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POLYSACCHARIDES AND FOOD PROCESSING*

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ABSTRACT

The rôle of polysaccharides during processing and for the quality of foods is discussed. Starch is the most important energy source for man. Most other polysaccharides are not metabolized for energy, but play an important rôle as dietary fibres. Pectins, alginates, carrageenans, and galactomannans are discussed as functional food additives in relation to their structure and their rheological behaviour, stability and interactions. Endogenous polysaccharides of fruits and vegetables and in products derived from them are responsible for such phenomena as texture (changes), press yields, ease of filtration and clarification, cloud stability, and mouth feel. To achieve desirable properties, the action of endogenous enzymes on polysaccharides must be inactivated and/or exogenous enzymes added as processing aids. This is also true for overcoming haze phenomena in clear juices or to break down undesirable microbial polysaccharides. Dough properties for bread baking can be improved by enzymic breakdown of a restrictive pentoglycan network. Network formation may come about by oxidative coupling of phenol rings of ferulic acid bound to hemicelluloses by ester links. Gels may be made by inducing oxidative coupling in natural or synthetic systems. Stagnation in development of new polysaccharide food additives is ascribed to difficulties in obtaining government approval for food use.

INTRODUCTION

Food processing means transformation of raw materials into food products having a specified nutritional, sensory, and use quality. For most foods, polysaccharides play an important rôle in processing steps and in quality aspects (see ref. 1 for general sources). Considering first nutritional quality, the most important energy supplier for the human body is the polysaccharide starch. Among the polysaccharides, it is also the principal supplier of energy, because the digestive system enzymes can attack only α-D-(1→4) glucosidic linkages. Other poly-

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saccharides used in foods as natural constituents and as polysaccharide additives and which used to be called ballast or roughage, are at present a subject of high interest in food technology and nutrition: dietary fibre. The dietary fibre hypothesis of Burkitt and Trowell suggests that the low-fibre diets of industrialized societies is an important causative factor in the development of so-called civilisation diseases (constipation, obesity, hemorrhoids, diverticulosis, cardiovascular trouble, colon cancer). Improved bowel activity achieved by high dietary fibre diets protects against these diseases and may even cure some of them. Dietary fibres are often analysed by treating a defatted food sample with amylases and proteases to imitate the human digestive system, and the high-molecular fraction of the remaining material is then calculated as dietary fibre. Some analysts further differentiate this into such groups as pectin, hemicelluloses, and cellulose. A good average value for fibre content of fruits and vegetables would be between 2 and 3%, pectin being about one third of this. Cereal preparations have much higher contents, e.g., rye flour 20% and wheat bran 40%, but the dry-matter content of cereals is also much higher. Clinical human experiments have shown that quantitative estimations are not sufficient, and the literature reflects the development and increasing use of methods to fractionate fibre material and to determine at least the monomer building-blocks; other laboratories are also determining the molecular structure of the polysaccharides.

DISCUSSION

As an example for well-defined fibre constituents, branched β-xylans are shown in Fig. 1. Glucuronoarabinoxylans are typical representatives of cereal pentoglycans, present e.g. in wheat bran, a very efficient dietary fibre in respect to digestive transit-time and bulk of feces, and is widely used by the consumer, who adds it to such foods as yoghurt, or by the food manufacturer in special breads. The physiological effect of cereal products has indeed been shown to be related to their content of pentoglycan. A fibre constituent of special interest is pectin (Fig. 2). Pectin does not show the action on digestion of many other hemicelluloses, but has the ability to decrease the cholesterol content of blood serum. It is essentially a (1→4) chain of α-D-galacturonic acid with most of the carboxyl groups esterified with methanol. Other structural features present are some L-rhamnose residues in the galacturonic chain, and of hemicellulose side-chains. Theories have been proposed to explain the hypocholesterolemic action by a binding of bile salts to the acid groups. However, an even stronger plasma-cholesterol decreasing action is obtained with such neutral polysaccharides as galactomannans (Fig. 2). Indeed, newer theories ascribe the plasma cholesterol-lowering effect to polysaccharide interference with reabsorption of bile salts in the lower gut. The food technologist uses, as a galactomannan, guar gum, the reserve carbohydrate in the seeds of guar beans, planted on a large scale mainly in India and Pakistan, or locust-bean gum, obtained from the seeds of locust beans, the fruits of the locust-bean tree grown in Mediterranean regions.

