

REVIEW PAPER

PREBIOTIC XYLOOLIGOSACCHARIDES FROM LIGNOCELLULOSIC MATERIALS: PRODUCTION, PURIFICATION AND APPLICATIONS – AN OVERVIEW

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This paper is a state-of-the-art review and a consolidated source of information regarding the prebiotic potential of xylooligosaccharides (XOS) derived from lignocellulosic materials (LCM) as bioactive molecules with high-added value for human health. XOS can be obtained by hydrothermal pretreatment (or autohydrolysis), a primary technological step in biological conversion of LCM into value-added products. Purification of XOS is a complex process which aims to remove unwanted compounds and to achieve the necessary degree of polymerization. Proven benefits and positive effects on the human health are mainly in the intestinal microbiota, where food-grade XOS stimulate the growth and proliferation of probiotic bacteria. The main objective of this study was to provide an in-depth overview of the recent published investigations reported in the scientific literature on the production of XOS from xylan-containing LCM by hydrothermal pretreatment, purification of hydrothermally produced XOS and, furthermore, evaluation of the bioactive properties of purified XOS.

Keywords: xylooligosaccharides, lignocellulosic materials, hydrothermal pretreatment, prebiotic, purification, bioactive properties, health beneficial effects

Xylooligosaccharides (XOS) production from xylan-containing lignocellulosic materials (LCM) by hydrothermal pretreatment

Lignocellulosic biomass is the most abundant organic material in nature with an estimated annual worldwide production of 10–50 billion dry tons (Zhao *et al.*, 2009), including agricultural residues (such as: corn stover, crop straws, sugar cane bagasse), forestry residues from the forest thinning, herbaceous energy crops (such as alfalfa, switchgrass), woody plants (hardwoods and softwoods), waste from the pulp and paper production, and municipal solid wastes (Huang *et al.*, 2008; Sluiter *et al.*, 2010). Biomass residues can be divided into two categories: (i) crop residues (plant residues that remain on the field after the collection of crops) and (ii) agro-industrial residues (by-products of the post-harvest processes) (Lim *et al.*, 2012). LCM are made up of three major components: between 15% and 30%

hemicellulose (an amorphous, branched polymer that is composed of several sugars, such as arabinose, galactose, glucose, mannose and xylose); between 35% and 50% cellulose (a linear polymer of glucose molecules linked together in a highly crystalline structure) and between 15% and 30% lignin (a complex phenyl-propane polymer) (Wyman & Yang, 2009).

A primary technological challenge in biological conversion of LCM into value-added products refers to hydrothermal pretreatment (Laser *et al.*, 2002; Saha *et al.*, 2013), also known as autohydrolysis (Lee *et al.*, 2009; Tunc & van Heiningen, 2011; Egüés *et al.*, 2012a; Xiao *et al.*, 2013a), hydrothermolysis (Dogaris *et al.*, 2009), hot compressed water treatment (Hashaikeh *et al.*, 2007; Goh *et al.*, 2012), hot water extraction (Hamzeh *et al.*, 2013; Borrega *et al.*, 2013), or liquid hot water pretreatment (Díaz *et al.*, 2010; Díaz *et al.*, 2011; Wan *et al.*, 2011).

Hydrothermal pretreatment represents a simple, low-cost and environmental friendly technology, which causes hemicellulose depolymerization (mainly converted into soluble oligomers as a main reaction products) and lignin transformation due to the high temperature profile (Lee *et al.*, 2010).

The pretreatment technology is a necessary step to remove lignin and hemicelluloses, to reduce cellulose crystallinity and to increase the porosity of the LCM. There are several key factors to take into consideration for an optimum pretreatment (Sun & Cheng, 2002; Alvira *et al.*, 2010; Sarkar *et al.*, 2012; Singh *et al.*, 2014) such as: (i) improve the formation of sugars or the ability to subsequently form sugars by hydrolysis; (ii) avoid loss or degradation of formed sugars; (iii) avoid minimum amount of toxic compounds; (iv) non-production of solid-waste residues; (v) obtaining high sugars concentration; (vi) lignin recovery; and (vii) cost effective requirements. From an economic point of view, the pretreatment step must improve the separation among cell wall components while avoiding the formation of inhibitory compounds (Soccol *et al.*, 2010).

Autohydrolysis is carried out with hot, compressed water, leading to a liquid phase rich in hemicelluloses-derived sugars, sugar decomposition products (furfural and hydroxymethylfurfural) and acetic acid (generated from acetyl groups) (Amendola *et al.*, 2012).

