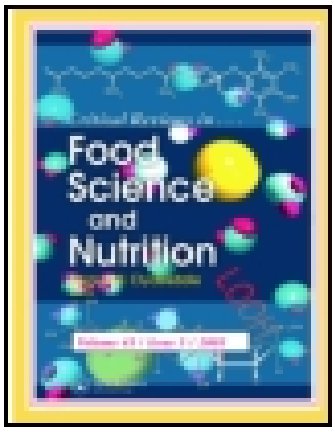

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Phenolic compounds of cereals and their antioxidant capacity

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Phenolic compounds of cereals and their antioxidant capacity

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Running head: Antioxidants of cereal grains

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Abstract

Phenolic compounds play an important role in health benefits because of their highly antioxidant capacity. In this review, total phenolic contents, phenolic acid profile and antioxidant capacity of the extracted from wheat, corn, rice, barley, sorghum, rye, oat and millet, which has been recently reported, are summarized. The review shows clearly that cereals contain a number of phytochemicals including phenolics, flavonoids, anthocyanins, etc. The phytochemicals of cereals significantly exhibit antioxidant activity as measured by trolox equivalent antioxidant capacity, 2,2-diphenyl-1-picrylhydrazyl radical scavenging, reducing power, oxygen radical absorbance capacity, inhibition of oxidation of human low-density lipoprotein cholesterol and DNA, Rancimat, inhibition of photochemilumenescence, and iron(II) chelation activity. Thus, the consumption of whole grains is considered to have significantly health benefits in prevention from chronic diseases such as cardiovascular disease, diabetes, and cancer because of the contribution of phenolic compounds existed. In addition, the extracts from cereal brans are considered to be used as a source of natural antioxidants.

Keywords: Phenolic compounds, Cereals, antioxidant, Reactive oxygen species

INTRODUCTION

Reactive oxygen species (ROS) are chemically reactive molecules containing oxygen including singlet oxygen, superoxide anion radicals, peroxide anions, and hydroxyl radicals which are involved in the etiology of many diseases as indicated by the signs of oxidative stress seen in those diseases. They can be generated during normal cellular respiration, by activated leucocytes as part of the immune response, and by exogenous oxidants such as air pollution and cigarette smoke (Finkel and Holbrook, 2000). They have an undoubted capability to be harmful by their action on vital cellular components including lipids, proteins and DNA (Temple, 2000). Fortunately, natural antioxidants, including phenolic compounds, vitamins and carotenoids, are proven to be the effective nutrients in the prevention of these oxidative stress related diseases. Phenolic compounds, a specific group of secondary metabolites, play an important role in combating oxidative stress in the human body by maintaining a balance between oxidants and antioxidants. Phenolic compounds possess one or more aromatic rings with one or more hydroxyl groups, and generally are categorized as phenolic acids, flavonoids, coumarins, and tannins. Phenolic acids are derivatives of benzoic and cinnamic acids (**Fig. 1**) and are predominant phenolic acids found in plants. (Dykes & Rooney, 2007). The most common hydroxycinnamic acids are caffeic, p-coumaric and ferulic acids, which frequently occur in foods as simple esters with quinic acid or glucose. Probably the most well-known bound hydroxycinnamic acid is cholorogenic acid, which is combined from caffeic and quinic acids. Unlike hydroxycinnamates, hydroxybenzoic acid derivatives are mainly present in foods in the form of glucosides; p-hydroxybenzoic, vanillic and protocatechuic acids are the most common forms (Clifford, 1999; Herrmann, 1989; Manach *et al.*, 2004). Phenolic acids in plants have been

connected with diverse functions, including nutrient uptake, protein synthesis, enzyme activity, photosynthesis, structural components, and allelopathy. Cinnamic and benzoic acid derivatives exist in virtually all plant foods including fruits, vegetables, and grains and are physically dispersed throughout the plant in seeds, leaves, roots, and stems (Macheix, 1990; Shahidi, & Nacsk 1995). In addition to their roles in plants, phenolic compounds in our diet may provide health benefits associated with reduced risk of chronic diseases such as anti-allergenic, anti-atherogenic, anti-inflammatory, anti-microbial, antioxidant, anti-thrombotic, cardioprotective and vasodilatory effects (Manach *et al.*, 2005). The beneficial effects derived from phenolic compounds have been attributed by their antioxidant properties which can protect against degenerative diseases such as heart disease and cancer involved in reaction oxygen species (i.e., superoxide anion, hydroxyl radicals and peroxy radicals) (Heim *et al.*, 2002). Likewise, the epidemiological evidence clearly shows that the strong inverse association between the intake of carotenoids such as α-carotene, β-carotene and lycopene, and the risk of several cancers, especially prostate, lung and stomach (Van Poppel & Goldbohm, 1995; Greenwald & McDonald, 1999; Giovannucci, 1999). In reality, carotenoids may be acting merely as surrogate measures of fruit and vegetables and it is other components of these foods that prevent cancer (Temple, 2000).

Cereals are the most important food for human in the world. Wheat, maize, rice and barley are the world's four major agricultural cereal grains in which three cereals (wheat, maize and rice) together comprise at least 75% of the world's grain production (Harlan, 1992). In addition, eight cereal grains: wheat, maize, rice, barley, sorghum, oats, rye, and millet provide 56% of the food energy and 50% of the protein consumed on earth (Stoskopf, 1985). Along with providing

the major caloric and protein source for humanity, recent researches indicate that cereal grains contain significant amounts of phenolic compounds which are related to reduced risk of chronic diseases (Hung & Hatcher, 2011; Liyana-Pathirana & Shahidi, 2006; Liyana-Pathirana & Shahidi, 2007; Farnochi *et al.*, 2005; Aguilar-Garcia *et al.*, 2007). These publications only reported the information of phenolic compounds and their antioxidants of individual cereal, while few papers reviewing about the existence and quantification of phenolic compounds and their antioxidants in all cereals have been done (Dykes and Rooney, 2007). Therefore, the objective of this paper focuses on recent researches on the phenolic compounds and their antioxidants of the major cereals to see the significant contribution of these cereals to human health.

