Bioactive compounds in whole grain barley: Nutraceutical properties and health benefits

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Abstract
Functional foods have recently received a lot of attention by both health professionals and the common population for improving overall well-being, as well as in the prevention of diseases including cancer and cardiovascular diseases. In this line, whole grain barley has been reevaluated and recognized as valuable sources of nutraceuticals. The great number of potentially active nutrients and their multifunctional properties make barley (Hordeum vulgare) are functional component for the production of health-promoting food and food supplements. Several data revealed the high content of some chemical constituents, which can give benefit to this cereal on a nutritional and technological functionality basis. High levels of dietary fiber mainly beta glucan, starch and phytochemicals are noteworthy.

INTRODUCTION

Today, the functions of foods are not intended to only satisfy hunger and to provide basic nutrients for humans but also to prevent nutrition-related diseases and improve the state of well-being of the consumers. Functional foods and nutraceuticals fit into this niche market as they are regarded as nutrients that provide unique beneficial effects through reducing the risk of chronic disease, beyond their basic nutritional functions (El Sohaimy, 2012). Nowadays, functional foods represent one of the most interesting areas of research and innovation in the food industry (Annunziatta and Vecchio, 2011; Corbo et al., 2014). Actually, all foods are functional, as they provide taste, flavor, or nutritive value. Recently, the term functional when applied to food has adopted a different connotation, which of providing an additional physiological health benefit beyond that of meeting basic nutritional needs. Epidemiological evidence suggests that higher consumption of whole-grain...
foods can significantly reduce the risk of chronic diseases such as cardiovascular diseases (CVD), type 2 diabetes and some cancers (Malla et al., 2014). There has been an increasing interest in the health-enhancing role of specific foods or physiologically active food components, so-called functional foods. In agricultural and biomedical research, functional foods and health-protecting materials (i.e., nutraceuticals including dietary fiber and phytochemicals) are perceived as offering some of the greatest opportunities for improving human health (Neelam et al., 2011). It is well known that populations consuming a large proportion of plant-based foods, including whole grains of cereals, have a lower incidence of cardiovascular diseases and certain types of cancer (Otles and Cagindi, 2006; Tuso et al., 2013). In recent years, cereals and its ingredients are accepted as functional foods and nutraceuticals because of providing dietary fiber, proteins, energy, minerals, vitamins and antioxidants required for human health. Cereals include dietary fiber such as β-glucan and arabinoxylan, carbohydrates such as resistant starch and oligosaccharides. In addition, cereals can be used as fermentable substrates or the growth of probiotic microorganisms (Charalammpopoulos et al., 2002; Jeremias et al., 2015). Preventing cancer and CVD, reducing tumor incidence, lowering blood pressure, risk of heart disease, cholesterol and rate of fat absorption, delaying gastric emptying and supplying gastrointestinal are the protective effect of the cereals (Susan et al., 2013). Several of the nutrients in cereals have known potential for reducing risk factors for CHD: the linoleic acid, fiber, vitamin-E, Selenium and folate. Cereals also contain phytoestrogens of the lignin family and several phenolic acids with antioxidant properties (Nyanzi et al., 2011). It is well known that populations consuming a large proportion of plant-based foods, including whole grains of cereals, have a lower incidence of cardiovascular diseases and certain types of cancer (Otles and Cagindi, 2006; Tuso et al., 2013). In recent years, cereals and its ingredients are accepted as functional foods and nutraceuticals because of providing dietary fiber, proteins, energy, minerals, vitamins and antioxidants required for human health.

