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Impact of milling and thermal processing on phenolic compounds in cereal grains

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Abstract

Consumption of wholegrain foods has been recommended for healthy diets. The beneficial health properties of wholegrain products have been associated with the presence of higher amounts of dietary fiber and antioxidants and lower calories as compared to their respective refined ones. Phenolic compounds are mainly attributed to antioxidant properties of wholegrain foods. This review article provides a single comprehensive source that describes effects of milling and thermal processing on phenolic compounds and antioxidant properties in cereals. In general, milling and pearling processes affect the distribution of phenolic compounds and thus antioxidant properties vary among the milling fractions. Thermal processes such as baking and extrusion could cause negative or positive effects on phenolic compounds and antioxidant

properties of the end product subject to grain type and processing conditions. Thus factors that enhance health benefits of wholegrain cereal products have been discussed.

Keywords: Wholegrain, products, bioactive, antioxidants.

Introduction

Cereal grains are rich in a variety of naturally occurring components known as phytochemicals. The most important groups of wholegrain phytochemicals are phenolics (phenolic acids, alkylresorcinols and flavonoids), carotenoids, vitamin E, γ-oryzanols, dietary fibers and β-glucan (Okarter and Liu, 2010). Antioxidant properties of cereal grains are mainly attributed to phenolic compounds and other phytochemicals. A body of evidences now exists for the protective functions of phytochemicals in human health and nutrition, in particular when they consume consistently at required daily amount (Chatenoud et al., 1998; Meyer et al., 2000, Anderson et al., 2000; Kasum et al., 2001; Anderson, 2003; Bazzano et al., 2005; Behall et al., 2006; Anderson et al., 2007; Chan et al., 2007; Cheng et al., 2009; De Moura, 2008; Alminger and Eklund-Jonsson, 2008; Binns, 2010;). These compounds possess a number of relevant biological properties that depends in part on their antioxidant capacity (Thompson, 1994; Przybylski et al., 1998). They may actively contribute to the control of oxidative reactions and provide protection *in-vivo* via their capacity as free-radical scavengers, reducing agents, potential ability to complex of prooxidant metals, and as quenchers of singlet oxygen (Kinsella et al., 1993; Xing and White, 1997; Lasztity, 1998; Przybylski et al., 1998; Watanabe, 1998).

The presence of phenolic compounds in cereals and their distribution, content and health benefits for humans have extensively been reviewed (Andreasen et al., 2000; Sanchez-Moreno, 2002;

Jacobs and Gallaher, 2004; Flight and Clifton, 2006; Naczk and Shahidi, 2006; Dykes and Rooney, 2007; Li et al., 2008; Bondia-Pons et al., 2009; Meulenberg 2009; Okarter and Liu, 2010). This review article provides a single comprehensive source that focuses on how different processing technologies affect phenolic compounds in cereal grains in terms of their content and antioxidant properties.

Phenolics in cereal grains

Phenolics are naturally occurring compounds that possess one or more aromatic rings with one or more hydroxyl groups. They include a wide range of groups such as phenolic acids, flavonoids, stilbenes, coumarins, and tannins. The content of phenolic compounds in grains broadly vary and is dependent on grain type, genotype, part of the grain sampled, grain handling and processing (Adom and Liu, 2002; Adom et al., 2003, 2005; Ragaee et al 2011a). The most common phenolic compounds found in grains are phenolic acids and flavonoids. Flavonoids exist as glycosides linked to various sugar moieties or in complexes with organic acids, amines, lipids, carbohydrates or other phenols. They are present in cereals in a free and/or conjugated form, and mainly concentrated in the aleurone layer of the cereal kernel. They can also be found in embryos and seed coat of grains (Shirley, 1998).

Phenolic acids are subdivided into two groups, hydroxybenzoic and hydroxycinnamic acid derivatives (Fig. 1) (Liu, 2007). Hydroxybenzoic acid derivatives include *p*-hydroxybenzoic, protocatechuic, gallic, syringic and vannilic acids. They are commonly present in a bound form as part of lignins and tannins. Hydroxycinnamic acid derivatives comprise *p*-coumaric, caffeic, ferulic, and sinapic acids. They are mainly present in a bound form, linked to cell wall structural components such as arabinoxylan, cellulose, lignin, and proteins through ester bonds. Ferulic

acid and its derivatives occur primarily in the seeds and leaves of plants, mainly covalently conjugated to mono- and di-saccharides, plant cell wall polysaccharides, glycoproteins, polyamines, lignin, and insoluble carbohydrate biopolymers. In the seeds, ferulic acid is predominantly present in the aleurone cell walls of kernel (Pussayanawin, et al., 1988) and is esterified to arabinose (Faurot, et al., 1995), stanols and sterols (Seitz, 1989) and glucose (Herrmann, 1989). Campestanyl and sitostanyl ferulates are the main steryl ferulates present in wheat grain (Hakala, et al., 2002).

Wheat

Wheat kernels contain a number of phenolic compounds (Table 1) (i.e. ferulic, vanillic, gentisic, caffeic, salicylic, syringic, *p*-coumaric, sinapic acids, vanillin and syringaldehyde). Of these, ferulic acid is the primary phenolic acid in the grain, accounting for up to 90% of total phenolic acids (Sosulski, et al., 1982; Abdel-Aal et al., 2001; Adom, et al., 2003; Kim et al., 2006;). Ferulic acid dehydrodimer is also found in wheat bran (Renger and Steinhart, 2000) to strengthen aleurone cell walls during maturation by bridging arabinoxylan chains together (Piot et al., 2000). The dehydrodimers are products of oxidative coupling of ferulic acid catalyzed by peroxidase (Geissmann and Neukom, 1973). The cross-linking of cell walls with phenolic acids provides a physical barrier against insects and microorganisms (Abdel-Aal et al., 2001). Alkylphenol compounds that contain 17, 19, 21, 23 and 25 carbon atoms coupled to a resorcinol ring at the 5 position are also identified in wheat grain (Naczk and Shahidi, 2006). Tricin or 5,7,4`-trihydroxy 3`,5`- dimethoxyflavone is known as the dominant flavone pigment in wheat. In addition, two C-glycosylflavones, 6-C-pentosyl-8-C-hexosylapigenin and 6-C-hexosyl-8-C-pentosylapigenin were isolated from wheat bran (Feng and McDonald, 1989). Total ferulic acid