WHEAT ANTIOXIDANTS

Wheat (*Triticum aestivum* L.) is one of the most important cereal grains in the world because of the universal use of wheat for a wide range of products such as bread, noodles, cakes, biscuits, cookies, etc. Wheat kernel is composed of endosperm (81–84%), bran (14–16%), and germ (2–3%) (Pomeranz, 1988). Endosperm is the inner part playing a role as storage of energy (starch) and functioning protein (gluten components). Bran is the outer layer protecting the grain and germ is the kernel's reproduction system. Wheat endosperm contains mostly starch and protein, whereas bran and germ are rich in dietary fiber, minerals and phytochemicals which play important roles in nutrition and health benefits for humans (Pomeranz, 1988). Therefore, the customers are strongly recommended to consume whole wheat flour and its related products. The significant health benefits are derived from the important diets in bran and germ such as dietary

fiber or phenolic acids. The results of TPCs in different milling fractions of wheat grains are shown in **Fig. 2**. The TPC of bran/germ fractions (2867-3120 μmol of gallic acid equiv/100 g) was 15-18-fold higher ($p < 0.01$) than that of respective endosperm fractions (176-195 μmol of gallic acid equiv/100 g of flour) in the five wheat samples tested (Adom *et al.*, 2005). Recently, the gradual milling method has been developed to grade whole grains from outer to inner parts without removal of germ and bran using a modified Japanese rice-polisher (Hayashi *et al.*, 1991). The graded flour fractions containing large amounts of nutrients such as dietary fibers and minerals were considered as the sources of nutrition for human beings (Maeda, 2001). Hung *et al.* (2009) reported that the graded flour fractions milled from the outer parts of grain contained significantly higher amount of phenolics and exhibited significantly higher antioxidant capacity than did the whole grain. Likewise, the inner flour fractions milled from mostly endosperm part had significantly higher amount of phenolics and exhibited significantly higher antioxidant capacity than did the white flour, which was milled by a conventional milling method. In addition, the roller milling method with or without debranning have been reported to increase the amount of phenolic compounds and improve antioxidant activity of the pearled wheat fractions (Beta *et al.*, 2005). Phenolic acids existed in cereal grains in free, soluble conjugate and insoluble bound forms. Organic solvents such as ethanol, methanol and acetone may be employed to extract the free and soluble conjugate phenolic acids, whereas bound phenolics may be released by alkali, acid, or enzymatic treatment of samples prior to extraction (Sosulski *et al.*, 1982; Krygier *et al.*, 1982a; Krygier *et al.*, 1982b; Andreasen **et al.**, 2001; Zupfer *et al.*, 1998; Bartolome, & Gomez-Cordoves, 1999). The previous studies reported that phenolic acids in wheat grains are mostly in the bound form and exist in bran associated with cell wall materials

(Adom & Liu, 2002; Liyana-Pathirana *et al.*, 2006). The bound phenolics were considered to have more health benefits because they may escape from upper gastrointestinal digestion conditions along with cell wall materials and are absorbed into blood plasma during digestion of intestinal microflora (Andreasen *et al.*, 2001). Therefore, the increased consumption of the outer layer fractions of wheat grains might increase in an amount of the bound phenolics absorbed. During germination of wheat, free phenolic acids in wheat increased, whereas bound phenolic acids significantly decreased. However, the steeped, then incubated sub-samples, in two Canadian wheat classes, Canadian Western Red Spring (CWRS) and Canadian Western Amber Durum (CWAD), exhibited significantly greater TPCs than their corresponding non-germinated sub-samples (Hung *et al.*, 2011). Thus, the germinated wheats exhibits better nutritional properties than un-germinated wheat and could be used to improve the nutrition value in food products

Phenolic acids in cereal grain extracts can be detected by liquid chromatography system. A high pressure chromatography system (HPLC) has been commonly employed to detect the phenolic acids in wheat extracts (Kim *et al.*, 2006; Hatcher and Kruger, 1997). Recently, the first report on the application of an ultra-performance liquid chromatography (UPLC) for the rapid separation and quantification of simple phenolic acids in wheat extract replacing the traditional high pressure liquid chromatography system (HPLC) has been published (Hung *et al.*, 2011). The UPLC system was developed by Waters Corp. to use sub 3-µm-particle chromatography columns resulting in analyses with short running time, high sensitivity and resolution. The UPLC system used includes a binary solvent manager which delivers up to 15,000 psi pressure, a photodiode array (PDA) detector with a spectra in a range of between 190 and 800 nm, a 1.8 lm

particle column and a sample manager with small injection volume used (0.5–5 μl). **Fig. 3** shows the typical chromatography of phenolic compounds extracted from the wheat flours and detected by the UPLC system. Twelve standards were separately detected in the running program for only 5 min (Fig. 1C) by using the UPLC system as compared to a 60-min running by a HPLC system reported by Kim *et al.* (2006). The main phenolic compound detected in wheats extracted by an aqueous of 80% ethanol was syringic acid, whereas the main phenolic compound detected in the extracts by alkaline hydrolysis was ferulic acid. These results confirm that the hydroxybenzoic acid derivatives can be easily extracted using alcohol, whereas the hydroxycinnamic acid derivatives are released from the bound form by alkaline hydrolysis. Using 80% aqueous ethanolic extraction, five phenolic compounds were found in wheat varieties with a decreasing order of syringic>sinapic>ferulic>coumaric>caffeic, whereas The phenolic profile of CWRS and CWAD flours after alkaline hydrolysis includes seven compounds with a decreasing order of ferulic>sinapic>vanillic>4-hydroxybenzoic>p-coumaric>syringic>ceffeic (Hung *et al.*, 2011). However, the phenolic acids in wheats were found to vary among the published reports which might be due to the different condition of extraction and chromatography system (Hung *et al.*, 2011; Liyana-Pathirana *et al.*, 2006; Hatcher *et al.*, 1997; Mattila *et al.*, 2005; Zhou *et al.*, 2004; Solsulski *et al.*, 1982).

The antioxidant activity of phenolic fractions was evaluated using Trolox equivalent antioxidant capacity (TEAC), 2,2-diphenyl-1-picrylhydrazyl radical scavenging (DPPH), reducing power, oxygen radical absorbance capacity (ORAC), inhibition of oxidation of human low-density lipoprotein cholesterol (LDL) and DNA, Rancimat, inhibition of photochemilumenescence (PCL), and iron(II) chelation activity (Liyana-Pathirana *et al.*, 2006).

In the methods of ORAC, PCL, and Rancimat, wheat phenolics may act as free radical scavengers by donating a hydrogen atom. In assays that determine the ability to inhibit LDL and DNA oxidation by wheat phenolics, the antioxidative properties may be rendered by both hydrogen donation and/or metal chelation. Wheat phenolics appeared to serve as powerful antioxidants by radical scavenging and/or metal chelation in a consistent manner. The antioxidant capacity is positively correlated to the TPCs of wheat extracts. The extracts with higher phenolic contents exhibited the stronger antioxidant capacity than the lower one. Liyana-Pathirana *et al.* (2006) reported that the 10% byproduct from the pearling of wheat demonstrated the highest antioxidant activity. Subsequent removal of external layers resulted in a decrease in phenolic content with concurrent lower antioxidant activity values for higher degrees of pearling. Likewise, Hung *et al.* (2009) reported that all fractions contained a part of bran by gradual milling resulting in improvement of antioxidant capacity of these flours as compared to the white flour. In addition, the bound phenolic extracts of wheats exhibited higher antioxidant capacity than did the free phenolic extracts. The total antioxidant capacity of all graded milling fractions were mainly contributed by the bound phenolic extracts (72.5 - 83.2%), which mostly existed in the outer fractions rather than the inner fractions of wheat grain. As phenolic compounds are concentrated in the outermost layers, the bran fractions resulting from pearling may be used as a natural source of antioxidants and as value-added products in the preparation of functional food ingredients or for enrichment of certain products (Liyana-Pathirana *et al.*, 2006).

