Cereal and pulse crops are staple foods that provide essential nutrients to many populations of the world. Traditionally, whole grains were consumed but most current foods are derived from refined fractions of cereal and pulse crops. Consumption of processed or refined products may reduce the health benefits of food. In wheat-based processed foods, for example, the removed 40% of the grain (mainly the bran and the germ of the wheat grain) contains the majority of the health beneficial components. These components, particularly non-essential phytochemicals such as carotenoids, polyphenols, phytosterols/stanols, and dietary fibers, have been shown to reduce the risk of major chronic diseases of humans, such as cancer, cardiovascular diseases, and Parkinson’s disease.

Such bioactives are therefore good candidates for ingredients of nutraceuticals and functional foods. There are many factors that can affect the bioactive content of cereal and pulse-based food ingredients, including genetics, growing and storage conditions, post-harvest treatments, food formulation and processing. All of these factors ultimately affect human health and wellness. Bioavailability is also important for these compounds for exerting their protective roles.

Cereals and Pulses: Nutraceutical Properties and Health Benefits provides a summary of current research findings related to phytochemical composition and properties of cereal and pulse crops. The nutraceutical properties of each major cereal and pulse are discussed. Coverage of cereals and pulse crops includes barley, oats, rice, corn, adlay, wheat, buckwheat, psyllium, sorghum, millet, common beans, field peas, faba beans, chickpea, lentil and soybeans. Chapters for each crop discuss methods to improve crop utilization, nutraceutical components and properties, bioactive compositions, antioxidant properties, beneficial health effects, disease prevention activities, and areas for future research. Also included are two chapters that examine the beneficial health properties of dietary fibers and antioxidants. Edited and written by an international team of respected researchers, this book is a reference guide for scientists working in food ingredients, food product research and development, functional foods and nutraceuticals, crop breeding and genetics, human nutrition, post-harvest treatment and processing of cereal grains and pulses. It will enable them to effect value-added food innovation for health promotion and disease risk reduction.

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Cereals and Pulses: Nutraceutical Properties and Health Benefits
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Cereals and Pulses
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1 Cereals and pulses – an overview

Rong Tsao, Liangli (Lucy) Yu, and Fereidoon Shahidi

1.1 Introduction

For thousands of years grains and pulses have been produced and consumed as staple foods. Bread, noodles, porridge, breakfast cereals, and other forms of food made from wheat, oats, barley, rice, corn, lentils, chickpeas, and soybean (and other dried seeds) are found in all cultures and cuisines around the world. Many of these foods continue to be home prepared, however, large amounts of the staple foods today, particularly in the industrialized countries, are also made commercially. The global market for breakfast cereals alone was $24.5 billion in 2008, and it is estimated to grow by roughly 17.1% to a total value of $28.7 billion by 2013 (Datamonitor, 2009).

The same report also showed that ready-to-eat cereals dominated, having an 87.8% share of the global breakfast cereals market. America leads the global breakfast cereals market, accounting for 64.9% of the market’s value, according to the same report. However, processing may reduce the health benefits of food and this depends entirely on the form in which the products are consumed. Most of the wheat-based foods, including bread, noodles and pasta, and cookies, are made from bleached white flour (60% extraction). What is more important is that the 40% removed grain, mainly the bran and the germ, contains the majority of the health beneficial components.

Cereal grains and leguminous seeds contain myriad components that are important and essential to human health. The macro-nutrients, carbohydrates, proteins, and fats serve as a rich source of energy and contain many essential nutrients such as vitamins, amino acids, and fatty acids. However, in recent years, some of these and other minor components have been found to play important roles beyond satisfying basic nutritional requirements. Studies have shown that dietary fibers and certain phytochemicals can be key to health maintenance and disease risk reduction. Intakes of dietary fibers and phytochemicals have been associated with reduced risk of cancer, cardiovascular disease, diabetes, chronic inflammation, neural degeneration, and other chronic ailments and illnesses. These bioactives are, therefore, good candidates as ingredients for nutraceuticals and functional foods.
Meanwhile, many factors can affect the composition and the potential health benefits of foods rich in these bioactives throughout the value chain. Genetics, growing and storage conditions, post-harvest treatments, food formulation, and processing can all affect the content of these bioactives in cereal- and pulse-based food ingredients, and related foods and food supplements, ultimately affecting human health and wellness. This monograph focuses on the chemical and nutraceutical compositions, and potential health beneficial properties, of commonly consumed cereals and legumes. The effects of growing conditions, post-harvest treatments, and food processing and formulation on nutraceutical properties of the cereals and legumes are also covered. In addition, the mechanisms involved in rendering the beneficial effects of cereal and legume components are discussed.

1.2 Chemistry and nutraceutical compositions

Intact kernels of grains or seeds contain three major parts: germ/embryo, endosperm/cotyledon, and bran/seedcoat. It is also important to know that most of the nutrients, including dietary fibers and polyphenols, are found in the germ and bran or seedcoat, therefore to receive maximum health benefits, food products made from whole grains or pulses are preferable. Refined grains and pulses often have the germ and bran or seedcoat removed, thus important dietary fibers, vitamins, minerals, and bioactive phytochemicals are lost; although in countries such as the US and Canada manufacturers are required to enrich white flour with several vitamins and iron.

Phytochemicals are plant-originated secondary metabolites that possess various biological activities. These natural products can be categorized into different chemical classes (Liu, 2004; Tsao, 2010). Cereal grains and pulses are a rich source of bioactive phytochemicals. While polyphenols and carotenoids are perhaps the most studied phytochemicals, particularly for their antioxidant activities, other groups such as phytosterols and saponins are major contributors to the health benefits of cereal grains and pulses.

