

Healthy Polysaccharides The Next Chapter in Food Products

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Received: December 1, 2005

Accepted: March 11, 2006

Summary

New lifestyles of modern countries have contributed to the appearance of chronic diseases such as obesity or cardiovascular diseases, which are mainly due to bad eating habits. Solutions can be found in providing the consumers with functional foods with health capability. With the supplementation of food products during the first step with for example vitamins, minerals (Ca^{2+} , Mg^{2+}) or essential fatty acids to improve their health properties, another strategy has grown up in the last decade with the development of low-fat products. These lipids, originally present in the food product (and removed), are responsible for its texture. The solution has been found in the discovery of the polysaccharides, so called fat replacers, with specific physicochemical behaviour, which also possess healthy properties as dietary fibres and prebiotics. The present review gives an overview of these available polysaccharides (plant, algal, bacterial and animal).

Key words: beneficial polysaccharides, health, nutraceuticals, dietary fibre, prebiotics, food industry, low-fat/calorie products, food mimetic, fat replacers, nutrition

Introduction

In 1997 in the USA, heart diseases accounted for approximately 31 % of deaths, cancer for 23 %, cerebrovascular diseases for 7 % and chronic obstructive pulmonary diseases for 5 %. The reasons for this are important to be known not only for individuals and their families, but also to control the high cost of medical care. Basic applied research in the area of nutrition and health has not only shown that certain traditional nutritional habits are associated with a major risk of prevailing chronic diseases, heart disease, stroke, and many types of cancer but also that understanding the underlying mechanisms can provide the basis for public health actions in their prevention.

In the past 30 years, there have been increases in the number of fast-food restaurants, popular especially with

young people because such restaurants offer relatively low-cost meals. It could be presumed that this phenomenon will not decrease if the actual lifestyle does not change. It is not yet known whether the high meat or sugar intake common in this type of foods can affect at later stage the increase of chronic diseases. Additionally, low-fibre diets represented 35 % of the main causes of cancer mortality in the USA in 1999 (1).

On the other hand, bran cereal fibres are known to lower the risk of heart diseases and several of the nutritionally linked cancers. A higher intake of vegetables (fruits and fibres), especially insoluble wheat bran fibres, could improve the situation, but the modern lifestyle is presently more and more dependant on processed and convenience foods (2). By 2005, there will have been an estimated 30 % increase in major health problems mainly

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due to the growing ratio of the aging and obese population (3). In fact, overweight and obesity are increasingly prevalent and are important contributors to cardiovascular disease, type II diabetes mellitus and several common cancers. Estimations of the global burden of disease attributable to excess body mass indicate a loss of healthy life causing 2.5 million of deaths in 2000 (4).

Based on those statements, the idea of physiological functions and functional foods was proposed around 1990 as the third function of food in Japan and in 1991 the Japanese government started an approval system for »Foods for Specified Health Use« (FOSHU) (5). Functional foods deliver the positive message of eating well, rather than the old messages to reduce and avoid. The health potential of foods is well perceived by European consumers even if they consider them as members of the general category (such as yogurt or spread) and only secondarily as a functional food (6). The world-wide opportunity for future growth and development of novel functional foods is tremendous. By 1997, 90 % of consumers were convinced that even slight modification of their diet could improve their health, and sales of functional foods increased by 15 % annually. Only during 1997, European sales of yogurt brought a profit of 2 billion dollars to manufacturers. Several foodstuffs with probiotics and prebiotics are available in the European, American and Asian markets, e.g. fresh milk, kefir, yogurt, fruit juices. This number and variety of products is expected to grow up extensively in the next 10 years (7). Advances in medical research, coupled with continuous new food-technology developments are expected to provide many opportunities for manufacturers to produce cutting-edge functional foods, thus addressing the needs of the health-conscious consumer. Potential markets for functional foods are bound to become a success (3).

Functional foods, designer foods and nutraceuticals refer to foods or food ingredients that provide non-nutritive physiological benefits that may enhance health. The need appears to find a means to optimize consumers' health through foods and herbs in an effort to offset the cost of drugs and health care. As the market is driven by an increased consumers' demand for these nutraceutical foods, research has risen in that field. Important to the approval of health claims is the necessity to identify the active component and generate enough scientific evidence to support the efficacy of the claim (8). Food companies are responding to the need for foods with enhanced satiability and lower energy density by allocating more resources for the development of dietary fibre-enriched products. The challenge for industry is to ensure that such foods are both palatable and attractive to the consumer, while maintaining nutritional benefits (9). Another challenge consists now in producing those healthy foods with different processes. From the research and development point of view, functional foods represent a territory where the expertise of food technologists, nutritionists, medical doctors and food chemists must be combined to obtain innovative products. For example, the dairy market has profoundly changed with the presence of fermented probiotic milk. Also in the field of bakery, soft drinks and baby food, a considerable number of new functional foods has been created (6). Many studies have examined the actual impact of new processes

on those molecules with nutritional value (10,11) or the influence of the combination of molecules on new properties and availability of interesting nutrients (12).

Basically, polysaccharides are the main components of dietary fibers. A lot of researches have been done (and continue to be done) to understand better the interactions of those polysaccharides with other macromolecules such as proteins [only interactions (13,14) or to understand glycation kinetics (15,16)] and lipids (17). This scientific knowledge helps to improve or to modify the initial properties of the interesting polysaccharides. In fact, one possibility to include those new compounds into enriched food products is to modify their initial physicochemical properties by chemical or physical treatments, as for example making starch soluble by acidic treatment (18) or to modify starch with unconventional methods (19–21). Another possibility is to find new sources containing new molecules with characteristic properties, for example resistant starch (22).

New information would open the way for the development of new food ingredients with prophylactic or health promoting activities, which could be used beside other pre- and probiotic substances (23). This review details the first ever dietary fibres that present physiological properties and are or can be used in the future in functional food products.

Healthy Food – Definitions of Terms and Actual State of Legislation

It is first important to define all the different terms accompanying the healthy food in more details. Currently, marketing »healthy« foods to otherwise healthy people has met with unprecedented success. The realization that attention to the diet as part of a healthy lifestyle can reduce the risk of disease and promote health has created a market for a whole range of new products called nutraceuticals, functional foods or novel foods. Many consumers opt for healthy versions of their favourite products, being unable or unwilling to adapt their diet to the suggested guidelines.

Nutraceuticals are natural, bioactive chemical compounds that are characterized by health-promoting, disease-preventing or medicinal properties. They are natural ingredients that exist in foods and are considered the source of health benefits beyond their nutritional contribution. Identification of these foods will allow their incorporation into a more healthy diet and may enhance development of new food products. In 1998, the only ingredients successfully incorporated into products were dietary fibre (polysaccharides) and carotenoids (8).

The second term used in healthy foods, »functional foods«, was first introduced in Japan in the mid-1980s and it referred to processed foods containing ingredients that aided specific bodily functions in addition to being nutritious. The precise definition of functional food is not universal and is still evolving. Functional foods have been more broadly defined as foods similar in appearance to conventional foods that are consumed as part of a normal diet and have demonstrated physiological benefits and/or reduce the risk of chronic diseases beyond basic nutritional functions (3). The term functional food des-

cribes foodstuffs which, apart from their nutritive value, evidently improve health and well-being of consumers. They may be applied in prophylaxis and therapy of certain diseases (7).

In recent years, accumulating evidence has pointed clearly to a role of certain dietary components (bioactive ingredients) in the prevention of cardiovascular disease, some kinds of cancer, osteoporosis, inflammatory conditions, obesity and modulation of the immune system. Bioactivity refers to the application of nutraceuticals or bioactive ingredients in food such as prebiotics, probiotics, bioactive carbohydrates (fibre), bioactive peptides and sterols. Functional foods are endowed with specific physiological benefits that discriminate them from traditional foods. Therefore, functional products can be classified into two main categories according to the expected effects: those aiming to improve physiological functions and those aiming to reduce the risk of specific pathologies (6).

They are expected to be in the form of ordinary food, whereas dietary supplement stands for a food not in its conventional form, providing a component to supplement the diet by increasing the total dietary intake of that component. Health conscious consumers are increasingly seeking functional foods in an effort to control and improve their own health and well-being. The field of functional foods, however, is in its infancy. Foods with novel health claims (supported by solid scientific substantiations) have the potential of becoming important components of a healthy lifestyle and therefore extremely beneficial to the public (3).

There are three main strategies for functional food design: (i) to modify the composition of raw material, (ii) to modify the technological processes (create specific processes to allow or enhance the formation of compounds having specific biological activities), and (iii) to modify the formulation of the recipes. In the last case, the addition of so-called functional ingredients to a traditional food matrix is the simplest and most common way to realize a functional food. However, the simple addition of a functional ingredient should be performed taking into account many variables such as the interaction with the food matrix, the stability of the process, and bioavailability of functional ingredients in the final product (6).