content of 11 wheat varieties was found to be significantly different (Adom et al., 2003) up to two folds. Similarly significant genetic variability in ferulic acid content in durum wheat (three-fold) and common wheat (two-fold) was reported (Lempereur et al., 1997). Significant differences in ferulic acid content between wheat cultivars have also been reported (Regnier and Macheix, 1996) which corresponded to levels of endogenous enzymes involved in phenolic acid metabolism in wheat plants. During successive phases of grain development, the ferulic acid content was similar but the final concentration differed between cultivars. In another study (Abdel-Aal et al., 2001) about 13% difference in mean ferulic acid contents was observed between different wheat cultivars (four spring wheat and three homozygous spring wheat breeding lines and Arin, a midgeresistant German cultivar) grown in Saskatchewan, Canada, in 1996 at four locations (Kernen, Wynyard, Kelvington, and Jedburgh).

Barley

In barley grains ferulic and *p*-coumaric acids are the most abundant phenolic acids (Hernanz et al., 2001; Madhujith, et al., 2006;) mainly found in the outer layers (husk, pericarp and aleurone) of the grain. The proanthocyanidins are found in the testa of the barley grain (Aastrup et al., 1984) and they exist in barley as an oligomeric mixture of prodelphinidins and procyanidins (McMurrough et al., 1996). These compounds are involved in the formation of haze in beer (McMurrough et al., 1992; Siebert et al., 1996).

Corn

In corn, insoluble bound phenolic acids constitute the predominant fraction of phenolic acids (Sosulski et al., 1982; Grabber et al 2000). Phenolic acids linked covalently to amine functionalities such as feruoylputrescine, *p*-coumarylputrescine, diferuloylputrescine, di-*p*-

coumarylputrescine, *p*-coumarylspermidine, diferuloylspermidine and diferuloylspermine are also found in the embryo and aleurone layer of corn kernels (Sen et al., 1994). Feruloylated disaccharides including *O*-(2-*O*-*trans*-feruoyl-l-arabinofuranosyl)-(1→3)-d-xylanopyronose,*O*-(2-*O*methoxyl-5-*O*-*trans*-feruoyl)-l-arabinofuranosyl-(1→3)-d-ylanopyronose and *O*-(2-*O*-methoxyl-5-*O*-*cis*-feruoyl)-l-arabinofuranosyl-(1→3)-d-xylanopyronose are detected in the acid hydrolysate of corn hulls (Honsey and Rosazza, 1997). Furthermore, 16 steryl cinnamic acid derivatives, mainly located in the interior portion of the inner pericarp layer and germ have also been identified [Seitz, 1989, 1990].

Oats

Oats contain a large number of phenolic compounds such as phenolic acids and their derivatives, avenanthramides quinones, flavones, flavonols, chalcones, flavanones, anthocyanins and amino phenolics. Bound-phenolic acids may be linked to sugars, polysaccharides, lignins, amines, and long-chain alcohols and omega-hydroxy fatty acids [Collins and Webster, 1986; Emmons and Peterson, 1999; Peterson, 2001; Mattila, et al., 2005). At least 25 and 20 avenanthramides, conjugates of cinnamic acid with anthranilic acids and *N*-acylanthranilate alkaloids were identified in oat groat and hulls (McKeehen et al., 1999).

Buckwheat

Whole buckwheat contains 2–5 times more phenolic compounds compared to oats or barley, (Holasova et al., 2002; Zdunczyk et al., 2006). The bran fraction of buckwheat contains large quantities of bound phenolic acids such as syringic, *p*-hydroxybenzoic, vanillic and *p*-coumaric acids (Durkee and Thivierge, 1977), while several free phenolic acids such as ferulic, *p*-hydroxybenzoic, caffeic and chlorogenic acids were detected in buckwheat grits (Mattila et al.,

2005). Rutin, quercetin, orientin, vitexin, isovitexin and isoorientin were also found in buckwheat (Dietrych-Szostak and Oleszek, 1999) in addition to four catechins, (−)-epicatechin, (+)-catechin 7-*O*-dglucopyranoside, (−)-epicatechin 3-*O*-*p*-hydroxybenzoate and (−)-epicatechin 3-*O*-(3,4-di-*O*-methyl) gallate that were identified in the ethanolic extracts of buckwheat groats (Watanabe, 1998). Rutin, quercetin, hyperin, and catechins are the primary antioxidants in buckwheat (Morishita et al., 2007). Oomah and Mazza (1996) reported an average of 387 and 13.1 mg/g of flavonoid and 0.47 and 0.77 mg/g of rutin in the seed and hull, respectively for four cultivars of buckwheat grown at three locations in western Canada

Effects of Storage

Cereal grains are biological materials that undergo biochemical changes but they can be stored for long time without having major changes in their quality. Under ideal conditions of low temperature, relative humidity and safe moisture content, cereal grains can be stored for several years. Thus harvesting, drying, storage and overall handling of grains before milling may influence the quality of grain products. Storage of dry cereal grains can affect their compositional properties including phenolics content and composition. Several studies have shown that storage affect concentration of total phenolic content in cereal grains (Table 2). For instance, Sosulski et al., (1982) reported about 66% reduction in the total phenolic content of wheat grains stored for 6 months. However, the same phenolic acids profile (free, conjugated and bound) was found in both fresh and stored samples. Apparently ferulic acid, even in the bound form, underwent destructive oxidation reactions during storage. Total and bound phenolic acid contents in brown and milled rice was also found to drop to a greater extent when was stored at 37^{o}C as compared with 4^{o}C (Zhou et al., 2004). Free, esterified and glycosylated phenolic acids

in rye, triticale, barley and oat decreased during storage for 6 months in dry conditions (Weidner et al., 1996). During storage of grains interactions of various parameters such as moisture content, grain respiration, microbial infestation, insects, germination, endogenous enzymes and storage conditions could occur showing the complexity of storage. A part or all these factors could contribute to the changes in phenolic and other compounds in grains.

