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Review

How does wheat grain, bran and aleurone structure impact their nutritional and technological properties?

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Wheat grain and its technological fractions—bran and aleurone—are rich in nutritional compounds such as dietary fibre and phytochemicals, which are recognized as having high health benefits. These bioactive compounds are embedded in the complex cellular and molecular structures of the wheat matrix. The matrix structure influences their bioaccessibility and bioavailability, probably altering their metabolic and health effects. In this review, we have gathered current knowledge on the influence of the structure of cereal matrices such as grain, bran or aleurone on their metabolic and health effects, as well as their impact on the quality of final cereal-based products.

Introduction

Epidemiological studies have reported that the consumption of whole grain products may reduce the risk of cardiovascular diseases, various types of cancer, type 2 diabetes and possibly improve body weight regulation (Giacco, Della Pepa, Luongo, & Riccardi, 2011; Jacobs, Marquart, Slavin, & Kushi, 1998; Mellen, Walsh, & Herrington, 2008; Ye, Chacko, Chou, Kugizaki, & Liu, 2012). Diverse potential mechanisms mediate the protective effects of whole wheat grain since grains are rich in many nutrients linked to disease prevention. It was recently suggested that, besides the effects of dietary fibres (DF), the synergistic action of several bioactive compounds also contributes to health protection and/or physiological function maintenance (Fardet, 2010).

In wheat, the most significant bioactive compounds with recognised health benefits are minerals, polyphenols (especially phenolic acids), sulphur amino acids, betaine, total choline, phytic acid, alkylresorcinols as well as vitamins B and E (Fardet, 2010). These bioactive microcomponents and also DF are mainly present in the outermost layers of wheat. Outer layers are recovered during the milling process in a technological fraction called bran. Among the outer layers, aleurone has been pinpointed as the most nutritionally interesting as it concentrates most DF and other bioactive compounds (Brouns, Hemery, Price, & Anson, 2012). Aleurone is normally recovered as part of bran during the milling process, but novel dry-fractionation techniques can now be used to isolate aleurone from the other bran layers (Hemery, Rouau, Lullien-Pellerin, Barron, & Abecassis, 2007).

The intake of bioactive compounds depends on their total content in food, but their release from food during digestion and absorption into the blood stream are also dependent on the food matrix microstructure (Palzer, 2009). Wheat bran and aleurone layer are matrices with a very complex structure. In these fractions, at the molecular level, DF and other bioactive compounds are mainly

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present in bound forms, not as free constituents. DF are mainly polysaccharides present on cell walls in the outermost layers. Other bioactive compounds are also embedded in these complex matrices, either encapsulated in the cells and/or cell-wall structures or chemically bound at the molecular level. For example, ferulic acid (FA), which is the major phenolic acid of wheat bran, is mainly ester-linked with arabinoxylan and embedded in bran and aleurone cell walls. The physiological and health effects of wheat grain and its fraction have been studied, but the importance of their structure, from macro *via* micro to molecular levels, is not often mentioned or taken into account in the scientific literature. Foods with greater nutritional properties could be obtained through proper assembly of the hierarchical structures (Zúñiga & Troncoso, 2012). These structures could be obtained by targeted desintegration or reconstruction of one or more components from the microscopic to macroscopic levels, *i.e.* the so called "bottom up" approach.

This review gathers current knowledge on how the structure of cereal matrices affects both their overall health effects and technological properties. We initially considered the macro, micro and molecular structures of wheat grain and fractions. Next, structural parameters that could affect targeted physiological responses of foods containing wheat grain or fractions, *i.e.* starting from the particle size of grains and fractions until the release of their bioactive compounds, are reviewed. In the last part, the effects of the cereal matrix structure on the processing and quality of cereal-based foods are discussed.

Structure and composition of wheat grain, bran and aleurone fractions

Wheat grain has three main parts: endosperm, germ and peripheral layers. The endosperm (80–85% of the grain) is mainly composed of starch granules embedded within a protein matrix. Glucose is the major monosaccharide (96%) of the starchy endosperm, which contains only 2% of arabinoxylans (AX) (Barron, Surget, & Rouau, 2007; Gebruers *et al.*, 2008). The germ (3% of the grain) is composed of the embryo and scutellum and is rich in lipids, proteins, neutral sugars, as well as minerals, vitamins and sterols. The peripheral layers (13–17% of the grain) which surround the endosperm include—in order from the inner to the outer parts—the aleurone layer, hyaline layer, seed coat, inner pericarp and outer pericarp (Evers & Bechtel, 1988).