According to an overview of García *et al.* (2014), autohydrolysis pretreatment resulted in different yields mass fraction for hemicelluloses-derived sugars, such as 29.7% in the case of eucalyptus bark, 32.6% for cotton stalks, and 53.9% for apple tree pruning, for the same operation conditions (30 min and 180 °C). Based on the results of Amendola *et al.* (2012), autohydrolysis of grape stalks at 180 °C for 30 min, without additional chemical catalysts, resulted in separation of a high portion of the hemicelluloses, partly as free reducing sugars (about 50% of the total solids of liquor) and partly as oligomers. Moreover, Sukhbaatar *et al.* (2014) found that the optimum condition for the extraction of sugarcane bagasse hemicelluloses with highest xylose content, lowest degradation products and dissolved lignin was also reached at 180 °C for 30 min. Ruiz *et al.* (2013a) reported that xylose was the most abundant sugar in the extracted hemicellulose from wheat straw after the autohydrolysis pretreatment at 180 °C for 30 min, indicating the presence of xylan

as the main polysaccharide. On the other hand, Ligeró *et al.* (2011a) showed that the maximum recovery of xylan (62% of initial xylan content) was obtained after the hydrothermal process of *Ulex europæus* at 180 °C for 30 min. In addition to xylose, xylan may contain other pentoses (such as arabinose) and uronic acids (such as glucuronic acid and galacturonic acid) (Agbor *et al.*, 2011).

The xylan composition from hardwood plants differs from that in softwood plants (Van Dyk & Pletschke, 2012; Peng *et al.*, 2012; Ebringerová, 2006): Xylan, a polymer with backbone chains of β -xylopyranose units linked β -(1 \rightarrow 4), extracted from hardwoods (such as beechwood, willow and poplar), occurs as O-acetyl-4-O-methylglucuronoxylan, having a higher acetyl composition than glucuronoxylan from different hardwoods such as *Eucalyptus globulus*, *Eucalyptus urograndis* and *Betula pendula* (Pinto *et al.*, 2005). In xyans of this type of woods, the hydroxyl groups may be substituted by 4-O-methylglucuronic groups linked α -(1 \rightarrow 2) and acetyl groups attached through ester bonds at positions 2 and 3 of the pentose ring. Glucomannans from hardwoods are linear polymers of glucose and mannose (predominantly) linked β -(1 \rightarrow 4) and do not present side branch or substituent groups. The xylan backbone from softwoods (such as spruce, pine, Douglas fir) is identical to that from hardwoods xylan, with 4-O-methylglucuronic groups linked α -(1 \rightarrow 3). Glucomannans from softwoods (namely galactomannans), with a higher mannan composition (as galactoglucomannan), have two types of substituents: O-acetyl groups attached by ester linkages at positions 2 and 3 of the sugar and galactose bounds linked α -(1 \rightarrow 6) (Figure 1).

The mechanism for the hydrolysis of xylan can be described as follows (Liu, 2010; Liu *et al.*, 2012): (i) hydrogen ions from the bulk liquor migrate to the surface of the solid particle; (ii) small strong hydrogen bond-forming molecules occurs on the solid surface; (iii) protons and xylan react at the surface; (iv) dissoluble xylooligomers cleaves; and (v) dissolved xylooligomers diffuses to the bulk liquor. Bose *et al.* (2009) performed an investigation regarding the wide range of reported values for the xylan content of sugar maple, obtaining an average xylan content of 18.7%. Furthermore, results having xylo-oligomers in solution indicated that secondary hydrolysis at 80 °C (with a H₂SO₄ concentration of 40 wt%) generated high monomer concentrations (Bose *et al.*, 2009). The acidic groups linked to the hemicelluloses (mainly acetic acid) participate in the process of xylan polymerization (the conversion of xylan into high and low-molecular weight XOS as the major reaction products) (Ruiz *et al.*, 2013a). Mittal *et al.* (2009) investigated the formation and degradation of XOS in the wood pores of sugar maple and aspen chips and observed that XOS are formed due to xylan solubilization and further degraded via hydrolysis to xylose. In fact, results showed that the maximum yield of xylooligomers and xylose after sugar maple autohydrolysis varied from 51% at 152 °C after 4.5 hours to 73% at 160 °C after 3 hours.

Depending on the xylan sources used for XOS production, the structures of XOS vary in degree of polymerization (DP), monomeric units and types of linkages (Aachary & Prapulla, 2011). Several studies reported that xylan depolymerisation depended also on the severity of the autohydrolysis pretreatment.