Effects of milling

In general, milling is the transformation of raw materials into finer primary products for secondary processing. In cereal grains, milling is a process to separate the bran and germ from the starchy endosperm to produce white flours for use in making bakery products. Thus pericarp, testa and aleurone layers are all removed from the flour fraction. Such process has a major impact on health-promoting components found in grains such as minerals, vitamins, fibers and phytochemicals. Therefore, the concentration of grain antioxidants was drastically reduced during the refining process. Many studies reported concentration of phenolic compounds in the outermost layers, which could prove that the bran fractions obtained as milling by-products is a very valuable high nutrition fraction that could be used as a natural source of antioxidants and as a value-added product in the preparation of functional food ingredients and/or for enrichment of certain products. The milling process for different cereals and its effect on phenolics concentrations (Table 2) will be discussed in the following section.

Wheat

Wheat milling consists of controlled breaking, reduction, and separation to produce a variety of milled products for various uses. The objective during wheat milling is to separate the pericarp

and germ of the wheat kernel from the endosperm. On the other hand durum wheat is milled into a granular product called semolina for pasta production. Significant differences in the composition and concentration of phenolic acids in eight durum wheat samples were observed between kernel parts (starchy endosperm, aleurone layer and pericarp) (Peyron et al., 2002). The starchy endosperm was characterized by a low content in ferulic acid; the aleurone layer was rich in trans-sinapic acid, while the pericarp exhibited a high content of ferulic acid dehydrodimers. In a study on two Canadian wheats, durum and bread wheat, bioactive constituents were mainly concentrated in the outer layers of grains with the bran fraction having the highest antioxidant activity compared with shorts and flours **(**Liyana-Pathirana and Shahidi, 2007).

Five milling fractions of waxy wheat were obtained using a modified Japanese rice-polisher and gradual milling process (Hung et al., 2009). Total phenolic and flavonoid contents of the free and bound phenolic extracts gradually increased in the order from inner to the outer fractions. The outer layers had significantly higher amounts of free and bound phenolics than the wholegrain flour and the white flour. As expected total phenolic and flavonoid content of bound extracts were significantly higher than that of the free extracts. Other phenolic acids rather than ferulic acid were found in the free phenolic extracts of the endosperm, whereas ferulic acid was the primary phenolic in both free and bound extracts of the bran. The study demonstrated that by gradual milling all the fractions that contain part of bran had improved antioxidant capacity compared with white flours. The total antioxidant capacity of all graded milling fractions were attributed to bound phenolics (72.5–83.2%), which mostly exist in the outer fractions rather than in the inner fractions of wheat grain.

The effect of pearling versus roller milling on the distribution of phenolics and antioxidant properties in wheat fractions was investigated (Beta et al., 2005). Phenolics were concentrated in fractions from the first and second pearling (>4,000 mg/kg). Wheat fractions from the third and fourth pearling still contained high phenolic content (>3,000 mg/kg). A similar trend was observed in antioxidant capacity of the milled fractions. Phenolic content of roller-milled wheats decreased in the order shorts > bran > flour > highly refined endosperm portion. This could be associated with pentosans in the wheat aleurone layer that tends to concentrate in the middling flour streams as the degree of refinement decreases (Fulcher et al., 1972; Symon and Dexter, 1993). The refined endosperm portion of the kernel had approximately half the total phenolic content of the 75% residue from wheat pearling. During pearling, inner layers of the crease are left intact, whereas the kernel is essentially ripped open by corrugated break rolls in roller milling. Therefore, during pearling there are significant levels of phenolics contained within the crease. The authors concluded that pearled fractions (5 and 10%) had similar or higher levels of phenolics compared with the bran and shorts obtained from roller milling.

Investigating fifteen different wheat samples of ten spring and five winter wheat varieties as wholegrains and their respective bran and flour grown in both conventional and organic conditions in Estonia, Vaher et al. (2010) reported total phenolic content of the bran layer to be the highest (1258-3157 µg/g), followed by that of grains (168 - 459 µg/g) and the lowest of flour (44 - 140 µg/g). They concluded that the content of bound phenolic acids of winter wheats to be significantly higher than that of spring wheats and that growing conditions have a certain effect on the biosynthesis and accumulation of phenolic compounds

Oat

Unlike other cereals grains, oat is generally used as wholegrain after the hull is removed to make oat flakes, flours and steel-cut groats. Oat kernels are always heated prior to milling to inactivate enzymes and prolong shelf life due to the high content of oil in oat.