Barley (Hordeum vulgare) play an important role in meeting the nutrient needs of the human population. Like any food, they are good to excellent sources of some nutrients and low or void in other nutrients (Newman and Newman, 2006; Adil et al., 2012). Barley grain is a good source of dietary fiber and phytochemicals. It is rich in starch and sugars, relatively poor in protein and very low in fat. The vitamins content varies from one part of grain to another. The quality of barley products is determined by a variety of characteristics, which may be assigned different significance depending on the desired and use or type of product (Rosemary et al., 2008; Sullivan et al., 2013). Whole grains barley is preferred not only for its nutritional importance but also for its nutraceuticals properties (Mehdi et al., 2008; Lahouar et al., 2011, 2012, 2014a, 2014b; Izydorczyk et al., 2014). The active component in barley having nutraceutical property is the soluble fiber (1-3) (1-4)-β-D-Glucan or β-Glucan. B-glucan is polysaccharides found principally in the cell walls of the aleurone layer and endosperm in barley kernels. In barley, they are more concentrated in the endosperm (Wood, 2007). Several hulls less barley cultivars containing low or high β-Glucan, variation degree of extract viscosity, and waxy or normal starch are found (Andersson et al., 2004). B-glucan, a soluble fiber implicated in hypercholesterolemia, hypoglycemia, and in reducing incidence of chemically induced colon cancer (Newman and Newman, 2008). The main objective of the present paper is review bioactive compounds in whole grains barley, to summarize its nutraceutical properties and describe the potential mechanisms by which barley may protect health.

**BARLEY: HISTORY, TYPES AND USES**

**History**

Man has used barley (Hordeum vulgare) as food since time immemorial. It is one of the cereal founder crops and it is believed that first plant domestication took place within the Fertile Crescent. Hordeum vulgare L. subsp. spontaneum (wild barley) is said to be the ancestor of today’s barley (Badr et al., 2000). The spread of barley most likely started in present-day, northern Syria, southern Turkey, eastern Iraq and western Iran. With the movement of civilizations accompanied by the establishment of trade routes, the use and cultivation of barley reached Europe. Barley was a popular food in ancient Greece and Italy and used as an ingredient for preparing porridge or unleavened bread. Greek and Roman scholars such as Hippocrates or Pliny the Elder, respectively, considered barley as a healthy and nourishing food and barley gained as well recognition for medical treatments. In the ancient Rome, gladiators believed that barley could increase strength and stamina and thus preferred it to other cereals.

Barley reached Spain around 5,000 BC and spread then over today’s Germany and France. Indications of domestication of barley on the British Isles date back until 3,000 BC and one millennium later, barley was introduced to Northern Europe. Probably due to the nourishing properties and the ruggedness of the crop, barley became a major food especially for poor people throughout history (Newman and Newman, 2005). In 2009, barley was the twelfth most important agricultural commodity of the world in terms of production. After maize, wheat and paddy rice it was the fourth most important cereal crop (Gubatz and Shewry, 2011). The annual production was about 152 million tons, of which the Russian Federation produced around 17.9 million.

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tons followed by France, Germany and Ukraine with 12.9, 12.3 and 11.8 million tons, respectively. In the European Union, barley still attains distinction as the second cereal crop after wheat (FAO, 2011).

Types

Covered barley: it has a tough, inedible outer hull around the barley kernel. A less common variety, referred to as "naked" barley, has a covering, or hull, that is so loose that it usually falls off during harvesting.

Hulled Barley: (sometimes called dehulled barley) is covered barley that has been minimally processed to remove only the tough inedible outer hull. It's challenging to remove the hull carefully so that some of the bran is not lost – but that's what must be done for covered barley to be considered whole grain.

Hulless Barley: This type of barley has an outer hull that's so loosely attached to the kernel that it generally falls off during harvesting. This cuts down on processing and ensures that all of the bran and germ are retained.

Barley Grits: When barley kernels are cut into several pieces, they become grits.

Barley Flakes: If barley flakes remind you of oatmeal (rolled oats), it's because they're created the same way, by steaming kernels, rolling them, and drying them. As with barley grits, flakes can be made from whole grain barley or from pearl barley, with only the former considered whole grains. Barley flakes cook faster, because they have been lightly steamed and because of their greater surface area.

Barley flour: is used in baked goods and as a thickener for soups, stews and gravies. While it contains gluten, the protein that helps baked goods rise, the type of gluten in barley flour does not promote adequate rising on its own, so barley flour is usually used with wheat flour. Look for whole grain barley flour, ground from hulled or hulless barley, not from pearl barley.