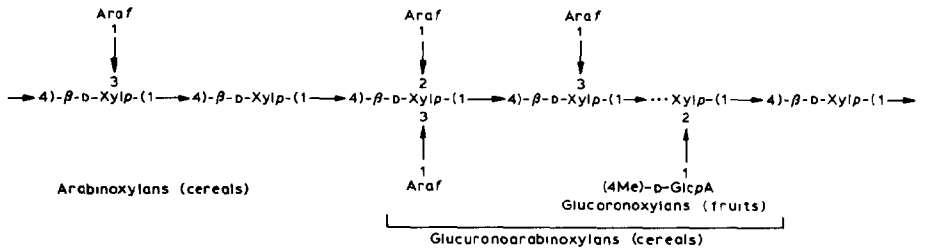


Fig. 1. Structure of branched xylans.

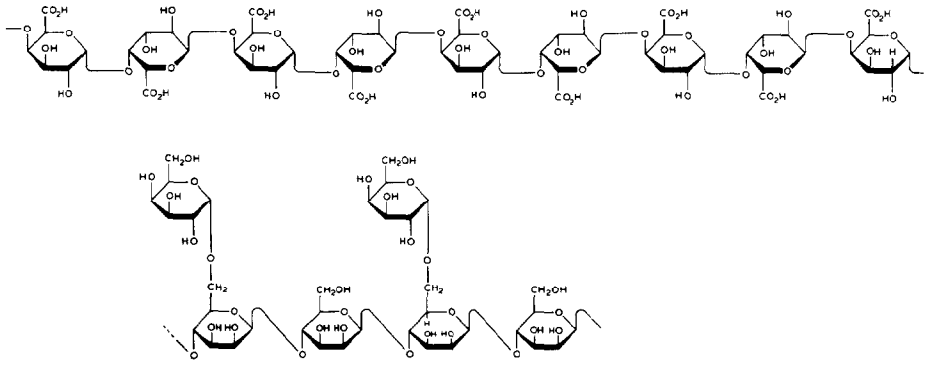


Fig. 2. Anionic and neutral polysaccharides. Top: α-(1→4)-D-galacturonan (pectin), bottom: β-(1→4)-D-mannan with α-(1→6)-D-galactose side groups, more or less regularly distributed along the mannan chain (galactomannan).

After a first period of enthusiasm, gum manufacturers are now reluctant to promote their products as dietary fibre, because of warnings from regulatory agencies that claims for cholesterol lowering and other effects may cause these products to be considered drugs. However, dietary-fibre promotion and consumption, and dietary-fibre research are still important factors in today's food industry. Research activities are in two directions–chemical structure/physiological action relationship, and formulation of palatable foods with high fibre content.

Pectin is also a well-known, functional food additive. As such it is produced industrially in many locations from apple or citrus pomace. It is used as gelling agent in jam and jelly manufacture and as a stabilizer to prevent flocculation of casein in acid milk products. The molecular weight of commercial pectin is ~80,000, corresponding to ~400 D-galacturonic acid (methyl ester) residues in the chain. Fig. 3 shows this chain to have a kink caused by the presence of (1→2)-linked L-rhamnose residues. Fig. 4 depicts our own view on the structure of apple pectin[2]. Smooth regions of pure homogalacturonan are interrupted by short, hairy regions rich in rhamnose and side chains. The rhamnose kink and the side chains are important for the gelling properties of pectin. According to modern theories of gel formation, junction zones are formed between chain segments with a regular

structure and under conditions favourable for such chain association (Fig. 5)[3]. In pectin gels, the chains are associated by hydrogen bridges, which are favoured by low water activity (therefore rationalising the necessity of a high sugar content in jam). The junction zones are terminated by an irregularity in the molecule such as a rhamnose residue or a hairy region–in this way free lengths of macromolecules are present and a three-dimensional net is formed rather than water-insoluble micelles. Some pectin manufacturers also partly deesterify pectin to afford low-methoxyl pectins that can form gels without sugar, as in low-sugar jams, an important dietetic food. Chain association then occurs by multiple bonding to calcium ions, which are situated between the pectin molecules like eggs in a box ("egg-box structure", Fig. 6). The diaxial glycosidic linkages between the α-D-galacturonic acid residues provide the spatial order between chain segments to accommodate the calcium ions.