Food compositions can be altered by targeted breeding. Grains and pulse crops can produce significantly more or less of certain components, for example, soybeans with low, medium, and high isoflavone contents have been developed and formulated into functional soy-breads that contain different levels of naturally occurring isoflavones (Shao et al., 2009). Environmental factors such as growing season, soil type, temperature, and agronomic practices (organic vs. conventional) have also been found to significantly affect the phytochemical compositions (Zhou et al., 2005). Phytochemicals such as polyphenols and carotenoids are relatively unstable under high temperature, thus food processing, such as production of breakfast cereals, can lead to loss of important bioactive compounds that are key to human health (Slavin et al., 2000; Muzhingi et al., 2008).

1.3 Potential health beneficial effects

Dietary fibers and phytochemicals are important components of a healthy diet. Dietary fibers, particularly soluble fibers such as β-glucans from barley and oats, have been found to significantly reduce the total and LDL (low-density lipoprotein) cholesterol levels (Brown et al., 1999; Chapters 2 and 3 in this volume); and the effect was discovered to be related to
An overview of the physicochemical properties such as the molecular weight of β-glucan (Wolever et al., 2010). Dietary fiber of rice bran also reduces LDL cholesterol, as discussed in Chapter 5. On the other hand, results of epidemiological studies of dietary fiber and cancer risks have not been consistent. For example, examining the consumption of dietary fiber and the risk of colorectal cancer, a recent Japanese study found that total, soluble, and insoluble dietary fibers were not measurably associated with overall risk or subsite-specific risk of colorectal cancer (Uchida et al., 2010). However, the same study suggested a decreased risk of distal colorectal cancer associated with rice consumption. Nevertheless, other studies have indeed shown a positive correlation between the consumption of dietary fibers and cancer risks. Howe et al. (1992) showed convincingly that intake of fiber-rich foods was inversely related to risk of cancers of both the colon and rectum. Among the 13 case–control studies, 12 showed significant correlation between dietary fiber intake and the decrease of risk of both left- and right-sided colon and rectal cancers, for men and women, and for different age groups, but no associations were seen for the intakes of vitamin C and β-carotene (Howe et al., 1992). A more recent study concluded similarly that the intake of dietary fiber was inversely associated with colorectal cancer risk. The authors also suggested that methodological differences (i.e. study design, dietary assessment instruments, definition of fiber) may account for the lack of convincing evidence for the inverse association between fiber intake and colorectal cancer risk in some previous studies (Dahm et al., 2010). Dietary fibers from pulse crops may also contribute to the reduction of LDL cholesterol and the risk of cancer, however, more research needs to be done in this area. Dietary fibers from other food crops including psyllium and sorghum are also known for similar health benefits (Chapters 11 and 12, respectively). Other forms of carbohydrates, such as resistant starch in corn (Chapter 7), also play important roles in alleviating health risks. The health properties of dietary fiber preparations and the potential molecular mechanisms involved in their beneficial actions are summarized in Chapter 18. In general, psyllium, oats, barley, and several edible legumes are important dietary sources of soluble fibers, while bran of wheat and corn are good sources of insoluble fiber. Soluble fibers may absorb moisture in the GI (gastrointestinal tract) track and form viscous fluid or gel, which may trap lipid and bile acids reducing their bioavailability and total energy intake. They may also be fermented in the large intestine and form short chain fatty acids, which can reduce the local pH and enhance the movement of intestinal contents. Such effects may lead to reduced absorption of energy and toxins, as well as changes of the microorganism profile in the large intestine. High intake of dietary fibers may reduce the risk of several human chronic diseases, such as cardiovascular diseases, diabetes, and colon cancer (Chapter 18).

While dietary fibers are an important ingredient contributing to the health benefits of cereal grains and pulses, ample evidence exists that phytochemicals may play greater roles. Many different classes of phytochemicals have been identified and their specific bioactivities reported. The major phytochemicals that have shown health benefits include various phenolic compounds, carotenoids, saponins, and phytosterols. Many of these secondary metabolites provide chemical defense against invading insects or microorganisms, or participate in wound healing in the plants.

Phenolic compounds, including the phenolic acids and flavonoids are responsible for the total antioxidant activity of cereals and pulses (Chapter 19). The majority of the phenolics are found in the bran or seed coat of the grains, therefore, consumption of whole grain and intact seed-based foods is of greater benefit. Diets rich in phenolics have been linked to the reduction of several chronic diseases, particularly those caused by
oxidative stress such as cancer, cardiovascular diseases, diabetes, and inflammatory illnesses. However, additional roles of phenolic compounds, particularly flavonoids, have been identified in recent years. In addition to the direct antioxidant activities, flavonoids, for example, have been shown to modulate cell signaling pathways at physiological concentrations way below those required to impact cellular antioxidant activities. Modulation of cell signaling pathways by flavonoids could help prevent cancer by stimulating phase II detoxification enzyme activity and by inhibiting proliferation and inducing apoptosis. Inhibition of biomarkers such as NFkB of inflammation and increase of the endothelial nitric oxide synthase (eNOS) activity may help prevent cardiovascular diseases.

