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Polysaccharides from macroalgae: Recent advances, innovative technologies and challenges in extraction and purification

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ABSTRACT

Polysaccharides obtained from macroalgae have promising prospects and could contribute greatly to the future of a marine based bio-economy. Specifically, laminarin and fucoidan from brown macroalgae have a wide variety of potential industrial applications including functional foods and nutraceuticals, due to their broad range of biological activities. These beneficial biological activities are related to the chemical composition and structure of the macroalgal polysaccharides. The molecular weight, monosaccharide composition and sulphate content of these polysaccharides could be influenced by both macroalgal biology (i.e. variations in polysaccharide composition due to macroalgae species and their biological cycle) and different extraction/purification techniques employed to obtain polysaccharide enriched products (i.e. de-sulphation or fragmentation of sulphated polysaccharides). This review focuses on the extraction and purification methods for the macroalgal polysaccharides laminarin and fucoidan used in the recent literature. The application of innovative extraction technologies (such as ultrasound, microwave and enzyme-assisted extractions), as well as new purification techniques (i.e. membrane separation), are also discussed together with the challenges concerning molecule structure-function relationship and macroalgal variability.

1. Introduction

Macroalgae are a large and diverse group of marine and freshwater organisms with >10,000 different species described to date (Collins, Fitzgerald, Stanton, & Ross, 2016). Marine macroalgae are able to adapt to the changing and extreme marine environmental conditions i.e. salinity, temperature, nutrients, radiation and combination of light and oxygen concentration by producing unique secondary metabolites including polysaccharides (Collins et al., 2016; Rajauria, Jaiswal, Abu-Ghannam, & Gupta, 2010). These macroalgal polysaccharides, particularly fucoidan and laminarin, show a wide range of biological activities such as antiinflammatory, anticoagulant, antioxidant, antiviral, antitumour, antiapoptosis, antiproliferative and immunostimulatory in in vitro and/or in vivo model systems (Collins et al., 2016; Gupta & Abu-Ghannam, 2011; Kadam, Tiwari, & O'Donnell, 2015a; Roohinejad et al., 2016; Sweeney & O'Doherty, 2016; Wijesinghe & Jeon, 2012). A representation of the chemical structure of laminarin from *Laminaria digitata* proposed by Adamo et al. (2011) is presented in Fig. 1. Laminarin is described as 1,3-linked β-D-glucose residues with different degrees of branching at β-(1,6) that influences the water solubility of the molecules (Rioux, Turgeon, & Beaulieu, 2010). The structure is composed of (1,3)-β-D-glucopyranose residues consisting some 6-O-branching (in the main chain) and β-(1,6) (intrachain links) (Kadam et al., 2015a). The laminarin structure may vary in degree of branching, the degree of polymerization and the ratio of (1,3)- and (1,6)-glycosidic bonds. They are uncharged molecules at neutral pH which are stabilized by inter-chained hydrogen bonds, hence it has been proposed that they are not hydrolysed in the upper gastrointestinal tract and are classified as dietary fibres (O'Sullivan et al., 2010). However, dietary supplementation with laminarin increased the expression of glucose transporters in the ileum (Heim et al., 2014a), suggesting that some hydrolysis is taking place in the small intestine. Laminarins are energy reserve polysaccharides that are present in reserve vacuoles inside the macroalgal cell and may constitute up to 35% of the dried weight of the macroalgal biomass (Kadam et al., 2015a).

The chemical structure of fucoidan from *Laminaria saccharina* proposed by Cumashi et al. (2007) is shown in Fig. 1. Fucoidan or fucose-containing sulphated polysaccharides have a backbone of (1 → 3)-linked α-L-fucopyranosyl or alternating (1 → 3)- and (1 → 4)-linked α-L-fucopyranosyl residues and also include sulphated galactofucans with backbones built of (1 → 6)-β-D-galacto- and/or (1 → 2)-β-D-mannopyranosyl units with fucose or fuco-oligosaccharide branching, and/or glucuronic acid, xylose or glucose substitutions (Ale,

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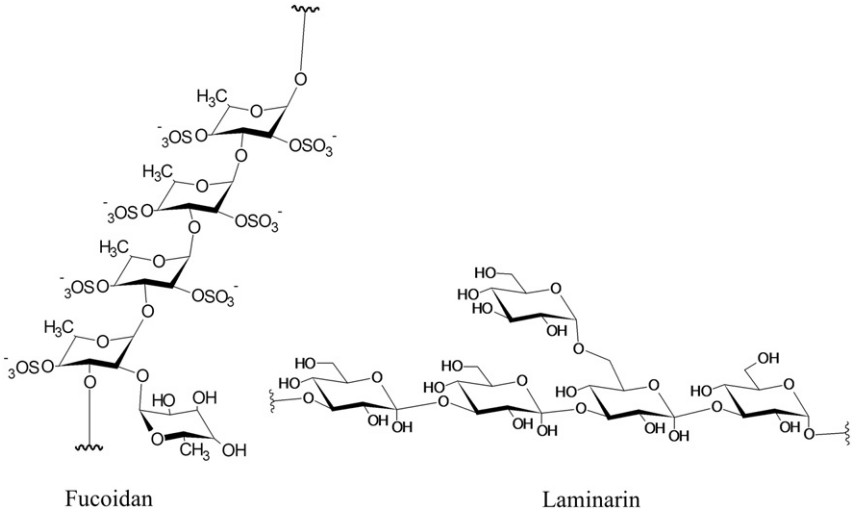

Fig. 1. Chemical structure of fucoidan from *Laminaria saccharina* and laminarin from *Laminaria digitata* proposed by Cumashi et al. (2007) and Adamo et al. (2011) respectively.