Another hydrocolloid glycuronan, industrially extracted from brown algae, is alginic acid, a heteropolysaccharide composed of varying and sometimes alternating sequences of L-guluronic and D-mannuronic acid (Fig. 7). The α-(1→4) glycosidic linkages between the L-guluronic acid molecules leads to a diaxial orientation similar to that in galacturonan and equally suitable for an egg-box type of chain association with calcium ions. This is not the case for the diequatorial

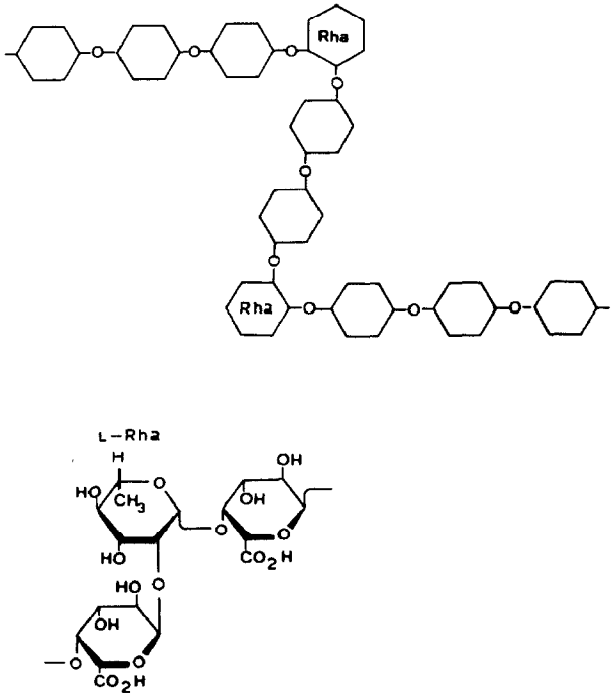


Fig. 3. Kinks in the pectin chain through (1→2)-bound rhamnose residues. The L-rhamnosyl residue is shown as α-linked, but the anomeric configuration has still to be established.

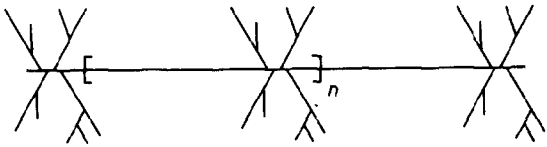


Fig. 4. Model of a pectin molecule having repeating units consisting of "smooth" homogalacturonan regions and "hairy" regions having a high concentration of neutral sugars[2].

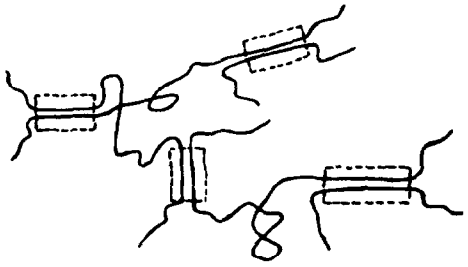


Fig. 5. Network formation of polysaccharides by junction zones[3].

