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Review

Spruce-derived mannans – A potential raw material for hydrocolloids and novel advanced natural materials

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Abstract

The history, analysis, recovery, and utilization of *O*-acetylgalactoglucomannans (AcGGM for short), which is the main hemicellulose present in softwoods, is reviewed. The water-soluble and hence easily extractable AcGGM from Norway spruce (*Picea abies*) is especially in focus. The influence of different extraction and purification methods on the yield and structure of AcGGM is discussed. Mild structure-preserving processing is vital to maintain the acetyl groups. Without acetyl groups, the water-solubility is decreased due to molecular orientation and the formation of inter- and intramolecular hydrogen bonds. Specific enzymes acting on AcGGM can be useful in targeted modifications, as well as in structure elucidation and structure–function studies. Large-scale recovery methods are also compared. Of particular interest is the recovery of dissolved AcGGM from process waters in mechanical pulp mills using Norway spruce as raw material. AcGGM has promising biological activity and physico-chemical properties suitable for various applications in, for example, food, health, papermaking, textile, and cosmetic industries.

Keywords: Enzymes; GGM; Isolation; Mannans; *O*-Acetyl galactoglucomannans; Recovery; Spruce; Wood

1. Introduction

Polysaccharides, i.e. cellulose, hemicelluloses, and pectins are together with lignin the main constituents of wood and wood pulps (Sjöström, 1993; Timell, 1967). Cellulose is a homopolymer of β-(1 → 4)-linked D-glucopyranosyl units, whereas the hemicelluloses are low-molar-mass heteroglycans built up of several different neutral and acidic monosaccharide units. Pectins are plant-derived substances that contain mainly galacturonic acid residues, are water-soluble to a high degree, and able to form gels.

Water-soluble polysaccharides are released and accumulated into process waters in the production of mechanical pulp and wood-containing paper and are partly removed with the waste waters. This is usually considered as a disadvantage, since it will give a lower pulp and paper yield and a higher impact load on the environment or waste water management. In kraft pulping, the non-cellulosic polysaccharides are converted into isosaccharinic acids or simple sugars and nowadays concentrated and burned in the recovery furnace (Vakkilainen, 1999). From sulfite pulping liquors, the sugars can be quite easily recovered and fermented into ethanol (Gullichsen, 1999a). The general trend towards sustainability in the forest industry, and a growing interest for the biorefinery concept, have recently brought forth the issue of utilizing wood hemicelluloses as a natural resource of specialty chemicals or for bioethanol production (Ragauskas et al., 2006; Raymond & Closset, 2004).

The current use of mannans in industry is mainly limited to guar gum, Konjac glucomannan, locust bean gum, tara gum, and fenugreek gum. These gums have European Union additive numbers (e.g. E412 for guar gum) and are applied in the food industry as emulsifiers, thickeners,

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stabilizers, and gelling agents (Wikipedia, 2007; http://en.wikipedia.org/wiki/). They are also claimed to have nutritional, medicinal, and health effects and, thus, they are applied also in various health products. Furthermore, especially guar gum is applied also in various areas such as in textile, paper, explosives, pharmaceutical, cosmetic, petroleum, and mining industries. The world market for guar gum is estimated to be about 150,000 tons per year. However, at the moment there is no industrial use of wood-derived mannans.

This review deals with the history, recovery, analysis, and utilization of *O*-acetylgalactoglucomannans (AcGGM for short), which is the main hemicellulose in softwoods. The water-soluble and hence easily extractable AcGGM from Norway spruce (*Picea abies*) is especially in focus. Various mannans from other sources are only briefly treated when a comparison to spruce AcGGM or GGM (deacetylated AcGGM) is appropriate.

2. Galactoglucomannans in Norway spruce and other tree species

O-Acetylgalactoglucomannans are the principal hemicelluloses in softwoods (Gymnospermae), the amount in stemwood usually being 10–25% (w/w) (Ebringerová, Hromádková, & Heinze, 2005; Fengel & Wegener, 1984; Sjöström, 1993; Timell, 1965, 1967; Willför, Sundberg, Hemming, & Holmbom, 2005a). Interestingly, the occurrence of a softwood glucomannan (lacking galactosyl side groups) was not proposed until 1956 (Anthis, 1956; Hamilton, Kircher, & Thompson, 1956) and of GGM first in 1958 (Hamilton, Partlow, & Thompson, 1958), even though the presence of mannose-containing polysaccharides, also containing galactose residues, had been suggested already earlier (Adams, 1957; Timell, 1965; Wise & Ratliff, 1948). Meier was the first to undoubtedly show the presence of galactosyl units linked to mannosyl units (Meier, 1960). GGM has later been found in a Chinese fossil tree species (*Metasequioa glyptostroboides*) (Wenda, Peiqing, & Pinyu, 1990) and even in several plants such as clubmosses, horsetails, and in whisk fern, which all are related to fossil tree species living some 400 million years ago (Timell, 1964a).

The amount and composition of wood substances, and hence also of AcGGM, in the living tree differs in the different macroscopic parts of the tree (branches, knots, tops, roots) (Fengel & Wegener, 1984; Vuorinen & Alén, 1999). Furthermore, there are variations within the tree stem; between earlywood and latewood, between sapwood and heartwood, between normal wood and compression wood, and between different fibers and parts of fibers (Bertaud & Holmbom, 2004; Fengel & Wegener, 1984; Pranovich, Konn, & Holmbom, 2003a; Sundberg, Pranovich, & Holmbom, 2003a; Timell, 1967, 1986; Vuorinen & Alén, 1999). The relative amount of AcGGM is larger in latewood than in earlywood and AcGGM is especially abundant in the S2 and S1 secondary cell walls. The chemistry of compression wood and thus also of AcGGM in compression wood has been reviewed by Timell (1986). The amount of AcGGM in compression is usually about half of the amount found in normal wood, which is closely corresponded to a larger amount of (1 → 4)-linked β-D-galactan in the compression wood. However, the structure of compression wood AcGGM is evidently similar to that of AcGGM found in normal stemwood. There may also be structural differences of GGM within the different layers in the cell wall, but undoubtedly proving this is difficult using the methods available today.