Polysaccharides: A Source of Oligosaccharides with Biological Activities

Traditionally, polysaccharides are used as thickening, emulsifying and stabilizing agents. But, nowadays, a huge market in healthy compounds has appeared with the production of oligo- or monosaccharide syrups (2,24,25) using physical methods or controlled enzymatic degradation of polysaccharides (e.g. starch). Some of them possess interesting biological properties (26,27) such as for example oligodextrins (anti-ulcer agents, lowering serum cholesterol in low saturated fat diet) (28), fructooligosaccharides (prebiotics, dietary fibre, stimulate mineral absorption, enhance defense mechanism) (29–34), xylooligosaccharides (35), mannoooligosaccharides (36,37) and galactooligosaccharides (38). This subject (oligosacchari-

des with biological activities) is out of our focus and will not be discussed in this review.

Dietary and Prebiotic Properties, Fat Replacers

Healthy polysaccharides are divided in three main categories regarding their beneficial impact on the organism: prebiotics, which play a role on probiotics (related action); dietary fibres with direct physiological properties (direct action); and the fat-mimics, which replace fat in products (indirect action).

Prebiotics and probiotics

Due to the potential synergy between probiotics and prebiotics, foods containing a combination of these ingredients are often referred to as synbiotics (3).

Probiosis can be defined as the positive effect of the consumption of fermented dairy products with cultures of lactic acid bacteria on the equilibrium of intestinal microflora. Functional foods, defined above, can contain probiotics or prebiotics, two terms important to define.

Probiotics are defined as living microorganisms in foodstuffs, which, when taken at certain levels in nutrition, provide equilibration of the intestinal flora, and hence have a positive effect on the health of the consumer. Probiotics are selected from the strains most beneficial for the host's intestinal bacteria (*Bifidobacterium*, *Lactobacillus*) and yeast (*Saccharomyces boulardii*). The criteria for microorganisms to be included in the probiotics group are listed in Table 1. Greater resistance of organisms to intestinal infection is another benefit from the use of probiotics, because they fill an ecological niche by adhering to intestinal wall, competitively use nutrients and decrease pH levels, thus inhibiting the growth of pathogenic bacteria. Under special conditions, this is further improved by the production of hydrogen peroxide and bacteriocins (nisin and pediocin). Probiotics can also digest lactose and the symptoms of lactose intolerance diminish as the lactose level in fermented dairy products decreases. Intensification of the production of antibodies in the gastrointestinal tract induced by probiotics and the activities of some carcinogenetic enzymes reduced in their presence have also been described (7).

Prebiotics are defined as nondigestible substances (dietary fibres) that exert some biological effect on humans by selective stimulation of the growth or bioactivity of beneficial microorganisms either present or therapeutically introduced in the intestine. In fact, prebiotics undergo fermentation by beneficial microflora in the large intestine (contrary to the dietary fibres). Inulin and resistant starch are the most known molecules to comprise the prebiotics group (7).

Dietary fibres (DFs)

A long tradition has associated dietary fibres (DFs) as being beneficial to human health and protective against a range of diseases that are common in the Western world, including colon cancer. However, their effects became controversial and further epidemiologist studies indicated that higher intakes of DFs did not protect against colon cancer. New DF-enhanced foods have the potential to enhance satiety and aid the regulation of

Table 1. Main characteristics of prebiotics, probiotics and dietary fibres

Prebiotics	Probiotics	Dietary fibres
Stimulation and activation of useful microorganisms	Survival on passing through gastrointestinal tract at low pH and on contact with bile	Reduce risk of breast or colon cancer
Improve quality of intestinal microflora	Survival in foodstuffs and possibility of production of pharmacopoeia lyophilized preparation	Nutrient and SCFA production by degradation of probiotics (vitamins, butyrate)
	Stabilization of the intestinal microflora	Anti-constipating agent
	Nonpathogenicity	Anti-pathogenic agent
	Adhesion to intestinal epithelial cells	Increase absorption of minerals in the intestine
	Fast multiplication, with either permanent or temporary colonization of the gastrointestinal tract	Binding excess bile acids and salts, interact with mutagens and carcinogens in the gut
	Generic specificity of probiotics	Reduce risk of cardiovascular disease
	Inhibition of growth of pathogenic bacteria	Decrease blood lipid level (cholesterol)

blood glucose for diabetic patients. Certain viscous soluble DFs (including guar gum and locust bean gum) have the potential to alter the rate of carbohydrate degradation during digestion by their effects on food structure, viscosity and composition. This is likely to have beneficial flow-on effects for the regulation of postprandial blood sugar and insulin levels, key events in the prevention and treatment of obesity and diabetes (9). Oppositely, recent studies show a protective effect of DFs on cardiovascular disease. Increased intake of certain DFs can be beneficial in reducing inflammation and particularly idiopathic inflammatory bowel diseases, Crohn's disease and ulcerative colitis (39). A range of DF-carbohydrates can also modulate the activity of the microbial flora through a range of different mechanisms (40). Several non-starchy polysaccharides such as pectins, guar gum or oat gum do not metabolize in the stomach, nor are they digested by the intestinal microflora. Therefore, they can not be considered as prebiotics. The multiple properties of DFs are detailed in Table 1. The products [oligosaccharides (FOS, MOS, GOS), cellobiose] formed during their bacterial fermentation are also beneficial to humans. Thus, food containing prebiotics and fibres is put into the group of products called nutraceuticals (7).

In the past, scientific evidence exalting the physiological effects of DFs [such as reduction of bowel transit time, prevention of constipation, reduction in risk of colorectal cancer by the increase of the caecal and colon mass, production of short chain fatty acids (SCFAs), lowering blood cholesterol, regulation of blood glucose levels for diabetes management, promotion of colon functionality, increase of beneficial colonic microflora growth (*i.e.* as prebiotic)] was shown to convince the food industry to use DFs not only to improve the physical characteristics of their products but also to improve food nutritional properties (41). For example, the introduction of DFs in a product like pasta provides many advantages. In fact, pasta is very popular, widely consumed due to its facility in transport, storing as well as cooking and used in many recipes. In Italy, the daily pasta intake is about 100 g. Therefore, functional pasta with added 5 %

of DFs would allow most of the people to reach the recommended dietary intake of 25–30 g/day. From the technological point of view, the major problem in the addition of DFs to pasta is a possible modification of the physicochemical and sensorial properties of both the added DFs and the final product. Technological treatments can modify fibre properties such as the viscosity and ion-exchange capacity (which are the main contributors to the fibre effect on glucose and lipid metabolism), thus varying the physiological effects of the final functional pasta. Also, water absorption and viscosity as well as the ability to maintain a compact structure and the characteristic flavours or taste after cooking can be severely affected by DFs added. In fact, the pastas enriched with low amounts of DFs in the EU market have very poor sensorial quality and a lot of work is necessary to obtain pasta products comparable with conventional ones (6).

There are two main types of fibres: insoluble and soluble. Bran cereal is mostly the insoluble type. It absorbs water, provides increasing intestinal bulk and leads to a large stool. This type of fibre prevents constipation, diverticulosis and related intestinal diseases. The large stool leads to the excretion of cancer-promoting substances such as bile acids and estrogen metabolites. Soluble fibres have little effect on stool bulk but do increase gel formation in the intestinal tract. The result is interruption of enterohepatic cycling and reabsorption of products that, at higher concentrations, could have adverse effects. Thus, fibres promote harmless excretion. Fruit and vegetables are good sources of soluble fibres (1). Research into DFs has broadly examined the effects of soluble and insoluble fractions as purified fibres, or in naturally fibre-rich whole foods. High-fibre foods have been related to the modulation of glycemic response using both purified fibres and food naturally rich in fibres. In particular, foods high in soluble DFs have been shown to have a positive effect on reducing hyperglycemia and hyperinsulinemia, in relation to the control of diabetes and the reduction of risk factors for degenerative diseases such as obesity, hyperlipidemia, cardiovascular disease, cancer and hypertension. Reasons proposed for the

reduction of the glycemic response are multiple: amount and quality of fibres used, increased intrinsic viscosity of the food in combination with fluids and the gastrointestinal environment, maintenance of physical integrity of the food material and incomplete starch gelatinisation (which increase the caecal and colon mass called a bulking effect). In the case of cholesterol lowering, the potential of fibres results from the effects manifested in the upper gastrointestinal tract, due to the ability of cereal fibres to form gel-like network and alter gastrointestinal viscosity. This bulking effect is due to the water-holding capacity of the fibre, which allows prolonging the post-prandial satiety, increasing stool bulk and relief of constipation. Soluble DFs lower the rate of intestinal absorption of metabolizable nutrients, thereby reducing the glycemic load on the body. In turn, this necessarily reduces the level of insulin response. DFs increase the number of colonic crypts (increase colonic surface area). They have been implicated in modulating the colonic mucus barrier, the first line of defence that the colonic mucosa has to luminal aggression (42).

