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Plant Cell Wall Polysaccharides: a Commentary on their Role as Agents for Food Structure and for Health†

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Abstract

The plant cell wall protects cells, provides structural support, assists with regulation of growth and provides a mechanism for cells to adhere to and communicate with each other. In plants eaten as food, the cell wall contributes texture and mouthfeel, and is a barrier which, when broken, allows flavours and moistness to be released and perceived in the mouth. The functional properties of polysaccharides that enable them to provide structural support around a cell also make them attractive hydrocolloids for improving texture, sensory and nutritional qualities of food. Isolated pectin, cellulose (modified) and a range of structural and storage polysaccharides (including galactomannans, glucomannans, xyloglucans) located in the cell walls of land plants can provide mouthfeel, viscosity, stabilisation, pouring properties and assistance in manufacture. They achieve these effects through interactions with water as well as their capacity to form gels through self-association or through inter-polymeric relationships. These same properties also determine their usefulness as non-digestible dietary fibre. In this review, we will outline the uses and functions of isolated land plant cell wall polysaccharides added to food products as ingredients to improve texture, and also summarise what is currently known about the mechanisms underlying the health benefits they provide as dietary fibres.

Keywords: cellulose, dietary fibre, food, gelation, hydrocolloids, mannans, pectin, viscosity, stabiliser, thickener

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Introduction

Polysaccharides originating from plant cell walls play an important role in the food we eat. For edible plants (fruit or vegetables), the condition of the polysaccharides in the cell wall makes a large contribution to texture and mouthfeel, whether eaten fresh or processed in some way to promote edibility (Kunzek et al., 1999; Sila et al., 2008; Toivonen & Brummell, 2008). Cell walls from fruit, vegetables and cereal grains are also the main source of non-digestible fibre in the human diet.

The gelling and thickening characteristics of plant cell wall-derived polysaccharides have led to their

increasing use as ingredients in food. Isolated pectin, cellulose and a range of structural and storage polysaccharides located in the cell walls of plants are proven additives that can, separately or in combination, provide mouthfeel, viscosity, pouring properties and assistance in manufacture. Isolation of these polysaccharides and chemical modification of their properties has led to a multi-billion dollar production industry that supplies food manufacturers world-wide.

A relatively new use of cell wall polysaccharides as ingredients is their addition *in toto* into prepared foods

to increase the dietary fibre content. These additions are not made with the aim of improving sensory or manufacturing qualities (although this may be an added benefit), but are mainly for improving the health quotient of foods. This takes advantage of the fact that all plant cell wall polysaccharides are indigestible in the human digestive system and are considered to be 'dietary fibre'. Cellulose and some associated hemicelluloses are insoluble and contribute bulk and water-binding properties to digesta, while most pectins and glucans can be solubilised and are fermentable by gut flora, also providing an array of health benefits. Health professionals currently advocate increased intake of dietary fibre to alleviate, or at least slow, the onset of many diet- or lifestyle-related diseases, and the addition of plant cell wall-based fibre to prepared foods is one way to achieve this.

This commentary will cover the uses and functions of isolated cell wall polysaccharides added to food products as ingredients to improve texture or as health-beneficial dietary fibre additives. We have restricted the scope to those polysaccharides that are sourced directly from land plants, rather than similar polysaccharides that are deliberately produced or engineered from bacteria, and those obtained from marine plant cell wall polysaccharides, both of which are also highly valuable and widely used in the food industry. There are a number of useful comprehensive textbooks available summarising the extraction, modification and application of polysaccharides for food, and all devote considerable space to those polysaccharides of land plant origin. These are listed in Table 1.

Food Ingredients from the Cell Wall: Their Role *in planta*

Structural wall polysaccharides in land plants

Depending on the source, the primary cell wall of land plants consists of three main groups of polysaccharides: (i) microfibrillar cellulose; (ii) non-crystalline polysaccharides with a high proportion of α -(1 \rightarrow 4)-linked galacturonic acid (termed pectins); and (iii) mainly neutral non-crystalline hemicelluloses which are polysaccharides of mixed residue and branching composition. The proportions of these three polysaccharide fractions can vary between species, and walls can be divided into Type I and Type II groups (Carpita & Gibeaut, 1993) dependent on their relative proportions. Type I walls are rich in pectin and the hemicellulose xyloglucan (typical of dicotyledons, non-graminaceous monocotyledons and gymnosperms) whereas Type II walls have little pectin and comparatively more hemicellulose, particularly glucuronoarabinoxylan and mixed-linkage glucans (typically found in cereals and grasses). Along with this general classification, there are variations in wall composition that are associated with specialised cell types and tissues of different organs within the plant. Direct visualisation techniques with polysaccharide epitope-specific antibodies have revealed a wide range of polysaccharide arrangements in cell walls, reflecting cell and polysaccharide functionality (reviewed by Knox, 2008).

TABLE 1: Comprehensive texts summarising the extraction, modification and application of polysaccharides in food.

Title	Editor	Year Published	Publisher
<i>Food Gels</i>	P. Harris	1990	Elsevier Applied Science, London, UK
<i>Industrial Gums: Polysaccharides and Their Derivatives</i> (3rd Edition)	R. L. Whistler & J. N. BeMiller	1992	Academic Press, San Diego, USA
<i>Food Polysaccharides and Their Applications</i> (1st Edition)	A. M. Stephen	1995	Marcel Dekker, New York, USA
<i>Polysaccharide Association Structures in Food</i>	R. H. Walter	1998	Marcel Dekker, New York, USA
<i>Gums and Stabilisers for the Food Industry 11</i>	P. A. Williams & G. O. Phillips	2002	Special Publication, Royal Society of Chemistry, Cambridge, UK
<i>Food Polysaccharides and Their Applications</i> (2nd Edition)	A. M. Stephen, G. O. Phillips & P. A. Williams	2006	CRC Press, Boca Raton, USA

Cellulose microfibrils form a network quite distinguishable from the other polysaccharides in the wall. Because strong hydrogen bonds form between the long chains of cellulosic β -(1 \rightarrow 4)-linked glucose units immediately after synthesis, cellulose exists as microfibrils with an inner crystalline core that is impenetrable to water. Cellulose is, therefore, highly insoluble under normal conditions, and the strong reagents required to solubilise it can cause a loss of crystallinity or molecular size.

In planta, pectin and hemicellulose polysaccharides also exist in an insoluble state but unlike cellulose they do not self-associate quite so strongly. Although insoluble, these polymers are hydrated and form a concentrated gel-like wall matrix. There are three basic groupings of pectin: homogalacturonan (HGA), rhamnogalacturonan I (RG-I) and rhamnogalacturonan II (RG-II) (Willats et al., 2001; Willats et al., 2006; Mohnen, 2008). homogalacturonan contains only α -(1 \rightarrow 4)-linked galacturonic acid residues which may be methoxylated at O-6 (creating an ester functional group), and may be acetylated at O-2 or O-3. The frequency and arrangement of the ester groups along the main galacturonan backbone is significant for wall cohesion. If there are continuous stretches of unesterified residues (at least 30 residues) then inter- or intra-chain association can occur through shared interaction with calcium ions. A galacturonan with xylose substitution, termed xylogalacturonan, has also been identified (Schols et al., 1995).