The antioxidant activity of the phenolics has been associated with many chronic diseases. Cinnamic acid and its derivatives, particularly ferulic acid, are the main phenolic acids in cereal grains (Zhou et al., 2005). Phenolic acids are found mostly in the bran, and the majority may exist in conjugated and bound forms (Liyana-Pathirana and Shahidi, 2006; Kim et al., 2006; Chandrasekara and Shahidi, 2010; Chapter 19). Cereal grains are also the major dietary source of lignans, a group of polyphenols that play important roles in human health, particularly as precursors of mammalian lignans. These compounds are mostly found in the bound form, thus are not normally extractable by organic solvents (Chapters 6 and 9). Flavonoids, mainly flavones and flavonols, have been found in cereal grains. Apigenin, kaempferol, and quercetin glycosides are major flavonoids, however, anthocyanins contribute significantly to the total flavonoid content in dark colored grains such as purple corn (Chapter 7). Catechins have also been identified in grains such as buckwheat (Chapter 10). Sorghum and millet, with their unique drought-resistance and high level of polyphenols, are considered important to combat the continuously increasing health problems of obesity, diabetes, cardiovascular diseases, and cancer. Sorghum is unique among cereals with its high content of condensed tannins that are oligomeric and polymeric flavonoids. These proanthocyanins are strong antioxidants and considered key for lowering risks of several chronic diseases (Chapter 12). Seed coat of pulses is also a good source of flavonoids (Chapters 14 and 15). Isoflavones, a subgroup of flavonoids, are only found in soybean and other legumes. Isoflavones and lignans are phytostrogens, therefore, in addition to other biological activities, their role in hormone-related diseases such as breast cancer and osteoporosis is also important (Chapters 17). Other legumes such as pulse crops have been studied in recent years and efforts have been made to determine the bioactives and their relationship with health benefits (Chapters 14 and 15).

Carotenoids are critical to the photosynthesis of plants, however, many of these compounds, such as β-carotene, are also important to humans as vitamin A precursors. In cereals and pulses, while many carotenoids have been identified, zeaxanthin and lutein are worthy of special mention. These two non-vitamin A precursors, found mainly in corn and other cereal grains such as wheat, are not only strong antioxidants, but can also inhibit cancer cell proliferation and prevent cell mutation. These compounds are especially critical to the health of the eye (Chapter 7).

Other phytochemicals, such as phytates, saponins, and phytosterols, have also been found to contribute to the potential health benefits of cereals and pulses. Policosanols and lactams are unique bioactives found in a minor cereal crop adley, among other commonly found phytochemicals that showed various health benefits (Chapter 8). D-chiro-inositol and fagopyritols in buckwheat have also been found to benefit diabetics (Chapter 10). However, it is generally understood that these and all other above-discussed active components play an
assorted role in various health problems, as pointed out in Chapter 18. Their composition and specific roles can be found in different chapters of this book. It is our hope that this book offers a focused discussion of cereals and pulses as important contributors to health, and how we can improve the quantity and quality of their functional components in the diet throughout the value-chain, i.e. breeding, production, postharvest storage, and food processing. Reviews on the chemistry, biochemistry, and mechanisms of action of the bioactives, including dietary fibers and the various phytochemicals, will also provide insights into future research.

References


2    Effects of barley consumption on cardiovascular and diabetic risk

Trust Beta, Qin Liu, and Yang Qiu

2.1    Introduction

Barley is one of the most important cereal crops cultivated in the world. In history, it has been consumed mainly as a staple food, whereas in modern times it is mostly used in the beer industry. In the human diet, barley not only provides protein and carbohydrate, but is also a good source of dietary fibre. There is growing evidence supporting a role for dietary fibre in lowering plasma cholesterol, improving lipid metabolism, and reducing glycemic index (Li et al., 2003; Behall et al., 2004, 2005, 2006). Therefore, consumption of barley whole grain and/or barley-based foods has been associated with lower risks of cardiovascular diseases, diabetes, and some types of cancer (Pins and Kaur, 2006; Ames and Rhymer, 2008).

In recent years, the health benefits provided by barley have led to an increased focus on the study of nutraceutical components in barley. The (1→3,1→4)-β-D-glucans, commonly known as β-glucans, are the major constituents in barley dietary fibre. They are structural components in barley endosperm cell walls. The molecular structures and physicochemical properties of β-glucans in barley have been characterized by Izydorczyk and Dexter (2008) and their effects on cardiovascular and diabetic risks have been reviewed by Pins and Kaur (2006). In addition to β-glucans, the other health promoting compounds mostly studied in barley are phenolic compounds. They are reported to play an important role in the prevention of and protection from oxidation-induced diseases.

Therefore, this chapter provides a review of the major nutraceutical components in barley grain and their roles in the maintenance of human health. Special attention will be paid to β-glucans.

2.2    Barley β-glucan and risk of cardiovascular diseases, diabetes and colon carcinogenesis

2.2.1    Chemical structure of barley β-glucan

Barley β-glucans are linear homopolysaccharides of D-glucopyranosyl residues linked mostly via two or three consecutive β-(1→4) linkages that are separated by a single β-(1→3) linkage.
Despite sharing the same general molecular structure, β-glucans from different genera of barley are varied in the length and branching. The ratios of β-(1→4)/β-(1→3) linkages are also different.

### 2.2.2 β-glucan content in barley grain

Barley grain contains remarkable β-glucan content ranging from 2.5 to 11.3% (Izydorczyk and Dexter, 2008). Izydorczyk and Dexter summarized the β-glucan contents in different genotypes of hulled and hulless barley, which are given in Table 2.1. It appears that barley genotypes with waxy or high amylose starch contain higher content of β-glucans than those with normal starch. There is no significant difference in total β-glucan content between hulled and hull-less barley types.

In addition to the genetic factor, the concentration of β-glucan in barley is also influenced by environmental factors (Andersson et al., 1999). The total content of β-glucans in barley generally increases when it is grown in hot and dry conditions (Morgan and Riggs, 1981).

