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The Nutritional Property of Endosperm Starch and Its Contribution to the Health Benefits of Whole Grain Foods

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Abstract

Purported health benefits of whole grain foods in lowering risk of obesity, type 2 diabetes, cardiovascular disease and cancer are supported by epidemiological studies and scientific researches. Bioactive components including dietary fibers, phytochemicals, and various micronutrients present in the bran and germ are commonly considered as the basis for such benefits. Endosperm starch, as the major constituent of whole grains providing glucose to the body, has been less investigated regarding its nutritional property and contribution to the value of whole grain foods. Nutritional quality of starch is associated with its rate of digestion and glucose absorption. In whole grain foods, starch digestion and glucose delivery may vary depending on the form in which the food is delivered, some with starch being rapidly and others slowly digested. Still, there are other inherent factors in whole grain products, such as phenolic compounds and dietary fibers, that may moderate glycemic profiles. A good understanding of the

nutritional property of whole grain endosperm starch is essential to the development of food processing technologies to maximize the health benefits of whole grain foods and to design functional foods with similar health benefits.

Key words

whole grain foods, whole grian starch, slowly digestible starch, dietary fiber, phytochemicals

Introduction

As the prevalence of obesity-related metabolic diseases such as type 2 diabetes continues to increase, dietary approaches to reduce their risk have become an active research area. Use of whole grain foods, defined by the United States Food and Drug Administration as "cereal grains that consist of the intact and unrefined, ground, cracked or flaked fruit of the grains whose principal components -- the starchy endosperm, germ and bran -- are present in the same relative proportions as they exist in the intact grain.", is one of the dietary approaches to combat metabolic diseases (Chatenoud et al. 1998; Cho et al. 2013). Intake of whole grain foods has been reported to result in reduction of postprandial glycemic and/or insulinemic responses in human studies (Alminger and Eklund-Jonsson 2008; Rosen et al. 2009). Epidemiological data support an association between whole grain intake and decreased risk of obesity and weight gain (Giacco et al. 2011) and type 2 diabetes (Fung et al. 2002; Aune et al. 2013). A reduction in cardiovascular disease indices (Tovar et al. 2013) and modulation in distal colorectal cancer incidence (Kyro et al. 2014) have also been observed. As for the basis of the health benefit of whole grains, bioactive phytochemicals (Okarter and Liu 2010) and functional dietary fibers (Anderson et al. 2009) are considered as the critical components (Fardet 2010). Whole grain endosperm starch, on the other hand, even though quantitatively the major constituent of whole grain, has not been researched extensively concerning its contribution to the health benefit of whole grain foods particularly in regard to what effect of the home-cooked or further processed form has on its digestion and absorption. Synergy between starch and other functional components in whole grain foods, such as phenolic compounds and dietary fibers, may also be a contributing factor to the health benefits of whole grain foods (Jonnalagadda et al. 2010). From the perspective of glycemic index (GI) (Jenkins et al. 1981), many whole grain foods are indeed low-GI foods (Foster-Powell et al. 2002) (Wolever 2013), and as well some refined cereal-based products are low-GI foods that may have similar health benefits. The nutritional property of starch, related to its digestion rate property, is likely a main factor related to reduced glycemic response and associated glucose homeostasis, lipid metabolism, and insulin sensitivity (Jenkins et al. 1983; Jenkins et al. 1988; Lagerpusch et al. 2013). Thus, such property of endosperm starch in a whole grain food context and its contribution to the health benefits needs to be considered (Wolever 2013).

Starch is composed of essentially linear amylose and highly branched amylopectin, and the relative amounts and composition of these two different polymers are important parameters determining the nutritional property of starch, most often expressed by proportion of rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) (Englyst et al. 1992). Amylose is associated with the content of RS, and amylopectin (particularly types containing higher amount of long or very short branch chains) to the content of SDS (Zhang et al. 2008). Nutritionally speaking, RS does not belong to the scope of available or glycemic carbohydrates, but is considered as a type of dietary fiber. RDS can produce large fluctuations in postprandial glycemia, which induces oxidative stress that may be a health concern (Monnier et al. 2006), while SDS is characteristic of a moderate and prolonged glycemic response that is beneficial to glycemic control. Considering the health implications of SDS (Lehmann and Robin 2007) and RS (Nugent 2005), their content is relevant to the health property of whole grain foods. In this article, the slow digestion property and RS content of endosperm starch in whole grain foods will be reviewed for a better understanding of its potential contribution to the health benefit. Aspects affecting starch nutritional property in a whole grain context will be reviewed including starch structure (different cultivars or mutants), botanical structure of the whole grain (kernel), impact by other food components (dietary fiber and phytochemicals), and the effect of food processing (food form or food structure).

Glucose Homeostasis Affected by Whole Grain Foods

Metabolic diseases such as obesity and type 2 diabetes are caused by an interplay between genetic background (including microbiota) and environmental conditions in which the diet is an important factor. Improved diet is critical for modulation of metabolic processes associated with these diseases. Weight gain or obesity caused by a long term positive energy balance is believed to be the initial step of disease development, which is accompanied by a low-grade inflammation associated with circulating cytokines such as tumor necrosis factor-alpha (TNF-α) and interleukin-6 (IL-6) (Gregor and Hotamisligil 2011). This type of inflammation eventually leads to insulin resistance (Festa et al. 2003), dyslipidemia, hypertension, and prothrombotic factors that are referred to as metabolic syndrome (Grundy et al. 1999). Insulin resistance (Taniguchi et al. 2006), with its directly linked abnormity in glucose homoeostasis, is a central pillar of type 2 diabetes (Reaven 1988).

