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Review

Functional properties, structural studies and chemo-enzymatic synthesis of oligosaccharides



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ABSTRACT

Oligosaccharides offer beneficial effects on immune system and gut health, such as anticancer activity, immunomodulatory activity, and complement activation. Functional oligosaccharides are widely found in plants, algae, bacteria and higher fungi. Milk oligosaccharides, especially human milk oligosaccharides, have considerable health benefits, such as the growth-promotion of the beneficial bacterial flora in the intestines, and developing resistance to bactertial and viral infections. Recent developments in high performance liquid chromatography, mass spectrometry, nuclear magnetic resonance and capillary electrophoresis techniques contribute to the analysis of the oligosaccharide identification and mixture quantification. Synthesis of oligosaccharides is becoming increasingly important to pharmaceutical industries, in which chemo-enzymatic synthesis is considered as an effective method. This article gives a brief summary of structures, accessible sources, physiological and chemical characteristics, and potential health benefits of functional oligosaccharides.

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1. Introduction

Personal health has become an ever-increasing important issue for consumers. Identification and characterization of functional food components have advanced nutrition science. Non-digestible dietary fibers and functional oligosaccharides are functional carbohydrates with various benefits (Bland, Keshavarz, & Bucke, 2004). According to the IUPAC-IUBMB Joint Commission on Biochemical Nomenclature, naturally occurring carbohydrates that consist of 3–10 monosaccharide units, linear or branched, connected by α - and/or β -glycosidic linkages, are defined as oligosaccharides (or glycans). However, the physiological or rational chemical reasons for setting these limits remains unclear. Carbohydrates, whose monosaccharide units are fructose, galactose, glucose and/or xylose, are recognized as the main classes of functional oligosaccharides available at present or under development (Mussatto & Mancilha, 2007) (Fig. 1). These molecules are well-

* Corresponding author. E-mail address: jianboxiao@yahoo.com (J. Xiao). known as prebiotics, because they promote the growth of beneficial bacteria, particularly *Bifidobacteria* species. These functional oligosaccharides have shown advantageous physicochemical and physiological properties that contribute to the improvement of consumer health. Thus, application of oligosaccharides as ingredients in functional foods has great potential for improving the quality of foods in relation to consumers' health.

2. Health benefit of functional oligosaccharides

Functional oligosaccharides have been applied for many purposes, such as nutrients, pharmaceuticals, feeds, cosmetics, immunostimulating agents and prebiotic compounds (Patel & Goyal, 2011; Sako, Matsumoto, & Tanaka, 1999), which incorporate 13 classes of commercially produced non-digestible oligosaccharides showing bifidogenic functions. In addition, known functional oligosaccharides also include arabino-oligosaccharides, arabinogalacto-oligosaccharides, arabinoxylo-oligosaccharides, galacturono-oligosaccharides, rhamnogalacturonoligosaccharides, and human milk oligosaccharides (HMOs) (Table 1). In particular,

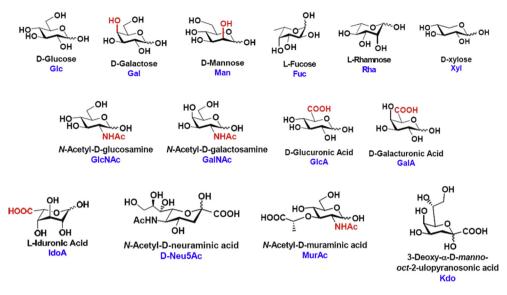


Fig. 1. Common monosaccharides components of the functional oligosaccharides.

Table 1
Natural functional oligosaccharides and their glycosidic linkages.

