



## Review

## Improving cereal grain carbohydrates for diet and health

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## ABSTRACT

Starch and cell wall polysaccharides (dietary fibre) of cereal grains contribute to the health benefits associated with the consumption of whole grain cereal products, including reduced risk of obesity, type 2 diabetes, cardiovascular disease and colorectal cancer. The physiological bases for these effects are reviewed in relation to the structures and physical properties of the polysaccharides and their behaviour (including digestion and fermentation) in the gastro-intestinal tract. Strategies for modifying the content and composition of grain polysaccharides to increase their health benefits are discussed, including exploiting natural variation and using mutagenesis and transgenesis to generate further variation. These studies will facilitate the development of new types of cereals and cereal products to face the major health challenges of the 21st century.

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## 1. Introduction

Cereals are the dominant crops in world agriculture, with a total of 2500 million tonnes being harvested globally in 2011, comprising 704 million tonnes of wheat, 723 million tonnes of rice, 883 million tonnes of maize (<http://faostat.fao.org/site/291/default.aspx>) and lesser amounts of a number of “minor cereals” (barley, oats, rye, sorghum and millets). They are the major source of calories and protein to the diets of humans and livestock (including poultry).

Major reasons for the success of cereals include their adaptability, high yields, and ease of harvest and storage, but their processing and eating properties are also important, with wheat in particular being processed into a range of foods including bread and other baked goods, noodles and pasta. Failure of cereal harvests due to adverse weather, pathogens or human actions has contributed to famines in many countries, and increasing cereal production is a key aim of national and international research efforts.

Although emphasis is rightly placed on increasing crop production to meet the needs of the growing global population it is important to also bear in mind that the major effect of food on the health of the population in the developed world, and increasingly

in rapidly developing economies such as India and China, relates not to lack of food but to over-consumption, particularly increased consumption of highly refined foods when associated with an increasingly sedentary life style. These include many starch-rich foods derived from cereals, which has conveyed a negative view of the contribution of cereals to diet and health to many consumers. In fact, this is far from the truth with cereals being important sources of many essential or beneficial components to the human diet. For example, the National Diet and Nutrition Survey of the UK showed that cereal products contributed 29/30% of the total daily energy intake of adult males/females, 22/21% of the intake of protein and 39/37% of the intake of non-starch polysaccharides (the major components of dietary fibre, DF) (NDNS, 2011). Similarly, Steer et al. (2008) showed that bread products alone contributed 12% of the protein, 20% of the fibre and 16% of the iron to the adult UK diet.

The present article therefore focuses on the contributions of cereal carbohydrates to a healthy diet, focussing on wheat with comparative data on other cereals being included where appropriate.

## 1.1. Introduction to grain carbohydrates

Carbohydrates can be classified according to their molecular size and degree of polymerisation, with each group being subdivided according to the number and composition of monosaccharide units.

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This classification includes sugars (monosaccharides and disaccharides), oligosaccharides, starch (amylose and amylopectin) and non-starch polysaccharides.

Carbohydrates account for about 65–75% of the mature wheat grain (Stone and Morell, 2009), with similar values being reported for other major cereals. Values reported for the amounts of individual groups in the wheat grain vary between different studies but are in the order of about 1% or less monosaccharides (glucose, fructose) and disaccharides (sucrose and maltose), about 1% oligosaccharides (raffinose and fructo-oligosaccharides), 1–2% fructans, 65–75% starch and about 10% cell wall polysaccharides (mainly cellulose, arabinoxylan and  $\beta$ -glucan), the latter forming the major DF components (Stone and Morell, 2009; Andersson et al., 2013). However, there are large differences between the compositions of the different grain tissues. In particular, the aleurone and outer layer (pericarp and testa), which form the bran fraction on milling of wheat, contain little starch but up to half of the dry weight is cell wall polysaccharides, while the starchy endosperm (the major storage tissue of the grain) comprises about 85% starch and only 2–3% cell wall polysaccharides.

Starch is composed of two different types of glucan polymers: amylopectin and amylose, present in a 3:1 ratio. Both polymers are formed of  $\alpha$ -D-glucose but they differ in their level of branching, with amylose being essentially linear and amylopectin being highly branched. These branches can directly affect starch characteristics and functionality as differences in their chain length distribution and clustering, and the ability to form a double helical conformation, may contribute to the crystalline features of the amylopectin (Jeon et al., 2010).

The major cell wall polysaccharides in the cell walls of wheat and related cereals (barley, oats and rye) grain are arabinoxylan

(AX) and (1  $\rightarrow$  3, 1  $\rightarrow$  4)- $\beta$ -D-glucan ( $\beta$ -glucan). AX comprises a backbone of  $\beta$ -D-xylopyranosyl residues linked through (1  $\rightarrow$  4) glycosidic linkages, with some residues being substituted with  $\alpha$ -L-arabinopyranosyl residues at either position 3 or positions 2 and 3 (Fig. 1). Substitution at position 2 alone occurs only rarely in wheat AX (Stone and Morell, 2009). The arabinose residues at position 3 of monosubstituted xylose residues may also be substituted with ferulic acid at the 5 position, allowing the formation of cross-links by oxidation of ferulate present on adjacent AX chains. This results in the formation of dehydrodiferulate (ferulate dimers) or, more rarely, triferulate residues which are stable to acid hydrolysis. A range of other modifications may also occur, including acetylation, substitution with galactose and glucuronic acid and substitution of the arabinose with *p*-coumaric acid instead of ferulic acid.