2.1. Water-soluble AcGGM

The amount of water-soluble AcGGM is only a small fraction of the total amount found in wood. However, treatments such as delignification, microwave treatment, steam-explosion or enzymatic treatment may enhance the dissolution of degraded polysaccharides and will briefly be considered here, even though this does not fall directly into our definition. We here define water-solubility as those polysaccharides that are dissolved from ground wood or pulp into non-boiling water at neutral or slightly acidic conditions. This water-solubility is greatly influenced by the amount of bulky substituents in the polysaccharide, which hinders the formation of intra- and intermolecular associations (hydrogen bonds) between the polysaccharide chains. For the AcGGM, the acetyl groups are more critical than the galactosyl side groups and the AcGGM will retain its solubility even though all galactose groups, but not the acetyl groups, are removed, for example, enzymatically (unpublished results).

Water-soluble polysaccharides play an important role in mechanical pulping and papermaking. Especially spruces, and there within Norway spruce, are considered to be the most suitable tree species for thermomechanical pulping (Varhimo & Tuovinen, 1999), and hence research has been focused also on the water-soluble AcGGM from Norway spruce. The occurrence and structure of softwood and spruce GGM was extensively studied in the 1950s and 1960s. Nonetheless, it was not until the late 1980s that the dissolution of spruce AcGGM in mechanical pulping caught a real attention. Starting from the PhD thesis of Sjöström (1990), where she showed that AcGGM actually were the main dissolved polysaccharides in mechanical pulp waters, our work has focused much on the occurrence and dissolution, properties and behavior especially in papermaking, and even isolation of AcGGM from spruce pulp and wood, as well as other important tree species (Holmbom, Ekman, Sjöholm, Eckerman, & Thornton, 1991; Thornton, 1993 and papers therein; Örså, 1995 and papers therein; Sundberg, 1995 and papers therein; Sundberg, 1999; Svedman, Lönnberg, Holmbom, & Jäkärä, 1995 and papers therein; Sundberg, Holmbom, Eckerman, & Adams, 2002; Willför, 2000, 2002 and papers therein; Hannuksela, 2004; Holmbom & Sundberg, 2003; Pranovich, Sundberg, & Holmbom, 2003b; Sundberg et al., 2003a; Willför, Rehn, Sundberg, Sundberg, & Holmbom, 2003b; Willför et al., 2003a and papers therein; Konn, 2006; Willför, Sundberg, Pranovich, & Holmbom, 2005b; Willför et al., 2005a; Xu & Willför, 2005 and papers therein; Xu, Willför, Sundberg, Pettersson, & Holmbom, in press).

Normally less than 0.3% (w/w) of spruce or pine wood or TMP pulp is dissolved in the form of AcGGM upon extraction with water at room temperature (Willför & Holmbom, 2004; Willför et al., 2003a). It is possible that part of this very easily water-soluble AcGGM is extracellular and thus deposited on the cell wall in the lumen (Timell, 1965). Raising the temperature to 50 °C or above will dissolve more AcGGM, also of larger molar mass, and in fact we have often used mild agitation in 60 °C as a "standard" method, which resembles the conditions in mechanical pulp mill process strains for comparison of the dissolution of polysaccharides (Sundberg, Holmbom, Willför, & Pranovich, 2000; Thornton, 1993; Willför et al., 2003a, 2003b, 2005a, 2005b). Nevertheless, the dissolution is to a large extent governed by the treatment time (Örså, Holmbom, & Thornton, 1997; Willför et al., 2003a, 2003b). Totally up to 1% and 1.3% (w/w) AcGGM is dissolved from spruce wood and TMP, respectively. For wood, this represents less than 5% of the total amount of AcGGM. By using microwave heat-fractionation or steam treatment to degrade the AcGGM to oligosaccharides or low-molar-mass polysaccharides, it is possible to get a yield even close to 80% of the total amount in the wood (Lundqvist et al., 2002, 2003; Palm & Zacchi, 2003). Another way of improving the dissolution of AcGGM oligosaccharides, and thus enhance the total yield, is by using different hemicellulase enzymes (Gübitz, Csom, Johansson, & Saddler, 1998; Perila & Bishop, 1961; Rättö, Siika-Aho, Buchert, Valkeajärvi, & Viikari, 1993; Tenkanen, Makkonen, Perttula, Viikari, & Teleman, 1997). Different endomannanases, and their combinations, dissolve a mixture of various AcGGM oligosaccharides. Larger amounts of linear oligosaccharides are obtained when α-galactosidases and acetyl mannan esterases are present to remove galactosyl and acetyl side groups, respectively (Biely & Tenkanen, 1998; Shallon & Shoham, 2003; Stålbrand, 2003; Tenkanen, 2004).

2.2. Hardwood glucomannans and GGM

Hardwoods (Angiospermae) usually contain 2–5% (w/w) only of glucomannans with no galactose side groups attached (Fengel & Wegener, 1984; Sjöström, 1993; Timell, 1964b, 1967; Willför et al., 2005b). So far, the presence of GGM has only been shown in the stemwood of one hardwood species, namely *Populus monilifera* (Kubačková, Karácsonyi, & Bilisics, 1992). Unfortunately, the isolation procedure used would have caused both deacetylation and hydrolysis of acid-labile side groups. It is, though, highly likely that the poplar GGM contained acetyl groups, since *O*-acetylated glucomannans have later been found in aspen and birch wood (Jacobs, Lundqvist, Stålbrand, Tjerneld, & Dahlman, 2002; Teleman, Nordström, Tenkanen, Jacobs, & Dahlman, 2003). The structure otherwise resembled that usually reported for softwood GGM, with a Man:Glc:Gal ratio of about 2.4:1:0.24 and a total yield of about 3% from stem saw dust. This poplar GGM has had much attention especially regarding the biological activity of hydrolyzed GGM oligosaccharides (see subsequent chapter).

3. Extraction, isolation, and analysis

For isolation and subsequent chemical analysis of wood polysaccharides, the wood must first be mechanically disintegrated to ensure a complete solvent penetration into the cell wall (Fengel & Wegener, 1984; Vuorinen & Alén, 1999). This is usually achieved by a first rough step such as chipping, sawing, stick preparation, or the like, followed by grinding in a suitable mill. However, heating and grinding to a very fine, dusty material should be avoided. A screening step may be added to ensure a homogeneous material, but this can cause loss of parts difficult to grind. The polysaccharides in commercial or laboratory-made pulps are also of interest, even though structural changes and degradation may have occurred. The fibers in mechanical pulps such as TMP have been thoroughly mechanically treated and the wood structure disintegrated at the high pressure (3–5 bar) and temperature (140–150 °C) applied. Hence, considerably larger amounts of AcGGM and other polysaccharides can be extracted compared to ground wood (Willför et al., 2003a).