The inner and outer pericarps contain empty cells, with cell walls mostly made of AX (∼46% w/w) with a high degree of branching, cellulose (∼25%), lignin, and also dimers of FA (around 2.5 mg/g of tissue) cross-linking polysaccharides (Barron *et al.*, 2007; Harris, Chavan, & Ferguson, 2005). The seed coat (or testa) is very rich in alkylresorcinols (Landberg, Kamal-Eldin, Salmenkallio-Marttila, Rouau, & Aman, 2008). The hyaline layer is mainly composed of AX (67% w/w) and is very rich in monomeric FA (10 mg FA/g tissue) (Barron *et al.*, 2007). Aleurone is an unicellular tissue layer with block-shaped cells (37–65 μm × 25–75 μm) (Evers & Bechtel, 1988) representing 7–9% (w/w) of the kernel and 45–50% of the bran fraction (Buri, von Reding, & Gavin, 2004). The intracellular aleurone content (70% of aleurone dry mass) is characterised by high contents of small vacuoles (aleurone grains), proteins, minerals, phytates, lipids and B vitamins (Buri *et al.*, 2004; Evers & Bechtel, 1988). The aleurone cell wall is mainly composed of AX, *β*-glucans and proteins (Bacic & Stone, 1981; Saulnier, Sado, Branlard, Charmet, & Guillon, 2007). Aleurone phenolic compounds are highly esterified with AX (98.5%), and minor amounts are present in conjugated or free forms (Rosa, Dufour, Lullien-Pellerin, & Micard, 2013). The structures of the cereal matrices (whole wheat grain, bran and aleurone layer) and their main DF (AX) and phenolic acid (FA) components are illustrated in Fig. 1.

Arabinoxylans (AX) and β-glucans are the most nutritionally relevant cell wall polysaccharides of wheat grain and fractions (Table 1). Wheat AX are formed by a linear backbone of (1->4)-linked β-D-xylopyranosyl units and generally divided into two groups: water-extractable AX (WE-AX) and water-unextractable AX (WU-AX). In wheat grain, the WE-AX and WU-AX contents are around 0.51 and 1.84 g/100 g flour, respectively (Saulnier *et al.*, 2007), but the proportion of WU-AX is even higher in wheat bran and aleurone (around 95% w/w) (Rosa, Aura, *et al.*, 2013). β-glucans account to 0.4–0.8 g/100 g wheat flour and most of them (80–90%) are water-unextractable (Nemeth *et al.*, 2010). FA is the most abundant polyphenol in wheat grain, representing over 95% of all the phenolic acids. Other phenolic acids such as sinapic, *p*-coumaric, vanillic and caffeic acids have also been detected in minor amounts (Table 1). FA and *p*-coumaric acid are mostly present in an insoluble form, esterified to AX, whereas sinapic and vanillic acid are mostly found in the conjugated form, *i.e.* linked with oligosaccharides (Barron *et al.*, 2007; Li, Shewry, & Ward, 2008; Parker, Ng, & Waldron, 2005). Flavonoids are mainly present in the bound form, mostly concentrated in the outer grain layer (Van Hung, Maeda, Miyatake, & Morita, 2009). Other important phytochemicals that have been associated with the health benefits of wheat grain are displayed in Table 1.

Nutritional properties of whole-grain wheat foods, bran and aleurone fractions

Epidemiological studies have linked whole grain consumption to a reduced risk of many diseases. The intake of wheat bran (represented by its percentage in whole grains, and also by bran-enriched products consumed by the studied population) was also reported in prospective epidemiological studies to have an inverse association with the risk of type 2 diabetes in women and coronary heart disease in men (Jensen *et al.*, 2004; de Munter, Hu, Spiegelman, Franz, & van Dam, 2007). However, there is still limited direct interventional evidence confirming the beneficial effects of whole wheat grain and fractions as