Improvement of glucose homeostasis has been evidenced to be one important mechanism related to the health benefit of whole grain foods. Epidemiological analysis showed that whole grain foods with lowered fasting glucose concentration is beneficial to the prevention of vascular disease (Ye et al. 2012), and abnormity of glucose homeostasis is intimately associated with type 2 diabetes and cardiovascular disease (Gerstein 1997). Epidemiological studies also revealed an inverse relationship between whole grain consumption and fasting insulin levels, and improved insulin resistance and glucose control (Murtaugh et al. 2003). Analysis of epidemiological studies from 1965-2010 demonstrates a reduction in risk of type 2 diabetes with high intake of cereal fiber or mixtures of whole grains and bran (Cho et al. 2013). In a large population postmenopausal women prospective study, an inverse dose-response relationship between whole grain consumption and incidence of type 2 diabetes was found (Parker et al. 2013). A randomized and controlled clinical trial showed whole grain foods are also beneficial to cardiovascular disease related to improved glucose, insulin and homocysteine levels, as well as lowered lipid peroxidation (Jang et al. 2001). A cross-sectional study in the Framingham Offspring Study showed an inverse relationship between whole grain food consumption and metabolic risk factors of body mass index, waist-to-hip ratio, total cholesterol, LDL level, and fasting insulin level (McKeown et al. 2002). A long term longitudinal study also showed favorable lipid profiles and glycemic control associated with whole grain and high fiber intake (Liu 2002). Taken together, these studies suggest that improved insulin sensitivity and glucose homeostasis are likely mechanistically important to the purported health benefits of whole grain food consumption.

Bioactive phytochemicals, functional dietary fiber, and food forms of whole grain foods may all affect starch digestion and glucose absorption, thereby impacting glucose homeostasis and insulin sensitivity. Bioactive polyphenols have been shown to increase insulin secretion (Li et al. 2006), modulate liver glucose release, and/or activate insulin receptors (Hanhineva et al. 2010). Regarding dietary fiber, their fermentation can induce the secretion of glucagon-like peptide-1 (GLP-1) to increase not only the release of insulin, but improve insulin sensitivity (Pereira et al. 2002) for better glucose homeostasis (Massimino et al. 1998; Johansson et al.

2013). The released GLP-1 also delays gastric emptying by affecting gut motility through a neural pathway (Imeryuz et al. 1997), which is beneficial to a slow glucose bioavailability (Zhang et al. 2015). Fermentable dietary fibers can also improve immunological health with a reduction of inflammatory factors, such as interleukin-6 (Martinez et al. 2012) that are associated with insulin resistance (Kim et al. 2009; Caricilli and Saad 2013). In whole grain foods, another important factor affecting the nutritional quality of starch is the food form as this is related to how starch is accessed by digestive enzymes. Processes that include high heat and shear tend to disperse gelatinized starch outside of matrices making it rapidly digestible. Conversely, those that retain botanical or starch structures of whole grains tend to digest slower (Liljeberg et al. 1992).

Recent metabolomics analysis after whole rye intake showed a favorable shift in branched amino acids, single carbon metabolism, LDL levels (Moazzami et al. 2012), and metabolites related to satiety and body weight control (Lankinen et al. 2011). Distinct metabolic profiles in a human study were shown between whole grain and refined grain foods after intake for 48 h (Fardet et al. 2007). Intake of whole grain foods delayed the occurrence of prediabetes from impaired glucose tolerance and this was related to modulation of the polymorphisms of transcription factor-7-like 2 (TCF7L2) encoding gene (Wirstrom et al. 2013). A genomics study on the effect of whole grain consumption on gene expression showed that rye pasta (with a low postprandial glycemic response) down-regulated genes of insulin signaling and β--cell apoptosis, while an oat-wheat-potato diet (high glycemic response) up-regulated genes related to stress and cytokine-chemokine-mediated immunity (Kallio et al. 2007). As the application of omicstechnologies in the study of whole grain foods, a deeper understanding may be gained of the contribution of starch to the health benefit of whole grain foods with different forms of starch or starches from different botanical sources.

Slowly Digestible Starch

Recently, there has been an increased awareness of the quality aspect of dietary carbohydrates, and this has even become a new target in dietary approaches to intervene or prevent metabolic diseases. Rate, extent, and location of carbohydrate digestion and absorption are likely more important to the health outcome than simply the amount of carbohydrate consumed. Glycemic index (GI), as developed by Jenkins (Jenkins et al. 1981), was the first concept to physiologically classify available glycemic carbohydrates based on the area under the 0-120 min postprandial glycemic response curve compared to a control food. Although the concept has been considered controversial by some (Pi-Sunyer 2002), others have studied low-GI foods (GI < 55) and found them related to health benefits (Ludwig 2002; Livesey 2005). In cereal-based foods, a positive correlation between GI and RDS-derived glucose (Englyst et al. 1999) and a negative correlation between RDS and SDS (Zhang et al. 2008) revealed that SDS is likely the material basis for cereal-based low-GI foods.