CORN ANTIOXIDANTS

Corn (*Zea mays* L.) is a major staple food in the world after wheat and rice, providing nutrients for humans and animals and serving as a basic raw material for the production of starch, oil and protein, alcoholic beverages, food sweeteners and, more recently, fuel. The kernels are often white or yellow in colour, although black, red and a mixture of colours are also found. There are a number of grain types, distinguished by differences in the chemical compounds deposited or stored in the kernel. White maize is biologically and genetically very similar to yellow maize, although there is a difference in appearance due to the absence of carotin oil pigments in the kernel which otherwise cause the yellow colour of the grain (FAO, 1992). In addition, mutant corn genotypes with different amylose contents (typical, waxy and high-amylose maize) have been genetically developed.

Corn has a greater total phenolic content (TPC) and total antioxidant activity than do wheat, oats, and rice. TPC of corn extract was 15.55 ± 0.60 mmol of gallic acid equiv/g of grain, which was higher than that of wheat (7.99 ± 0.39 μmol of gallic acid equiv/g of grain), oats (6.53 ± 0.19 μmol of gallic acid equiv/g of grain), and rice (5.56 ± 0.17 μmol of gallic acid equiv/g of grain). The bound phenolics were also found to be significantly higher than free phenolics in corn extract. About 69% of the total phenolics present in corn is in the insoluble bound forms, with ferulic acid being the major phenolic compound present. The bound phenolic content was also highest for corn (13.43 ± 0.59 μmol/g of grain), followed by wheat (6.10 ± 0.39 μmol/g of grain) and then oats (4.76 ± 0.14 μmol/g of grain) (Adom et al., 2002). Li *et al.* (2007) studied on the phenolic contents and antioxidant capacity of their compounds extracted from the typical and mutant corn genotypes and reported that the TPCs in the mutant corns were higher than the amount found in the typical corn in all extraction (methanol, HCl/methanol extraction and

alkaline hydrolysates). The TPC was found to be greater in alkaline hydrolysates than in methanol and HCl/methanol extracts and high-amylose corn (F4-HA) had the highest TPC among the genotypes. The phenolic acids found in corn genotypes included *p*-hydroxybenzoic, vanillic, cafefic, syringic, *p*-coumaic, *m*-coumaric, *o*-coumaric, and ferulic acids, in which ferulic acid was the predominant phenolic acid present in all four types of corn. Other major phenolic acids were *o*-coumaric acid (126.53-575.87 mg/kg) and *p*-coumaric (97.87-211.03 mg/kg) present in corn. Free and bound ferulic acids in corn were higher than those of wheat, rice and oat (Adom *et al.*, 2002), whereas mutant corns were found to have greater ferulic acid levels than their typical parents. The total antioxidant activity of corn was the highest ($p < 0.01$) of those of the grains tested including corn, wheat, oat and rice. Free phenolic compounds were the major contributors to the total antioxidant activity in methanol and HCl/methanol extracts, whereas bound phytochemicals were responsible for the free radical scavenging activity of alkaline hydrolysates (Li *et al.*, 2007). The total antioxidant activity of the bound extraction highly correlated with phenolic content ($R^2 = 0.991$, $p < 0.01$) and ferulic acid content ($R^2 = 0.999$, $p < 0.01$), while there was a low correlation between parameters measured for free extracts (Adom *et al.*, 2002). For the mutant corn genotypes, the high-amylose corn had a better antioxidant capacity than did typical (nonmutant) corn genotypes (Li *et al.*, 2007). In addition, purple pigmented corn kernels are very rich in anthocyanins with well established antioxidant and bioactive properties (Tsuda *et al.*, 2003). Also, the total antioxidant activity of sweet corn becomes elevated by 44% after thermal processing (Dewanto *et al.*, 2002).

RICE ANTIOXIDANTS

Rice is one of the oldest food crops in the world. Most of the rice varieties cultivated today belong to the species, *Oryza sativa* L. Rice harvested from the field is called paddy. The paddy consists of the hull and the rice caryopsis, also known as brown rice. The brown rice is the edible part of the rice grain and furthermore milled into white rice and bran. The white rice is starchy endosperm part of rice grain, which mostly contains carbohydrate and protein, whereas rice bran consists of germ, pericarp, aleurone cells and seed coat, which is rich in dietary fibers, minerals and B vitamins. Rice bran also contains high levels of several phytochemicals such as vitamin E and γ-oryzanol fractions that have antioxidant activities and health-related benefits. **Fig. 4** shows the structures of vitamin E and *γ*-oryzanol components in rice bran analyzed by liquid chromatography/mass spectrometry/mass spectrometry (Yu *et al.*, 2007). A natural form of vitamin E in rice bran consists of eight homologues, four of which are tocopherols and the other four comprising tocotrienols (Jariwalla, 2001). Gamma-oryzanol is a mixture of ferulic acid esters of triterpene alcohols and sterols (Evershed *et al.*, 1988; Diack, & Saska, 1994; Rogers *et al.*, 1993; Xu, & Godber, 1999). Both *γ*-oryzanol and vitamin E in rice bran had significant antioxidant activities, which protect cells from the oxidative damage of plasma very low-density lipoprotein, cellular proteins and DNA and from membrane degeneration (Akihisa *et al.*, 2000; Topinka *et al.*, 1989; Xu *et al.*, 2001). Among the vitamin-E homologues, α-tocotrienol has known to have more than three times the in vitro free radical scavenging activity of α-tocopherol (Packer, 1995). Tocotrienols have also reported to have significantly health benefits in inhibiting cholesterol synthesis, lowering serum-cholesterol levels in various animal models, and

suppressing tumor-cell proliferation (Qureshi *et al.*, 2000). In addition, γ-oryzanol has been found to be 13 to 20 times (w/w) greater content in rice bran than total tocopherols and tocotrienols (Bergman and Xu, 2003) and has reported to decrease animal serum-cholesterol levels, have anti-inflammatory activity, and inhibit cholesterol oxidation in vitro (Rong *et al.*, 1997; Akihisa *et al.*, 2000; Xu *et al.*, 2001).

