Picea abies* Karst.) was felled in Southwest Finland in May 2008. Knot-free stem discs were sawn out. Sticks were cut out from the sapwood of the discs, and were ground in a Wiley mill equipped with a 2-mm cut-off screen, and further with a 1-mm screen. The ground wood was stored in sealed polyethylene bags in the dark at −24 °C.

2.2. Hot-water extraction of spruce wood

Approximately 25 g (oven-dry weight) ground wood was extracted with water using an ASE apparatus (ASE-300, cell volume 100 ml, Dionex, Sunnyvale, CA, USA) at 170 °C for 20 min. The extract solution, about 80 ml, was purged out with nitrogen and rinsed with about 50 ml of water.

Altogether about 4.5 l of water extracts was obtained by multiple ASE extraction (43 batches) from a total amount of about 1 kg spruce wood. The water extracts were then centrifuged and the finest sediments were removed (mostly lignin and lignin-related substances, Song et al., 2011a). The volume and end-pH of the extract solutions were measured at room temperature shortly after the extraction. All water extracts were stored in closed test tubes at 4 °C in the dark.

2.3. Separation of GGMs by membrane filtration

The water extracts were purified by membrane filtration using Jumbosep™ Centrifugal Devices (Pall Corporation, New York, US). The devices were designed originally for globular solute filtration of protein and virus solutions. Modified polyethersulfone membranes with five pore sizes (300, 100, 30, 10 and 3 kDa based on globular solute filtration ability, low protein-binding) were used. The device was assembled as illustrated in Fig. 1 after adding the water extracts into the sample reservoir. The assembled device with contents was then centrifuged at about 1575 g for 24 h. The filtration was started with the largest pore size membrane (300 kDa) (Fig. 1). After each filtration, the extracts in the reservoir and the filtrates in the receiver were both transferred to test tubes and stored at 4 °C in the dark. The filtrate passing each membrane filter, first the 300 kDa membrane, was used for the next filtration with the next smaller size membrane (100 kDa), and so forth.

2.4. Separation of GGMs by precipitation in ethanol

Centrifuged water extracts with a reduced content of lignin was used for precipitation of GGMs. High-molar-mass hemicelluloses were precipitated by adding the water extracts to different volumes of ethanol (99.5 % purity) to obtain different ethanol–water ratios. The total volume of the ethanol–water solution was 400 ml.

After precipitation, the suspensions were left to stand overnight. The supernatants were decanted and the precipitates filtered and washed with ethanol, acetone and MTBE, and finally vacuum-dried. The dried precipitates were white powders. The precipitates were stored at 4 °C in the dark. About 20 mg of each precipitate was weighed and dissolved in 10 ml distilled water. Aliquots of sample solutions were taken for different analyses.

2.5. Structural characterisation by ^{13}C NMR spectroscopic analyses

Hydrophobic substances including lignin and other aromatic substances were removed from the hot-water extract of spruce wood by adsorption on column packed with XAD-7 resin (Pranovich et al., 2005). A pure hemicelluloses-rich white powder

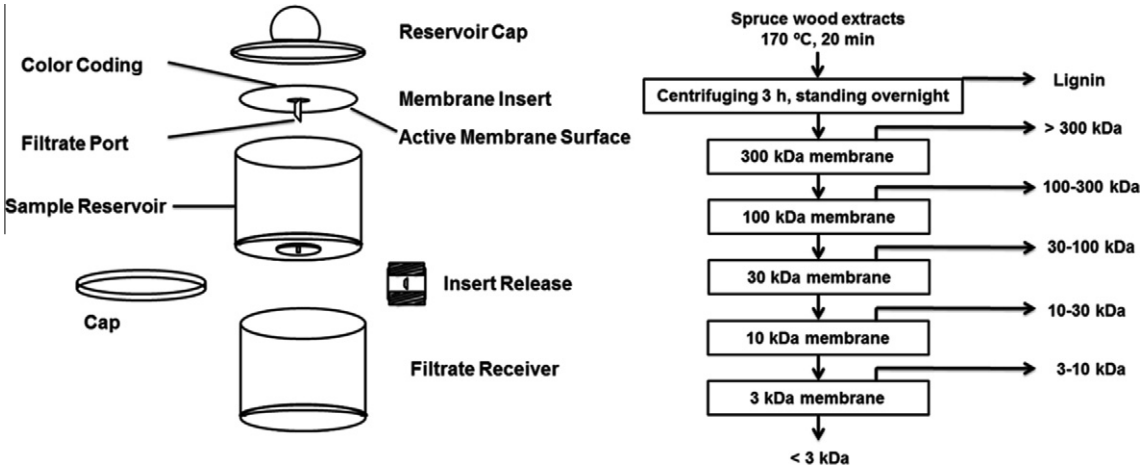

Fig. 1. Set-up of Jumbosep™ Centrifugal Devices and filtration scheme.