Rhamnogalacturonan I is a branched domain of pectin thought to be glycosidically linked to HGA, although the possibility has been raised that HGA could be better considered a side-chain of RG-I (Vincken et al., 2003). The typical structure of RG-I is a backbone of alternating galacturonic acid and rhamnose units, with the rhamnose being the site of side-branches of varying lengths consisting of galactose, arabinose or a combination of the two. The side branches themselves may also be branched.

Rhamnogalacturonan II is a small domain consisting of a nine-membered galacturonan backbone substituted with 11 different sugar residues, in a highly conserved branching pattern. While only a small motif, RG-II can dimerise through borate esters, therefore creating sites of interpolymeric association which are critical for plant growth (O'Neill et al., 2004).

The hemicelluloses of plant cell walls are quite diverse, often containing more than one sugar residue type and with a plethora of linkages. Polysaccharides include xyloglucans, mannans (including gluco- and galactogluco-derivations; Melton et al., 2009), (1 \rightarrow 3),(1 \rightarrow 4)- β -D-glucans, xylans (including arabinoxylans and glucuronoarabinoxylans; Brummell & Schröder, 2009), as well as long-chain galactans, arabinans

and arabinogalactans. Arabinogalactan proteins (AGPs) consist of a highly branched carbohydrate portion composed of a (1 \rightarrow 3)- β -D-galactan backbone with (1 \rightarrow 6)- β -D-galactan side chains further substituted with arabinose and other sugars, conjugated to a diverse family of protein backbones which tend to contain a high proportion of hydroxyproline (Showalter, 2001). The structure of this carbohydrate moiety is often termed Type-II arabinogalactan.

Apart from cellulose, which is synthesised by a plasma membrane complex, the other cell wall polysaccharides are assembled in the Golgi apparatus, through the action of a range of transferases that specifically add nucleoside diphosphate-activated sugars to growing chains. Once synthesised, the polysaccharides within Golgi vesicles are released to the cell wall, where integration via polysaccharide interaction occurs (described by Fry, 2004; Farrokhi et al., 2006; Geisler et al., 2008). This assembly may take the form of self-interaction through ionic bonds (e.g. calcium-mediated junction zones in pectin), and inter-polymeric associations through hydrogen bonding or van der Waals forces (e.g. xyloglucan with cellulose). There is still debate about whether the covalent linkages that occur between polysaccharides of different types (e.g. pectin with xyloglucan; RG-II association through borate ester formation; the incorporation of RG-I and RG-II domains into HGA chains) occur inside the cell during synthesis or in the wall after synthesis. Cell wall transglycosylases, (i.e. enzymes that can break one linkage and reform this linkage at another site, such as xyloglucan endotransglycosylase), are active in the cell wall, and enable the wall to maintain its ability to be loosened in growing tissues. Other developmentally regulated changes in the wall undoubtedly occur, such as the loss of pectin ester groups through the action of pectinmethylesterase, the loss of RG-I side-branch substituents via exo-acting glycosidases, and the breakdown of polymer backbones through endo-acting hydrolases.

Storage Polysaccharides in the Walls of Land Plants

Seeds and tubers contain large quantities of carbohydrate for supporting the growth of a new germinating plant or initiated shoot. Most frequently this reserve carbohydrate is starch or fructan and is located within the cell but, in some species, storage polysaccharides are located in the cell wall. These storage polysaccharides do not contain the α -(1 \rightarrow 4)-linked glucose typical of starches, nor fructose in any form, but tend to have hemicelluloses such as mannans (especially galacto- or gluco- derivatives), mixed-linkage glucans and xyloglucan filling this role. Some of these seeds have been found to have polysaccharides with desirable qualities and in sufficient quantities to be of great value to the food industry.

The endosperm of some legume seeds, e.g. *Cyamopsis tetragonolobus* (guar), *Caesalpinia spinosa* (tara), *Ceratonia siliqua* [locust bean gum (LBG) or carob] and *Trigonella foenum-graecum* (fenugreek), contains large quantities of galactomannan which is used in the food industry. Galactomannan has a β -(1 \rightarrow 4)-linked mannose backbone with variable amounts of α -galactose residues linked (1 \rightarrow 6) to it. The molar ratio of mannose to galactose is species-specific, and is important in the way the galactomannan polymers interact with water and hence their value during seed imbibition, as well as their usefulness in affecting textures in foods. Key elements of the synthesis of galactomannan have been established, including identification of genes encoding enzymes responsible for the synthesis of the mannan backbone and the addition of the galactose side chains (Reid, 2000; Dhugga et al., 2004; Gidley & Reid, 2006).

The cotyledons of the *Tamarindus indica* (tamarind) seed contain large quantities of xyloglucan as a storage polysaccharide. The general structure of tamarind xyloglucan is a β -(1 \rightarrow 4)-linked glucan backbone, with three of every four glucose units substituted with xylose, and one or two of every three xylose units further substituted with galactose (York et al., 1990). Arabinose substitutions are possible (Niemann et al., 1997), although the addition of fucose to galactose substituents, a feature often present in structural xyloglucans, is not found in tamarind.

Although glucomannan is a structural component of cell walls (particularly in the secondary walls of hardwoods), it is also a storage polysaccharide in primary walls of some roots, tubers and bulbs. The tubers of *Amorphophallus konjac* (konjac) are the main source of glucomannan as a food ingredient. This linear polysaccharide of β -(1 \rightarrow 4)-linked mannose is interspersed with frequent β -(1 \rightarrow 4)-linked glucose residues with a glucose : mannose molar ratio of 2 : 3. There is acetylation at O-6, although this does not occur in a regular manner (Davé & McCarthy, 1997). The presence of acetyl groups can prevent self-association and improve water solubility. Konjac glucomannan is synthesised as chains of more than 300 kDa (Izydorczyk et al., 2005) but the synthetic pathway has yet to be determined for glucomannan either as a storage or structural component of the cell wall.

Applications in Food

Functionality of Hydrocolloids

Redgwell and Fischer (2005) described hydrocolloids as "those substances which influence the physical properties of water", being able to "swell and produce a viscous solution or dispersion when exposed to water". This means that individually or in combination, hydrocolloids can be used to change the fluid

texture of products, by binding water, or swelling and taking up space in water or solutions. Plant-derived polysaccharides fit this hydrocolloid definition and contribute to food texture and structure through their ability to aggregate, gel and bind water (Dickenson, 2003). With the exception of cellulose, plant cell wall-derived polysaccharides are readily able to act as hydrocolloids in foods, often mimicking the interaction they have in an aqueous environment of a living plant cell wall. Cellulose, however, requires physical or chemical modification to be able to act as an effective hydrocolloid.