The phenolic profiles of both brown and milled rice were dominated by ferulic and p-coumaric acids with lesser amounts of gallic, vanillic, caffeic and syringic acids. The total phenolic acids in the ‘‘bran’’ (calculated as the difference in contents of brown and milled rice) typically contributed 70–90% of the total phenolic acids in the grain, depending on cultivar and the particular phenolic acid. These results suggest that the concentrations of phenolic acids increased from endosperm to the aleurone (Zhou *et al.*, 2004). The free phenolic content of rice was lower than that of corn but higher than those of wheat and oat. However, rice had the lowest bound phenolic content as compared to other grains (Adom *et al.*, 2002). Ferulic acid was the dominant phenolic acid, both in total and bound states, in brown and milled rice, followed by p-coumaric acid (Zhou *et al.*, 2004). The antioxidant capacity of the rice extracts, both in the bound and total phenolics, was the lowest compared to that of corn, wheat or oat. The lowest antioxidant activity of rice extracts compared to those of other cereals was due to the low amount of phenolic acids, ferulic and p-coumaric acids, in the bound phenolic extracts (Adom *et al.*, 2002). However, the total antioxidants in rice are significantly contributed by tocopherols, tocotrienol and γ-oryzanol, which has not been examined by Adom and Liu (2002). Thus, brown rice and rice bran containing large amount of phytochemicals derived from the outer layer of rice grain are considered to have significantly impact on human health. The brown rice should

be consumed instead of the white rice and the extracts of rice bran and its oil could be used as a functional food or as additives to improve the storage stability of foods.

BARLEY ANTIOXIDANTS

Barley (*Hordeum* V*ulgare* L.) is one of the first agricultural domesticates together with wheat, pea, lentils dating from about 10,000 years ago (Smith, 1998). It is the fourth most important cereal in the world in terms of world production after wheat, rice and corn. Barley has been known to be used in the beer industry, malting and animal feed with 80-90% of barley production is used for malting and animal feedstocks (Baik, & Ullrich, 2008). Recently, barley is considered to be used as an ingredient for production of functional foods (Holtekjolen *et al.*, 2008) due to its high contents of bioactive compounds such as β-glucans, tocopherols, tocotrienols (Jadhav *et al.*, 1998) and many classes of phenolic compounds such as benzoic and cinnamic acid derivatives, proanthocyanidins, quinones, flavonols, chalcones, flavones, flavanones and amino phenolic compounds (Goupy *et al.*, 1999; Hernanz *et al.*, 2001). The abundant content of phenolic compounds in barley reveals that it may serve as an excellent dietary source of natural antioxidants with antiradical and antiproliferative potentials for disease prevention and health promotion (Madhujith & Shahidi, 2007; Zhao *et al.*, 2008).

Like other cereals, the content of insoluble-bound phenolics was significantly higher than those of soluble conjugate and free phenolic fractions among all barley extracts tested as evaluated by Madhujith and Shahidi (2009). Free phenolic content ranged from 0.18 to 0.42 mg ferulic acid equivalents per gram defatted material while soluble conjugates ranged from 0.42 to 0.81 mg ferulic acid equivalents per gram of defatted material and insoluble-bound fraction

ranged from 2.03 to 3.36 mg ferulic acid equivalents per gram of defatted material. The TPC of barley grains is also concentrated in bran other than the endosperm part. The TPCs of the pearling byproducts decreased when moving from the outermost layer to the center of the barley grain. The outermost layer (F1), which is basically the bran, contained the highest TPC while F2 also showed a significantly higher TPC compared to the rest of the inner fractions (Madhujith *et al.*, 2006). Sharma and Gujral (2010) also reported that the TPC in barley bran was highest followed by whole flour and refined flour in all the germinated and ungerminated samples. In whole flour the TPC was less compared to the bran as the endosperm diluted the concentration of phenolic compounds from the outer layers. A similar effect was also observed for the refined flour that showed the lowest TPC as compared to the bran and the whole flour.

Phenolic acids from 30 barley varieties (combination of hulled/hulless/two-row/six-row/regular/waxy) were investigated by HPLC following four different sample treatments have been reported by Yu *et al.* (2001). Seven major phenolic acids including the benzoic acid (*p*-hydroxybenzoic, vanillic, and protocatechuic acids) and cinnamic acid derivatives (coumaric, caffeic, ferulic, and chlorogenic acids) were found in the barley varieties. *p*-Hydroxybenzoic acid was the major phenolic acid in the 30 barley varieties studied by using acid, α-amylase, and cellulase hydrolysis treatments, followed by ferulic acid. By hot water extraction, the protocatechuic acid and chlorogenic acid were the two major compounds that existed in free form in barley grain even though their concentrations were very low (<2.9 μg/g for protocatechuic acid and <16.3 μg/g for chlorogenic acid). After acid hydrolysis, the concentrations of protocatechuic, vanillic, chlorogenic, and ferulic acids could be quantified. On the other hand, *p*-hydroxybenzoic, caffeic, and *p*-coumaric acids could be detected but not

quantified because of poor resolution or low levels of those compounds. After acid hydrolysis with α-amylase hydrolysis, a better separation for all phenolic acids in the complex medium was obtained. All six phenolic acids could be separated except for protocatechuic acid. The treatment combining acid, α-amylase, and cellulase yielded the highest concentration for most phenolic acids, indicating that most phenolic acids in barley are primarily bound to other grain components (for example, starch, cellulose, *β*-glucan, pentosans, and others) (Yu *et al.*, 2001). In another study, Kim *et al.* (2007) has found 17 phenolic acids and 7 flavonoids present in 127 lines of colored (black, blue, and purple) barley (**Table 1**). In the tested barley, chlorogenic acid and phloroglucinol were present in hulled and unhulled groups as the major compounds, respectively. All barley groups had very low concentrations of syringic acid, *o*-hydroxyphenylacetic acid, ferulic acid, and 3,4-dimethoxybenzoic acid. The concentrations of phloroglucinol acid, vanillic acid, syringic acid, *o*-hydroxyphenylacetic acid, 3,4-dimethoxybenzoic acid, salicylic acid, and *o*-coumaric acid in the blue and purple groups were significantly higher than those in the black groups.

There are a number of publications reported on the antioxidant capacity of phenolic extracts from barley in the literature (Goupy *et al.*, 1999; Kim *et al.*, 2007; Madhujith *et al.*, 2006; Madhujith *et al.*, 2007; Madhujith *et al.*, 2009; Zhao *et al.*, 2008). The insoluble phenolic fraction exhibited significantly higher TEAC and ORAC values and DPPH radical scavenging capacity than the free, soluble conjugate phenolic fractions of barley extracts. A similar trend was observed against inhibition of LDL cholesterol oxidation and radical-induced DNA breakage (Madhujith *et al.*, 2009). The antioxidant and antiradical activities are mainly concentrated in the outer fractions (F1-F3 fractions), which are counted approximately up to 25%

of the grain on weight basis (Madhujith *et al.*, 2006). In colored barley, the DPPH radical scavenging activities varied from 46.4 to 86.3%. Average radical scavenging activity in the unhulled barley groups (66.5%) was higher than that of hulled barley (63.5%). Although the total concentration of anthocyanins in the colored barley varied among the tested groups, the radical scavenging activity among colored barley groups was not significantly different. This results indicate that antioxidant capacity of the colored barley is related to the concentration of phenolic compounds such as chlorogenic acid, 3,4-dimethoxybenzoic acid, homogentisic acid, protocatechuic acid, and rutin (Kim *et al.*, 2007). Zhao *et al.* (2008) also reported that the TPC showed strong correlations with DPPH radical scavenging activity, ABTS radical cation scavenging activity, and reducing power ($P < 0.01$), whereas its correlations with superoxide anion radical scavenging activity and metal chelating activity were poor ($P > 0.05$) using the Pearson correlation analysis.

