SPECIAL SECTION: Molecular Diversity and Health Benefits of Carbohydrates from Cereals and Pulses

REVIEW

Variability in Fine Structures of Noncellulosic Cell Wall Polysaccharides from Cereal Grains: Potential Importance in Human Health and Nutrition

Helen M. Collins,[1] Rachel A. Burton,[1] David L. Topping,[2] Ming-Long Liao,[3] Antony Bacic,[3] and Geoffrey B. Fincher[1,4]

ABSTRACT

Cereal Chem. 87(4):272–282

Noncellulosic polysaccharides from the cell walls of cereal grains are not digested by human small intestinal enzymes and so contribute to total dietary fiber intake. These polysaccharides are becoming recognized increasingly for their potential to lower the risk of serious diet-related conditions such as type II diabetes, cardiovascular disease, colorectal cancer, and diverticular disease. The effectiveness of noncellulosic cell wall polysaccharides in improving health outcomes is related to the fine structure and associated physicochemical properties. The two most nutritionally relevant wall polysaccharides of cereal grains are the arabinoxylans and the (1-3,1-4)-β-D-glucans. These polysaccharides have high molecular mass values but are nevertheless soluble in aqueous media, at least in part, where they adopt highly asymmetrical conformations and consequently form high viscosity solutions. Thus, arabinoxylans and (1-3,1-4)-β-D-glucans contribute to the soluble fiber component of human diets. The molecular size, solubility, and viscosity of the polysaccharides vary widely not only between different cereals but also within a single species. The variability in these properties reflects differences in the chemical structure of the polysaccharides, which in turn influences the beneficial effects of arabinoxylans and (1-3,1-4)-β-D-glucans in human diets. Here, we summarize information on the variability of fine structures of the arabinoxylans and (1-3,1-4)-β-D-glucans in common cereals and relate these to solubility, viscosity, and health benefits. The recent identification of genes involved in the biosynthesis of the (1-3,1-4)-β-D-glucans opens the way for the genetic improvement of cereal quality parameters that are important in human health.

Cereal grains contain macronutrients such as protein, fat, and carbohydrate that are required by humans for growth and maintenance, but cereals also supply important minerals, vitamins, and other micronutrients that are essential for optimal health. Indeed, a major proportion of these nutrients for humans is obtained from foods prepared from cereal grains including rice (*Oryza sativa*), wheat (*Triticum aestivum*), barley (*Hordeum vulgare*), sorghum (*Sorghum bicolor*), and the millets (*Panicum miliaceum* and *Pennisetum americanum*).

In traditional agrarian societies, cereal starches remain the principal sources of energy, where they are largely consumed as whole grains, which includes the pericarp-seed coat and the aleurone layer and so are relatively high in fiber content. This is not the case in industrialized countries where refined, low-fiber foods are the norm (Marquart et al 2007). It is becoming clear that whole grain cereal foods in general have considerable potential to improve human health and to substantially lower the risk of serious, diet-related diseases. One of the most important components of whole grain cereals from this standpoint is a complement of indigestible complex carbohydrates (dietary fiber). Within the grain nonstarch polysaccharides (NSP), resistant starch (RS), and oligosaccharides (OS) are the major contributors to total dietary fiber (TDF). Of these, human intestinal enzymes can digest only starch. All other plant polysaccharides have a monomeric composition or stereochemistry that renders them resistant to human digestive enzymes. Thus, arabinoxylans and (1-3,1-4)-β-D-glucans are NSP that constitute the noncellulosic component of cell walls and cell wall residues in cereal grains, but they are not digested by human enzymes, and make up an important proportion of dietary fiber in many diets.

Dietary Fiber and Human Health

Dietary fiber reduces the risk of contracting serious human diseases and reduces the adverse social and personal impact of conditions such as colorectal cancer (CRC), cardiovascular disease (CVD), and diabetes. These are global issues and are established as the main causes of morbidity and mortality in affluent, developed economies (Jemal et al 2005). There is strong evidence that they are also emerging as serious problems in developing countries through growing affluence that is flowing from industrialization (Mascie-Taylor and Karim 2003). This time-trend not only supports the role of diet and lifestyle as risk factors for these conditions, but is also informative as to opportunities for prevention.

The strongest evidence for the contribution of dietary fiber to disease prevention comes from prospective cohort studies such as the European Prospective Investigation into Cancer and Nutrition (EPIC). Typically, these involve the assessment of the diet and lifestyle characteristics of large groups of people who are monitored for an extended period of time and are also assessed for clinical events. Data from EPIC show very strong, dose-dependent reduction in the risk of CRC with greater dietary fiber consumption (Bingham et al 2003). Other studies have shown similar re-

[1] Australian Centre for Plant Functional Genomics, School of Agriculture, Food and Wine, University of Adelaide, Waite Campus, Glen Osmond, SA 5064, Australia.
[2] CSIRO Food Futures National Research Flagship, Kintore Avenue, Adelaide, SA 5000, Australia.
[3] Australian Centre for Plant Functional Genomics, School of Botany, University of Melbourne, Parkville, VIC 3052, Australia.
[4] Corresponding author. Fax +61-8-8303-7102. E-mail: geoff.fincher@adelaide.edu.au

doi:10.1094/CCHEM-87-4-0272

ductions in the risk of obesity (Lui et al 2003; Koh-Banerjee et al 2004), diabetes (Jacobs and Gallaher 2004), diverticular disease (Aldoori et al 1998), and CVD (Jacobs and Gallaher 2004).

Some of the effects of dietary fiber reflect NSP indigestibility. This is particularly the case for insoluble NSP, which are major constituents of plant cell walls. Products such as wheat bran are extremely effective at relieving constipation through a stool bulking effect. However, it is clear that not all NSP are equal, and fractions containing pentosans are particularly effective over other polysaccharides in increasing fecal bulk (Cummings 1992). The reason for this is not clear but may reflect water-holding capacity. However, NSP have effects above and beyond simple indigestibility and they can be subdivided further on the basis of aqueous solubility into soluble and insoluble NSP. It must be emphasized that this solubility may be demonstrated under conditions that do not occur in the human small intestine (Topping 1991).

NSP in Plasma Cholesterol and Cardiovascular Disease

The terms "soluble fiber" and "insoluble fiber" have entered into common usage and also serve to segregate NSP on the basis of the best-documented physiological effect, lowering of plasma cholesterol, an established risk factor for CVD (Clearfield 2006). CVD is characterized by infiltration of lipoprotein cholesterol into major arteries. This process is known as atherosclerosis and can lead to progressive occlusion of the circulatory system, which results in impaired cardiac or brain function and, if unchecked, to tissue necrosis and death. CVD has a number of risk factors such as age and gender that cannot be altered. Modifiable risk factors include cigarette smoking, physical activity, and raised plasma low density lipoprotein (LDL) cholesterol. LDL is the major plasma vehicle for transporting cholesterol to the tissues and its connection to atherosclerosis is clear. Cereals high in soluble NSP can lower plasma cholesterol effectively. At the least, these reductions are ≈3–5% and are obtained through the consumption of foods in quantities that consumers are likely to eat (Kestin et al 1990). The lowering of total and LDL cholesterol has been demonstrated particularly through the consumption of oats and to a lesser extent barley (Truswell 2002).

Both cereals contain soluble NSP (1-3,1-4)-β-D-glucans, which are thought to be the active agents (Dikeman and Fahey 2006). Studies in humans and animals with isolated (1-3,1-4)-β-D-glucans have shown reductions supporting this hypothesis. However, there are some contradictory data generated using (1-3,1-4)-β-D-glucan-enriched fractions (Keogh et al 2003). The reasons for this uncertainty are very important and may reflect isolation procedures, food production methods, or other factors.

NSP and Diabetes

The (1-3,1-4)-β-D-glucans and other soluble NSP, such as arabinoxylans, are thought to modulate digestion by relatively high viscosity in aqueous media (Dikeman and Fahey 2006). The high viscosity is believed to slow the flow of digesta, which would attenuate fat and cholesterol absorption and the reabsorption of bile acids. It is also thought to contribute to the effects of soluble NSP through the absorption of other nutrients including glucose, which leads to a lowering of the glycemic response. The glucose released during starch digestion is absorbed and enters the circulation, raising blood concentrations and stimulating the secretion of insulin, which maintains homoeostasis through uptake of glucose by peripheral tissues. The speed and magnitude of the rise in blood glucose concentration are of considerable significance, especially in individuals with diabetes, where insulin secretion is inadequate or insulin action is impaired. The effect of soluble NSP in slowing glucose absorption is therefore of considerable benefit in terms of diabetes risk and management but also has implications for overall starch digestion. The presence of soluble NSP in foods, even at very modest levels, limits amylolysis so that the RS content is increased (Topping 2007). This leads to an area of growing interest for human health, the relationship between undigested fiber carbohydrates and the large bowel microflora.