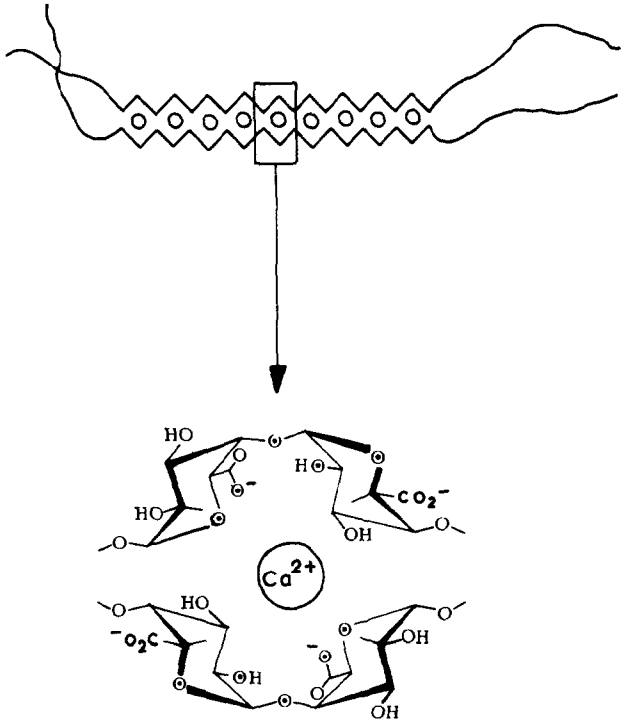
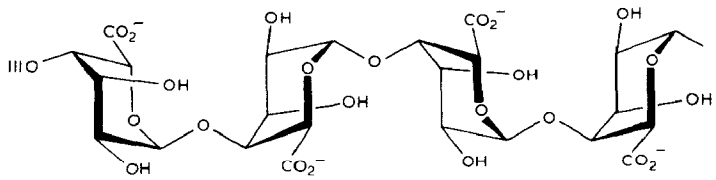


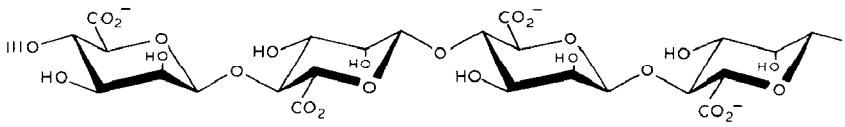
Fig. 6. Junction zones between low-methoxyl pectin chains induced and stabilized by calcium ions. ⊙ denotes sites for calcium binding.

disposition of the linkages between the β-D-mannuronic acid residues, and it may therefore be understood that the gelling properties of alginates depend on the amount and distribution of the guluronic acid residues, which varies between species of algae. Despite these similar properties, alginates and low-methoxyl pectin do not really compete with one another because of their different heat stability under various pH conditions (Fig. 8). Among all of the gelling hydrocolloids, pectin is unique for its stability under acid conditions, but it breaks down readily under neutral conditions[4] because of eliminative scission of the pectin chain at glycosidic linkages next to an esterified carboxyl group. Under these pH conditions, alginates are heat stable and are therefore widely used as binding agents in such restructured foods as meat loafs or pet foods, and in applications where they are included in a mass that is extruded into a calcium salt bath, where it gels and preserves a given form. In this way, artificial onion rings are made from small pieces of onions, a byproduct of the manufacture of natural onion rings.

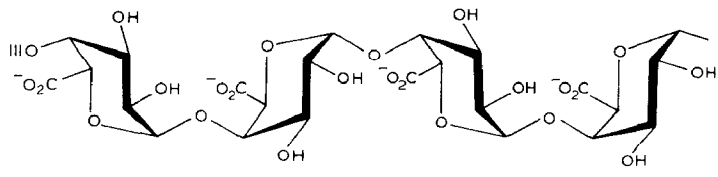
Other examples for gelling and thickening agents obtained from seaweed are



(1→4)-Linked α-D-guluronic acid residues in alginates



(1→4)-Linked β-D-mannuronic acid residues in alginates



(1→4)-Linked α-D-galacturonic acid residues in pectins

Fig. 7. Block shapes in alginates and pectins.