Pearl Barley: (not a whole grain) has been polished, or "pearled" to remove some or the entire outer bran layer along with the hull. If it is lightly pearled, pearl barley will be tan colored; if it is heavily pearled, barley will be quite white (bottom photo). Most of the barley found in the typical supermarket is pearl barley. Although it is technically a refined grain, it is much healthier than other refined grains because (a) some of the bran may still be present and (b) the fiber in barley is distributed throughout the kernel, and not just in the outer bran layer. Pearl barley cooks more quickly than whole grain barley.

Quick Pearl Barley: (not a whole grain) is a type of barley flake that cooks in about 10 minutes, because it has been partially cooked and dried during the flake-rolling process. Although barley flakes can be whole grain and technically it would be feasible to create quick whole grain barley (similar to quick oats, which are whole grain), the quick barley commercially available today is made from pearl barley and so is not whole grain (USDA, 2010).

Uses

Barley is the fourth most important cereal crop in the world after wheat, maize and rice. Originally, barley was mainly cultivated and used for human food, but it is now used primarily for animal feed. It is estimated that about two-thirds of the barley crop has been used for feed, one-third for malting and about 2% for food directly. Barley is also used for the production of starch, either for food or for the chemical industry (Öztürk et al., 2007). Barley is a valuable grain for finishing beef cattle in the United States and is used in swine diets particularly in geographic regions where maize cannot be economically produced, thus it competes with wheat as a feed in those climates. In some countries, such as Morocco, India, China and Ethiopia, barley is used as an important food crop in daily diets. Furthermore, ‘barley tea’ has a longer history of use than green tea in Japan. 'Barley tea' is consumed in many Asian countries. Six-rowed barley, two-rowed barley and six – rowed naked barley are processed to barley tea in Japan. Modest quantities of non-alcoholic drinks based on barley and malt are consumed in various parts of the world (Ullrich, 2011). In addition, barley has some useful by-products, the most valuable being the straw, which is used, mainly for bedding in developed countries, but also for animal feed in developing and under-developed countries. Barley malt can be added to many food stuffs such as biscuits, bread, cakes and desserts. Food barley is generally found in regions where other cereals do not grow well due to altitude, low rainfall, or soil salinity. In Western countries, barley is increasing in popularity as a food grain and is used in flours for bread making or other specialties such as baby foods, health foods and thickeners (Sullivan et al., 2013).

NUTRITIONAL CONTENTS OF WHOLE GRAIN OF BARLEY

Knowing about grain quality starts with knowing the anatomy of a single grain. Whether the grain is to be used for feed or for human consumption, the key characteristics of a grain still apply (Gubatz and Shewry, 2011). Have you ever wondered how the anatomy of a grain affects its quality characteristics? Figure 1 shows the anatomy of a
typical grain. Here we will discuss the parts of seed from the inside out starting with the embryo. The anatomical structure of whole grain of barley is presented in Figure 2 (Biel and Jacyno, 2013). Whole grains of barley consist of the entire grain seed of barley, including the bran, the germ, and the endosperm. Usually the kernel is cracked, crushed, or flaked during the milling process. If the finished product retains the same relative proportions of bran, germ and endosperm as the original grain, it is considered a whole grain (Fardet, 2010).

The embryo: also known as the germ, is the beginnings of a new plant, including the genetics, and early plant structures (leaves and roots) that will get the plant started. The embryo contains various protein, phytochemicals, oils, enzymes and vitamins. It makes up approximately 3% of the seed. The enzymes it contains helps to trigger the release of nutrients from the remainder of the seed when the embryonic plant starts to grow. The germ is typically removed during milling of refined flour because it can influence bread-making quality, and the oils in the germ can go rancid if the flour is stored for a long time (MacDougall and Selvendran, 2001).

