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Chemical characteristics, physical and functional properties of some β -bonded polysaccharides: A review

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Abstract

β -bonded polysaccharides are biopolymer substances used as functional ingredients that provide nutritional benefits and health implications. They are extracted from several sources which include higher plants, yeasts, fungi, etc. Applications of β -bonded polysaccharides cover a wide range of benefits, which include new sensorial properties, texture, less use of fat, and improvement to gut health. Incorporation of β -bonded polysaccharides in food formulations is set to grow worldwide and some of them are already used as food ingredients. In this article, we attempted to review recent studies on chemical characteristics, functional properties, and therapeutic values of different β -bonded polysaccharides. Some gaps in knowledge that require further research are also highlighted.

Keywords: Carbohydrates, β -bonding polysaccharides, gut health, prebiotics

Introduction

Polysaccharides are biopolymers occurring in the nature to perform various functions. They act as nature's energy reserves and form hydrated cross-linked three-dimensional network to give mechanical strength to plant tissues. Starch, glycogen and plant gums such as guar gum, gum Arabic and locust bean gum are some of the energy storage polysaccharides. There are several non-starch polysaccharides, which serve as principal components responsible for structure of the plant tissues. Cellulose is the most abundant cell wall polysaccharides, followed by hemicellulose and pectin^[100]. These polysaccharides are a non- α -glucan type that reach the human colon where they are indigestible by the human digestive tract enzymes. A variety of substances occurring in the nature including β -glucan, arabinoxylan, inulin, mannaans, gums etc. fall under the category of β -bonded polysaccharides. β -glucan comprises of linear chain of β -D-glucopyranosyl units that are linked by (1 \rightarrow 3) and (1 \rightarrow 4) linkages^[94]. Arabinoxylan is the next major component of the cell walls of wheat and rye and consists of a linear backbone of (1 \rightarrow 4)-linked β -D-xylopyranose units. The third most important example of β -bonded polysaccharides is inulin that consists primarily of β - (2 \rightarrow 1) fructosyl fructose units with a reducing end formed in an individual glucopyranose unit^[89]. There are other polysaccharides types of animal origin, namely chitin, chitosan and glycosaminoglycans. Chitin is apparently a linear polymer of *N*-acetyl-glucosamine units, which form covalent β -(1 \rightarrow 4)-linkages. According to reports, it is said to be a major component of the shells of crustaceans and some insects^[104]. Chitosan, which is made by treating the chitin shells of shrimp and other crustaceans with an alkaline substance, is linear polymer of β - (1 \rightarrow 4)-linked D-glucosamine and *N*-acetyl-D-glucosamine. Glycosaminoglycans are yet another type of long linear β -bonded polysaccharides consisting of repeating disaccharide units^[23]. These are, however, exempted from the current focus due to over details of their subject matter. Over the years, several efforts have been made to study different aspects of β -bonded polysaccharides occurring in plant and microbial sources. All these have led to the accumulation of considerable amount of knowledge on their chemical structure, functional properties, nutritional benefits, etc. As this information are largely scattered in the literature, it has become a necessity to compile them in an orderly manner. Hence, a systematic review of the available literature detailing out the influence of chemical characteristics on the functional properties of different β -bonded polysaccharides is of great value for further advancement of research and product applications.

β -glucan

Extraction sources

Cell walls of cereals (e.g. oat, barley), certain types of mushrooms (e.g. reishi, shiitake, Maitake), yeast, seaweed, and algae are the major sources of β -glucan^[1]. According to Maheswari *et al.*^[62], both oats and barley are found to contain significant amount of β -glucan [3-5% (w/w, dry basis)] when compared to other major cereals. However, groat of some oat (6-7%) and barley (12%) cultivars might have much more. A lesser amount of beta-glucan could be found in other grain types such as wheat, rye, sorghum, etc. After evaluating ten different yeast strains, Pengkumsri *et al.*^[76] concluded that β -glucan yield recovery from various yeast strains might vary from 3.11 to 3.78%. Apart from sources, method of extraction might also influence the yield of β -glucan. Recently, Maheswari *et al.*^[62] reviewed different β -glucan extraction methods employed for various grain sources mainly oats and barley. As per the analysis by this review, among the four classes of extraction methods namely aqueous, acidic, alkaline, and enzymatic, the recovery of β -glucan extracted were remarkably high only for aqueous and alkaline methods.

Chemical structure

Depending on the source of origin, the molecular weight (Mw) range of β -glucan might vary from ten to thousands of kilodaltons. Sources of origin, extraction protocol, including the solvents, reaction conditions, etc. are said to cause large variation in the Mw of β -glucan. The Mw differences might also affect the molecular conformations as for instance the β -