Pearling of oat groats for 5 to 180 s to remove approximately 1-15% of the kernel weight was investigated (Peterson, 2001). Most of the material obtained from pearling for short time was bran, and longer time increased the amount of starchy endosperm in the pearling fractions. Antioxidant capacity of 80% ethanol extracts, measured by β-carotene bleaching and the reduction of the free radical, 2,2-diphenyl-1- picrylhydrazyl (DPPH) was highest in the short time pearling fractions and decreased as more endosperm tissue was included. Likewise, there was a decreasing concentration in total phenolics and several simple phenolic acids, as more material was pearled from the groats. In contrast, the concentration of avenanthramides was not correlated with pearling time, indicating that they were more uniformly distributed in the groats. Ten milling products were prepared from either heated or non-heated oat groats using a Satake laboratory pearler following by milling and sieving on a Retsch mill equipped with a 0.5 mm screen (Handelman et al., 1999). The different fractions included the outer (hairy) surface of the groat followed by removal of 1.6, 3, 5 and 7% of the starting groat in addition to the bran, flour, wholegrain flour, concentrated bran fraction, and oat flaking filter fines were assessed in terms of antioxidant capacity. The aleurone or outermost layer was found to contain the greatest concentration of antioxidants in the oat groat. All fractions derived from the aleurone layer, were strongly active in the Low Density Lypoprotein oxidation and oxygen radical absorbing capacity (ORAC) assays. This indicates that oat bran consists principally of the aleurone layer and, consequently, possesses an antioxidant capacity comparable to that of pearling. However,

commercial preparations of oat bran are often mixed with the starchy endosperm, a mixture that could dilute the total antioxidant capacity of these fractions (Wood et al., 1991; Wood and Beer, 1998).

Rye

Rye is traditionally consumed as wholegrain food products in the Nordic countries, and thus it is rich in dietary fiber and bioactive compounds such as phenolic acids and lignin. The profile and concentrations of antioxidants in the whole rye grain and its morphological fractions were determined in different rye varieties grown in Poland (Zielinski et al., 2007). Pericarp and testa fraction was a good indicator for antioxidant properties for the selection of rye variety of high technological quality, rather than these of the wholegrain, or endosperm with embryo fraction. When rye was milled using Buhler mill to its botanical fractions (yield of 49, 16, 16, and 19% for bran, shorts, flour C and flour B, where flour B was the milling fraction from break rolls and flour C was the milling fraction from reduction rolls, the distribution of total phenolic compounds was 127 mg/100g in bran, 49.4 mg/100g in shorts, 4.6 mg/100g in flour C, 3.6 mg/100g in flour B compared to 65 mg/100g in the rye wholegrain flour (Heiniö et al., 2008). Therefore, the amounts of bioactive compounds can be concentrated in the bran fraction through the milling process (Nilsson et al., 1997; Glitsø and Knudsen, 1999).

Barley

Pot and white pearled barley are used as food ingredients in a variety of foods. They are prepared by abrasive milling to remove part or all the kernel outer layers. The total amounts of phenolic acids in wholegrain barley flour ranges from 604 to 1346 μg/g fresh weight depending on variety, with ferulic acid being as the dominant compound. Most of the phenolic acids in the

barley fractions are present in the esterified or bound form. Phenolic acids content varies according to occurrence or lack of hull, with significantly higher levels in the hulled varieties (Holtekjølen et al., 2006). Despite accounting for only 10-20% of the total grain weight, the hulls represent about 45% of the total antioxidant capacity measured in the covered wholegrain flours (Holtekjølen et al., 2011).

Antioxidant properties of pearled barley fractions obtained from two barley varieties (Falcon and AC Metcalfe) and measured based on Trolox equivalent showed that the concentration of antioxidant and antiradical activities in the outer fractions is approximately up to 25% of the grain on weight basis. When barley grains were abraded using Vertical Schelling Machine, the total phenolic content decreased as the number of the fraction increases. Most of the total phenolics were concentrated in the outer layers, husks, pericarp, testa and aleurone layers which contained the highest concentrations of total phenolic acids (0.6-0.9%) while the endosperm layers contained the lowest concentration (0.1% or less) (Nordkvist et al., 1984). In the current industrial practice up to 50% of the outer parts may be removed which may lead to substantial loss of bioactive compounds (Madhujith et al., 2006) which has to be changed to boost antioxidants and other health-promoting components in barley products**.**

Corn

Corn is fractionated into its components either by dry milling process (mechanical separation of constituents) or wet milling process (combined chemical and mechanical separation of constituents). The objective of dry milling corn is to separate the kernel into its anatomical parts (endosperm, bran, and germ), while the objective of wet milling is to separate corn into largely chemical constituents (starch, protein, fiber, and oil). Dry milling products of corn that are

suitable for food use and account for 50% of the total yield are flaking grits, coarse, medium and fine grits, meal, cones, and flour. Crude fiber content of all these fractions could vary from 0.4 to 0.7% (Singh et al., 2006). which indicates a very low concentration of dietary fiber, antioxidants and bioactive compounds. On the other hand, germ and hominy feed fractions account for 10 and 35% of the total yield, respectively are rich in crude fiber (4.6 and 5.4%, respectively) which are considered good source of dietary fiber, antioxidants and bioactive compounds. The most valuable fractions from wet milling process are starch and germ accounting for 67.5 and 7.5% of total yield, respectively. Refined corn bran has 92% dietary fiber, and it is used in dietary beverages, extruded breakfast cereals bread and snack foods. The phenolic composition of corn kernels is qualitatively similar to that of other cereal grains (McDonough et al., 1983). The bulk of phenolics (phenolic acids, flavonoids, and conjugated amines) are concentrated in the pericarp and aleurone layers as well as the germ, with traces in the endosperm.

Corn bran contains heteroxylans (approximately 50%), cellulose (approximately 20%) and phenolic acids (approximately 4%, mainly ferulic and diferulic acids) (Saulnier et al., 1995; Carvajal-Millán et al., 2007). Ferulic acid (FA) is the predominant phenolic compound in corn bran, and is mainly bound to cell wall polysaccharides (Adom and Liu, 2002).

Sen et al. (1994) employed microspectrofluorometry as a method of mapping the location of phenolic substances in corn kernels. Autofluorescence due to phenolic acids was detected mainly in the embryo, aleurone, and pericarp of corn kernel cross sections. Resistant corn types showed higher intensities of phenolic fluorescence but no unusual distributions. Ehrlich's reagent

revealed phenolic acid amide fluorescence in the embryo and aleurone. The localization of phenolic amines was confirmed by HPLC analysis.