The intra- and inter-polymeric associations that are possible for polysaccharides in an aqueous environment are influenced by molecular size and charge, as well as pH and ionic conditions, and the presence of other solutes. Added into foods, these polysaccharides are further affected by the presence of other components (especially fats and protein), as well as by variations in temperature, atmosphere and product handling.

Table 2 lists the types of roles plant-derived polysaccharides can have in food systems, and these functionalities are described further below.

An emulsifier prevents separation of two immiscible phases, such as oil and water. For a hydrocolloid to act as an emulsifier in an oil : water system it needs to be a block copolymer with a small proportion of strongly absorbing hydrophobic character (to bind to the oil droplets), and a large proportion of non-absorbing hydrophilic character (Dickenson, 2003). While many polysaccharides do have the required amphiphilic character, they are not generally considered to have the fast surface-acting characteristics required of true emulsifiers, as their macromolecular size hinders rapid attachment to droplets. Dickenson (2003) has argued strongly that any true surface activity for polysaccharides, such as the galactomannans (guar, LBG), is the result of small amounts of co-extracted protein. Stabilisers provide long-term support for emulsions, and many plant cell wall polysaccharides that have hydrophobic and hydrophilic domains can be used in this role because of their affinity for water, and their large molecular size which can keep droplets at maximum separation distances. Stabilisation can also be achieved through providing thickening properties to a fluid-solid matrix of a foam (e.g. in ice cream) and interacting with protein micelles (e.g. acidified milk beverages).

Thickening is achieved by increasing the viscosity of a fluid without altering other properties. Water binding characteristics, and the ability to self-interact and aggregate in solution, make many cell wall polysaccharides useful in this regard. A high molecular weight can also assist with thickening - some polysaccharides (e.g. pectins) may have the structural and aggregation properties suitable for thickening but their comparatively low molecular

TABLE 2: Food additive functions for polysaccharides of cell wall origin.

Role	Action
Emulsification	Enables immiscible phases to form and retain a homogeneous mixture. An emulsifier acts as a surfactant positioned between the two immiscible phases, promoting a stable dispersion of one phase into the other.
Stabilisation	Maintains the desired physico-chemical state over a long time frame. A stabiliser may provide a firmer texture for foams, assist emulsifiers by inhibiting separation of an emulsion, and add bulk to prevent loss of textural quality.
Thickening	Causes an increase in viscosity without affecting other properties of the fluid.
Gelation	Provides texture through the formation of an internal structure which appears to be a solid but is actually formed by liquid.
Water binding	Enables retention of water in a product with or without swelling, affecting product texture and shelf-life.
Syneresis control	Prevents unbound water being eliminated from a gel.
Fat mimetic	Provides structure and texture in the product or sensation in the mouth resembling that provided by normal addition of fat; due to a combination of water binding, gelation and thickening properties.
Dietary fibre	Ingredient that is not digestible by gastric enzymes and does not contribute to energy requirements, but may be fermentable by gut bacteria.

weights rule them out of this texturing function.

Many polysaccharide hydrocolloids can form gels, i.e. they can self-associate, or associate with other polysaccharides to build stable networks in a solution (Wang & Cui, 2005; Burey et al., 2008). There are two main types of gelation mechanisms employed by polysaccharides of plant cell wall origin. Ionotropic gelation describes the cross-linking of chains via interactions of negatively charged areas on the polysaccharide with cations to form stable junction zones. Gels that form after heated polysaccharide solutions are cooled are termed cold-set gels, and the junction zones that form associated networks are stabilised by hydrogen bonds and hydrophobic interactions at preferred sites between the polysaccharides. Setting properties of gels are influenced by the types of polysaccharides (size, side groups, charge) and formulations (including variations in concentration, pH, solute, ions) used. Gels can be thermoreversible (i.e. will melt on reheating after gelation has occurred), or will be unresponsive to added heat. If the temperature of melting of a thermoreversible gel is higher than the temperature of set as it is cooling then the gel exhibits thermal hysteresis, and this can be a

valuable property if gels need to be pumped at elevated temperature. Syneresis of a gel occurs when unbound water is excluded from the gel some time after it has formed and this usually has poor quality connotations. To provide different textural properties in food, gels are often broken into particles within a solution or within a food matrix. To achieve this, either gels are dispersed (often using shearing) into droplets as aggregation occurs, or the droplets are formed prior to gelation conditions being induced (Burey et al., 2008). These gel particles can increase the viscosity and mouthfeel of foods, and they can be spray-dried and introduced into foods, adopting the gel structure when rehydrated again. Polysaccharides that do not gel, or cannot gel due to unsuitable environment conditions, can act as fluid viscosifiers, and their effectiveness is enhanced by increasing molecular weight and concentration and decreasing temperature (Izydorczyk et al., 2005).

A fat mimetic imparts a similar texture and mouthfeel to that normally provided by fat. This sensation is achieved by a combination of functions, most importantly the ability to interact with available water in food formulations in such a way as to generate various textural properties e.g. cohesiveness,

smoothness, dryness. Polysaccharides can be used as fat mimetics through the combination of their water-binding, gelation and thickening properties.

All plant cell wall polysaccharides are considered to be dietary fibre. The usual quantity of polysaccharides added to food as structuring agents may not provide a physiologically useful health impact. However, as polysaccharides have multifunctional properties they can be added (as individual ingredients or as whole cell walls) to foods in much larger quantities to provide a significant health impact without adversely affecting texture. This can be accomplished by deliberately replacing the function of other standard ingredients (e.g. as fat mimetics), by providing additional texture, or by use of a polysaccharide derivative that does not adversely affect texture. This area is discussed in more detail further in the text.

Sources, Modifications and Uses

Isolation of polysaccharides from plants for use as food ingredients has been described by Izydorczyk et al. (2005) and Harris and Smith (2006), while Waldron et al. (2003) have reviewed the role of these polysaccharides in terms of consumer quality requirements. While plant polysaccharides important to the food industry are generally available from most plants, it has become more viable to use only particular plant sources for reasons of economy and consistent quality. Even when there are better or more functional polysaccharide types available, the cost of extraction from an unusual or more specialised source has to be weighed against the economy of introducing such elements through chemical modification after extraction. For example, while researchers are finding new possibilities for pectin extraction (particularly from fruit processing

industries), as well as new functionalities, it is still more economically viable and dependable to extract pectin from the waste of citrus and apple beverage production (Lopez da Silva & Rao, 2006; Daniells, 2008).

Table 3 lists common food applications for plant cell wall-derived polysaccharides, and these are discussed in detail in the following sections. A specialised area of food ingredient is the addition of isolated plant cell wall material to foods with the primary aim of increasing dietary fibre intake.