glucan with low Mw exhibits a random coiled conformation while those with high Mw exists either in single or triple helix conformations^[34]. Cereal based (1 \rightarrow 3) (1 \rightarrow 4)- β -D-glucans contain 70% (1 \rightarrow 4)-linked and 30% (1 \rightarrow 3) linked β -D-glucopyranosyl residues structured mainly in a sequence of β -(1 \rightarrow 3)-linked cellotriosyl and cellotetraosyl units (Figure 1). β -glucan of oats, barley, rye and wheat can be distinguished based on the differences in the ratios of major products of hydrolysis, 3-O- β -cellobiosyl-D-glucose and 3-O- β -cellotriosyl-D-glucose^[98]. Cereal-based β -glucan might display significant diversity in their structures, including the ratio of tri- to tetramers, the amount of longer cellulosic oligomers and the ratio of β -(1 \rightarrow 4): β -(1 \rightarrow 3) linkages^[51]. Mixed linkages (1 \rightarrow 3, 1 \rightarrow 4)- β -D-glucans are linear homopolymers of D-glucopyranosyl (GlcP) residues, which are linked mostly via two or three consecutive β -(1 \rightarrow 4) linkages that are separated by a single β -(1 \rightarrow 3) linkage (Figure 1)^[52]. Presently, there is hardly any proof for appearance of two or more adjacent β -(1 \rightarrow 3) linkages in the β -glucan chains^[27]. β -glucans extracted from oats, wheat, barley and rye are differentiated from lichenins through differences in the ratios of the major products of hydrolysis; 3-O- β -cellobiosyl-D-glucose and 3-O- β -cellotriosyl-D-glucose^[98]. A (1 \rightarrow 3), (1 \rightarrow 4)- β -glucan-4-glucanohydrolase also known as lichenase would hydrolase the linkage of 3-O-substituted glucose unit in the β -glucan. The products of the hydrolysis will be represented by the building blocks of native β -glucan^[40].

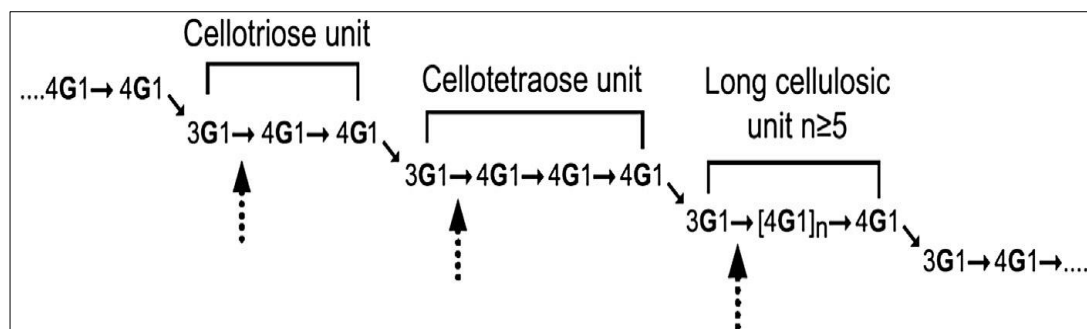


Fig 1: General molecular structure of β -glucan^[44]

Physical and functional properties

Multiple functionalities and uses of β -glucan are mainly due to the mixed linkage (1 \rightarrow 3) (1 \rightarrow 4) - β -D-glucan (β -glucan), which make it unique as a plant cell wall component and a source of dietary fiber^[98]. Based on the sources of origin and macromolecular structure, β -glucan is said to exhibit significant differences in their properties^[34]. The long chain of β -glucan is dominated by cellulose like β 1 \rightarrow 4 links, and interrupted every third or fourth glucose unit by a β 1 \rightarrow 3 linkage. This structural feature gives it a high-water binding capacity and ability to form high viscous solutions^[34]. The presence of multiple-OH groups is also attributed to β -glucan's strong affinity towards water molecules. Among various physical properties, gelation is an important property of β -glucan. Generally, β -glucan's gelation rates are varied with Mw as for instance, the β -glucan of oat with low Mw displayed high gelation rates and short gelation times when compared to its high-Mw counterparts. The β -glucan with low Mw exhibiting increased gelation rate is said to be due to less spatial hindrance^[61]. Some β -glucan were found to display antioxidant properties subject to Mw and source of origin. For

instance, β -glucan of yeast with low Mw had higher antioxidant property Lei *et al.*^[59] while β -glucan from *Chlorella pyrenoidosa* with higher Mw exhibited better immune-stimulatory activity Suárez *et al.*^[91].

β -glucans can also function as hydrocolloids, which could contribute to gelling and thickening behavior in food systems^[40]. Previous studies demonstrated that β -glucan samples with different Mw exhibited variations in their gelation rate. However, Doublier and Wood^[33] previously pointed out that the gel-forming properties of β -glucan with low Mw could also be influenced by the self-association via cellulose-like sequences. β -glucan has been used in different food formulations due to its water binding capacity and emulsion stabilizing properties to improve the textural and rheological properties^[57]. The poor stability of bread can be improved by adding β -glucan to the flour mixture to increase the resting period in making quality doughs. Besides this, in all types of dough, it can also stimulate an increase in water absorption^[87]. Generally, the high water absorbing capacity of β -glucan could suppress the amount of steam produced, resulting in the reduced loaf volume and greater crumb firmness^[38].

Table 1: Sources, technological properties and health effects of β -bonded polysaccharides