3.1. Extraction, isolation, and purification

The extraction and isolation of GGM for analytical purposes has traditionally been achieved through alkaline extraction of holocellulose after delignification with chlorine (chlorous acid) or acidic chlorite (Browning, 1967; Fengel & Wegener, 1984; Sjöström, 1993; Timell, 1967; Vuorinen & Alén, 1999). Unfortunately these treatments will always cause more or less oxidation, hydrolysis, and dehydration of sensitive sugars in the hemicelluloses. Especially the α-D-galactose side groups, but also the β-D-mannose units, are acid labile and may be split off during the holocellulose preparation. A relative hydrolysis rate of about 1:2–3:4–5 for β-D-glucose:β-D-mannose:α-D-galactose for the main sugar units in GGM is suggested in the literature (BeMiller, 1967; Harris, 1975; Shafizadeh, 1963). This has also been shown for isolated GGM upon partial acid hydrolysis (pH around 2, boiling water), where galactose units were the first monomers to appear, followed by mannose and finally glucose (Hamilton, Partlow, & Thompson, 1960; Timell, 1961, 1962). The galactose side groups in GGM are also acid labile during microwave treatment of spruce chips (Lundqvist et al., 2003; Stålbrand et al., 2004). During acid bisulfate cooking of spruce, the yield of galactose in the pulp also decreases much faster than the glucomannan yield (Gullichsen, 1999b), which also supports the acid sensitivity of the galactose groups. The amount of galactose side groups in AcGGM from spruce TMP was also smaller than from AcGGM isolated from wood (Willför et al., 2003a), indicating hydrolysis of these groups during pulping. Acetyl groups can also be split off at acid conditions (Vuorinen & Alén, 1999). Nevertheless, Katz (1965) isolated AcGGM from Paraña pine chlorite holocellulose using dimethyl sulfoxide (DMSO).

Alkaline extraction conditions will cause deacetylation of acetyl groups in the GGM (Browning, 1967; Ebringerová et al., 2005; Fengel & Wegener, 1984; Pranovich et al., 2003b; Sjöström, 1993; Thornton, Ekman, Holmbom, & Petterson, 1994b; Timell, 1965), which is a natural explanation for the lack of such groups in isolated GGM in older works. Pranovich et al. (2003b) recently showed that pH values of 9–10 are sufficient enough to cause deacetylation already at temperatures below 50 °C. Furthermore, alkaline conditions will always cause some hydrolysis of glycosidic bonds and sensitive side groups, as well as degradation and decomposition of dissolved polysaccharides. Hence, the yield and structure of alkaline-extracted GGM may not be representative for the native GGM. The co-extraction of other polysaccharides, which here should be considered as impurities, is also increased. Alkaline solutions of sodium and potassium hydroxide at various concentrations (successive extractions) can be used to isolate different fractions of GGM (Browning, 1967; Fengel & Wegener, 1984; Sears, Alexander, Goldscmid, & Hamilton, 1978; Sjöström, 1993; Timell, 1965; Vuorinen & Alén, 1999). Addition of borate (e.g. boric acid) can enhance the dissolution of GGM, because the borate ions form complexes with the C-2 and C-3 hydroxyl groups in the mannose units. The borate ions can be readily removed on acidification afterwards.

Only a few neutral (non-destructing) solvents, which also preserve most acetyl groups, have been successfully used for extraction of polysaccharides and AcGGM. Especially dimethyl sulfoxide has been applied for extraction of GGM and AcGGM even from holocellulose preparations (Annergren, Croon, Enström, & Rydholm, 1961; Browning, 1967; Fengel & Wegener, 1984; Hägglund, Lindberg, & McPherson, 1956; Katz, 1965; Puls, Schorn, & Schuseil, 1992). Nevertheless, the best solvent for extracting unmodified AcGGM is water at slightly acidic or neutral pH (pH 5.5–7) (Örså, 1995; Örså et al., 1997; Sjöström, 1990; Sundberg et al., 2000; Thornton, Ekman, Holmbom, & Örså, 1994a; Thornton et al., 1994b; Willför, 2000; Willför & Holmbom, 2004; Willför et al., 2003a, 2003b, 2005a). Water extraction has been used also earlier for obtaining GGM, but without investigating the presence of acetyl groups at that time (Adams, 1957; Aspinall & Wood, 1963; Thompson, Becher, & Wise, 1953a, 1953b). Combinations of DMSO and water have also been applied for extracting GGM from spruce holocellulose (Hägglund et al., 1956; Lindberg & Meier, 1957), while Cafferty, Glaudemans, Coalson, and Marchessault (1964) used water to extract AcGGM from pre-swollen holocellulose.

GGM can be selectively precipitated from an alkaline extract using barium hydroxide, which forms insoluble complexes with the C-2 and C-3 hydroxyl groups in the mannose units (Browning, 1967; Fengel & Wegener, 1984; Sjöström, 1993; Timell, 1965; Vuorinen & Alén, 1999). Other precipitating agents used are Fehling's solution or other alkaline copper salts. Another approach may be to first selectively precipitate other polysaccharides from the solution. Cetyl trimethyl ammonium hydroxide or cetyl pyridinium chloride has been used for precipitation of acidic polysaccharides. Browning (1967) lists some other precipitating agents that have been used. A rough fractionation from an alkaline solution can also be achieved by neutralization and/or precipitation by addition of a miscible organic solvent, commonly ethanol. A ratio of ethanol to water around 4:1 will precipitate the polysaccharides and leave oligomeric and monomeric carbohydrates in the water solution. Ethanol is also useful for precipitation of AcGGM from water solutions (e.g. Sundberg et al., 2000; Willför et al., 2003a, 2003b). Repeated precipitations in ethanol can increase the purity, but this is not always the case since co-precipitation of other dissolved polysaccharides can be a problem. Acetylation and fractionation of the acetylated GGM using different organic solvents has also been applied (Aspinall, Begbie, & McKay, 1962; Browning, 1967; Hamilton et al., 1960; Linnell, Thompson, & Swenson, 1966).