Cellulose

Cellulose for food use is isolated from cotton and wood. Waste from the cotton industry is ideal for this use as it is free from lignin, but wood-derived cellulose requires harsh pulping and washing to provide a pure substance. Cellulose is only useful to the food industry if it is modified after extraction. Physical modification makes its hydroxyl groups more able to interact with water, while chemical modification enables better dispersion and solubility and introduces new functionalities that are useful in foods (Izydorczyk et al., 2005; Coffey et al., 2006; Harris & Smith, 2006).

Microcrystalline cellulose is obtained after cellulose has been treated with hydrochloric acid to remove amorphous cellulose (of less crystallinity). These particles are dried or sheared to produce highly crystalline microfibril aggregates that are used in foods along with a hydrophilic carrier such as guar gum to assist with dispersal. Microcrystalline cellulose is used as a bulking agent (it carries no taste and is inert) and thickener. It can also be used as a fat replacer where necessary due to its bulking properties as well as the mouthfeel it produces when used to assist in the suspension of insoluble particles in fluids.

TABLE 3: Use of cell wall-derived polysaccharides in foods.

Polysaccharide	Function	Item
Cellulose derivatives	stabilisers, thickeners, water-retention	ice cream, batters, syrups, cake mixes, meat products
Pectins	gelation, stabilisers	jams, preserves, beverages, bakery items, confectionery, dairy products
Galactomannans	stabilisers, water retention	dairy products, ice cream, desserts, bakery items
Glucomannans	emulsifier, thickener	noodles, pet food, confectionery
(1→3),(1→4)-β-D-Glucans	thickener, gelation, fat mimetic, health benefit	low calorie/low fat frozen desserts, processed meats, bakery items, dressings, beverages
Whole cell walls	thickener, gelation, health benefit, fat mimetic	low calorie/low fat bakery items, cheese, mayonnaises, frozen desserts, sauces, meat products, beverages

Chemically modified celluloses are produced by firstly swelling the cellulose in strong alkali to break down the hydrogen bond formation that holds the microfibrils together, then substituting certain hydroxyls of the glucose ring (usually at O-2 or O-6 and occasionally at O-3) with methyl, ethyl, hydroxypropyl, or carboxymethyl groups. These reactions are controllable and derivatised products can be tailored to end-use requirements. This derivatisation enables the cellulose to become soluble and act as a hydrocolloid although the different groups add quite different properties. Carboxymethyl cellulose is highly negatively charged, which makes it more hydrophilic, whereas the addition of alkyl groups creates sites of hydrophobicity, and the resulting amphiphilic molecules can be used to stabilise fat : water emulsions. Methyl and hydroxypropyl/methyl derivatives, in particular, tend to form thermoreversible gels at high temperature (increasing concentrations of salts can lower the temperature of gelation) and can aggregate at air : water and oil : water interfaces, which makes them particularly useful to stabilise foams and emulsions. The location of the substituent groups, as well as the degree and frequency of the substituents and the molecular weight (controlling viscosity in solutions) are important elements in the subsequent uses of these cellulose derivatives in foods. Carboxymethyl cellulose is used as a thickener and as a stabiliser (in breads, and in ice creams and other low-temperature products). The high-temperature gelation qualities of methyl celluloses makes them useful in avoiding boil-over in liquid fillings of baked goods, while they also add gelation and thickening qualities to low fat salad dressings.

Pectin

Most pectins are extracted from the waste products (peel and pomace) of the citrus and apple juicing industries (May, 1990; Voragen et al., 1995; Harris & Smith, 2006; Lopez da Silva & Rao, 2006). These are reliable sources, and generate pectins with consistent qualities that can be modified for particular end uses. The insoluble remnants from juicing are extracted in strong mineral acid at high temperature, and the solubilised material is precipitated with alcohol, dried, and powdered. Typically the molecular weight of pectin is too low (in comparison to other viscosifying polysaccharides) to be of value in effecting bulk changes in viscosity without inducing gelation, and it is this ability to gel which is pectin's most useful function as a food ingredient.

The main factor determining the functionality and types of uses for pectin is the degree of esterification of the polygalacturonan residues. High methoxyl (HM) pectins generally have more than 50% of the galacturonic acid residues esterified, while low methoxyl (LM) pectins have less than 50% of the galacturonic acid residues esterified. Extraction to preserve high endogenous levels of esterification requires shorter times with

higher temperatures, while lower esterification contents can be achieved with lower temperatures for extended times (May, 1990; Voragen et al., 1995; Lopez da Silva & Rao, 2006). Esterification levels can be reduced after extraction by careful treatment with acid or alkali, and in some cases esterification can be increased by treatment with methanol. Pectins are formulated (usually with sucrose which also enables good dispersion in solution) to provide setting concentrations within industry standard criteria.

High methoxyl pectin is mostly used for setting high solute/low pH gels and these gels are thermo-irreversible (i.e. once formed they cannot be returned to a liquid state by re-heating). The higher the degree of methoxylation in HM pectin, the faster the set. High methoxyl pectins cause gelation through the formation of junction zones between pectin molecules (Voragen et al., 1995; Lopez da Silva & Rao, 2006). This is brought about through the presence of high solute contents which induce regions of low water activity, forcing the polymers to interact more with each other than with the solvent. The junction zones are reinforced by areas of hydrophobic interaction (between neutral carboxyls and secondary alcohols) and hydrogen bonding (between methoxyl groups). This process is affected by pH. The number of charged unesterified carboxyl groups on the pectin is reduced at a pH around 3-3.5 (which is generally most favourable). Longer chain lengths (higher molecular weight) create more chances for junction zone formation so the gel will be stronger, with a higher rupture (breaking) strength. Rhamnose residues, which can occur in the RG-I areas of the extracted pectin backbone, introduce kinks in the molecule and can, therefore, prevent excessive junction zone formation, which could result in gel particle formation and possible syneresis (a split of the gelled areas and exclusion of water) of the product.

Low methoxyl pectin can form gels with the addition of calcium, and these pectins are especially valuable under conditions of lower (or no) sugar and at higher pH than is possible with HM pectin. Gels form due to the formation of intermolecular junction zones where stretches of non-esterified (anionic) galacturonic acid residues line up and bind together via calcium ions, in a similar manner to the way these pectins are thought to interact in the native cell wall (Voragen et al., 1995; Rinaudo, 2008). The current model is described as a "shifted egg box" (Lopez da Silva & Rao, 2006). Low methoxyl pectin gels are thermo-reversible.

After extraction the carboxyl groups on LM pectin can be amidated by treatment with ammonia, and amidated LM pectins can form firmer gels with less calcium than their non-amidated counterparts. This provides flexibility to tailor pectin formulations for circumstances where the quantity of calcium cannot be fixed.

Gel set parameters such as gelation temperature, time

to set, strength of set and thermostability, are influenced not only by the level of esterification and the molecular weight of the pectin, but by the presence of pectin side-branches and acetyl groups, the concentration used, as well as the amount and type of solute, the pH and the order of adding components together (Voragen et al., 1995; Lopez da Silva & Rao, 2006). Willats et al. (2001) showed that a simple quantitation of esterification content alone may be misleading in terms of gelation ability, because the arrangement of the esterified groups along the chain has a profound influence on the gelation capability of the pectin. Unfortunately there is no easy way for the industry to measure the distribution of esterification at the moment.