Polysaccharide type	Sources	Technological properties	Health and physiological effects	Reference
β -glucan	Cereals; mushrooms; yeast; seaweed; algae	Thickening and gelling behavior; High water absorption capacity	Remedial role in the etiology of colorectal cancer; Reduced serum cholesterol levels; Postprandial blood glucose control; Reduce high blood pressure	[6, 13, 18, 22, 32, 39, 40, 52, 54, 56, 58, 72, 86, 88, 99]
Inulin	Chicory; Jerusalem artichoke; wheat; bananas; asparagus; garlic; onion	Sugar replacer; Fat replacer; Texture modifier	Improved bowel habitats; Enhance the growth of bifidobacteria and lactobacilli and enhance the gut environment; In particulate form, possesses anti-cancer and immune enhancing properties	[9, 10, 12, 17, 20, 26, 29, 30, 37, 38, 43, 55, 57, 68, 69, 77, 85, 89, 95, 101]
Arabinoxylan	Millet; wheat; barley; oat; rice; rye; sorghum; maize	Shelf-life extension; Rheological properties of dough; Improvement of bread loaf volume; Retro-gradation of starch	Reduction of serum cholesterol; Promoting absorption of calcium and magnesium; Anti-HIV activity; Increased T and B cell proliferation; Immunomodulatory function	[35, 41, 44, 53, 66, 78, 90, 103]
Gum	Endosperm of plant seeds; plant exudates; seaweeds; microbes	Texture modifiers; Gelling agents; Thickeners; Emulsifiers; Stabilizers; Coating agents or packaging films	Reducing serum cholesterol level; Accelerating wound healing; Strengthening the immune system	[16, 31, 47, 65, 70, 75, 97]

Health impact

Several beneficial health influences of β -glucan have been compiled through various studies (Table 1). β -glucans can play a remedial role in prevention of colorectal cancer due to the effects of increasing caecal and colon mass owing to the increasing resistance of starch digestion. This might vary depending on the quantity of fermentable material reaching the cecum. The high amount of fermentable material in the caecum will lead to an increased production of short chain fatty acids [28]. β -glucan is also capable of flattening the postprandial blood glucose level and proven to reduce serum cholesterol levels [17, 97]. After studying the potential of oats to lower the cholesterol level, Anderson *et al.* [6-7] reported that oat bran-rich in β -glucan could reduce the total serum cholesterol in hypercholesterolemic subjects by about 23% with minimal changes in HDL cholesterol level [6-7]. According to another study by Keenan *et al.* [56], intake of whole grain cereals such as oats might lower the blood pressure.

The physiological effects of cereal-based β -glucan on type 2 diabetic subjects have been demonstrated through several previous studies. For instance, intake of both oat bran and cream of wheat plus oat gum meals significantly reduced the postprandial plasma glucose compared to the control diet of wheat [13]. Oat bran providing 7.3 g of β -glucan in a breakfast cereal was able to lower postprandial glucose in non-insulin-dependent diabetes mellitus (NIDDM) subjects than an oat bran breakfast cereal providing 3.7 g β -glucan [52]. According to another study by Murphy *et al.* [72], β -glucan is found to display immune-potential properties, but their connection to health benefit is not proven. Separately, Kahlon *et al.* [54] stated that β -glucan could assist in improving blood glucose regulation as well as serum cholesterol reduction in diabetic and hypercholesterolemic patients due to their solubility in water and capacity to make a highly viscous solution.

Inulin

Extraction source

Inulin is a mixture of linear fructose polymer with different chain length and a glucose molecule at each C2 end. It occurs in many plant species, which include chicory, Jerusalem artichoke, wheat, bananas, asparagus, garlic, onion, etc. Inulin occurs in high amounts in the roots and tubers of chicory (15-20%), Jerusalem artichoke (14-19%), dahlia (15-20%),

shatwaar (15-20%), salsify (15-20%), kuth (18-20%), garlic (9-16%) etc. [87]. Although root of chicory is the main source for commercial production of inulin [73], use of Jerusalem artichoke and dahlia has been widely investigated. The conventional process of inulin extraction involves high thermal agitation (70-80 °C) and prolonged extraction time (1-2 h). As large amounts of impurities are present in the juice extracted through the conventional process, further purification steps are required. As such, researchers looked into non-conventional technologies such as enzyme assisted extraction, ultrasound assisted extraction, microwave assisted extraction, supercritical fluid extraction, and pulsed electric fields as alternative environmental friendly methods [105]. Although these are said to be greener approaches when compared to the conventional method, their cost-effectiveness needs to be studied for their commercial viability.

Chemical structure

In nature, inulin occurs as a polysaccharide consisting of fructose units which are linked with β - (2, 1) -D-fructosyl-fructose bonds of varying chain lengths with a glucose molecule at the end of each fructose chain (Figure 2) [24]. Inulin extracted from plants are known to have chains of 2-100 or more fructose units. When compared to plant inulin, microbial inulin are found to have a larger degree of polymerization ranging from 10,000 to 100,000 [84]. Garlic fructan, on the other hand, has a (2, 1) -linked β -D fructosyl backbone with (2, 6) -linked β -D-fructosyl side chain [14]. Native Dahlia inulin has longer chain than Chicory inulin, while Jerusalem artichoke inulin is known to have a much shorter chain [20]. In chicory, inulin has a degree of polymerization (DP) ranging from 3 to 60 monosaccharides units. Non-fractionated inulin extracted from fresh roots might contain glucose, fructose, sucrose and small oligosaccharides. Inulin from chicory roots can be modified chemically to yield shorter chain fractions known as fructo-oligosaccharides (FOS) [102].

Physical and functional properties

The physical and functional properties displayed by inulin in food and pharmaceutical systems are strongly connected to their Mw and the nature of bonding. Occurrence of multiple hydroxyl groups in its chemical structure contributes greatly to its strong affinity towards water molecules. This

characteristic feature helps in the formation of gel, which is a three-dimensional network of insoluble particles. This ensures

physical stability as the liquid water.