ANTIOXIDANTS OF OTHER CEREALS

Other cereals such as sorghum, oats, rye, and millet have also contributed to supply the major caloric and protein source for humanity and are main materials for food and non-food processing due to their high production in the world. In addition, these cereals have been reported to have significantly antioxidant capacity associated with the health benefits. Therefore, it is very important to evaluate TPCs of these cereals and their antioxidant capacity.

Sorghum (*Sorghum bicolor* M.) is the fifth leading cereal food crop in the world and is particularly important as a human food resource in Asia and Africa (Rooney & Waniska, 2000). Sorghum is a rich source of various phytochemicals including tannins, phenolic acids,

anthocyanins, phytosterols and policosanols (Awika & Rooney, 2004). Tannin content of sorghum grain ranged from 10.0 – 68.0 mg/g (Awika *et al.*, 2004), in which only sorghums containing a pigmented testa had significant amounts of condensed tannins (Dykes *et al.*, 2005). Like other cereals such as wheat, corn and barley, the sorghum phenolic compounds are mostly concentrated in the bran and in bound forms. Ferulic acid is the most abundant bound phenolic acid in sorghum (Hahn *et al.*, 1983), while other phenolic acids including syringic, protocatechuic, caffeic, p-coumaric, and sinapic are also found in sorghum as the more abundant (Waniska *et al.*, 1989). The most common anthocyanins in sorghums are the 3-deoxyanthocyanidins, which include orange luteolinidin and yellow apigeninidin. Both compounds have good potential for use as natural colorants due to their pH stability (Dykes *et al.*, 2005). Recently, a number of studies on health-related benefits of sorghum reported that sorghum has significantly antioxidant activity (Choi *et al.*, 2006), antimicrobial activities (Kil *et al.*, 2009), anticarcinogenic effects (Kwak *et al.*, 2004), and cholesterol-lowering effects (Ha *et al.*, 1998), and can reduce the risk of cardiovascular disease (Cho *et al.*, 2000).

Rye (*Secale cereale L.*) is a grass grown extensively as a grain and as a forage crop with low requirements regarding soil and fertilization, as well as a relatively good overwinter ability. Therefore, it is grown primarily in Eastern, Central and Northern Europe (Salovaara & Autio, 2001). Rye grain, like other cereal grains, contributes significant quantities of energy, protein, selected micronutrients and non-nutrients to a human diet (Edge *et al.*, 2005). Therefore, it is widely used for flour, rye bread, rye beer, some whiskeys, some vodkas, and animal fodder. Phytochemicals of rye include tocopherols and tocotrienols (Zielinski *et al.*, 2007), phenolic acids and ferulic acid dehydrodimers (Andreasen *et al.*, 2000), and alkylresorcinols (Gliwa *et al.*,

2011). Tocopherol contents in rye ranged from 2.43 – 10.2 μg/g (db) with the main tocopherols were α-tocopherol and β-tocopherol. The whole grain contained higher tocopherol content than did endosperm with embryo or pericarb with testa. Tocotrienol contents with only α- tocotrienol and then β- tocotrienol ranged from 9.53 – 28.8 μg/g (db), in which tocotrienol contents of the whole grains and the fraction of endosperm with embryo of the investigated cultivars were twice as low as that of pericarb and testa fraction (Zielinski *et al.*, 2007). Total phenolic content of rye is in a range of 2.16 – 4.01 mg/g (db), in which the pericarb with testa fraction was about twice richer in TPC than was the endosperm with embryo fraction or the whole grain (Zielinski *et al.*, 2007). The phenolic acids existed in rye grain include ferulic, sinapic, *p*-coumaric, caffeic, *p*-hydroxybenzoic, protocatechuic, and vanillic acids. The concentration of ferulic acid, the most abundant phenolic acid, ranged from 900 to 1170 μg/g dry matter, followed by sinapic acid ranging from 70 to 140 μg/g dry matter, *p*-coumaric acid ranging from 40 to 70 μg/g dry matter, and caffeic, *p*-hydroxybenzoic, protocatechuic, and vanillic acids, which were all detected in concentrations less than 20 μg/g dry matter (Andreasen *et al.*, 2000). The highly positive correlation coefficient between the TPCs and antioxidant capacity of the whole grains, pericarb with testa fractions and endosperm with embryo fractions of rye were also observed. The results obtained indicate the possibility of using antioxidant contents and antioxidant properties of pericarb with testa fraction, rather than these of the whole grain, for the selection of rye variety of high technological quality (Zielinski *et al.*, 2007). Andreasen *et al.* (2001) reported that the most abundant phenolic acids in rye, ferulic acid, sinapic acid, and the dimer 8-*O*-4-diFA, exert antioxidant activity to inhibit low-density lipoprotein (LDL) oxidation in vitro. The rye bran extracts highly inhibited LDL lipid oxidation rather than the whole flour extract.

Alkylresorcinols (ARs), compounds which were demonstrated to occur in cereal grains and related materials such as whole-grain cereal products, are similar to tocopherols except that they have a straight aliphatic hydrocarbon side chain and a single phenolic ring (**Fig. 5**). ARs are well-known antioxidants, which also possess antimicrobial, antibacterial, antifungal, and antitumor activities (Kozubek & Tyman, 1999). In rye bran, and the presence of AR homologues C15:0, C17:0, C19:0, C21:0, C23:0, and C25:0 was confirmed, in which the AR homologue C19:0 was the most common and C15:0 was the least common (Gliwa *et al.*, 2011). Rye bran is known to have a high amount of ARs compared to the inner part of rye grain. ARs in rye bran is a range of 360 - 3200 μg/g, higher than those of triticale (580 - 1630 μg/g), wheat (317 - 1010 μg/g), and barley (44 - 500 μg/g) (Ross *et al.*, 2003). DPPH radical reduction varied from ~10% to ~60% for the rye bran alkylresorcinol homologues (C15:0–C25:0) at concentrations from 5 to 300 μM and was not dependent on the length of the alkyl side chain of the particular homologue. Values of EC_{50} for all the alkylresorcinol homologues were significantly higher than those for Trolox and α-, δ-, and γ-tocopherols, compounds with well-defined antioxidant activity and used as positive controls (Korycinska *et al.*, 2009). The antioxidant activity using oxygen radical absorbance capacity (ORAC) of rye extracts decreased from the outermost fraction to the innermost fraction. From a comparison of the results for antioxidant properties obtained using the ORAC assay and the total amount of ARs using GC-MS, it is confirmed that ARs are in fact the components that give rye its antioxidant activity (Gliwa *et al.*, 2011).