It is typical in the food industry for pectins to be sold as formulations, so very specific grades of HM, LM and amidation may be combined to meet specific quality and end-use needs. For jams and jellies, the condition of native pectin in the fruit can vary from season to season, making the choice of amount and type of added pectin as much an art as it is science. In fillings for baked products, the choice of pectin type depends on the manufacturing process, and whether the filling is to be baked with the product or injected after baking. Rapid-set HM pectins set at high temperatures, are bake-stable (do not melt during cooking) and have a cuttable texture. Pumpable fillings need to have a gelation structure that can withstand mechanical stresses, and LM pectins, which are thermoreversible, are often chosen for this application. For fruit bases that are part of cold dairy desserts, LM pectins (particularly the amidated types) are used as the base material can be pumped and the restructuring of the gel is rapid, allowing for clean layering or suspension within the dessert.

In addition to gelation, pectins can interact with proteins and prevent protein aggregation. This stabilising activity does not require pectin to form a gel, but instead the anionic domains, particularly in LM pectins, bind electrostatically to casein micelles, with the esterified domains of the pectin extending out into the solution to prevent the micelles from attracting each other. This is valuable in acidified milk beverages to prevent the separation of casein at low pH.

Pectins also can act synergistically with other added polysaccharides (such as the mannuronic acid- and guluronic acid-rich alginates obtained from certain species of brown alga) that are widely used in the food industry. The pectin/alginate interaction is a combination of two quite similar polysaccharide types, with both containing regions capable of ionic interactions with divalent ions. The strongest mixed gels are obtained with HM pectins and alginates that contain a high proportion of guluronic acid blocks, in conditions under which neither polysaccharide would gel – low pH, low sugar content and in the absence of ions (Williams & Phillips, 1995; Walkenström et al., 2003; Lopez da

Silva & Rao, 2006). The interaction is thought to be due to a promotion of inter-chain association with the pectin chains arranging themselves to have the methyl groups in the HM areas lined up opposite the hydrogens on C-1 and C-2 of the guluronic acid blocks – this arrangement is one that excludes water, and reduces electrostatic interactions. These are 'cold set' gels and require the introduction of food-grade acid, often D-glucono- δ -lactone, which is a slow release acidifier. Low methoxy pectin and high-mannuronic acid alginates can also form gels, even in conditions of high sugar solute, but these require calcium. These mixed gels are more bake-stable than those of the separate components used individually, and prevent syneresis. This "mixed independent" synergism is attributed to the presence of two independent but complementary gel networks occurring within the same system (Young et al., 2003), rather than the chain : chain compatibility of the HM pectin/high guluronic acid alginate synergy described above.

Mannans

Galactomannan gums for the food industry are isolated primarily from guar and locust beans, although tara and fenugreek are also sources. Most of the world's supply of guar comes from Pakistan and India, where the legume has a particular tolerance of hot dry conditions, whereas most LBG is produced around the Mediterranean. For extraction, the seeds or beans are cracked and the endosperm is ground to a fine flour. The gums are solubilised in hot water, and then purified by precipitation. Little extraneous material is co-extracted with the gums from these sources.

Galactomannans from guar and locust bean have quite different properties, arising from the extent of galactose substitution on the mannan backbone, with higher substitution rates resulting in greater water solubility (Izydorczyk et al., 2005; Gidley & Reid, 2006; Harris & Smith, 2006; Rinaudo, 2008). Guar gum has the highest rate of galactose substitution (one for every two mannose backbone residues), whereas LBG has around half this substitution rate and with a more random distribution. The non-gelling LBG can self-associate in regions with little or no galactose presence, whereas guar gum cannot. Thus, LBG requires heating for complete solubilisation, whereas guar gum is readily water-soluble and equimolar solutions have greater viscosity than LBG. Nevertheless, both types of galactomannan are used as thickeners, and are effective in small amounts. Galactomannans can act as emulsifiers in oil : water systems, but there is confusion regarding the mechanism of this activity as there is no hydrophobic region on the polysaccharide. It is thought that the degree of galactose substitution on the mannan backbone may influence the emulsification properties, but to date this mechanism is unresolved (Wang and Cui, 2005). As stabilisers, galactomannans can prevent 'creaming' in salad dressings. Locust

bean gum is widely used in low temperature products such as ice creams to assist in stabilising the oil : water and air : liquid phases present and in slowing the rate of melt. Locust bean gum increases the viscosity of the ice cream matrix, which has the added benefit of masking the perception of large ice crystal grittiness, as well as forming a low-temperature gel around ice crystals which prevents their aggregation. Guar gum is also used for thickening in dairy foods, and prevents syneresis of fillings in baked goods.

Locust bean gum is often used in conjunction with kappa-carrageenan, a substituted galactan polymer obtained from certain species of red alga, and used extensively as a food texturising agent. The synergistic effects of mixtures result in greater viscosity and gelation than is possible with either component alone. The nature of the enhanced gel properties that result from interaction of LBG and kappa-carrageenan are still not fully understood. Current models suggest it is an interactive effect, arising due to the coil structure of LBG being accommodated within the network formed by carrageenan (Williams & Phillips, 1995; Williams & Langdon, 1996). There is no evidence of intermolecular binding, and synergistic effects may not occur if LBG is added to the kappa-carrageenan under conditions that do not favour kappa-carrageenan gelation. Synergistic responses are increased as the ratio of mannose to galactose in LBG is increased. Whatever the nature of the interaction, addition of LBG softens the texture of the normally brittle kappa-carrageenan gel and can prevent its syneresis. Interestingly, guar gum does not interact with kappa-carrageenan.

Partially hydrolysed guar gum is produced by endo- β -D-mannanase-mediated hydrolysis of guar during extraction (Harris & Smith, 2006; Yoon et al., 2008). It is added to foods to enhance the dietary fibre component and in this regard its value lies more with its ability not to affect texture or colour rather than with any viscosification or gelation characteristics.

Glucomannan is extracted from the dried, pulverised roots of the konjac plant, which grows mainly in China and Japan. Extraction conditions can vary, since much unwanted material can be co-extracted under aqueous conditions, and the more acetylated the glucomannan the more freely soluble in water it will be (Stephen & Churms, 1995; Renn & Blake, 2003; Morris, 2006). Recent advances include extraction with high shear, and use of hydrogen peroxide to reduce solution viscosities during extraction (Renn and Blake, 2003). The average molecular weight of konjac glucomannan is very high and consequently it can be used to increase fluid viscosity where thickening is needed. The presence of acetylation is also the basis of konjac gel formation (Williams et al., 2000; Nishinari & Takahashi, 2003; Morris, 2006). When konjac glucomannans are heated under alkaline conditions (which causes removal of acetyl groups) the polymer

becomes insoluble and a gel develops. Such gels have extraordinary thermal stability. Glucomannan from konjac is used in noodles, pet food, and in confectionery although the latter use has declined somewhat in recent years due to concerns about the lack of softening of the gel during chewing and swallowing. Glucomannans are also able to interact with kappa-carrageenans in a synergistic manner as well as with other plant hydrocolloids, such as starches, and bacterial polysaccharides, such as xanthans, used in prepared foods. These gels are thermoreversible.

