

# Chapter 1

## Important Antioxidant Phytochemicals in Agricultural Food Products

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### **Abstract**

Antioxidant phytochemicals are secondary plant metabolites widely present in the plant kingdom. Most of the phytochemicals are phenolic derivatives with monohydric or polyhydric phenols. Numerous clinical studies have confirmed that antioxidant phytochemicals can prevent some cholesterol-related and oxidation-induced chronic diseases. The antioxidant properties and health benefits of phytochemicals in different agricultural food plants have been intensively studied in recent years. This chapter will discuss the phytochemicals in common fruits, vegetables, and grains and their potential to reduce the risk of epidemiological disease. As more and more consumers are becoming concerned about health functions of foods, the information of this chapter will be useful for scientists in the food, plant breeding and physiology, medicine, and epidemiology areas to understand and utilize natural antioxidant phytochemicals in health-promoting food and other products.

*Keywords:* antioxidant; phytochemical; phenolic; polyphenolic; antioxidation; plants

### **1.1 Introduction**

Antioxidant phytochemicals generally possess one or more hydroxylated aromatic or phenolic rings, which contribute to their antioxidant

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activity. They are widely distributed in plants and synthesized by shikimate and chorismate biosynthesis from the essential precursor L-phenylalanine (Haslam, 1993; Herrmann, 1995). The synthesis reaction involves a series of deamination, enzymatic conversion, and enzymatic hydroxylation reactions, and generates a variety of the phytochemicals with one or more phenolic rings (Herrmann, 1989). Based on the number and pattern of phenolic rings in the structure, antioxidant phytochemicals may be simple structures such as phenolic acids, which have only one phenolic ring, or complicated polyphenolics and tannins, which have two or more than two phenolic rings, respectively. The phenolic phytochemicals can also link with different moieties, such as sugars, long carbon chains, and phytosterols to form complex phenolic derivatives. Thousands of phenolic derivative phytochemicals have been found in the plant kingdom. The major physiological function of antioxidant phytochemicals in plants is to defend against oxidative and environmental stress, such as UV radiation, microbes, pathogens, parasites, etc. (Croteau et al., 2000). Most phytochemicals are also responsible for the colors of plants. For example, anthocyanins, one class of polyphenolics are purple, black, or red pigments. In edible plants such as fruits and vegetables, phytochemicals also contribute to attributes like astringency, bitterness, or a spicy taste (Lule and Xia, 2005).

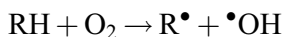
Phenolic acids, derivatives of hydroxybenzoic and hydroxycinnamic acids, are divided into subgroups and may be found in many different types of agricultural products. Protocatechuic, caffeic, coumaric and chlorogenic acids are phenolic acids found in abundance in fruits and vegetables. Ferulic acid is a phenolic acid commonly found in grains, especially in grain bran. Polyphenolics are a group of flavonoids, which are divided into anthocyanins, isoflavones, flavones, flavonols, flavanols, and flavanones. Anthocyanins are present in high levels in berries, and isoflavones are abundant in beans. The flavonol quercetin is largely present in apples, while catechin, a flavanol, is found in teas and coffees. Grapefruits are rich in flavanones, such as naringenin. Tannins are a group of polymerized polyphenolics present in berries and red wines. Some tannins existing in fruit juice and wine have a molecular weight over 2000 daltons and are not water-soluble (Khanbabaee and van Ree, 2001). Also, some antioxidant phytochemicals in grain germ and bran, such as tocopherols and oryzanols, are lipid-soluble.

Antioxidant phytochemicals have recently become an attractive subject for scientists in many different research areas. The scope of research in phytochemicals is no longer limited to the functionality associated with plants and organoleptic properties, but has been expanded to include their functionality in human health, which is linked to various epidemiological diseases and micro-nutrition. Most phytochemicals in natural agricultural sources have been generally recognized as bioactive or health-promoting compounds, which play an important role in preventing cardiovascular diseases, cancers, obesity and diabetes, lowering blood cholesterol level, and reducing inflammatory action (Halliwell, 1996).