Mikkelsen, & Meyer, 2011b). The l-fucopyranose residues may be substituted with sulphate on C-2, C-4 and rarely on C-3 positions (Ale, Maruyama, Tamauchi, Mikkelsen, & Meyer, 2011a). Fucoidans are an integral part of the cell walls of brown macroalgae, playing a crucial role in the protection of the macroalgae against environmental challenges (Senthilkumar, Manivasagan, Venkatesan, & Kim, 2013).

There is a marked relationship between the chemical structure of both macroalgal polysaccharides (i.e. molecular weight, monosaccharide composition, sulphate content and position) and their biological activity. These differences could be attributed to factors such as macroalgal species, structural variation in the parts of the macroalgae sampled and differences in polysaccharide content and composition depending on the season (Kim, 2012; Men'shova et al., 2012; Skriptsova, Shevchenko, Tarbeeva, & Zvyagintseva, 2011). Furthermore, it was also observed that structural modifications to these molecules (i.e. molecular weight and degree of sulphation) can occur during the processes of extraction and purification; for instance, the use of different extraction solvents and experimental conditions (such as pH, time, temperature and pressure) (Ale et al., 2011a; Foley, Szegezdi, Mulloy, Samali, & Tuohy, 2011; Hahn, Lang, Ulber, & Muffler, 2012; Lorbeer, Lahnstein, Bulone, Nguyen, & Zhang, 2015).

Therefore, for the extraction and purification of different fractions of laminarin and fucoidan, details of the macroalgal biomass used as well as the methodology followed are extremely important in order to achieve the bio-activities required, as well as complying with good manufacturing practices. The lack of standardized extraction methodologies has prevented the official approval of polysaccharides or their derived fractions for pharmaceutical, dermatological, nutraceutical or other commercial applications to date (Ale & Meyer, 2013).

Thus, the present review focuses on the extraction and purification techniques of laminarin and fucoidan from macroalgae described in the recent literature. New processes, technologies and optimized extraction and purification procedures are reported together with the challenges concerning molecule structure-function relationship and macroalgal variability.

2. Extraction of polysaccharides from macroalgae

The process of extraction of macroalgal polysaccharides could include several steps summarized in Fig. 2. These extraction steps include preparation of the macroalgal biomass, pre-treatment of the macroalgae, extraction techniques (traditional solvent extraction versus the current innovative technologies including ultrasound, microwave and enzyme-assisted extractions) and purification techniques to obtain the polysaccharides of interest and then proceed to test its biological activity and potential industrial uses.

2.1. Preparation of macroalgal biomass

The procedure for the extraction of polysaccharides from macroalgae involves cleaning of the macroalgae with either sea water or distilled water to remove sand and epiphytes followed by drying (oven-drying or freeze-drying). The dried biomass is then milled to obtain the highest surface-to-volume ratio during the latter extraction procedures (Hahn et al., 2012; Imbs, Ermakova, Malyarenko, Isakov, & Zvyagintseva, 2016).

As an alternative to drying processes, Hjelland, Andersen, and Yang (2012) patented the exudate method which obtains laminarin and fucoidan at commercial amounts from live macroalgal tissue. Using this technique, the fresh macroalgae is cut in pieces of ≥1 cm and pilled in a dark-humid place to obtain the exudate from the live macroalgae tissue. After this step, the polysaccharides laminarin and fucoidan, could be extracted and purified from the exudates obtained.

2.2. Pre-treatment of macroalgae

Different pre-treatments applied to the dried biomass, together with the detailed description of the extraction techniques described in the recent literature are presented in Table 1. The most commonly performed pre-treatments in the literature were washing of the dried biomass with a mixture of methanol, chloroform and water (4:2:1; *v*/v/v) (Ale, Mikkelsen, & Meyer, 2011c; Lim et al., 2014), or with acetone alone (Dore et al., 2013). More recently, a number of alternatives at different temperatures have been explored including: a mixture of acetone and ethanol (Shan et al., 2016); a single ethanolic pre-treatment; or several ethanolic pre-treatments (Imbs et al., 2016; Yuan & Macquarrie, 2015). These alcohol treatments were applied to remove lipids (defatted), proteins (deproteinated) and phenols (dephenolated), but also mannitol and chlorophyll, compounds that are highly bound to the polysaccharides, contaminating the target compounds (Hahn et al., 2012). Other novel pre-treatments recently described in the literature include the compressional-puffing-hydrothermal process which consists of heating at atmospheric pressure (140 °C, 180 °C and 220 °C), followed by a rapid reduction of pressure in a vessel containing superheated water, which allows the modification of the cellular structure of the macroalgae prior to extraction of fucoidan (Huang et al., 2016).