(1→3),(1→4)- β -D-Glucans

Oats, barley and other cereals are the principal sources of the hemicellulosic (1→3),(1→4)- β -D-glucan (mixed linkage glucan, MLG) for the food industry (reviewed by Lazaridou & Biliaderis, 2007). Mixed linkage glucan has a basic structure of short blocks of three or four β -(1→4)-linked glucose residues with the blocks joined by β -(1→3) linkages. The ratio of β -(1→4) : β -(1→3) linkages is around 7 : 3, although intervening sequences of solely β -(1→4)-linked glucan may also be present within the polysaccharide (Izydorczyk et al., 2005). Unlike the previously described polysaccharides, MLG is an extracted hydrocolloid added to food to boost non-digestible fibre content for positive health effects, such as cholesterol-lowering and slowing the absorption of glucose produced during digestion (see below) rather than for its food structuring qualities per se. Nevertheless, it can be added to foods without negative textural effects (central to consumer acceptance) and in some cases can act as a fat replacer, and this is due to its ability to bind water and create areas of thermoreversible gelation.

Various types of MLG are used in foods. For example, GlucageTM is purified MLG from barley obtained using a simple aqueous extraction followed by freeze-thaw precipitation (Morgan & Ofman, 1998; Morgan, 2006). Molecular size of the extracted glucans can be controlled by extraction conditions (the longer the time of extraction the smaller the chain length), due to the activity of endogenous hydrolases. The longer chain length MLGs (e.g. 500 kDa) can be used to increase fluid viscosity, while much shorter chain lengths favour gel formation due to increased polymer mobility in solution and opportunity to form junction zones (Lazaridou et al., 2003; Vaikousi et al., 2004). Junction zone formation is governed by the regularity of distribution of blocks of celotriose and cellotetraose and their interaction through hydrogen bonds with similar segments on other chains. These properties enable gelling and fat replacement when added to foods.

Another form of MLG is present in cell wall preparations derived from amylase digestion, heat, alkali and/or high shear treatment of oats and barley. These products are marketed as 'Oatrim', 'Nutrim' and 'C-trim' and have MLG as a central component and are based on a

number of patents from the USDA since the 1990s (e.g. Inglett, 1991; Inglett, 1992). Kim et al. (2008) recently analysed the content and molecular weight of glucans in the 'Trim' products and found that glucan chain-length reductions occurred during the manufacturing process. Depending on the extraction process, these products have high water binding capacity, which influences product flow properties and creamy mouthfeel. They can be used to replace the texture provided by solid or liquid fats, and are found in a range of diet foods including dairy and baked products.

Whole cell walls

The availability and impact of the addition of isolated whole cell walls from plants to processed foods for the improvement of dietary fibre content has been reviewed by Kunzek et al. (2002), Redgwell and Fischer (2005), Rodríguez et al. (2006) and Harris and Smith (2006). The health benefits associated with dietary fibre are described in the next section. The dietary fibre supplementation of prepared food is a relatively recent trend in the food industry and, as with MLG, is an addition with the primary aim of improving the health value of foods. For successful incorporation and maximum consumer acceptance, however, there must be no adverse effect on product texture (the food needs to have the normal expected texture). Recent improvements in cell wall isolation and treatment have generated whole cell wall materials with enhanced technical properties that provide the required texture, to the point where they can be used to substitute some of the textural and mouthfeel properties provided by fat, therefore providing an additional health benefit.

Cell wall material for inclusion into food is sourced from a diverse range of plant species, organs and tissues, and is generally a by-product of extraction for other valuable materials. This means, as Harris and Smith (2006) have pointed out, that there is a very wide range of constituent polysaccharides present in "fibre preparations", and that the nomenclature used by the industry does not usefully describe the potential health or food benefits. Citrus, apple, tomato, wood, cotton, bamboo and cereals are some of the commercial sources of whole cell walls for dietary fibre ingredients (Redgwell & Fischer, 2005) and many more could be used (McKee & Latner, 2000, Rodríguez et al., 2006). The quality of the fibre can vary with the quality of the raw material because cell wall composition and rheology can change dramatically during plant development, and must be closely monitored to ensure the products have consistent, expected quality. Generally speaking, walls from parenchyma cells (as in fruit flesh) are rich in pectin and hence contain a high proportion of fermentable dietary fibre, those that are highly vascular (e.g. woody stems) contain more cellulose and other insoluble dietary fibre constituents, whereas cereals contain less pectin but more hemicelluloses and cellulose. This translates into different functionalities in

food structure and texture. 'Invisible' incorporation into food is reliant on particle size and the water-binding capacity of the fibre, both of which can be controlled, either by mechanical means (such as grinding or high-rate shearing), or by formulation to meet particular end requirements. As described above for the 'Trim' products that are enriched in MLG and other hemicelluloses, shearing of whole cell wall material in water can produce a remarkable capacity to bind water into a form that can range from a viscous liquid to highly gelled (Redgwell & Fischer, 2005). Whole cell walls are included in foods such as breads and biscuits, as well as dairy and meat products and beverages.

Plant Cell Wall Polysaccharides as Dietary Fibre

According to the latest guidelines of the 2008 Codex Committee on Nutrition and Foods for Special Dietary Uses (Cummings et al., 2009), the term 'dietary fibre' encompasses carbohydrate polymers (degree of polymerisation of ≥ 10) which are not hydrolysed by endogenous enzymes in the human small intestine; are naturally occurring in food consumed, extracted from raw material, or synthesised to have these carbohydrate characteristics; and which have been shown to provide a physiological benefit to health when consumed. These guidelines do not currently include oligosaccharides (degree of polymerisation 3–9), although there is recognition that these can also be non-digestible and provide health benefits. Earlier definitions of dietary fibre, summarised by Buttriss and Stokes (2008), have included such oligosaccharides, as well as other non-carbohydrate materials such as lignins. As there has been considerable debate on what is and is not dietary fibre (Cummings & Stephen, 2007; Mann et al., 2007; Gray, 2008) it seems likely this latest Codex definition may also evolve over time. Whatever the limits of the definition of dietary fibre (and its consequent implications on nutritional labelling and public health messages), it is clear that plant cell wall polysaccharides in foods, either intrinsically present (e.g. whole fruit, vegetables or grains,) or added as individual ingredients or as isolated whole cell walls, have the chemical and physiological properties that qualify them as dietary fibre.