Further purification can be done using chromatography (Browning, 1967; Fengel & Wegener, 1984; Sjöström, 1993; Vuorinen & Alén, 1999). Size-exclusion chromatography (gel permeation chromatography) can be used for fractionation according to molar mass or more correctly according to hydrodynamic volume. Acidic polysaccharides can be removed using anionic exchange chromatography. Sjöström (1990) and Thornton et al. (1994a) used different hydrophobic, cationic, and anionic columns for fractionation of polysaccharides, mainly AcGGM, from Norway spruce. Nevertheless, the strength of chromatographic methods is more in removing non-polysaccharide substances, such as lignin and lipophilic extractives, than in separating different polysaccharides in pure fractions. Upscaling of chromatographic methods is also difficult and has so far not been successfully applied for GGM, except for a removal of extractives and lignin impurities (Willför et al., 2003b). Micro- or ultrafiltration has also been used to remove impurities from AcGGM (Sundberg et al., 2000; Willför et al., 2003a, 2003b).

In view of recent results on lignin–carbohydrate complexes (LCCs) it is now established that AcGGM are partly covalently linked to lignin in the native wood, and thus also in pulps (Laine, Tamminen, & Hortling, 2004; Lawoko, Henriksson, & Gellerstedt, 2005, 2006a, 2006b). Nevertheless, it has also been suggested that GGM is mainly associated with the cellulose in the fiber walls (Salmén & Olsson, 1998), so the number of covalent bonds between GGM and lignin can be rather small. There also appears to be different networks of GGM and xylans bound together through

LCCs. For example, even quite pure AcGGM preparations always contain small amounts of xylans and pectins (Willför et al., 2003a, 2003b; Hannuksela & Hervé du Penhoat, 2004). This evidently also means that obtaining a truly pure AcGGM, without any aromatic structures or other sugars attached to the backbone, will be extremely difficult and result in loss of yield and thus also a possible loss of native structural elements.

3.2. Analytical methods

In earlier works, the analytical methods applied for structural investigations of GGM and other polysaccharides were mainly permethylation and hydrolysis, periodate oxidation, partial hydrolysis, and hydrolysis, as well as different fractionation and purification steps including precipitation, complex formation, and separation on chromatographic columns or by electrophoretic methods (Browning, 1967; Timell, 1965). Paper chromatography and thin-layer chromatography were also frequently applied.

The analytical methods have evolved and nowadays several sophisticated techniques can be used more or less routinely. For determination of the monosaccharide composition, cleavage of the glycosidic bonds by acid hydrolysis, acid methanolysis, or enzymatic hydrolysis is first required (Bertaud, Sundberg, & Holmbom, 2002; Sundberg, Sundberg, Lillandt, & Holmbom, 1996a; Tenkanen, Hausalo, Siika-Aho, Buchert, & Viikari, 1995b; Vuorinen & Alén, 1999). Especially acid hydrolysis and also methanolysis can be applied directly on wood samples, while enzymatic degradation works well only on delignified samples (Dahlman, Jacobs, Liljenberg, & Olsson, 2000). The main problem with acid hydrolysis, which is less copious than acid methanolysis, is the degradation of labile uronic acids and also other sugar units. The obtained monosaccharides are then analyzed using gas chromatography (GC), high-performance liquid chromatography (HPLC), or capillary electrophoresis (CE) (Dahlman et al., 2000; Sundberg et al., 1996a; Vuorinen & Alén, 1999).

Linkage analysis is preferably done by permethylation followed by hydrolysis or methanolysis and finally analysis using GC–MS (Brasch, 1983; Brasch & Wilkins, 1985; Capek, Alföldi, & Lišková, 2002; Capek et al., 2000; Laine, Tamminen, Vikkula, & Vuorinen, 2002; McDonald, Clare, & Meder, 1999; Vuorinen & Alén, 1999; Willför et al., 2003a). Different NMR spectroscopy techniques are nowadays also applied directly on the polysaccharides, giving valuable structural information without risk of loss of sensitive compounds during partial hydrolysis. NMR spectroscopy is also a convenient technique to determine the amount and position of *O*-acetyl groups in AcGGM, as well as linkage sequences (Capek et al., 2002; Hannuksela & Hervé du Penhoat, 2004; Lundqvist et al., 2002; Willför et al., 2003a). Linkage and sequence analysis is also convenient when combining with an initial step of enzymatic hydrolysis (Stålbrand et al., 2004; Tenkanen, 2004; Tenkanen et al., 1997). Nevertheless, since all analytical procedures have some disadvantages, the best approach towards complete structural characterization is to combine different analytical techniques.

Molar mass has traditionally been determined with a range of physical (e.g. osmotic pressure or ultracentrifugation) and chemical methods (based on reactions with the reducing end group) (Browning, 1967). Nowadays, the preferred methods are different forms of size-exclusion chromatography (SEC), also called gel permeation chromatography, which depends mainly on the hydrodynamic volume and requires polymers with similar structure for calibration (Vuorinen & Alén, 1999). The expression apparent molar mass has been used for this hydrodynamic volume (e.g. Thornton, Eckerman, & Ekman, 1991; Willför et al., 2003a). The molar masses of poly- or oligosaccharides separated by SEC are then determined by refractive index, UV, laser light-scattering, or matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF-MS) using standard compounds for calibration where appropriate (Dahlman, Jacobs, & Nordström, 2004; Dahlman, Rydlund, & Lindquist, 1997; Hannuksela & Hervé du Penhoat, 2004; Jacobs & Dahlman, 2001; Jacobs et al., 2002; Lundqvist et al., 2002, 2003; Willför et al., 2003a, 2003b). Unfortunately, the large number of different techniques applied makes a comparison between results difficult (Ebringerová et al., 2005).

3.3. Structural characterization

The main structural features of softwood GGM and AcGGM have been known and documented for a long time (Fengel & Wegener, 1984; Sjöström, 1993; Timell, 1965). Nonetheless, recent research has given new details on the structural differences also for differently isolated GGM samples mainly from Norway spruce, but also different pine species (Brasch, 1983; Brasch & Wilkins, 1985; Capek et al., 2000, 2002; Hannuksela & Hervé du Penhoat, 2004; Lundqvist et al., 2002; McDonald et al., 1999; Stålbrand et al., 2004; Tenkanen, Puls, Rättö, & Viikari, 1993; Tenkanen et al., 1997; Willför et al., 2003a).