Fat replacers

Low-calorie/fat foods were initially introduced in the market to serve specific dietary and slimming needs. This food category was originally developed for diabetics and individuals with specific medical problems, such as obesity and heart diseases. Actually, there is a stronger shift towards healthier foods with less fat and sugar and more fibres. Research has clearly revealed a pronounced preference of Americans for foods and drinks of low calories and fat. The most popular are low-fat dairies, including cheese, non-fat milk, yogurt and sour cream, although soft drinks with no sugar continue to be on the top of desired products. The main reason for the consumption of these products continues to be the improvement of health. In order to limit coronary heart diseases, it is recommended to decrease the amount of saturated fatty acids and cholesterol in the product and to replace them with carbohydrates and fats rich in essential fatty acids. Fat replacers (or fat mimetics) can also be used to replace fat in the food systems. The food industry has developed a wide variety of fat mimetics to replace fat in the food system. They consist of carbohydrates or proteins regarding their organoleptic properties and the improvement of texture (primarily furnished with fat). Most of the carbohydrates are modified starch, gums or fibrous polysaccharides. The use of fibre in the technology of low-calorie foods can be attributed to the enhancement of consistency and the texture of the water phase in food systems and to the restoration of mouth-feel that is lost when fat is removed. They aim at compensation of fat functionality, water control and development of the desired bulk. The properties of fat mimetics result from association of water with the structure of carbohydrate particles, which should bind and orientate water in such way to provide in the oral cavity a sensation similar to that of fat. They furnish a desired cohesiveness, viscosity, dryness, juiciness and a certain moisture of the end-product that mimic fat (43).

Prebiotics, dietary fibres and fat replacers as well comprise polysaccharides as described above. It is clear that those macromolecules can have various origins and

structures. Despite these variations, they can exhibit or induce similar (or different) health properties that are discussed in details below. These polysaccharides can be divided in two main groups: the starch family and the non-starch polysaccharides (NSP).

Starch and Derivatives

Starch

Starch is one of the most important but flexible food ingredients possessing attributes for innumerable industrial applications. For example, the direct use of starch in foods accounts for 18.7 % (beer brewing, surimi production, confectionery) of the total starch consumption in Japan with 3 million tonnes in 2000. Starch is the least expensive agricultural commodity and the majority of oligosaccharides are derived from starch (5). It can be extracted from multiple resources such as cereal grains (e.g. corn, wheat and sorghum), and tubers or roots (potato, tapioca). Starch contributes to the texture and sensory properties of processed foods (2). Numerous studies have been realised about the structure and properties of starch and it is still continuing to evolve. Starch granules are composed of 2 types of α -glucan: amylose and amylopectin (Figs. 1A and 1B). The ratio of the 2 polysaccharides varies according to the botanical origin. Thus, the content of amylose varies from 15 % (waxy starches), 20–35 % (normal starches) to more than 40 % (high-amylose starches). Amylose is a long linear chain (molar mass of $1 \cdot 10^5$ – $1 \cdot 10^6$ g/mol) containing around 99 % of α -(1 \rightarrow 4) and a few α -(1 \rightarrow 6) linkages. Amylopectin consists of much larger molecules ($M=1 \cdot 10^7$ – $1 \cdot 10^9$ g/mol) with a branched structure built from 95 % α -(1 \rightarrow 4) and 5 % α -(1 \rightarrow 6) linkages. Both amylose chains and exterior chains of amylopectin can form double helices which may in turn associate to form crystalline domains. The complex structure is well described by the recent review of Tester *et al.* (44). Starch in the endosperm of rice kernel has a composition of about one-third amylose and two-thirds amylopectin. The bran and the oil lower serum LDL cholesterol. Commercially, the starch granules are very fine and may be useful in other applications such as fat substitutes and rice components for sports beverages or energy bars (8). A blend of 3 % potato starch is used in the production of low-fat frankfurters and waxy starch in low-fat muffin (43).

Resistant starch (RS)

In the last decade, a new type of starch called resistant starch (RS) has been discovered. This fraction is formed upon food processing treatments and has been shown to have beneficial nutritional effects (indigestible) on humans (2). Counting RS in the group of prebiotics reflects the current tendency toward joint consideration of the physiological activity of dietary fibres and prebiotics. In the large bowel, RS positively influences the rate of fermentation of prebiotics by the colonic microflora. It is itself fermented by microflora into fatty acids. This action is accompanied by removal of secondary bile acids. RS may be divided into 4 groups: (i) seed starches that are physically inaccessible because entrapped within the whole or partly milled grains or seeds (RS1); (ii) granu-

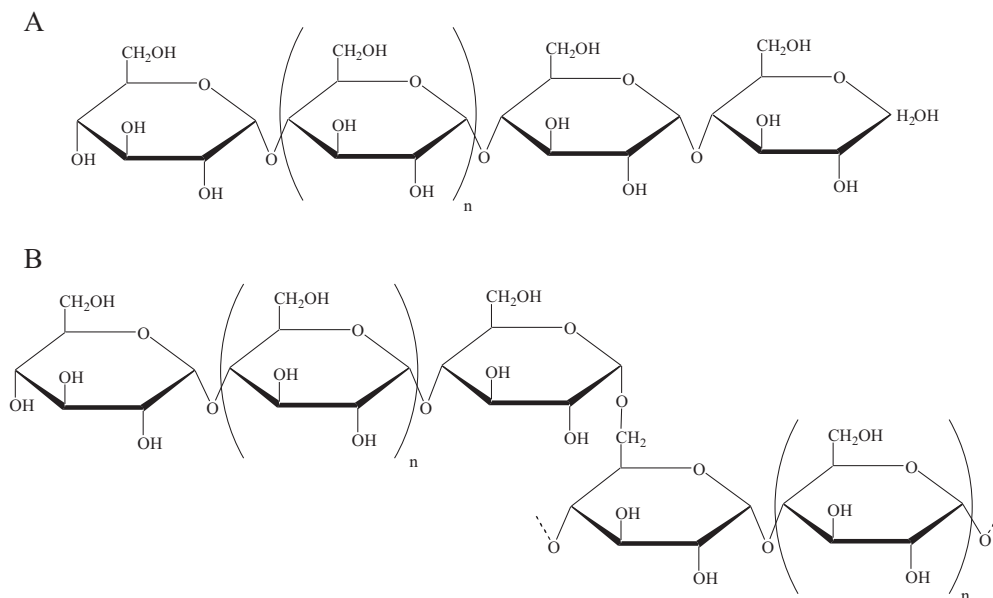


Fig. 1. Structures of starch macromolecules (A: amylose, B: amylopectin)

lar starches or crystalline region (mainly B-types), particularly high-amylose and banana starches, with a resistance depending on tendency of swelling (RS2); (iii) highly retrograded starches, produced either by extrusion cooking or by liberation from cereals by enzymatic digestion (RS3); (iv) chemically modified starches (45).

High-amylose corn starch is another possibility of a less-digestible starch. Its physiological properties were recognized almost a decade ago (7). Due to the long term consumption of high amylose starch, increasing the amylose levels in starch appears to lower the rate of glucose delivery in blood and the glycemic index (GI) (45). Low GI foods exhibit favourable effects on the control of diabetes and also reduce risk factors for cardiovascular diseases. It has been shown that RS may also contribute to dietary energy, growth enhancement and elevation of fat deposition (2).

Derivatized starches

Surface derivatization of starch granules is another approach for bringing in desirable property changes. The complexation of amylose by lipid molecules influences both thermal and rheological properties of wheat starch, where the leaching of amylose molecules from the granules to the water is restricted. Recently, a lot of concern has been shown by health-conscious people about reducing the dietary calorie intake to avoid complications of obesity and diabetes.

Hydrogenated starch is used in low calorie snacks and candies. Some of the starch derivatives have been increasingly used as fat replacers or fat substitutes. Treatment with stearyl-chloride has been reported to give a starch derivative with a fatty feel (mouth-feel or touch-feel likes). It creates a carbohydrate-water network that can mimic the texture of fat. They are of use as fat replacers in frozen desserts and in high-moisture systems due to their slippery mouth-feel when hydrated (salad dressings, meat emulsions, bakery products). They are either partially or totally undigested, thus contributing zero

calories to the food when eaten. Some chemically modified starches (phosphorylated starches, citrate starches) have been categorized as RS because they are nondigestible too. Oxidized starches have potentially several nutritive applications of considerable value and are useful in dietetic food (2). Fat replacers based on modified starch (hydrolyzed or substituted) can provide the finished product with the organoleptic characteristics of their fully fat counterparts. They are used in salad dressings, meat, dairy products and baked goods. The use of modified starch and also carrageenan in low-fat meat products allows retaining the soft texture, juiciness and flavour with a reduced level of fat (to limit the risk of cardiovascular heart diseases and to lose mass) (43).