### 2.2.3 Barley β-glucan in the prevention and management of cardiovascular diseases

Cardiovascular disease (CVD), primarily in the form of heart disease and stroke, is the Nation's leading killer for both men and women among all racial and ethnic groups. The major risk factors associated with CVD include high levels of total cholesterol and low-density lipoprotein (LDL) cholesterol (Ames and Rhymer, 2008). Consumption of barley β-glucan enriched foods has been associated with the reduced incidence of CVD due to the ability of β-glucan to lower serum cholesterol and LDL cholesterol levels.

McIntosh et al. (1991) reported that when 21 patients with light hypercholesterolemia were given 8 g of β-glucan through a barley diet (170 g/d) for four weeks, the total cholesterol...
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and LDL levels were reduced by 6% and 7%, respectively. More recently, Behall et al. (2004) conducted two studies on the effect of barley β-glucans among hypercholesterolemic patients. In one of their studies, 7 men and 18 women were supplemented with a diet containing 0, 3 or 6 g/day of barley β-glucan with equivalent levels of total dietary fiber for 15 weeks. The total cholesterol was decreased by 5% and 6% when the diet contained 3 g or 6 g barley β-glucan/day, respectively, and LDL cholesterol level was reduced by 10% and 13%. In another study (Behall et al., 2004), a five-week diet with low, medium, and high-soluble barley fiber reduced total cholesterol by 14%, 17%, and 20%, respectively, and LDL cholesterol by 17%, 17%, and 24%, respectively. Based on these human clinical trials, the US Food and Drug Administration (FDA) released an announcement that daily intake of 3 g of soluble β-glucan from barley or certain dry milled barley products would decrease plasma total cholesterol level by 5–8% (FDA, 2005).

The mechanism by which barley β-glucan lowers serum cholesterol has not been completely understood. However, two possible mechanisms were proposed including the delayed intestinal absorption of glucose and lipids and the inhibition of absorption and re-absorption of cholesterol and bile acids (Anderson et al., 1984, 1988; Wilson et al., 2004).

### Table 2.1 Beta-glucan contents in different genotypes of hulled and hull-less barley

<table>
<thead>
<tr>
<th>Barley genotype</th>
<th>Total beta-glucan</th>
<th>Water-soluble beta-glucan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hullled, normal starch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC Metcalfe</td>
<td>4.5</td>
<td>1.2</td>
</tr>
<tr>
<td>CDC Kendall</td>
<td>4.4</td>
<td>1.3</td>
</tr>
<tr>
<td>Legacy</td>
<td>5.1</td>
<td>1.2</td>
</tr>
<tr>
<td>Xena</td>
<td>4.9</td>
<td>1.4</td>
</tr>
<tr>
<td>Hull-less, normal starch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDC McGwire</td>
<td>4.7</td>
<td>1.3</td>
</tr>
<tr>
<td>AC Millhouse</td>
<td>4.5</td>
<td>1.2</td>
</tr>
<tr>
<td>CDC Dawn</td>
<td>3.9</td>
<td>1.2</td>
</tr>
<tr>
<td>AC Bacon</td>
<td>4.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Falcon</td>
<td>3.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Hull-less, waxy starch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDC Alamo</td>
<td>7.5</td>
<td>2.8</td>
</tr>
<tr>
<td>CDC Rattan</td>
<td>7.5</td>
<td>2.9</td>
</tr>
<tr>
<td>CDC Fibar</td>
<td>9.7</td>
<td>3.5</td>
</tr>
<tr>
<td>CDC Candle</td>
<td>6.9</td>
<td>2.5</td>
</tr>
<tr>
<td>Enduro</td>
<td>6.8</td>
<td>2.4</td>
</tr>
<tr>
<td>Hull-less, high amylose starch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SH99250</td>
<td>8.9</td>
<td>2.0</td>
</tr>
<tr>
<td>SB94893</td>
<td>8.9</td>
<td>1.5</td>
</tr>
</tbody>
</table>

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2.2.4 Barley β-glucan in the treatment of diabetes

Diabetes is a chronic disease characterized by high blood glucose level (hyperglycemia). There are three type of diabetes; type 1 is caused by T-cell mediated autoimmune destruction of islet insulin-secreting β-cells (Rother, 2007), type 2 is characterized by the resistance to
insulin with both hyperglycemia and hyperinsulinemia followed by the deficiency of insulin, and type 3 has both decreased insulin and increased resistance to insulin (Carpenter, 2007; Schinner et al., 2005). Among the three types of diabetes, type 2 accounts for 90% of the total incidences of diabetes. The major causes of type 2 diabetes involve lifestyle factors as well as genetics.

