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Functionality of spruce galactoglucomannans in oil-in-water emulsions

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ABSTRACT

For a sustainable food chain, the demand for plant-based, functional, and cost-effective food hydrocolloids is on a high-rise. Hemicelluloses from the renewable lignocellulosic biomass are available in abundance from side-streams of the forestry industry to fulfill this demand. Their effective valorization requires a safe, economic extraction method that can be up-scaled to an industrial scale and, simultaneously, understanding of their functionality to develop applications. In this study, an aqueous-based extraction method, pressurized hot water extraction (PHWE) of spruce saw meal was used to obtain galactoglucomannans (GGM), "spruce gum". Ethanol precipitation was performed to remove non-polysaccharide extractives such as free phenolic compounds, and the emulsion component ratio-dependent interfacial saturation capacity of the remaining purified fraction was studied to understand its functionality. GGM resulted in good to excellent emulsification and stabilization of oil-in-water emulsions and exhibited adsorption at the oil droplet interface, which depended on the amount of oil and droplet size of emulsions. The adsorbed GGM content was determined by gas chromatography after acid methanolysis, and their macromolecular characteristics were studied by size-exclusion chromatography. At GGM to oil ratios 2, 1, and 0.4, stable emulsions with predicted several months of shelf life at room temperature were achieved. The results indicated mechanisms affecting the physical stabilization and breakdown of emulsions containing spruce gum, a novel sustainable hydrocolloid.

1. Introduction

The market of food hydrocolloids is growing rapidly, and its value is expected to reach $7.56 billion by 2020 (MarketsandMarkets, 2016). As consumers are more conscious than ever about health and environment, the demand for innovation and "clean" food products has increased significantly. Hydrocolloids are integral ingredients in a wide range of processed food products and beverages and include polysaccharides from plants, seaweeds, microbes, plant exudates, and modified biopolymers from starch, and cellulose. Most are high-molar-mass hydrophilic biopolymers and are able to stabilize emulsions by modifying the rheological properties of continuous phase. Only a few of them (namely, gum arabic, some pectins, some galactomannans, modified starch, and modified cellulose) function as emulsifiers (Dickinson, 2003). For example, gum arabic is an established hydrocolloid emulsifier but an expensive ingredient, and replacements such as corn fiber gum, an arabinoxylan (hemicellulose)-rich product from corn milling, are being sought (Yadav, Johnston, Hotchkiss, & Hicks, 2007).

Under the framework of sustainable bioeconomy, a wood-based bioeconomy is envisioned to tackle major global challenges of depleting natural resources in various sectors. As paper consumption has declined over the past years, traditional mills are in the process of becoming biorefineries for the efficient valorization of all lignocellulosic components (Ministry of Economic Affairs and Employment, 2017). Spruce is an industrially important softwood variety for pulping and papermaking process, where cellulosic fibers are the main product, and hemicelluloses and lignin are usually burned for energy. Additionally, sawdust is available as a by-product from sawmills which is currently either burned or used in low-value products. About 25–35 wt% of softwood tissues consist of extractable non-cellulosic polysaccharides (hemicelluloses), mainly acetylated galactoglucomannans (GGM)

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(Willför, Sundberg, Tenkanen, & Holmbom, 2008). They have a linear backbone of β (1 → 4) linked D-Man*p* and β (1 → 4) linked D-Glc*p* substituted by the α-D-Gal*p* residues at the C-6 position, preferably at mannose units that are acetylated at C-2 or C-3 with a degree of substitution of 0.3. GGM with a molar mass ranging from 12,000 to 60,000 g/mol (Mikkonen et al., 2016; Mikkonen, Xu, Berton-Carabin, & Schroën, 2016) have been extracted with different methods; from process water during thermomechanical pulp treatment (Willför, Rehn, Sundberg, Sundberg, & Holmbom, 2003; Xu, Willför, Holmlund, & Holmbom, 2009), pressurized hot water extraction (PHWE) of sawdust (Kilpeläinen et al., 2014) and a pending patent from CH-Bioforce Oy (Von Schoultz, 2015). With an intermediate viscosity in aqueous solutions, and interfacial activity between to that of conventional, amphiphilic, small molecular surfactants and large macromolecular hydrocolloids, GGM is an interesting option that is yet to be commercially utilized.

The abundantly available GGM, or "spruce gum", can be valorized as novel, functional hydrocolloids in oil-in-water emulsions in pharmaceuticals, cosmetics, paints, and coatings, for example. In previous studies, GGM exhibited higher emulsification and stabilization capacity against both physical breakdown and lipid oxidation compared to the current gold standard polysaccharide hydrocolloid, gum arabic, and its suggested replacement, corn fiber gum (Lehtonen et al., 2016; Mikkonen, Merger et al., 2016; Mikkonen, Xu et al., 2016). In contrast to functionality of most polysaccharide-based emulsifiers that originates from the residual contaminants (e.g., protein fractions in gum arabic and galactomannans) (Dickinson, 2003), in earlier studies, the emulsification and stabilization abilities of GGM were strongly hypothesized as a mixed effect from inter- and intra-molecular polysaccharide assemblies inducing particle-type stabilization (Pickering effect) and the presence of co-extracted phenolic residues in GGM acting as hydrophobic anchor groups inducing steric stabilization. GGM obtained by PHWE method consist of 75 wt% polysaccharides, and the rest are other wood-derived compounds, primarily lignins and extractives (Kilpeläinen et al., 2014). Phenolic residues contribute to but are not alone responsible for the observed stability of GGM emulsions (Lehtonen et al., 2018) thus, the role of the polysaccharide-rich fraction of GGM on the stabilizing functionality remains unresolved.