SDS is defined by an *in vitro* starch digestion method (Englyst et al. 1992), though human studies on raw corn starch (Seal et al. 2003; Wachters-Hagedoorn et al. 2006), which is a naturally pure SDS material, showed that SDS does produce a prolonged and sustained low postprandial glycemic and insulinemic response, which is similar to that found with low-GI foods. Indeed, the health benefits of SDS are also similar to low-GI foods (Lehmann and Robin 2007). Regarding physiological response, SDS epigenetically caused a shift of the gene expression peak of the sodium-glucose cotransporter 1 (SGLT1) from the upper jejunum to ileum (Shimada et al. 2009) leading to increased glucose transporter in the ileum (Woodward et al. 2012). SDS from raw corn starch also caused sustained release of GLP-1 (Wachters-Hagedoorn et al. 2006) that is important to glucose homeostasis and insulin sensitivity (Larsen 2008). In a recent rat study in our laboratory (unpublished data) on SDS, we showed improved feeding behavior and a decreased expression of hypothalamic orexigenic neuropeptide Y (NPY) and Agouti-related peptide (AgRP) that are appetite stimulators favoring food intake. Thus, SDS not only generates a modulated postprandial glycemic response, but influences a variety of physiological processes that are related to digestion, food intake, and health.

Slow Digestion Property of Endosperm Starch in Whole Grain Foods

Compared to cereal grain-derived refined flours, the matrix of whole grain foods and the functional components of dietary fiber and phytochemicals may contribute to the slow digestion property of the endosperm starch. The physical barrier formed by some whole grain food matrices, the *in vivo* physiological effects resulted from phytochemicals and fermentation of dietary fibers, starch structures, and food processing will be the focus of the following sections.

1. Physical structure of whole grain and starch digestion

Whole grain kernels or coarse particles of whole grain are more effective than milled flour to reduce the rate of starch digestion for postprandial glycemic control (Liljeberg et al. 1992). This is consistent with the *in vitro* study of Heaton et al (Heaton et al. 1988) showing that particle size from milling of wheat, corn, and oat grains influences starch digestion rate. Literature report (Björck et al. 1994) showed that food structure is a key parameter to postprandial glucose and insulin response, and any disruption of the physical or botanical structure of the cereal grain

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ingredients substantially increases the postprandial glycemic and insulinemic responses. Thus, the physical structure of the whole grain food plays an important role in the rate of starch digestion and is a key determinant of metabolic responses to most products (Bjorck et al. 1994).

Cereal grains, biologically speaking, are the life carrier of their next plant generation and all the nutrients needed for seed germination and the plant's early life development are present in the grain. This is the botanical structure of grain kernels. Starch, as the energy provider for seed germination, is nearly all located in the endosperm cells (Kamal-Eldin et al. 2009) (Fig 1), and it may or may not be embedded in a continuous protein matrix that is found inside the cell wall structures. In the raw state when starch is within a dense protein matrix, there is decreased degree of starch digestibility (Lopes et al. 2009). This impact of the protein matrix on the starch digestion property may still exist even the grain has been milled to flour (which consists of a large portion of matrix-entrapped starch in the form of small particles) and cooked, as evidenced by our study showing 20% SDS was produced when flour was cooked compared to 0-2% SDS if isolated starch was cooked (Zhang et al. 2008). In addition to the internal physical structure in the endosperm, whole grain kernels have a fiber-rich bran layer that conceivably could decrease accessibility of degrading enzymes to starch. Thus, retaining the ordered botanical structures of whole grain kernel is a natural way to gain slowly digestible, or perhaps even resistant, starches during food processing (Figure 2).

Although the botanical structures can act as a physical barrier to starch degrading enzymes, most whole grain foods are substantially processed before consumption. One strategy to retain some SDS property would be to process whole grain foods to maintain some degree of physical barrier property. As mentioned above, food processing with high temperature and shear, such as flaking or extrusion, disrupts the internal grain structure and substantially increases RDS content. On the other hand, moderate processing such as thick rolled or cut oats (Mishra and Monro 2009) retains some degree of slow starch digestion property due to minimal disruption of the physical structure of the grain. Similarly, a dense and low porosity food form is another way to maintain a physical barrier to retard starch digestion rate, such as a dense *al dente* cooked pasta in which a two-step sequential digestion kinetics of starch in pasta is caused by the compact microstructure and gluten network-entrapped starch granules (Zou et al. 2015). If intact kernels are cooked and consumed, the native grain structure with cell wall-encapsulated starch will be retained and the expansion of starch may also be limited, and both have been shown to contribute to an increase in content of SDS and RS (Figure 3).

2. The structure of starch granules

As mentioned above, certain raw starches have intrinsically high SDS that is based on the inner structure of starch granule itself. The A-type semi-crystalline granular structure formed by amylopectin in most cereal starches, along with their highly channelized gross structure, is the basis for their slow digestion properties (Zhang et al. 2006). On the other hand, most raw B-type starches, such as potato and banana starches, have high RS content. There are also a variety of starches with different granular structures such as commercial waxy starches (no amylose) and high-amylose starches (30-70% amylose), and a range of experimental starch mutants (e.g. *aewx* corn starch). Additionally, amylose content can differ within a normal population of the same cereal species or among different botanical sources (Table 1). Normal native A-type cereal starches (amylose, 20-30%) contain a good amount of SDS, and high-amylose starches are a source of RS (Szczodrak and Pomeranz 1991).