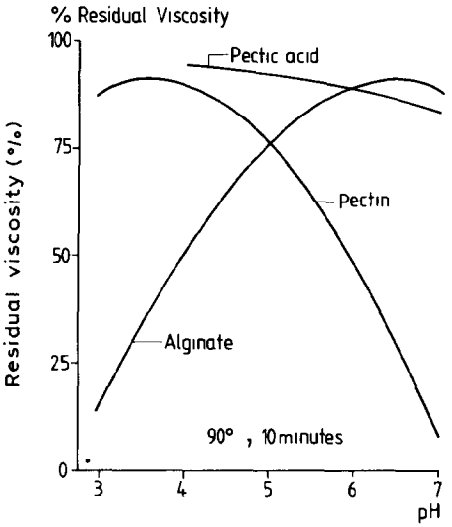


Fig. 8. Heat stability of pectin and alginate[4].

the carrageenans, a group of compounds extracted from several families and genera of red algae. Not all members of this family have the capacity to gel. In Fig. 9, mu-carrageenan illustrates the non-gelling types and kappa-carrageenan the gelling types. Kappa-carrageenan is insoluble in cold water, but dissolves in hot water and sets to a gel on cooling in the presence of potassium cations. The basic unit is a (1→4)-linked dimer, several hundred of which are linked to each other by (1→3) linkages; the orientation of all the linkages is diequatorial. This gives the polymer the regularity necessary for the formation of junction zones. It is noteworthy that the equatorial positions of the hydroxyl groups involved in the glycosidic linkages of the 3,6-anhydrogalactose moiety arise from the fact that the ether ring forces the molecule into the unusual $^1C(D)$ conformation. No such regularity exists in the non-gelling carrageenans, where the axial–equatorial linkages result in a chain having kinks already apparent in the dimer. Under alkaline conditions, the 6-*O*-sulfated galactose is converted to the 3,6-anhydro sugar; it should be understood that alkali treatment is an important step in the manufacture of gelling carrageenans. The junction zones in the case of a carrageenan gel are double helices and while in Fig. 10 the transitions from the state of unordered coils to double helices and to aggregates are simply indicated by arrows, it must be realized that this is an area to which much research effort is dedicated[3]. Carrageenan gels tend to become brittle, probably because the aggregates are prone to associate further. Galactomannans can serve as spacing agents–smooth regions of the galactomannan with few or no galactose side-groups associate with a helix, preventing another helix from doing so (Fig. 11)[3]. Gels made in this way are beautifully elastic; in many cases the carrageenan manufacturer already adds an appropriate amount of galactomannan to his product, which is sold for uses in pie fillings, dessert gels, gelled milk

products, and the like. The high-molecular-weight, highly viscous, water-soluble galactomannans do not gel by themselves but find many food uses as thickening agents in sauces and soups, as body builder in soft drinks, and as stabilizer in ice creams to prevent growth of ice crystals. For improving the gelling characteristics of carrageenans, locust bean gum is chosen. It has fewer side groups than guar gum and therefore a better potential for smooth regions necessary for associating with a helix. Such associations are also formed with xanthan gum, resulting in a dramatic increase in viscosity. Solutions of xanthan gum, alginate, and carrageenan are widely used as stabilizers, to prevent fruit-pulp particles from settling in fruit beverages, to keep cocoa particles in suspension in chocolate milk, or to prevent the creaming up of oil droplets in bottled, ready-to-use salad dressings. This is attributable to an interesting rheological property, the formation of weak gels; it might be said that the particles or the oil droplets are gelled-in in a liquid system.

The functional properties of polysaccharides are often improved by derivatization. Table I shows[5] 20 derivatives of starch made to improve or to impart functionality, for instance freeze–thaw stability if starch is used as a thickening and binding agent for sauces in frozen meals, or for better stability against high temperature and shear forces if starch is a binding agent in extruded snacks. Much money has been and is being spent on toxicity testing of polysaccharides and polysaccharide derivatives to obtain approval for food use. These costs can be gained back only on very large-volume uses, and the risk of failing to overcome toxicological and/or red-tape barriers for food clearance must be carried by non-food uses. These aspects are a major concern of gum manufacturers.