Туре	Monosaccharides	Number of monosaccharides	Bonds indicative of functions
Arabino-oligosaccharides	Arabinose	2-8	α-1,5
Arabinogalacto-oligosaccharides	Arabinose, galactose	2-9	β-1,4
Arabinoxylo-oligosaccharides	Xylose, arabinose	5-10	α-1,2, α-1,3, β-1,4
Clycosylsucrose	Glucose, fructose	3	α-1,2, β-1,4
Cyclodextrins (CDs)	D-glucopyranose	6 (α-CD),7 (β-CD),8 (γ-CD)	α-1,4
Fructo-oligosaccharides	Sucrose, fructose	2-5	β-1,2
Galacto-oligosaccharides	Galactose	2-5	β-1,2, α-1,4
Galacturono-oligosaccharides	Galactosamine	2-9	α-1,4
Gentio-oligosaccharides	Glucose	2-10	β-1,6
Glucose-oligosaccharides	Glucose	2-10	α-1,2, β-1,3, β-1,6
Human milk oligosaccharides	Glucose, galactose, GlcNAc	2-8	α-1,2, α-1,3, α-1,4, α-2,3, β-2,6, β-1,3, β-1,4
Isomalto-oligosaccharides	Glucose	2-5	α-1,4
Lactosucrose	Galactose, fructose	2-3	β-1,4
Lactulose	Galactose, fructose	2	β-1,4
Malto-oligosaccharides	Mannitose, glucose	2-10	α-1,2, α-1,4
Palatinose	Glucose, fructose	2	β-1,6
Raffinose	Galactose, fructose, glucose	3	β-1,2, α-1,4
Rhamnogalacturon-oligosaccharides	Rhamnose, galactose	4-8	α-1,2, α-1,4, β-1,4
Soybean oligosaccharides	Fructose, galactose, glucose	2-4	α-1,6
Stachyose	Galactose, fructose, glucose	4	α-1,4
Xylo-oligosaccharides	Xylose	2-7	α-1,4

cyclodextrins produced from starch through enzymatic conversion in nature is a family of macrocyclic oligosaccharides (Astray, Gonzalezbarreiro, Mejuto, Rial-Otero, & Simal-Gandara, 2009; Radu, Parteni, & Ochiuz, 2016). Cyclodextrins (α , β , and γ) are cyclic α -(1 \rightarrow 4)-glucans with degrees of polymerization of 6, 7, and 8 monosacharide units, respectively. Macrocyclic carbohydrates have been widely applied as building-blocks in supramolecular chemistry, drug carriers, molecular reactors, and artificial receptors (Muthana, Yu, Cao, Cheng, & Chen, 2009). The use of functional oligosaccharides improves the balance of the intestinal microflora and greatly decreases the gastrointestinal infections (Xu, Chao, & Wan, 2009). Additionally, the consumption of functional oligosaccharides can reduce the risk of lifestyle-related diseases, such as cardiovascular disease, cancer, obesity and type 2 diabetes, which are related to obesity (Mussatto & Mancilha, 2007) (Table 2). Thus, functional oligosaccharides are widely cited to be important dietary fibers in nutritional advice for metabolic syndromes induced specific disorders.

3. Sources of functional oligosaccharides

Plants and algae are the richest sources of functional oligosaccharides (Van Laere, Hartemink, Bosveld, Schols, & Voragen, 2000) (Table 2). Depolymerization of suitable raw materials or partial enzymatic hydrolysis of purified pectins can produce the pectic oligosaccharides (Gullón et al., 2013). Some typical feruloylated oligosaccharides could be prepared from plant sources, e.g., wheat, maize bran, sugarcane bagasse and rice (Qu & Sun, 2014). Particularly, marine oligosaccharides have attracted attention in drug development (Zhao, Wu, Yang, Liu, & Huang, 2015). Carrageenans, extracted from marine red algae, belong to an anion polymers family and share a common backbone of alternating $(1 \rightarrow 3)$ -linked β -D-galactopyranose and $(1 \rightarrow 4)$ -linked α -D-galactopyranose (Yao, Wu, Zhang, & Du, 2014). Carrageenans are well-known for their valuable biological activities, mainly attributed to the presence of sulphates (Kim & Rajapakse, 2005). Chitosan and its derivatives show potential in various fields such as food, cosmetics,

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