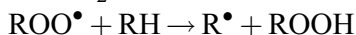
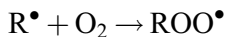
## **1.2 Lipid Oxidation and Antioxidant Property of Phenolic Derivative Phytochemicals**

Antioxidants are substances that inhibit the generation and reduce the number of oxidation-initiating free radicals, which eventually helps to prevent or delay oxidation reactions, such as lipid auto-oxidation. Lipids, essential components in animal and human cell membranes, are very vulnerable substances that are readily oxidized when exposed to free radicals, light, oxygen, pro-oxidants, and high temperatures (Frankel, 1999). In food systems, lipid oxidation causes serious deterioration in food quality during the storage of lipid-containing foods (Decker and Xu, 1998). The oxidation of lipids produces undesirable rancid odors and oxidation products, and decreases the sensory and nutritional quality of food. The primary products of lipid oxidation are hydroperoxides, which are unstable and further decompose into various secondary compounds such as alkanes, alkenes, aldehydes, ketones, alcohols, esters, acids, and hydrocarbons. Also, some lipid oxidation products are harmful to a variety of mammalian cells. They can affect cell division and proliferation, resulting in cell inflammation, and increase the risk of developing chronic diseases (Berliner et al., 1995). Lipid auto-oxidation is a major type of lipid oxidation, in which lipids react with oxygen through a free radical mechanism (Asghar et al., 1988). Below are the steps of free radical lipid auto-oxidation (RH indicates a fatty acid; ROOH indicates a hydroperoxy fatty acid; • denotes a free radical):

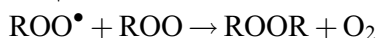
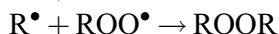
*Radical initiation:*



*Radical propagation:*



*Radical termination:*



Lipid oxidation is not restricted to the fatty acids and triglycerides of foods. Another important food lipid, cholesterol, can also be oxidized by free radicals (Maerker, 1987; Xu et al., 2001). Cholesterol is present at significant levels in food from animal sources, such as egg yolk, meat, and milk products. It is an essential molecule for humans as a component of cell membranes and as the precursor of steroid hormones and bile acids. Most cholesterol in the human bloodstream is carried by low-density lipoprotein (LDL) particles. High levels of LDL cholesterol, known as “bad cholesterol,” is directly associated with various cardiovascular diseases. Cholesterol oxidation products from foods, or those produced by human metabolism, are toxic and harmful to blood vessel tissue cells (Kumar and Singhal, 1991; Lyons and Brown, 1999). They can trigger the development of a progressive thickening of the artery wall due to the accumulation of the oxidation products in LDL particles. Eventually, this can lead to the formation of plaque, which results in cardiovascular diseases and the formation of certain types of cancers (Morel and Lin, 1996; Wilson et al., 1997). Lipid oxidation reactions that occur in the cell membrane may also lead to various types of cancer, as these reactions result in damage to the membrane due to mutations that arise during the cell-duplication process (Jadhav et al., 1996).

Phenolic antioxidants can quench and terminate the free radicals without being transformed to new free radicals in the system.

The hydroxyl groups on the phenolic ring contribute to the antioxidant function by donating electrons to eliminate free radicals in a system. As the phenolic radical intermediates are relatively stable due to resonance occurring on the phenolic ring, they do not initiate a new free radical chain reaction. Furthermore, the phenolic radical intermediates can react with other free radicals to terminate the chain reaction. Phenolics may also suppress reactive oxygen and nitrogen species formation by deactivating related enzymes and chelating free radical-producing metal ions. The number of free hydroxyl groups on phenolic rings is correlated to the antioxidant activity of a phenolic compound (Cotelle, 2001). Hydroxycinnamic acid derivatives were found to have higher antioxidant activity than their corresponding hydroxybenzoic acid derivatives because the  $-\text{CH}=\text{CH}-\text{COOH}$  linked to the phenyl ring may enhance the stability of the resonance (Rice-Evans et al., 1996). The number and position of hydroxyl groups in phenolic rings are also important to the antioxidant activity of flavonoids (Bors and Michel, 2002).

