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BIOCHEMISTRY

Cereal Bioactive Compounds: A Review

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ABSTRACT

Cereal grains and wholegrain cereal products (rich in fibrous polymers) are the excellent sources of numerous unique substances rating among biologically active compounds such as dietary fiber (arabinoxylans, beta-glucans, cellulose, lignin and lignans), sterols, tocopherols, tocotrienols, alkylresorcinols, phenolic acids, vitamins and microelements. Cereals have been staple foods both directly for human consumption and ready available to the human diet. The major cereals consumed worldwide are wheat, rice, maize, barley, oats, rye, millet, sorghum. Bioactive compounds of whole-grains are present in the bran/germ fraction of cereal-grains and least in endosperm. The bioactive components in cereals help in reducing the risk of chronic diseases act as a functional ingredient. Bioactive compounds in whole-grain cereals have not received as much attention as in fruits and vegetables due to difficult in extractions and some have antinutritional role. These health benefits are achieved through multifactorial physiological mechanisms including antioxidant activity, mediation of hormones, enhancement of immune system and facilitation of substance transit through the digestive tract, butyric acid production in the colon, and absorption.

Highlights

- Cereals are the staple foods both directly for human consumption with bioactive compounds present in the bran/germ fraction of cereal-grains and least in endosperm.
- Cereal grains and wholegrain cereal products (rich in fibrous polymers) are the excellent sources of bioactive compounds with biologically active and health importance.

Keywords: Arabinoxylans, Beta-glucans, Bioactive, Antioxidant, Immune system

Cereal grains and cereal products (rich in fibrous polymers) are the excellent sources of numerous unique substances rating among biologically active compounds such as dietary fiber (arabinoxylans, b-glucans, cellulose, lignin and lignans), sterols, tocopherols, tocotrienols, alkylresorcinols, phenolic acids, vitamins and microelements. Cereals are edible seed of the grass family (Bender & Bender 1999). Cereals are grown for their highly nutritious edible seed, which are often referred to as grain. Some cereals have been staple foods both directly for human consumption and indirectly via livestock feed since the beginning of civilization (British Nutrition Foundation 1994). The major cereals consumed worldwide are wheat, rice, maize, barley, oats, rye, millet, sorghum. Apart from being an important part of diet, these cereals are also rich in various health promoting components (Slavin 2003). Cereals are staple foods providing major sources of carbohydrates, proteins, B vitamins and minerals for the world's population. Cereals contain a range of substances which may have health promoting effects, these substances are often referred to as phytochemicals or plant bioactive substances (Goldberg 2003). Although concentrations of these substances in foods are usually small, they have attracted attention of researchers because of their biological activities and positive impacts on human health. Around 1970, Trowell and Burkitt noticed that native residents of African countries whose diet was rich in dietary fiber did not suffer from civilization diseases such as malfunction of cardiovascular system, cancers and obesity (Anderson *et al.* 2000). Bioactive compounds are extra nutritional elements that typically occur in small quantities in foods. These substances are beneficial to human health but are not essential for the human body (Kris-Etherton 2002). Whole-grains or foods made from whole-grains contain all the essential parts, the bran, the endosperm and rarely germ in contrast to the refined grains, in which the bran and the germ of the grains are removed during the milling process. Whole-grains are rich sources of fiber, vitamins, minerals and phytochemicals. The majority of bioactive compounds of whole-grains are present in the bran/germ fraction of cereal-grains. These fractions of whole-grain may therefore help in reducing the risk of chronic diseases. Bioactive compounds in whole-grain cereals have not received as much attention as in fruits and vegetables. These health benefits are achieved through multifactorial physiological mechanisms including antioxidant activity, mediation of hormones, enhancement of immune system and facilitation of substance transit through the digestive tract, butyric acid production in the colon and absorption.

Bioactive Compounds Present in Whole-Grain Cereals

Whole-grains contain unique bioactive compounds that complement those in fruits and vegetables when consume together. The major bioactive compounds in whole-grain cereals are phenolic compounds, phytosterols, tocols, dietary fibers (mainly beta-glucan), lignans, alkylresorcinols, phytic acid, γ-oryzanols, avenanthramides, cinamic acid, ferulic acid, inositols and betaine (Jones 2002). Some bioactive compounds are quite specific to certain cereals; γ-oryzanol in rice, avenanthramide and saponins in oats, beta glucans in oats and barley and alkylresorcinol in rye, although these are also present in other cereals like wheat but relatively in fewer amounts. The important bioactive compounds in whole-grain cereals are discussed under:

Phenolic Compounds

Phenolic are compounds possessing one or more aromatic rings with one or more hydroxyl groups and generally are categorized as phenolic acids, flavonoids, stilbenes, coumarins and tannins (Liu 2004). Phenolics are the products of secondary metabolism in plants, providing essential function in the reproduction and growth of the plant, acting as defense mechanisms against pathogens and parasites, also contributing to the color of plant. In addition to their role in plants, phenolic compounds in our diet provide health benefits associated with reduced risk of chronic diseases. Phenolic compounds have antioxidant properties and protect against degenerative diseases like heart diseases and cancer in which reactive oxygen species i.e., superoxide anion, hydroxyl radicals and peroxyl radicals are involved [Harborne & Williams 2000; Rhodes & Price 1997)] The concentration of phenolic compounds in whole-grain cereals is influenced by grain types, varieties and the part of the grain sampled (Adom & Liu 2002; Adom *et al.* 2005). The most common phenolic compounds found in whole-grain cereals are phenolic acids and flavonoids.

Phenolic Acid in Cereals

Phenolic acids are derivatives of benzoic and cinnamic acids and are present in all cereals. Phenolic acids can be subdivided into two major groups, hydroxybenzoic acids and hydroxyl- cinnamic acid derivatives. Hydroxybenzoic acid derivatives include P-hydroxybenzoic, protocatechins, vannilic, syringic and gallic acids. Hydroxyl cinnamic acid derivatives include p-coumaric, caffeic, ferulic and sinapic acids. The phenolic acids reported in cereals occur in both free and bound form. Sorghum and millet have the widest variety of phenolic acids. Free phenolic acids are found in outer layer of the pericarp (Mattila 2005; Hahn 1983). Bound phenolic acids are esterified to cell walls; acid or base hydrolysis is required to release these bound compounds from the cell matrix (Kim 2006; Robbins 2003). The major phenolic acids in cereals are ferulic acids and p-coumaric acid (Holtekjølen 2006). Ferulic acid is the most abundant hydroxycinnamic acid found in cereal grains. It is the main poplyphenol present in cereals in which it is esterified to the arabinoxylans of the grain cell wall. The ferulic acid content of wheat grain is near about to 0.8 - 2 g/kg dry weight basis, which may represent 90% of total polyphenols (Lempereur *et al.* 1997). Ferulic acid can provide health benefits because of its antioxidant properties (Thompson 1994). Coumaric acids are hydroxyle derivatives of cinnamic acid. There are three forms of coumaric acids: p-coumaric acid, o-coumaric acid and m-coumaric acid. The three forms differ by the position of the hydroxyl substitution of the phenolic group (Garrait *et al.* 2006). Since p-coumaric acid is a hydroxyl derivative of cinnamic acid, p-hydroxycinnamic acid is synonym for p-coumaric acid (Madhujith *et al.* 2006). p-coumaric acid is present in the lowest amount in the centre of the grain kernel and in increasing amount towards the outer layers (Awika& Rooney 2004). Coumaric acids are suggested to have antioxidant effect and researches have shown that there is free radical scavenging property in p- coumaric acids (Ferguson 2006). Coumaric acid also has been suggested to have antitumor activity against human malignant tumors. Coumaric acid induces cytostasis and inhibits the malignant properties of humantumor cells in vitro.

Flavonoids in Cereals

Flavonoids are compounds with a C6-C3-C6 skeleton that consists of two aromatic rings joined by a three carbon link; they include anthocynins, flavonols, flavones, flavanone and flavonols. More than 5000 flavonoids have been identified in nature (Yao *et al*. 2004). Flavonoids are located in the pericarp of all cereals. Sorghum has the widest varieties of flavonoids reported. Flavonones found in fruits and vegetables are also reported in cereals. For example, the flavones epigenin, a compound found in barley and celery is also reported in millet, oat and sorghum (Rice-Evans *et al.* 1997). Cereals have only small quantities of flavonoids, except that barley contain measurable amounts of catechin and some di and tri pro-cyanidins (McMurough & Baert 1994). Flavonoids are reported to have antioxidant, anticancer, anti allergic, anti-inflammatory, anti-carcinogenic and gastro protective properties (Cook & Sammans 1996).

Avenanthramides in Cereals

Avenanthramides are specific polyphenols from oats. They are substituted cinnamic acid amides of anthranilic acids and there are at least 25 distinct entities. The three major aventhramides reported in oats are aventhramide-1, 3 and 4, which are also known as aventhramids B, C and A respectively (Collins 1989). Levels of aventhramide 1 range from 40-132μg/g in the grain. Oat flakes have more aventhramides (26-27μg/g) than oat bran (13μg/g) (Mattila *et al.* 2002). Avenanthramide are bioavailable and they have anti inflamatory, antiatherogenicand anti-oxidant properties (Peterson *et al.* 2002).