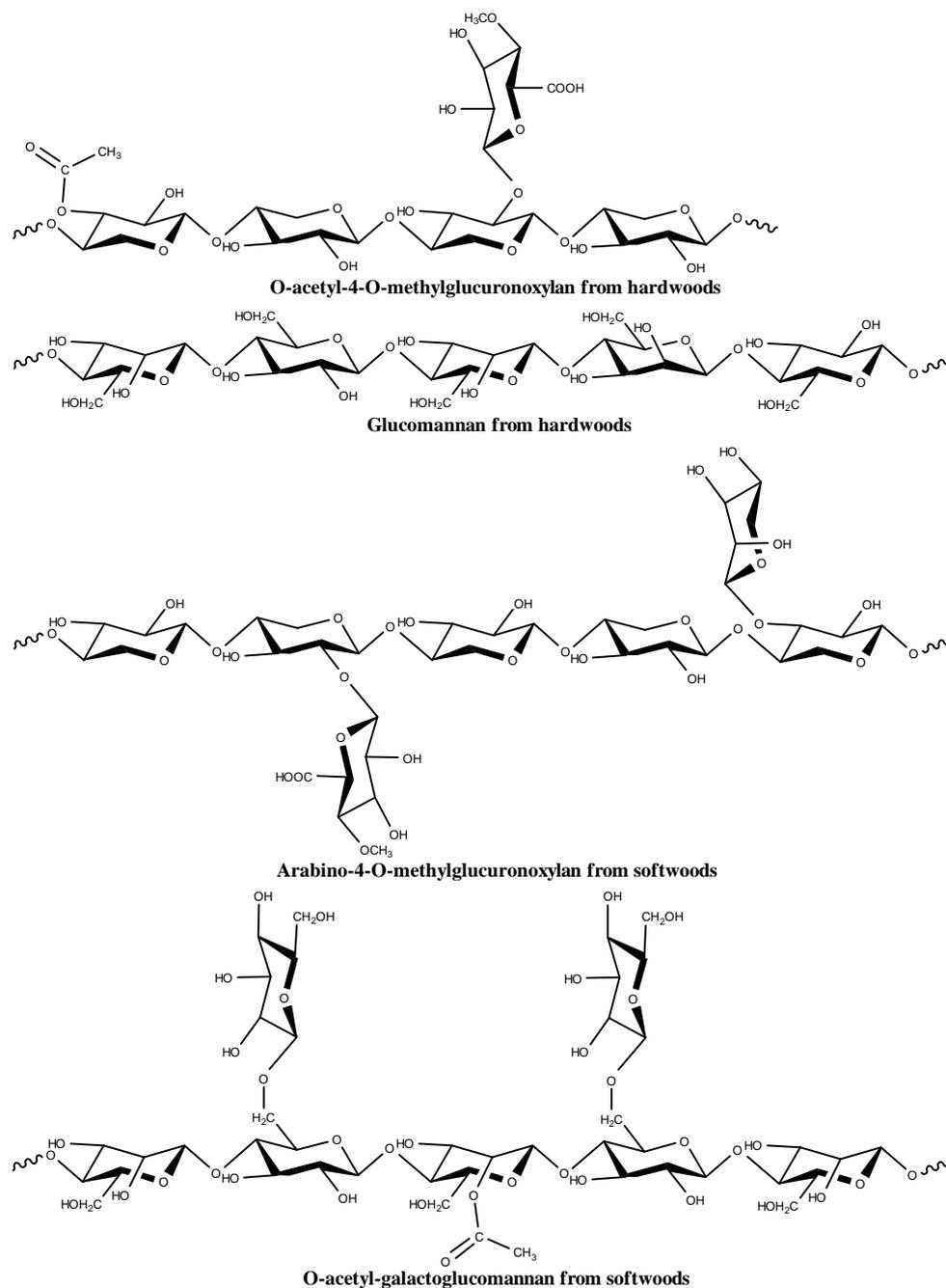


Figure 1. Structure of xylans and glucomannans from hardwoods and softwoods
(adapted after: Vázquez et al., 2000; Ebringerová, 2006)

Phaiboonsilpa *et al.* (2013) found that xylose (X1 with DP = 1) and XOS, such as xylobiose (X2 with DP = 2), xylotriose (X3 with DP = 3), xylotetraose (X4 with DP = 4) and xypentaose (X5 with DP = 5), containing two to five xylose

molecules linked by β -(1 \rightarrow 4) bonds (Carvalho *et al.*, 2013) (Figure 2), were obtained in the first stage of hot compressed water treatment of rice husk at 230 °C for 15 min.