NSP, Bowel Microflora, and Fermentation

The human cecum and colon support a numerically large, taxonomically diverse, and metabolically active bacterial population that ferments unabsorbed dietary carbohydrates. The main metabolic end products include short chain fatty acids (SCFA), in particular acetate, propionate, and butyrate. Many of the health benefits of NSP and other complex carbohydrates accrue from the presence of these acids (Topping and Clifton 2001). SCFA are absorbed during passage of the fecal stream and <10% of those produced appear in excreted feces. The SCFA taken up from the large bowel are metabolized by the viscera and contribute to energy needs. While major SCFA acids make a general metabolic contribution, butyrate in particular has attracted considerable in-

TABLE I
Composition of Cell Walls of Cereal Grains (% by wt)[a]

Cereal	Cellulose	Glucomannan	(1-3,1-4)-β-D-Glucan	Heteroxylan	Pectin	Lignin	Protein[b]
Wheat (*Triticum aestivum* L.)							
Aleurone	2	2	29	65	–	–	1
Starchy endosperm	2	2	20	70	–	–	–
Bran	29	–	6	64	–	8.3	9.2
Barley (*Hordeum vulgare* L.)							
Aleurone	2	2	26	71	–	–	6
Starchy endosperm	2	2	75	20	–	–	5
Rice (*Oryza sativa* L.)							–
Starchy endosperm	28	15[c]	20[d]	27[d]	3	–	18
Bran	9	3	6	60	8	12	8
Maize (*Zea mays* L.)						–	–
Bran	22.5	–	–	67.5	–	–	–
Oats (*Avena sativa* L.)[e]							
Starchy endosperm	–	–	85	–	–	–	–
Rye (*Secale cereale* L.)[f]							
Aleurone	8	–	13	68	–	–	–
Starchy endosperm	6	–	12	65	–	–	–

[a] Extracted from Fincher and Stone (2004).
[b] Values for wall protein may include cellular proteins.
[c] Some genotypes had very low glucomannan content.
[d] Xyloglucan/mannan.
[e] Millar et al (1995).
[f] Extracted from Glitso and Knudsen (1999), based on percentage of total nonstarch polysaccharides.

terest for its potential to promote large bowel health. It is the preferred metabolic substrate for colonocytes and its oxidation is thought to provide energy for the uptake of cations and for the salvage of water. This is an important function for the normal gut but has a considerable therapeutic potential in infectious watery diarrhea (Ramakrishna et al 2000).

Butyrate is also believed to make an important contribution to lowering the risk of chronic diseases. A substantial body of experimental evidence indicates that it acts to promote a normal colonocyte phenotype through the repair of damaged DNA and induction of programmed cell death, or apoptosis, in transformed cells. These and related actions are thought to lower the risk of CRC and help to explain the protective effect of fiber. While it appears that RS fermentation favors the production of butyrate, evidence is emerging that arabinoxylans may also be fermented to a substantial degree and may have a role to play in regulating SCFA production in humans (Lu et al 2000a,b).

NSP and Emphysema

It is clear that cereal NSP have an established and growing connection to human health which is of considerable socioeconomic importance through the reduction of diet-related disease. A population study has shown a new and unexpected relationship in the lowering of risk of emphysema by greater fiber consumption (Kan et al 2008). This disease is found most commonly in cigarette smokers and the protection mechanism is unclear. This is just one of the emerging drivers for a more thorough understanding of the relationship between the chemical structure of NSP, their physical properties, and mode of action in the gastrointestinal tract.

(1-3,1-4)-β-D-Glucans and Arabinoxylans in Cereal Grains

The NSP of cereal grains include cellulose, (1-3,1-4)-β-D-glucans, heteroxylans, glucomannans, xyloglucans, pectic polysaccharides, callose, fructans, and arabinogalactan-proteins. However, the heteroxylans and the (1-3,1-4)-β-D-glucans usually predominate, and attention is focused on these two polysaccharides in this review. Substituents on heteroxylan chains of the starchy endosperm and aleurone cells of cereal grains are mostly α-L-arabinofuranosyl residues and therefore these polysaccharides will be referred to as arabinoxylans. The absolute amounts of these major NSP of cereal grains, the arabinoxylans and (1-3,1-4)-β-D-glucans, vary considerably depending on the cereal species (Table I), the genotype of the individual cereal species, and on environmental conditions during grain development and maturation.

Among cereal grains, barley and oats contain the highest level of (1-3,1-4)-β-D-glucans (Table II), with contents on a dry basis reported to be 3–20% and 3–7% (Welch and Lloyd 1989; Wood et al 1991; Rudi et al 2006), respectively. The (1-3,1-4)-β-D-glucans are the major endosperm cell wall components of both species, where they contribute ≈75% of the total cell wall material. Wheat is not recognized as a significant source of (1-3,1-4)-β-D-glucan because of it has much lower content in the grain. These are usually <1% on a dry weight basis, although values ≤2.3% have been reported (Fincher and Stone 2004). Rice, rye, and maize also contain levels <2% (Table II).

Arabinoxylan is a major component of the cell walls of the endosperm in most cereal species and is the dominant component of wheat, rye, and maize endosperm walls (Table I). Rye and wheat have the highest content with reported ranges of 7.1–12.2% and 4–9%, respectively. This is followed by barley, maize, rice, and oats. The lowest levels are found in sorghum, which has levels of <2% (Table III).

Molecular Diversity of (1-3,1-4)-β-D-Glucans

Chemical Structure

Cereal (1-3,1-4)-β-D-glucan consists of long chains of glucosyl residues linked through both (1-3)- and (1-4)-β-linkages, in proportions of 1:2.2 to 1:2.6 (Fig. 1A) (Fincher 1975; Bacic and Stone 1981). The distribution of the two linkage types is neither random nor is it a strictly repeating arrangement. The (1-3)-linkages appear to be occurring singly, while most of (1-4)-linkages occur in groups of two or three, leading to a structure of predominantly (≈90%) (1-3)-β-linked cellotriosyl and cellotetraosyl units. Longer blocks of 4–14 contiguous (1-4)-β-linked glucosyl residues account for the rest of the structure (Cui and Wood 2000). The presence of irregularly spaced (1-3)-linkages prevents extensive alignment or crystallization of otherwise long glucan chains by introducing molecular kinks and bestows apparent water solubility on the cereal β-glucan.

Distribution in Cereal Kernels

In general (1-3,1-4)-β-D-glucan in cereals occurs in the subaleurone and endosperm cell walls (Cui and Wang 2009). Different cereals exhibit different distribution patterns in the kernels:

Oats. The distribution of (1-3,1-4)-β-D-glucan in the oat kernel appears to vary between low and high (1-3,1-4)-β-D-glucan cultivars, showing concentrations in the subaleurone layer in the low (1-3,1-4)-β-D-glucan cultivars, and an even distribution across the endosperm in the high (1-3,1-4)-β-D-glucan cultivars (Fulcher and Miller 1993).

Barley. There is no particular concentration of (1-3,1-4)-β-D-glucan in the subaleurone layer in barley as there is in oats and the distribution appears to be even across the endosperm (Autio 2006; Cui and Wang 2009).

Wheat. There is a significant concentration of (1-3,1-4)-β-D-glucan in the subaleurone layer in wheat with little found in the rest of the endosperm (Beresford and Stone 1983; Autio 2006).

TABLE II
Properties of (1-3,1-4)-β-D-Glucans in Cereal Species

Cereal	Total β-Glucan (g/100 g flour)[a]	Water-Extractable (g /100 g flour)[a]	Water-Extractable % Total β-Glucan[a,b]	Intrin. Viscosity (dL/g)[a]	Molecular Wt (kDa)[c]	DP3:DP4 Ratio[d]	(1-4),(1-3) Linkages
Wheat (*Triticum aestivum* L.)	0.5–2.3	0.02	1–4	4.96	350–800	3.0–4.5:1	2.2–2.6:1[a]
Barley (*Hordeum vulgare* L.)	2.0–20.0[e]	1.7–2.6[f]	36–54	4.6-6.9	800–2,000	2.8–3.3:1	–
Oats (*Avena sativa* L.)	3.8–6.1	3.7–5.0	82–97	2.0-9.6	800–2,000	1.8–2.4:1	–
Rice (*Oryza sativa* L.)	0.13	0.03	23		–	–	–
Rye (*Secale cereale* L.)	1.0–2.0	–	–	5.9	–	2.7–3.2:1	–
Sorghum (*Sorghum bicolor* L.)	1.1–6.2	–	–	–	–	–	1.15:1[g]
Maize (*Zea mays* L.)	0.8–1.7	–	–	–	–	–	–

[a] Extracted from Fincher and Stone (2004) and Fincher and Stone (1986).
[b] Calculated as a percentage of the water-extractable (1-3,1-4)-β-D-glucan of the total (1-3,1-4)-β-D-glucan.
[c] Cui et al (2000); Rimsten et al (2003); Li et al (2006a); Li et al (2006b).
[d] Wood (2007).
[e] Rudi et al (2006).
[f] Lazaridou et al (2008).
[g] Ramesh and Tharanathan (1998).

Rye. In rye, the overall (1-3,1-4)-β-D-glucan content is much lower than in oats and barley, and seems to be evenly distributed throughout the grain (Autio 2006).

Molecular Size

A very wide range (48,000–3,000,000) of weight average molecular weights (M_w) has been reported for cereal (1-3,1-4)-β-D-glucans (Fincher and Stone 2004), with the values depending very much on the history of the source material, the isolation procedure employed to obtain (1-3,1-4)-β-D-glucan, and the method used for molecular mass estimation. Therefore a cautious approach is needed when comparing published molecular mass data.

When comparing molecular size data of cereal (1-3,1-4)-β-D-glucan samples prepared in a similar manner and determined by defined methods, the average M_W of wheat (1-3,1-4)-β-D-glucan is in the range 350,000–800,000, and appears to be significantly lower than the values of 800,000–2,000,000 reported for oat and barley (1-3,1-4)-β-D-glucans (Table II) (Cui et al 2000; Rimsten et al 2003; Li et al 2006a,b). It is noteworthy that the health benefit of NSP, such as lowering of blood glucose, insulin, and cholesterol levels, is closely linked to viscosity and is thus dependent on both molecular size and concentration.

Fine Structure

The ratio of (1-4)- to (1-3)-linkages is fairly constant for most cereals at ≈2.2–2.6:1, except for sorghum where the ratio is 1.15:1 (Table II) (Ramesh and Tharanathan 1998). Little more is known about the fine structure of (1-3,1-4)-β-D-glucan in sorghum and how this difference might influence the physicochemical properties of the sorghum (1-3,1-4)-β-D-glucan. However, one study has proposed that sorghum (1-3,1-4)-β-D-glucan also contains (1-6)-branch points (Onwurah 2001).