There are strong and accepted indications that fibre is important for normal digestive and cardiovascular functions. Improvements and/or lowered risk profiles for colorectal cancers, inflammatory bowel diseases and other metabolic disorders such as coronary heart disease, obesity and Type-II diabetes may result from increased intake of dietary fibre. Effects may be direct and physical (e.g. faecal bulking, water binding, adsorption of mutagens produced during digestion, viscosification of digesta) or indirect (e.g. through modulation of glycaemic and inflammatory responses, changes in fat and bile salt absorption profiles following digestion, nourishment of gut microflora). Among the

key issues in quantifying the impact of dietary fibre on human health, however, are the varied composition of the polysaccharides making up the dietary fibre portion of the diet of trial subjects, as well as the impact of the rest of the food matrix that may be consumed at the same time. Some consideration has been given to whether the health benefits of dietary fibre from whole cell wall-containing foods (vegetables, fruits, wholegrain cereals) are augmented by the other (often unknown) phytochemicals present in these foods, and that consequently, fibre supplements or isolated non-digestible polysaccharides could be unable to provide the full spectrum of possible health benefits (Mann, 2007; Buttriss & Stokes, 2008), but these relationships are still unclear. Some fibre (or combinations of fibres) may also have negative effects on health, including promotion of carcinogenesis in some circumstances, bloating, and the reduction of sulphates to potentially toxic sulphides (Harris & Ferguson, 1999; Lunn & Buttriss, 2007). The dietary and health effects of fibre may also depend on variations in gut microflora populations between individuals (Rose et al., 2007).

Dietary fibre is chemically classified as 'soluble' (e.g. pectins, MLGs) and 'insoluble' (e.g. cellulose, xylans and other hemicelluloses). These solubility distinctions are reflected in quite different physiological effects, leading to the often-used terms 'fermentable' and 'non-fermentable' (or 'poorly fermentable') dietary fibre. The mechanisms that underpin these effects are discussed below, and for this commentary we have referred to recent comprehensive reviews to outline the latest viewpoints about plant cell wall polysaccharides that act as dietary fibre, and their contribution to health.

Normal Gastrointestinal Activity

The human digestive system does not contain enzymes to hydrolyse cell wall polysaccharides into component sugars to provide energy and support metabolism. Therefore, all consumed cell wall polysaccharides move intact, along with digested material, out of the stomach and into the small intestine, where the products of digestion are absorbed into the bloodstream. Cell wall polysaccharides, which may have been solubilised through cooking of plant foods (e.g. pectins, MLGs, mannans) or are present already solubilised as food ingredients, viscosify the digesta in the stomach and small intestine (Dikeman & Fahey, 2006). This physical property influences stomach emptying and the movement of digesta through the small intestine, consequently affecting the rate of metabolite absorption (Brennan, 2005; Lazaridou & Biliaderis, 2007; Lunn & Buttriss, 2007; van Dam & Seidell, 2007). In a normal healthy gastrointestinal system, this provides a moderate, prolonged level of glucose absorption, an opportunity for cholesterol and bile salts to be absorbed and then recycled, and a sense of fullness (satiety). The viscosification of digesta caused by increased quantities of soluble fibre in the diet accelerates the

transit time of digesta through the small intestine, significantly slowing the rate of glucose absorption and thereby flattening and prolonging the peak in glycaemic and insulin responses and providing a more gradual increase in blood glucose levels (Brennan, 2005; Lunn & Buttriss, 2007; van Dam & Seidell, 2007; Buttriss & Stokes, 2008; Galisteo et al., 2008). It can also reduce the amount of cholesterol and bile salts absorbed (discussed in more detail below). These responses are especially important in the control of diabetes, obesity and hypercholesterolemia. Brennan (2005) also suggests the presence of additional soluble fibre in starchy foods can alter the accessibility of starch to degrading enzymes.

Soluble fibre, while not digestible by human enzymes, is fermentable by gut microflora present in the proximal colon (Guarner & Malagelada, 2003; Lunn & Buttriss, 2007; Rose et al., 2007; Scott et al., 2008; Buttriss & Stokes, 2008). The ultimate products of such fermentation are short-chain fatty acids (SCFAs) primarily acetate, propionate and butyrate. The term 'prebiotic' has been used to describe soluble oligo- and poly-saccharides that are preferred by bifidobacteria that produce butyrate (Buttriss & Stokes, 2008), although Lim et al. (2005) suggest the criteria for prebiotics is not necessarily restricted to those with an end product of butyrate. The type of SCFAs produced and rate of fermentation are influenced to some degree by the sugar residues present in the polysaccharides making up the fibre, but may depend more on linkages present (including cross-linkages), and in the case of pectin, the degree of methylation (Rose et al., 2007).

The benefits promoted by fermentation of soluble fibre appear to either stem directly from the support of the gut microflora population, or from the improved condition of the cells of the colon (which are nourished in particular by the butyrate byproduct of bacterial fermentation). The specific impact of this on the reduced risk of colorectal cancers is outlined in more detail below. In addition, the lowered pH induced in the colon by the production of SCFAs improves conditions for mineral absorption, inhibits the growth of pathogens, as well as possibly preventing the formation of toxic breakdown products (Lim et al., 2005; Rose et al., 2007; Buttriss & Stokes, 2008; Scott et al., 2008). Short-chain fatty acids produced by bacterial fermentation of soluble dietary fibres have also been reported to contribute to the lowered glycaemic response (Guarner & Malagelada, 2003) and to directly interfere with cholesterol synthesis in the liver (Lunn & Buttriss, 2007; Aleixandre & Miguel, 2008; Scott et al., 2008).

Insoluble fibre from plant cell wall polysaccharides (cellulose, xylans and other hemicelluloses) directly contributes to a normal, healthy digestive system through the ability to bind/trap water as digesta moves along the intestine and by providing faecal bulk (Young et al., 2005; Lunn & Buttriss, 2007; Rose et al., 2007;

Scott et al., 2008). Insoluble fibre can bind bile acids and dietary carcinogens, and with increased insoluble fibre in the diet, transit times are decreased, reducing the length of time that potential carcinogens are in contact with the luminal epithelium (Young et al., 2005; Lunn & Buttriss, 2007; Rose et al., 2007; Scott et al., 2008). Insoluble fibre can be very slowly fermented by bacteria in the distal colon (Young et al., 2005), although Guarner and Malagelada (2003) and Lim et al. (2005) suggest the depletion of polysaccharide and altered pH conditions of the distal colon are more suitable for putrefaction than fermentation.

Risk of Colorectal Cancers

The effects of both insoluble and soluble fibre of plant cell wall origin can contribute to reduced risk of colorectal cancers, although more research is needed to provide conclusive connections and underlying mechanisms. As previously mentioned, the physical interaction of insoluble fibre with potentially toxic and carcinogenic compounds derived from food combined with the influence of such fibre on water binding and bulk flow properties minimises the contact time such compounds have with susceptible gut epithelial cells (Lim et al., 2005; Young et al., 2005; Rodriguez et al., 2006; Lunn & Buttriss, 2007; Rose et al., 2007; Buttriss & Stokes, 2008; Scott et al., 2008). The effectiveness of insoluble fibre in this regard appears to be dependent on the composition of the fibre, and particularly its presence as part of whole foods, compared with isolates or supplements (Harris & Ferguson, 1999).