Sorghum

Sorghum grains are milled into three fractions, gross, medium and fine, along with a very fine particle dust. Each of these fractions possesses different characteristics and uses and the gross fraction (mainly bran high in protein) is used as animal feed. The bran fraction is rich in tannin that is removed to produce tannin-free bran and a quantity of tannin which can be used for dyes, creams and cosmetics. The medium fraction is coarse flour, and would be returned to the mill for further processing, although it is used in making bran-based cereals. The fine fraction produced by the mill is used as gluten-free flour, for making special bread, biscuits and cakes for celiac patients. Awika et al. (2005) decorticated specialty sorghums using a tangential abrasive dehulling device to remove successive bran layers collected at 1 min intervals. The decorticating products were assessed in terms of phenols, tannins, 3-deoxyanthocyanins, dietary fiber, and antioxidant capacity. The first two bran fractions had the highest levels of phenols and antioxidant activity (3-6 times higher than that of wholegrain). Brown (tannin-containing) and black sorghums had at least 10 times higher antioxidant capacity than white sorghum or red wheat bran. Black sorghum had the highest 3-deoxyanthocyanin content (up to 19 mg/g bran). Dietary fiber in sorghum bran was 36-45%, as compared to 48% in wheat bran. Also milling fourteen commercial hybrid cultivars of sorghum grains (Ali and Wills, 1982) to 10% total loss in weight using abrasion resulted in concentration of the pigments in the pericarp indicating bran rich in dietary fiber. Concentration of phenolic compounds in the bran fraction of sorghum grain also been reported by other researchers (Taylor et al., 2006). Therefore, sorghum bran could be

considered as rich source of valuable dietary components and present promising opportunities for improving health attributes of food.

Buckwheat

Buckwheat is a good source of phenolic compounds and other phytochemicals (Dietrych-Szostak and Oleszek, 1999; Baumgertel et al., 2003,). Buckwheat bran and hulls have 2–7 times higher antioxidant activity than barley, triticale, and oats (Holasova et al., 2002; Zdunczyk et al., 2006). The antioxidant properties of 80% methanolic extracts of buchwheat, wheat, rye, oat and barley originated from whole grain was in the order of buckwheat > barley > oat > wheat = rye (Zieliński and Kozłowska, 2000). The authors reported total phenolic compounds for dehulled grain and hulls to be as follow: barley, 28.7 and 36.8 µg/mg; oat, 16.3 and 45.0 µg/mg and buckwheat, 90.7and 381.9 µg/mg.

Unlike most cereals, the majority of phenolic compounds in buckwheat are present in the free form distributed throughout the entire grain (Quettier-Deleu et al., 2000; Hung and Morita, 2008). Therefore, extracts from flour, hull, and whole buckwheat would exhibit high antioxidant activity (Quettier-Deleu et al., 2000; Holasova et al., 2002). Using 50% ethanol extraction (for free phenolics) followed by alkaline extraction (for bound phenolics), the antioxidant activity, free, bound and total phenolic content of commercial buckwheat flours (Farinetta, Supreme, and Fancy) and whole buckwheat was investigated (Inglett et al 2011). The results demonstrated that Farinetta flour contained the highest free (5.1 mg/g), bound (8.5 mg/g) and total (23.6 mg/g) phenolic content, followed by Supreme (free = 7.6 mg/g, bound = 5.4 mg/g and total = 13.0 mg/g), whole buckwheat (free =5.4 mg/g, bound = 3.1 mg/g and total = 8.5 mg/g), and Fancy flour (free =2.6 mg/g, bound = 2.8 mg/g and total = 5.3 mg/g), respectively. In another study

using 80% methanol containing 1% hydrochloric acid at room temperature the total phenolic content of dehulled buckwheat seeds and hulls was 7.3 and 39.0 mg/g, respectively (Velioglu et al., 1998). Hung and Morita (2008) evaluated phenolic content of both free and bound phenolic extracts of buckwheat flour fractions (obtained by gradual milling) and reported significant increase in the order from the center of the grain to the outer layer. In conclusion, attention has to be paid during the milling process regarding the removal of the outer layers of all cereal grains. This would help in reducing the loss of bioactive compounds and increasing the health benefits of the final products.

Effect of thermal processing

Cereal thermal processes such as baking, roasting and extrusion cause a number of physical and chemical changes due to starch gelatinization, protein denaturation, components interactions and browning reactions, These changes would result in improved organoleptic properties, increased nutrient availability, improved antioxidant properties and inactivation of heat labile toxic compounds and enzyme inhibitors. Earlier research on cereal products has shown that thermal processing might assist in releasing bound phenolic acids by breakdown of cellular constituents and cell walls (Dewanto et al., 2002). In addition, browning during thermal processing causes increase in total phenolic content and free radical scavenging capacity. This increase could be due to the dissociation of conjugated phenolic moiety during thermal processing followed by some polymerization and/or oxidation reaction and the formation of phenolics other than those endogenous in the grains. Other reactions such as Maillard reaction (non-enzymatic browning), caramelization and chemical oxidation of phenols could also contribute to the increase in total phenols content.

Processing may also change the ratio between various phenolic compounds due to thermal degradation. Vanillin and vanillic acid can be produced through thermal decomposition of ferulic acid (Fiddler et al., 1967; Pisarnitskii et al., 1979; Peleg et al., 1992), while *p*-hydroxybenzaldehyde can be formed from *p*-coumaric acid (Pisarnitskii et al., 1979). Caffeic acid is heat-sensitive and could be reduced during heat processes, while ferulic- and *p*-coumaric acids are susceptible to thermal breakdown (Steinke and Paulson, 1964; Pisarnitskii et al., 1979; Huang and Zayas, 1991). Heat stress (100 °C) could also increase some phenolics such as ferulic, syringic, vanillic, and *p*-coumaric acids or simple phenolics in wheat flour due to degradation of conjugated polyphenolic compounds such as tannins (Cheng et al., 2006). Some phenolics are also known to accumulate in the cellular vacuoles (Chism and Haard, 1996), and thermal processing may release such unavailable phenolics. The processing operating conditions also affect changes in phenolic compounds. For instance, the release of phenolic compounds is highly dependent on moisture content, time and temperature during extrusion processing (Dimberg et al., 1996).