The (1-3,1-4)-β-D-glucan 4-glucanohydrolase (E.C.3.2.1.73; lichenase; endo-β-D-glucanase) is an enzyme that specifically cleaves (1,4)-β-glycosidic linkages that immediately precede (1-3)-linked glucosyl residues in (1-3,1-4)-β-D-glucans (Fig. 1A). This class of enzyme is particularly useful insofar as it can be used to provide quantitative "fingerprint" information on the lengths and relative proportions of the blocks of adjacent (1-4)-β-glucosyl residues in different (1-3,1-4)-β-D-glucans. The fine structural fingerprint can subsequently be related to the physicochemical properties of the polysaccharide in aqueous media. The (1-3,1-4)-β-D-glucans of oat, barley, and wheat and noncereal (1-3,1-4)-β-D-glucan lichenin are distinguished by differences in the ratios of the two major products of (1-3,1-4)-β-D-glucan endohydrolase hydrolysis: 3-O-β-cellobiosyl-D-glucose (G4 G3G; DP3) and 3-O-β-cellotriosyl-D-glucose (G4G4G3G; DP4) (Fig. 1A). The DP3/DP4 ratios in these (1-3,1-4)-β-D-glucans are 1.8–2.4 for oats, 2.8–3.3 for barley, 3.0–4.5 for wheat, and >20 for lichenin (Cui and Wood 2000; Lazaridou et al 2004). These ratios correspond to the relative solubility of the four (1-3,1-4)-β-D-glucans, which range from the high-soluble oat polysaccharide, through barley and wheat (1-3,1-4)-β-D-glucans, to the relatively insoluble lichenin (Table II) (Cui and Wood 2000). Lichenin has long been used as a standard (1-3,1-4)-β-D-glucan but is synthesized by the fungal symbiont of the Icelandic moss lichen (Honegger and Haisch 2001; Olafsdottir and Ingólfsdottir 2001) and, as mentioned above, has a relatively high DP3/DP4 ratio. The (1-3,1-4)-β-D-glucan that was recently detected in the cell walls of the fungal pathogen *Rhynchosporium secalis* also has a very high DP3/DP4 ratio (Pettolino et al 2009).

Conformation and Solubility

The solubility of cereal (1-3,1-4)-β-D-glucans will depend on the overall conformation of the polysaccharide, which in turn will be determined by molecular size and molecular fine structure. The G4G3G trisaccharides and the G4G4G3G tetrasaccharides in a water-soluble barley (1-3,1-4)-β-D-glucan were arranged essentially at random along the polysaccharide chain (Staudte et al 1983), and this indicated that (1-3)-β-D-glucosyl residues were inserted at random along the (1-3,1-4)-β-D-glucan chain (Fincher 2009a,b). The irregular insertion of (1-3)-β-D-glucosyl residues would result in the formation of irregularly spaced kinks in the polysaccharide chain that would severely limit the capacity of the chains to align into regular aggregates and would probably account for the high solubility of polysaccharides with such a large DP (Staudte et al 1983). If it is assumed that the tri- and tetrasaccharides in other cereals (1-3,1-4)-β-D-glucans are also randomly arranged, it would follow that DP3/DP4 ratios will provide an indication of solubility. The (1-3,1-4)-β-D-glucans with ratios close to 1:1 would be expected to be more soluble than (1-3,1-4)-β-D-glucans with either very high or very low DP3/DP4 ratios because as the proportion of either the trisaccharide or the tetrasaccharide increases, the polysaccharide would become more regular in shape and this would allow increased levels of molecular alignment and hence lower solubility (Lazaridou et al 2004; Fincher, 2009a). This suggestion is supported by observations that lichenin has a

TABLE III
Properties of Arabinoxylans in Cereal Species

Cereal	Total Arabinoxylan (g/100 g flour)[a]	Water-Extractable (g/100 g flour)[a]	Water-Extractable % Total Arabinoxylan[a,b]	Ara/Xyl Ratio	Intrin. Viscosity (dL/g)[a]
Wheat (*Triticum aestivum* L.)					
Whole grain	4.0–9.0	0.3–0.9	7.5–10	0.7[c]	0.8–5.5
Flour	1.4–2.1	0.54–0.68	34		–
Bran	19.4	0.88	4.6		–
Barley (*Hordeum vulgare* L.)	3.4–8.0	0.32–0.42	5.3–9.4	0.4–0.5[d]	–
Barley (*Hordeum vulgare* L.) hulless	–	–	–	0.6–0.7[d]	–
Oats (*Avena sativa* L.) whole grain	2.2–4.1	0.2	4.9–9.1		–
Rice (*Oryza sativa* L.)			–		–
Whole grain	2.6	0.06	2.3		–
Bran	4.8–5.1	0.35–0.77	7.3–15	–	–
Rye (*Secale cereale* L.)					
Whole grain	7.1–12.2	0.6–2.4	8.5–19.7	–	–
Flour	3.10–4.31	1.05–1.49	34	0.7–0.8[e]	–
Bran	12.06–14.76	1.04–1.47	8.6–10.0	0.5–0.6[e]	–
Sorghum (*Sorghum bicolor* L.) whole grain	1.8	0.08	4.4	–	–
Maize (*Zea mays* L.) whole grain	5.1–6.8	0.46	6–9	–	–

[a] Extracted from Fincher and Stone (1986), Fincher and Stone (2004) and Biliaderis and Izydorczyk (2006).
[b] Calculated as a percentage of water-extractable arabinoxylan of the total arabinoxylan.
[c] Barron et al (2007).
[d] Knutsen and Holtekjølen (2007).
[e] Nystrom et al (2008).

DP3/DP4 ratio of ≈20 and is relatively insoluble. Conversely, the (1-3,1-4)-β-D-glucans in the primitive horsetail group of plants, including *Equisetum arvense*, have relatively low DP3/DP4 ratios, typically of the order of ≤0.1 and are also relatively insoluble (Fry et al 2008a; Sørensen et al 2008).

Thus, a significant proportion of (1-3,1-4)-β-D-glucan from barley and oat grain is extractable by water at 40°C. For example, water-soluble (1-3,1-4)-β-D-glucan extracted at 40°C accounts for ≤20% of the total (1-3,1-4)-β-D-glucan in some barley cultivars, and the soluble fraction increases ≤50–70% when extracted at 65°C (Fincher 1975; Fleming and Kawakami 1977). In contrast, the (1-3,1-4)-β-D-glucan of wheat is very difficult to solubilize, being practically unextractable with water at 65°C (Beresford and Stone 1983; Li et al 2006a).

Genetic Determinants of (1-3,1-4)-β-D-Glucan Fine Structure

Members of both the cellulose synthase-like F (*CslF*) and cellulose synthase-like H (*CslH*) gene families in cereals mediate in the synthesis of (1-3,1-4)-β-D-glucan (Burton et al 2006; Doblin et al 2009). In barley, there are seven members of the *CslF* gene family and only a single *CslH* gene. All of these genes show variable patterns of transcription across a wide range of tissues (Burton et al 2008; Doblin et al 2009) and it is far from clear what role each gene may play in the synthesis of this polysaccharide. It is likely that the products of these genes do not act in isolation but rather function in a complex, either with additional members of the family or with proteins from other families (Schreiber et al 2008).

The availability of sequences for barley *CslF* and *CslH* gene family members has enabled the expression patterns of the genes to be monitored through transcript abundance in developing barley grain. At about eight days after pollination (DAP), when cellularization of developing endosperm is essentially complete (Wilson et al 2006), there is a transient increase in *CslF9* transcripts; these subsequently decrease to very low levels by 16 DAP (Burton et al 2008). The levels of *CslF6* transcripts are high throughout endosperm development and actually increase during the latter stages of grain maturation (Burton et al 2008). Transcripts of the other members of the *CslF* gene family, as well as the *CslH* genes, remain low throughout endosperm development in barley, but this is not to dismiss them as unimportant in (1-3,1-4)-β-D-glucan biosynthesis (Burton et al 2008; Doblin et al 2009).

The abundance of transcripts for the individual *CslF* genes and their developmental patterns during grain filling appear to vary between barley cultivars and this is consistent with quantitative trait locus (QTL) mapping data. Depending on the mapping population used, QTL for barley grain (1-3,1-4)-β-D-glucan content are found near the *CslF9* locus on chromosome 1H and close to the *CslF6* locus on chromosome 7H, as expected from the expression data (Burton et al 2008). However, other QTL have been reported