Unlike natural antioxidant phytochemicals, which are accumulated and excreted in biological systems, there is a group of antioxidants that are artificially synthesized. The most common synthetic antioxidants used in foods are butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tertiary butylhydroquinone (TBHQ), and propyl gallate (PG). They are all phenolic derivatives and have either a mono- or polyhydroxyl group on the phenolic ring. The use of synthetic antioxidants is restricted because of food safety concerns, which are increasing around the world. Even though only a small amount of these artificial antioxidants are used, they are still a concern owing to of potential harmful health problems from long-term consumption (Kotsonis et al., 2001). They could be the promoting agents that target liver, lung, and stomach tissues to alter their gene expression (Pitot and Dragon, 2001). However, the antioxidant phytochemicals from agricultural products are usually considered to be GRAS (generally recognized as safe). With this advantage, more and more consumers and food developers prefer using phytochemicals as natural antioxidants to replace synthetic antioxidants in food products. Foods labeled “all natural” or “no artificial” ingredients are becoming common in the markets. Furthermore, the benefits of reducing the risk of chronic diseases by a higher daily consumption of fruits, vegetables and grains have been confirmed in a number of studies. Many studies have suggested that antioxidant phytochemicals in these agricultural food

plants play an important role in preventing chronic diseases (Block et al., 1992; Boyer and Liu, 2004; Delgado-Vargas and Paredes-Lopez, 2003; Harborne and Williams, 2000; Ness and Powles, 1997; Steinmetz and Potter, 1996).

### **1.3 Antioxidant Phytochemicals in Fruits**

#### **1.3.1 Berries**

The most important antioxidant phytochemicals in berries are anthocyanins, a group of polyphenolics responsible for the black, purple, or red colors of these fruits. The profiles of anthocyanins and health benefits of different berry varieties – such as blackberries, raspberries, blueberries, cranberries, bilberries, and strawberries – have been studied extensively (Seeram, 2009). Compared to other berries, bilberries have more than 15 different types of anthocyanins (Lätti et al., 2008; Yue and Xu, 2008), and the content and composition of anthocyanins in berries is largely dependent on the growth environment. There is large variation of total anthocyanin content in bilberries harvested in different geographic areas, ranging from 19.3 to 38.7 mg/g dry weight (Lätti et al., 2008). Delphinidin and cyanidin sugar-conjugated derivatives dominated in those bilberry samples. Also, the total anthocyanin content in the concentrated bilberry extracts could be up to 24% (Zhang et al., 2004). Besides anthocyanins, berries also have significant quantities of flavan-3-ols, hydroxybenzoic and hydroxycinnamic acid derivatives, condensed and hydrolyzable tannins, and other antioxidant phytochemicals (Howard and Hager, 2007). These compounds and anthocyanins directly contribute to the antioxidant capacity of berries. The order of antioxidant activity from high to low of different berries using a LDL oxidation model was blackberries, raspberries, blueberries, and strawberries (Heinonen et al., 1998). This study also suggested that the bioavailability and bioactivity of different anthocyanins was variable. The health function of anthocyanins in preventing obesity and diabetes was also reported. Mice that were fed cyanidin-3-O-glucoside in their diet had significantly lower body weight gain typically induced by the high-fat diet, and white and brown adipose tissue weights were also significantly lower after 12 weeks (Tsuda et al., 2003). In another study, mice fed a high-fat (35%) diet plus purified anthocyanins from blueberries also had lower body weight gains and less body fat than the

high-fat controls (Prior et al., 2008). In general, the antioxidant activity of wild berries, such as crowberries, cloudbberries, whortleberries, lingonberries, rowanberries, and cranberries, was higher than that of cultivated berries, such as strawberries and raspberries (Määttä-Riihinen et al., 2004). In a thermal stability study, degradation of the ten anthocyanins, delphinidin, cyanidin, petunidin, peonidin, and malvidin derivatives with different conjugated sugars at heating temperatures of 80, 100, and 125 °C were similar at the same heating temperature (Yue and Xu, 2008). However, the degradation of each compound increased drastically when the heating temperature was increased to 125 °C, with half-lives of all anthocyanins reported to be less than 8 min.