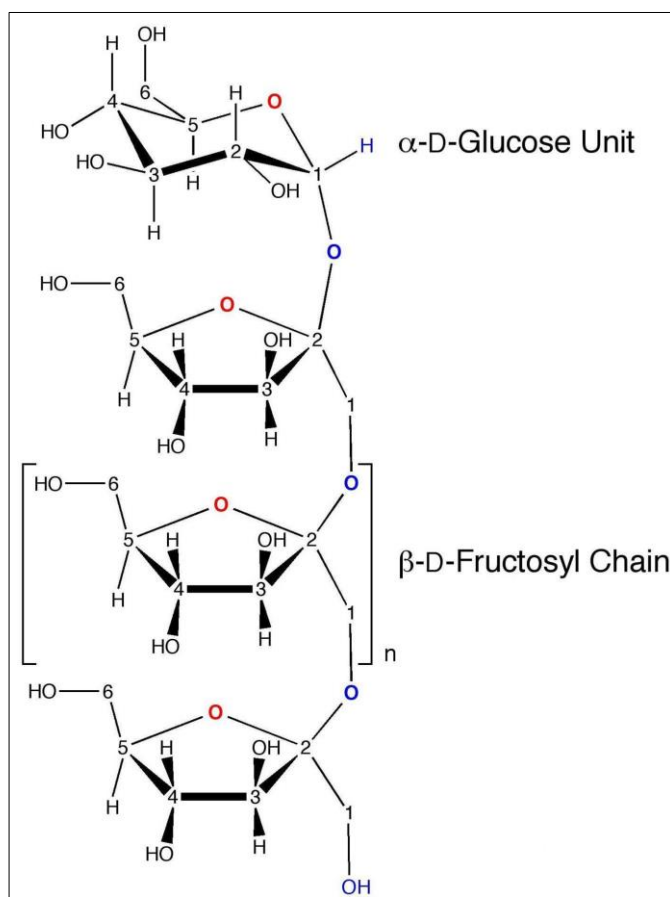


Fig 2: Inulin polymers ^[11]

becomes immobilized within these particles ^[21]. The unique drug delivery capability of inulin is due to stability and strength of the β- (2-1) glycosidic linkages which can withstand to the extreme pH and ionic strength conditions in the human GI tract avoiding the action of endogenous enzymes ^[48]. There has been a growing interest among food industries for inulin due to its functional properties, which include fat replacement, sweetening synergies, rich soluble fiber, and enhancement of bowel health (Table 1) ^[20]. Apart from being a low-calorie sweetener, inulin contributes to bland neutral flavors, fat-like texture and mouth feel ^[95]. Potential applications of inulin to substitute sugar and fat include milk-based products, breakfast spreads, frozen desserts, chocolate and baked items ^[29]. Mixing of certain inulin-type probiotics with water could produce a potential fat replacer because the combination will have the same mouth feel and texture like a fat. However, it can only be used in water-based food products such as spreads and dairy products rather than dry foods ^[26]. High Performance (HP) inulin having high molecular weight and longer chain is mostly desired for application as fat replacers ^[55]. However, solubility of inulin-type fructans is reduced with longer chain length, resulting in the inulin microcrystals formation when mixing with water or milk. They have a smooth, creamy mouth feel, which are not discretely perceptible. Inulin HP has no sweetness contributions but it has almost twice the fat mimetic features of a standard inulin ^[55]. In baking application, addition of inulin has an effect on the rheological characteristics, water absorption capacity, and dough development. Addition of roughly 2.4 - 7.5% of inulin would

decrease water absorption in the dough; this is more obviously seen with shorter chain inulin due to their lubricating effects on sugars and oligosaccharides present ^[77]. Meyer and Peters ^[68] noticed that inulin with different degrees of polymerization has increased the dough stability. For instance, addition of 1 - 4% inulin TEX (long chain length) has increased the dough development time and stability, resulting in strengthening of the dough.

Health impact

The prebiotic properties of inulin are well-recognized ^[95] as it can influence the colonic microbiota, giving beneficial effects on human gut health (Table 1) ^[38]. Owing to the β-configuration of the anomeric carbon at C-2 position of fructose monomers, inulin resists hydrolysis by human digestive enzymes in the small intestine ^[30]. As a consequence, inulin can enhance the growth of lactobacilli and bifidobacteria, which help improve the gut environment ^[20]. A specific increase in bifidobacteria in human of all ages ^[69] are linked to physiological effects such as improving the bowel habitats, lowering of serum cholesterol, increasing the absorption of calcium, etc. In some food formulations, replacing certain cholesterol raising fatty acids through supplemental inulin has been shown to be beneficial in the management of hypercholesterolemia. Substituting fats or sugar partly by inulin could have a direct influence on serum lipids as well as reducing the calorific density of selected foods ^[29].

The widening application of inulin in pharmaceutical fields is due to its β (2-1) glycosidic bonds, which make it indigestible

by enzymes present in humans and other higher animals [12]. According to studies conducted by Davidson *et al.* [29], there was no increment of both total cholesterol (1.3%) and low-density lipoprotein cholesterol (LDL-C) (2.1%) during inulin intake while total cholesterol and LDL-C increased to 7.4% and 12.3%, respectively during the control phase. Based on the study conducted among 18 subjects with Type II diabetes mellitus, daily intake of 8.0 g of fructo-oligosaccharides for 14 consecutive days was shown to lower the total blood cholesterol by 0.49 mmol/L (8%) and LDL-C by 0.44 mmol/L (10%) [101]. All these findings suggest that consumption of insoluble dietary fiber might reduce serum total cholesterol and LDL-C in a subject [29]. Further to this, inulin can act as a slow release drug delivery medium [89] as well as function as a stabilizer for protein and peptide-based drugs and vaccines [43]. Apart from an immune-modulator [85], other interesting biological effects of being a potent complement pathway activator and anti-cancer agent were also evidenced from the intake of inulin [57]. Hence, they were able to suppress the growth of colon cancers in animal models. Complementary effects of tumor inhibition were also seen with fermentation products of inulin. Particularly, the formation of short chain fatty acids such as butyric and propionic acids is reported to inhibit the growth of colon cancer [12]. According to another report, dietary inulin can also suppress methylnitrosourea-induced mammary carcinogenesis in Sprague-Dawley female rats [92].