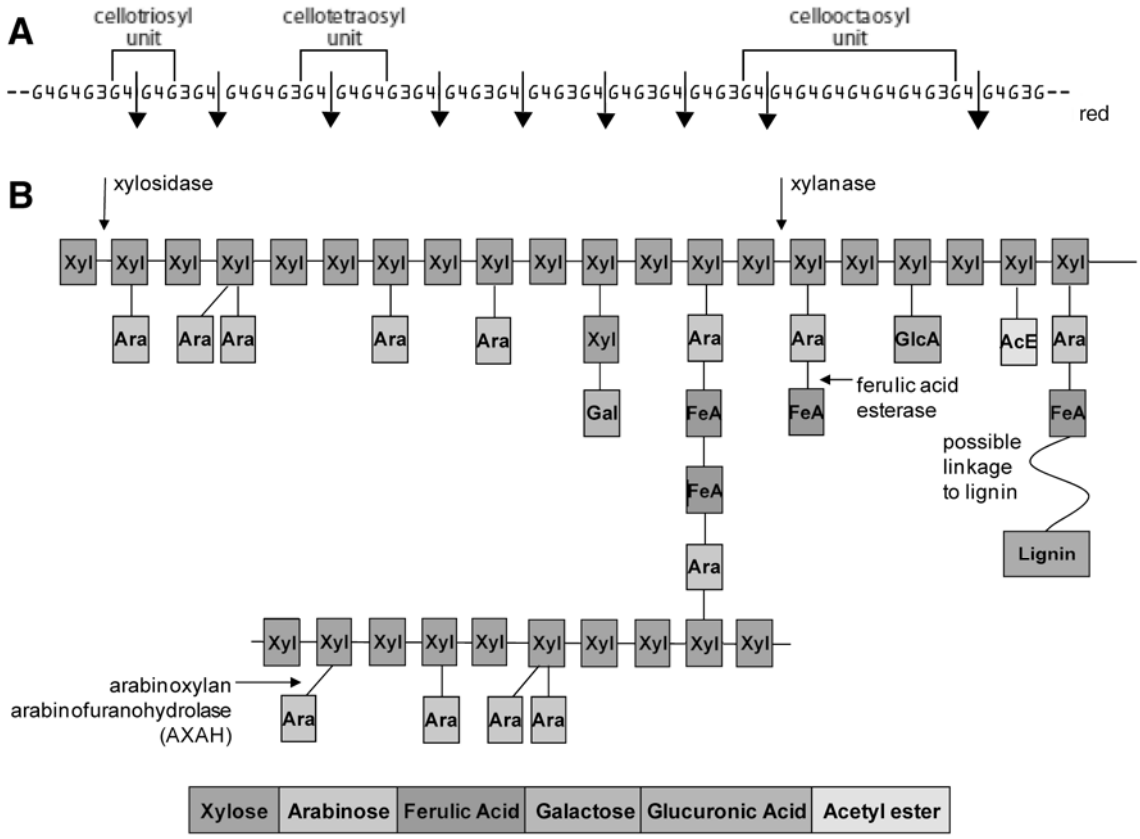

Fig. 1. A, Structure of a typical (1-3,1-4)-β-D-glucan, where G indicates a glucosyl residue, 3 indicates a (1-3)-β-glucosyl linkage, 4 indicates a (1-4)-β-glucosyl linkage and "red" indicates the reducing end of the polysaccharide. Polysaccharide may contain randomly arranged cellotriosyl and cellotetraosyl units linked by (1-3)-β-linkages. A small proportion of the molecule consists of blocks of ≤12 or 14 adjacent (1-4)-β-glucosyl linkages, as suggested here by inclusion of a cellooctaosyl residue. Arrows show linkages hydrolyzed by the family GH17 (1-3,1-4)-β-D-glucan endohydrolase group of enzymes. Because these enzymes only hydrolyze (1-4)-β-glucosyl linkages adjacent to a (1-3)-β-glucosyl residue toward nonreducing end of polysaccharide, they can be use to quantitatively determine the proportion of tri- and tetrasaccharide units in the molecule. This figure was adapted from Fincher and Stone (2004). **B,** Structure of a typical cereal arabinoxylan, showing α-L-arabinofuranosyl (Ara) units attached to O-2 or O-3 of (1-4)-linked β-D-xylopyranosyl (Xyl) residues. Some arabinofuranosyl residues are esterified at O-5 by a hydroxycinnamic acid, which may be either *p*-coumaric or ferulic acid (FeA). D-Glucuronosyl residues (GlcA) were reported as substituents at O-2 of the xylopyranosyl residues in some cereal arabinoxylans. Galactosyl (Gal) substituents are also present in plant arabinoxylans, mostly in monocots. Acetyl ester groups (AcE) have also been reported but their locations are not well defined. Diagram provided by Hunter Laidlaw.

on chromosome 2H near a cluster of *CslF* genes that are not highly expressed during endosperm development in the cultivars studied by Burton et al (2008) and in positions of the genome where there are no *CslF* or other genes that might be expected to be involved in (1-3,1-4)-β-D-glucan biosynthesis (Burton et al 2008).

Biosynthesis of (1-3,1-4)-β-D-Glucan and Regulation of Fine Structure

At the moment, it is not clear exactly where in the cell the biosynthesis of the polysaccharide takes place, although there are any number of hypotheses relating to both the mechanism and the location of (1-3,1-4)-β-D-glucan synthesis in the cereals (Burton and Fincher 2009; Fincher 2009a,b). The traditional view that noncellulosic wall polysaccharides such as the cereal (1-3,1-4)-β-D-glucans are synthesized solely in the Golgi apparatus is not easily reconciled with recent data on the location of the polysaccharide and the putative synthase enzymes. Specific antibodies against the (1-3,1-4)-β-D-glucans bind only to the cell wall in barley tissues; no binding is observed over Golgi bodies (Wilson et al 2006). However, antibodies against the CslH protein itself bind to the ER and Golgi (Doblin et al 2009). These observations have been rationalized through a two-phase assembly system for (1-3,1-4)-β-D-glucan synthesis. Thus, the (1-3,1-4)-β-D-glucans of barley might be synthesized first as a series of short cellodextrins that are covalently linked to a membrane protein or to a membrane lipid in the Golgi apparatus. The series would consist predominantly of cellotriosyl residues and cellotetraosyl residues, but would also include longer cellodextrins in steadily decreasing abundance. In the second phase of biosynthesis, the membrane-linked cellodextrins may be translocated to the plasma membrane, where a transferase polymerizes them into the final (1-3,1-4)-β-D-glucan polysaccharide (Doblin et al 2009; Fincher 2009a,b). The fine structure of the final (1-3,1-4)-β-D-glucan would be determined by the relative abundance of the cellodextrins synthesized in phase I of the putative assembly process. Candidate transferases include glucan synthase-like enzymes (Gsl), which are also known as callose synthases, and xyloglucan endotransglycosylases (XET). Such a two-phase assembly mechanism involving both the Golgi and the plasma membrane would explain why antibodies against (1-3,1-4)-β-D-glucans do not bind to the Golgi (Wilson et al 2006), where the (1-3)-β-D-glucosyl residues necessary for antibody recognition are not yet present. The antibody would only bind to the final (1-3,1-4)-β-D-glucans in the wall, after the formation of the (1-3)-β-D-glucosyl linkages. At this stage, there is only indirect evidence to support such an assembly mechanism and that other plausible mechanisms of (1-3,1-4)-β-D-glucan assembly have been proposed (Buckeridge et al 2001).

As a result of these uncertainties, we are not currently able to describe precisely the molecular and cellular processes that are involved in (1-3,1-4)-β-D-glucan synthesis and, in particular, we can only speculate on the way in which the fine structure of the polysaccharide is determined. Different CslF and CslH enzymes, either alone or in combination with other enzymes, might synthesize (1-3,1-4)-β-D-glucans with different ratios of (1-3)-β-D-glucosyl to (1-4)-β-D-glucosyl residues or with different proportions of cellotriosyl and cellotetraosyl units (Fincher 2009b). Indeed, we have recently obtained evidence in transgenic barley lines to suggest that transformation with specific *CslF* genes results in (1-3,1-4)-β-D-glucans with markedly different fine structures, especially with respect to the ratio of tri- to tetrasaccharide units (Burton et al 2010). It is possible that the mechanisms that control fine structure differ between species, and even within species, depending on the tissue location of the (1-3,1-4)-β-D-glucan and on the prevailing environmental conditions. We are accumulating knowledge and experimental technologies that will enable these questions to be addressed in the immediate future.

Alterations to (1-3,1-4)-β-D-Glucans *in Muro*

Molecular interactions between (1-3,1-4)-β-D-glucans and other types of wall polysaccharides in cereals have generally been assumed to be noncovalent. However, covalent linkages between different classes of wall polysaccharides, including (1-3,1-4)-β-D-glucans, might occur in the cereals, although unequivocal evidence is not yet available to support this possibility (Fincher 2009a). Nevertheless, a potential role in the formation of covalently linked wall polysaccharide complexes has recently been assigned to the xyloglucan endotransglycosylases (XET) and if in vivo evidence for this proposed function is subsequently obtained, it will carry important implications for the solubility of cereal grain (1-3,1-4)-β-D-glucans and hence for commercial applications. Hrmova et al (2007) showed that a highly purified barley XET catalyzed the formation of covalent linkages between xyloglucans and celluloses, and between xyloglucans and (1-3,1-4)-β-D-glucans, albeit at relatively low rates. Fry et al (2008b) later showed that an XET from *Equisetum* spp. has a preference for transferring (1-3,1-4)-β-D-glucans to xyloglucans but also concluded that cereals lack this activity. These observations provide some incentive for closer examination of the interactions between wall polysaccharides and for the potential to alter the properties of the polysaccharides following their deposition into the wall.

Importance of (1-3,1-4)-β-D-Glucan Fine Structure in Human Health

Health claims are now permitted in the United States and many other countries for oats and barley, based on the fact that both cereals and their derived products are good sources of (1-3,1-4)-β-D-glucans. In contrast, wheat is not only low in (1-3,1-4)-β-D-glucan content (<1%), but the physicochemical properties of the native (1-3,1-4)-β-D-glucan from wheat are very poor compared with those of oat or barley (1-3,1-4)-β-D-glucans. Consumption of wheat fiber (or wheat bran) does not lower plasma cholesterol and thus is often used as a control in human feeding trials (Anderson et al 1991; Topping 2007).

The water hydration capacity of wheat bran (1.67 ± 0.13 g/g) is much lower than those of barley (2.33 ± 0.19 g/g) and oat (4.12 ± 0.23 g/g) bran (Wood 1993). Moreover, because of the low solubility, essentially no wheat (1-3,1-4)-β-D-glucan will be extracted into solution at physiological temperatures. Recently, a protocol was reported that enables the isolation of high purity (>90%) (1-3,1-4)-β-D-glucan from wheat bran powder (Li et al 2006a). The extended isolation procedure, involving α-amylase digestion to remove starch, alkali (1.0*M* NaOH) extraction at room temperature, β-xylanase treatment to partially hydrolyze coextracted arabinoxylan, and fractional precipitation by ammonium sulfate, produces purified wheat (1-3,1-4)-β-D-glucan at <1% yield. Notably, without the aid of alkali or other hydrogen-bond-breaking agents, the wheat (1-3,1-4)-β-D-glucan obtained needs to be stirred at high temperature (≥85°C) for a couple of hours to achieve sufficient dissolution. Furthermore, wheat (1-3,1-4)-β-D-glucan is relatively unstable in a solution state, showing a strong tendency to aggregate or form gels (Cui and Wood 2000; Lazaridou et al 2004).