### ***1.3.2 Grapes***

The major antioxidant phytochemicals in grapes are anthocyanins, catechin, gallic acid, and resveratrol (Carle et al., 2004). The antioxidant capacity of grape extract or red grape wine in inhibiting lipid oxidation has been studied intensively. Both commercial grape juices and fresh grape extracts were reported to have the ability to lower human LDL oxidation, which was significantly correlated with the level of antioxidant phytochemicals in the juices and extracts (Frankel et al., 1998). Resveratrol is a polyphenolic present in much higher quantities in grapes than in other fruits. It is found in the vines, roots, seeds, and stalks, but its highest concentration is in the grape skin (Carle et al., 2004). The contents of polyphenolic antioxidants in red wine are variable and depend on the grape variety, vineyard location, cultivation system, climate, soil type, vine practices, harvesting time, and enological practices (Ribéreau-Gayon, 2006). Resveratrol and catechin in red wine are in ranges of 0.2–5.8 and 10–250 mg/L, respectively (Gu et al., 1999). Malvidin-3,5-diglucoside, an anthocyanin, was identified and isolated from wild grapes and was found to have higher antioxidant activity than alpha-tocopherol (Tamura and Yamagami, 1994). Red wines that contain both types of phenolics demonstrated greater efficacy in preventing LDL lipid oxidation than tocopherol alone (Frankel et al., 1993). In red wine, the anthocyanin-containing fraction had greater activity in inhibiting LDL oxidation than other phenolic fractions without anthocyanins (Ghiselli et al., 1998). Recently, the capacities of red and white wines to inhibit cholesterol oxidation were compared (Tian et al., 2011), and it was found that the ability of red wine was

50 times higher than that of white wine in preventing cholesterol oxidation induced by free radicals. These studies support the notion that daily intake of the appropriate amount of red wine may lower the risk of cardiovascular diseases.

### ***1.3.3 Grapefruits***

Flavanone, narirutin, naringin, hesperetin, and hesperidin are the major antioxidants in grapefruit and grapefruit juices (Miller and Rice-Evans, 1997). Naringin was present in a range of 407–1548 mg/100 g fresh weight while narirutin was present in amounts from 28 to 2059 mg/100 g fresh weight in different varieties of grapefruit (Ortuno et al., 1995). White grapefruit had higher concentrations of naringin and furanocoumarins located in the albedo and flavedo than red grapefruit varieties (Castro et al., 2006). The juice of grapefruit exhibited higher antioxidant activity than the juice from orange in a free radical scavenging model. In a LDL model, juices from orange, tangerine, and grapefruit did not show any antioxidant capability in reducing the lipid oxidation of LDL (Wang et al., 1996). Also, a diet supplemented with fresh red grapefruit positively influenced serum lipid levels, especially serum triglycerides and serum antioxidant activity (Gorinstein et al., 2006). However, it was found that narirutin, hesperetin, and hesperidin may have lower antioxidant activity when compared with the phenolics in berries or grapes (Scarлата and Ebeler, 1999).

### ***1.3.4 Apples***

A variety of antioxidant phytochemicals in apples include catechin, procyanidins, hydroxycinnamates, flavonols, anthocyanins, and dihydrochalcones. The consumption of apple contributes to the reduced risk of diseases such as cardiovascular disease and some forms of cancer (Boyer and Liu, 2004). In a recent study, the phenolic phytochemical composition and antioxidant activity of 67 varieties of apple cultivars were examined by Wojdylo et al. (2008). The total content of these phytochemicals varied from 0.5 to 2.7% of dry weight. In apple juice, the total phenolic content ranged from 0.02 to 0.1% of juice. Catechin and procyanidins are the major classes of apple phenolics, representing more than 80% of the total content. A small amount of anthocyanin was also found in red apples. The results of this study demonstrated that new varieties of apple, such as Ozark Gold, Julyred, and Jester, had the same



or higher values of bioactive compounds in comparison with the old varieties, such as Golden Delicious, Idared, and Jonagold. Antioxidant phytochemicals in apple peel were reported to have the capabilities of preventing macro- and microscopic damage and of barrier dysfunction along the gastrointestinal tract in an animal study (Carrasco-Pozo et al., 2011). A recent study investigated the effect of apple polyphenolics on the lifespan of fruit flies and their interaction with gene expressions of superoxide dismutase, catalase, and cytochrome-c oxidase (CcO) subunits III and VIb (Peng et al., 2011). The results showed that the mean lifespan was significantly extended by 10% in fruit flies fed an apple polyphenolics diet.