The main structural features of spruce AcGGM are outlined in Fig. 1. The main chain consists of randomly distributed $(1 \rightarrow 4)$-linked β-D-mannopyranosyl and $(1 \rightarrow 4)$-linked β-D-glucopyranosyl units (Capek et al., 2000, 2002; Hannuksela & Hervé du Penhoat, 2004; Lundqvist et al., 2002; Stålbrand et al., 2004; Willför et al., 2003a). α-D-Galactopyranosyl units are linked as single units to mannosyl units in the main chain, which also has been reported for GGM in pine kraft pulp (Tenkanen et al., 1993). Nevertheless, small differences, such as galactosyl groups linked by $(1 \rightarrow 6)$-bonds to glucosyl units in the main chain have been reported for AcGGM from some species, also spruce (e.g. Annergren et al., 1961; Aspinall & Wood, 1963; Brasch, 1983; Hamilton et al., 1960; Hoffmann & Timell, 1970; Lindberg, Rosell, & Svensson, 1973; Mills & Timell, 1963;

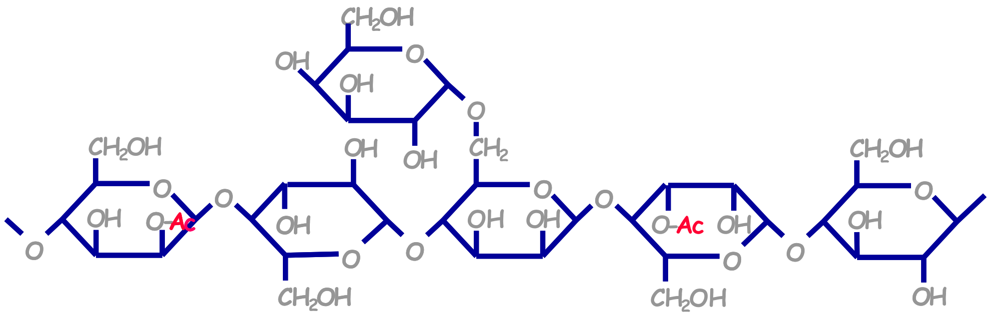

Fig. 1. Structural features of Norway spruce water-soluble *O*-acetylgalactoglucomannans. Specific features are: Gal:Glc:Man ratio ≈ 0.5:1:4; Acetyl groups at C-2 and C-3, exclusively in mannosyl units; Molar mass 20–60 kDa.

Timell, 1962, 1965, 1967; Timell & Hoffmann, 1972). Nevertheless, most of these studies have been done using only permethylation combined with paper chromatography, or the like, and the results have not been verified using modern NMR techniques. It has also been suggested that some β-D-galactosyl units are linked to the main chain of spruce AcGGM and are attached also to the glucosyl units (Capek et al., 2000; Willför et al., 2003a). However, other results suggest that these features would have appeared from a β-D-galactan present as an impurity (Hannuksela & Hervé du Penhoat, 2004).

Generally, the GGM is suggested to be linear, except for the occasional galactosyl side groups. However, it has also been suggested that some longer side chains, also containing non-GGM sugar units, can occur in small amounts (Fengel & Wegener, 1984; Sjöström, 1993; Timell, 1965; Willför et al., 2003a). The problem is to ensure that the GGM sample is absolutely free from impurities and that there are not any covalent bonds to other sugar units.

The sugar unit ratio differs between studies and between species, but typically it is 3.5–4.5:1:0.5–1.1 (Man:Glc:Gal) for water-soluble AcGGM from Norway spruce (Hannuksela & Hervé du Penhoat, 2004; Lundqvist et al., 2002; Stålbrand et al., 2004; Sundberg et al., 2000; Thornton et al., 1994a, 1994b; Willför et al., 2003a, 2003b). An average ratio of 4:1:0.5 has been used for AcGGM dissolved in mechanical pulping of spruce (Holmbom & Sundberg, 2003). Similar ratios (4.5:1:1.3 and 3.6:1:0.8) were suggested also for radiata pine (Brasch, 1983; McDonald et al., 1999). It is, nonetheless, clear that the starting material (wood, pulp, process waters) and the extraction and isolation procedures will influence these ratios (Willför et al., 2003a). Traditionally it has been suggested that there are two different GGM present in softwoods; one with a Man:Glc:Gal ratio of approximately 3:1:1 and an other with a ratio of approximately 4:1:0.1 (Fengel & Wegener, 1984; Sjöström, 1993). There are also suggestions that there are differences between the GGM that is alkali-soluble and that which is water-soluble. However, most probably these differences are caused by the methods of extraction and isolation, and from uncertainties in the analytical methods, rather than from the existence of two different polysaccharides. There may be a difference between the AcGGM that is easily water-soluble and that which needs rougher extraction methods, but this is still to be proved analytically.

It has been suggested that all native softwood GGM contain acetyl groups (Timell, 1967). Water-soluble Norway spruce AcGGM has been shown to have a degree of acetylation of around 0.3, again with variations due to the raw material and method of isolation (Capek et al., 2002; Hannuksela & Hervé du Penhoat, 2004; Lundqvist et al., 2002; Willför et al., 2003a, 2003b). It is now documented that only the mannosyl units bear acetyl groups in position C-2 and C-3. Different ratios of distribution between the C-2 and C-3 position have been suggested. However, that discussion is rather dispensable, since it has been shown that acetyl groups can migrate between these positions and supposedly also to the C-6 position (Garegg, 1965; Lindberg et al., 1973; Reicher, Corréa, & Gorin, 1984; Tanaka, Yaku, Iyoda, & Koshijima, 1990). Katz (1965) suggested acetyl groups also in the glucosyl units of AcGGM from Paraña pine, while McDonald et al. (1999) suggested them only at the C-3 position of the mannosyl units in radiata pine AcGGM.

The mean molar mass for water-extracted AcGGM has been reported to be between 30 and 60 kDa (Sjöström, 1993; Willför et al., 2003a, 2003b; Xu et al., in press), while numbers of 20 and 78 kDa was reported for a low-molar-mass and a high-molar-mass fraction of spruce AcGGM, respectively (Hannuksela & Hervé du Penhoat, 2004). Lower masses have obviously been reported for fractions isolated from holocellulose and for AcGGM isolated after stem treatment or microwave treatment (Jacobs & Dahlman, 2001; Lundqvist et al., 2002, 2003; Palm & Zacchi, 2003, 2004). As for the other structural features, it is clear that the starting material and way of extraction and isolation will strongly influence the molar mass. It is also well known that many polysaccharides exhibit a broad molar mass distribution, and therefore it is also difficult to give a definite molar mass for isolated water-soluble AcGGM.

