Chapter 1

AGRICULTURAL BY-PRODUCTS AS IMPORTANT FOOD SOURCES OF POLYPHENOLS

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ABSTRACT

Polyphenols are secondary metabolites of plants. Dietary phenolics are not only classified as human nutrients, but play important roles in human health and are therefore called nutraceuticals. Both epidemiological studies and controlled human studies have shown that regular intakes of diets rich in phenolics are inversely related to some chronic diseases such as certain cancers and coronary heart diseases. Types and contents of phenolics in different food system vary greatly and foods of plant origin including fruits, vegetables, legumes and some beverages are good sources of bioactive phenolics. Beside the edible part of plant foods, some agricultural by-products usually contain higher levels of polyphenols, particularly, flavonoids than products themselves. This chapter describes the major classes of dietary phenolics, and their occurrence in the commercially important agricultural by-products including peanuts skin, grape pomace, apples pomace, citrus processing by-products, and cranberry pomace. The possible applications of the polyphenolics from these agricultural by-products in food system are also discussed.

Keywords: Polyphenols, Agricultural by-products, Dietary polyphenolics, Food processing, applications

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1. INTRODUCTION

Polyphenols are secondary metabolites of plants. They are produced by the plant defense system to protect plants from invading insects and microorganisms, and to give the plants their specific organoleptic properties such as color, taste and flavor (Freeman and Beattie. 2008). Polyphenols are not classified as human nutrients, but they play important roles in human health and, therefore, are called nutraceuticals. Chemically, phenolics can be defined as substances possessing an aromatic ring bearing one or more hydroxyl groups, including their functional derivatives (Shahidi and Naczk, 2004). Polyphenols are compounds that have more than one phenolic hydroxyl group attached to one or more benzene rings (Vermerris and Nicholson, 2006). Most food phenolics possess more than one hydroxyl group; therefore, phenolics are also called polyphenols. In this review, phenolics and polyphenols are used interchangeably.

Epidemiological studies have shown that regular intake of diets rich in phenolics is inversely related to some chronic diseases such as certain cancers and coronary heart diseases, but the biological effects and activities of various phenolics are not equal. Numerous studies have been conducted to identify and quantify polyphenols in different agricultural products. Over 8000 of individual polyphenols have been identified (Rackova et al., 2005) and the number is still increasing due to the availability of advanced analytical equipment such mass spectrometer and NMR. Foods of plant origin including fruits, vegetables, legumes and some beverages are good sources of bioactive phenolics. The most complete database on dietary flavonoids in different foods was released by USDA in January 2007 (USDA Database Release 2.1. 2007). The database contains individual flavonoid contents in the edible portions of 380 selected foods. Phenol-Explorer is a comprehensive web-based database on polyphenol content in foods. It contains more than 37,000 original data points collected from 638 scientific articles published in peer-reviewed journals (Neveu et al., 2010).

Types and contents of phenolics in different food system vary greatly, depending on the type of food, environmental conditions of product growth, and processing/cooking conditions. The richest sources of dietary polyphenols were various spices and dried herbs, cocoa products, some darkly coloured berries, some seeds (flaxseed) and nuts (chestnut, hazelnut) and some vegetables, including olive and globe artichoke heads (Pérez-Jiménez et al., 2010). Medicinal herbs and spices also contain different types of health promoting phenolics (Huang et al., 2010). Beside the edible part of plant foods, some agricultural by-products/residues such as apple pomace, cranberry pomace, grape pomace, citrus peels, peanut skin, soy pulp/okara and sweetpotato peels usually contain higher levels of polyphenols, particularly, flavonoids than products themselves (Schieber, et al., 2001a; Nepote, et al., 2002; Wolf and Liu. 2003; Rossi. 2003; Yu et al., 2005; Montealegre et al., 2006; Park and Zhao. 2006; Vattem and Shetty, 2006; Makris et al., 2007; He and Liu. 2008). The mass production of juices, wine, peanut oil, and wide use of peanuts in different food products gernerated large quantities of these by-products. These by-products are usually decomposed in the landfill, which poses economic loss and causes environmental problems. Recovery of polyphenols for value added utilization of these by-products will not only add value to the respective commodities but also lessen the environmental burden associated with the disposal of these agricultural residues.

2. CLASSIFICATION OF FOOD PHENOLICS

Natural phenolics are classified by different ways, and different scientists have different preference in the classification of polyphenols. Harborne and Simmonds (1964) classified phenolic compounds into 20 groups based on the number of carbons in the molecule. Handique and Baruah (2002) divided natural polyphenols into 4 groups: 1) proanthocyanidin derivatives-these are oligomers containing two to six units of flavan-3-ol or high molecular weight polymer of flavan-3-ol, 2) galloyl and hexahydroxydiphenyl ester derivatives, 3) hydroxycinnamic acid derivatives, and 4) Phloroglucinol derivatives. In the classification of Dewick (1995), polyphenols were divided into tannins, lignins, and flavonoids. Each of these groups contains many subclasses (Khanbabaee and van Ree, 2001; Spencer et al., 2008). In the book of Shahidi and Naczk, 2004) phenolics are classified into 7 groups: 1) Cinnamic and benzoic acid derivatives and simple phenols, coumarins, flavonoids and stilbens, lignans and lignins, suberins and cutins, Tannins, and tocopherols and tocotrienol. In food science research, natural polyphenols are generally classified into groups and sub-classes based on the similarity of their chemical structures, that is, the types of building blocks that appear as repeated units. Four major classes of polyphenols found in foods are phenolic acids, flavonoids, lignans, and stilbenes (Spencer et al., 2008). Besides these 4 groups, Tyrosols and tyrosol esters form a group of polyphenols found exclusively in olives and virgin olive oils and have antioxidant and anti-inflammatory properties (Giovannini et al. 1999). Specific foods rich in polyphenols can be found in the USDA Database Release 2.1 (2007), USDA Database for proanthocyanidins (2004), and some wonderful review articles (Dimitrios, 2006; Balasundram et al., 2006; Karakaya 2004).

2.1. Phenolic Acids

Phenolic acids are phenols that possess one carboxylic acid functional group and are divided into two subclasses: hydroxycinnamic acids and hydroxybenzoic acids. Hydroxy-benzoic acids are characterized by the presence of a carboxyl group substituted on a phenol (Vermerris and Nicholson, 2006). Ellagic acid, gallic acid, salicylic acid, tannic acid, vanillic acid are common hydroxybenzoic acids found in food system (Shahidi and Naczk, 2004).

Structures of these phenolic acids are given in Figure 1. Gallic acid exists in grape, tea, strawberries, rhubarb, and soybean, hops and oak bark. Ellagic acid is a fused four-ring polyphenol. Plants produce ellagic acid to protect themselves from microbiological infection and pests. Ellagic acid is present in many red fruits and berries, including raspberries, strawberries, blackberries, cranberries, grapes, pomegranates and some nuts including almonds, peanuts, pecans and walnuts, but the highest levels of ellagic acid are found in raspberries (Vattem et al. 2004;).

The hydroxycinnamic acids are more common than are hydroxybenzoic acids and they mainly include *p*-coumaric, caffeic, ferulic and sinapic acids (Mattila et al., 2006; El-Seedi et al., 2012). These acids are rarely found in the free form, except in food that has undergone freezing, sterilization, or fermentation. The bound forms are glycosylated derivatives or esters of quinic acid, shikimic acid, and tartaric acid (Vermerris and Nicholson, 2006). The structures of these hydroxycinnamic acids are shown in Figure 2. Caffeic acid is found in