Non-Starch Polysaccharides (NSP)

Algal source

Whereas numerous seaweed species have been consumed since ancient times, it is only in the late 1980s that France authorized the human consumption of some brown, red and green seaweeds as vegetables and seasonings. The fibre content of Japanese and European edible seaweeds demonstrates the richness of these plants in soluble fibres called alginate (brown seaweeds), carrageenan (red seaweeds) and ulvan (green seaweeds). Soluble and insoluble amounts of dietary fibres vary respectively from 17.2 to 58.6 % and from 4.7 to 25.6 % of the seaweed mass. The fermentation of seaweed soluble dietary fibres by human colonic bacteria has been studied and discussed separately below (46). The role of NSP in the small bowel is essentially a physical one, in which the algal cell wall acts as a barrier to the release of nutrients and thus slows their absorption (especially for starch digestion and for the control of glucose and insulin metabolisms) (23).

Alginate

Alginate is a polyuronic saccharide that is isolated from the cell walls of a number of brown seaweed species (Phaeophyta) but can also be produced from bacterial sources (*Azotobacter*). While large quantities of seaweed are eaten in Southeast Asia, the inclusion of algal phycocolloids (alginate, carrageenan and agar) as thickeners and stabilizing or emulsifying agents is the main use in the Western world (desserts, dairy, sauces, beer, fruit drinks, extruded foods). Alginate is the most widely produced algal polysaccharide, with 27 000 tonnes/year (5–20 \$/kg in the USA) compared to 15 000 tonnes/year for carrageenan and 11 000 tonnes for agar (42). Alginates are a family of unbranched copolymers of (1→4) linked α -L-guluronic acid (G) and β -D-mannuronic acid (M) pyranose residues of widely varying composition and sequential structure (Fig. 2A). They can form true block copolymers, composed of homopolymeric region of M or G blocks, interspaced with a region of alternative structure (MG blocks). The content and distribution of these uronic acids depend on the species, the growth

conditions, the age and the tissue considered in the algae. The molar mass varies between $2 \cdot 10^5$ and $1.6 \cdot 10^6$ g/mol (23). Alginate properties (viscosity and gel-forming capacities) are dependent on the molar mass and the M:G ratio (polyguluronate forms rigid gels in the presence of calcium). The gelling properties are due to their capacity to bind various divalent or multivalent cations, the most important being calcium ions (47). Their solubility depends on the pH: insoluble below 4 (precipitation) and stable between 6–9 (highly viscous solution) (23). Alginate may reduce the activity of proteases in the upper gastrointestinal tract (pepsine activity by up to 80 % and weak effect on trypsin activity). Relatively few studies have considered the effects of alginates in lowering cholesterol. Alginate supplementation (7.5 g/day, M:G=1.5) of a low fibre diet has previously been shown to more than double (140 % increase) the mean fatty acid excretion in the digesta of a small cohort of human ileostomy patients. Alginate decreases the uptake of fats in the small intestinal lumen and reduces plasma cholesterol (under zero cholesterol, low fat and high fat diets).

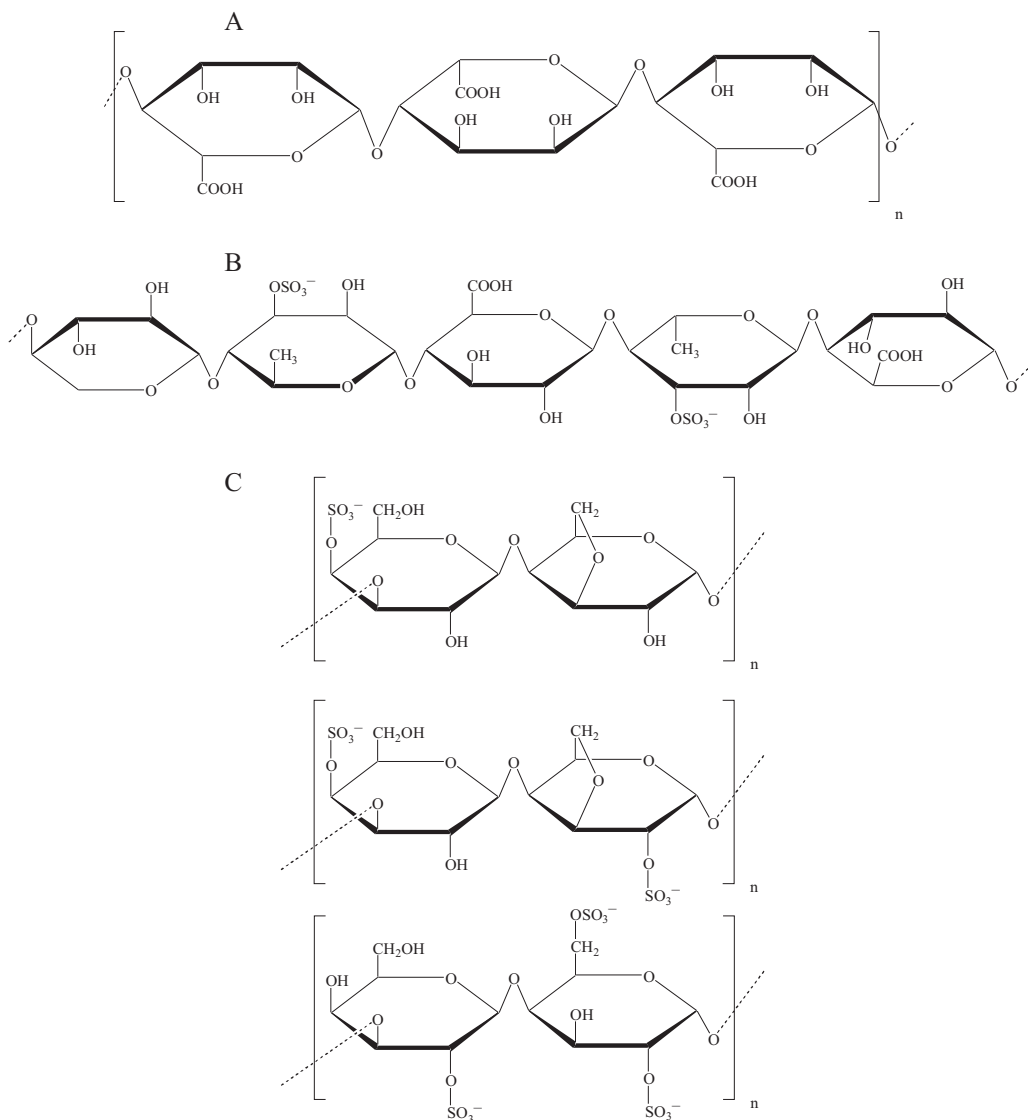


Fig. 2. Structures of algal polysaccharides [A: alginate, B: ulvan, C: carrageenan: kappa (up), iota (middle) and lambda (down)]

This is due to the increased levels of faecal bile and cholesterol excretions. They could also be of benefit in reducing the blood cholesterol levels in the general population. Na-alginate (1–3 %) was shown to have less hypocholesteremic effect (reduction in plasma cholesterol from fibre free controls of 8.5–20.5 %) than carrageenan (14.5–29.9 %). Increased G block content will lead to an increased gel forming capacity of the alginate, which would be expected to reduce intestinal absorption. Alginate causes a reduction in blood peak glucose and plasma insulin rises in diabetes patients (by 31 and 42 %, respectively). Similar results were found with healthy nondiabetic human subjects. Alginate may therefore reduce the likelihood of the onset of diabetes type II and/or obesity and possible cardiovascular disease as well as reduce systemic risk factors in patients with these diseases. It may also reduce hypertension in a high fat and/or high sodium diet. Incorporation of 5 % viscous alginate to standard meals modifies both the glycemic and insulenic indices of Large White pigs (23). These effects were attributed to the reduction in intestinal absorption and its prolongation of gastric emptying, and the inhibition of gastrointestinal proteases. Alginate can have low viscosity in liquid form and becomes a gel once it is in contact with acid in the stomach (42). Na-alginates are very little digested in the stomach and small intestine. The acidic content of the stomach converts sodium alginate to alginic acid. Sandberg *et al.* (48) have suggested an indirect role of the alginate gel through the reduction of bile acid excretion to the colon and the protection against colon cancer due to secondary bile acids acting as promoters of colon cancer (23). The reduced nutrient absorption due to alginate might suggest that the inclusion of high levels of alginate in the diet may outweigh any potential health benefits for pregnant women and infants. Alginates have been reported to adsorb a range of potential food and chemical mutagens (dioxin isomers, heterocyclic amine food mutagens), thereby not only lowering colonic exposure to these agents but also the rest of the body. They reduced accumulation of toxic pentachlorobenzenes and increased excretion of bile acids. Secondary bile acids are more damaging to the colon than primary acids, and their binding by alginate may help prevent mucosal damaging occurring in the colon. Alginate can alter the colonic microflora in term of populations (species) and the quantities of short chain fatty acids produced [even if its degradation has not been correlated with the production of short chain fatty acids (SCFA) expected from the classical metabolic pathways (46)], depending on the time and levels of alginate exposure. Faecal bifidobacteria levels increased while the number of some potentially pathogenic bacteria decreased during alginate consumption. As alginates are hydrocolloids that escape full bacterial fermentation, they are expected to greatly increase stool water content and bulk. Cellulose, pectin and gum arabic did not cause a significant increase in total colonic mucin output *vs.* controls as opposed to Na-alginate. A maximal mucus thickness and significantly higher mucus replenishment were obtained with 1 % alginate diet. Recent studies have suggested that certain alginates may enhance repair of mucosal damage in the gastrointestinal tract.