Oat (*Avena sativa L.*) and millet (*Eleusine coracana*) are also rich in phenolic compounds which possess antioxidant capacity. Phenolic acids of the oat are *p*-hydroxybenzoic acid, vanillic acid, caffeic acid, vanillin, *p*-coumaric acid, and ferulic acid (Emmons *et al.*, 1999), whereas

diadzene, gallic, coumaric, syringic and vanillic acids were identified as major phenolic acids from the extracted phenolics of the millet (Viswanath *et al.*, 2009). In addition, three avenanthramides and an unidentified ferulate derivative were also detected in oat extracts (Emmons *et al.*, 1999). Phenolic compounds in oat and millet are also concentrated in outer layer (bran) of grains. Like other cereal grains, the extracts of oat and millet also exhibited significantly antioxidant capacity, which was correlated with measures of oxygen radical absorbance capacity and low-density lipoprotein oxidation. The millet extract also showed higher antimicrobial activity against *Bacillus cereus* and *Aspergillus flavus*. Total phenolic content of the phenolic extracts of both oat and millet was significantly positively correlated with antioxidant activity (Emmons *et al.*, 1999; Viswanath *et al.*, 2009). In addition, avenanthramides, substituted *N*-cinnamoylanthranilate alkaloids isolated only from oats, have also shown antioxidant activity in an *in vitro* linoleic acid oxidation system (Dimberg *et al.*, 1993).

CONCLUSION

In all cereals, phenolic compounds are found mostly in the outer layer rather than in the endosperm. Therefore, the extracts from the bran always contained higher total phenolic contents as compared to the endosperm. The highly positive correlation between TPCs and antioxidant activity of the phenolic extracts were observed in literature. Ferulic acid was abundant acid in the bound form of the wheat, corn, rice, sorghum and rye, whereas *p*-hydroxybenzoic is the major acid in the barley and oat, and diadzene is dominant acid in the millet. The phenolic extracts from cereal grains exhibit significantly antioxidant capacity evaluated using trolox equivalent antioxidant capacity, 2,2-diphenyl-1-picrylhydrazyl radical scavenging, reducing power, oxygen

radical absorbance capacity, inhibition of oxidation of human low-density lipoprotein cholesterol and DNA, Rancimat, inhibition of photochemilumenescence, and iron(II) chelation activity. Nowadays, the whole grain and whole-grain products are encouraged to consume instead of the white flour because they contain large amount of nutrients such as dietary fibers, vitamins, minerals and phytochemicals derived from the outer layer of grains. The consumption of whole grains is considered to have significantly health benefits in prevention from chronic diseases such as cardiovascular disease, diabetes, and cancer. In addition, the extracts from the bran is considered to be used as a source of natural antioxidants, which can be used to produce functional foods or used as additives in food storage.

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Fig.1. Basic of (a) hydroxyhydroxybenzoic and (b) hydroxycinnamic acid derivatives

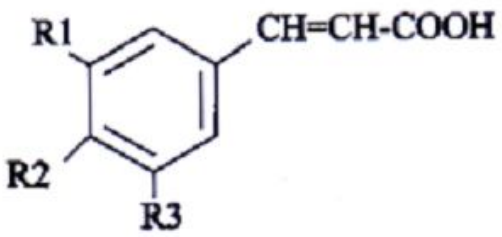
Fig. 2. Total phenolic content of milled fractions of wheat varieties (Adapted with permission from Adom et al. (2005). Copyright ©2005 American Chemical Society).

Fig. 3. Typical chromatography for phenolic compounds from alcohol extract (A), alkaline extract (B) and a mixed standard (C) detected at 280 nm. 1, Gallic acid; 2, Protocatechuic acid; 3, 4-Hydroxybezoic acid; 4, Gentisic acid; 5, Vanillic acid; 6, Syringic acid; 7, p-Coumaric acid; 8, Ferulic acid; 9, Sinapic acid; 10, Rutin; 11, Quercetin.

Fig. 4. Structures of vitamin E and g-oryzanol components. 7a, β-tocotrienol; 7b, γ-tocotrienol; 9, δ-tocopherol; 10, γ-tocopherol; 11, α-tocopherol; 3, (24S)-cycloart-25-ene-3*β*,24-diol-3*β*-trans-ferulate; 4, (24R)-cycloart-25-ene-3*β*,24-diol-3*β*-trans-ferulate; 6, cycloart-23Z-ene-3*β*,25-diol-3*β*-trans-ferulate; 12, cycloartenol trans-ferulate; 14, campesterol trans-ferulates; 15, 24-methylenecycloartanol trans-ferulate; 16, sitosterol trans-ferulate; 17, stigmastanol trans-ferulate (Adapted with permission from Yu et al. (2007). Copyright ©2007 American Chemical Society).

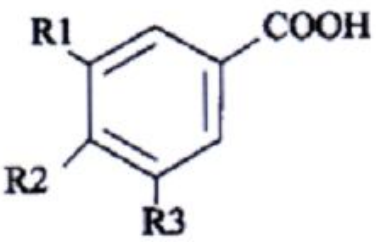
Fig. 5. Chemical structure of the alkylresorcinols. R - the alkyl side chain. R = 15, 5-n-pentadecylresorcinol (C15:0); R = 17, 5-n-heptadecylresorcinol (C17:0); R = 19, 5-n-nonadecylresorcinol (C19:0); R = 21, 5-n-heneicosylresorcinol (C21:0); R = 23, 5-n-tricosylresorcinol (C23:0); R = 25, 5-npentacosylresorcinol (C25:0)

a



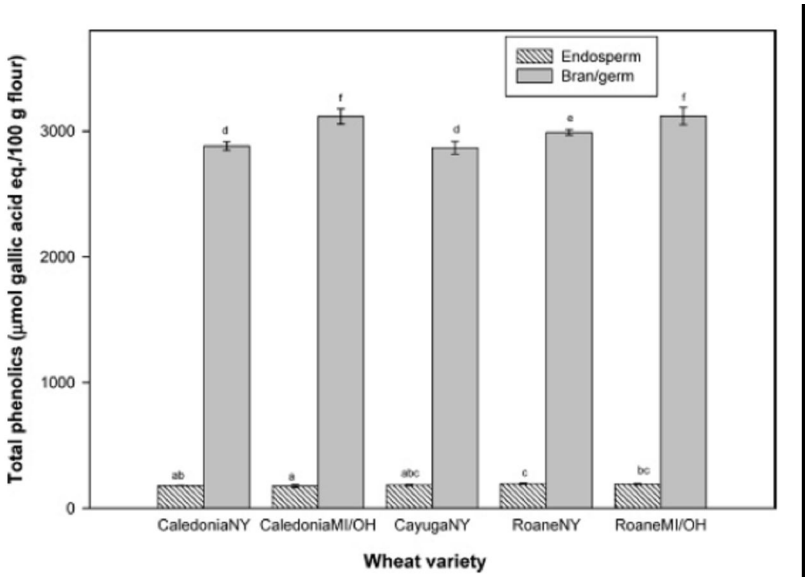
R1	R2	R3	Compound
H	OH	H	*p*-Hydroxybenzoic acid
OH	OH	OH	Gallic acid
H	OH	OH	Protocatechuic scid

b



R1	R2	R3	Compound
H	OH	OH	Caffeic acid
CH_3O	OH	OH	Ferulic acid
H	OH	H	*p*-Coumaric acid