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While the granular structure is of importance to the nutritional property of raw starch, when it is cooked and gelatinized, it tends to form high levels of RDS. Starch molecular structure then becomes an important factor related to the digestion rate and nutritional properties of starch. When gelatinized starch retrogrades, B-type crystalline structures form that have a slow or perhaps sometimes a resistant digestion property. Zhang et al. (Zhang et al. 2008) found a parabolic relationship relating amylopectin fine structure to SDS amount. Amylopectin from starch mutants of corn with either a high content of branched short chains or high content of long chains had a comparatively slow digestion property (Figure 4). This also explains why starches from different botanical sources may have different glucogenic properties (Lin et al. 2012). Both whole grain properties and starches with certain molecular structures could be important to the slow digestion property of starch, and selection of whole grain crops containing molecular structure-based slowly digestible starch might be a strategy to boost the health benefit of whole grain foods, at least for the purpose of glycemic control.

When normal starch is gelatinized, amylose releases from the starch granule and retrogrades as the temperature decreases. These amylose-retrograded crystallites are termed type 3 RS. Beyond reducing caloric content, RS has a prebiotic property (Bird et al. 2010; Fuentes-Zaragoza et al. 2011) that modulates the composition of the gut microbiota (Haenen et al. 2013), increases butyrate-producing bacteria, and decrease pathogenic bacteria. Butyrate has been shown to be important to colon health by inhibiting inflammation and carcinogenesis, decreasing oxidative stress in humans (Hamer et al. 2009), improving colonic defense barriers (Hamer et al. 2008) and insulin sensitivity, and promoting energy expenditure (Gao et al. 2009). Butyrate also has the potential to be used as a therapeutic agent to treat metabolic diseases and neurological disorders with its ability to modulate expression of related genes through an epigenetic mechanism(Berni et al. 2012) Thus, selection of whole grains with a comparably high content of amylose might be another way to increase their health benefit. Examples are high-amylose barley (Szczodrak and Pomeranz 1991), high-amylose rye (Mohammadkhani et al. 1999), and high-amylose maize (Maki et al. 2012).

3. Contributing factors that influence starch digestion in whole grain foods

3.1. Cereal dietary fiber

Even though the mechanistic underpinnings of the health benefits of whole grain foods are not completely elucidated, dietary fibers such as arabinoxylan, pectin, cellulose, β-glucan, and resistant starch are often mentioned (Lattimer and Haub 2010; Cho et al. 2013). As noted above, a few of the fibers (e.g. β-glucans, water-soluble arabinoxylans) found in some whole grains are viscous-forming fibers that, through changes in diffusion kinetics of enzymes and digested products (Blackburn and Johnson 1981; Johnson and Gee 1981), might lead to a lower rate of gastric emptying, nutrient absorption, and probably glucose liberation and absorption in the upper gastrointestinal tract (Ray et al. 1983). Indeed, high viscosity of β-glucans did affect *in vitro* starch digestion (Kim and White 2013), and the zero-shear viscosity of jejunal digesta was found negatively correlated with glucose absorption in a pig study (Ellis et al. 1995). On the other hand, the presence of soluble dietary fiber (1% and 2% arabinoxylans and β-glucans with 10 times difference of viscosity) did not significantly affect the liberation of glucose from starch digestion (Dhital et al. 2014), indicating that the established benefits of soluble fibers on postprandial glycemic response are not primarily due to the direct effect of viscosity. Additionally, many if not most whole grain sources do not have appreciable amounts of viscous-forming fibers. Regarding the water insoluble fiber of cellulose, it inhibited α-amylase for starch digestion with a mixed type of inhibition kinetics resulted from a nonspecific binding to the enzyme (Dhital et al. 2015).

Soluble dietary fiber and RS are fermented in the colon to produce short chain fatty acids that trigger the release of gut hormones PYY and GLP-1 (Tolhurst et al. 2012) with the resulting effect of regulating gastrointestinal tract activity (Imeryuz et al. 1997), energy metabolism (Flint et al. 2000), insulin sensitivity (Parlevliet et al. 2010), and appetitive response (Gutzwiller et al. 1999). Short chain fatty acids (SCFAs) directly regulate energy metabolism (den Besten et al. 2013) and insulin-mediated fat accumulation (Kimura et al. 2013), appetite through regulating neuropeptidies in hypothalamus (Frost et al. 2014), and food intake through an intestinal gluconeogesesis mechanism (Vadder et al 2014). Dietary fibers also act as a selection pressure to modulate the ecology and composition of colonic microbiota (Pieper et al. 2009; Koropatkin et al. 2012) that has been shown to have a critical role in metabolic syndrome (D'Aversa et al. 2013).