Technology developments in the milling industry, including applying specially designed machines with a friction or abrasion action to debran grains, using air classification to achieve separation based on particle density difference, and sieving to separate particles of different sizes, has been able to generate cereal fractions enriched in (1-3,1-4)-β-D-glucan (Cubadda and Marconi 2008; Verado et al 2008). Thus, for oats and barley cultivars with (1-3,1-4)-β-D-glucan at 3–7%, fractions with (1-3,1-4)-β-D-glucan contents of ≈20% can be obtained through these physical approaches. For example, Barley Balance is a natural (1-3,1-4)-β-D-glucan concentrate consisting of >23% (1-3,1-4)-β-D-glucan that is prepared from waxy barley by a dry-milling and separation process (PolyCell Technologies, http://www.poly-cell.com/index.html). Simi-

larly, through the use of a newly developed pearling technology, wheat bran fractions with >3% (1-3,1-4)-β-D-glucan may be produced (www.nelstrop.co.uk/peritec.asp).

The potential health benefits of increased (1-3,1-4)-β-D-glucan levels in wheat-based products such as bread, pasta, and cookies have been demonstrated in numerous studies using added milling fractions from oat and barley to elevate the (1-3,1-4)-β-D-glucan content of the products (Cavallero et al 2002; Gill et al 2002; Kerckhoffs et al 2003; Andersson et al 2004; Trogh et al 2004, Sinesio et al 2008).

Molecular Diversity of Arabinoxylans

Chemical Structure

Arabinoxylans of the cereals typically consist of a main chain of (1-4)-linked β-D-xylopyranosyl (Xyl*p*) residues (Fig. 1B). With each Xyl*p* residue in the $^4C_1$ chair conformation (Nieduszynski and Marchessault 1971), every hydroxyl group, including those involved in glycosidic linkages, will be in the equatorial configuration. The molecular structure will therefore adopt an extended chain conformation similar to cellulose, albeit with more flexibility than a cellulosic chain, and chains will have a propensity to aggregate through the formation of extensive interchain hydrogen bonding. Varying amounts of α-L-arabinofuranosyl (Ara*f*) units can be attached to O-2 or O-3 of Xyl*p* residues, giving rise to Xyl*p* residues that may be unsubstituted, monosubstituted or disubstituted. In wheat and rye arabinoxylans, only small amounts of O-2 substituted Xyl*p* residues are present (Andersson et al 2006). The arabinose-to-xylose (Ara/Xyl) ratio has been regarded as an important indicator of the physicochemical properties of arabinoxylans because degree of substitution of the main xylan chain will influence the ability of chains to aggregate and hence affect solubility. Thus, one would expect that highly substituted arabinoxylans would be more soluble than those with fewer arabinosyl substituents. For example, when a water-soluble arabinoxylan from wheat flour was treated with α-L-arabinofuranosidase, the resulting products have fewer Ara*f* substituents and more readily aggregate into insoluble complexes (Andrewartha et al 1979).

The distribution of arabinosyl substituents along the xylan backbone will also influence the physicochemical properties of the polysaccharide. In many cereal arabinoxylans, substitution patterns appear to be nonrandom, with different regions showing different substitution patterns (Gruppen et al 1993; Izydorczyk and Biliaderis 1994). In some regions, mono- and di-substituted Xyl*p* residues are clustered together, often separated by 1–2 unsubstituted Xyl*p* residues. Other regions contain relatively few arabinosyl substituents and therefore are susceptible to hydrolysis by xylanases (Fig. 1B).

Cereal arabinoxylans also bear hydroxycinnamic acid substituents including ferulic acid and *p*-coumaric acids at O-5 of Ara*f* substituents attached to the O-3 atoms of backbone Xyl*p* residues (Smith and Hartley 1983). The feruloyl moiety is susceptible to oxidative cross-linking through a free-radical mechanism catalyzed by enzymes and oxidizing agents such as peroxidase/H_2O_2. This can lead to gel formation through dimerization of neighboring arabinoxylan chains (Stone and Morell 2007). In addition, acetyl ester groups can be present on Xyl*p* or Ara*f* residues but the locations are not well-defined because of the labile nature of the esters (Stone and Morell 2007). Other substituents on Xyl*p*, including glucuronosyl residues, 4-*O*-methyl-glucuronosyl residues and short oligomeric side chains consisting of two or more arabinosyl residues, or an arabinosyl residue with a terminal xylosyl residue, have been reported at low levels for some cereal arabinoxylan extracts (Viëtor et al 1992; Andersson et al 2006).

Molecular Size

As for (1-3,1-4)-β-D-glucans, the molecular mass of arabinoxylans depends on the cereal species, the cell wall type, the method of extraction, and the method used to determine the molecular size of the polysaccharide preparation. Average molecular mass values have been reported at 65,000–5,000,000 with M_w/M_n ratios of 1.3 for alkali-soluble wheat arabinoxylan to 8.5 for rye arabinoxylan (Fincher and Stone 2004). Thus, the arabinoxylan, in common with other cell wall polysaccharide preparations, represent polydisperse populations of molecules that probably originate from imprecise mechanisms of chain termination during biosynthesis or through postsynthetic enzymic and nonenzymic modifications.

Solubility

Cereal arabinoxylans have been broadly divided into two groups: water-soluble or water-extractable arabinoxylans (WE-AX) and water-insoluble of water-unextractable arabinoxylans (WU-AX). The WE-AX components are usually extracted with water at <40°C, while alkali is needed to extract WU-AX. The solubility of arabinoxylans will undoubtedly be determined by the molecular size and the fine structure of the polysaccharide. For the latter, differences in structural or molecular features, including the degree and patterns of arabinofuranosyl substitution, and the various forms of covalent bonding such as ester and diferulic acid bridges will contribute to solubility characteristics of the polysaccharides.

On a dry weight basis, WE-AX and total arabinoxylan comprise 0.3–0.9% and 4.0–9.0%, respectively, of wheat grain (Stone and Morell 2007) and 0.6–3.0% and 7.0–12%, respectively, of rye grain (Table III) (Bengtsson and Aman 1990). This shows clearly that the soluble fraction only accounts for a small proportion of total arabinoxylan in grains from both of these cereals.

Unfractionated WE-AX exhibit large variations in the Ara/Xyl ratio, with typical average values of 0.5–0.7, but extreme values of 0.3–1.1 have been reported for their subfractions (Philippe et al 2006; Stone and Morell 2007). Less information is available for the WU-AX preparations. The structures of WU-AX preparations, obtained from alkali extraction (Gruppen et al 1991, 1992, 1993) or xylanase extraction (Ordaz-Ortiz and Saulnier 2005), appear to be similar to those of WE-AX, with only small differences in molecular weight and Ara/Xyl ratio.

Genetic Determinants of Arabinoxylan Fine Structure

At this stage, we know less about the synthesis of AX than we do about (1-3,1-4)-β-D-glucan synthesis. There are a number of reports detailing the perturbation of genes that cause a lower accumulation of AX in plants, as summarized for wheat by Saulnier et al (2007). The need for the synthesis of a backbone that is subsequently substituted by the addition of a number of differently configured side-chains, some of which may contain multiple constituents (Fig. 1B), ensures that the unraveling the mechanism of AX synthesis will pose a major challenge to plant biologists. Recent bioinformatical analyses of mutant lines and transcript profiles during periods of arabinoxylan synthesis in the Poaceae, suggest that genes in GT43 families might encode (1-4)-β-D-xylan synthases, genes in the GT47 family encode xylan (1-2)-α- or (1-3)-α-L-arabinosyl transferases, and genes in the GT61 family encode feruloyl-arabinoxylan (1-2)-β-D-xylosyl transferases (Brown et al 2007; Mitchell et al 2007; Pena et al 2007; Persson et al 2007). However, experimental confirmation of the participation of these genes in the process of AX biosynthesis has so far proved elusive and these suggestions challenge traditional views as to how heteroxylans in plants are assembled (York and O'Neill 2008; Fincher 2009a).

Although the genes that encode xylan synthases and the key glycosyl transferases that together mediate the synthesis of AX in plants have not been identified, QTL mapping has revealed that genes involved in the Ara-to-Xyl ratio of the water-extractable AX from wheat grain are located on chromosome 1BL and elsewhere (Martinant et al 1998), while examination of wheat-rye addition lines indicate that genes controlling AX levels are located on chromosome 6R (Boros et al 2002). A QTL contributing to dough viscosity and soluble AX is located on chromosome 7A of wheat

(Groos et al 2007). However, the genes involved in AX synthesis in these regions of the genome have not been identified and this has limited our ability to explain the differences in AX fine structure and in its regulation. Furthermore, uncertainties regarding the enzymic determinants of Ara-to-Xyl ratios, AX chain length and solubility (Saulnier et al 2007) place serious interpretative constraints on the genetic data that have so far been published for AX levels and fine structure in cereals.

Remodeling of Arabinoxylan *in Muro*

There are a number of reports to suggest that newly synthesized AX has a high degree of arabinosyl substitution, and that differing numbers of arabinosyl residues are subsequently removed, possibly by the action of arabinoxylan arabinofuranohydrolases (Carpita 1984; Lee et al 2001; Gibeaut et al 2005). These are extracellular enzymes (Lee et al 2001) and have the potential to significantly alter the physicochemical properties of the AX after they are deposited into the wall. As a result, it is unclear whether the degree of arabinosyl substitution of AX is regulated at the biosynthetic level through the activity of arabinosyl transferases, or at the remodeling level through the postsynthetic removal of arabinosyl residues, or if both processes are important for the determination of AX fine structure. Also, the evidence that arabinoxylan arabinofuranohydrolases remove arabinosyl residues from AX in vivo is not strong (Lee et al 2001) nor can the participation of other as yet unidentified hydrolytic enzymes cannot be ruled out. In any case, the removal of arabinosyl residues from AX would presumably increase the potential for intermolecular interactions, both between AX molecules themselves, or between AX and other wall constituents. This in turn would affect AX solubility and the overall properties of the wall.