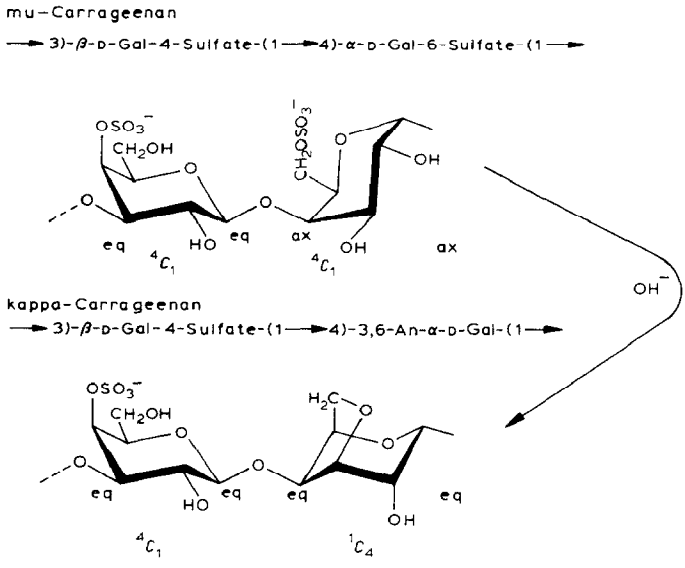


Fig. 9. Gelling (Kappa) and non-gelling (Mu) carrageenans.

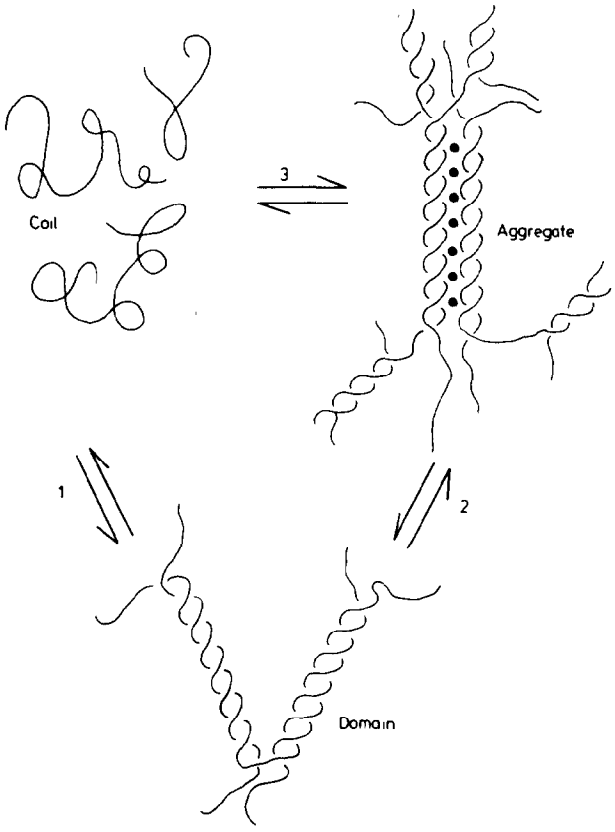


Fig. 10. The domain model of carrageenan gelation. Interchain association of iota carrageenan occurs primarily through double helices (domains) which, with certain cations (●), can aggregate to form a gel. From ref. 3, with permission.

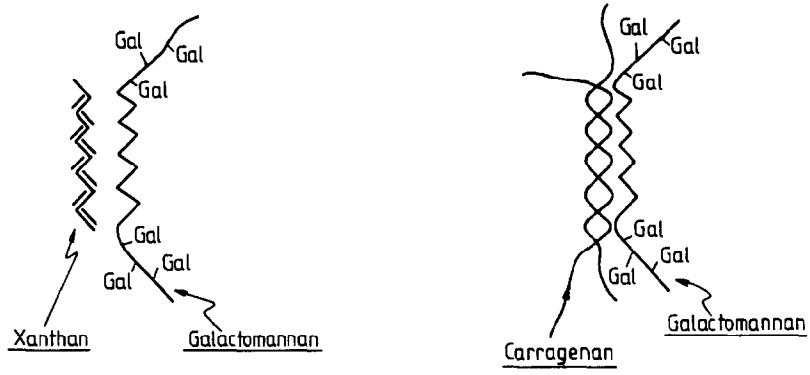


Fig. 11. Models proposed for the interaction between chains of xanthan and carrageenan with galactomannan[3].