Slowly digestible starch is not just an *in vitro* method-oriented concept, but manifests itself in an *in vivo* postprandial glycemic response profile characterized by a slow and prolonged elevation of plasma glucose concentration (Zhang and Hamaker 2009). Apart from factors reviewed above that impact digestion rate (i.e. physical structure of grain, starch granular and molecular structures, dietary fiber), the physiologically controlled process of gastric emptying, if slowed, creates a slowly digestible effect on postprandial glycemic response (Horowitz et al. 2002). Dietary fiber can substantially affect the motility of the gastrointestinal tract in which the viscosity either directly affects gastric emptying or through the ileal brake and/or colonic brake

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feedback control systems (Zhang et al 2015). Ileal brake and colonic brake are negative feedback loops purported to maximize the absorption of nutrients. Typically, most of the macronutrients are digested and absorbed in duodenum and jejunum and, if the nutrients are present in the ileum, the ileal brake is employed by the body to slow the gastric emptying and duodeno-jejunal motility so as to maximize nutrient absorption (Maljaars et al. 2008). The colonic brake, which can be directly induced by SCFA, produces a similar function of slowing down colonic motility, gastric emptying and upper small intestine motility (Cherbut et al. 1997; Topping and Clifton 2001). Dietary fiber with a high viscosity (if possible *in vivo*) can cause reduced rate of glucose absorption (Ellis et al. 1995) and more nutrients deposition in the ileum to trigger the release of GLP-1 through the ileal brake mechanism (Schirra and Göke 2005). SCFAs generated through fiber fermentation by the colon microbiota induces the release of the gut hormone peptide YY (PYY) (Wen et al. 1998) and GLP-1 (Tolhurst et al. 2012) to slow gastric emptying, promote insulin secretion, and flatten glycemic response. This creates a ‘second-meal effect’ first described by Jenkins et al. (Jenkins et al. 1982; Brighenti et al. 2006). Thus, dietary fibers can slow the absorption of glucose or other nutrients from both its physiochemical property such as high viscosity (Zijlstra et al. 2012) and the elicited ileocolonic brake system.

3.2. Impact of phytochemicals on starch metabolism

The anti-inflammation and antioxidative stress function of whole grain foods has been ascribed to their diverse range of phytochemicals (Table 2) (Belobrajdic and Bird 2013). Phytochemicals are the bioactive small compounds that reside mostly in the outer bran part of cereal grains, particularly the pericarp seed coat and aleurone layers. They include phenolic compounds, phytosterols, tocols, betaine, and folate and are of great diversity in chemical structures and physiochemical properties. The phenolic compounds of cereal grains are composed of numerous derivatives of benzoic and cinnamic acids, as well as flavonoids, flavones and flavanols, anthocyanidins, avenanthramide, lignans, and alkylresorcinols. They have antioxidant property that is important to fight against oxidative stress associated with metabolic diseases. A recent investigation showed that many phenolic compounds also have indirect antioxidative functions by inducing the expression of endogenous protective enzymes such as superoxide dismutase, glutathione peroxidase, and catalase (Wang et al. 2013). These compounds can modulate many stages of carcinogenesis (Surh 2003) and cancer-related inflammation signaling pathways by suppressing NF-κB activation, inhibiting STAT-3 activation, and down-regulating COX-2, iNOS, or inflammatory cytokines (Pan et al. 2009; Kim et al. 2011). Thus, phytochemicals are considered functional compounds related to the health function of whole grain foods, even though many clinical trials using whole grain cereals have not shown significant improvement in health-related biomarkers (Belobrajdic and Bird 2013).

Beyond the *in vivo* post-absorptive metabolic functions of phytochemicals mentioned above, the polyphenols in whole grain foods may have other functions related to carbohydrate digestion and absorption in the gastrointestinal tract. Starch is first hydrolyzed by salivary and pancreatic α-amylases to cleave the large starch molecules into maltose and maltooligosaccharides that are then further digested by brush border α-glucosidases to produce absorbable glucose. Glucose is then transported into the small intestine enterocytes through SGLT1, and into the blood system through GLUT2. Polyphenols such as tannins and catechins may be involved in all of these steps due to their affinity to proteins/enzymes (Bandyopadhyay et al. 2012). They have at least some inhibitory function on the activity of the α-amylases and α-glucosidases comprised of maltase-glucoamylase and sucrase-isomaltase (Mohamed Sham Shihabudeen et al. 2011; Mohamed et al. 2011; Forester et al. 2012; Mkandawire et al. 2013; Tu et al. 2013; Wang et al. 2013; Simsek M et al. 2015; Simsek et al. 2015). Polyphenols can interrupt the uptake of glucose by interacting with glucose transporter SGLT1 (Kobayashi et al. 2000) and GLUT2 (Kwon et al. 2007; Stelmanska 2009; Manzano and Williamson 2010) or by reduction of the expression of glucose transporters (Alzaid et al. 2013). Thus, conceptually, both starch digestion and glucose absorption may be interfered by polyphenols, and in turn affect postprandial glycemia. This is consistent with a recent human study showing that green tea extract (mainly polyphenols) decreases starch digestion and absorption (Lochocka et al. 2015). However, our recent study using a mouse model did not find significant impact of polyphenols (from green tea) on postprandial glycemic response to normal or waxy corn starch. Regarding the impact of tea polyphenols on high-amylose starch (naturally a resistant starch), an increased glycemic response was found (Liu et al. 2011), which is likely due to its interaction with polyphenols to prevent the association of amylose molecules (Chai et al. 2013). However, when octenyl succinic anhydride modified waxy starch was used, an *in vivo* α-glucosidase inhibitory function of polyphenols with decreased postprandial glycemia was found (Peng et al. 2015). It is possible that appropriate food forms may be needed to ensure specific binding of phenolic compounds to starch digestion enzymes and glucose transporters in the gastrointestinal tract for phenolic compounds to exert their inhibitory functions on starch digestion and glucose absorption to attenuate postprandial glycemia.