3.4. Enzymes for AcGGM hydrolysis and modification

Several hydrolytic enzymes are capable of degrading AcGGM. Specific AcGGM-acting enzymes are useful for example in targeted modifications of AcGGM as well as in structure elucidation or structure–function studies. The degree of hydrolysis is dependent on the enzyme applied, the amount of the enzyme used, and the length of the treatment.

Endomannanases (EC 3.2.1.78) catalyze the random hydrolysis of β-D-1,4 mannopyranosyl linkages within the main chain of AcGGM. The hydrolysis products are mannose, mannobiose, and various mixed oligosaccharides. Their amount and type depend on the degree of substitution of AcGGM as well as on the distribution of the substituents. Some endomannanases are able to hydrolyze not only the β-1,4-bond between two mannosyl units, but also the bond between the adjacent glucosyl and mannosyl units (Kusakabe, Park, Kumita, Yasui, & Murakami, 1988; Tenkanen et al., 1997). Several endoglucanases, which hydrolyze mainly cellulose, are also able to cut the linkage between glucosyl and mannosyl units in GGM (Biely & Tenkanen, 1998; Tenkanen, 2004).

The side groups connected to the AcGGM main chain can be removed by α-galactosidase (EC 3.2.1.22) and acetyl (mannan) esterase (EC 3.1.1.6) (Puls et al., 1992; Stålbrand et al., 2004; Tenkanen, 1998; Tenkanen, Thornton, & Viikari, 1995a). Some accessory enzymes are able to hydrolyze only short-chain oligomers, which first must be produced by the backbone depolymerizing endoenzymes, whereas others are capable of attacking intact polymeric AcGGM. The synergism between different enzymes is often observed by the accelerated action of endomannanse in the presence of accessory enzymes and vice versa. Enzymes participating for further hydrolysis of the AcGGM and GGM oligomers are β-mannosidase (EC 3.1.1.25) and β-glucosidase (EC 3.2.1.21), which remove mannose and glucose residues, respectively, from the non-reducing termini of oligosaccharides. Enzymatic deacetylation results in decreased solubility of GGM, which subsequently leads to adsorption of GGM onto the wood fibers (Thornton, Tenkanen, Ekman, Holmbom, & Viikari, 1994c). Removal of galactose substituents does not lead to the precipitation of GGM, if still acetylated.

An interesting possibility for controlled modification of AcGGM is oxidation with galactose oxidase (EC 1.1.3.9) which selectively oxidizes the C-6 hydroxyl group of the galactosyl side group to an aldehyde group (McPherson, Parsons, Spooner, & Wilmot, 2001). Formed aldehyde groups can form intra- and intermolecular hemiacetal bonds and may thus alter the physical properties of AcGGM solution. The aldehyde functionality may also increase the interactions with other polymers, as well as with cellulose fibers (Hartmans et al., 2004). In addition, carbonyl groups facilitate further chemical modifications and grafting of various functional groups to AcGGM.

4. Large-scale recovery of AcGGM

Traditionally, the isolation of AcGGM has been done only in small-scale for analytical purposes. The lack of appropriate amounts of isolated polymeric AcGGM has long been an obstacle for more extensive research or up-scaling towards industrial applications. Even the search for suitable enzymes has been hindered by the lack of substances (Puls et al., 1992). Different batch-wise laboratory isolation procedures have been used by, for example, our group for pulping and papermaking research (Hannuksela, Tenkanen, & Holmbom, 2002; Sundberg et al., 2000; Thornton et al., 1994a; Willför et al., 2003a). Nonetheless, the procedures as such are suitable only for gram-scale preparation and they are unfortunately tedious and require a lot of patience of the researcher.

Starting from a combination of bench-scale methods (unpublished results) and a method for interstage washing in a pulp mill (Sundberg et al., 2002), the first successful large-scale recovery method for AcGGM was developed and published in 2003 (Sundberg, Willför, Rehn, & Holmbom, 2003b; Willför et al., 2003b) (Fig. 2). Although it was limited to apparatuses available to our group, which enabled treatment of 5-kg batches, the method enabled recovery of AcGGM in 100-g scale in a couple of working weeks. Using Norway spruce TMP as starting material, the AcGGM yield of 95 mole% purity was about 5 kg/ton pulp. This method could also be scaled-up, if suitable equipment was procured.

Our next thought was that process waters in mechanical pulp mills already contain substantial amounts of dissolved AcGGM. In fact, during mechanical pulping of spruce wood, about 50% of the dissolved matter consists of AcGGM, which corresponds to about 5000 tons/year in a large mechanical pulp mill. The AcGGM could be recovered from a carefully selected process water stream that would not disturb the normal operations of the mill, especially since a removal of substances providing steric stability to colloidal wood resin could have severe consequences for the mill operations. Two mill-scale trials in Finnish TMP mills during 2005 confirmed this (unpublished results) (Fig. 2). We managed to recover AcGGM of 70–80 mole% purity (the main impurities being arabinogalactans and pectic acids) and an apparent average molar mass

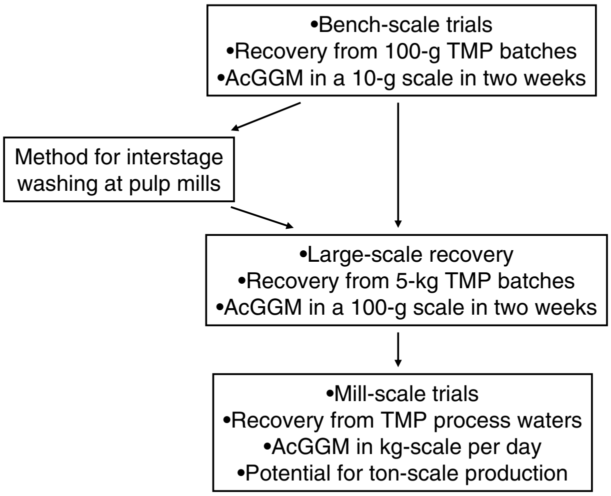

Fig. 2. Development of methods for AcGGM recovery.

around 60 kDa, in an appreciable yield by a combination of different filtration and ultrafiltration steps followed by spray drying or precipitation in ethanol (Xu et al., in press). Thus we now have kg-amounts of wood-derived AcGGM available for research purpose. Attempts have been made to further purify the AcGGM (unpublished results), but this has proved to be difficult without losses in yield or solubility (due to deacetylation). Later, Persson, Matusiak, Zacchi, and Jönsson (2006) used a similar approach to isolate deacetylated GGM from process waters from the production of masonite. Hartman, Albertsson, Söderqvist-Lindblad, and Sjöberg (2006a) and Hartman, Albertsson, and Sjöberg (2006b) also isolated AcGGM from TMP process waters using ultrafiltration and freeze-drying.