Other dietary fibre effects appear to be less direct, and are aligned with the SCFA products of bacterial fermentation of soluble fibre although not all studies have shown a positive effect (Young et al., 2005; Rose et al., 2007). Apart from the general benefits provided by the production of SCFAs produced by these bacteria (mentioned above), butyrate, a product of fermentation of soluble fibre by gut microflora, has been shown to interfere with the cell cycle and to promote apoptosis in cells of the gut epithelium. These processes may enable either repair of damaged DNA or complete death of non-repairable cells (Young et al., 2005; Lunn & Buttriss, 2007; Scott et al., 2008) and this vigilance may provide a 'front line' defence against cancer. Promotion of calcium absorption by the epithelial cells, which is induced by the lowered pH created by the production of SCFAs is also thought to be linked, along with butyrate, to inhibition of cell proliferation, and to enhanced cell differentiation (Lim et al., 2005). Lowered pH may also interfere with enzymes involved in cancer induction (Lim et al., 2005; Rose et al., 2007).

Inflammatory Bowel Diseases

Inflammatory diseases of the colon are complex, but appear to be linked to a deficiency in the amount and use of butyrate to nourish and maintain functionality

of epithelial cells as well as to impaired tolerance of the range of bacteria present in the colon (Guarner & Malagelada, 2003; Galvez et al., 2005; Rose et al., 2007; Hamer et al., 2008). Increasing the quantity of soluble, fermentable dietary fibre to colonic microflora has been proposed to increase the amounts of SCFAs (particularly butyrate) available to promote normal functioning of the epithelial cells. There are also indications that dietary fibre (via SCFA production) has anti-inflammatory effects, particularly interfering with activation of factors that induce production of cytokines that mediate the full inflammatory response in these conditions (Galvez et al., 2005; Rose et al., 2007; Hamer et al., 2008). While more research is required for a greater understanding of the underlying nature of inflammatory bowel diseases, increasing intake of soluble dietary fibres has proved a successful therapy for symptom control for some individuals.

Cardiovascular Health

In a healthy system, much of the cholesterol and bile salts from digested food are absorbed from the ileum, with a small proportion excreted in the faeces. The cholesterol conjugates to lipoproteins (e.g. high/low density lipoproteins) on entering the bloodstream. A large proportion of this reabsorbed cholesterol is converted to bile in the liver, and then re-secreted into the digestive system. High levels of cholesterol conjugated to lipoproteins, particularly the low density lipoproteins in the blood, can lead to atherosclerosis which increases the risk of heart disease, strokes and clots. However, the hastened transit of digesta through the small intestine in response to the viscosification provided by an increased intake of soluble dietary fibre reduces the amount of cholesterol and bile acids that are re-absorbed before excretion, therefore less is circulated back to the liver (Lunn & Buttriss, 2007; Mann, 2007; Galisteo et al., 2008). The SCFAs produced by bacterial fermentation of soluble fibres can also interfere with *de novo* cholesterol synthesis in the liver (Lunn & Buttriss, 2007; Aleixandre & Miguel, 2008; Scott et al., 2008) – acetate and propionate are thought to be particularly effective in this regard.

There also appears to be a connection between dietary fibre intake and the reduction of inflammatory processes that are connected to coronary heart disease. C-Reactive protein is a clinical marker of inflammation, and studies in humans have shown that increased levels of dietary fibre are associated with reduced amounts of serum levels of C-reactive protein (King, 2005; Galisteo et al., 2008). A comprehensive demonstration of any direct anti-inflammatory effect of fibre, however, may depend on the experimental conditions used (Mann, 2007). The biochemical mechanism connecting dietary fibre to regulation of C-reactive proteins and other downstream inflammatory processes has yet to be resolved.

Future Trends

The use of plant-based hydrocolloids in foods in the next decade of the twenty-first century will need to support global food trends, especially those of health and convenience. It is likely that these polysaccharides will continue to be used as texturisers, stabilisers and fat replacers. However, we predict there will also be increased use of their ability to 'carry' other health-supplementing ingredients (as in emulsions, perhaps in association with proteins), and more research will be needed to optimise this functionality without negatively affecting texture or taste.

We expect that nanotechnology will influence the use of cell wall-based hydrocolloids in food, e.g. milling technologies to produce smaller, more dispersible particles, better understanding of surface activities of the polymer molecules, and new knowledge to induce synergies between polysaccharides that are not usually compatible.

Although there is constant research interest in identifying new, highly functional polysaccharides from exotic sources, as well as in using waste streams as sources of polysaccharide hydrocolloids, whether this interest persists will depend on the ultimate economic benefit to the food industry. Currently there is little enthusiasm in the industry for this. We anticipate that chemical modifications will extend the applications of hydrocolloids in the future, such as the introduction of cross links (e.g. Littoz & Clements, 2008), and quite possibly the conjugation of health-beneficial small molecules. There is also considerable interest in finding new applications for polysaccharides previously thought of as unsuitable for foods. For example, the level of acetylation in sugar beet pectins prevents gelation even under ideal HM or LM conditions, and consequently this abundant source of pectin has not been used in the food industry. However, this lack of self-association has been found to be of benefit when sugar beet pectins are used to encapsulate fish oil (Drusch, 2007).

In the future it may be possible to achieve modifications or improvements to the functionality of plant polysaccharides *in planta* through genetic modification (so-called 'designer' polysaccharides), as suggested by Willats et al. (2006). Certainly, there is increasing molecular information on transferases that specifically add sugars to growing polysaccharide chains, and the identification and functional expression of suites of genes encoding enzymes associated with complex branched polysaccharide assembly (Scheible & Pauly, 2004; Farrokhi et al., 2006; Lerouxel et al., 2006). Whether this direction can be taken up by the food industry in the next few decades depends on extensive fundamental and applied research to develop suitable plants with reliably altered wall synthesis, as well as public acceptance of food

materials generated through genetic engineering. Along similar lines, as more is known about the synthetic pathways of plant polysaccharides, it may become possible to introduce the enzyme complexes required into bacteria to synthesise large quantities of relatively pure polysaccharide in a controlled manner, thus bypassing the plant altogether. All these areas present significant research challenges before they can be applied within the food industry.

Conclusive proof of the health efficacy of cell wall polysaccharides that act as dietary fibre clearly rests with identification of the actual beneficial components of dietary fibre, the manner in which it operates in the gut, the wider impact of these effects and the potential for negative consequences (Ferguson & Harris, 2003; Ferguson & Harris, 2005). Future research will focus more fully on these elements, as well as the interactions of fibre with other foods in the diet. This information, together with a greater understanding of cell wall polysaccharide synthesis in plants, may lead to the breeding of plant species with enhanced and targeted beneficial dietary fibre properties.

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