Importance of Arabinoxylan Fine Structure in Human Health

WE-AX is believed to be the main NSP responsible for the perceivable viscosity-enhancing property of wheat grain because wheat (1-3,1-4)-β-D-glucan is mostly insoluble in water at body temperature (Beresford and Stone 1983). There are a limited number of reports in which health benefits were demonstrated for wheat arabinoxylan concentrate that was isolated as a by-product during starch and gluten production from wheat flour (Lu et al 2000a,b, 2004; Zunft et al 2004). However, it is still not clear as to whether or not cereal arabinoxylans in grain or milling fractions are able to produce the health benefits that are well-established for oat and barley (1-3,1-4)-β-D-glucans (Brennan and Cleary 2005; Topping 2006). Based on the data compiled in review articles (Autio 2006; Stone and Morell 2007), wheat WE-AX does not compare favorably with oat or barley (1-3,1-4)-β-D-glucans with respect to viscosity.

Wheat WE-AX preparations have viscosities of 0.8–5.5 dL/g, while those of oat and barley (1-3,1-4)-β-D-glucan are ≤9.6 dL/g (Tables II and III). For the agronomic improvement of wheat, rye has served as a valuable donor of genes (Dhaliawal and MacRitchie 1990). The wheat 1B/1R lines seem to contain more WE-AX than normal wheats, but the translocation of the rye 1R chromosome fragment appears to have a negative effect on the molecular size of the WE-AX in these lines (Biliaderis et al 1992; Selanere and Andersson 2002).

It should be reemphasized that WE-AX only accounts for a small proportion of the total arabinoxylan found in wheat grain. Extraction of arabinoxylan from whole grain meal or the bran fraction is thus difficult and unlikely to be commercially feasible. It is generally accepted that arabinoxylan plays a significant role in the baking performance of cereals, and various microbial xylanases are already widely utilized in breadmaking to overcome the detrimental effect of WU-AX on product quality (Courtin and Delcour 2002; Selinheimo et al 2006). Xylanases not only hydrolyze the xylan backbone of WU-AX to release WE-AX, they also reduce the molecular size of the WE-AX group (Courtin and Delcour 2001). However, it is unclear whether this enzymic depolymerization will damage or destroy physiological efficacy of arabinoxylan.

Concluding Remarks

Recent advances in the identification of genes involved in (1-3,1-4)-β-D-glucan synthesis have opened up opportunities to dissect the molecular mechanisms that control the fine structure of the polysaccharide, including parameters such as the ratio of (1-4)-β-D-glucosyl to (1-4)-β-D-glucosyl residues, the ratio of trisaccharide to tetrasaccharide units along the chain, and the final molecular size of the polysaccharide. It is highly likely that the genes that mediate AX biosynthesis in cereals and grasses will soon be identified. Of particular importance will be genes that encode xylan synthases, arabinosyl transferases, and feruloyl transferases. Once these genes are characterized, we will be in a better position to unravel the molecular mechanisms for AX biosynthesis and to define the determinants of AX fine structure.

A more thorough understanding of the molecular mechanisms for both (1-3,1-4)-β-D-glucan and AX synthesis should enable us to isolate or prepare polysaccharides with well-defined structures, which in turn could be used in animal and human feeding trials to assess in detail the underlying factors that contribute to the beneficial effects of these wall polysaccharides on human health.

ACKNOWLEDGMENTS

This work has been supported by grants from the Australian Research Council, the Grains Research and Development Corporation, and the CSIRO Flagship Collaboration Fund. We thank Hunter Laidlaw for preparation of Fig. 1B.

LITERATURE CITED

Aldoori, W. H., Giovannucci, E. L., Rockett, H. R. H., Sampson, L., Rimm, E. B., and Willett, W. C. 1998. A prospective study of dietary fiber types and symptomatic diverticular disease in men. J. Nutr. 128: 714-719.

Anderson, J. W., Gilinsky, N. H., Deakins, D. A., Smith, S. F., Neal, D. S., Dillon, D. W., and Oeltgen, P. R. 1991. Lipid responses of hypercholesterolemic men to oat-bran and wheat-bran intake. Am. J. Clin. Nutr. 54:678-683.

Andersson, A., Armo, E., Grangeon, E., Fredriksson, H., Andersson, R., and Aman, P. 2004. Molecular weight and structure units of (1-3,1-4)-β-glucans in dough and bread made from hull-less barley milling fractions. J. Cereal Sci. 40:195-204.

Andrewartha, K. A., Phillips, D. R., and Stone, B. A. 1979. Solution properties of wheat-flour arabinoxylans and enzymatically modified arabinoxylans. Carbohydr. Res. 77:191.

Autio, K. 2006. Functional aspects of cereal cell-wall polysaccharides. Page 167 in: Carbohydrates in Food. A. C. Eliasson, ed. Taylor and Francis: New York.

Bacic, A., and Stone, B. 1981. Isolation and ultrastructure of aleurone cell walls from wheat (*Triticum aestivum* cultivar Insignia) and barley (*Hordeum vulgare* cultivar Clipper). Austr. J. Plant Physiol. 8:453-474.

Barron, C., Surget, A., and Rouau, X. 2007. Relative amounts of tissues in mature wheat (*Triticum aestivum* L.) grain and their carbohydrate and phenolic acid composition. J. Cereal Sci. 45:88-96.

Bengtsson, S., and Aman, P. 1990. Isolation and chemical characterization of water-soluble arabinoxylans in rye grain. Carbohydr. Polym. 12:267-277.

Beresford, G., and Stone, B. A. 1983. (1-3),(1-4)-β-D-glucan content of *Triticum* grains. J. Cereal Sci. 1:111-114.

Biliaderis, C. G., and Izydorczyk, M. S. 2006. Arabinoxylans: Technologically and nutritionally functional plant polysaccharides. Page 251 in: Functional Food Carbohydrates. C. G. Biliaderis and M. S. Izydorczyk, eds. CRC Press: Boca Raton, FL.

Biliaderis, C. G., Izydorczyk, M. S., Lukow, O. M., and Bushuk, W. 1992. Pentosans in flours of 1B-1R translocation wheats. Cereal Chem. 69:226-228.

Bingham, S. A., Day, N. E., Luben, R., Ferrari, P., Slimani, N., Norat, T., Clavel-Chapelon, F., Kesse, E., Nieters, A., Boeing, H., Tjonneland, A., Overvad, K., Martinez, C., Dorronsoro, M., Gonzalez, C. A., Key, T. J., Trichopoulou, A., Naska, A., Vineis, P., Tumino, R., Krogh, V., Bueno-de-Mesquita, H. B., Peeters, P. H. M., Berglund, G., Hallmans, G., Lund, E., Skeie, G., Kaaks, R., and Riboli, E. 2003. Dietary fibre in food and protection against colorectal cancer in the European Prospective Investigation into Cancer and Nutrition (EPIC): An observational study. Lancet 361:1496-1501.

Boros, D., Lukaszewski, A. J., Aniol, A., and Ochodzki, P. 2002. Chromosome location of genes controlling the content of dietary fibre and arabinoxylans in rye. Euphytica 128:1-8.

Brennan, C., and Cleary, L. 2005. The potential use of cereal (1-3,1-4)-β-D-glucans as functional food ingredients. J. Cereal Sci. 42:1-13.

Brown, D. M., Goubet, F., Vicky, W. W. A., Goodacre, R., Stephens, E., Dupree, P., and Turner, S. R. 2007. Comparison of five xylan synthesis mutants reveals new insight into the mechanisms of xylan synthesis. Plant J. 52:1154-1168.

Buckeridge, M. S., Vergara, C. E., and Carpita, N. C. 2001. Insight into multi-site mechanisms of glycosyl transfer in (1-4)-β-D-glycans provided by the cereal mixed-linkage (1-3),(1-4)-β-D-glucan synthase. Phytochemistry 57:1045-1053.

Buliga, G. S., Brandt, D. A., and Fincher, G. B. 1986. Sequence statistics and solution conformation of a barley (1-3,1-4)-β-D-glucan. Carbohydr. Res. 157: 139-156.

Burton, R. A., and Fincher, G. B. 2009. (1-3,1-4)-β-D-Glucans in cell walls of the *Poaceae*, lower plants and fungi: A tale of two linkages. Molecular Plant 2:873-882.

Burton, R. A., Wilson, S. M., Hrmova, M., Harvey, A. J., Shirley, N. J., Medhurst, A., Stone, B. A., Newbigin, E. J., Bacic, A., and Fincher, G. B. 2006. Cellulose synthase-like CslF genes mediate the synthesis of cell wall (1-3,1-4)-β-D-glucans. Science 311:1940-1942.

Burton, R. A., Jobling, S. A., Harvey, A. J., Shirley, N. J., Mather, D. E., Bacic, A., and Fincher, G. B. 2008. The genetics and transcriptional profiles of the cellulose synthase-like HvCslF gene family in barley. Plant Physiol. 146:1821-1833.

Burton, R. A., Collins, H. M., Kibble, N. A. J., Smith, J. A., Shirley, N. J., Jobling, S. A., Henderson, M., Singh, R. R., Pettolino, F., Wilson, S. M., Bird, A. R., Topping, D. L., Bacic, A., and Fincher, G. B. 2010. Over-expression of specific *HvCslF* cellulose synthase-like genes in transgenic barley increases the levels of cell wall (1,3;1,4)-β-D-glucans and alters their fine structure. Plant Biotechnol. J. doi: 10.1111/j.1467-7652.2010.00532.x

Carpita, N. C. 1984. Cell wall development in maize coleoptiles. Plant Physiol. 76:205-212

Cavallero, A., Empilli, S., Brighenti, F., and Stanca, A. M. 2002. High (1-3,1-4)-β-glucan barley fractions in bread making and their effects on human glycemic response. J. Cereal Sci. 36:59-66.

Clearfield, M. 2006. Statins and the primary prevention of cardiovascular events. Current Atheroscler. Rep. 8:390-396.