Another approach has been to maximize the total yield of AcGGM from spruce using microwave heat-fractionation or steam treatment of spruce wood (Lundqvist et al., 2002, 2003; Palm & Zacchi, 2003, 2004; Stålbrand et al., 2004; Söderqvist-Lindblad, Albertsson, & Ranucci, 2004). These treatments degrade the polysaccharides to oligosaccharides or low-molar-mass AcGGM. Addition of dilute alkali up to $\leqslant$0.05% NaOH still allowed recovery of AcGGM, but at higher alkalinity, the acetyl groups were destroyed. However, yields as high as 70–80% of the total amount of AcGGM could be attained this way. Gel filtration has been applied for separation of the oligomeric AcGGM or GGM substances. The first stage in the original two-stage Organocell process has also been proposed as a suitable source of AcGGM (Bennani, Rigal, & Gaset, 1991; Puls & Saake, 2004). Unfortunately, the process has nowadays been modified and is no longer suitable for recovery of AcGGM.

Unfortunately, all methods described above have the same problem with impurities, either other polysaccharides, lignin fragments, or salts and proteins, in the AcGGM. It is obvious that up-scaling will give a less pure AcGGM compared to analytical scale isolations. Nevertheless, in view of some resent studies of LCCs (Laine et al., 2004; Lawoko et al., 2005, 2006a, 2006b), it may be more or less impossible to obtain a completely aromatic-free AcGGM.

5. Physico-chemical characteristics of AcGGM

Most of the data available on the physico-chemical characteristics of AcGGM is actually from the field of pulping and papermaking. One characteristic of AcGGM and GGM that has received much attention throughout the years is the sorption of AcGGM and GGM to different fiber surfaces (Annergren & Rydholm, 1960; Clayton & Phelps, 1965; Hannuksela, Fardim, & Holmbom, 2003; Hannuksela, Holmbom, Mortha, & Lachenal, 2004; Hannuksela et al., 2002; Hansson, 1970; Holmbom & Sundberg, 2003; Holmbom et al., 1991; Holmbom, Åman, & Ekman, 1995; Laffend & Swenson, 1968a, 1968b; Sundberg & Holmbom, 1997, 2004). Especially GGM, but also AcGGM, is sorbed preferably to cellulose surfaces. The sorption of mannans, including AcGGM and GGM, to different fibers was recently reviewed by Hannuksela and Holmbom (2004a). The sorption of GGM to cellulose surfaces alters the properties of paper, e.g. by increasing the tensile strength and decreasing the tear strength (Hannuksela et al., 2004; Holmbom et al., 1995; Laffend & Swenson 1968b; Sundberg et al., 2000; Suurnäkki, Oksanen, Kettunen, & Buchert, 2003). Residual GGM on cellulose surfaces in the production of carboxymethyl cellulose (CMC) has also been suggested to influence the swelling properties of the pulp, as well as the amount of unreacted residuals (Jardeby et al., 2005).

Another interesting property of AcGGM is the ability to stabilize colloidal wood resin emulsions in papermaking against electrolyte-induced aggregation and also to lower the deposition tendency of resin aggregates (Hannuksela & Holmbom 2004b; Holmbom & Sundberg, 2003; Johnsen, Lenes, & Magnusson, 2004; Otero et al., 2000; Rundlöf, Eriksson, Ström, & Wågberg, 2002; Sihvonen, Sundberg, Sundberg, & Holmbom, 1998; Sundberg & Holmbom, 1997; Sundberg, Thornton, Holmbom, & Ekman, 1996b; Sundberg, Thornton, Pettersson, Holmbom, & Ekman, 1994). AcGGM-stabilized wood resin droplets form colloidal emulsions, which are not aggregated even at high salt concentrations. These specific properties are an essential part of the papermaking process and removal of all AcGGM from the process would probably cause insuperable pitch problems. Furthermore, AcGGM and GGM also interact with and adsorb fillers used in papermaking (Willför, Sundberg, Holmbom, & Sihvonen, 2000).

Xu et al. (in press) have studied the physico-chemical properties of the mill-scale isolated AcGGM mentioned earlier. The AcGGM was readily soluble in water even up to 20% concentration, although at a concentration above 0.1% the solutions were first colloidal to their nature before filtration. After filtration, almost a complete dissolution occurred, indicating that flocks or networks of the polymers were destroyed due to the shear forces applied during filtration. The solutions were stable even after 11 days and addition of NaCl did not affect the stability. However, deacetylation caused flocculation, as expected. The surface activity in water was low. The viscosity was low and concentration-dependent. An interesting feature, which will be studied more in-depth, was that a small addition of AcGGM to a solution of Konjac glucomannan dramatically decreased the viscosity.

The applicability of AcGGM as stabilizer for oil-in-water emulsions has recently been studied. Mikkonen et al. (2007a) evaluated the potential of AcGGM as emulsifier of hydrophobic beverage flavors. AcGGM was found to be almost as good stabilizer as the commercially widely used gum arabic (arabinogalactan).

The film formation of AcGGM, or modified AcGGM, have also been studied (Cafferty et al., 1964; Hartman et al., 2006a, 2006b; Mikkonen et al., 2006). Proper film formation of AcGGM requires, however, a substantial addition of plasticizer. AcGGM is reported to form cohesive transparent self-supporting films in the presence of glycerol, xylitol, or sorbitol. The film plasticized with sorbitol has shown low oxygen gas permeability at intermediate relative humidity (50% RH) (Hartman et al., 2006a). However, films from AcGGM are rather weak. Thus blend films, with improved mechanical properties, from AcGGM and other polysaccharides, alginate, carboxymethyl cellulose and Konjac glucomannan, have been prepared (Hartman et al., 2006a; Mikkonen, Yadav, Willför, Hicks, & Tenkanen, 2007b). The moisture sensitivity of AcGGM films has been improved with further chemical modifications (Hartman et al., 2006b).