Fig.1. Basic of (a) hydroxyhydroxybenzoic and (b) hydroxycinnamic acid derivatives



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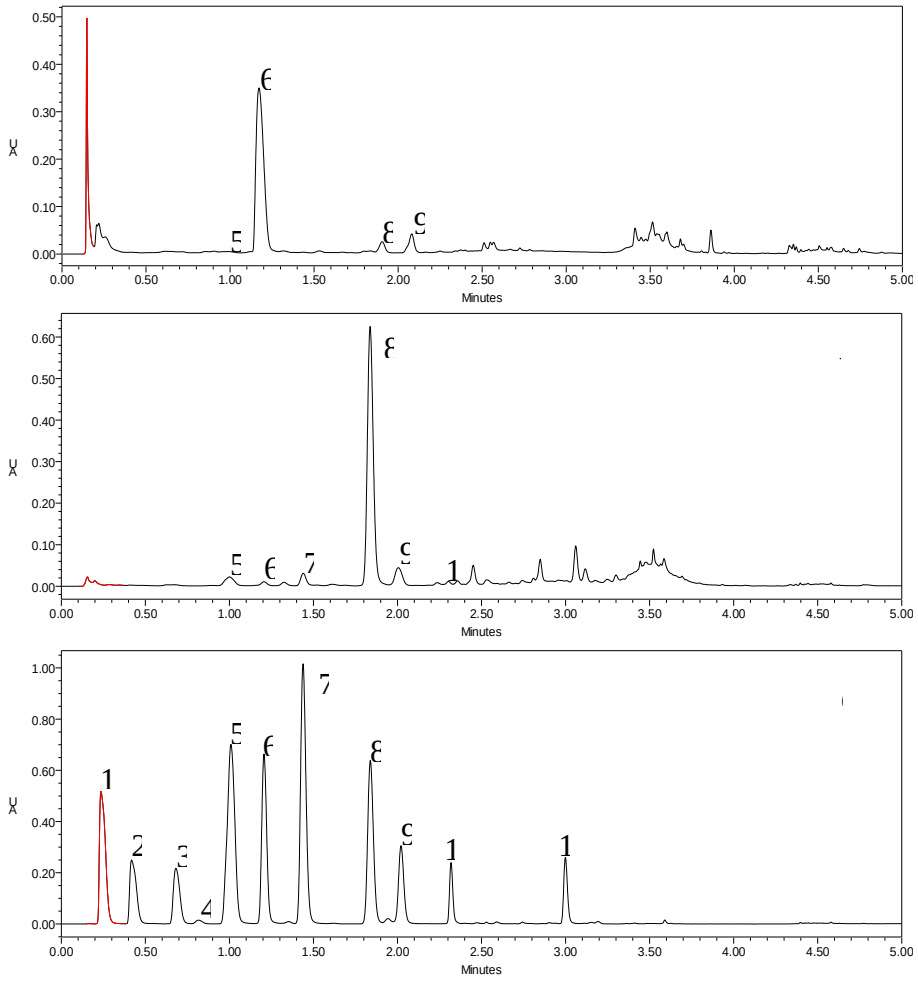

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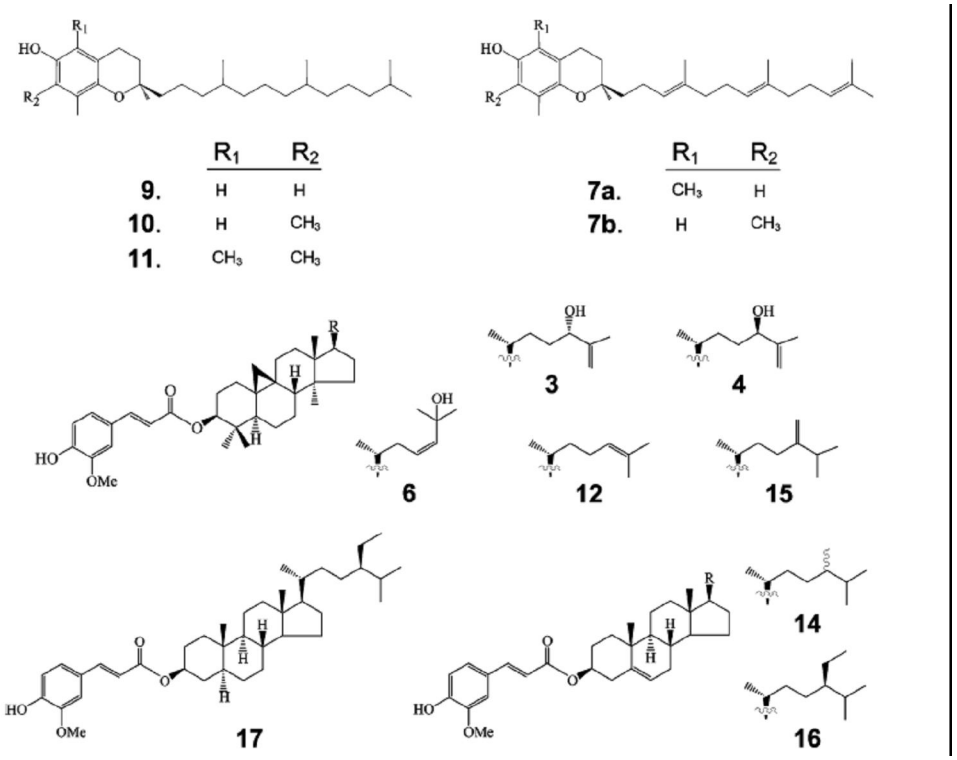

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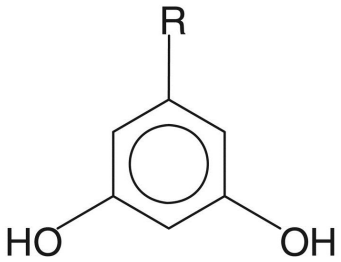