many fruits (apple, pear, plum, grape and tomato), vegetables (artichoke, burdock) seasonings (basil, oregano, thyme) and beverages such as coffee consumed by humans principally in conjugated forms such as chlorogenic acid. Chlorogenic acid is formed by the esterification of caffeic acid with quinic acid. It is rich in fruits such as apple, peach, prues, berries, pineapple, but also present in coffee at very high concentrations (Kroon and Williamson 1999; Stacewicz-Sapuntzakis et al., 2001). Ferulic acid is found in cereal brans in the water insoluble form because it is covalently linked to plant cell walls (Adam et al., 2002; Quinde-Axtell and Baik, 2006). Ferulic acid is also found in some vegetables and sweet corn (Srinivasan et al., 2007).
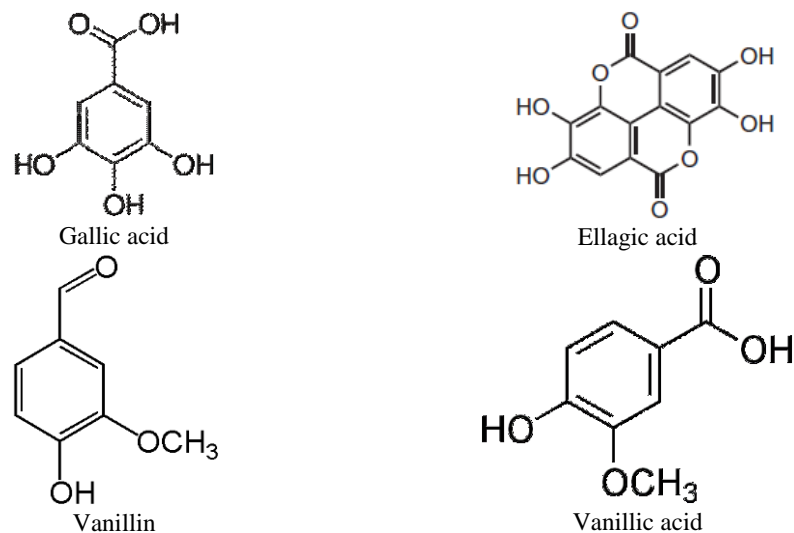
Figure 1. Chemical structures of selected hydroxybenzoic acids commonly found in foods.
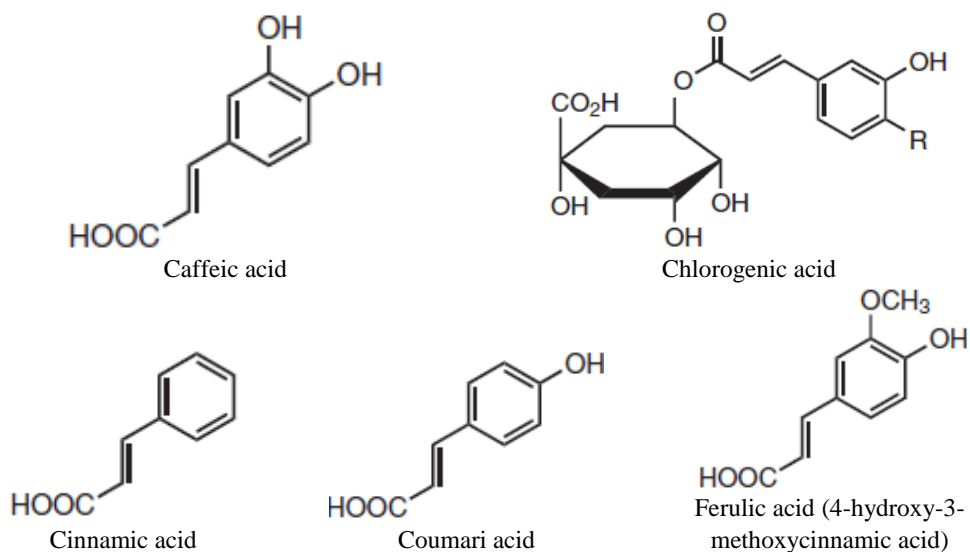
Figure 2. Chemical structure of selected hydroxycinnamic acids commonly found in food systems.
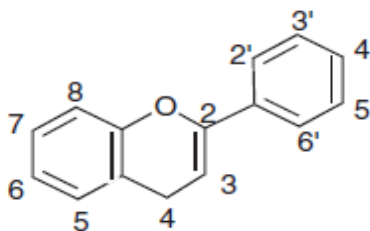
Figure 3. General structure of flavonoids. The basic structure consists of the fused A and C ring, with the phenyl ring B attached - through its 1' position to the 2-position of the C ring (numbered from the pyran oxygen).

2.2. Flavonoids

The largest and best studied polyphenols are the flavonoids. All flavonoids possess a three-ring diphenylpropane ($C_6C_3C_6$) core structure (Figure 3). Usual modifications of the basic core structure include hydroxylation and/or methylation at positions C-3, C-5, C-7, C-3′, C-4′, and/or C-5′ (Vukics and Guttman, 2008). Flavonoids occur as aglycones, glycosides and methylated derivatives. Based on their molecular structures, flavonoids are divided into seven subclasses: flavones, flavanones, flavonols, isoflavones, anthocyanidins/anthocyanins, flavanols (or catechins and procyanidins) and chalcones (Karakaya, 2004). Another group of flavonoids, which are not included in this classification, are proanthocyanidins, also called, procyanidins, condensed tannins or oligomeric procyanidins (Prior and Gu. 2005).

Flavanones: The C-ring of flavanones contains a ketone group, but no unsaturated carbon-carbon bond. The A- and B-rings can be substituted by sugar or methyl groups in the manner analogous to that of the flavones, as shown in Figure 4. Citrus fruits are good sources of flavanones. The flavanones account for approximately 95% of the total flavonoids in the citrus (Peterson et al., 2006a). Citrus flavanones are typically present in the glycoside or aglycone forms. The main aglycones are naringenin (5,7,4′-Trihydroxyflavanone) in grapefruit, hesperetin (4′-methoxy-3′,5,7- trihydroxyflavanone) in orange and tangerine, and eriodictyol (5,7,3′,4′-tetrahydroxyflavanone) in lemon (Majo et al., 2005; Peterson et al., 2006a). The flavanones in citrus fruits are generally glycosylated by a disaccharide at position 7: either a neohesperidose, which imparts a bitter taste, such as naringin in grapefruit, or a flavorless rutinose, such as hesperidin in oranges (Manach et al., 2004; Peterson et al., 2006a; Chanet et al., 2012).

Flavones are a class of flavonoids with the backbone of 2-phenylchromen-4-one (2-phenyl-1-benzopyran-4-one). Natural flavones include apigenin (4',5,7-trihydroxyflavone), Luteolin (3',4',5,7-tetrahydroxyflavone) and tangeritin (4',5,6,7,8-pentamethoxyflavone) as shown in Figure 5. Good sources of flavones are celery parsley, tangerine and other citrus peels (Manach et al., 2004).

Flavonols are a class of flavonoids characterized by the presence of a 3-hydroxyflavone backbone (3-hydroxy-2-phenylchromen-4-one (IUPAC)). Their diversity stems from the different positions of hydroxyl (-OH) groups. The most common flavonols are quercetin, myricetin, and kaempferol, and their structures are given in Figure 6. Flavonols are present in many fruits and vegetables such as apple, grape, berries, onion, kale, broccoli, lettuce, tomato,

tea, and red wine (Häkkinen, et al. 1999; Aherne and O'Brien, 2002). Greener leaves contain more flavonols.
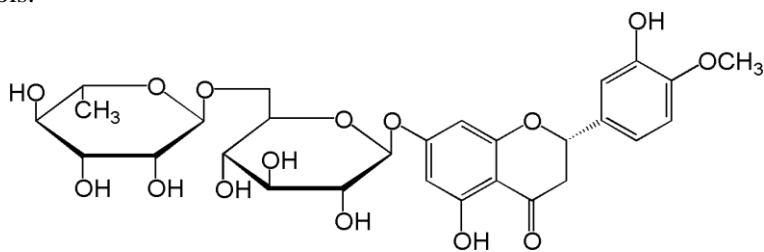
(1) Hesperidin (Hesperetin 7-rhamnoglucoside, hesperetin-7-rutinoside)
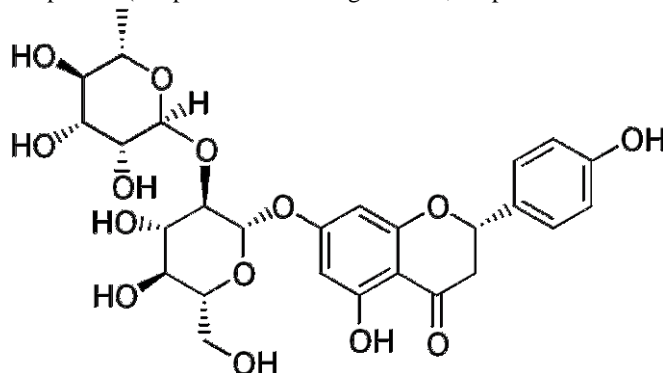
(2) Naringin (4',5,7-Trihydroxyflavanone-7-rhamnoglucoside)

Figure 4. Chemical structure of two major flavanoids found in citrus fruits (1) hesperidin, and (2) Naringin.
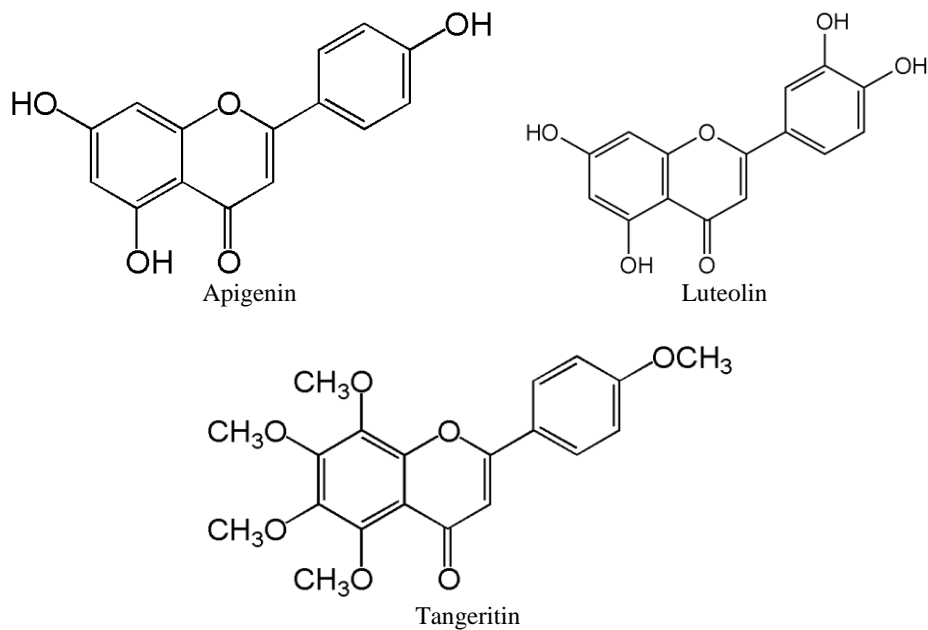
Apigenin