TABLE I

MODIFIED STARCHES (INCLUDING AMYLOSE AND AMYLOPECTIN)[5]

Acetylated distarch adipate
Acetylated distarch glycerol
Acetylated distarch phosphate
Acid-treated starches
Alkali-treated starches
Amylose and amylopectin
Bleached starches
Dextrins, white and yellow
Distarch glycerol
Distarch phosphate
Enzyme-treated starches
Hydroxypropyl distarch glycerol
Hydroxypropyl distarch phosphate
Hydroxypropyl starch
Monostarch phosphate
Oxidized starch
Phosphated distarch phosphate
Starch acetate
Starch sodium octenyl succinate
Starch sodium succinate

Endogenous polysaccharides also play an important rôle in food processing. In this respect, pectin is again important in its function as a structural cell-wall element. Softening of the texture of vegetables and sloughing of potatoes as a consequence of heat treatment is because of eliminative breakdown. On the other hand, an increase of the hardness of canned vegetables is obtained by adding a calcium salt to the liquid; the food technologist speaks of calcium firming. The calcium ions bind the pectin chains together and thus increase cell cohesion. If plant tissue is disintegrated for the preparation of fruit or vegetable juice, a pulpy, viscous liquid is obtained in which pectin is present in the liquid and in the solid phase. Technologically it is then a substrate for endogenous and exogenous enzymes. In, for example, orange juice there is strong native pectinesterase activity–if this is not inhibited, the originally high-ester juice pectin is de-esterified and precipitates with the calcium ions of the juice[6]. The consequence is self clarification of the juice, a serious quality defect. The only practical means against this has thus far been heat inactivation or freezing, both not very satisfactory, the first for quality and the second for economic reasons. The consumer wants orange juice having a stable cloud. For such juices as apple, grape, and blackcurrant, a stable, clear juice is desired. Filtration of the juice and concentration for storage and transport can only be achieved by complete depolymerization of the pectin molecules. For this purpose, fungal pectinases have been in use for ~50 years. These enzymes are also used to achieve better press yields and to manufacture cloud-stable fruit nectars and vegetable juices[7]. Juice from enzyme-treated apple pulp sometimes causes a haze problem. Analysis shows that the major component

(90%) of the haze material is L-arabinan, 88% of which has the (1→5)-linkage. This result indicates an arabinan consisting primarily of linear glycosidic sequences. Fig. 12 shows this linear sequence as the backbone of a branched arabinan having (1→2)- and (1→3)-linked arabinan side-chains. It is this branched, water-soluble α-L-arabinan that is originally present in apples; the commercial fungal pectic enzyme-preparations contain an arabinosidase that detaches the side chains; the remaining unbranched arabinan chains then associate to insoluble micelles, the haze material[8]. A confirmation of the absolute and the anomeric configuration of the arabinose molecules and the type of glycosidic linkages is seen in the fact that the haze material can be broken down by an endo-(1→5)-α-L-arabinanase, and enzyme manufacturers are now investigating whether they can prepare arabinosidase-free pectinase preparations or whether they should add an endo-arabinase to their preparations, as they do add amylases to prevent starch-haze formation. This is an example of a plant polysaccharide that is troublesome in foods.

Some microbial polysaccharides also cause difficulties in food processing, for example, *Botrytis cinerea* gum[9]. This black mold develops on grapes when picking is delayed. It exudes pectolytic enzymes that cause perforation of the grape skin. More water can then evaporate, and crushing yields grape juice having a high sugar content. This is fermented to a wine having a very particular flavour, formed partly by the yeasts in this high-sugar system, and partly by the mold itself. It is highly appreciated by German wine connoisseurs who pay premium prices for such wines which carry the designation Edelfäule (noble rot). The difficulty is that a polysaccharide is formed by the mold, a (1→3)-β-D-glucan having (1→6)-β-D-glucosyl side groups. This high-molecular-weight gum gives very viscous musts, and wines that are difficult to filter and to clarify. An enzyme firm has recently marketed an exo-(1→3)-β-D-glucanase that will be a very welcome processing aid.