The endosperm: makes up 75-83% of the seed. It contains the starch, which is held in a matrix of protein. This is the energy source of the seed for germination, and the proportion of protein and starch in the endosperm will dictate its characteristics for feed and food processing. Surrounding the endosperm is the aleurone layer, which makes up a relatively small part of the seed. The aleurone layer contains enzymes that can start the reaction that changes starch into sugar, a key step in using grains for specialized uses such as brewing beer (MacDougall and Selvendran, 2001).

The husk: is the next layer, which accounts for approximately 14% of the seed. This part is the skin of the seed and helps to protect it from disease and pests. It is mainly made up of dietary fibers (β-glucan, cellulose, arabinoxylan and lignin) and contains some vitamins. The husk can affect protein content and milling quality, so it is typically removed when
making refined flour. Small seeds will have a larger amount of bran compared with the inside of the seed, whereas larger or plumper seeds will have a smaller ratio of surface area (bran) to inside. This means that larger seeds are often more desirable, especially from a milling perspective (Fardet, 2013).

### BIOACTIVE COMPOUNDS OF BARLEY GRAIN AND ITS NUTRACEUTICAL PROPERTIES IN DISEASES PREVENTION

Barley cultivars vary widely in their chemical composition due to differences in genotype, growing environment and the interaction between the two. Whole barley grain consists of about 65–68% starch, making starch the most abundant constituent and found mostly in the endosperm (Griffey et al., 2010). The next chief constituents are total fiber ranging from 11–34% and protein 10–20%. Other constituents include 2–3% free lipids and 1.5–2.5% minerals. Barley also contains a myriad of other components including a number of antioxidants and phenolic compounds (Figure 3) (Borneo and Leon, 2012).

#### β-glucan

In barley, fiber represents the second major constituent of the grain after starch, but unlike starch, fiber is found throughout the kernel (Brownlee, 2011). Fiber can be classified into soluble and insoluble forms. The content of total fiber in barley ranges from 11–34% of which 3–20% is soluble dietary fiber mostly in the form of β-glucan (Jalili et al., 2000; Andersson et al., 2004; Makeri et al., 2013). Barley is preferred not only for its nutritional importance but also for its nutraceutical properties. The active component in barley having nutraceutical property is the soluble fiber (1-3) (1-4)-β-D-Glucan or β-Glucan (Figure 4) (Storsley et al., 2003; Brennan and Cleary, 2005). β-glucan is polysaccharides found principally in the cell walls of the aleurone layer and endosperm in barley kernels. In barley, they are more concentrated in the endosperm (Izydorczyk and Dextor, 2008).

#### Starch

The physical, chemical and enzymatic processing of barley modifies the characteristics of starch, which is the major storage carbohydrate of all higher plants and is the major constituent of barley and impart the nutraceutical properties (Copeland et al., 2008). The starch granules, embedded in the protein, are then encased within individual endosperm cells and protected by a cell wall. Many of these cells are packed tightly within the grains starchy endosperm (the white bit found in the middle of a grain). In addition, the endosperm itself is protected by the aleurone layer and finally the entire structure is covered by the seed coat (Figure 5) (International Starch Institute, 2012).
However, it has been found that a part of starch, consumed in the diet, escapes digestion and absorption in the small intestine and is fermented in the large intestine with the production of short chain fatty acids (Wong and Jenkins, 2007). This fraction is called resistant starch (RS) which is associated with a reduction of the glycemic index, low absorption of cholesterol, and prevention of colon cancer (Leu et al., 2003). RS can be added as a functional ingredient (Thompson, 2007). RS concentration of barley increases during processing. Process heating and cooling cycles are used for promoting starch retrogradation, which, in turn, increases RS content. Another method for RS production involves starch gelatinization, enzymatic debranching of the gelatinized polymer, deactivation of the debranching enzyme, and separation of the resultant product by either drying, extrusion, or crystallization. Extrusion has been claimed as a unit operation for RS production; however, the RS levels obtained with this procedure are lower than those prepared using autoclaving (Asare et al., 2011). The nutraceutical characteristics associated with the fermentation of the indigestible RS. However, there is another nutraceutical property associated to the fermentation, which is the probiotic effect. RS may also act as a prebiotic because it favorably influences the ecology of the microbial flora in the large intestine. When RS and probiotics are consumed together, a symbiotic effect takes place; a prebiotic role of RS is to protect some of the ingested organisms on their hazardous path to the colon, effectively increasing the initial levels of the desirable species, once the colon is reached. When both the probiotics and the RS are present in the colon, then the RS may initiate its role as substrate for a portion of the probiotic organisms (Topping et al., 2003; Slavin, 2013).