The direct adherence of calcium alginate leads to the formation of a gel over a wound. Exchange of calcium ions from the alginate gel with sodium from the plasma is believed to stimulate platelet activation and clotting at the wound site, thereby aiding hemostasis (42). Alginates stimulate interleukine (1 and 6) and TNF- α production by isolating human monocytes (47).

Ulvan

Ulvan is produced by green seaweeds *Ulva* (Chlorophyta). It is composed of uronic acids, rhamnose (sulphated or not), xylose and the disaccharide composed of \rightarrow 4)- β -D-glucuronic acid-(1 \rightarrow 4)- α -L-rhamnose-(1 \rightarrow), which is a major repeating structure [Fig. 2B: \rightarrow 4)- β -D-Xyl-(1 \rightarrow 4)- α -L-Rha-3-sulphate-(1 \rightarrow 4)- β -D-GlcA-(1 \rightarrow 4)- α -L-Rha-3-sulphate-(1 \rightarrow 4)- α -L-IduA-(1 \rightarrow)]. It is sulphated on C3 of the rhamnose residue, and the glucuronic acid can be partially replaced by iduronic acid or xylose more or less sulphated on C2. The solubility of ulvan in water is improved at higher temperatures (80–100 °C) and they cannot markedly thicken the solutions. They form weak thermo-reversible gels in the presence of boric acid and calcium at pH=7.5 (23). Ulvans are poorly or not degraded by faecal bacteria (46). Ulvan could serve as a stabilizer and promoter for the binding of growth factors to the high affinity receptors of the cells in the intestinal membrane. Those growth factors are known to be involved in the intestinal epithelial growth and repair of wounds (23).

Carrageenan

Carrageenan is produced by red seaweeds and is an alternation of 1,3-linked β -D-galactose (B) and 1,4-linked α -D-galactose (A) units. In most cases (not for lambda type), this last sugar (A) occurs as 3,6-anhydro- α -D-galactose and the repeating disaccharide is referred to as carrabiose (Fig. 2C). Three types of carrageenans are commercially available as thickening and gelling agents for the food industry: kappa- (KC), iota- (IC) and lambda (LC) carrageenans. They differ in the position of a sulphate group as substituent. KC is mainly built on kappa-carrabiose repeating units sulphated on C-4 of the 1,3-linked sugar (49). Commercial carrageenans have a molar mass between 10^5 and 10^6 g/mol. They are soluble in water but it depends on the type and concentration of ions that are present in the solution or as counter-ions (because they are polyelectrolytes). This solubility is favoured by high temperatures (80–100 °C). KC and IC form thermo-reversible gels in the presence of ions (K^+ and NH_4^+ for KC, Ca^{2+} for IC) or in association with proteins (23). Carrageenans are not metabolized in the colon. Those anionic algal soluble fibres, with ulvan, will be present in the colon unmodified and will potentially be in contact with the epithelial cells of this organ and affect the biology of the colonocytes (46). IC favours the proliferation of large intestinal mucosa (23). IC is recommended for use in the formulation of low-fat meat products because it forms an elastic and clear gel with calcium, displays a stability in regard of freeze-thawing, increases water-holding ability and cold solubility. All types of carrageenan are used in low-fat frankfurter sausages, beef burgers and beef patties (43).

Bacterial source

A number of bacterial exopolysaccharides (EPS) have industrial applications as gelling and emulsifying agents. Three of them have been approved as food adjuncts by the United States Food and Drug Administration: curdlan (produced by *Agrobacterium*), xanthan (produced by *Xanthomonas campestris*) and gellan (produced by *Sphingomonas paucimobilis*) (50).

Curdlan

Curdlan is a neutral, essentially linear (1→3)-β-glucan which may have a few intra- or inter-chain (1→6)-linkages (Fig. 3A). Curdlan’s unusual rheological properties among natural and synthetic polymers underlie its use as a thickening and gelling agent in foods. Apart from being tasteless, colourless and odourless, the main advantages are that in contrast to cold-set gels and heat-set gels, the heating process alone produces different forms of curdlan gel with different textural qualities, physical stabilities and water-holding capacities. Gels of variable strength are formed depending on the heating temperature, time of heat-treatment and curdlan concen-

tration. In most food applications, curdlan is used in the high-set, thermo-reversible gel form and is stable during retorting, deep-fat frying and cycles of freeze-thawing. Curdlan gels have been used to develop new food products (freezable tofu noodles) and calorie-reduced food, since there are no digestive enzymes for curdlan in the upper alimentary tract and curdlan can be used as a fat-substitute. The safety of curdlan has been assessed in animal studies and *in vitro* tests and it is approved in food use in Korea, Taiwan and Japan as an inert dietary fibre. It is registered in the USA as a food additive (50). When feeding rats with curdlan, the caecal mass increased significantly, as the amount of SCFA and lactic acid in the caecal content (51). The significant increase in the mass of the caecum was accompanied by a decrease in faecal mass. The transit time of the gastrointestinal tract was extended by curdlan supplementation (52). Significant decrease was observed in the total hepatic cholesterol and low values were measured in the proportion with secondary bile acids. All those parameters revealed that curdlan is easily degraded and fermented by intestinal bacteria in the caecum and lowers cholesterol concentration in the liver (51).

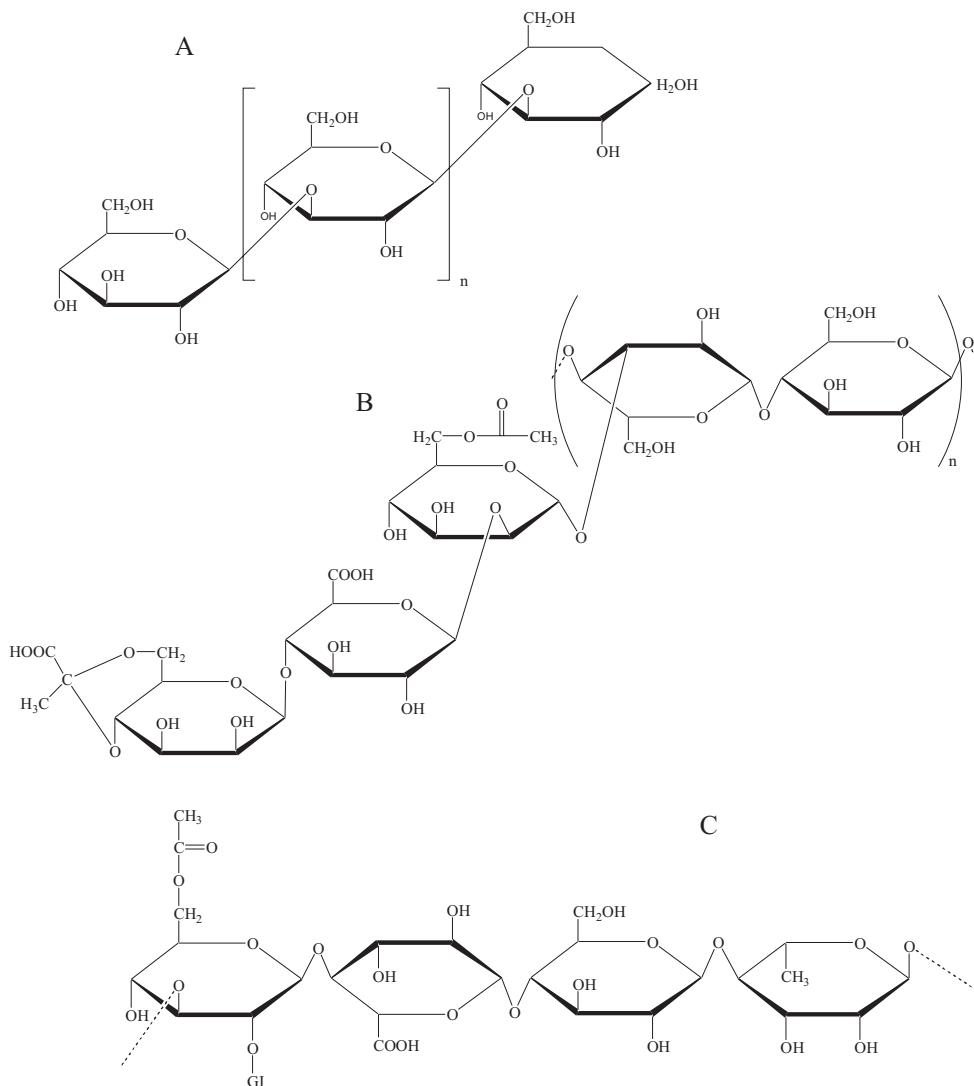


Fig. 3. Structures of bacterial polysaccharides (A: curdlan, B: xanthan, C: gellan)