Baking

Baking is used for the production of breads, cakes, pastries, pies, tarts, quiches, cookies and crackers. Wholegrain bakery products are expected to be better sources of phenolic compounds compared with refined flour products due to the concentration of phenolic compounds in the outer layers of the wheat kernel. Baking could result in an increase in the concentration of phenolic compounds of wholegrain bread regardless baking time (10, 20 or 35 min) (Gelinas and McKinnon, 2006). The crust of bread was found to contain slightly more phenolic compounds than its crumb. Other studies reported negligible changes in total phenolics caused by baking

(Menga et al., 2010). Maillard reaction was found to produce a dramatic increase of molecules possessing free radical scavenging properties in butter cookies (Bressa et al., 1996). The authors investigated the generation of a chain-breaking antioxidant capacity as a function of the cooking time using a kinetics approach. In this study a diazo compound (an organic compound that has two linked nitrogen atoms (azo) as a terminal functional group) was used to generate peroxyl radicals at constant rate, and the reporting reaction was the bleaching of crocin in the presence of these radicals. They reported that "during the first 20-30 min of cooking, when browning takes place, an antioxidant capacity accounting for up to 5 g of Trolox was produced in 100 g of dried aqueous extracts of the cookies"

The effect of bran particle size, dough fermentation time and baking time and temperature on total phenolic content, ferulic acid and antioxidant properties was investigated in whole wheat pizza crust made from two different hard white winter wheat varieties, Trego and Lakin (Moore et al., 2009). Antioxidant properties included oxygen radical absorbing capacity (ORAC), hydroxyl radical scavenging capacity (HOSC), relative 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging capacity (RDSC), and cation 2,2′-azinobis (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) radical scavenging capacity. Bran particle size had no effect on the antioxidant properties tested. Increasing dough fermentation time from 0 to 48 h also showed no significant influence on antioxidant properties except for HOSC (increased by about 28%) which could be a result of the increase in soluble free ferulic acid (up to 130%). Increasing thermal treatment, by increasing the time from 7 to 14 min at 204^{o}C or by increasing the temperature from 204 to 288^{o}C with a 7 min bake time, resulted in significant increase in ABTS scavenging properties and RDSC for both wheat varieties compared with the unbaked dough.

ORAC values were only affected by increasing the temperature to 288^{o}C for 7 min. The significant differences found between unbaked and baked pizza dough samples or between total phenolic contents of crusts prepared under different baking conditions were very few. Total phenolic content of the baked pizza crusts were highly correlated with all antioxidant capacities (r= 0.476, $p < 0.05$, r= 0.429, $p < 0.05$, r = 0.601, $p < 0.01$, and r = 0.711, $p < 0.01$ for RDSC, ABTS scavenging capacity, HOSC, and ORAC, respectively). In general longer dough fermentation time and increased baking time or temperature could be considered potential approach to enhance antioxidant properties in whole wheat pizza crust.

The extraction rate or flour yield obtained from cereal grains also has impact on changes in phenolic compounds and antioxidant capacity of end products. For instance, high extraction rate of rye flour enhanced the formation of antioxidant compounds during breadmaking (Michalska et al., 2008). Cookies baked from 100% extraction rate sorghum flours contained 2-3 folds more total phenolics compared with those made from 70% extraction rate flours and antioxidant capacity was higher by 22-90% depending on the sorghum cultivar (Chiremba, et al., 2009). Germination of rye wholegrain before sourdough baking produced bread with increased phenolic compounds content (Liukkonen et al., 2003; Michalska et al., 2008).

Extrusion

Extrusion cooking is simultaneous actions of temperature, pressure and shear; their intensities and interactions variey enormously depending on feed ingredients, extruder configuration and the desired characteristics of endproducts. High-temperature short-time extrusion cooking may be regarded as a hydrothermal process even it works at comparatively low content of moisture in the raw material. Hydrothermal processing of cereal grains may liberate phenolic acids and their

derivatives from the wall cells or convert them from one form into another subject to technological process and conditions (Khan and Ungar, 1986).

Nowadays several breakfast cereal products are produced by flaking, oven- and gun-puffing, baking, shredding and direct expansion. As a multi-step, multi-function thermal/mechanical process, extrusion could have beneficial or detrimental changes on bioavailability and content of nutrients of cereal products. Extrusion would enhance stability of food due to enzyme inhibition (lipase and lipoxidase), apparently increase dietary fiber content due to the formation of resistant starch and redistribution of insoluble to soluble dietary fiber, increase protein and starch digestibility, and reduced lysine availability due to Miallard reaction which results in increased antioxidant capacity and phenolic compounds content (Cheftel, 1986). Little research has looked into effects of extrusion process on antioxidant properties and phenolics. A study on dark buckwheat flour reported no change in antioxidant capacity after extrusion at 170^{o}C (Sensoy et al., 2006). Another study showed a significant reduction in both antioxidant capacity (60-68%) and total phenolics (46-60%) in all barley extrudates compared with that of the unprocessed barley flour (Altan et al., 2009).

The behavior of phenolic compounds present in selected cereals (wheat, barley, rye and oat) during extrusion cooking at different temperatures (120, 160, 200^{o}C) significantly changed (Zielinski et al., 2001). Significant increases in phenolic acids content and free and bound phenolic acids except for sinapic and caffeic acids which were not detected in the extruded grains. The highest content of free and bound phenolic acids was reported in rye and oat. The changes in free phenolic acids were more pronounced when compared to the bound ones. The liberated phenolic acids may contribute to the high antioxidant potential of extrudates when they

are considered as a dietary antioxidant. Ferulic acid was found as a predominant compound in raw wholegrain as well as in extruded grain.