By contrast,  $\beta$ -glucan has a simpler structure, comprising only glucose residues which are linked by (1  $\rightarrow$  4) and (1  $\rightarrow$  3) bonds. In general, single (1  $\rightarrow$  3) linkages are separated by 2 or 3 (1  $\rightarrow$  4) linkages but the linkage ratio may vary between tissues and species and longer “cellulose-like” regions of continuous (1  $\rightarrow$  4) linkages (up to 14) have been reported in wheat bran  $\beta$ -glucan (Li et al., 2006). The ratio between (1  $\rightarrow$  4) and (1  $\rightarrow$  3) linkages differs between different cereal species (Cui et al., 2000; Lazaridou et al., 2004; Lazaridou and Biliaderis, 2007), with the relative proportion of trisaccharide (DP3) decreasing from wheat (67–72%), to barley (52–69%) and oats (53–61%). It is probable that such variation in linkage pattern determines the differences that occur in the properties, including the solubility and viscosity, of  $\beta$ -glucans from various sources.

## 2. Contributions of grain carbohydrates to diet and health

### 2.1. Nutritional value of grain carbohydrates

All organisms require energy to maintain their life cycles. For humans, carbohydrates are the major energy sources, typically accounting for 45–70% of the total energy intake and expenditure. Being quantitatively the most important dietary energy source for most populations, carbohydrates have a special role to play in energy metabolism and homeostasis. Cereals are the dominant source of carbohydrates in the human diet, providing the major source of energy and contributing significantly to protein intake.

In addition to their classification based on degree of polymerisation and sugar composition, carbohydrates can also be classified based on the extent to which they are digested and absorbed in the human small intestine, thus contributing directly or indirectly to the body carbohydrate pool and influencing post-prandial glycaemia (glycaemic carbohydrates). In this classification, carbohydrates which are not digested and absorbed in the human small intestine are distinguished from glycaemic carbohydrates, forming the major part of DF (Mann et al., 2007).

The carbohydrates that have the greatest impact on post-prandial blood glucose are those that are absorbed relatively quickly from the small intestine. In fact, most metabolic parameters are adversely affected by an abrupt perturbation in the post-prandial period of a metabolic steady state present in the fasting condition. The greater and more rapid the perturbation, the more pronounced are the effects. Therefore this metabolic perturbation could be minimised if carbohydrate digestion and absorption were slowed down. This has resulted in interest in understanding the properties of foods that are able to retard digestion. The type of starch is certainly relevant in this respect, with amylose being slowly digested by  $\alpha$ -amylases present in the human duodenum and amylopectin being very rapidly digested because the branched structure provides multiple sites for enzymatic hydrolysis. Moreover, amylose is structurally organised in the form of the double

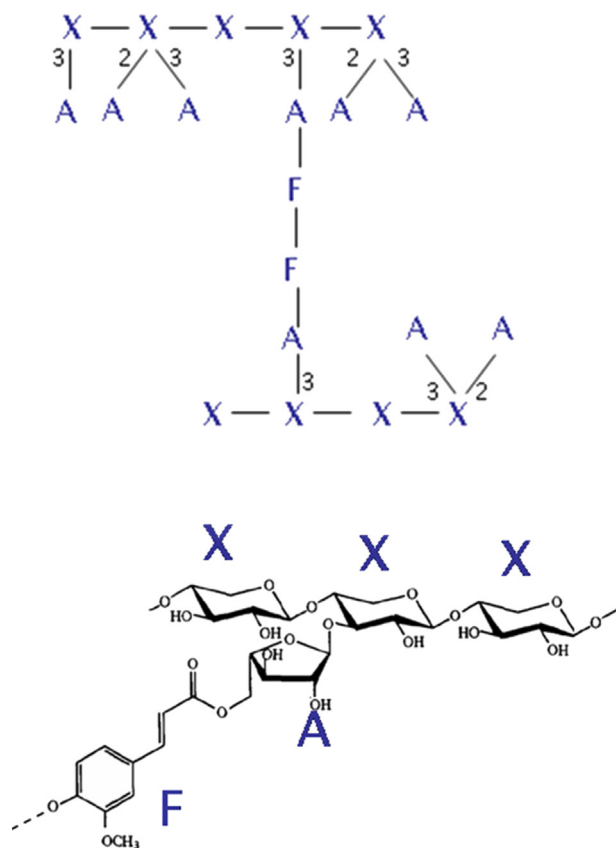


Fig. 1. Schematic (top) and detailed (bottom) structures of wheat starchy endosperm arabinoxylan.

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