Arabinoxylan

Extraction sources

Arabinoxylan (AX) serves as the structural polysaccharides in the cell walls of several plant including woods and cereal grains. Millet, wheat, barley, oat, rice, rye, sorghum, and maize are some of the well-known sources of AX. Total AX content of grains might vary from 1.37% in wheat flour to 29.86% in maize bran [74]. In the past, byproducts of the food industry such as sugar beet pulp, banana peels, cereal bran,

corncoobs, etc. have also been used for the extraction of AX. Although different methods are available for isolation of AX from various plant sources, aqueous or alkali treatments are quite frequently used.

Chemical structure

AX are branched heteroglycan made up of pentose sugars, arabinose and xylose. They are composed of a linear backbone of β - (1 \rightarrow 4) linked D-xylopyranosyl residue (Xylp), which are linked through (1 \rightarrow 4) glycosidic linkages. α -L-arabinofuranose units (Araf) are attached to some of the Xylp residue at O-3, O-4, and/or at both O-2, 3 positions [74]. This will result in four structural elements in the molecular structure of arabinoxylans: monosubstituted Xylp at O-2 or O-3 with ferulic acid residue esterified, disubstituted Xylp O-2, 3, and unsubstituted Xylp (Figure 3) [51]. Although arabinose residues are attached as single substituents, a small portion of oligomeric side chains containing two or more Araf linked via 1 \rightarrow 2, 1 \rightarrow 3, and 1 \rightarrow 5 linkages have been reported for AX extracted from wheat and rye [51]. The distributions of arabinosyl substituents and the degree of the substitution along the xylan backbone are vital, since they can affect the capacity of AX to interact with each other or other polysaccharides. Thus, they can alter physical and functional properties of the macromolecules [51]. AX of wheat-endosperm comprises of highly branched regions, where singly (C-3) or doubly (C-2, 3) substituted xyloses are separated by singly unsubstituted xylose residues [42]. Generally, most highly branched xylan backbones are found in AX of rice compared to those extracted from barley, rye, and wheat. Other than this, they may also contain glucuronic acid moieties and galactose along with pentose sugar. The most important factor in determining physiochemical properties of AX are the degree and the distribution of side chain [46]. Unsubstituted xylose residue that segmented continuously permit intermolecular realignments and interchain associations [51].

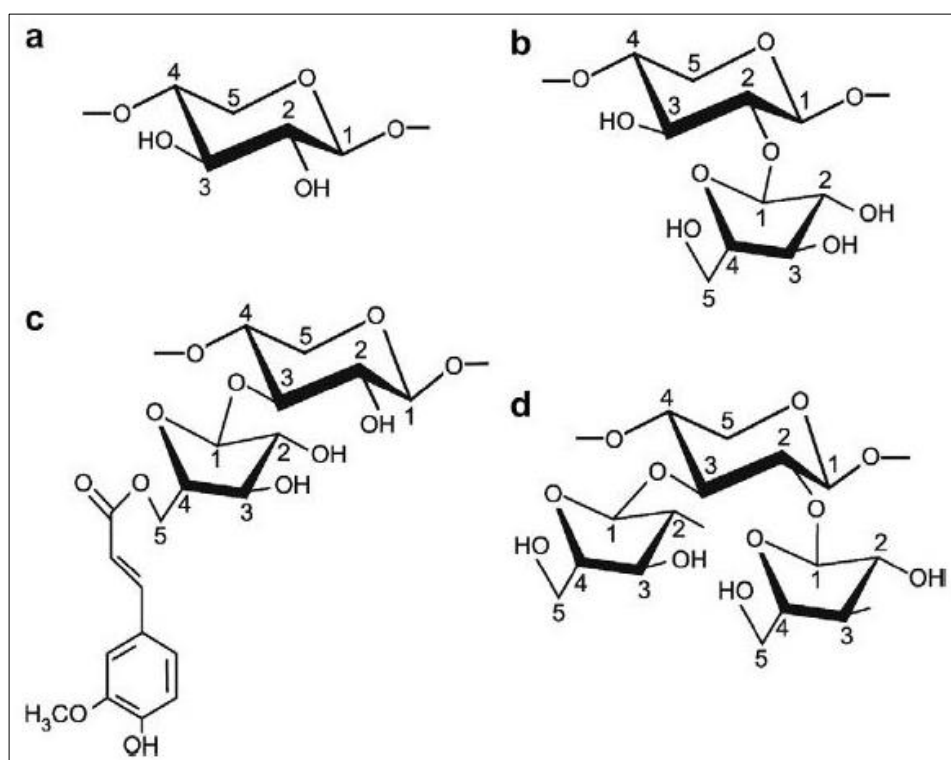


Fig 3: Structural elements present in arabinoxylans: (a) unsubstituted Xylp; (b) monosubstituted Xylp at O-2; (c) monosubstituted Xylp at O-3 with ferulic acid residue esterified to Araf and (d) disubstituted Xylp at O-2, 3 [51]