**Phytochemicals in barley**

Over the last decade, fruits, vegetables and cereals have been studied for various bioactive compounds such as phenolics and flavonoids as health promoting and disease preventing effects were found in both in vitro and in vivo studies (Stratil et al., 2007). Phytochemicals, per definition, are substances that are likely to contribute to health or are essential for the maintenance of health (Cooke et al., 2002; Dvořáková et al., 2008). In contrary to vitamins or minerals, there is no evidence that they are essential or even required to sustain life. It is hypothesized that phytochemicals that are located in the fiber matrix, in addition to or instead of the fiber itself, are responsible for the reduced risk of various diseases associated with oxidative stress, such as cancer, cardiovascular and neurodegenerative diseases (Jacobs and Steffen, 2003). Thus, the consumption of whole grains is seen as health-promoting (Slavin, 2003), because whole grains and products thereof present a good source of natural antioxidants (Decker et al., 2002).

Polyphenols constitute together with carotenoids the only dietary antioxidants present in the colon in valuable concentrations (Scalbert and Williamson, 2000; Manach et al., 2004). The release of phenolics in the colon may explain the inverse association between whole grain consumption and incidence of certain chronic diseases (Andreassen et al., 2001; Kern et al., 2003, Lahouar et al., 2014b). Moreover, an apparent increase of antioxidant release during enzymatic incubation was found in vitro studies (Pérez-Jiménez and Saura-Calixto, 2005; Nagah and Seal, 2005; Menga et al., 2010). Barley grains contain a wide range of phenolic acids, which are either derivatives of benzoic acid (C6-C1) or cinnamic acid (C6-C3). In general, higher levels of phenolic compounds were reported for barley and...
are supposed to protect against age-related visual acuity. Hence, dietary lutein and zeaxanthin (‘yellow spot’) of the retina, the area of maximal lipid peroxidation. Lutein and zeaxanthin are polyphenols (Shahidi and Naczk, 2004). Also Hernanz et al. (2001) and Naczk and Shahidi (2006) reported that ferulic acid is the dominant free phenolic acid in barley seeds. The composition of phenolic acids in 30 barley varieties was investigated by Yu et al. (2002) where they found varying levels of benzoic and cinnamic acids. Phenolic compounds are said to exhibit one or more of the following roles: free radical scavenger, reducing agent, potential producer of prooxidant metals and quencher of singlet oxygen formation. Anthocyanins in wheat and barley are found either in the pericarp or in the aleurone layer causing purple and blue hues of kernel colour, respectively. The black pigmentation of the lemma and pericarp of barley, however, is described to be due to melanin-like pigment, which may overlap other pigments. Black kernel colour due to melanin-like pigment is unknown to wheat species. Lutein and zeaxanthin are the two main carotenoids identified in barley (Panfili et al., 2004). The electron rich chain makes them effective radical scavengers and inhibits free radical propagation reactions such as lipid peroxidation. Lutein and zeaxanthin are responsible for the coloration of the macula lutea (‘yellow spot’) of the retina, the area of maximal visual acuity. Hence, dietary lutein and zeaxanthin are supposed to protect against age-related macular degeneration and cataract (Beatty et al., 2000). Furthermore, lutein and zeaxanthin possibly act together with other bioactive compounds against cancer, cardiovascular risk and other diseases (Mares-Perlman et al., 2002; Calvo, 2005). Vitamin E or tocopherols are also present in markedly concentrations (Cavallero et al., 2004; Andersson et al., 2008).