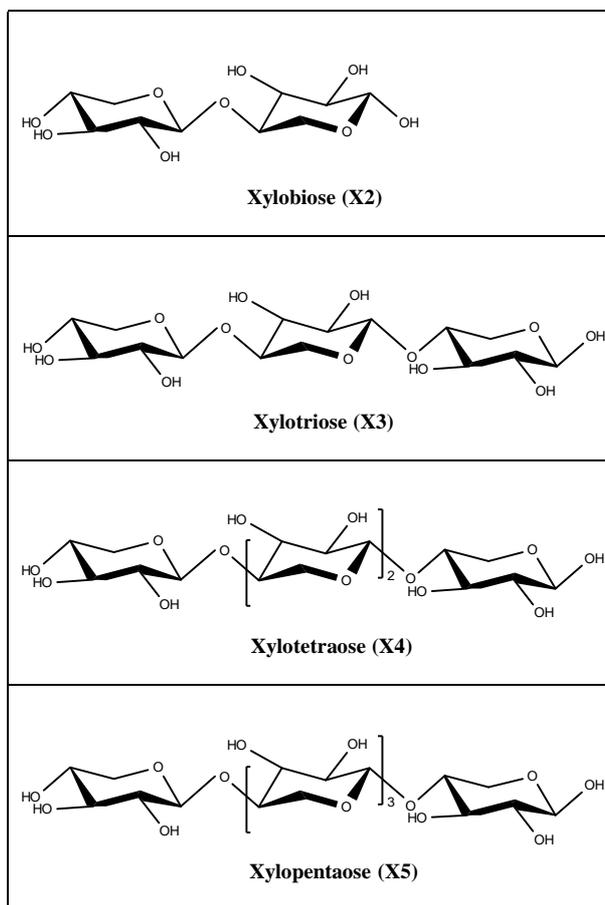


Figure 2. Structure of xylooligosaccharides (XOS) from lignocellulosic materials
(adapted after: Carvalho *et al.*, 2013)

According to Nabarlitz *et al.* (2007a), XOS isolated from autohydrolysed almond shells comprise a mixture of partially O-acetylated neutral and acidic oligomers derived from the 4-O-methylglucuronoxylan polymers. A comparative assessment showed that the characteristics of the raw material determined the yield and composition of the XOS. In fact, after autohydrolysis of different lignocellulosic residues at 179 °C for 23 min, Nabarlitz *et al.* (2007b) found that the most suitable substrate for XOS preparation was almond shells, with an elevated yield of 55% of the initial xylan content. Furthermore, Nabarlitz *et al.* (2005) studied the production of XOS from almond shells by autohydrolysis at temperatures ranging from 150 °C to 190 °C and reported different yields varying from 42% at 150 °C for 300 min to 63% at 190 °C for 19 min. According to Moniz *et al.* (2013), high

recovery of XOS (53% of the initial xylan content) from autohydrolyzed corn straw could be obtained at 215 °C. Moreover, Borrega *et al.* (2011) suggested that the maximum amount of XOS formed after autohydrolysis of birch wood at temperatures between 180 °C and 240 °C was about 15% of the dry wood mass (corresponding to a conversion of 70% of the initial xylan). Xiao *et al.* (2013b) reported that the maximum XOS yield of 47.49% was achieved at 180 °C for 30 min, after the autohydrolysis of bamboo culm. On the other hand, Chen *et al.* (2014) showed that the maximum XOS yield of 13.5% of the initial dry biomass (with a maximum conversion of 69.2% of the initial xylan content) was observed after the autohydrolysis of *Miscanthus x giganteus* at 200 °C for 5 min. In addition, Ligeró *et al.* (2011b) reported that the autohydrolysis of *Miscanthus x giganteus* at 160 °C for 60 min could be a suitable method for obtaining high yields of XOS (about 65% of the initial xylose).