Phytochemicals, especially polyphenols, generally have a very low bioavailability (Manach et al. 2005), and most are delivered into the colon where they may be re-absorbed after modification by the microbiota. Additionally, it has been reported that polyphenols or their metabolites in the colon alter the ratio of *Bacteroidetes/Firmicutes* (Cardona et al. 2013). As the gut microbiota is important to health, including its action related to the gut-brain axis (Cryan and Dinan 2012), potential modulation of the gut microbiota by phytochemicals could affect its composition and SCFA production (Parkar et al. 2013), which might affect SCFA-induced ileocolonic brake and the gut-brain axis mechanisms.

4. Whole grain food processing and starch digestibility

Food physical or matrix barriers, inherent structure of starch, dietary fiber, and phytochemicals potentially could affect the nutritional property of starch as discussed above. Yet, food processing depending on the type can markedly increase starch digestion rate through simultaneous starch gelatinization and disruption of the physical barriers around starch. It is not well known from the literature, however, to what degree retention of fiber and phytochemicals in processed whole grain foods reduce starch digestion/glucose absorption rate. This is a topic that needs more study.

It is also conceivable that food processing may create some new food forms that could modulate starch digestion. A study using whole grain rye bread, pasta, and β-glucan-containing rye bread showed that food forms, including ones developed through processing, were more important than the amount of dietary fiber to reduce the postprandial glycemia and insulin concentration (Juntunen et al. 2002). Food forms from traditionally processed wheat (parboiling) and rye (whole grain) were found to reduce postprandial glycemia (Jenkins et al. 1986). More work needs to be done to understand how processing of whole grains can be used to slow starch digestion property.

The process of transforming raw whole grains to food products involves multiple steps that influence the starch component. Milling, as the first step in grain processing, disrupts much of the physical barrier in the whole grain kernel by breaking the bran layer and the endosperm tissue. Larger particles generally have a comparably slow digestion property. Other processing methods such as cutting or crushing can be used to produce even larger particles and slower digestion. Other commonly used food processing methods such as extrusion, flaking, and gun-puffing involving high temperature and high shear stress often gelatinize starch and destroy the semicrystalline structure of granules leading to a rapid digestion. Processes involving a high amount of water such as breadmaking or rice steaming also gelatinize the starch making it rapidly digestible. Some novel processing technologies such as non-thermal processing might be applied to partially retain the slow digestion property of starch. After starch gelatinization, there is the possibility that starch retrogradation can be manipulated to provide a slow digestion property (Zhang et al. 2008), which might be increased by interaction with other food components such as lipid to form starch-lipid complex (Hasjim et al. 2013), protein to form starch-protein complexes through the Maillard reaction, and a starch-lipid-protein three-component complex that had altered starch digestibility (Zhang et al. 2010). Interaction between high-amylose starch and polyphenols was also shown to modulate starch digestion property in a concentration-dependent manner (Chai et al. 2013).

Starch gelatinization and retrogradation during whole grain food processing might also be modulated through interaction with dietary fiber, related to its high water absorption property, to alter distribution of water or limit water availability for starch gelatinization and retrogradation so as to modulate starch digestibility. In this regard, water-soluble arabinoxylans were shown to increase retrogradation and rigidity of starch gels by reducing water availability of the starch (Gudmundsson et al. 1991), perhaps by accelerating chain ordering of starch molecules (Biliaderis and Izydorczyk 1992). Stabilization of starch granular structure during heating was also observed with increased phase transition temperature (Biliaderis et al. 1997) due to the effect of fiber on water absorption and its liquid crystal phase transition (Randzio et al. 2003). This is consistent with our finding of an increase of starch gelatinization temperature in whole grain flour samples compared to refined flour (unpublished data). β--Glucan, found in oats and barley, affected oat flour pasting property and starch digestibility, and was associated with its molecular weight and the β-(1→4)/β-(1→3) glycosidic linkage pattern (Liu and White 2010; Regand et al. 2011). Thus, the impact of dietary fiber on starch gelatinization and retrogradation behavior during food processing could be another way to modulate starch digestibility in whole grain foods.

Contribution of Slowly Digestible Starch to the Health Benefits of Whole Grain Foods

Starch is the sole provider of available carbohydrate in whole grain foods, and it is an important, though often overlooked, component to whole grain food quality. Although many health benefits have been attributed to dietary fiber and phytochemicals in whole grains, relatively little attention has been paid to their impact on starch degradation to glucose and its absorption, and more generally how starch is utilized by the body from different whole grain foods. Improved glucose metabolism resulting from synergistic interactions between phytonutrients and macronutrients in which starch is the main energy component (Jonnalagadda et al. 2011) is likely a central feature to whole grain foods' health benefit.