Many studies have shown that β-glucan in barley is helpful in controlling blood glucose and insulin response. Pick et al. (1998) studied the long-term effects of incorporating high β-glucan content (β-glucan = ~7%), waxy, hulless barley bread products in every day diets of non-insulin-dependent diabetic (type 2) subjects. The results showed that mean blood glycemic response area (AUC) was lower (NS) and insulin response area was higher (\( P \leq 0.05 \)) when subjects were fed barley bread as opposed to refined wheat flour bread. Incorporating barley bread products (5 g/d β-glucan) into the diet of the type 2 diabetics improved their glycemic response and increased insulinenic response leading to some subjects reducing their dose of oral hypoglycemics. In another study, the effect of barley breakfast cereal made by a hulless barley on blood glucose and insulin response was reported (Rendell et al., 2005). In their study, Prowashonupana, a barley variety with low starch, high fiber, high protein, and relatively high concentration of free sugars, containing 3 times as much β-glucan as other standard hulless barley, was used. The results showed that the post-prandial glycemic index was reduced for Prowash compared to commercial liquid meal replacer (LMR) or oatmeal for both diabetics and non diabetics. In the non-diabetic subjects, the maximal rise in glucose from baseline was 26.3 ± 3.9 mg/dL after LMR, 41.3 ± 3.9 mg/dL after oatmeal, and 6.4 ± 2.7 mg/dL after Prowash (\( p < 0.01 \)). The maximal increase in glucose in the diabetic patients was 69.9 ± 4.5 mg/dL after LMR, 80.8 ± 8.8 mg/dL after oatmeal, and 28.4 ± 3.5 mg/dL after Prowash (\( p < 0.01 \)). The maximal increase in insulin post-LMR was 33.9 ± 3.6 mIU/mL in the diabetic patients and 54.0 ± 9.8 mIU/mL in the non-diabetic controls. Oatmeal elicited a maximal insulin increase of 29.9 ± 4.2 mIU/mL in the control subjects and 21.4 ± 2.5 mIU/mL in the diabetic patients. In contrast, the maximal insulin increase after Prowash was 8.6 ± 1.5 mIU/mL in the non-diabetic controls and 6.8 ± 1.2 mIU/mL in the diabetic patients (\( p < 0.01 \)). The reduced post-prandial glucose levels in the subjects consuming Prowash were similar to those observed in diabetic patients treated with alpha-glucosidase treatment. In insulin-dependent type 1 diabetics, lower post-prandial blood glucose permits equivalent reduction in insulin doses. For many individuals, a food product is highly preferable compared to pharmacological agents. Behall et al. (2005) also reported that when barley Prowashonupana and oatmeal were given to ten women with average age of 50 years old and body mass index of 30 (overweight), peak glucose and insulin levels were significantly lower after barley meals than oat, suggesting that high β-glucan was the key factor in those reductions. In another report, the breakfast made by β-glucan-enriched barley exhibited favorable responses on glucose metabolism, and particularly on insulinenic responses compared with whole grain wheat breakfast in a group of ten healthy volunteers (five males, age 25.4 ± 0.5 yrs, BMI 22.6 ± 0.7 kg/m²) (Casiraghi et al., 2006).

According to the above literature, it is believed that daily intake of barley β-glucans helps lower blood glucose and that barley β-glucans can be used in the treatment of diabetic patients. However, a detailed mechanism of action of β-glucans is still to be established. A possible theory is that β-glucans increase the viscosity of the intestinal contents resulting in the reduced postprandial insulin and glucose levels. Over time, lower ambient insulin levels improve cellular insulin sensitivity, causing improved glucose metabolism (Pins and Kaur, 2006).
2.2.5 β-glucan and chemoprevention of colon carcinogenesis

The chemoprevention of colon carcinogenesis by β-glucans has been mostly studied in vitro. Kim et al. (2009) reported that bacterial β-glucans induced 1) the apoptosis of colon cancer SNU-C4 cells and 2) changes of cell morphology and of the expression of apoptotic genes. The same β-glucans also increased the activity of caspase-3 enzyme. In other reports, β-glucans inhibited the activity of isozymes of cytochrome family (phase I enzyme) involved in the first activation of carcinogens (Hashimoto et al., 2002; Okamoto et al., 2004). Barley β-glucans may have protective effects against damage induced by methyl methanesulfonate (MMS) in the CHO-K1 cell line (deficient in drug metabolism) and 2-aminoanthracene (2AA) in the HTC cell line (proficient in drug metabolism) (Oliveira et al., 2006). The antitumor activity and immune responses of β-glucans depend on their molecular structures and physical properties. There is need for elaborate clinical trials to assess the effectiveness of purified β-glucans among cancer patients.

Several studies have shown that β-glucan extracts from barley can prevent chemical agent-induced tumor. Earlier studies have shown that barley bran could reduce 1,2-dimethylhydrazine (DMH) intestinal tumor incidence and burden (McIntosh, 1996). Co-administration with β-glucan from barley enhanced efficacy of photodynamic therapy in treatment of Lewis lung carcinoma (Akramiene et al., 2009). Pre-incubated barley β-glucan reduced the DNA damage in CHK-K1 cell line when induced by methyl methanesulfonate (MMS) (Oliveira et al., 2006). The protection of barley β-glucan against 2AA (2-aminoanthracene) and MMS was also observed in CHO-K1 (Angeli et al., 2006).

The mechanism involved in antitumor activity may be attributed to the antioxidant properties of β-glucans, thereby preventing oxidant injury by reactive oxygen species, which lead to formation of cancers. Moreover, β-glucans showed protection effects against genotoxicity and cytotoxicity induced by chemotherapy drugs such as cyclophosphamide, abriamycin, and cisplatin (Tohamy et al., 2003). This protective effect may be due to the ability to trap free radicals or other reactive species during metabolism of the drugs.

2.3 Other nutraceutical components and properties in barley

In addition to β-glucans, barley grain also contains a wide range of phenolic compounds. According to Madhujith and Shahidi (2007) and Bellido and Beta (2009), phenolic extracts from barley showed high antioxidant activity. By using the extracts from barley, the cell proliferation of Caco-2 colon cancer cell was inhibited 29.3–51.2% and 9.3–15.9% at 0.5 and 0.05 mg/ml, respectively (Madhujith and Shahidi, 2007). Therefore, the full characterization of phenolic compounds in barley is important.