Courtin, C. M., and Delcour, J. A. 2001. Relative activity of endoxylanases towards water-extractable and water-unextractable arabinoxylan. J. Cereal Sci. 33:301-312.

Courtin, C. M. and Delcour, J. A. 2002. Arabinoxylans and endoxylanases in wheat flour bread-making. J. Cereal Sci. 35:225-243.

Cubadda, R. E., and Marconi, E. 2008. Developing functional foods enriched with natural barley β-glucans: A review. Ingred. Aliment. 7:6-13.

Cui, S. W., and Wang, Q. 2009. Cell wall polysaccharides in cereals: Chemical structures and functional properties. Struc. Chem. 20:291-297.

Cui, S. W., and Wood, P. J. 2000. Relationships between structural features, molecular weight and rheological properties of cereal β-D-glucans. Pages 159-168 in: Hydrocolloids (1): Physical Chemistry and Industrial Applications of Gels, Polysaccharides and Proteins. K. Nishinari, ed. Elsevier: Amsterdam.

Cui, S. W., Wood, P. J., Blackwell, B., and Nikiforuk, J. 2000. Physicochemical properties and structural characterization by two-dimensional NMR spectroscopy of wheat β-D-glucan—Comparison with other cereal β-D-glucans. Carbohydr. Polym. 41:249-258.

Cummings, J. H. 1992. The effect of dietary fiber on fecal weight and composition. Pages 263-349 in: Dietary Fiber in Human Nutrition. G. A. Spiller, ed. CRC Press: Boca Raton, FL.

Dhaliawal, A. S., and MacRitchie, F. 1990. Contributions of protein fractions to dough handling properties of wheat-rye translocation cultivars. J. Cereal Sci. 12:113-122.

Dikeman, C. L., and Fahey, G. C. 2006. Viscosity as related to dietary fiber: A review. Crit. Rev. Food Sci. Nutr. 46:649-663.

Doblin, M. S., Pettolino, F. A., Wilson, S. M., Campbell, R., Burton, R. A., Fincher, G. B., Newbigin, E., and Bacic, A. 2009. A barley cellulose synthase-like CSLH gene mediates (1-3,1-4)-β-D-glucan synthesis in transgenic Arabidopsis. Proc. National Acad. Sci. U.S.A. 106:5996 - 6001.

Fincher, G. B. 1975. Morphology and chemical composition of barley endosperm cell walls. J. Inst. Brew. 81:116-122.

Fincher, G. B. 2009a. Revolutionary times in our understanding of cell wall biosynthesis and remodeling in the grasses. Plant Physiol. 149:27-37.

Fincher, G. B. 2009b. The evolution of (1-3,1-4)-β-D-glucans in cell walls of grasses. Curr. Opin. Plant Biol. 12:140-147.

Fincher, G. B., and Stone, B. A. 1986. Cell walls and their components in cereal grain technology. Pages 207-295 in: Advances in Cereal Science and Technology. Y. Pomeranz, ed. AACC International: St. Paul, MN.

Fincher, G. B., and Stone, B. A. 2004. Chemistry of nonstarch polysaccharides. Pages 206-223 in: Encyclopedia of Grain Science. C. Wrigley, H. Corke, C. E. Walker, eds. Elsevier: Oxford.

Fleming, M., and Kawakami, K. 1977. Studies of the fine structure of β-D-glucan of barleys extracted at different temperatures. Carbohydr. Res. 57:15-23.

Fry, S. C., Nesselrode, B. H., Miller, J. G., and Mewburn, B. R. 2008a. Mixed-linkage (1-3,1-4)-β-D-glucan is a major hemicellulose of *Equisetum* (horsetail) cell walls. New Phytology 179:104-115.

Fry, S. C., Mohler, K. E., Nesselrode, B. H., and Franková, L. 2008b. Mixed-linkage β-glucan: Xyloglucan endotransglucosylase, a novel wall-remodelling enzyme from *Equisetum* (horsetails) and charophytic algae. Plant J. 55:240-252.

Fulcher, R. G., and Miller, S. S. 1993. Structure of oat bran and distribution of dietary fiber components. Page 1 in: Oat Bran. P. J. Wood, ed. AACC International: St. Paul, MN.

Gibeaut, D. M., Pauly, M., Bacic, A., and Fincher, G. B. 2005. Changes in cell wall polysaccharides in developing barley (*Hordeum vulgare*) coleoptiles. Planta 221:729-738.

Gill, S., Vasanthan, T., Ooraikul, B., and Rossnagel, B. 2002. Wheat bread quality as influenced by the substitution of waxy and regular barley flours in their native and extruded forms. J. Cereal Sci. 36:219-237.

Glitso, L. V., and Knudsen, K. E. B. 1999. Milling of whole grain rye to obtain fractions with different dietary fibre characteristics. J. Cereal Sci. 29:89-97.

Groos, C., Bervas, E., Chanliaud, E., and Charmet, G. 2007. Genetic analysis of bread-making quality scores in bread wheat using a recombinant inbred line population. Theor. Appl. Genet. 115:313-323.

Gruppen, H., Hamer, R. J., and Voragen, A. G. J. 1991. Barium hydroxide as a tool to extract pure arabinoxylans from water insoluble cell wall material of wheat flour. J. Cereal Sci. 13:275-290.

Gruppen, H., Hamer, R. J., and Voragen, A. G. J. 1992. Water unextractable cell wall material from wheat flour. 2. Fractionation of alkali extracted polymers and comparison with water extractable arabinoxylans. J. Cereal Sci. 16:53-67.

Gruppen, H., Kormelink, F. J. M., and Voragen, A. G. J. 1993. Water unextractable cell wall material from wheat flour. 3. A structural model for arabinoxylans. J. Cereal Sci. 18:111-128.

Honegger, R., and Haisch, A. 2001. Immunocytochemical location of the (1-3,1-4)-β-glucan lichenin in the lichen-forming ascomycete *Cetraria islandica* (Icelandic moss). New Phytology 150:739-746.

Hrmova, M., Farkas, V., Lahnstein, J., and Fincher, G. B. 2007. A barley xyloglucan xyloglucosyl transferase covalently links xyloglucan, cellulosic substrates and (1-3,1-4)-β-D-glucans. J. Biol. Chem. 282:12951-12962.

Izydorczyk, M. S., and Biliaderis, C. G. 1994. Studies on the structure of wheat endosperm arabinoxylans. Carbohydr. Polym. 24:61-71.

Jacobs, D. R., and Gallaher, D. D. 2004. Whole grain intake and cardiovascular disease: A review. Curr. Atheroscler. Rep. 6:415-23.

Jemal, A., Ward, E., Hao, Y. P., and Thun, M. 2005. Trends in the leading causes of death in the United States, 1970-2002. JAMA 294:1255-1259.

Kan, H. D., Stevens, J., Heiss, G., Rose, K. M., and London, S. J. 2008. Dietary fiber, lung function, and chronic obstructive pulmonary disease in the atherosclerosis risk in communities study. Am. J. Epidemiol. 167:570-578.

Keogh, G., Cooper, G., Mulvey, T., McArdle, B., Coles, G., Monro, J., and Poppitt, S. 2003. Randomized controlled crossover study of the effect of a highly β-glucan-enriched barley on cardiovascular disease