**FUTURE STUDIES**

The future viability and success of functional food contain in the future marketplace depends on several elements. Consumers’ attitudes and beliefs about functional foods should be examined in relation to sources of information and trust. The majority of modern consumers are particularly concerned of whether health claims on food labels are appropriate in relation to the nutritional information provided on the food products. New categories of barley-based products will certainly be object of research and development for future markets. These will probably include more target-specific and age-specific products and it will be important to study techno-functional properties of bioactive fractions of barley how these substances can retain their functional properties in different food matrices. Future technological innovations will essentially find solutions for stability and viability problems connected to the formulations, microencapsulation, packaging materials and biological incorporation of bioactive compounds into foods. Regarding the effects in health, it seems that it considerably affects the consumer’s behaviors in the purchase of certain foods in detriment of others. However, certain studies describe that consumers purchase essentially from habit, experience and past behavior. Therefore, it seems important to make a global effort to streamline regulations with the respective health claims. Indeed, there are still major difficulties in assessing the potential of functional foods because of the lack legal interpretations of this concept. In fact, there are discrepancies between producers and consumers regarding the understanding and applying of the concept of sustainability of food systems, including functional foods. By definition, sustainable food related practices do not increase risks to human health but substances added to make functional foods are biologically active with potential to affect human physiological responses. This issue of food security and food safety is still a difficulty in measuring and controlling the efficacy of functional foods. Today it is evident that functional foods can become an important portion of people’s dietary intake, and this should lead the public health authorities to issue recommendations concerning the consume of more healthy foods, like barley. Literature has already showed the manifest improvements in health, either by interference with oxygen species, their ability to lower cholesterol or by other mechanisms. Nevertheless, it is important to demonstrate the clinical beneficial effects of functional compound of barley to correctly attribute their mechanisms of action and to quantify their influence in the individual’s health. For example, the thorough study of the relationship between the consumption of these foods with morbidity and mortality is of the utmost importance, although this is not an easy task. Meanwhile, the boundaries between these nutraceuticals and drugs have become slimmer and sometimes overlapping. This is an important matter once even the distribution channel may be affected when a given product is classified as drug or as nutraceutical. Also, this affects another important feature which is the major role that governments may have, promoting the use of functional foods by children in kindergartens and old people in third age residences, for example with appropriate regulamentation for their feeding needs.
CONCLUSIONS

All the studies reviewed in this manuscript demonstrate that a higher intake of whole grains of barley is associated with lower chronic diseases. However, so far, the results from a few intervention trials investigating whether a whole grain-low calorie diet is able to reduce body weight, have failed to demonstrate a cause/effect relation. For this reason, further intervention studies with adequate methodology are necessary to answer this question. Based on the scientific evidence so far available, the characteristics of a satisfactory study can be summarized in three points. The first two are the sample size- which should be adequate, and the duration of the intervention which should be sufficiently long (probably at least two years). Thus, the model of the study should consider two steps: first, the participants are treated with a low caloric diet, able to achieve at least 5-10% of body weight loss, and second, subjects are treated with a whole grain diet ad libitum, in order to evaluate body weight loss maintenance. For the time being, however, whole grain consumption can be recommended as one of the features of the diet that may help control body weight. This is consistent with epidemiological evidence, which compared regular whole grain consumption vs. refined cereals, with respect to a lower risk of developing overweight, and other major diseases of affluent societies, like type 2 diabetes, cardiovascular diseases and cancer. Barley grain is rich in starch and sugars, relatively poor in protein and very low in fat. However, because human consumption of barley and barley-containing food products has been insignificant as compared to other cereal grains, the development of new processes and food products has been neglected and there has been little effort to define quality requirements for food uses. The significance of β-glucan and tocols for human nutrition is well known, but little is known about the functional properties of β-glucan for making food products. Some of the traits preferred for specific food applications are known through investigations on incorporating barley into wheat-based food products.

CONFLICT OF INTEREST

All other authors declare no conflict of interest.

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