## **1.4 Antioxidant Phytochemicals in Vegetables**

### **1.4.1 Tomato**

Tomatoes have been recognized as a rich source of beta-carotene, provitamin A, ascorbic acid and vitamin C (Hanson et al., 2004). In recent years, another important carotenoid in tomatoes, lycopene, has received considerable attention. Lycopene is responsible for the red color of tomatoes and watermelons (Rao and Agarwai, 2000). Lycopene consists of eight units of isoprene to form a long carbon chain, which has eleven conjugated double bonds and two non-conjugated double bonds. Although the beta-carotene and ascorbic acid in tomatoes have been confirmed as being free radical scavenging antioxidants, lycopene has been reported to quench free radicals twice as efficiently as beta-carotene, making it one of the most potent antioxidants of the carotenoids (Breeman et al., 2002). The antioxidant capacity of lycopene has led to promising results in decreasing the risk of some illnesses and cancers. Several studies showed that lycopene is able to prevent the oxidation of LDL, which causes the atherogenic process and heart disease (Delgado-Vargas and Paredes-Lopez 2003). In fresh tomatoes, the content of lycopene was reported to range from 2.5 to 200 mg/100 g of raw tomato (Takeoka et al., 2001; Dewanto et al., 2002; Seybold et al., 2004). Although a decrease in lycopene content has been observed during cooking processing in some studies, an increase was found in other studies. This may be because cooking temperatures below 80 °C increase free lycopene by disrupting cell walls or hydrolyzing lycopene

derivatives rather than degrading the lycopene (Thompson et al., 2000). In a high temperature thermal stability study using pure lycopene, 50% of lycopene was degraded at 100 °C after 60 min, 125 °C after 20 min and 150 °C after less than 10 min. Only 64.1 and 51.5% lycopene was retained when the tomato slurry was baked at 177 and 218 °C for 15 min, respectively. At these temperatures, only 37.3 and 25.1% of lycopene was retained after baking for 45 min. In 1 min of high power microwave heating, 64.4% of lycopene still remained. However, greater degradation of lycopene in the slurry was found with frying. Only 36.6 and 35.5% of lycopene was retained after frying at 145 and 165 °C for 1 min, respectively. Thus, different cooking conditions could have various impacts on the stability of lycopene in tomato (Mayeaux et al., 2006).

#### **1.4.2 Root Vegetables**

Carrot, potato, and sweet potato are the most common root vegetables in our daily diet. Generally, carotenoids are the most abundant phytochemicals in these root vegetables. However, anthocyanins are also largely present in carrot and sweet potato varieties having intense purple colors. Although raw carrot has been reported to have lower antioxidant activity than other vegetables (Kähkönen et al., 1999), boiling significantly improved their antioxidant activity (Gazzani et al., 1998). Potato and sweet potato, especially in the peels, contain significant amounts of antioxidant phytochemicals, such as chlorogenic, gallic, protocatechuic, and caffeic acids (Rodriquez De Sotillo et al., 1994). Purple potatoes and peels have exhibited greater antioxidant activities than the white and yellow varieties due to the contribution of high levels of anthocyanins (Kähkönen et al., 1999). Pelargonidin glucoside and peonidin glucoside were identified as the major anthocyanins in red-flesh sweet potatoes (Rodriquez-Saona et al., 1998). Anthocyanins from purple sweet potato were reported to suppress the development of atherosclerotic lesions and oxidative stress in mice (Miyazaki et al., 2008).

#### **1.4.3 Peppers**

Peppers are rich in vitamins C and E, provitamin A, and carotenoids (Materska and Perucka, 2005). Peppers also contain various antioxidant phytochemicals, such as ferulic and sinapic acids, quercetins, luteolins, and apigenins (Marin et al., 2004; Materska and Perucka, 2005).