Physical and functional properties

Arabinoxylan (AX) drew attention of several researchers owing to their role in improving physical properties of food systems. The Mw, substitution pattern, the xylose to arabinose ratio, amount and sequence of glycosidic bonds, and presence of other substituents would normally influence the physicochemical properties of AX [81]. Apart from arabinose and xylose, some residues of galactose and glucuronic acid could also be found as side branches in the main chain of AX. According to Li and Du [60], the molecular characteristics of AX could also be influenced by genetics as well as isolation techniques. Most AX from wheat endosperm are water extractable but result in highly viscous aqueous solutions [25]. In aqueous solution, they are presumed to have a wormlike structure, which characterize their behavior as semi-flexible polysaccharides [51]. Presence of covalent-linkages between side chains of AX are believed to be responsible for higher water solubility [51]. Generally, changes of concentration and molecular weight of the polymers would influence the viscosity of the AX solution [82]. Hydrolysis of arabinoxylan by endoxylanase might alter its chemical structure and Mw causing changes in its solubility and viscosity. The main reason was the fact that xylanase was able to degrade AX to small oligosaccharides [79]. There are several interesting technological properties of AX, which have been beneficially used by food industries (Table 1). AX may be incorporated into foods to add nutritional enhancement or improving quality in terms of shelf life stability [90]. They were found to impart beneficial effect on bakery products because of their high-water absorbing capacity and ability to form hydrated networks [53]. They not only affect the retrogradation of starch, but also might influence moisture distributions, rheological properties of dough, and the loaf volume of bread [53]. AX may also be incorporated into pharmaceutical products owing to their interesting biological activities such as prebiotic, antioxidant, and anticancer properties [106]. The demonstrated antioxidant properties of AX are attributed to the high ferulic acid content in their molecular structure. Other than this, there is possibility of cumaric acid residues being esterified to arabinose units at the O-5 position.

Health impact

Arabinoxylan (AX) could have physiological effect similar to that of β -glucans upon consumption by human [52]. According to Table 1, a host of beneficial functional properties of AX are demonstrated through research work. Several studies previously reported the physiological effects of arabinoxylans from wheat, rye and maize on cecal fermentation including production of short chain fatty acids, reduction of serum cholesterol and improvement of absorption of calcium and magnesium [66]. Farhan *et al.* [35] stated that AX displayed their ability to form viscous solutions, which might slow down the rate of digestion in monogastrics. As they are indigestible in the small intestine, they could provide fermentable carbon sources to bacteria living in the large intestine [44]. Some other in vitro studies also indicated that a specific concentrate of long-chain water-extractable AX (LC-AX) could stimulate specific intestinal microbes such as *Bifidobacterium longum* [78]. According to some studies, a modified AX such as BioBran/MGN-3, acted as a potent biological response modifier (BRM), exhibiting anti-HIV activity, which helped to increase T and B cell proliferation and NK

immunomodulatory function. BioBran/MGN-3 also notably influence the macrophage activity. The researchers first studied the intestinal microbiota in children by investigating the degradation of cross linked and non-cross linked AX. According to reported findings, ferulic acid cross-linking reduced the rate of AX fermentation. A modified AX from rice bran was a potent inducer of phagocytic function by macrophage but the effects were dependent on the type of macrophages and the concentration of the BioBran/MGN-3 [41].

Gums

Extraction sources

Gums are non-starch water-soluble polysaccharides with considerable commercial interest. Depending on the source of extraction, gums broadly categorized as exudate and non-exudate gums. When used as ingredients in processed foods, they are sometimes called hydrocolloids [15]. Gum Arabic, gum ghatti, fenugreek gum, gums of guar and locust bean etc. are polysaccharides of considerable commercial importance. They originate from different sources such as the endosperm of plant seeds (e.g. guar gum, fenugreek gum, locust bean gum), plant exudates (e.g. gum Arabic), seaweeds (e.g. agar), and bacteria (e.g. Xanthan gum) [5]. Different geographical regions of world are famous for production of these gums and their prices are generally affected due to fluctuations in demand and supply. Africa is World's largest supplier of GA, mostly of them come from Sudan (80%) and throughout the Sahel, from Senegal to Somali. In the case of guar gum, India (80%) is the world's largest producer, followed by Pakistan (15%) and some other Asian countries. After studying three Indian guar cultivars, Sharma *et al.* [83] stated that the gum extraction yields of G 80, HG 365, and Ageta 112 were 41.19, 37.32, and 31.19%, respectively. Extraction of gums from non-conventional sources such as fenugreek and durian seeds was an interest for some research groups. When defatted fenugreek seeds were subjected to extraction of gum at 10 °C for 2h, it was found to give a yield of 22% [19]. Gum extracted from fenugreek seeds is already well-known for their properties and utilization in various food and pharmaceutical products [63]. According to another report, Amid and Mirhosseini [5] succeeded in extracting gum from durian seeds thrown away in abundance after consumption. The researchers stated that under the optimal condition of extraction, the yield of gum from durian seed was found to be 56%.