Luteolin

Tangeritin

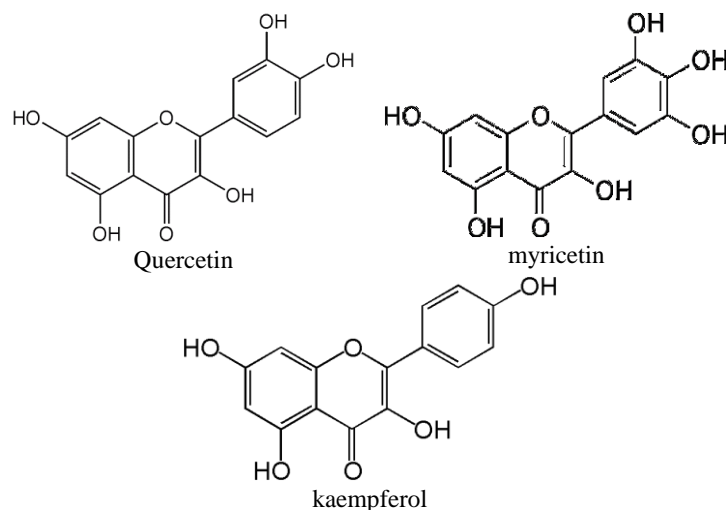Figure 5. Chemical structures of common dietary flavones.

Figure 6. Chemical structures of common dietary flavonols.

Flavanols (also referred to as Flavan-3-ols) belong to a class of flavonoids that contain the 2-phenyl-3,4-dihydro-2H-chromen-3-ol skeleton. These compounds include the catechins and procyanidins. Green tea is rich in all catechins including (+)- catechin, (-)-epicatechin (EC), (-)-epicatechin gallate (ECG), (-)-epigallocatechin (EGC) and (-)-epigallocatechin gallate (EGCG). They are present in almost all teas including green tea, white teat, black tea and oolong tea. Catechins constitute about 30% of dry weight of fresh tea leaves (Balentine et al., 1998). Other foods such as grapes, wine, coco, choclate and coffee also contain catechins (Hammerstone et al., 2000; Ruidavets et al., 2000). In black tea and oolong tea catechins are oxidized into orange-red theaflavins including a mixture of theaflavin (TF_1), theaflavin-3-gallate (TF_2A), theaflavin-3'-gallate (TF_2B) and theaflavin-3,3'-digallate (TF_3) (Leung et al., 2001). Procyanidins are polypmers of catechin and/or epicatechin. A-type procyanidins are formed through a 4→8 C-C bond and an interflavonid C-O bond (Lou et al., 1999) while B-type procyanidins are formed through 4→8 or 4→6 C-C bonds of flavan-3-ol monomers (Figure7). They can be found in many plants, most notably apples, cranberry, pine bark, cinnamon, cocoa, grape seed, grape skin, wine, and peanut skin. The procyanidin contents of different food items can be found in USDA database (USDA, 2004). Grape seed and apple skins are rich in B-type procyandins, while cranberry, peanut skin and almond skin are rich in A-type procyanidins (Prior et al., 2001; Lazarus et al., 1999; Yu et al., 2006; Garrido et al., 2008).

Anthocyanins (ACNs) are water-soluble plant pigments responsible for the blue, purple, and red color of many plant tissues. They occur primarily as glycosides or acylglycosides of their respective aglycone anthocyanidins (Mazza and Miniati, 1993). Anthocyanidins are typically not found as free aglycones, with the exception of the following 6 compounds: pelargonidin (orange-red), cyanidin (red), peonidin (rose-red), delphinidin (blue-violet), petunidin (blue-purple), and malvidin (purple) (Figure 8). About 17 anthocyanidins and over 600 naturally occurring ACNs have been reported (Mazza and Miniati, 1993; Anderson, 2004), and they are known to vary in (1) the number and position of hydroxy and methoxy groups on the basic anthocyanidin skeleton; (2) the identity, number, and positions at which sugars are attached; and (3) the extent of sugar acylation and the identity of the acylating

agent (Wu et al., 2006). Anthocyanins were found to be the main phenolic constituents of many berries. (Kähkönen, 2001), red apples, grapes, egg plants and red cabbage (Wu et al., 2006).
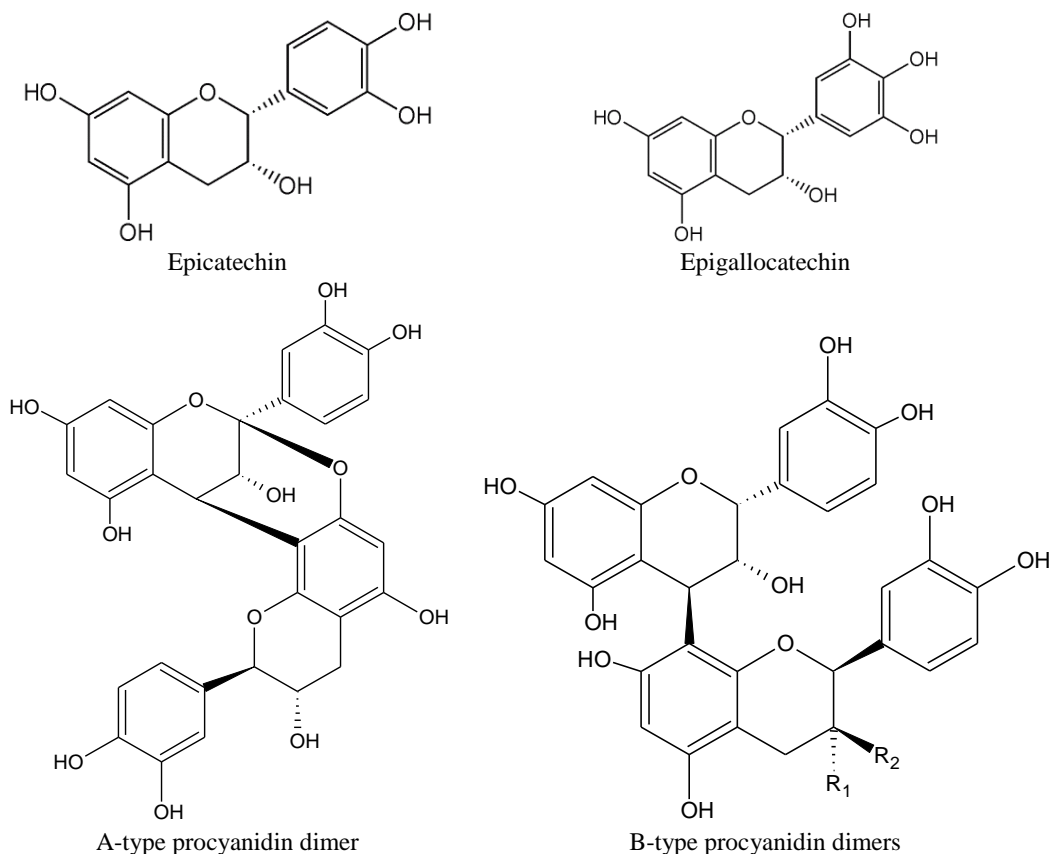
Figure 7. Representative structures of catechins and procyanidins.

Isoflavonoids: The isoflavonoids are one of the most distinctive and important classes of the naturally occurring flavonoids. Their distribution in plants is limited compared to other flavonoids, and they are found predominantly in legumes, particularly, soybeans, chickpea, peanuts and alfalfa. Other sources of isoflavonoids include kudzu and red clover (Wuttke et al., 2002). Isoflavones constitute the largest group of natural isoflavonoids. The major isflavonoids found in nature are daidzein (4', 7-dihydroxyisoflavone), genistein (5,7,4'-trihydroxyisoflavone) and glycitein (7,4'-dihydroxy-6-methoxyisoflavone). They are the aglycones of genistin, daidzin and glycitin (Pratt and Birac1979; Ruiz-Larrea.1997). They belong to the group of isoflavones with a typical C6-C3-C6 structure. Molecular structures of common isoflavones are shown in Figure 9. The isoflavones are also called phytoestrogens because they have weak estrogen activity.