These compounds were reported to have the capability of reducing harmful oxidation reactions in the human body and preventing various diseases associated with free radical oxidation, such as cardiovascular disease, cancer, and neurological disorders (Doll, 1990; Hollman and Katan, 1999; Harborne and Williams, 2000; Delgado-Vargas and Paredes-Lopez, 2003; Shetty, 2004). Green, yellow, orange, and red sweet bell peppers are commonly available in markets, with green bell pepper being the most produced and consumed (Frank et al., 2001). Carotenoids and flavonoids are the colorants that impart the orange and red colors of peppers (Delgado-Vargas and Paredes-Lopez, 2003). The yellow–orange colors of peppers are formed by alpha- and beta-carotene, zeaxanthin, lutein, and cryptoxanthin (Howard, 2001). The red color of peppers is due to the presence of carotenoid pigments capsanthin, capsorubin, and capsanthin 5,6-epoxide. All four colored peppers exhibited significant capability in preventing the oxidation of cholesterol or polyunsaturated fatty acid (docosahexaenoic acid – DHA C22:6) during heating (Sun et al., 2007).

#### ***1.4.4 Culinary Herbs***

Culinary herbs have been used to enhance and complement the flavors of various foods for hundreds of years. Recently, culinary herbs were found to have functionality not only with their unique flavor characteristics, but also in their medicinal benefits such as antioxidant activity, and anti-inflammatory and antimicrobial capability (Shan et al., 2005). A number of studies have confirmed that rosemary, sage, oregano, basil, ginger, turmeric, and thyme show strong antioxidant activity. Unique antioxidant phytochemicals, including carnosic acid, carnosol, rosmarinic acid, curcumin, eugenol, and other common phenolic compounds, are present in the culinary herbs (Hirasa and Takemasa, 1998; Hinneburg et al., 2006; Kikuzaki and Nakatani, 1993; Frankel, 1999). The antioxidant capacity of the phenolic compounds in these herbs is responsible for their beneficial health effect of preventing some chronic diseases (Kähkönen et al., 1999; Shan et al., 2005). Their antioxidant activity also helps to retard or prevent lipid oxidation or rancidity in a variety of food products mixed with the culinary herbs (Birch et al., 2001; Rababah et al., 2004). Ginger and turmeric extracts have higher antioxidant activity than synthetic alpha-tocopherol (Kikuzaki and Nakatani, 1993). Bhale et al. (2007) found that rosemary and oregano

demonstrated their capability in inhibiting oxidation of susceptible long-chain unsaturated fatty acids in menhaden oil, and they also found that the amount of the herb extracts used in foods has to be carefully examined, as the extracts might contain some pro-oxidants. The ability of oregano extract to prevent lipid oxidation was increased with a higher extract concentration in menhaden oil. However, the capacity for rosemary extract to prevent lipid oxidation was highest at an extract concentration of 2.5% and decreased when the concentration was increased to 5% in both heating and room temperature incubation studies. At room temperature, the antioxidant capacity of rosemary extract is much higher than that of oregano extract. Thus, for food preservation purposes, rosemary extract may be more effective than oregano extract. However, at higher cooking temperatures, the antioxidants in oregano extract are more stable and stronger than those in rosemary extract in retarding fish oil oxidation. This study provided useful information relative to the natural herb antioxidants used in stabilizing lipid-rich foods during cooking and storage.

## **1.5 Antioxidant Phytochemicals in Grains**

### ***1.5.1 Soybean***

Soybean is one of the major protein and lipid sources in the diets of most developing countries. Soy-containing foods have received considerable attention for their potential role in reducing the formation and progression of certain types of cancers and some chronic diseases such as cardiovascular disease, Alzheimer disease, and osteoporosis (Messina, 1999; Zhao et al., 2002). Also, soy has the capability of lowering oxidative stress, stimulating or inhibiting estrogen activity and preventing the harmful proliferation of cells (Mitchell et al., 1998; Hwang et al., 2000; Maggiolini et al., 2001). The major antioxidant phytochemicals in beans are isoflavones, of which soybean is the richest source among beans. The total level of isoflavones in soybean is up to 0.5% (Liu, 1997). The hydroxyl groups on the two phenolic rings of isoflavones provide excellent antioxidant activity (Meng et al., 1999). The various types of isoflavones are distinguished by the different substitute groups and sugar moieties on the two phenolic rings. As isoflavones are not lipid-soluble, the level of isoflavones in soybean oil