Low-molar-mass spruce AcGGM from heat-fractionation of spruce has also showed promising potential in hydrogels together with poly(2-hydroxyethyl methacrylate) (PHEMA) (Söderqvist-Lindblad et al., 2004).

6. Biological activity

Wood-derived GGM has not attracted much attention regarding possible biological effects (Xu & Willför, 2005), at least compared to other mannans such as acemannan commonly found in leafs of the aloe vera plant (e.g. Femenia, García-Pascual, Simal, & Rosselló, 2003) or high-molar-mass Konjac mannans (e.g. Vuksan et al., 1999, 2000). The work conducted at the Slovak Academy of Science, together with co-workers, concerning the biological activity of hydrolyzed and deacetylated GGM oligosaccharides (GGMOs) from *P. monilifera* and Norway spruce makes an interesting exception. The effect of GGMOs on the elongation growth of pea (*Pisum sativum*) and spruce stems and the interaction with plant growth regulators such as auxins have been studied (Auxtová et al., 1995; Auxtová-Šamajová et al., 1996; Lišková et al., 1995). GGMOs showed a distinct effect, which was concentration and pH dependent. More recently, the effect of GGMOs and auxins on the elongation growth and root formation of pea and mung bean (*Vigna radiata*) cells was studied (Kollárová, Henselová, & Lišková, 2005; Kollárová, Lišková, & Capek, 2006). The effects of the GGMO structure and galactosyl side chains were also evaluated. Furthermore, GGMOs induce changes in glycosidase activities during auxin-induced growth in pea stems (Bilisics, Vojtaššák, Capek, Kollárová, & Lišková, 2004). Especially changes in intracellular α-D-galactosidase and β-D-galactosidase activities were noted. GGMOs have also been shown to induce a non-specific resistance in plants (cucumber cells, *Cucumis sativus*) to local viral infection (tobacco necrosis virus) on leaf surfaces (Slovákova et al., 2000). Spruce GGMOs were recently shown to be involved in the signaling pathways of vascular (tracheary element) differentiation in xylogenic cultures of zinnia (*Zinnia elegans*) (Beňová-Kákošová et al., 2006). It is evident that wood-derived GGMOs have a wide biological activity in plants and also a potential for other biological applications. However, an in-depth study of the use of such compounds in pharmaceutical or health-promoting applications is still missing.

The biological activity of naturally acetylated or deacetylated polymeric GGM has recently been a subject of interest. A first study shows that especially deacetylated GGM have a dose-dependent immunological activity, which makes GGM and its derivatives potentially interesting as biological-response modifiers and therapeutic agents (Ebringerová et al., in press).

Another example of immunological activity of AcGGM has been the raising of antibodies against spruce AcGGM (Lappalainen, Tenkanen, & Pere, 2004). These selective antibodies can be used for chemical mapping of pulp fibers, which is of interest since most technical properties of paper are largely governed by the surface chemistry of the fibers.

7. Possible applications of AcGGM in novel advanced natural materials, as well as in bioactive substances and hydrocolloids

In view of the discussions above and considering applications of other mannans (Hannuksela and Holmbom, 2004a, 2004b; Xu & Willför, 2005), it is quite simple to pinpoint some potentially interesting areas of applications for spruce AcGGM, or wood-derived AcGGM in general. In papermaking or in the textile industry, and for medical applications, i.e. areas that deal with cellulose surfaces, the potential lies within a possible surface modification using native or modified AcGGM. Specialty paper grades, abrasion-resistant clothing, or antibacterial bandage could be high-value products obtainable through sorption of modified AcGGM to the cellulose surfaces. Other interesting applications could be as barriers against oxygen gas, water vapor, or fat barriers in food pack. For example, a blend of chitosan and AcGGM could have interesting properties where now only chitosan have been tested (Kjellgren & Engström, 2006; Kuusipalo, Kaunisto, Laine, & Kellomäki, 2005).

The potential bioactivity of AcGGM or GGM oligosaccharides, as well as of the polysaccharides as such, should also be further investigated. For health applications, the best possible source for recovery may be another one than process waters from the paper industry, but using softwood as raw material is still promising. The range of possible applications is broad: from plant growth regulators to health-promoting agents, such as prebiotic substances, and even pharmaceuticals. Emulsion stabilization in food and feed applications should also be considered as potential areas of use. In cosmetics and selected technical applications, a natural polysaccharide of modest molar mass could be used for emulsion stabilization or control of viscosity. Controlled polymerization and derivatization, as recently was demonstrated for hydrogels of AcGGMO's and PHEMA (Söderqvist-Lindblad et al., 2004) and for polysaccharide films (Hartman et al., 2006b) is a way to further broaden the applicability of AcGGM.

8. Conclusions

O-Acetylgalactoglucomannans (AcGGM) constitute the principal hemicellulose type in softwoods, the amount in stemwood normally being 10–25% (w/w). AcGGM has a main chain of $(1 \rightarrow 4)$-linked β-D-mannopyranosyl and $(1 \rightarrow 4)$-linked β-D-glucopyranosyl units, with α-D-galactopyranosyl units linked as single side units to mannosyl units in the main chain. Water-soluble Norway spruce AcGGM has a degree of acetylation of around 0.3 in the C-2 and C-3 positions of the mannosyl units. The amount of easily water-soluble AcGGM is only a small portion of the total amount found in wood. The water-solubility is greatly influenced by the amount of bulky substituents, i.e. acetyl groups, which hinder the formation of intra- and intermolecular hydrogen bonds between the polysaccharide chains.

Norway spruce, which is widely used in mechanical pulping, is most interesting as a source of AcGGM. Different extraction and purification methods will influence the yield and structure of the recovered AcGGM. During isolation, structure-preserving methods are vital to maintain the acetyl groups and hence the water-solubility. An interesting large-scale method is the recovery by ultrafiltration of dissolved AcGGM from process waters in mechanical pulp mills using Norway spruce as raw material.

Specific GGM-acting enzymes are useful in targeted modifications of AcGGM, as well as in structure elucidation or structure–function studies. AcGGM has promising biological activity and physico-chemical properties enabling various applications in, for example, food, health, papermaking, textile, and cosmetic industry.

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