Roasting

Roasting has been a traditional practice for several centuries. It is a popular process for corn, check peas and other grains to produce a variety of snack foods such as popcorn, aadun, dankuwa, guguru and elekute (Ayatse et al., 1983; Ihekoronye and Ngoddy, 1985). Traditional roasting of grains is used primarily to increase nutritional value and enhance flavour, in addition to the reduction of antinutritional factors and extension of storage life (Huffman and Martin, 1994). Roasting resulted in a marked reduction in phenolic content (13.2 and 18.3%), and antioxidant capacity (27.2 and 13.5%) in yellow and white sorghum, respectively (Oboh et al., 2010). While a significant increase in both antioxidant capacity and total phenols content of barley grains was obtained after roasting 2 layers of grains or 61.5 g in a microwave oven at 600W power for 8.5 min (Gallegos-Infante et al., 2010a; Omwamba and Hu, 2010). The increase of phenolic compounds could be attributed to the release of bound phenolics from the breakdown of cellular constituents. A significant decrease in total phenolic content (8.5 to 49.6%) and antioxidant activity (16.8 to 108.2%) was observed after sand roasting of eight barley varieties (Sharma and Gujral, 2011). Because the majority of phenolic compounds in buckwheat are in the free form, roasting would cause reduction in antioxidant capacity (Sensoy et al., 2006; Zielinski et al., 2009).

Other cooking techniques

A number of cereal grains are thermally processed by canning technology such as corn or sorghum. Canning of grains causes several changes in nutrient bioavailability and characteristics

including phenolic compounds. Significant increase in the content of free phenolics, free ferulic acid and total antioxidant capacity were found following heating canned corn in a retort at 115°C for 10, 25, or 50 min (Dewanto et al., 2002). In addition pressure cooking of corn (autoclaved for 40 min at 15 *psi*) caused substantial increase in the amounts of free ferulic acid, *p*-coumaric acid and vanillin (Steinke and Paulson, 1964). Boiling red sorghum and finger millet at atmospheric pressure resulted in significant reduction in total extractable phenolics, while barley showed increase in total phenolic content and antioxidant capacity (Gallegos-Infante et al., 2010a). A summary of changes in phenolics and antioxidants during thermal processing is presented in Table 3.

Other phenolic sources

Many natural antioxidant ingredients are being used in the baking industry. These include coco powder, cranberries, apple skin, grapes, black beans, red beans, wheat bran, rice bran, barley flour, soya flour, flaxseed, amaranth, quinoa, and so many more. The inclusion of these antioxidant sources in the formula of bread, cookie, or muffin would result in a significant increase in phenolics and antioxidant capacity of baked products. For instance incorporation of 40 or 30% barley flour with wheat flour increased antioxidant properties of the composite breads compared with the control (100% wheat flour) bread (Holtekjølen, et al., 2008; Ragaee et al., 2011b). The antioxidant properties were found to be dependent on the variety of barley and the extraction rate of barley flour. With regards to phenolics in bread, the amount of free phenolics decreased during baking process, while the amount of bound phenolics increased. The antioxidant properties determined as ferric reducing/ antioxidant power were relatively constant during baking process. Incorporating bean flour at 30% level increased total phenolic content in

cooked pasta from 5 to 9.7 mg catechin equivalent/g freeze dried cooked pasta (Gallegos-Infante et al., 2010b). The replacement of potato starch with a pseudocereal flour (amaranth, quinoa and buckwheat) resulted in gluten-free breads with significantly high content of polyphenol compounds and antioxidant capacity in addition to high nutritional properties (high in protein, fiber, calcium, iron and vitamin E) and good baking characteristics (Alvarez-Jubete et al., 2009; Alvarez-Jubete et al., 2010a &b).

Other ingredients such as dried apple skin powder was incorporated as a value-added food ingredient in muffin up to 24% (w/w) replacement level increased the concentration of total phenolics and antioxidant capacity in the final product while did not affect its overall acceptability (Rupasinghe et al., 2009). Rice bran might be a good source of antioxidnts compared with other commonly used antioxidants (Bhanger et al., 2008). When rice bran was added to cookies it showed appreciable contribution towards stabilization of cookies and enhanced shelf life (Bhanger et al., 2008). Incorporation of sugar beet molasses or powders of osmotically dehydrated powders of fruits/vegetables improved the antioxidant properties of the wheat breads (Filipcev et al., 2010).

Future perspective and conclusion

Cereal grains undergo physical and chemical changes during storage and processing so, careful considerations should be taken to minimize or prevent any unfavorable changes in phenolic compounds. Most of bioactive and phenolic substances are mainly concentrated in the outer layer of cereal grains, and thus wholegrain products are considered the best solution to reduce the loss of bioactive compounds and increase the health benefits of cereal products. Different thermal processing technologies have been found to produce various effects, and thus

the choice of cereal recipe and thermal process is crucial in preserving health-enhancing properties of cereal products.

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Fig.1 Chemical Structures of Common Phenolic Acids in Cereals

Table 1. Common Phenolic Acids in Cereal Grains

Derivatives of Hydroxybenzoic acid		
Group	**Position**	**Name**
OH	2	Salicylic acid
OH	3	3-Hydroxybenzoic acid
OH	4	*p*-Hydroxybenzoic acid
OH	3,4	Protocatechuic acid

OH	2,5	Gentisic acid
OH	3,4,5	Gallic acid
OCH_3 OH	3,5 4	Syringic acid
OCH_3 OH	3 4	Vanillic acid
Derivatives of Hydroxycinnamic acid		
Group	**Position**	**Name**
OH	2	*P*-Coumaric acid
OH	3	*m*-Coumaric acid
OH	3,4	Caffeic acid
OCH_3 OH	3,5 4	Sinapic acid
OH	3,4	Chlorogenic acid (ester of caffeic acid and quinic acid)
OH OCH_3	4 3	Ferulic acid

Table 2. Summary of Effects of Storage, Milling and Pearling on Total Phenolic Content in Cereal Grains.