Cereal pentoglycans that have been mentioned as dietary fibre are also substrates for polysaccharide depolymerases in connection with bread making. These hemicelluloses seem to inhibit dough development by forming a restrictive network

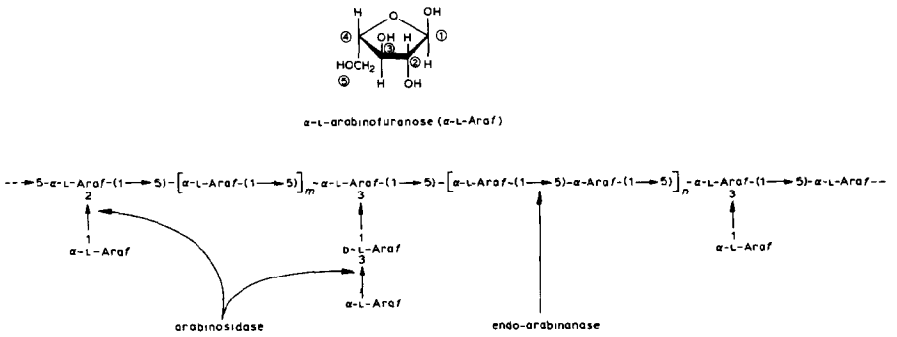


Fig. 12. Schematic structure of arabinan isolated from apple-juice concentrate. Points of attack of arabinan-degrading enzymes[8].

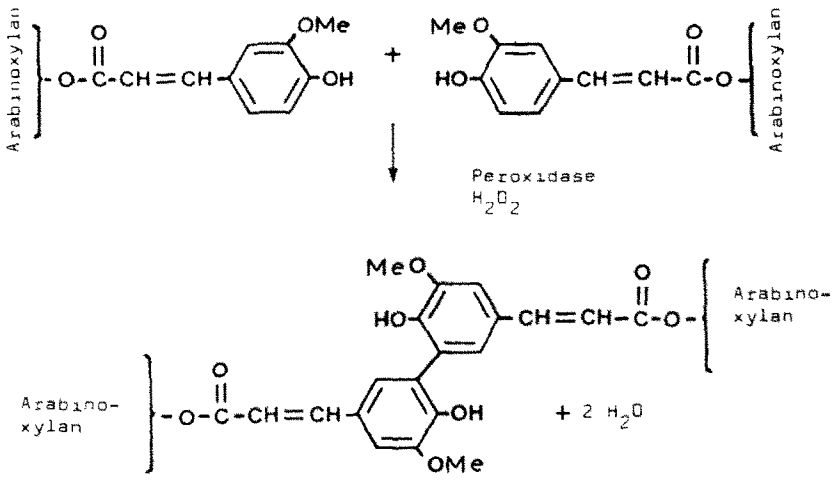


Fig. 13. Crosslinking of arabinoxylan chains by oxidative phenolic coupling of two ferulic acid residues[10].

in the dough, and there are enzyme preparations on the market with mainly pentoglycanase activity that are used as dough-improving agents. It is not yet clear which pentoglycans are involved, but Fig. 13 shows how these molecules might be coupled to each other[10]. Cereal pentoglycans are often found to be esterified with ferulic acid, and gelation of an aqueous flour extract may be achieved by oxidative coupling of the phenol rings with hydrogen peroxide and peroxidase. It is very probable that this coupling also happens naturally in flour, as diferulic acid has been found in flour after alkali treatment. This gelling mechanism is not restricted to pentoglycans. Side chains of sugar-beet pectin also carry ferulic acid substituents, and gels may be obtained by adding hydrogen peroxide and peroxidase[11]. Esterification of guaran with phenolic acids and gelling of solutions of these esters by oxidation have been described[12]. Can cheap, new gelling agents be made in this way?

CONCLUSIONS

There is very little activity in respect to new polysaccharides for food uses except in the field of microbiological polysaccharides. Will the need for new functions or new raw materials become greater than the deterrent factors connected with obtaining food approval? We do not know. At any rate the extensive research efforts on structure and properties of existing food polysaccharides have great importance for the rational production of wholesome food.

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