Chemical structure

The chemical structure of GA is complex; being a mixture of polyelectrolytes associated with calcium, magnesium and potassium salts, GA consists of both proteins and polysaccharides subunits. The backbone of GA is composed of 1, 3-linked β D-galactopyranosyl units. The side chains are mainly composed of two to five 1, 3-linked β D-galactopyranosyl units, joining to the main chain by 1, 6-linkages. α -L-arabinofuranosyl, α -L-rhamnopyranosyl, and β -D-glucopyranosyl units are present in their main and side chains [49]. Gum ghatti has very complex arrangements of neutral sugar units consists of Galp, Araf, and Arap and GlcA. They are attached to a molecular core of alternating β -D-GlcA and D-Man residues, the former linked through O-4 and the latter through O-2 (Figure 4).

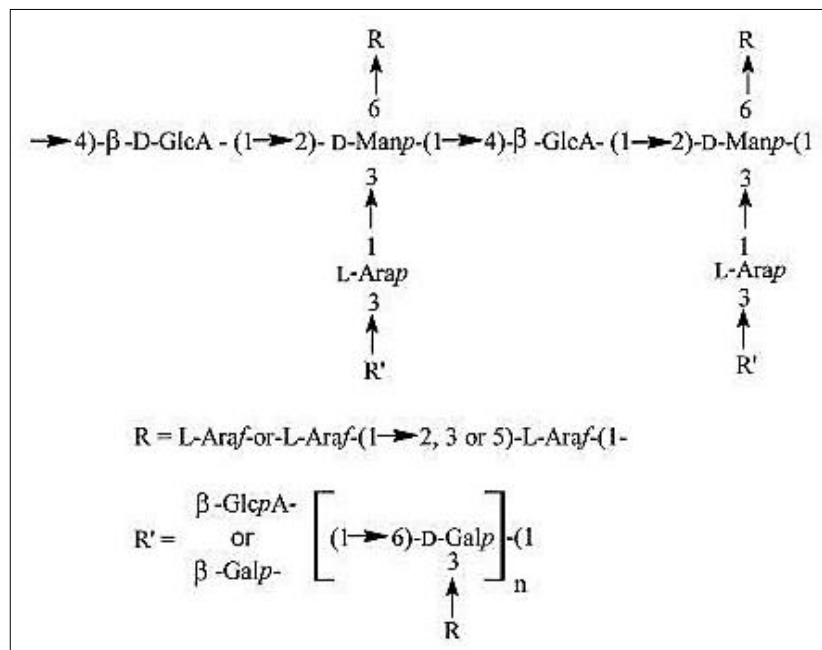


Fig 4: Structural features of gum ghatti ^[11]

D-Man residues are present as double branch-point of (1, 3)- and (1, 6)-linked Gal units that occupy the side chains. According to Tischer *et al.* ^[93], the substituents at O-4 of the -Glc pA- units were comprised of 6% of rhamnose in the polysaccharides. As a common feature of many plant gum polysaccharides, it contributes substantially to its structure as an α -Rhap- (1 \rightarrow 4)- β -Glc pA-group. Guar gum mainly consists of the high molecular weight polysaccharides of galactomannans which are linear chain of (1 \rightarrow 4)-linked β -D-mannopyranosyl units with (1 \rightarrow 6)-linked α -D-galactopyranosyl residues as side chains ^[64]. Garti and Leser ^[36] stated that the mannose to galactose ratio of the units was 2:1. According to various other research studies, the ratio is found to be in the range of 1.6:1 to 1.8:1. Owing to greater branching of guar, it is reported to be known for greater hydrogen bonding and gelation activity. Locust bean gum resembles Guar gum as it being composed of the complex carbohydrate polymer of galactose and mannose, but with different proportions of these two sugars ^[64]. Xanthan being a gum of microbial origin has a hetero-polysaccharide with a very high molecular weight. Its main chain is made up of glucose units and the β -D-glucoses are linked (1 \rightarrow 4) to form the backbone similar to cellulose. Its side chain consists of α -D-mannose that contains an acetyl group, β -D-glucuronic acid, and a β -D-mannose terminal unit, linked to a pyruvate group.

Physical and functional properties

Gums are used for a variety of purposes such as gelling agents, texture modifiers, thickeners, emulsifiers, stabilizers, or as coating agents (Table 1) ^[65]. Water absorption and swelling are two essential characteristics of natural gums. Occurrence of plenty of hydroxyl groups in their molecular structure confers them the natural ability to form hydrogen bonds with water molecules, resulting in high viscosity of their aqueous solutions. According to Aphibanthammakit *et al.* ^[8], the charged portion of the carbohydrate moiety of plant gums also contributes to viscosity because the dipolar water molecules participate in strong electro static interaction, leading to the formation of hydration shells. It is hypothesized that the strong water binding effects coming from their

hydrophilic carbohydrate moiety of gums can prevent organoleptic defects in products like ice cream ^[45].

According to multiple reports, plant gums were found to contain variable amounts of proteins (0.30 and 22.75%). Hydrophobic nature of the protein moieties adsorbs onto the surface of oil droplets while the hydrophilic carbohydrate moiety inhibits the flocculation and coalescence of molecules through electrostatic and steric repulsions. The combination of highly branched polysaccharide chains and the affinity of the covalently linked protein moieties for the oil phase explain why some of the gums are excellent emulsifiers in oil-in-water emulsions.

There has been an increasing trend in using GA as a food additive in bakery and confectionary products as well as drinks. According to Verbeke *et al.* ^[96], GA has been used as thickener, stabilizer, and emulsifiers as it can effectively modify the rheological properties of aqueous food systems. For instance, incorporation of GA in frozen products like ice cream can prevent the undesirable formation of larger crystals. It is also used for the purpose of encapsulation, and coatings in pharmaceuticals. In pharmaceutical industry, it is used as an excipient, an adhesive, and binder in tableting. It is used in drinks due to such advantages as low viscosity, low calorie, and stabilizing property in oil in water emulsion. It is as good as inulin, with regard to prebiotic function.