Xanthan

Xanthomonas campestris is a plant pathogenic bacterium that produces the exopolysaccharide xanthan. Xanthan has attracted particular attention because it has found many applications as a thickener and emulsifier (salads and dressings, ice cream, frozen foods, jams, sauces, syrups, beer) as a result of its unique rheological properties in industrial food sector (53). Xanthan is an acidic polymer made up of pentasaccharide subunits, forming a cellulose backbone with trisaccharide side chains composed of mannose- β -(1 \rightarrow 4)-glucuronic acid- β -(1 \rightarrow 2)-mannose attached to alternate glucose residues in the backbone by α -(1 \rightarrow 3) linkages (Fig. 3B). On approximately half of the terminal mannose residues a pyruvic acid moiety is joined by a ketal linkage. Acetyl groups are often present as 6-O substituents on the internal mannose residues. Some external mannoses contain a second 6-O acetyl substituents. The levels of pyruvate and acetyl substitution vary with bacterial growth conditions and other parameters. It is already a well-established product (10–20 000 tonnes/year) with more than 1600 patents on production and applications only in the USA. Xanthan is approved by the USFDA and EU for food use. Solutions of xanthan have high viscosity at low concentrations and are pseudoplastic. Xanthan is insensitive to a broad range of temperature, pH and electrolyte concentrations. It is mainly added as a stabilizing, thickening, gelling and emulsifying agent in the food industry (beer, cheese, ice cream, sauces, juice drinks, salad dressings and bakery fillings) (54). The study of Osilesi *et al.* (55) reports the action of xanthan against diabetes mellitus. Mixtures of xanthan with guar gum and locust bean gum demonstrated improved effects and are described elsewhere (56). Experiments made with xanthan alone showed a postprandial serum glucose lowering but with fewer effects than other dietary fibres such as wheat bran or resistant starch (retardation of glucose diffusion, adsorption of glucose to prevent its diffusion, inhibition of the activity of α -amylase) (57).

Gellan

Gellan is produced by *Sphingomonas paucimobilis*. It is a linear anionic heteropolysaccharide based on a tetrasaccharide repeat unit composed of two molecules of D-glucose, one of L-rhamnose, and another of D-glucuronic acid. The native gellan is partially esterified. The 1,3-D-Glc residue can be linked to L-glycerate at C2 and/or to acetate in C6 (Fig. 3C). It has approval in the USA and EU for food use as a gelling, stabilizing and suspending agent, either alone or in combination with other hydrocolloids (58). It yields very clear and strong gels (53). It is produced and marketed by some companies under trade names such as »Gelrite«, »Phytigel« and »Kelcogel« (59). Study in rats demonstrated that gellan shortens the gastrointestinal transit time, in that way promoting evacuation. The caecal mass diminished (52), but the serum total cholesterol concentration and the HDL cholesterol were not affected by the gellan diet (51).

Plant source

Cereal grains and β -glucans

Whole grains are traditionally used in nutrition as carriers of fibres in addition to other molecules (vitamins, microelements, *etc.*). In the past 30 years, numerous stu-

dies have documented a beneficial role in controlling blood pressure, arterial health and insulin level. Their proper use may also facilitate mass loss. Even if cereal products were not considered as prebiotics, they have been recommended recently as healthy food for their strong hypocholesterolemic properties. The fat replacer OatrimTM combines the activity of typical dietary fibres with prebiotic activity (7). The water-insoluble dietary fibre present in wheat bran is very efficient in increasing the faeces mass, while the water-soluble β -glucans, which represent a great part of the oat dietary fibre, are not (6).

The content of (1 \rightarrow 3, 1 \rightarrow 4)- β -D-glucan, commonly referred to as β -glucan, ranges from 1 % in wheat grains to 3–7 % in oats, and 5–11 % in barley. Thus, barley is a rich source of β -glucans. World production of barley in 2000/2003 was approximately 134 million metric tonnes (EU=52 Mt, Russia=25 Mt, Canada=13 Mt). The barley crop may be considered relatively under-utilised with regard to its potential use as an ingredient in processed human foods. Recent attention has focussed on the potential use of β -glucan as functional food ingredient. Oats have been linked to the health claims attributed to the use of β -glucans and are a valuable source of β -glucans, as barley, because they are the predominant components of cell walls of these cereal grains. In the linear β -glucan chain, the (1 \rightarrow 3)-linkages occur singly whereas the (1 \rightarrow 4) are found mostly in sequences of 2 or 3 (Fig. 4A). Hence, the molecules may be regarded as being composed of (1 \rightarrow 3)- β -linked cellotriosyl and cellotetraosyl units. Oat β -glucans generally have an upper M (0.065–3 \cdot 10⁶ g/mol) compared to barley (0.15–2.5 \cdot 10⁶ g/mol). Much more recent interest in the use of β -glucans in food systems has stemmed from their use as a functional dietary fibre (41). A lot of research has been done on the role of oat β -glucan, a viscous soluble polysaccharide, which may reduce cholesterol in hypercholesterolemic patients, thereby reducing the risk of heart disease. Rolled oats, oat bran and other products have sufficient β -glucans to be beneficial to health. Wheat bran contains insoluble fibres, which have been recognized for stimulating regularity and prevention of constipation by increasing faecal bulk. Prevention of colon cancer remains controversial but appears more effective with wheat bran than with other types of fibre (8). β -glucans have been shown to reduce serum cholesterol levels (total and LDL-cholesterol). The physiological responses appear to be affected by solution concentration and the molar mass of glucan. The mechanism is still not clear, although the role of viscosity alteration in digesta is important because it increases intestinal viscosity, which may decrease the absorption of cholesterol and the reabsorption of bile acids. Inclusion of oat β -glucan into breakfast cereals, even at low levels (below 5 %), could reduce the postprandial glycaemic response by up to 50 %. This response appears to be dose-dependent. Increased amounts did not show large reductions (saturation point). β -glucans (2.5–5 %) have also been used in other cereal based food systems such as bread. Significant reductions in starch degradation and sugar release were demonstrated proportional to the amount of β -glucans incorporated into the breads. The ability of β -glucans to influence the rate of starch degradation and hence the glycaemic index of foods has

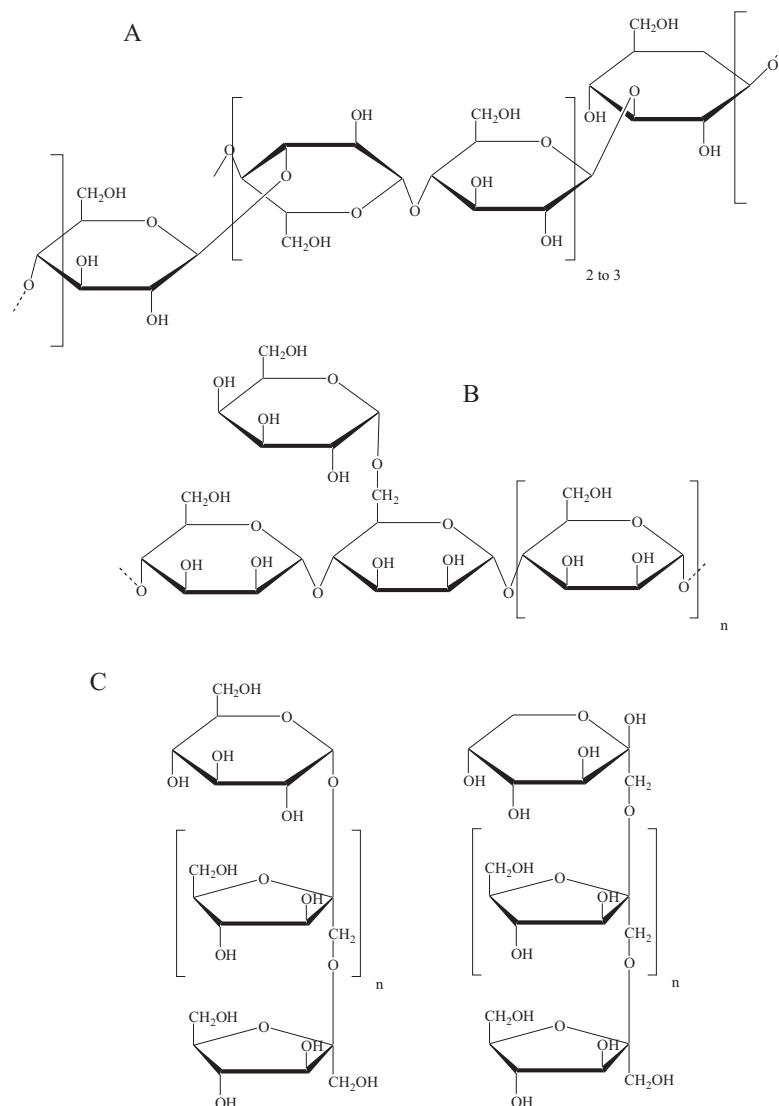


Fig. 4. Structures of plant polysaccharides (A: β -glucan, B: galactomannan, C: inulin [$G_{pyr}Fn$ (left) and $F_{pyr}Fn$ (right)])

obvious benefits with regard to obesity and diabetes. Thus blood glucose levels of diabetic and prediabetic individuals can be moderated by using food rich in β -glucans. According to the FDA, the use of dietary fibre containing oat β -glucan reduces the glycemic and cholesterol responses of individuals. They recommended 3 g/day of β -glucan to have a nutritional effect and 30–35 g/day of dietary fibre by the American Dietetic Association. Oatrim™ is an oat β -glucan concentrate which reduced glycemic responses in men and women, but is less effective than the Nutrim™ from the barley β -glucans in the regulation of glucose and insulin responses (41). β -glucans have also been shown to stimulate immune responses by the alteration they cause in the colonic microflora or the alteration in SCFA production by the microflora (42).