2.3. Stilbenoids

Major stilbenoids found in foods of plant origin are resveratrol and its glycosides. Resveratrol (trans-3,5,4'-trihydroxystilbene) is a phytoalexin, a class of antibiotic compounds synthesized from p-coumaroyl CoA and malonyl CoA in response to fungal infection (Soleas and Diamandis.1997). Resveratrols are found largely in the skins of red grapes, and in other foods such as mulberries and peanuts (Sanders, et al., 2000). Resveratrol's most abundant natural sources are *Vitis vinifera, labrusca*, and *Muscadine* grapes. Resveratrol occurs in the vines, roots, seeds, and stalks, but its highest concentration is in the skin (Ector et al., 1996), which contains 50-100 micrograms per gram of dry mass (Jang et al., 1997). The structures of trans-resveratrol and its glycoside are given in Figure 10.
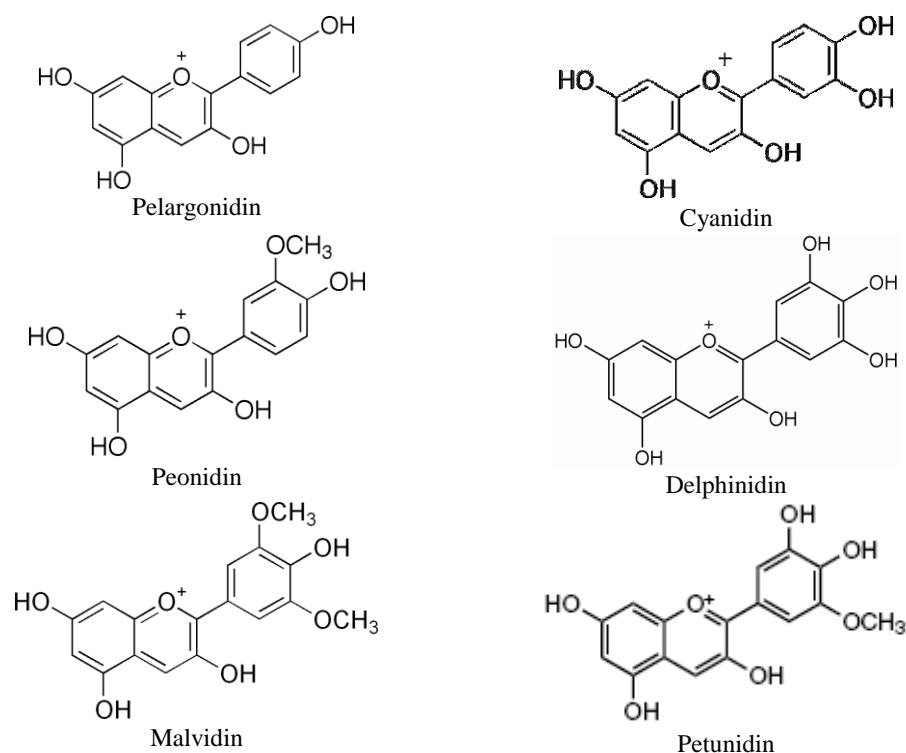
Figure 8. Chemical structures of naturally occurring anthocyanidins.

2.4. Lignans

Lignans are one of the major classes of phenolic phytoestrogens, but they also act as antioxidants. Flax seeds and sesame seeds are among the best known sources of lignans. Other sources of lignans include cereals (rye, wheat, oat, barly), pumpkin seeds, soybeans, broccoli, beans, and some berries, with nuts and oil seeds containing higher total lignan content (Smeds et al., 2007; LPI, 2005). Secoisolariciresinol and matairesinol were the first identified plant lignans in foods while pinoresinol and lariciresinol are recently identified plant lignans that contribute substantially to the total dietary lignan intakes (LPI, 2005).

Typically, Lariciresinol and pinoresinol contribute about 75% to the total lignan intake whereas secoisolariciresinol and matairesinol contribute only about 25% (Milder et al., 2005). These plant lignans are the precursors of mammalian lignans enterodiol and enterolactone. The chemical structures of major lignans found in foods are shown in Figure11.

Daidzein

Genistein
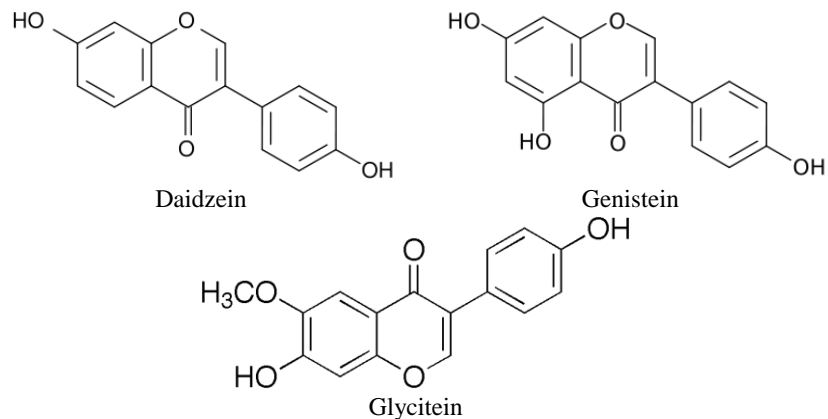
Glycitein

Figure 9. Structures of major isoflavones: daidzein, genistein and glycitein.

Trans-Resveratrol

Resveratrol glycoside (Piceid)
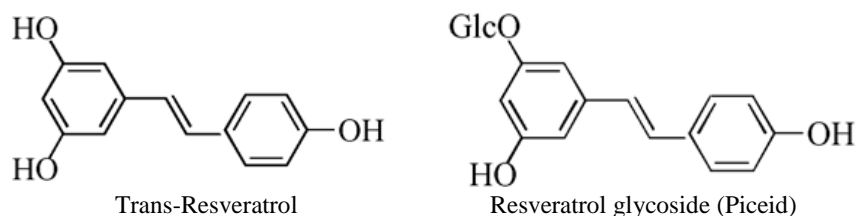
Figure 10. Structures of trans-resveratrol and resveratrol glycoside (piceid).

2.5. Tyrosol and Tyrosol Esters

Tyrosol is a phenolic antioxidant present in a variety of natural sources. The principal source in the human diet is olive oil. The major tyrosols found in olive oil are tyrosol, hydroxytyrosol and tyrosol acetate (Figure 12). Hydroxytyrosol and tyrosol are structurally identical except that hydroxytyrosol possesses an extra hydroxy group in the ortho position (Azabou et al., 2007). Hydroxytyrosol has been reported to possess different biological properties such as antioxidant (Aruoma et al., 1998; Visioli et al., 2001) and anticarcinogenic activities (Della Ragione et al., 2000; D'Angelo et al., 2005) as demonstrated by *in vitro* studies. However, *in vivo* and human studies are needed to confirm possible health benefit claimed by the *in vitro* studies.

Secoisolariciresinol

Matairesinol

Lariciresinol

Pinoresinol
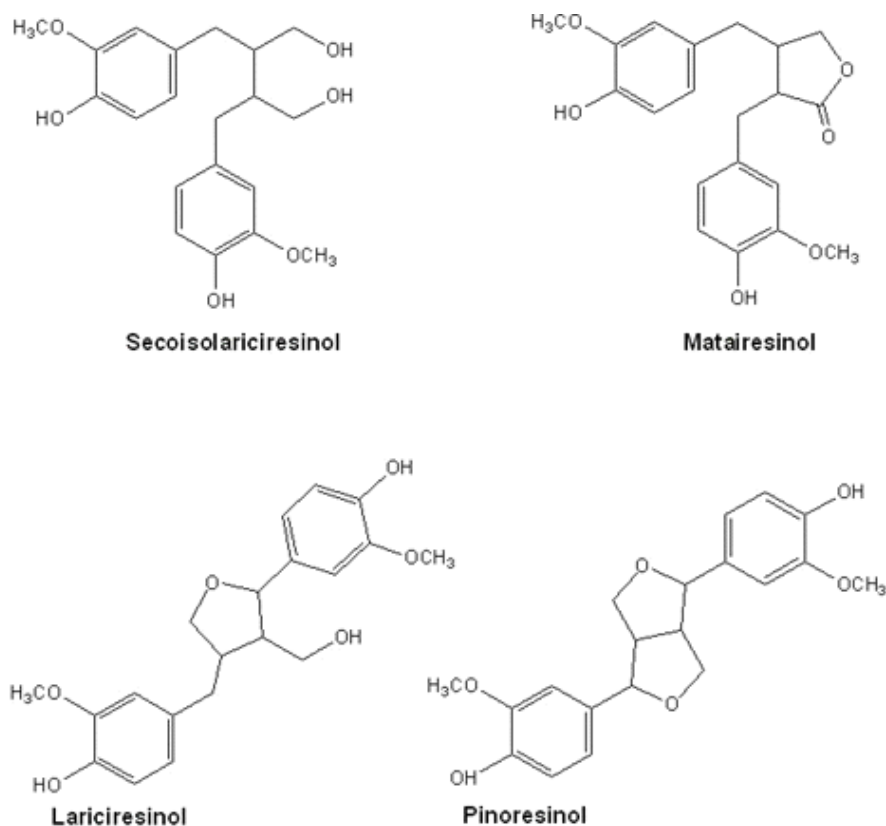
Figure 11. Chemical structure of some common dietary lignans (LPI, 2005).