2.3.1 Phenolic acids in barley grain

Phenolic acids can be classified as hydroxylated derivatives of benzoic and cinnamic acids. Hydroxycinnamic acids are more common than hydroxybenzoic acids and mainly consist of p-coumaric, caffeic, ferulic, and sinapic acids (Manach et al., 2004). Ferulic acid is the most abundant phenolic acid in cereal grains. As one of the cinnamic acid derivatives, ferulic acid
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shows high antioxidant because of CH = CH-COOH group. Several studies have shown that ferulic acid have anti-inflammatory (Sakai et al., 1999), skin photoprotection, and tumor inhibition (Priefert et al., 2001; Murakami et al., 2002) properties. Ferulic acid also exhibits potential chemopreventive effect on oral (Mori et al., 1999) and large bowel carcinogenesis (Kawabata et al., 2000). It may protect against coronary heart disease because of the antioxidant and cholesterol-lowering activities (Sakamoto et al., 1987). Therefore, the high content of ferulic acid in outer layers of cereal kernels may be associated with the health benefits of whole grains.

Phenolic acids in barley have been studied extensively (Holtekjlen et al., 2006; Quinde et al., 2006; Hernanz et al., 2001). As with other cereal grains, phenolic acids in barley occur in free, conjugated (soluble) and bound (insoluble) forms with their concentrations in the order of bound > conjugated > free. The bound form makes up more than 60% of the total phenolic acid (Adom and Liu, 2002; Li et al., 2008). Nine phenolic acids have been detected in barley flour, including caffeic acid, ferulic acid, sinapic acid, protocatechuic acid, vanillic acid, p-coumaric acid, p-hydroxybenzoic acid, syringic acid, and ferulic acid dehydrodimers (Mattila et al., 2005). Ferulic acid (FA) is the major phenolic acid constituting 90% of the total, while p-coumaric and vanillic are minor acids in barley grain (Table 2.2). A wide range in total phenolic acid content (254–675 \(\mu\)g/g) was observed across different barley samples analyzed under the European HEALTHGRAIN program. Bound phenolic acids make up approximately 73% of the total phenolic acid content with concentrations ranging from 133 to 523 \(\mu\)g/g. Soluble conjugated phenolic acids comprised approximately 25% of the total phenolic acid content with levels ranging from 86 to 198 \(\mu\)g/g. Free phenolic acids comprised only a very small proportion (<3%) ranging from 4.6 to 23 \(\mu\)g/g. The free phenolic acids comprised ferulic (27%), vanillic (28%), syringic (17%), and p-coumaric acid (22%). Ferulic

<table>
<thead>
<tr>
<th>Barley genotype</th>
<th>Ferulic acid (ug/g)(^1)</th>
<th>p-Coumaric acid (ug/g)(^1)</th>
<th>Vanillic acid (ug/g)(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peru 3</td>
<td>650.3 ± 28.65</td>
<td>24.5 ± 7.82</td>
<td>42.5 ± 22.99</td>
</tr>
<tr>
<td>Peru 5</td>
<td>838.9 ± 62.61</td>
<td>11.9 ± 4.79</td>
<td>58.8 ± 4.59</td>
</tr>
<tr>
<td>Peru 16</td>
<td>745.6 ± 100.44</td>
<td>53.9 ± 8.39</td>
<td>66.8 ± 4.99</td>
</tr>
<tr>
<td>Peru 35</td>
<td>877.1 ± 108.06</td>
<td>22.2 ± 3.35</td>
<td>50.6 ± 9.86</td>
</tr>
<tr>
<td>Peru 45</td>
<td>797.1 ± 20.61</td>
<td>21.8 ± 5.14</td>
<td>45.5 ± 1.03</td>
</tr>
<tr>
<td>Ex 116</td>
<td>589.8 ± 0.25</td>
<td>39.0 ± 2.00</td>
<td>28.9 ± 2.34</td>
</tr>
<tr>
<td>Ex 127</td>
<td>749.4 ± 218.60</td>
<td>16.6 ± 5.03</td>
<td>66.6 ± 32.54</td>
</tr>
<tr>
<td>Cl 4325</td>
<td>706.8 ± 58.59</td>
<td>70.2 ± 29.11</td>
<td>65.6 ± 0.15</td>
</tr>
<tr>
<td>Ex 82 x Cl 19973</td>
<td>642.9 ± 66.44</td>
<td>15.4 ± 4.30</td>
<td>99.6 ± 51.60</td>
</tr>
<tr>
<td>Ex 87 x Cl 19973</td>
<td>723.3 ± 21.51</td>
<td>14.5 ± 2.78</td>
<td>94.7 ± 12.11</td>
</tr>
<tr>
<td>Ex 83</td>
<td>675.1 ± 64.47</td>
<td>37.0 ± 10.14</td>
<td>45.5 ± 16.23</td>
</tr>
<tr>
<td>Cl 1370</td>
<td>704.9 ± 116.63</td>
<td>9.4 ± 2.01</td>
<td>75.7 ± 38.97</td>
</tr>
<tr>
<td>Cl 4374</td>
<td>693.9 ± 101.05</td>
<td>14.5 ± 2.59</td>
<td>77.4 ± 28.79</td>
</tr>
<tr>
<td>Cl 9977</td>
<td>607.4 ± 85.91</td>
<td>9.6 ± 1.22</td>
<td>58.1 ± 16.33</td>
</tr>
<tr>
<td>Cl 10151</td>
<td>848.6 ± 22.24</td>
<td>10.1 ± 1.12</td>
<td>93.1 ± 44.27</td>
</tr>
<tr>
<td>Cl 2318</td>
<td>978.7 ± 133.17</td>
<td>11.1 ± 0.75</td>
<td>79.1 ± 26.92</td>
</tr>
<tr>
<td>Cl 1248</td>
<td>732.5 ± 46.05</td>
<td>12.2 ± 1.05</td>
<td>62.2 ± 10.07</td>
</tr>
<tr>
<td>Cl 2230</td>
<td>703.1 ± 94.68</td>
<td>10.3 ± 0.13</td>
<td>78.4 ± 16.67</td>
</tr>
<tr>
<td>Cl 4013</td>
<td>908.3 ± 58.54</td>
<td>11.7 ± 0.35</td>
<td>62.8 ± 3.98</td>
</tr>
<tr>
<td>Hokuto Hadoka</td>
<td>745.5 ± 91.68</td>
<td>12.3 ± 0.96</td>
<td>69.0 ± 6.10</td>
</tr>
<tr>
<td>Shiga Waseh</td>
<td>863.3 ± 13.1</td>
<td>20.9 ± 0.49</td>
<td>81.7 ± 1.35</td>
</tr>
</tbody>
</table>