Purification of hydrothermally produced xylooligosaccharides

According to Aachary & Prapulla (2011), the autohydrolysis liquors must be refined by removing mono-saccharides and non-saccharide compounds in order to obtain the highest possible XOS content or to achieve the necessary degree of polymerization. Aachary & Prapulla (2011) also reported that the usual purity of commercial XOS can vary in the range of 75% to 95%. According to Peng *et al.* (2012), a variety of purification procedures have been proposed to prepare hemicelluloses of desired purity from plant cell walls, such as: (i) ethanol precipitation (Peng *et al.*, 2013; Shi *et al.*, 2013); (ii) ammonium sulfate precipitation; (iii) iodine-complex precipitation; (iv) supercritical anti-solvent precipitation; (v) column chromatography, including size-exclusion chromatography (SEC) (Jacobs *et al.*, 2003; Nacos *et al.*, 2006) and anion-exchange chromatography (AEC); and (vi) membrane fractionation technologies, including: microfiltration (MF), diafiltration (DF) (Patil *et al.*, 2014), ultrafiltration (UF) (Iwasaki & Matsubara, 2000), nanofiltration (NF) (Goulas *et al.*, 2002) and reverse osmosis (RO). Furthermore, Cara *et al.* (2012) reported that olive tree pruning hydrolysate was subjected to purification by preparative gel filtration chromatography (GFC) in order to produce oligosaccharides (mostly XOS) with a different degree of polymerisation. In a recent research by Xie *et al.* (2014), ultrafiltration was compared with the ethanol precipitation and gel filtration chromatography techniques for the separation of polysaccharides from *Cyclocarya paliurus* (sweet tea tree) and results showed that ultrafiltration was a separation process with more advantages than other techniques, including: (i) high-efficiency; (ii) low cost; (iii) energy saving; and (iv) environmental friendly.

Purification of saccharides by ultrafiltration and nanofiltration can be accomplished by use of organic and ceramic membranes (Pinelo *et al.*, 2009). Akpınar *et al.* (2010) reported that the fractionation of XOS (obtained from tobacco stalk xylan) within a given degree of polymerization range can be easily carried out by using ultrafiltration with membranes of different molecular weight cut off in order to remove oligosaccharides. In fact, results showed that membrane separation successfully removed the high molecular weight polysaccharides. Because

hemicelluloses extracted from corn residues are mainly composed of hemicellulosic sugars (such as xylan and arabinoxylan-type polysaccharides), Egüés *et al.* (2012b) found that it was possible to improve the physicochemical characteristics of brute autohydrolysis liquor (resulting from the corn waste hydrolysis treatment) by ultrafiltration technology with ceramic membrane. Furthermore, Arkell *et al.* (2013) also confirmed that hemicelluloses extracted from wheat bran can be concentrated and purified by ultrafiltration with ceramic membrane. Nabarlantz *et al.* (2007c) reported that ultrafiltration using commercial thin-film polymeric membranes is a suitable process for the purification of XOS solutions produced by autohydrolysis of almond shells. Wan *et al.* (2012) showed that ultrafiltration removed the minerals and monosaccharides from extracted soluble rice bran fiber, which resulted in higher viscosity and soluble solids content.

In order to obtain food grade XOS with a high degree of polymerization, Makishima *et al.* (2009) and Sato *et al.* (2010) applied several purification processes for hydrothermal water soluble fraction of corncob and waste medium after mushroom cultivation, respectively, as follows: (i) ultrafiltration with membranes for decolorization; (ii) nanofiltration with membranes for elimination of monosaccharide and concentration of XOS; (iii) activated carbon treatment for second decolorization; (iv) ion exchange demineralization and second activated carbon treatment; and (v) vacuum evaporation for concentration. On the other hand, Nabarlantz *et al.* (2005) showed that XOS were recovered from the hydrolysis liquor of almond shells by spray drying, accounting for 60% of the recovered non-volatile compounds.

The literature also mentions some of the purification methods based on adsorption techniques using various adsorbents, such as: activated carbon, bentonite, aluminium hydroxide or oxide, titanium, silica and porous synthetic materials (Qing *et al.*, 2013). One of these adsorption processes has been described by Chen *et al.* (2014), where activated carbon was used for recovering XOS from *Miscanthus x giganteus*, followed by ethanol elution. In fact, results showed that using a 10% activated carbon with ethanol/water elution recovered 47.9% of XOS from pretreated liquid phase.

According to Otieno & Ahring (2012), the purity levels of XOS can be obtained also through further purification processes of the pretreated liquor containing xylose, such as: centrifugation, filter filtration, membrane filtration, decoloration, and spray drying. Furthermore, the purification of different compounds in liquid media depends on their solubility, molecular weight and the type of intermolecular bonding (Otieno & Ahring, 2012). According to Liu *et al.* (2012), several methods for low molecular weight liquid constituents separation could be employed, such as: (i) distillation; (ii) chemical separation; (iii) centrifugation; (iv) pervaporation; and (v) filtration. On the other hand, Pinelo *et al.* (2009) investigated the applicability of novel separation techniques in relation to high-performance separation of oligosaccharides such as: (i) membrane bioreactors; (ii) vibrating membrane module; (iii) electro-ultrafiltration; and (iv) backflushing (or backshocking).