Gum ghatti has several applications in food and pharmaceutical fields. They are excellent emulsifying agents because of the proteinous molecular components that is bound to oil ^[47]. The high viscosity of the gum ghatti has been considered as an ideal characteristic feature to be used as a stabilizer for dense pharmaceutical emulsions and suspensions. As an emulsifying agent and stabilizer, gum ghatti has been widely used in beverages, butter containing table syrups, and flavor fixative for specific applications ^[31]. Unlike GA, Gum ghatti is not completely soluble at concentrations of $\geq 5\%$ in water. The viscosity of gum ghatti dispersions increases with time, probably due to increases in the degree of aggregation of the polysaccharide molecules.

Guar seed endosperm is a source of water-soluble gum known as guar gum. Guar gum finds uses as an additive in bakery products, ice cream, yoghurt, sauces and sausages. In chapatti,

pasta and bread making, it acts as a dough improver and texture improver. As a food additive, it emulsifies, binds water, prevents ice crystals in frozen products, moisturizes, thickens, stabilizes and suspends many liquid-solid systems. In industrial frying, it can be used to reduce the oil uptake by fried products. Guar gum found applications as thickener and stabilizer due to its ability to form hydrogen bonding with water molecule [64]. The ability to hydrate rapidly in cold water systems to give highly viscous solutions is the most significant characteristic of guar gum. In cheese making, guar gum has been successfully incorporated to produce low-fat cheese without changing the rheology and texture being compatible with full-fat cheese [64].

Health impact

Gums from plant sources are known for their multifarious health implications (Table 1). Some researchers perceived the behavior of several plant gums during metabolism as similar to those of dietary fibre. Dietary fibre intake already found to minimize the risk of cardio vascular complications, help enhance immune function and weight management [45]. GA, for instance, is considered as a dietary supplement that can help in weight management and prevention of obesity. In normal experimental rats, it is reported to enhance the absorption of sodium in the small intestinal [80]. According to some other animal model studies, administration of GA was found to help maintain several blood lipid profile in both human [71] and mice [1-2]. GA is also found to have the capability to alter the expression of mRNA levels of genes involved in lipid metabolism to suppress the diet-induced obesity [3].

Guar gum and Gum ghatti are reported to play some significant role in the control and management of a number of health issues like chronic ailments and bowel related disorders. It might also be beneficially used for weight management and prevention of obesity. Guar gum can help to reduce serum cholesterol and postprandial blood glucose due to its gel forming properties. According to an in vitro study, Guar gum was found to significantly decrease the starch digestion as it can act as a barrier between starch and starch hydrolyzing enzymes [28]. Gum ghatti has been found to be effective in strengthening the immune system and reducing serum cholesterol level. As it helps in stimulating the immune system, it can reduce the effects of many neurological diseases. It has been found to be effective in patients undergoing chemotherapy to help prevent or lessen the side effects of the treatment. Apart from this, it also found to exert some influence to help reduce or slow down the ageing process and weight gaining.

Conclusions and future prospects

In this review, chemical structure, physical and functional properties and health impacts of β -bonded polysaccharides such as β -glucan, arabinoxylan, inulin, and selected gums have been discussed. Most of the studies provided evidence for multiple benefits of β -bonded polysaccharides in terms of functional and technological properties such as thickening and stabilizing property along with high water-holding capacities, which might help improve food texture and quality. Since some of these biopolymers are indigestible in small intestines, they will serve as substrate for partial fermentation in the large intestine, which will bring about physiological effects such as reducing cholesterol level, reducing postprandial blood glucose level, accelerating the wound healing, and strengthening the immune system. This review concluded that

the properties and functions of individual β -bonded polysaccharides are strongly linked to their chemical structure and composition. It should be noted that there are further prospects and challenges in this field. For instance, the applications of some of the β -glucans are reported to be limited due to their high molecular weight and viscosity. In such cases, employment of emerging technologies of altering the molecular structure might be attempted to render improvement in their solubility. Introducing suitable ionic groups with appropriate degrees of substitution might be a good strategy to enhance the water solubility of β -glucans. Exploration of β -glucan and inulin from under-utilized grains and medicinal plants and other marine resources is a promising area. Particularly, investigation of the occurrence of β -bonded polysaccharides in microbial sources, thriving in marine environment, is an exciting area for new initiatives. Lack of biomedical expertise to identify and facilitate development is one of the impediments. Use of molecular and bioinformatics methods to explore the distribution of β -bonded polysaccharide producing bacteria in the marine environment can address this issue. Further, the tropical forest resources are known to provide ample opportunities for exploration of novel β -bonded polysaccharides. Particularly, there would be several forest species, which could yield exudate gums and their seeds might contain non-exudate gums. Profiling of their composition, bioactivities and functional properties could provide leads for future exploitation and developments.

Author Contributions

Nur'Ain Najwa Mohd Nor: Writing - Original Draft Preparation; Nazrim Marikkar: Conceptualisation, Writing - Review & Editing, Supervision; Yanty Noorzianna Manaf: Writing - Review & Editing; and Shuhaimi Mustafa Supervision, Project Administration, Funding Acquisition. All authors have read and agreed to the published version of the manuscript.

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Conflicts of interest

The authors declare no conflicts of interest.

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