3. OVERVIEW OF SELECTED AGRICULTURAL BY-PRODUCTS RICH IN POLYPHENOLS

3.1. By-Products of Peanut Processing

Peanut is an important crop grown in the U.S. and worldwide. The productions of other nuts are rather small compared to peanuts. The average global peanut production in 2012-2013 was about 39.93 million metric tons (FAS-USDA, 2014). In 2012, peanut production in the United States was about 3.06 million metric tons (6.74 billion pounds, USDA-NASS, 2013). The large scale commercial utilization of peanuts to produce peanut oil, peanut butter, roasted snack peanuts, and peanut confections generates significant amount of peanut shell and skin. The skin has a pink-red color with astringent taste, and is typically removed before peanut consumption. Peanut skin represents 3-7% of peanut kernel weight depending on the variety and size of the peanuts. Peanut skin, as a low value peanut processing industry, contains 12% protein, 16% fat, 72% of carbohydrate (Nepote et al., 2002), and is rich in polyphenols (Yu et al., 2005; Wang et al., 2007).- It is mainly used as animal feed (West et al., 1993).

Some studies have been carried out to evaluate the content and activity of peanut skin phenolics. For instance, six A-type procyanidin isomers were identified in peanut skin by Lou

and others using ^{13}C NMR (Lou et al., 1999). These six compounds were found to inhibit the activity of hyaluronidase, an enzyme that responsible for the release of histamine which causes inflammation. Catechins, B-type procyanidin dimers, procyanidins trimers, tetramers, and oligomers with higher degree of polymerization were also reported to be present in peanut skin (Lazarus et al., 1999; Yu et al., 2006). Peanut skin and cranberry are the only food sources reported to contain A-type procyanidins (Lazarus et al., 1999; Lou et al., 1999; Prior and Gu, 2005; Yu et al., 2006). In addition, resveratrol, a stilbene found in grape skin and wine, was also found in peanut skin at much higher concentration than in peanut kernels (Sanders et al., 2000).

The content of phenolics in peanut skins depends on the variety of peanuts and the type of processing. Usually, red skins contain higher amounts of phenolics than pink skins (Chukwumah et al., 2009). The extraction yield of total phenolics is affected by the solvent used and the processing methods used to remove the skin. Our research has revealed that the total phenolics (including phenolics acids, flavonoids and resveratrol) of non-defatted peanut skin was about 90-125 mg/g dry skin (Yu, et al. 2005), while total extractable phenolic content in defatted peanut skin was reported to be 144.1-158.6 mg/g dry skin (Nepote et al., 2002) depending on the solvent used.

The major phenolics in red peanut skins were found to be procyanidins including A-type and B-type procyanidin dimmers, trimers, and tetramers, while catechins occur in relatively small amounts. Two procyanidin monomers, eight B-type procyanidins dimers (MW=578), six A-type procyanidins dimers (MW=576), six A-type procyanidin trimers, ten B-type procyanidin trimers, four A-type procyanidin tetramers and 7 isomers of B-type procyanidin tetramer were identified in the work of Yu et al. (2007). Procyanidins with high degree of polymerization (e.g., pentamers, hexamers, heptamers and octamers) were reported by Lazarus et al. (1999). Phenolic acids (including caffeic acid, chlorogenic acid, and ellagic acid) and resveratrols were not quantified.

Tyrosol   Hydroxytyrosol
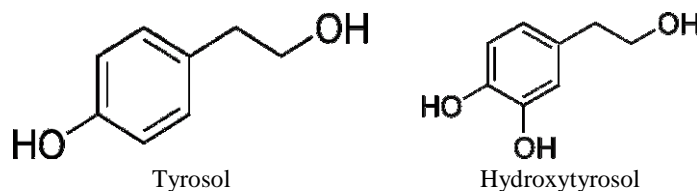
Figure 12. Chemical structures of Tyrosol and Hydroxytyrosol.

The polyphenol composition of peanut skins is affected by processing methods. Roasting had limited effects on total phenolics while blanching caused 89% loss of total phenolics. Total phenolics in directly peeled, roasted, and blanched peanut skins were 130.8, 124.3, and 15.1 mg/g, respectively (Yu et al., 2006). This indicates that procyanidins in peanut skin are highly soluble in hotwater. However, the composition changes caused by roasting (dry heat) are more complicated, and it may involve the polymerization of monomers, degradation and structure rearrangement of polymers.

Gamma radiation used to reduce the risk of microbial contamination of peanut skin changed total phenolic content, total condensed tannins, total flavonoid content, and the antioxidant activity (de Camargo et al., 2012).

Peanut skin also contains other polyphenol compounds. Lou and others (Lou et al., 2001) identified eight rare water soluble flavonoids from peanut skin extracts. Among these compounds, quercetin-3-O-[2-O-β-glucopyranosyl-6-O-α-rhamnopyranosyl]-β-glucopyrano-side and 3',5,7-trihydroxy-4'-methoxyisoflavone-3'-O-b-glucoside exhibited inhibitory effects on protein glycation which is related to the complication of diabetes.

Peanut skin polyphenols exhibited very high antioxidant activity in food products and moderate antibacterial activity. Addition of peanut skin polyphenol extract in ground beef significantly reduced the formation of peroxide and TBARS during cooking and slowed down lipid oxidation during storage of cooked meat. The effectiveness of peanut skin polyphenol as antioxidant at concentration 0.06% and higher was about the same as 0.02% BHT in cooked ground beef (O'Keefe and Wang, 2006; Yu et al., 2010). Peanut skin polyphenols also inhibited the oxidation of meat pigments myoglobin and hemoglobin and preserved the fresh redness of meat (Papadopoulou et al., 2005). Our recent study with fresh ground beef found that 0.4% of peanut skin extract reduced the growth of *E.Coli* 4066 and *S. Typhimurim* by 1 LogCFU during 12 day storage (Yu et al., 2010).

Despite measureable differences in procyanidin and phenolic content, peanuts kin polyphenol extracts from different extraction systems possessed similar antioxidant activity as determined by chemical assays and anti-inflammatory activity in an *in vitro* model of inflammation. The addition of peanut skin extract to lipopolysaccharides (LPS) challenged macrophages resulted in decreased pro-inflammatory enzyme, Cyclooxygenase-2 (COX-2) expression, as well as in decreased prostaglandin E2 (PGE2) and nitrous oxidase (NO) levels (Lewis et al., 2013). Water soluble polyphenolic extract of peanut skin (PSE) also showed hypolipidemic properties in rats on a Western diet. Rats receiving 300 mg/kg body weight showed significantly reduced body weight and epididymal fat. Plasma and liver triglyceride (TG) and cholesterol (TC) levels were significantly reduced while faecal secretion of TG and TC was greatly increased upon PSE administration. Liver mRNA expression of enzymes involved in fatty acid synthesis, and lipid uptake genes, such as PPARγ, were decreased, while PPARα was up-regulated by administration of PSE (Bansode et al., 2012). Due to their low cost, peanut skins have great potential to serve as an economical source of natural antioxidants for the food and nutraceutical industries.

3.2. By-Products of Wine and Grape Juice Processing - Grape Pomace

Grape pomace is the residue of grapes from wine and grape juice industry and poses disposal problems. According to USDA-NASS (2013), total grapes processed for wine and juice in 2012 was 4.753 million tons. About 20-30% of grapes used for wine making ends up as pomace (Amico et al., 2004; Kammerer et al., 2004; Makris, et al., 2007). Based on this percentage, the US wineries produced about 0.95-1.426 million tons of grape pomace. Grapes offer a richer polyphenol profile than many other fruits. Grape pomace is composed of grape skin, seeds and stem that are rich in both extractable and non-extractable phenolic compounds (10-11% of dry weight) (Makris, et al. 2007). The polyphenol contents and composition of grape skin and grape seeds vary with grape variety, climate condition, soil type, maturity and length of merceration (Fuleki 1997; Kennedy et al., 2000; Shi, 2003; McCalluma et al., 2007; Montealegre et al., 2006). The majority portion of grape pomace polyphenols has been

reported to be highly polymerized condensed tannin, and some polyphenols form complex with fiber, and are non-extractable unless strong acidic treatments are applied (Arranz et al., 2010).

Effects of grape variety on polyphenol composition of grape pomace

Polyphenol composition of grapes varies greatly with grape varieties, so does the polyphenol composition of grape pomace derived from grapes of different varieties or cultivars (Ruberto et al. 2007; Deng et al., 2011; González-Centeno et al., 2013).