is much lower. In defatted soy flour extract, soy isoflavones could be more than 100 times higher than in soybean oil (Yue et al., 2008). This study also found that the overall antioxidant activity of soy oil was lower than the defatted soy flour, although soy oil contained higher levels of vitamin E. The chemical structures of soy isoflavones are not consistent during food processing. The isoflavones with beta-glucoside, daidzin, glycitin, and genistin – which are the major isoflavones in unprocessed soy flour — could release the beta-glucoside and become their aglycone forms during thermal processing (Xu et al., 2002). At the same time, they could also be produced by the de-esterification from malonyl and acetyl beta-glucoside soy isoflavones in the soy flour. Factors induced in soy food processing, such as enzymes in raw soy flour, heating and additives, could affect the stabilities of soy isoflavones (Kudou et al., 1991; Mahungu et al., 1999, Tipkanon et al., 2010; Wang and Murphy, 1996; Yue and Xu, 2010).

### ***1.5.2 Wheat***

Wheat bran possesses various natural antioxidant phytochemicals that contribute toward preventing cardiovascular disease and certain cancers (Halliwell, 1996; Truswell, 2002). Phenolics, tocopherols, and fibre in wheat bran are generally believed to be primarily responsible for its positive effects on cardiovascular disease. Undesirable lipid oxidation reactions in the body contribute to these disease conditions (Moller et al., 1988; Alabaster et al., 1997; Andreassen et al., 2001). Many studies have found that these compounds of wheat bran exhibit significant capabilities in scavenging free radicals, chelating metal ion oxidants, and reducing lipid oxidation at different conditions (Yu et al., 2002; Zhou and Yu, 2004; Adom and Liu, 2005). Similar to other cereal grains, wheat bran contains many different types of antioxidant phytochemicals, such as ferulic, vanillic, caffeic, coumaric, and syringic acids (Li et al., 2005; Kim et al., 2006), as well as relatively high levels of carotenoids, tocopherols, and phytosterols (Nystrom et al., 2005; Zhou et al., 2005). A recent study identifying the most important antioxidant fractions of wheat grain found that the aleurone content in the fractions was highly correlated with the antioxidant capacity of the fractions (Anson et al., 2008). Ferulic acid was considered to be the major contributor to the antioxidant capacity in fractions with higher antioxidant capacity.

### **1.5.3 Rice**

Rice is one of the most important commodities in most Asian countries. Its edible part, white rice kernel, is produced during rice mill processing, which removes rice hull and rice bran from the harvested rough rice. Although rice bran accounts for up to 10% of the rice grain, it is considered a waste product of rice milling to be discarded or used as animal feed. However, it was found that rice bran contains a much higher level of antioxidant phytochemicals than rice kernel (Godber and Juliano, 2004). Rice bran lipid fraction consists of unsaponifiable material that seems to present a positive health function, mainly because of its high levels of alpha- and gamma-tocopherol, alpha- and gamma-tocotrienol, and gamma-oryzanol (Xu and Godber, 1999). Tocopherols and tocotrienols, known as vitamin E homologues, are recognized as antioxidant compounds that are able to prevent chronic degenerative illness, cardiovascular diseases, and tumors (Bramley et al., 2000; Qureshi et al., 2001). Gamma-oryzanol is a mixture of compounds derived from ferulic acid with sterols or triterpene alcohols (Xu and Godber, 1999). The levels of tocopherols, tocotrienols, and gamma-oryzanol in rice bran are variable and depend on factors such as cropping areas and varieties (Bergman and Xu, 2003). Many studies have demonstrated that gamma-oryzanol compounds could reduce serum cholesterol level, the risk of tumors incidence and inflammatory action (Rong et al., 1997; Wilson et al., 2002; Tsuji et al., 2003). Gamma-oryzanol in rice bran exhibited significant antioxidant activity in the inhibition of cholesterol oxidation, compared with the four vitamin E components. Because the amount of gamma-oryzanol could be up to ten times higher than vitamin E in rice bran, it may be the more important antioxidant of rice bran in reducing cholesterol oxidation, even though vitamin E has been traditionally considered the major antioxidant in rice bran. The higher antioxidant activities of gamma-oryzanol components may be due to their structure, which is very similar to cholesterol. The analogous structure of gamma-oryzanol components and cholesterol leads to similar chemical characteristics in a system. The gamma-oryzanol components may have a greater ability to associate with cholesterol in the small droplets of an emulsion system and become more efficient in protecting cholesterol against free radical attack (Xu et al., 2001). In addition to those lipophilic antioxidant phytochemicals, black- or purple-colored rice bran or rice contain

significant amounts of the hydrophilic antioxidant phytochemicals known as anthocyanins (Jang and Xu, 2009).