Lignans in Cereals

Lignans are polyphenolic bioactive compounds. They are a group of dietary phytoestrogen compounds that are present in a wide variety of plant foods including flax seeds, whole-grains like corn, oats, wheat and rye (Thompson *et al.* 1991). The common plant lignin in the human diet includes secoisolariciresinol, matairesinol, lariciresinol, pinoresinol and syringaresinol. When ingested, secoisolariciresnol and matairesinol are converted into the mammalian lignansenterodiol and enterolactone respectively by microbial enzymes in the colon (Hooper & Cassidy 2006). Mammalian lignans have strong antioxidant activity and weak oestrogenic activity that may account for their biological effects and health benefits (Wang *et al.* 1994) and makes them unique and very useful in promoting health and combating various chronic diseases.

Alkylresorcinols in Cereals

Alkyleresorsinols are plant derived phenolic lipids, especially found in whole-grain cereals. Rye contains the highest amount of alkylresorcinols, which can be twice as that of wheat (Ross *et al.* 2002). They are 1, 3 - dihydroxybenzene derivatives with an alkyle chain at position 5 of the benzene ring, which gives them an amphiphilic feature. Alkylresorcinols have antibacterial and antifungal properties and antioxidant property *in vitro* (Ross *et al.* 2004).

Carotenoids in Cereals

Carotenoids are the most wide spread pigments in nature with yellow, orange and red colors and have also received substantial attention because of both their role as pro-vitamins and antioxidants. Carotenoids are classified into hydrocarbons (carotenes) and their oxygenated derivatives (xanthophylls). The structure may be cyclised at one or both ends, have various hydrogenation levels, or possess oxygen containing functional groups. Carotenoids occur most commonly in trans form. Carotenoids commonly found in whole-grain cereals are lutein, zeaxanthin, beta-cryptoxanthin, beta carotene and alpha carotene (Britton 1995). Lutein is the carotenoid present in highest concentration in wheat followed by zeaxanthin and then beta cryptoxanthin. Rice bran contains both lutein and zeaxanthin, which improves eye sight. Cereals are the source of carotenoids (Saikia & Deka 2011). Maize is the best source with about 11μg/kg on dry weight basis (Panfili *et al.* 2004). Carotenoids are more evenly distributed within the grain, with significant quantities within endosperm, in contrast to other micro nutrients such as minerals, trace elements and polyphenols (Konopka *et al.* 2004). Carotenoids perform important functions in plants. They provide color in whole-grain flour. They also act as antioxidants in lipid environments of many biological systems.

Phytic Acid in Cereals

Phytic acid is bioactive compound which is also known as Inositol hexaphosphate (IP6). When IP6 is in salt form, it can also be called phytate. lnositol with lower phosphate groups, IP1-IP5 are called phytates. Almost all mammalian cells contain IP6 and its lower phosphorylated forms (IP1-5) (Vucenik & Shamsuddin 2006). It may account for more than 70% of the total kernel phosphorus (Zhou & Erdman 1995). Phytic acid is mainly located in the bran fraction of whole-grain cereals, especially within the aleurone layer. In corn, IP6 is mostly found in the germ (Febles *et al.* 2002). Phytic acid from whole-grain cereals has long been considered to be nutritionally negative, since it chelates minerals such as Zn, Fe, Ca and /or Mg, thus limiting their intestinal bioavailability (Lopez *et al.* 2002). However phytic acid is also a strong antioxidant *in vitro* (Graf & Eaton 1990). It suppresses Fe catalysed oxidative reactions, because of its capacity to chelate free Fe (Fenton reaction) and may be a potent antioxidant *in vivo*, by suppressing lipid peroxidation (Graf *et al.* 1987).

Phytosterols in Cereals

Phytosterols are a collective term for plant sterols and stanols, which are similar in structure to cholesterol, differing only in the side chain groups. In cereals, plant sterols occur as free sterols, steryl esters with fatty acids, or phenolic acids, steryl glycosides, and acylatedsteryl glycosides. The level of these components varies in different cereals and in different parts of the kernel (Toivo *et al.* 1999). The most important natural source of plant sterols in human diets are oils and margarines. Cereal products are recognized as significant plant sterol sources than vegetables (Normén *et al.* 1999). Plant sterols are one of the bioactive components currently being actively studied. They have decreased serum cholesterol levels in several studies and they may also be beneficial in preventing colon cancer (Awad *et al.* 1998).