Galactomannans

Galactomannan gums can often be used in different forms and functions (gelling, thickening, emulsifying) for human consumption. The gums vary from each other in different Man/Gal ratios. They are long chain molecules

composed of β -(1 \rightarrow 4)-mannose backbone with galactose molecules attached at C6. Within this family of molecules, fenugreek galactomannan (*Trigonella foenum-graecum* L.) is unique and possesses a ratio of galactose to mannose molecules around 1:1. Other sources of galactomannan, guar gum (*Cyanopsis tetragonoloba*) and locust bean gum (or carob from *Ceratonia siliqua*) have ratios of 1:2 and 1:4, respectively (Fig. 4B) (60).

Fenugreek, also known as Greek hay, is a member of the pea family. In addition to culinary use, fenugreek has a long history of use as a herbal medicine. Fenugreek is a very high dietary fibre (50 %) of which 15 to 20 % is galactomannan. In literature, the galactomannan fraction is often referred to as gum. Many studies have demonstrated fenugreek's ability to lower blood sugar levels. Ground fenugreek (15 g) mixed with water was shown to lower postprandial blood glucose levels in type II diabetic subjects. It has also been demonstrated that the hypoglycemic effect of fenugreek is largely due to the galactomannan fraction, which was confirmed by recent studies performed with a standardized fenugreek galactomannan extract (Fenulife). Although the galacto-

mannan is a major factor, researchers believe that it is not the only component of fenugreek with hypoglycemic benefit. Fenugreek galactomannan can form a gel in the stomach when consumed, which increases the viscosity of stomach contents. This slows gastric emptying (satiety feeling due to the viscosity) and delays the absorption of glucose in intestines. As a result it decreases the rise in blood sugar following a meal. Conversely, galactomannan has a potential to promote mass loss, through its effect as a soluble fibre. Delayed nutrient absorption, particularly of glucose, can reduce the glycemic index (GI) of the consumed food. Low GI meals have been associated with feelings of satiety in studies. The fibre content of fenugreek may contribute positively to the mass loss plan by helping individuals feel satiated longer after a meal, allowing them to control food intake. Other potential health benefits of fenugreek galactomannan include improved cholesterol health and gastro-protective effects. Fenugreek galactomannan has been reported to inhibit bile acid absorption, leading to lower cholesterol levels. It is thought that the galactomannan may form a gel layer on the surface of stomach cells that protects against damaging compounds. While the fenugreek galactomannan extract reduced glycemic response at low doses, neither psyllium husk powder or oat bran concentrate have an effect at the same dosages. The efficacy of a galactomannan depends on its ability to bind water and create viscosity in the digestive tract. This property varies with the size of galactomannan. Fenugreek galactomannan was more resistant to enzymatic degradation, staying more intact than either locust bean or guar gum. This test suggests that fenugreek galactomannan will have a more sustained water binding capacity throughout the digestive tract and will thus be able to exert health effects to a greater extent (61).

Guar gum (GG) is one of the most viscous galactomannans that is not digested in the mammalian small intestine and is particularly effective in exerting a hypocholesterolemic effect. GG possesses effects on the glucose metabolism in humans with diabetes mellitus. GG has been used successfully for the treatment of hypercholesterolemia, however, clinical application has not become widespread because a large amount of GG is unpalatable (56). In addition to this capability to control the blood glucose, guar gum is used for controlling the body mass or energy balance (43). Although guar has these positive benefits, its high viscosity makes it difficult to incorporate into food products. On the contrary, after enzymatic hydrolysis a partially hydrolyzed guar gum (PHGG) can be produced with a smaller M and less viscosity (62). They presented prebiotic activities and increased production of *Bifidobacterium* in the gut. They have been used in cereals, juices, shakes, yogurt, meal replacements, soups and baked goods and as a fibre source in enteral nutrition products.

Inulin

A wealth of information exists regarding the significance of inulin-type fructans, such as chicory inulin and oligofructose in modulating various functions of the human body. Targets for their effects include the colonic microflora, gastrointestinal physiology, immune function, bioavailability of minerals, lipid metabolism and

gastrointestinal tract health. Potential human health benefits resulting from their ingestion include reduction of risk of colonic diseases, insulin-independent diabetes, obesity, osteoporosis and cancer. Inulin is a blend of fructan chains found widely distributed in nature as plant storage carbohydrates. They are present in more than 36 000 plant species (63). Most of the commercial inulin is extracted from chicory roots or Jerusalem artichoke (64). Inulin is a polydisperse β -(1 \rightarrow 2) fructan (Fig. 4C). A glucose molecule typically resides at the end of each fructose chain and is linked by α -(1 \rightarrow 2) bonds as in sucrose. The chain lengths of these chicory fructans range from 2 to 60 residues with an average degree of polymerization (DP) of 10 but the average DP is much dependent on the plant source and the moment of harvesting this plant. In native inulin, most of the plants have a terminal glucose unit [GF(n)] but a small fraction [F(m)] does not contain any glucose units at all (65). The specific linkage prevents inulin from being hydrolytically digested in the upper part of the gastrointestinal tract (66) making it available for fermentation to SCFA by the intestinal bacteria in the colon. The colonic microflora is of crucial importance to any consideration of the role of feed ingredients in health and disease because many physiological effects of such compounds influence their activities. Prebiotics are nondigestible food ingredients that selectively stimulate growth and/or activity of potentially health-enhancing intestinal bacteria. Inulin has the ability to modify the composition of the intestinal flora (*i.e.* by increasing the number of bifidobacteria) and its metabolic activity in the large intestine. Prebiotic oligosaccharides such as inulin are fermented in the colon where they promote the growth of bacterial populations associated with a healthy, well-functioning colon. This selective stimulation occurs because oligosaccharides are readily fermented by beneficial types of colonic bacteria (bifidobacteria, lactobacilli and eubacteria) and are not used as effectively by potentially pathogenic bacteria species which cause diarrhea and produce ammonia, amines, indoles and phenols (staphylococci, *Salmonella*, *Listeria*, *Shigella*, *E. coli*). Bifidobacteria have been shown to inhibit pathogenic bacteria *in vivo*. They control the growth of invasive or otherwise harmful bacteria. Shifts in composition of the microflora (bifidobacteria in faecal samples increased) appear in humans fed with inulin (doses between 5 and 20 g/day over 15- to 65-day period). With increasing the chain length (*i.e.* long chain chicory inulin with average DP=28), the fermentation rate decreases (twice more slowly than the oligofructose), but qualitatively the modification of the composition of the intestinal flora is similar (bifidogenic). Inulins are fermented in the large intestine and therefore have properties similar to dietary fibre. Degradation of the longer chains will be slower which results in their arrival into more distal parts of the intestine. Despite their common properties with higher molar mass dietary fibres, they are not recovered during classical fibre analysis because of their relatively low molar mass and solubility in water and alcohol. Inulin and oligofructose do not result in long-term effects. They must be consumed on a regular basis in order to be effective. In a long-term study (over 2 months) with human volunteers, it was shown that as long as oligofructose or inulin is consumed

the bifidogenic properties persisted (63). Van Loo *et al.* (67) reported that inulin in common foodstuffs and garlic appears to contain the greater concentration of fructan (0.98–1.60 mg/g). However, inulin is present with oligofructose in significant amounts in a wide variety of common foods and food ingredients like confectionery, fruit preparations, milk desserts, yogurt and fresh cheese, baked goods, chocolate, ice cream and sauces (64).

Experiments with animals revealed that diets containing either inulin or resistant starch (5–20 %) improve the uptake of calcium, iron and zinc. On the other side, inulin stimulates absorption of calcium in humans. Rats supplied with inulin at a level of 10 % in the diet showed a decrease in the level of triglycerides and cholesterol after a meal. However, relevant data in healthy people are equivocal. At a daily intake of 10 g of inulin neither decreases in triglycerides and cholesterol nor changes in blood lipid level were observed. Significant decreases in total cholesterol and LDL cholesterol, for unclear reason, were observed in patients with hypercholesterolemia at an inulin supply of up to 18 g/day. This might result from a decrease of the activity of lipogenic enzymes of the liver. In rats, inulin also inhibited production of carcinogenic sialomucins and stimulated synthesis of anti-carcinogenic sulfomucins. Inulin improves colonic action because facilitation of defecation is achieved by osmotic increase in the volume of the stool. Inulin is already present in the market as prebiotic with probiotics in different yogurts (7) or dressings (3).