Ruberto et al. (2007) analyzed the methanolic extracts obtained from de-stemmed grape pomace samples of five Sicilian red grape cultivars (Nero d′Avola-NA, Nerello Mascalese-NM, Nerello Cappuccio-NC, Frappato-FR and Cabernet Sauvignon-CS) by HPLC–UV–DAD and HPLC–MS–ESI and found a large variability in the total anthocyanin and flavonol contents.

The total phenolics, total flavonoids and total flavanols in grape pomace from the vinification by-products of white (Roditis) and red (Agiorgitiko) cultivars (Vitis vinifera sp.) in Greece were determined to be 4826, 3522, and 1258 mg/100g dry pomace for the white grape pomace, respectively, and 5402, 5289 and 1551 mg/100g dry pomace for the red grape pomace, respectively. Besides the lack of anthocyanins in white grape pomace, no major differences between red and white grape varieties were observed (Makris et al., 2007). Significant differences ($p < 0.05$) of the total phenolic content, total tannin content, and antioxidant capacity were observed among pomaces from the different white grape varieties studied by González-Centeno et al. (2013).

The phenolic compounds in seeds and skins of 10 *Vitis vinifera* grapes including six white varieties (Chardonnay, Sauvignon blanc, Moscatel Gewürztraminer, Riesling and Viogner) and four red grape varieties (Cencibel, Cabernet Sauvignon, Merlot and Shiraz) grown in the warm climate of Spain were studied by Montealegre et al. (2006).Up to 13 anthocyanins, 11 hydroxybenzoic and hydroxycinnamic acids, 13 catechins and flavonols, as well as 2 stilbenes were identified and quantified in the skins and seeds from vintages by HPLC-DAD. Among the anthocyanins identified in grape pomace, 5 of them are the 3-o-monoglucosides of delphinidin, cyanidin, petunidin, peonidin and malvidin; another five are the acetylglucosides of five anthocyandins. Among the 10 anthocyanins, malvidin 3-O-glucoside was the predominant anthocyanin (Montealegre et al., 2006). The total amount of catechins of grape seeds ranged from 28.0 ± 4.1(Cabernet Sauvignon and Shiraz) to 73.0 ± 20.7 (Chardonnay) mg/100g fresh grape, and procyanidin dimmers ranged from 21.0 ± 2.2 (Cabernet Sauvignon and Shiraz) to 79.0 ± 17.8 (Riesling) mg/100g fresh grape, depending on the variety. The skin of Viogner had the least of total hydroxycinnamates, catechin and procyanidin dimmers, while Moscatel skin had the most of total hydroxycinnamates and flavonols. Chardonnay and Gewürztraminer skins were the richest in catechin and procyanidins among white grape varieties. Red grape skin contains much higher amount of hydroxycinnamates than white grape skin (3.1 to 5.5 mg/100g fresh grape), but much lower amount of catechins (0.9 to 1.8 mg /100g fresh grape), procyanidin dimmers (0.8 to 1.8 mg/100g fresh grape) and total flavonols (1.2 to 1.9 mg /100g fresh grape).

Significant amounts of free anthocyanidins including delphinidin, cyanidin, petunidin, peonidin and malvidin were found in Muscadine Nobel pomace with peonidin being the predominant (Wang et al., 2010). Flavonol profiles of 21 *Vitis vinifera* white grape cultivars

in Spain were dominated by quercetin-type flavonols, but some cultivars (e.g., Pedro Ximénez, Gewürztraminer, Verdejo, Albillo, and Riesling) were characterised by relatively high and significantly different proportions of isorhamnetin-type flavonols (Castillo-Muñoz et al., 2011).

In addition to the phenolic acids, anthocyanins, catechins and procyanidins, both white and red grape contain resveratrols (3-4'-5-hydroxystilbene). The resveratrol content in grapes differs according to the variety of grape (Ector et al., 1996) and the grape maturation (Moreno et al., 2008). Dark-skinned Muscadine products had higher concentrations of resveratrol than the bronze-skinned counterparts. Although certain amount of resveratrols in grape transfers into wine during grape maceration (Feijóo et al., 2008), significant amount of resveratrols remain in the pomace. Grape skins and seeds had higher resveratrol contents than juice and wine. The trans-resveratrol content was found to be 1.11 - 12.3 mg/100 dry mass in grape skin, 8.64±4.5 mg/100 dry mass in white grape skin and 1.42± 0.18 mg/100g dry mass in white grape seeds (Kammerer, et al., 2004).

Distribution of polyphenols in different parts of grape pomace

Phenolic compound distribution in different parts of grapes was reviewed by Xia et al. (2010). Overall, grape seeds contained lower amount of phenolic acid and anthocyanins than grape skin, but higher amount of Flavan-3-ols including catechins and procyanidins.

The grape skins are proven to be rich sources of anthocyanins, hydroxycinnamic acids, flavanols, and flavonol glycosides, whereas flavanols were mainly present in the seed portion of pomace (Kammerer et al., 2004). The total anthocyanin content in red grape pomace ranged from 248 to 13,187 mg/100g dry pomace, depending on the variety of grape and crop year. About 96-99% of the total anthocyanins could be recovered by polymeric resin adsorption technology (Kammerer et al., 2005). The amount of total phenolics, total flavonoids and total flavanols in red grape peels separated from grape pomace were 3,625, 3,587 and 626 mg/100g dry peels, respectively, and were significantly higher than those in white grape peels (970, 922, 197 mg/100g dry peels, respectively) (Makris et al., 2007). When evaluated separately, the contents of the same phenolic groups were 11,108, 11,090 and 4,605 mg/100g dry mass, respectively, in the white grape seeds, and 10330, 10258 and 5,836 mg/100 g dry mass in the red grape seeds, respectively. These data show that grape seeds contain the majority of polyphenols in grape pomace and flavonoids are the main phenolic compounds in grape seeds.

Six phenolic acids in skins of Cencibel grapes were identified with t-coutaric acid, t-caftaric acid and c-coutaric acid being the dominants, and proteocatechic acid and gallic acid were the major phenolic acids in grape seeds (Gómez-Alonso e al., 2007). Specific flavanols in the grape seeds include catechin, epicatechin, catechin gallate, epicatechin gallate, procyanidin B1 and procyanidin B2. The skins of fresh red wine grape also contains significant amount of catechins and procyanidins, but the majorities of these polyphenols transferred into wine during mersaration of red wine production (Gómez-Alonso e al., 2007). The polyphenol compositions of muscadine and Cabernet pomaces were also different. The contents of total polyphenol, total anthocyanin and total flavonoid were 36.42, 0.88 and 21.02 mg/g DM in Muscadine Nobel seeds, 19.39, 8.15 and 4.78 mg/g DM in muscadine skin, respectively (Yu et al., 2011).

Effects of processing on polyphenol compositionof grape pomace

The phenolic compositions of grape pomace from juice processing and from wine making may be significantly different depending on the type of wine produced. During the red wine vintage, the crushed grapes are macerated with juice, and the majority of soluble polyphenols dissolve in the wine, leaving complex polyphenols in the pomace. Anthocyanin content of grape pomace varies with wine vinification method and contact time. The longer the contact time, the lower the anthocyanin content remains in the pomace (Gómez-Plaza et al., 2006).

Because grapes are seasonal agricultural products and the freshly pressed pomace is perishable, it has to be dried or stored at freezing temperature for use at later time. Depending on the type of dehydration methods, significant loss in polyphenols may occur during drying. Heating decreased procyanidin and anthocyanin concentrations in freeze dried grape pomace significantly ($p < 0.05$). Reduction occurred when heated at 60°C or above for 8 hours with no further reduction when heating temperature increased from 105 to 125°C. No significant loss of both procyanidin and anthocyaninin were observed when heated at 40°C for up to 3 days (Khanal, Howard & Prior, 2010). Compared to freeze drying, vacuum drying of fresh grape pomace at 60°C for 24 hours also caused significant loss of total polyphenol, flavonoid and anthocyanin in variety dependent manner (Yu et al., 2011). Extrusion of grape pomace and grape seeds was reported to increase the biologically important small molecule fractions of polyphenols in grape pomce considerably by degrading the condensed tannin (Khanal et al., 2009).

Application of grape pomace polyphenols

Although grape pomace is rich in anthocyanins, procyanidins, flavonol glycosides and resveratrols which are considered the valuable bioactive compounds, the utilization of grape pomace is limited. Only small amount of grape pomace, specifically, grape seeds, is currently used to make dietary supplements and grape seed oil. The recovered anthocyanins are usually used as food colorants. Grape seed procyanidin extract (GSPE) modulates dyslipidemia associated with a high-fat diet in rats and repress genes controlling lipogenesis and VLDL assembling in liver (Martin-Carrón et al., 2000; Baiges et al., 2010). Low dose (25mg per kg body weight per day) GSPE treatment of high-fat-diet (HFD) fed rats significantly reduced the adiposity index and the weight of all the white adipose tissue depots and reversed the increase in plasma phospholipids induced by the HFD feeding (Caimari et al., 2012). Chronic consumption of grape phenolics has been shown to reduce obesity development and related metabolic pathways including adipokine secretion and oxidative stress in a rat model (Décordé et al., 2009). GSPE has also shown to have a modulatory role on age related oxidative DNA damage and lipid peroxidation in the central nervous system of rats (Feng et al., 2005). Cancer chemopreventive and anticancer efficacy of grape seed extract and other grape-based products were summarized by Kaur et al. (2009). Grape seed extract was tested as antioxidant to inhibit the oxidation of meat products (Ahn et al., 2002; Mielnik et al., 2006; Brannan & Mah, 2007) and bread (Peng et al., 2010), and antimicrobial in fresh ground beef (Ahn et al., 2007).