\(^1\)Mean ± SD.
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Acid is the major bound phenolic acid with the concentrations ranging between 149 and 413 μg/g and comprising 68% of the total fraction. p-Coumaric acid is the second most abundant phenolic acid in barley ranging from 5.25 to 115.5 μg/g (Andersson et al., 2008). In another report (Holtekjlen et al., 2006), total phenolic acids in barley ranged from 604 to 1346 μg/g including ferulic dehydrodimers, and the content of ferulic acid and p-coumaric acid ranged from 403 to 723 μg/g and 15 to 374 μg/g, respectively. The ferulic acid and p-coumaric acid contents in hulled varieties are considered higher than in hulless barley. Quinde et al. (2006) also reported that the total phenolic acid and ferulic acid content in hulled barley were higher than in hulless barley (Quinde et al., 2006). Phenolic acids in three wild genotypes of barley, Odens Aker, Abed Archer, and Rostov, were studied in Dr Beta’s laboratory. The results showed that the total phenolic acid content ranged from 784 to 1131 μg/g, and hulless variety Odense Aker had the lowest content of 784 μg/g. Ferulic acid and p-coumaric acid content ranged from 589 to 666 μg/g and 17.9 to 348 μg/g. Two hulled barleys, Abed Archer and Rostov, had significantly higher p-coumaric acid of 341.8 and 331.4 μg/g, results consistent with those reported by Holtekjlen et al. (2006).

Besides the monomers of phenolic acids, ferulic dehydrodimers have been reported in barley after alkali hydrolysis. In the cell walls, diferulic acids (DiFA) can be formed via a radical oxidative mechanism or intracellular peroxidases (Andreasen et al., 2000) and provide cross-linking between the cell wall polymers (Fry et al., 2000). The esterified and cross-linked diferulic acids protect the cell wall polysaccharides from degradation by enzymes and control the mechanical properties of the cell wall (Grabber et al., 1998). Cano et al. (2002) reported that the superoxide scavenging capacity of ferulic acid was enhanced by dimerization. To date, six common ferulic acids have been found in plants. They are 8-O-4 diFA, 8,5-diFA open form, 8,5-diFA dehydrobenzofuran form, 5,5-diFA, 8,8-diFA noncyclic form, and 4-O-5-diFA; with the first four having been reported in cereal grains (Hernanz et al., 2001). The extent to which bound phenolics are bioavailable has not been well-established as cell wall materials are challenging to digest. However, Andreasen et al. (2001) have shown that both human and rat colonic microflora can release diferulic acids from dietary cereal bran, and that esterified phenolics can be cleaved by esterase from the human gut (Andreasen et al., 2006). The results imply that some bound phytochemicals may be released and absorbed in the intestine, thereby contributing to human health improvement attributable to whole grains. The DiFA in barley ranged from 158 to 261 μg/g, with 8,5′-diFA (50–88 μg/g) and 4-O-5′-diFA (72–114 μg/g) as the major diferulates (Holtekjlen et al., 2006).

2.3.2 Flavonoids in barley grain

Flavonoids are a large group of phenolics sharing a C6-C3-C6 skeleton. In cereal grains, the most common flavonoids are flavones, flavonols, flavanone, flavanols, flavan-3-ols, and anthocyanidins.

Proanthocyanidins (PAs) also known as condensed tannins, are oligomers of flavan-3-ols. Compared to monomeric flavan-3-ols, PAs have higher antioxidant capacity in vitro (Hagerman et al., 1998), with 20 and 50 times more antioxidant capacity than vitamins C and E, respectively (Shi et al., 2003). They likely possess a wide range of biological properties through against oxidative stress (Fine, 2000).

Dvorákůvá et al. (2008) studied the flavan-3-ols for ten barley varieties including eight malt and two hulless, and the results showed that proanthocyanidin oligomers, including two dimers (procyanidin B3 and prodelphinidin B3) and four trimers (procyanidin C2,
prodelphinidin C2, and two other prodelphinidins), are the main proanthocyanidins found in barley. The trimers are the most abundant species. Among these, prodelphinidin B3 is the most plentiful with the content varying from 90 to 197 mg/kg, while procyanidin C2 is a minor constituent with the content ranging from 5 to 19 mg/kg. Holtekjlen et al. (2006) also reported the proanthocyanidin content in different barley varieties, which included hulled, hulless, normal, waxy, and high-amylose starch varieties as well as two-rowed and six-rowed genotypes. The total flavanols ranged from 325 to 527 μg/g, with two dimers and four trimers as the major flavanols in those varieties. There was no association between the proanthocyanidin level and different barley genotypes. In another study, catechin was detected only in hulled PA-free barley (Quinde et al., 2006). The total flavanols in hulless barley were higher than in hulled PA-containing barley. Hulless regular barley contained higher total flavanols than waxy varieties.