risk factors in mildly hypercholesterolemic men. Am. J. Clin. Nutr. 78:711-718.
Kerckhoffs, D., Hornstra, G., and Mensink, R. 2003. Cholesterol-lowering effect of β-glucan from oat bran in mildly hypercholesterolemic subjects may decrease when β-glucan is incorporated into bread and cookies. Am. J. Clin. Nutr. 78:221-227.
Kestin, M., Moss, R., Clifton, P. M., and Nestel, P. J. 1990. Comparative effects of three cereal brans on plasma-lipids, blood-pressure, and glucose-metabolism in mildly hypercholesterolemic men. Am. J. Clin. Nutr. 52:661-666.
Knutsen, S. H., and Holtekjolen, A. K. 2007. Preparation and analysis of dietary fibre constituents in whole grain from hulled and hull-less barley. Food Chem. 102:707-715.
Koh-Banerjee, P., Franz, M. V., Sampson, L., Liu, S. M., Jacobs, D. R., Spiegelman, D., Willett, W., and Rimm, E. 2004. Changes in whole-grain, bran, and cereal fiber consumption in relation to 8-year weight gain among men. Am. J. Clin. Nutr. 80:1237-1245.
Lazaridou, A., Biliaderis, C. G., Micha-Screttas, M., and Steele, B. R. 2004. A comparative study on structure-function relations of mixed-linkage (1-3),(1-4) linear β-D-glucans. Food Hydrocolloids 18:837-855.
Lee, R. C., Burton, R. A., Hrmova, M., and Fincher, G. B. 2001. Barley arabinoxylan arabinofuranohydrolases: Purification, characterization and determination of primary structures from cDNA clones. Biochem. J. 356:181-189
Li, W., Cui, S. W., and Kakuda, Y. 2006a. Extraction, fractionation, structural and physical characterization of wheat β-D-glucans. Carbohydr. Polym. 63:408-416.
Li, W., Cui, S. W., and Wang, Q. 2006b. Solution and conformational properties of wheat β-D-glucans studied by light scattering and viscometry. Biomacromolecules 7:446-452.
Liu, S. M., Willett, W. C., Manson, J. E., Hu, F. B., Rosner, B., and Colditz, G. 2003. Relation between changes in intakes of dietary fiber and grain products and changes in weight and development of obesity among middle-aged women. Am. J. Clin. Nutr. 78:920-927.
Lu, Z. X., Gibson, P. R., Muir, J. G., Fielding, M., and O'Dea, K. 2000a. Arabinoxylan fiber from a by-product of wheat flour processing behaves physiologically like a soluble, fermentable fiber in the large bowel of rats. J. Nutr. 130:1984-1990.
Lu, Z. X., Walker, K. Z., Muir, J. G., Mascara, T., and O'Dea, K. 2000b. Arabinoxylan fiber, a byproduct of wheat flour processing, reduces the postprandial glucose response in normoglycemic subjects. Am. J. Clin. Nutr. 71:1123-1128.
Lu, Z. X., Walker, K. Z., Muir, J. G., and O'Dea, K. 2004. Arabinoxylan fibre improves metabolic control in people with Type II diabetes. Eur. J. Clin. Nutr. 58:621-628.
Marquart, L., Miller Jones, J., Cohen, E. A., and Poutanen, K. 2007. The future of whole grains. Pages 3-16 in: Whole Grains and Health. L. Marquart, D. R. Jacobs, Jr., G. H. McIntosh, K. Poutanen, and M. Reicks, eds. Blackwell: Ames, IA.
Martinant, J. P., Cadalen, T., Billot, A., Chartier, S., Leroy, P., Bernard, M., Saulnier, L., and Branlard, G. 1998. Genetic analysis of water-extractable arabinoxylans in bread wheat endosperm. Theor. Appl. Genet. 97:1069-1075
Mascie-Taylor, C. G. N., and Karim, E. 2003. The burden of chronic disease. Science 302:1921-1922.
Mitchell, R. A., Dupree, P., and Shewry, P. R. 2007. A novel bioinformatics approach identifies candidate genes for the synthesis and feruloylation of arabinoxylan. Plant Physiol. 144:43-53
Nieduszynski, I., and Marchessault, R. H. 1971. Structure of β-D-(1-4') xylan hydrate. Nature 232:46-47.
Nystrom, L., Lampi, A. M., Andersson, A. A. M., Kamal-Eldin, A., Gebruers, K., Courtin, C. M., Delcour, J. A., Li, L., Ward, J. L., Fras, A., Boros, D., Rakszegi, M., Bedo, Z., Shewry, P. R., and Piironen, V. 2008. Phytochemicals and dietary fiber components in rye varieties in HEALTHGRAIN diversity screen. J. Agric. Food Chem. 56:9758-9766.
Olafsdottir, E. S., and Ingólfsdottir, K. 2001 Polysaccharides from lichens: Structural characteristics and biological activity. Planta Medica 67:199-208.
Onwurah, I. N. E. 2001. Crystallinity and polysaccharide chains of β-glucan in white sorghum, SK5912. Int. J. Biol. Macromolecules 29:281-286.
Ordaz-Ortiz, J. J., and Saulnier, L. 2005. Structural variability of arabinoxylans from wheat flour. Comparison of water-extractable and xylanase-extractable arabinoxylans. J. Cereal Sci. 42:119-125.
Pena, M. J., Zhong, R., Zhou, G. K., Richardson, E. A., O'Neill, M. A., Darvill, A. G., York, W. S., and Ye, Z. H. 2007. Arabidopsis irregular xylem8 and irregular xylem9: Implications for the complexity of glucuronoxylan biosynthesis. Plant Cell 19:549-563.
Persson, S., Caffall, K. H., Freshour, G., Hilley, M. T., Bauer, S., Poindexter, P., Hahn, M. G., Mohnen, D., and Somerville, C. 2007. The Arabidopsis irregular xylem8 mutant is deficient in glucuronoxylan and homogalacturonan, which are essential for secondary cell wall integrity. Plant Cell 19:237-255
Pettolino, F., Sasaki, I., Turbic, A., Wilson, S. M., Bacic, A., Hrmova, M., and Fincher, G. B. 2009. Hyphal cell walls from the plant pathogen *Rhynchosporium secalis* contain (1-3,1-6)-β-D-glucans, galacto- and rhamnomannans, (1-3,1-4)-β-D-glucans and chitin. FEBS J. 276:3698-3709.
Philippe, S., Saulnier, L., and Guillon, F. 2006. Arabinoxylan and (1-3), (1-4)-β-glucan deposition in cell walls during wheat endosperm development. Planta 224:449-461.
Ramakrishna, B. S,, Venkataraman, S., Srinivasan, S., Dash, P., Young, G. P., and Binder, H. J. 2000. Amylase-resistant starch plus oral rehydration solution for cholera. N. Eng. J. Med. 342:308-313.
Ramesh, H. P. and Tharanathan, R. N. 1998. Structural characteristics of a mixed linkage β-D-glucan from sorghum (*Sorghum bicolor*). Carbohydr. Res. 308:239-243.
Rimsten, L., Stenberg, T., Andersson, R., Andersson, A., and Aman, P. 2003. Determination of β-glucan molecular weight using SEC with calcofluor detection in cereal extracts. Cereal Chem. 80:485-490.
Rudi, H., Uhlen, A. K., Harstad, O. M., and Munck, L. 2006. Genetic variability in cereal carbohydrate compositions and potentials for improving nutritional value. Anim. Feed Sci. Technol. 130:55-65.
Saulnier, L., Sado, P. E., Branlard, G., Charmet, G., and Guillon, F. 2007. Wheat arabinoxylans: Exploiting variation in amount and composition to develop enhanced varieties. J. Cereal Sci. 46:261-281.
Schreiber, A. W., Shirley, N. J., Burton, R. A., and Fincher, G. B. 2008. Combining transcriptional datasets using the generalized singular value decomposition. BMC Bioinformatics 9:335.
Selanere, M. L., and Andersson, R. 2002. Cell wall composition of 1B/1R translocation wheat grains. J. Sci. Food Agric. 82:538-545.
Selinheimo, E., Kruus, K., Buchert, J., Hopia, A., and Autio, K. 2006. Effects of laccase, xylanase and their combination on the rheological properties of wheat doughs. J. Cereal Sci. 43:152-159.
Sinesio, F., Paoletti, E., D'Egidio, A. G., Moneta, E., Nardo, N., Peparaio, M., and Comendador, F. J. 2008. Flavor and texture as critical sensory parameters of consumer acceptance of barley pasta. Cereal Foods World 53:206-213.
Smith, M. M., and Hartley, R. D. 1983. Occurrence and nature of ferulic acid substitution of cell wall polysaccharides in graminaceous plants. Carbohydr. Res. 118: 65-80.
Sørensen, I., Pettolino, F. A., Wilson, S. M., Doblin, M. S., Johansen, B., Bacic, A., and Willats, W. G. 2008. Mixed-linkage (1-3),(1-4)-β-D-glucan is not unique to the Poales and is an abundant component of *Equisetum arvense* cell walls. Plant J. 54: 510-521.
Staudte, R. G., Woodward, J. R., Fincher, G. B., and Stone, B. A. 1983. Water-soluble (1-3),(1-4)-β-D-glucans from barley (*Hordeum vulgare*) endosperm. III. Distribution of cellotriosyl and cellotetraosyl residues. Carbohydr. Polym. 3:299-312.
Stone, B. A., and Morell, M. 2007. Carbohydrates. Pages 299-362 in: Wheat: Chemistry and Technology. K. Khan and P. Shewry, eds. AACC International: St. Paul, MN.
Topping, D. L. 1991. Soluble fiber polysaccharides—Effects on plasma-cholesterol and colonic fermentation. Nutr. Rev. 49:195-203.
Topping, D. L. 2007. Cereal complex carbohydrates and their contribution to human health. J. Cereal Sci. 46:220-229.
Topping, D. L., and Clifton, P. M. 2001. Short-chain fatty acids and human colonic function: Roles of resistant starch and nonstarch polysaccharides. Physiol. Rev. 81:1031-1064.
Trogh, I., Courtin, C. M., Andersson, A. A. M., Aman, P., Sorensen, J. F., and Delcour, J. A. 2004. The combined use of hull-less barley flour and xylanase as a strategy for wheat/hull-less barley flour breads with increased arabinoxylan and (1-3,1-4)-β-D-glucan levels. J. Cereal Sci. 40:257-267.
Truswell, A. S. 2002. Cereal grains and coronary heart disease. Eur. J. Clin. Nutr. 56:1-14.
Verardo, V., Bonoli, M., Marconi, E., and Caboni, M. F. 2008. Distribution of bound hydroxycinnamic acids and their glycosyl esters in barley (*Hordeum vulgare* L.) air-classified flour: Comparative study between reversed phase-high performance chromatography-mass spectrometry (RP-HPLC/MS) and spectrophotometric analysis. J. Agric.

Food Chem. 56:11900-11905.
Viëtor, R., Angelino, S., and Voragen, A. 1992. Structural features of arabinoxylans from barley and malt cell wall material. J. Cereal Sci. 15:213-222.
Welch, R. W., and Lloyd, J. D. 1989. Kernel (1-3),(1-4)-β-D-glucan content of oat genotypes. J. Cereal Sci. 9:35-40.
Wilson, S. M., Burton, R. A., Doblin, M. S., Stone, B. A., Newbigin, E., Fincher, G. B., and Bacic, A. 2006. Temporal and spatial appearance of wall polysaccharides during cellularization of barley (*Hordeum vulgare*) endosperm. Planta 224:655–667.
Wood, P. J. 1993. Comparisons of dietary fiber and selected nutrient compositions of oat and other grain fractions. Page 83 in: Oat Bran. P. J. Wood, ed. AACC International: St. Paul, MN.
Wood, P. J. 2007. Cereal β-glucans in diet and health. J. Cereal Sci. 46:230-238.
Wood, P. J., Weisz, J., and Fedec, P. 1991. Potential for β-glucan enrichment in bran derived from oat (*Avena sativa* L.) cultivars of different (1-3),(1-4)-β-D-glucan concentrations. Cereal Chem. 68:48-51.
York, W. S., and O'Neill, M. A. 2008. Biochemical control of xylan biosynthesis—Which end is up? Curr. Opin. Plant Biol. 11:258-265.
Zunft, H. J., Lueder, W., Koebnick, C., and Imhof, D. 2004. Reduction of the postprandial glucose and insulin response in serum of healthy subjects by an arabinoxylan concentrate isolated from wheat starch plant process water. Asia Pacific J. Clin. Nutr. 13:S147.

[Received August 19, 2009. Accepted March 9, 2010.]