Tocols in Cereals

Tocopherols and tocotrienols, commonly named tocols are chemical compounds known as vitamin E. Tocolsare natural antioxidants present in food of plant origin including cereals. Tocols include tocopherols and tocotrienols and are naturally occurring antioxidants present in cereal grain and are well recognized for their bioactivity (Nielson & Hansen 2008). Tocols occur in eight forms; α-tocopherol (αTP), β-tocopherol (βTP), γ-tocopherol (γTP), δ-tocopherol (δTP) and α-tocotrienol (αTT), β-tocotrienol (βTT), γ-tocotrienol (γTT) and δ-tocotrienol (δ TT) that differ in the number of methyl groups attached to the ring of 6-chromanol. Side chains of tocols consist of three isoprenoid units, and are saturated in tocopherols while tocotrienols con- tain three double bonds (Engelsen and Hansen, 2009). Tocols are synthesized only by photosynthetic plants and have to be contained in the diet. The richest sources of vitamin E in human diet are cereal grains that contain more tocotrienols than tocopherols. This proportion is advantageous because health benefits exerted by tocotrienols which display anticancerogenic and neuro- protective activities and reduce cholesterol level in blood serum surpass benign effects of tocopherols (Sen *et al.* 2007). Investigations of Zielin′ ski *et al.* (2001) revealed that the richest sources of tocols were grains of wheat and rye, which contained 27.81 and 27.78mg db, respectively. Barley and oat grains contained lesser quantities of these compounds – 18.73 and 11.59mg db, respectively. Not only the contents but also profiles of tocols in these grains were different. Rye, wheat and barley were the richest sources of a-tocopherol, b-tocotrienol and a-tocotrienols, respectively.

Gamma-Oryzanol in Cereals

γ-Oryzanol is a component of rice-bran oil and it was first presumed to be a single compound (Kaimal 1999). It was later determined that it is a mixture of substances including sterols and Ferulic acid, and at least 10 Pyhtosterylferulates (e.g. methyl sterols esterified to ferulic acid). Its content in whole-grain rice is 18-63mg/100g (DW) (Britz *et al.* 2007). Its concentration in rice-bran is 185-421mg/100g, depending on the rice variety, milling time, and stabilization process and extraction methods (Yu *et al.* 2007). It also lowers serum cholesterol. It is also associated with decreasing cholesterol absorption, decreasing platelet aggregation (Seetharamaiah *et al.* 1997). Oryzanol has also been used to treat hyperlipidemia, disorders of menopause, and to increase the muscle mass [Bonner *et al.* 1990].

Beta-Glucan in Cereals

β-glucan are polysaccharides found principally in the cell walls of the aleurone layer and endosperm in barley and oat kernels. In barley they are more concentrated in the endosperm while in oats they are concentrated in the aleurone layer (Bhatty 1993). These are the linear polymers of glucose molecules connected by 70% of β-(1-4) and 30% of β-(1- 3) - linkages. The largest amounts of β-glucan are found in barley (3-11%) and oats (3-7%), with lesser amounts reported in rye (1-2%) and wheat (<1%). Only trace amount have been reported in corn, sorghum, rice and other cereals of importance as food (Wood 1992). Oat-based breakfast cereals have also gained considerable attention in recent years as they are rich in β-glucan, which has been considered as a bioactive component and has been promoted as a means of reducing serum and plasma cholesterol levels (Behall *et al.* 2006) and reducing the postprandial glycemic response. Due to both linkages i.e., β-(1-4) and β-(1-3) linkages in β-glucan as compared to cellulose, the β-glucan is more flexible, soluble and viscous. It has been shown to have effects in lowering blood cholesterol. Due to both linkages i.e., β-(1-4) and β-(1-3) linkages in β-glucan as compared to cellulose, the β-glucan is more flexible, soluble and viscous. It has been shown to have effects in lowering blood cholesterol level and controlling blood sugar, probably mainly due to its high viscosity property as a soluble fiber to bind cholesterol and bile acids and facilitate their elimination from the body.

CONCLUSION

In the recent decades, there has been a growing interest in cereal bioactive substances as components of our diet, which is related to their beneficial effects on human health. Cereal grains and wholegrain cereal products (rich in fibrous polymers) are the excellent sources of numerous unique substances rating among biologically active compounds such as dietary fiber (arabinoxylans, b-glu- cans, cellulose, lignin and lignans), sterols, tocopherols, tocotrienols, alkylresorcinols, phenolic acids, vitamins and microelements. This study also tries to explain the impact of most important bioactive compounds found in cereal grains on selected technological processes. Special attention was devoted to arabinoxylans, b-glucans, alkylresorcinols, phytosterols and compounds known as tocols. Based on the current knowledge, it can be concluded that increasing the amount of whole grain products in our diet can prevent the development of diet-dependent diseases, such as cardiovascular and cancer diseases. In the light of these facts, it is recommended to obtain food products made from wholegrain cereals or fractions of whole grains as it generally positively affects our health.

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