How can a slow release and absorption of dietary glucose be beneficial to health? Glucose is important to higher life forms as preferred energy source. However, high blood sugar for even a short time period (acute postprandial hyperglycemia) can generate excessive reactive oxygen species and free radicals to cause oxidative stress, endothelial dysfunction (Kitasato et al. 2012), and inflammatory reactions (Ceriello 2005). Chronically high blood sugar is an etiological factor for vascular failure (Node and Inoue 2009) and is related to risk for cardiovascular disease (Ceriello 2009) and cancer (Stattin et al. 2007). Postprandial hyperglycemia control is a critical point in the control of diabetes (Hanefeld and Temelkova-Kurktschiev 2002). Diets containing a high amount of rapidly digestible starch often cause postprandial hyperglycemia followed by a hypoglycemic episode with correspondingly large fluctuations in insulin levels that may be even more harmful than sustained hyperglycemia, as evidenced by a higher degree of apoptosis and dysfunction of pancreatic β-cells (Kohnert et al. 2012). Thus, moderated starch digestion and glucose absorption are likely an important dietary factor related to health.

Comparative studies between whole grain foods and refined grains have demonstrated that differences in carbohydrate quality are important to health. For example, refined grain products were not as favorable to glycemic control and lipid metabolism (Liu 2002) and were not as beneficial as were a whole grain products to control of diabetes (Liu et al. 2000). Another epidemiological study showed that increased intake of refined carbohydrates and decreased intake of dietary fiber paralleled an increasing trend of higher incidence of type 2 diabetes (Gross et al. 2004). Refined grain intake was significantly associated with visceral adipose tissue compared to whole grain intake in the Framingham Heart Study (McKeown et al. 2010) Thus, diets high in whole grains and with high carbohydrate quality, that is with considerable amounts of SDS and/or RS, are important to their health benefit.

Perspective and Future Trends

The health benefit of whole grain foods have been built on the basis of numerous epidemiological and *in vivo* studies. Although starch is quantitatively the major component of whole grains, there are relatively few studies on whole grains and carbohydrate quality as it relates to health. Considering government recommendations that whole grain foods should be the main carbohydrate provider in the diet (USDA 2015 Dietary Guideline Advisory Committee (http://health.gov/dietaryguidelines/2015-scientific-report/), the quality of starch as the glycemic carbohydrate in whole grain foods should be better studied and understood related to whole grain value. If, in fact, SDS and/or RS are found to be critical to the health benefit of whole grain foods, then more needs to be known regarding how processing affects carbohydrate quality, and accordingly how to retain or maximize SDS/RS amounts. Additionally, further studies are required to elucidate the relationship between the starch component in the whole grain package and its digestion and absorption relative to dietary fibers and phytonutrients. In this way, novel functional whole grain, and likely even refined grain, foods can be designed to combat the metabolic diseases for improved health.

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Table 1. The content and composition of cereal carbohydrates(Kulp and Ponte 2000)

Samples	**Starch (%)**	**Amylose (%)**	**Pentosan (%)**	**β-Glucan (%)**	**Total dietary fiber (%)**
Wheat	63-72	23.4-27.6	6.6	1.4	14.6
Barley	57.6-59.5	22-26	5.9	3-7	19.3-22.6
Brown rice	66.4	16-33	1.2	0.11	3.9
Sorghum	60-77	21-28	1.8-4.9	1.0	10.1
Pearl millet	63	17	2-3		8.5
Corn	64-78	24	5.8-6.6		13.4
Oats	43-61	16-27	7.7	3.9-6.8	9.6
Rye	69	24-31	8.5	1.9-2.9	14.6
Triticale	53	24-26	7.1	1.2	18.1

Handbook of cereal science and technology, 2nd edition. Marcel Dekker, Inc. 2000

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Table 2. The contents of phenolic compounds in some cereals (Belobrajdic and Bird 2013).

Phenolic compounds	**Wheat**	**Barley**	**Rice**	**Rye**	**Oat**
Polyphenols (mg/100g)	70-1459	50-196	54-313	125-255	9-34
Phenolic acid (total)(μg/g)	200-900	100-550	N/A	200-1080	350-874
Phenolic acid (free)(μg/g)	5-39	5-23	N/A	10-35	50-110
Ferulic aicd (mg/100g)	16-213	110-120	30	39-50	21-24
Flavanoids (mg/100g)	30-43	12-18	N/A	67-75	56-82

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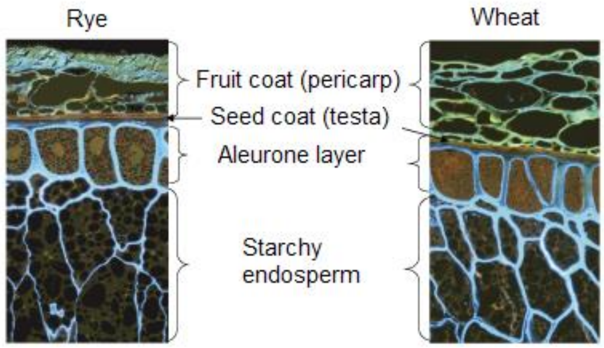

Figure 1. The cellular structure of grain kernels from rye and wheat. (Kamal-Eldin et al. 2009)