Evaluation of the bioactive properties of purified xylooligosaccharides

Bioactive properties of XOS can be described as: (i) prebiotic effect (also known as bifidogenic effect); (ii) anti-inflammatory activity; and (iii) antioxidant activity (Moniz *et al.*, 2013). XOS are bioactive molecules with high-added value and great prebiotic potential as ingredients for functional foods (Ruiz *et al.*, 2013b).

Prebiotic XOS can be defined as “a non-digestible food ingredient that beneficially affects the host by selectively stimulating the growth and/or activity of one or a limited number of bacteria in the colon” (Manisseri & Gudipati, 2010).

Functional foods can be defined as “natural or processed foods that contain known or unknown biologically-active compounds which provide health benefit for the prevention and treatment of chronic disease” (Qiang *et al.*, 2009).

XOS have potential applications in many fields, including: (i) agricultural applications: to stimulate and accelerate growth; (ii) animal feed formulations; (iii) pharmaceutical: to prevent gastrointestinal diseases, and also for different treatments (such as osteoporosis, otitis, hair and skin problems); and (iv) human consumption: as ingredients for functional foods, special foods (in diets against obesity) and synbiotic foods (containing microorganisms with positive effects on health) (Li *et al.*, 2003).

XOS are considered prebiotics when they selectively promote the growth of probiotics such as *Bifidobacteria* and *Lactobacilli* spp. According to Manisseri & Gudipati (2010), the growth characteristic pattern (such as decrease in pH and increase in cell mass) showed that *Bifidobacterium adolescentis* NDRI 236 and *Lactobacillus plantarum* NDRI strain 184 were able to efficiently utilize the XOS liberated from wheat bran soluble polysaccharides. Falck *et al.* (2013) reported that the XOS hydrolysates from hardwood (birch) and cereal (rye) xylans were successfully fermented by *Lactobacillus brevis* DSMZ 1264 and *Bifidobacterium adolescentis* ATCC 15703. Furthermore, Moura *et al.* (2007) showed that XOS of low molecular weight from corn cobs autohydrolysis exhibited a potential bifidogenic capability (similar to commercial XOS) as carbon and energy source in order to promote the growth of *Bifidobacterium adolescentis*.

The main advantages of XOS as functional ingredients for human health are as follows (Nabarlatz *et al.*, 2004; Mussatto & Mancilha, 2007; Carvalho *et al.*, 2013): (i) modulation of the colon microbiota (can be used as a source of soluble dietary fiber because are not metabolized by the human digestive system); (ii) a protective effect against infections in the gastrointestinal tract (inhibition of gastrointestinal pathogenic bacteria and growth of health-promoting bacteria in the intestinal tract); (iii) a decrease of pH in the colon; (iv) nutrient production; (v) an increase in absorption of different minerals; (vi) a benefic effect on the carbohydrates and lipids metabolism; and (vii) biological effects (such as immunological, anti-oxidant, anti-inflammatory and antiallergic activity).

Furthermore, XOS are important in decreasing the blood lipids, protecting liver functions, decreasing blood pressure and regulating blood sugar (Adsul *et al.*, 2009). Chung *et al.* (2007) indicated that commercial XOS supplementation at 4 g per day for 3 weeks did not adversely influence gastrointestinal symptoms,

hematologic and biochemical parameters, and nutrient intakes in elderly subjects. XOS can also be used as antioxidants against oxidative stress, anemia, arteriosclerosis, atherosclerosis, type II diabetes, osteoporosis and certain types of cancers (Deutschmann & Dekker, 2012).

Conclusions

This study has attempted to provide a comprehensive overview on the production, purification and applications of XOS derived from LCM. XOS are bioactive molecules with high-added value and great prebiotic potential as ingredients for functional foods. XOS are considered prebiotics when they selectively promote the growth of probiotics in the colon. XOS production from xylan-containing LCM by autohydrolysis pretreatment, having prebiotic potential for human health, offers an exciting opportunity for future applications. These high value-added products are becoming important in different commercial sectors such as food, pharmaceutical, and chemical industries. Future perspectives regarding the use of XOS as ingredients for functional foods based on their health benefits remains a challenge.

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