Cereal/ Conditions	**Changes in Phenolic Compounds**	**References**
Storage		
Wheat, at Room temperature	66% reduction after 6 month in the total phenolic content.	Sosulski et al. (1982)
brown and milled rice, at 37°C	Sever reduction in total and bound phenolic acids.	Zhou, et al. (2004)
Rye, triticale, barley and oat, dry condition	Free, esterified and glycosylated phenolic acids decreased after 6 months.	Weidner et al., (1996); Weidner, and Paprocka, (1996)
Oat, at 8% relative humidity	Phenolic acids and aldehydes significantly increased after 1 year (in non-heat treated oat. While significant increase in heat treated oat with hulls.	Dimberg et al. (1996)
Milling		
Wheat	Phenolics concentrated in the outer layers.	Barron et al. (2007); Liyana-Pathirana and Shahidi, (2006), (2007)

	The germ fraction possessed the highest total phenolic content, followed by bran, shorts, wholegrain and flour.	Barron et al. (2007)
Rye	Phenolics concentrated in the bran fraction.	Liukkonen et al. (2003); Glitsø and Knudsen, (1999)
Buckwheat	Mainly located in the outer layers of grain.	Hung and Morita, (2008); Dietrych-Szostak and Oleszek, (1999)
Pearling		
Wheat	The flours milled from the outer parts of grain contained significantly higher amount of phenolics and exhibited significantly higher antioxidant capacity than did the wholegrain.	Beta et al. (2005)
Buckwheat	Phenolic concentrated in the outer layer.	Hung et al. (2009); Skrabanja et al. (2004)
Barley	Phenolic concentrated in the outer layer.	Madhujith et al. (2006)
Oat	Phenolic concentrated in the outer layer of oat.	Peterson (2001); Liukkonen et al. (2003)
Wheat	Phenolic concentrated in the outer layer.	Liyana-Pathirana et al. (2006, 2007)
Wheat, rye, oat and buckwheat	total phenolic content are concentrated in Pericarp and Testa fractions from wheat, oat, buckwheat, rye , but in barley it was similar to the concentration in the endosperm.	Zielinski and Kozłowska, (2000)
Sorghum (decorticated)	Phenolics are concentrated in the pericarp and the testa of sorghum.	Dlamini et al, (2007), Awika et al. (2005)

Table 3. Summary of Effects of Different Thermal Processing on Total Phenolic Content in Cereal Grains.

Cereal/ Conditions	Changes in Phenolic Compounds	References
Baking		
Wheat purple wheat bran- or heat-treated	Slight increased the concentration of phenolics in bread crust in white bread than wholemeal bread.	Gelinas and McKinnon, (2006) Li et al. (2008)

purple wheat bran-enriched muffins	significant reduction in total phenolic contents and ORAC values.	
40% barley replacement in wheat bread	Reduction in the amount of free phenolics, while increase in the amount of bound phenolics.	Holtekjølen et al. (2008)
Rye, Sourdough	Increased in bound phenolics content. Slight or no increase in bound phenolic compounds. Slight reduction in bound phenolic acids content while no change in the amount of ferulic acid dehydrodimers.	Liukkonen et al. (2003) Kariluoto et al. (2006) Hansen et al. (2002)
Wheat, oat, barley	No asserting that baking modified the total phenolic content and total antioxidant capacity.	Menga et al. (2010)
Extrusion		
Regular corn flour, corn starch,	Reduction in total antioxidant capacity value.	Ozer et al. (2006)
Rye, oat, barley, wheat	Significant decrease in all the bioactive compounds tested, except for phenolic compounds.	Zielinski et al. (2001); Ozer et al. (2006)
Buckwheat, at 170^{o}C	No change.	Sensoy et al. (2006)
Barley and barley–fortified products	Reduction in total phenolic content.	Altan et al. (2009)
Rye, at 14% moisture content/120 or 180^{o}C	Significant increase in total phenolic content.	Gumul and Korus, (2006)
Sorghum	Reduction in antioxidant activity of the products than conventionally cooked porridges.	Dlamini et al. (2007)
Barley	Reduction in total phenolic content.	Altan et al. (2009)

Roasting		
Barley, microwave	Increase in total phenolic content. Increase antioxidant activity and total phenolic content.	Gallegos-Infante et al. (2010a); Omwamba and Hu, (2010)
Buckwheat,at 200^{o}C/10min	Slight reduction in antioxidant activity.	Sensoy et al. (2006); Zhang et al. (2010)
Cooking		
Barley	Increase in total phenolic content.	Gallegos-Infante et al. (2010a)
Sweet corn	Significant increase in total phenolic content.	Dewanto et al. (2002)

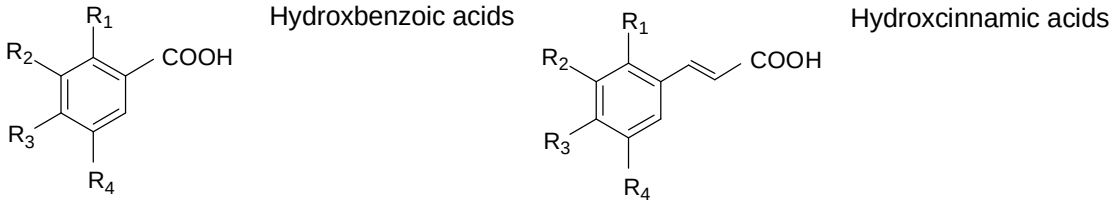

Fig.1 Chemical Structures of Common Phenolic Acids in Cereals