Polysaccharides form a thick adsorbed layer generating good steric barriers against coalescence in emulsions due to their large molecular volume (Dickinson, 2017) compared to small molecular surfactants (Wilde, Mackie, Husband, Gunning, & Morris, 2004). However higher amounts of polysaccharides are required for the complete saturation of interfaces due to their lower surface activity (McClements, Bai, & Chung, 2017). This result in instability in emulsions from either bridging or depletion flocculation exhibited by different nature of association of droplets – open or closed flocs (McClements, 2007). The former is due to sharing of polysaccharide chains between droplets due to their incomplete saturation that can largely promote coalescence and the latter is due to a high concentration of unadsorbed polysaccharides in the continuous phase (Dickinson, 2003). Similarly, unadsorbed polysaccharides also re-stabilize emulsions if present in sufficiently high concentrations by conferring a very high apparent viscosity to the continuous phase and/or generating a reversible gel network. Recently, they have also been accounted for in their role in stabilization by forming interfacial barriers in the form of aggregates (Dickinson, 2017).

In this study, the PHWE extract of spruce was ethanol-precipitated to remove free phenolic compounds (those not bound with GGM) and other non-polysaccharide extractives. We aim to understand the emulsification and stabilization mechanisms of the polysaccharide-rich fraction of spruce extract through characterizing the optimal component ratios of GGM stabilized emulsions for desired interfacial saturation. The component ratios in emulsions were correlated with droplet size, interfacial area, surface load, emulsion stability, and breakdown mechanisms using chemical and physical methods. The emulsion stability is discussed in relation to the adsorption of GGM at the interface and to the macromolecular characteristics of distributed polysaccharides.

2. Materials and methods

2.1. Materials

GGM was extracted using the pressurized hot water extraction (PHWE) process on spruce sawdust (Kilpeläinen et al., 2014). The sawdust was obtained from a sawmill (Herralan Saha, Herrala, Finland). A 96.9 kg (43.5 kg dry weight) spruce sawdust was extracted at 170 °C for 70 min with a 20 kg/min flow rate. A total of 1050 kg of extract was collected. The extract was filtered by an ultrafiltration system (PCI-membranes) using tubular modified polyethersulfone membranes (EM006). Before ultrafiltration, the extract pH was adjusted to neutral with sodium hydroxide to increase permeate flow through the membrane. As pH lowered during the ultrafiltration, NaOH was added to keep the pH of the concentrate neutral for a stable permeate flow. In this way, concentrated GGM was obtained from PHWE extract.

Concentrated GGM was precipitated with ethanol (1/8 concentrate/ethanol v/v) by slowly adding concentrate to an ethanol phase that was mixed thoroughly. When all concentrate was added to the ethanol, the solution was mixed for 15 min and left to precipitate overnight. The ethanol was siphoned away and the precipitated polysaccharide slurry was transferred to a filter bag (Eaton NMO-25-P01R-50 S, Hyxo Oy, Finland) where excess ethanol was removed. The slurry was filtered through a Buchner funnel using a pore 2 cellulose filter (Whatman) followed by drying in a vacuum oven at 40 °C for 2 days. This purified sample consisted mainly of polysaccharides and is referred to as GGM in this study. A summary of the extraction and purification method is illustrated in Fig. 1.

Rapeseed oil was purchased from a supermarket and purified by adsorption chromatography according to the previously described method (Lampi, Dimberg, & Kamal-Eldin, 1999). The oil was stored at −18 °C for further use. The purification was performed to remove any possible surface-active species (e.g., tocopherols) in commercial rapeseed oil to obtain a clear insight into the functional role of polysaccharide entities alone in the dispersed systems.

2.2. Reagents

Citric acid monohydrate was from Sigma-Aldrich (St. Louis, MO, USA). Sodium azide and sodium nitrate were from Merck (Darmstadt, Germany). Sodium dodecyl sulfate (SDS) was obtained from VWR's BDH Chemicals (Belgium). All solvents used were HPLC grade. Heptane, methanol, and anhydrous methanol were from Sigma-Aldrich (St. Louis, MO, USA). Pyridine and Bis(trimethylsilyl) trifluoroacetamide (BSTFA) were from Merck (Darmstadt, Germany), and trimethylsilyl chloride (TMSCl) was from Fluka (St. Louis, MO, USA).

Monosaccharide standards D-xylose, D-glucose, D-galactose, D-mannose were from Merck (Darmstadt, Germany), D-galacturonic

Fig. 1. Schematic diagram of extraction and purification process of GGM.

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