#### **1.5.4 Oat**

The soluble fiber compound of oat, beta-glucan, is generally believed to be responsible for its beneficial effects on cardiovascular disease and certain cancers (Handelman et al., 1999; Gray et al., 2002). Some studies have suggested that some of the health-promoting capabilities of oat are due not only to its antioxidant phytochemicals, but also its beta-glucan gum (White and Armstrong, 1986; Peterson and Qureshi, 1993; Wood et al., 2000). Similar to other cereal grains, oat contains relatively high levels of tocopherols, tocotrienols and phytosterols (Peterson, 2001). It is also a good source of a variety of phenolic antioxidants such as avenanthramides, *p*-hydroxybenzoic acid, and vanillic acid (Shahidi and Naczk, 1995; Peterson et al., 2001). Oat extracts, along with highly concentrated antioxidants, could be used as a natural preservative in preventing food oxidation during cooking and storage, especially for foods rich in unsaturated long-chain fatty acids and cholesterol (White and Armstrong, 1986; Sun et al., 2006). The oat extract showed the greatest capability of preventing cholesterol and DHA oxidation during heating in a model study (Sun et al., 2006). It significantly reduced cholesterol decomposition and DHA degradation, and prevented the production of harmful toxic cholesterol oxidation products. Therefore, oat extract has the potential to maintain the stability of cholesterol- and fatty acid-rich foods during cooking or storage.

#### **1.5.5 Corn**

Corn is also recognized as an excellent source of phytochemicals, such as tocopherol, phytosterols, and carotenoids, which generally possess the ability to prevent oxidation (Truswell, 2002; Martinez-Tome et al., 2004). Corn is a rich source of lutein, which is a non-provitamin A carotenoid and acts as a yellowish pigment (Johnson, 2004). Lutein is predominately transported by high-density lipoprotein (HDL) of plasma because of its relatively higher polarity. One major health function of lutein is to prevent age-related macular degeneration (AMD) and cataracts (Johnson, 2000). Lutein was also reported to have the capability of reducing the risk of certain cancers such as colon cancer (Slattery et al., 1988), and this may be due to its antioxidant function,

which makes lutein an effective free radical scavenger to prevent cell mutation (Schunemann et al., 2002). In addition to lutein, corn also contains other carotenoids, such as alpha- and beta-carotene, beta-cryptoxanthin, and zeaxanthin, which are not found at a significant level in most other cereals. Corn germ, a common source for producing vegetable oil, has 95% of the total vitamin E content in raw corn (Grams et al., 1970; Wang et al., 1998) and corn oil has even higher levels of vitamin E, up to 900 ppm. The major vitamin E homologues found in corn are alpha- and gamma-tocopherol. Although less than 5% of the vitamin E in corn is distributed in the corn endosperm, the major vitamin E homologues present in the endosperm were gamma-tocopherol and gamma-tocotrienol (Grams et al., 1970), which is similar to rice bran. Adom and Liu (2005) found that the total antioxidant activity of corn was the highest compared with wheat, oat, and rice. It was approximately three times higher than wheat or oat and twice as high as rice.

Traditionally, the benefits of grains, vegetables, and fruit have been associated with their nutrients, proteins, lipids, carbohydrates, and vitamins. However, many evidences suggest that, in fact, the antioxidant phytochemicals in these edible agricultural plants are the true beneficial components of these plants. Phytochemicals are not only responsible for preventing oxidation reactions but also play an important role in maintaining human health. Additional studies in this area are still needed for discovering new phytochemicals that are effective as antioxidants, and for utilizing these antioxidants in food systems and nutrition supplements. Also, further studies for comprehensively understanding their bioactive mechanisms of health-promoting functions are necessary. The information obtained from these studies could be used to expand the market of agricultural products, which would appeal to consumers who recognize the importance of diet as a means of promoting health. In turn, this would increase economic benefits for producers and manufacturers, as well as expand the utilization of agricultural commodities and their by-products as value-added materials.

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