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Table 1. Total concentrations (microgram per gram) of phenolic compounds in coloured barley groups. (Reprinted with permission from Kim et al. (2007). Copyright© 2007 American Chemical Society)

	hulled				unhulled			LSD (0.05)
	black 1	black 2	black 3	purple	black	blue	purple	
Phenolic acids								
Phl[a]	2.4 ± 7.0d[b]	0.8 ± 2.8d	3.6 ± 10.4d	19.3 ± 27.3c	46.3 ± 21.4ab	52.8 ± 59.6a	34.2 ± 16.5bc	15.41
Gal	14.6 ± 0.5a	15.2 ± 0.9a	15.0 ± 1.0a	14.6 ± 0.5a	15.6 ± 0.9a	15.7 ± 13.3a	15.7 ± 1.6a	2.42
Pyr	15.7 ± 8.0a	19.7 ± 4.4a	23.3 ± 11.0a	15.2 ± 0.4a	21.8 ± 11.0a	22.2 ± 3.1a	22.5 ± 9.0a	8.96
Hom	5.5 ± 3.3c	7.8 ± 4.3abc	10.3 ± 4.5ab	7.2 ± 1.4ab	11.3 ± 5.1ab	11.9 ± 0.4a	9.8 ± 2.7ab	4.24
Pro	8.1 ± 6.6a	7.7 ± 5.4a	13.2 ± 5.7a	8.6 ± 1.8a	9.3 ± 1.7a	12.2 ± 7.4a	10.7 ± 7.0a	6.28
Chl	30.0 ± 7.1ab	33.3 ± 9.4ab	38.8 ± 12.7a	25.0 ± 2.6b	29.2 ± 6.2ab	35.6 ± 6.1a	30.6 ± 6.1ab	10.16
Res	4.5 ± 1.8b	4.0 ± 1.0b	5.1 ± 4.3b	6.3 ± 2.0b	4.0 ± 1.3b	19.5 ± 18.7a	4.1 ± 2.0b	4.18
Van	0.5 ± 0.8b	0.4 ± 0.5b	0.3 ± 0.8b	0.4 ± 0.6b	0.2 ± 0.3b	9.3 ± 9.0a	1.1 ± 1.4b	1.71
Syr		0.0 ± 0.1b				1.4 ± 1.1a	0.0 ± 0.2b	0.20
Caf	10.3 ± 2.3a	10.3 ± 2.5a	8.4 ± 4.8a	11.1 ± 0.5a	11.6 ± 1.1a	11.0 ± 0.4a	8.1 ± 5.1a	3.86
Hyd		0.1 ± 0.3a	0.1 ± 0.5a			0.1 ± 0.1a	0.2 ± 0.7a	0.43
pCo	3.4 ± 0.5ab	3.0 ± 0.4bc	2.9 ± 0.3cd	3.3 ± 0.3ab	2.6 ± 0.1d	3.5 ± 0.9a	2.7 ± 0.3cd	0.41
Fer	0.2 ± 0.3b	0.2 ± 0.2b	0.1 ± 0.2b			2.6 ± 3.5a		0.62
Dim	0.1 ± 0.3c	0.1 ± 0.3c	0.2 ± 0.4c	1.9 ± 2.6a		0.9 ± 1.3b	0.2 ± 0.4c	0.60
Sal	10.9 ± 6.9b	11.0 ± 7.0b	14.2 ± 4.3b	15.8 ± 0.7b	16.4 ± 0.6b	28.1 ± 15.3a	15.5 ± 4.1b	6.43
Ben	2.0 ± 3.5c	4.4 ± 7.6c	1.9 ± 1.6c	12.4 ± 9.5a	4.6 ± 6.3bc	9.2 ± 13.1ab	2.3 ± 5.4b	6.11
Co	4.1 ± 1.0c	3.8 ± 1.3c	4.5 ± 1.6c	10.4 ± 5.7a	4.3 ± 0.2bc	5.2 ± 1.2bc	7.5 ± 4.7b	2.46
total	112.3 ±	121.8 ±	142.0 ±	151.5 ±	177.2 ±	241.3 ±	165.2 ±	28.74

	23.6e	17.3cd	30.6cd	20.0bc	24.4b	62.2a	30.6bc	
Flavonoids								
Cat	17.7 ± 6.0ab	17.6 ± 6.7ab	16.7 ± 6.9ab	13.1 ± 3.3b	16.8 ± 6.1ab	23.8 ± 13.3a	20.0 ± 10.3ab	7.90
Rut	3.2 ± 1.7a	3.0 ± 1.4a	3.7 ± 2.2a	4.6 ± 1.2a	0.7 ± 1.1b	4.6 ± 2.9[a]	3.4 ± 2.7a	2.10
Nar	0.0 ± 0.0a	0.1 ± 0.2a	0.1 ± 0.2a				0.1 ± 0.2a	0.17
Hes	0.4 ± 1.3b	0.2 ± 0.7b	0.2 ± 0.8b	2.4 ± 3.4a		1.0 ± 1.5b	0.4 ± 1.0b	1.13
Myr	28.0 ± 1.1c	27.7 ± 1.0c	27.7 ± 1.1c	39.1 ± 1.6a	33.4 ± 8.6b	42.6 ± 16.0a	31.4 ± 2.2bc	4.29
Que	17.4 ± 1.1b	17.1 ± 3.0b	17.4 ± 0.7b	19.3 ± 2.0b	14.8 ± 6.0b	66.6 ± 69.8a	17.9 ± 1.6b	11.76
Kae	12.7 ± 2.0b	12.3 ± 0.6b	12.2 ± 0.9b	13.4 ± 2.1b	11.9 ± 0.2b	23.9 ± 16.9a	13.1 ± 2.3b	3.14
total	79.3 ± 8.4b	78.1 ± 7.9b	77.9 ± 7.9b	91.9 ± 19.9b	77.6 ± 10.2b	162.5 ± 98.3a	86.3 ± 12.8	18.99
total phenolic compounds	191.6 ± 26.2c	199.9 ± 20.2c	220.0 ± 34.7bc	243.4 ± 15.2b	254.7 ± 26.1b	403.8 ± 144.9a	251.4 ± 38.0b	39.02

[a]Phl, phloroglucinol; Gal, gallic acid; Pyr, pyrogallol; Hom, homogentisic acid; Pro, protocatechuic acid; Chl, chlorogenic acid; Res, β-resorcylic acid; Van, vanillic acid; Syr, syringic acid; Caf, caffeic acid; Hyd, o-hydroxyphenylacetic acid; pCo, p-coumaric aicd; Fer, ferulic acid; Dim, 3,4-dimethoxybezoic acid; Sal, salicylic acid; Ben, benzoic acid; oCo, o-coumaric acid; Cat, catechin; Rut, rutin; Nar, naringin; Hes, hesperidin; Myr, myricetin; Que, quercetin; Kae, kaempferol. [b]Mean in the same row with different letters are significantly different ($p < 0.05$).