Because of the high cost of using polyphenol extracts, direct incorporation of grape pomace powder in food formula has attracted great interest to both researchers and food industry. Recently, a number of studies exploring the use of grape pomace as an ingredient in food products have been reported and are described here. It was found that addition of up to 10% of deseeded grape pomace in cookie formula increased dietary fiber and reduced true

digestibility of cookies without affecting the acceptability of the cookies (Canett Romero et al., 2004). Incorporation of 0.5-5% of grape seed flour in frankfurters reduced the oxidation level, increased protein and total dietary fiber contents, and enhanced water holding capacity of the products (P<0.05) (Özvural & Halil Vural, 2011). Grape pomace was also used in sourdough (Mildner-Szkudlarz, et al., 2011) and minced fish (Sánchez-Alonso et al., 2007) to increase the dietary fiber contents and phenolic compounds of these products. Using 10% grape pomace with barley flour to develop nutritious extruded foods produced products with acceptable sensory acceptable rating (Altan et al., 2008). A study of the extrusion of grape pomace/seeds with decorticated white sorghum found that extrusion conditions had significant effects on the procyanidin and total anthocyanin compositions of grape seeds and grape pomace, respectively (Khanal et al., 2009). Inclusion of grape pomace in food products could results in functional foods with beneficial effects of dietary fiber and grape polyphenols.

3.3. By-Product of Apple Juice Processing

Apple is one of the most consumed fruits worldwide. In addition to direct consumption, large quantities of apples are used to make apple juice, cider, source, vinegar, apple pie and canned apples. World apple production was more than 75 million tons (FAOSTAT, 2014). The commercial use of apples to produce these apple-based products resulted in huge amount of apple pomace which is a complex mixture of peel, core, seed, calyx, stem, and soft tissue and represents up to 30% of the original fruit (Vendruscolo et al., 2008). Owing to the high carbohydrate and low nitrogen content, apple pomace has been used as a substrate in a number of microbial processes for the production of organic acids, enzymes, single cell protein, ethanol and low alcoholic drinks. There is an increase in the utilization of apple pomace to produce value added products such as dietary fibre, protein, natural antioxidants, biopolymers, pigments and compounds with unique properties (Bhushan et al., 2008). Apple pomace is mainly composed of apple peels and seeds and has been shown to be a good source of polyphenols which are predominantly localized in the peels and are extracted into the juice to a minor extent (Schieber et al., 2001a).

The polyphenol contents of apple vary greatly depending on variety and growing conditions, so does the apple pomace. Quantitative analysis of phenolic compounds from four apple varieties (Golden and Red Delicious, Granny Smith and Green Reineta) using high-performance liquid chromatography found that high levels of catechins and flavonol glycosides, especially rutin, were found in apple peels, while chlorogenic acid was the major phenolic acid in the pulp for all apple varieties studied except for Granny Smith. Significant differences in phenolic contents among the apple varieties were also found with the Golden Delicious showing the lowest content of phenolic compounds and Green Reineta the highest (Escarpa and Gonzalez. 1998). Polyphenols in eight most widely cultivated varieties (Renetta, Red Delicious, Granny Smith, Morgenduft, Royal Gala, Braeburn and Fuji) in western Europe were determined by Vrhosek and colleagues (2004) using reversed-phase HPLC and LC-MS. The mean content of total polyphenols was in the range of 66.2 to 211.9 mg/100 g of fresh weight depending on the variety. The Renetta apple had the highest polyphenol concent followed by Red Delicious, but Fuji apples showed the lowest phenolic content. Flavanols (catechin and proanthocyanidins) were the major class of apple polyphenols (71-90%),

followed by hydroxycinnamates (4-18%), flavonols (1-11%), dihydrochalcones (2-6%), and in red apples anthocyanins (1-3%).

Polyphenols composition in the fleshs and peels of 8 apple cultivars grown in Ontario Canada including Golden Delicious, Red Delicious, McIntosh, Empire, Ida Red, Northern Spy, Mutsu, and Cortland were determined by Tsao et al. (2003). The highest phenolic content was found in Red Delicious (235 mg/100g fresh apple) and Northern Spy (207.6 mg/100g fresh), while Empire was found to contain the least (101.6 mg/100g fresh) of total phenolics. Five major polyphenolic groups, hydroxycinnamic acids, procyanidins, anthocyanins, flavonols and dihydrochalcones were identified and quantified. Among them the dihydroxycinnamic acid esters, phloretin glycosides, and flavan-3-ols were found in both flesh and peel, whereas quercetin glycosides were almost exclusively found in the peel. Cyanidin 3-galactoside was unique to and found only in red apple peels. In both apple peel and flesh, the predominant group of polyphenolics was procyanidins, followed by quercetin glycosides in the peel and hydroxycinnamic acid esters in the flesh.

Major compounds isolated and identified from Gala apple pomace from a New Zealand juice processing company were found to be epicatechin, caffeic acid, phloretin-2′-glucoside (phloridzin), phloretin-2′-xyloglucoside, 3-hydroxyphloridzin, quercetin-3-arabinoside (avicularin), quercetin-3-xyloside (reynoutrin), quercetin-3-galactoside (hyperin), quercetin-3-glucoside (isoquercitrin) and quercetin-3-rhamnoside (quercitrin) (Lu and Foo, 1997).

The study of Schieber's group (Schieber et al., 2001b) showed that commercial apple pomace actually contains extremely high amount of phloredin followed by quercetin glycosides, chlorogenic acid, 5-hydroxymethylfurfural (5-HMF) and quercetin. It should be noted that 5-HMF is not a compounds naturally present in apple but a sugar degradation product due to the harsh drying condition of commercial apple pomace. Other phenolic compounds found in significant amount were catechin, epicatechin, p-Coumaroyl quinic acid and procyanidin B2. Kołodziejczyk et al. (2007) found that red apple pomace had higher Flavan-3-ols, procyanidins, quercetin glycosides, and phloridzin contents, but lower hydroxycinnamic acids content than Antonówka White apple pomace growni in Poland.

It was found that 100 g of freeze dried peels from Rome Beauty apples contained 3,342±12 mg of total phenolics (as gallic acid equivalent), 2,299 ± 52 mg of flavonoids (as catechin equivalent), and 169.7±1.6 mg of anthocyanins (as cyanidin equivalent) (Wolf and Liu, 2003). Twenty-nine compounds, including triterpenoids, flavonoids, organic acids and plant sterol, were isolated from Red Delicious apple pomace. On the basis of the yields of isolated flavonoids, the major flavonoids in apple peels are quercetin-3-O-β-D-glucopyranoside (82.6%), then quercetin-3-O-β-D-galactopyranoside (17.1%), followed by trace amounts of quercetin (0.2%), (−)-catechin, (−)-epicatechin, and quercetin-3-O-α-L-arabinofuranoside (He and Liu, 2008).

Another study determined the total phenolics, total flavonoids and total flavan-3-ols of dry apple pomace from six apple cultivars grown in Novi Sad, Serbia, and the contents of these groups of polyphenols in the pomace ranged from 422 to 867, 45 to 119, and 227 to 951 mg/100g, respectively, depending on the variety of apples (Ćetkovic et al., 2008). Six high-purity polyphenols were identified by HPLC/MS from the pomace of apples growing in China by Cao et al. (2009). They were chlorogenic acid (1, m/z 354), quercetin-3-glucoside/quercetin-3-glacaside (2, m/z 464), quercetin-3-xyloside (3, m/z 434), phloridzin (4, m/z 436), quercetin-3-arabinoside (5, m/z 434), and quercetin-3-rhamnoside (6, m/z 448).

However, the apple cultivar was not specified in this study. Major phenols of the pomaces of four different apple cultivars (Gala v. Royal Gala Tenroy, Golden v. Golden, Granny Smith, and Pink Lady v. Cripps Pink) were benzoic acids (gallic acid), hydroxycinnamic acids (chlorogenic acid), flavanols (catechin), flavonols (rutin) and chalcones (phloridzin) (Grigoras et al., 2013).

The studies discussed above show that the number of phenolics identified and the content of a specific phenolic compound may vary from one study to another due to the difference in polyphenol extraction methods or analytical methods used, but what is in common is that apple pomace contains higher Flavan-3-ols, procyanidins, quercetin glycosides, phloridzin and hydroxycinnamic acid contents. The specific amount of each group of these polyphenols in apple pomace varies with apple variety. In addition to many types of polyphenols, apple pomace contains about 51% of dietary fiber due to high pectin content (Figuerola et al., 2005; Sudha et al., 2007; Kołodziejczyk et al., 2007).