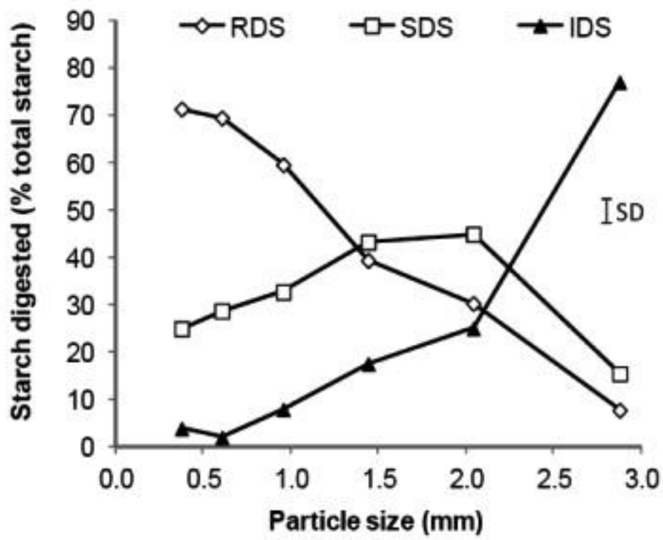

Figure 2. The effect of cereal particle size on the digestibility of starch. RDS: rapidly digestible starch, SDS: slowly digestible starch, IDS: indigestible starch (RS).(Suman et al. 2012)

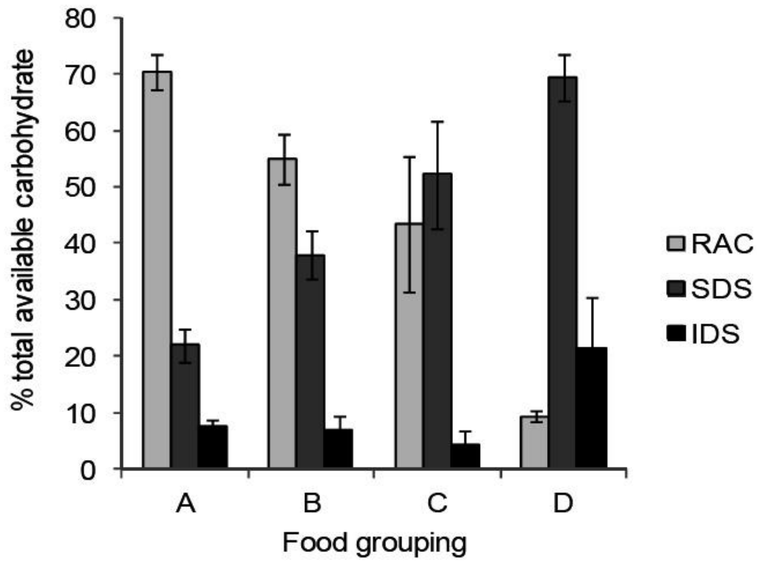

Figure 3. Impact of food forms on starch digestion. A: Little structure, starch gelatinized e.g. extruded, puffed and flaked precooked cereal products, B: Some structure, minimally processed, incomplete starch gelatinization e.g. rolled oats, C: Dense secondary structure, non-porous, surface digestion e.g. pasta, D: Intact, robust cell walls encapsulating starch in native tissue structure(Suman et al. 2012)

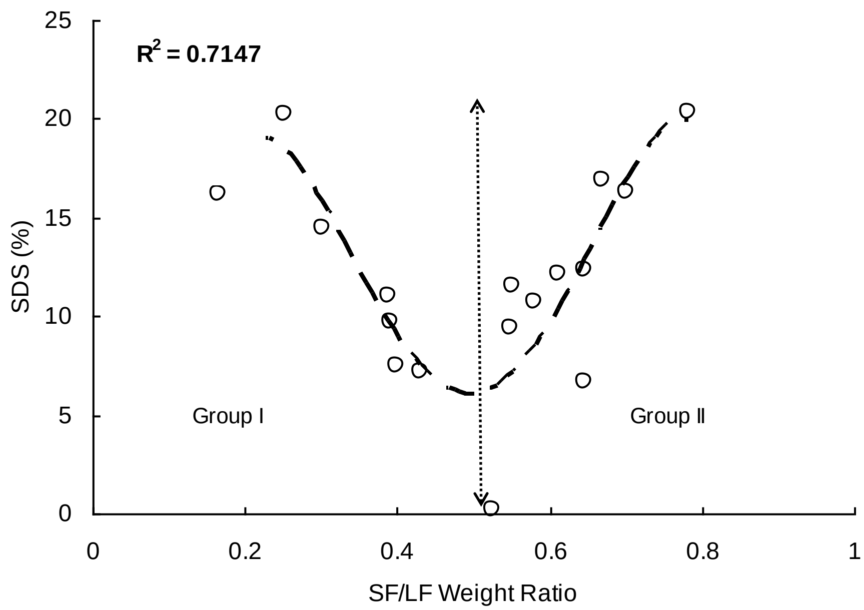

Figure 4. The parabolic relationship between SDS percentage and the weight ratio of short chain (SF) to long chain fraction (LF) of a range of starch mutants of corn and normal corn starch.(Zhang et al. 2008)