Pectin

Few studies have demonstrated the effect(s) of pectin molecules alone whereas several have reported some impacts but in mixtures with other polysaccharides. Brownlee *et al.* (42) described that pectin had a greatest effect in lowering total cholesterol levels per gram of four common viscous fibre sources (reduction in 70 μ M/L plasma/g fibre) such as oat, psyllium and guar gum. These effects appeared to be almost entirely due to a reduction in LDL cholesterol rather than HDL cholesterol. Pectin and carrageenan have been applied successfully to the development of low-calorie foods, especially soft drinks, jams, jelly, confectionary, dairy and meat products (43).

Cellulose

Microcrystalline cellulose (MC), constituted of long chains of β -(1 \rightarrow 4)-glucose, is a multifunctional ingredient that can be used in low-fat/calorie foods to enhance sensory properties. The size of crystallites is 0.2 μ m and they provide the creamy mouth-feel of fat in oil-in-water

emulsions. The beneficial functions of MC in the formulation of low fat products are emulsion stabilization, control of water mobility, formation of ice crystals, viscosity increase, suspension of solids and heat stability. Therefore, their applications are in bakery products, confectionery and dairy products, salad dressings, frozen desserts and beverages (43).

Animal source

Of the truly abundant polysaccharides in nature, only chitin has yet to find utilization in large quantities. Chitin is the second most abundant natural biopolymer derived from exoskeletons of crustaceans and also from cell walls of fungi and insects (68). Every year, about 5 to 100 billion tonnes of chitin are produced by crustaceans, molluscs, insects and fungi. Chitin is the most under-exploited biomass resource available on earth, even after it had been approved by USFDA as food additive in 1983 (69). It is a cationic aminopolysaccharide essentially composed of *N*-acetyl-D-glucosamine (GlcNAc) residues (5000 to 8000 in crab; 100 only in yeast due probably to chitin degradation during deproteinisation process) linked β -(1 \rightarrow 4) (Fig. 5). Depending on the polysaccharide source and isolation conditions, chitin has a different degree of acetylation. In native chitin, as many as one in 6-*N*-acetyl-D-glucosamine residues is deacetylated (68). Chitosan, a copolymer of 80 % D-glucosamine (GlcN) and 20 % *N*-acetyl-D-glucosamine units is a product derived from the *N*-acetylation of chitin in the presence of hot alkali. Chitosan represents in fact the family of *N*-acetylated chitins soluble in acidic conditions. The molar mass of these polysaccharides can be as high as 10⁶ g/mol. The degree of *N*-acetylation and the DP are the two important parameters dictating the use of chitins for various applications. Generally, they have an α -linear structure. Mostly, individual chains are arranged together in anti-parallel fashion. Due to the availability of reactive free amino-groups, chitin/chitosan molecules tend to associate *in situ* with several other (macro-) molecules and give rise to new types of structures and physicochemical characteristics. Chitosan is amenable for a variety of chemically modified derivatives that find widespread utilisation in many applications among which in the food and agriculture field. It has the properties to bind anions at low pH (bile acids or free fatty acids) allowing it to be used in reduction of lipid absorption or as an anti-gastritis, a hypocholesterolemic, an anti-carcinogenic or an anti-ulcer agent and a dietary fibre (70). Thus, Japan produces dietary coolies, potato chips and nood-

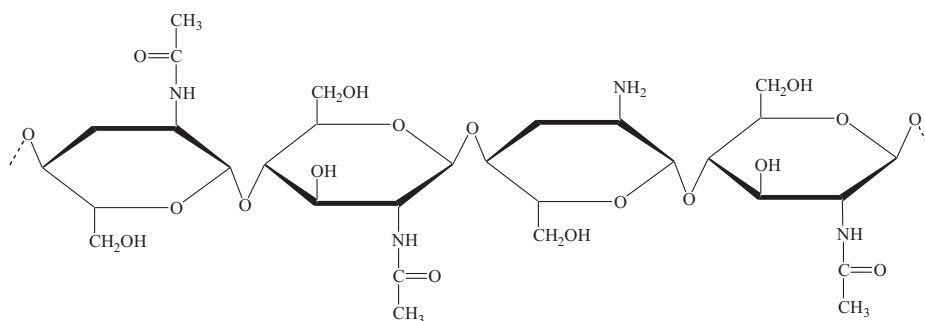


Fig. 5. Structure of the animal polysaccharide used as dietary fibre (chitin)

les enriched with chitosan because of its hypocholesterolemic effect (69). In fact, in the intestines, chitosan precipitates in the form of those complexes created (through ionic interactions) with fatty acids, bile acids, cholesterol and lipids. Then, they are excreted into the faeces decreasing the availability of bile acids (68). Although the use of chitin and chitosan in processed food is currently limited, valuable by-products of chitinous polymers (from crustaceans for example) have been identified and associated with numerous possible food applications (as additive) such as for example: texture controlling agent, emulsifying agent, thickening and stabilizing agent, food mimetic, *etc.* (69). These biopolymers offer the possibility in the production of value-added food products with for example the preservation of food products from microbial deterioration. The growing demand for foods without chemical preservatives has focussed efforts in the discovery of new natural antimicrobials. The USFDA has approved chitosan as food additive. Chitosan is used as a food quality enhancer in Japan, Italy and Norway. It has shown lower cholesterol and triacylglycerol values in animal fed with chitin or chitosan (2 %) (rabbits, hens, broilers). The lowering of cholesterol was attributed to enhanced reverse cholesterol transport in response to intestinal losses in dietary fats (70). Chitin has also enhanced the growth of bifidobacteria in the guts of chicken, which are important as they inhibit the growth of other types of microorganisms (68). The use of chitin as a functional food ingredient has been reported in bread dough fermentation. Chitin shows most of the criteria of dietary fibre: indigestibility in the upper gastrointestinal tract, polymeric nature and high water-binding properties leading to high viscosity (responsible for the hypocholesterolemic potential of chitin) (69). Chitosan may have a small effect on body mass of approximately 1.7 kg of loss in short-term treatment of overweight and obesity (4). The binding of bile or fatty acids made them escape the hydrolysis by lipase promoting their excretion including cholesterol, sterols and triacylglycerols. Moreover,

inside the digestive tract, chitosan forms micelles with cholesterol resulting in the double decrease of the absorption of dietary cholesterol and circulation of cholic acid to the liver. This implies the synthesis of cholic acid in the liver (from cholesterol), which tends to decrease the blood cholesterol concentration at a dose of 3–6 g/day (70,71). On the contrary, some studies have demonstrated that a long term intake of chitosan especially in high amount, may have deleterious effect on growth (71). This supports the need of additional research on these health properties and also on the possible detrimental aspects.

Conclusion

Polysaccharides are widespread macromolecules that can provide »healthy« properties in addition to the traditional nutritional aspect. Those functional properties, summarized in Table 2, include their ability to be used in food products as fat replacers, dietary fibres or prebiotics. Nowadays, dietary fibres are by far the most underexploited and promising field. This lack of exploitation is probably due to the recent discoveries of those physiological activities, such as prevention of cancers or obesity and diminution of cardiovascular diseases, of which the mechanism of action is still not well explicated. Hypotheses (and debates) continue, as to the viscous origin of those properties, but no correlation has been done yet. Moreover, the diversities in the origins (plant, animal, algal, bacterial), physicochemical (soluble or not, various viscosity levels) and structural (size, global charge, three-dimensional configuration) properties of the polysaccharides presented in this review tend to highlight that the viscosity is not the only cause of their action. The need to diminish public health problems as obesity and cardiovascular diseases accompanied by the tremendous increase of the consumer's demand for functional food products will certainly accelerate the development of studies on that subject. In a more industrial

Table 2. Health-effects induced by polysaccharides (actually demonstrated)

	CL	FS	PA	RFA	GL	REA	AM	SF	BPL	SIR	IWR
Native starch	X	X									
Starch derivatives		X	X	X	X						
Alginate	X		X	X	X	X	X	X	X	X	
Ulvan											X
Carrageenan										X	X
Curdlan	X	X	X					X			
Xanthan					X						
Gellan											
β -glucans	X		X		X				X	X	
Galactomannans	X		X		X			X			
Inulin	X		X		X	X					
Pectin	X				X						
Cellulose		X									
Chitin	X		X	X							

CL: cholesterol lowering; FS: fat substitute; PA: prebiotic activities; RFA: removal of fatty acids; GL: glucose lowering; REA: reducing enzyme activity in the upper gut; AM: absorption of mutagens; SF: satiety feeling; BPL: blood pressure lowering; SIR: stimulation of immune response; IWR: intestinal wound repair

aspect, the diversity of the »healthy« polysaccharides will allow the development of a wide range of functional applications (textures, mouth-feel, etc.) and make them one of the biggest potential of the next decade.

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