Anthocyanins are a major group of water-soluble pigments normally found in purple, blue, pink, and red colored flower, fruit, and vegetable as well as pigmented cereals. Some of the health benefits associated with anthocyanin consumption by humans, as reviewed by Lila (2004), include protection from DNA cleavage, alteration of development of hormone-dependent disease symptoms, enzyme inhibition, enhancement of the production of cytokines, lipid peroxidation, membrane strengthening, and reduction in capillary permeability and fragility. Jing et al. (2008) suggested that the structure of anthocyanin affected chemoprotection, which was measured as inhibition of colon cancer cell proliferation. Non-acylated anthocyanins had greater inhibitory effect on HT-29 cell proliferation than anthocyanins with pelargonidin, triglycoside, and/or acylation with cinnamic acid. Anthocyanin pigments and anthocyanin-rich foods have been reported to lower the risk of colon cancer through the inhibition of proliferation of human colon cancer in vitro (Zhao et al., 2004). The role of anthocyanins in inhibiting colon cancer in vivo has also been reported (Jing et al., 2008). In addition, the inhibition of cancer cell growth through induction of apoptosis by anthocyanins has been reported (Katsube et al., 2003).

In barley, anthocyanins are found in the pericarp or in the aleurone layer causing the kernel color to appear blue. Some barley varieties (Hordeum vulgare) have black pigmentation due to a melanin-like pigment that may overlap purple or blue color as a result of anthocyanins (Siebenhandl et al., 2007). As reported by Kim et al. (2007), the content of anthocyanins in barley varied from 13.0 to 1037.8 μg/g. Purple and blue barley groups contained higher average contents of anthocyanins than black barley. Unhulled genotypes had higher total anthocyanins than hulled genotypes. Purple barley bran had at least twice as high the level of anthocyanins than yellow barley bran (Bellido and Beta, 2009) confirming that pearling is effective in obtaining barley fractions high in antioxidant activity and phenolic contents (Rosa et al., 2007). The most common anthocyanin in the purple barley groups was cyanidin 3-glucoside, whereas delphinidin 3-glucoside was the most abundant anthocyanin in the blue and black groups (Kim et al., 2007).

### 2.3.3 Lignans in barley grain

Lignans are precursors to enterodiol and enterolactone in the mammalian system and this conversion is done by their gut microflora (Kuhnle et al., 2009). The structure and function of lignans are similar to 17 β-estradiol. The latter is an estrogen that is important in reproductive and sexual functioning. It also influences other organs including the bones
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in addition to acting as phytoestrogens (Kuhnle et al., 2009). Epidemiological studies have concluded that lignans as phytoestrogens might play a role in the prevention of breast (Ingram et al., 1997; Lime and Speirs, 2004), prostate, and colon (Aldercreutz, 2002) cancers through mechanisms likely based on alteration of hormone production, metabolism, and actions at the cellular level leading to reduction of cancer risks (Aldercreutz et al., 2004; Orcheson et al., 1998) and antioxidant properties that reduce cardiovascular diseases and mortality (Aldercreutz et al., 2004). Lignans were found to improve menopausal symptoms. Phytoestrogens including lignans (matairesinol and secoisolariciresinol) were found to have beneficial roles in obesity and diabetes through mechanisms that modulate pancreatic insulin secretion or via antioxidant actions (Bhathena and Velasquez, 2002).

The major types of lignans found in barley include (−)-7-hydroxymatairesinol, (+)-syringaresinol, (+)-lariresinol, (+)-pinoresinol, (−)-secoisolariciresinol (Kuhnle et al., 2009; Meagher and Beecher, 2000), (−)-matairesinol, cyclovariciresinol, 7-oxomatairesinol, secoisolariciresinol-sesquiglycerin, (+)-medioresinol, todolactol A, α-conidendrin, nortrachelogenin, and lariresinol-sesquiglycerin, in order of decreasing concentration (Smeds et al., 2007).

2.4 Potential of hulless barley in health promotion and disease prevention

2.4.1 Hulled versus hulless barley

The caryopsis of hulless barley is not covered with a husk unlike the hulled types. The dehulling is largely eliminated due to the absence of husk in the hulless varieties. Hulled varieties will need to be dehusked, a pre-processing step necessary to obtain hulless whole grain barley that is edible. The elimination of the dehulling step is attractive to food processors when it comes to hulless varieties. However, the brewing industry has preference for hulled varieties as the husk protects the grain during malting and serves as a filter during mashing.

2.4.2 The newly developed varieties of barley with enhanced macro-nutrients and phytochemicals for health promotion and disease prevention

Varieties such as Prowashonupana, a waxy, hulless barley developed during the late 1970s through a conventional barley breeding program at Mantana State University, are higher in fiber and protein, and lower in starch content, than many common cereal grains. They have four times more β-glucan than regular hulless barley.

2.5 Future studies

Barley is one of the major cereal grains produced in various parts of the world for food and nonfood uses. As whole grain, it is a source of nutrients, dietary fiber, and other phytochemicals. β-glucans from different sources are associated with health benefits. Compared with β-glucans derived from bacteria, fungi, and oats, studies on β-glucan from
barley are limited. Literature reports on β-glucan from barley have focused on its effects on lipid cholesterol and blood glucose level and insulin responses. With respect to anti-cancer properties, more clinical trials on barley β-glucans are needed. Detailed relationships between barley β-glucan structure, molecular weight, viscosity, and biological activity need further studies.

Studies on bioavailability of barley phenolic compounds and lignans are still limited. More epidemiological evaluation and animal studies as well as clinical trials need to be done to establish the health promoting properties of barley grain.

References