Many studies show that apples may reduce the risk of chronic disease by various mechanisms, including antioxidant, antiproliferative, and cell signaling effects. Consumption of apples and apple products has been associated with beneficial effects on risk, markers, and etiology of cancer, cardiovascular disease, asthma, and Alzheimer's disease. Recent work suggests that these products may also be associated with improved outcomes related to cognitive decline of normal aging, diabetes, weight management, bone health, pulmonary function, and gastrointestinal (Hyson, 2011). These make apple pomace a potential functional ingredient in the development of healthy food products.

3.4. By-Product of Citrus Processing

Citrus is an important crop with world production estimated at 115 million tons per year (FAOSTAT, 2012). Oranges, grapefruits, lemons, limes and tangerine are the most important fruits in world, particularly, in tropical areas. Citrus fruits are very nutritious because they contain very high concentrations of vitamin C, flavonoids, carotenoids and pectin (Wang, et al., 2010). Oranges, lemons, grapefruits and mandarins represent approximately 98% of industrial cultures, and oranges represent 82% of total (Marin et al., 2007). About 50-55% of the citrus fruit is juice; the remainder consists of by-products such as peels and pulp (Goodrich and Braddock, 2006). The wet peels produced from citrus juice processing contains significant amount of sugar, essential oil, limonoids and flavonoids. Sugar, essential oil and limonoids are typically recovered as value added by-products by the citrus industry, but polyphenols, specially primary flavonoids, are left in the peel which is usually pressed and dried as cattle feed (Braddock, 1995).

Five classes (flavones, flavanones, flavonols, flavans, anthocyanins and a number of phenolic acids) and over 60 flavonoid compounds have been identified and quantified in the edible portion and peels of different cultivars of citrus fruits (Peterson et al., 1998; Tripoli et el., 2007; Wang et al., 2007). The flavonoid composition of various citrus fruits differs greatly with highest amount of flavonoids occuring in the peel. Lemon, lime, sweet orange, tangerine, tangor are rich in hesperidin, whereas sour orange and grapefruit are rich in Naringin. Narirutin is present in all citrus fruit in significant amount. Neoeriocitrin and neohesperidin are present only in sour orange and tangelo, while eriocitrin exists in both lemon and lime. In citrus fruits, flavanones account for approximately 95% of the total

flavonoids. Information regarding the detailed flavanone compositions of grapefruit, lemon, lime oranges, tangerines (mandarins), tangors, and tangelos published before 2006 is presented in the reviews of Peterson et al. (2006a; and 2006b) and will not be repeated here.

Neoeriocitrin, naringin and neohesperidin are the main flavanones in the peels of sour orange (*C. aurantium*), lemon (*C. limon*) and bergamote (*C. bergamia Fantastico*) (Bocco et al., 1998; Mandalari, et al., 2006). Diosmetin derivatives are the major flavones in navel orange, bergamot and lemon peels (Mandalari et al., 2006; Lin and Harnly, 2007; Miyake et al., 1997). Hesperidin and narirutin are the most abundant flavonoid in sweet orange peels (Sawalha et al., 2009), while naringin is the most abundant flavonoid in grapefruit and bitter orange peels (Wu et al., 2007).

The major flavanones in the citrus peels from the citrus fruit growning in Taiwan are naringin, hesperidin and a small amount of neohesperidin while the flavones are diosmin, luteolin and sinensetin. The most common flavonols are rutin, quercetin and kaempferol, and the phenolic acids including caffeic acid, chlorogenic acid, ferulic acid, sinapic acid and p-coumaric acid are present in very low concentration (Wang et al., 2008). Total phenolics in edible portion and peels of citrus fruit were determined to be in the range of 913-2,160 and 3,270-4,920 mg/100g dry mass, respectively, depending on the species of the citrus. Among the species tested, peels from *C. reticulate Blanco* (Tangerines), *C. Tankan Hayata* and *C. sinensis* (sweet oranges) had the highest hesperidin content (2,950, 2,340 and 2,070 mg/100g dry mass, respectively), while *C. grandis* had highest naringin content (2,390-2,980 mg/100g dry mass). Lagha-Benamrouche et al. (2013) found that total phenolics in the peels of seven cultivars of oranges growing in Algeria varied from 9.62 to 31.62 mg GAE/g dry mass with Bigarade had the highest levels of total phenolics followed by Thomson. In summary, total phenolics and flavanone account for 0.91-4.92% and 2-3% of dry citrus peels, respectively.

Citrus flavonoids have emerged as promising therapeutic agents for the treatment of metabolic dysregulation. Many *in vitro* (cell culture) and *in vivo* (rat/mouse model) studies have shown that citrus flavanone glycosides have many health benefits such as apoptosis of cancer cells, prevention of endothelial dysfunction and oxidative stress, attenuation of lipopolysaccharide-induced hepatotoxicity (Park et al., 2008; Yamamoto et al., 2008; Kaur et al., 2006). In fact, epidemiological studies reported an inverse relationship between flavanones intake and the risk of cardiovascular diseases. Clinical and experimental data further showed their antihypertensive, lipid-lowering, insulin-sensitizing, antioxidative, and anti-inflammatory properties, which could explain their antiatherogenic action in animal models and have been used to treat allergy, heammorrhoids, hormonal disorder and ulcer (Chanet et al., 2012). In animal models, citrus flavonoid supplements prevent hepatic steatosis, dyslipidemia and improve insulin sensitivity primarily through inhibition of hepatic fatty acid synthesis and increased fatty acid oxidation (Assini et al., 2013). Therefore, the by-product of citrus processing industry could serve as a cheap source of health promoting flavanones that can be used in food ingrdients or as dietary supplements, thus adding values to this by-product.

3.5. By-Product of Cranberry Juice Processing

Cranberry is an important fruit in North America. The American cranberry is a prominent agricultural food crop produced in the US states of Massachusetts, Wisconsin, Michigan,

New Jersey, Oregon, and Washington, as well as Canada. The cranberry production in the United States in 2012 was 768.45 million pounds (equivalent to 349,000 metric tons) (USDA-NASS, 2013). Canada produced 79,163 metric tons of cranberries in 2007. Cranberry products have long been used for prevention and treatment of urinary tract infection in North America as a folk remedy. About 95% of cranberries are processed into products such as juice, sauce, and sweetened dried cranberries. Among all applications, 60% of cranberries are used to make juice, and the resulting cranberry pomace consisting of processed skins, seeds and stems has low nutritive and economic value due to the low protein and carbohydrate content (Vattem and Shetty, 2006). Its disposal into soil and in the landfill causes potential environmental problems due to its high acidity. However, cranberries are rich in biologically active phenolics including flavonols, anthocyanins, proanthocyanidins, phenolic acids and triterpenoids (Seeram et al., 2004; He and Liu, 2006; Mckay and Blumberg, 2007).

Similar to grapes and apples, cranberry skins and seeds are interesting sources phenolic compounds. For example, 100 g fresh cranberry peels contain 60-110 mg of pentacyclic triterpenoid ursolic acid depending on the cultivars, while considerably less amount of urolic acid was detected in cranberry sauce and none was detected in commercial cranberry juice (Kondo, 2006). Fifteen benzoic and phenolic acids including benzoic, o-hydroxybenzoic, cinnamic, m-hydroxybenzoic, p-hydroxybenzoic, p-hydroxyphenyl acetic, phthalic, 2,3-dihydroxybenzoic, vanillic, o-hydroxycinnamic, 2,4-dihydroxybenzoic, p-coumaric, ferulic, caffeic, and sinapic acid were identified using GC-MS (Zuo et al., 2002). Among 20 compounds identified from purified fractions of cranberry extract, ursolic acid, quercetin and 3,5,7,3'4'-pentahydroxylflavonol-O-β-D-glucopyranside showed potent antiproliferative activities against HepG2 human cancer cell and MCF-7 human breast cancer cell growth (He and Liu, 2006). Six anthocyanins, 13 flavonols and 8 procyanidins were identified and their contents in cranberry pomace were quantified on the dry mass using HPLC-ESI-MS. Total anthocyanin, flavonal and procyanidin contents were 121.4±5.9, 358.4±16.3 and 167.3±5.9 mg/100g DM, respectively (White et al., 2010; Roopchand et al. 2013).The anthocyanins were glycosides of cyanidin and peonidin; the flavonals were myricetin, quercetin and their glycosides; the procyanidins included larger quantities of A-type procyanidin dimer, trimer, pentamer and hexamer, and small quantities of catechin/epicatechin, B-type procyanidin dimer, trimer and tetramer.

Most phenolics in cranberry pomace exist in the bound form of glycosides with reduced biological activity. Works has been done to release the free phenolics from their glycosides. Solid-state bioconversion/fermentation using food grade fungus such as *Lentinus edodes* and *Rhizopus oligosporus* to produce free phenolic antioxidants in cranberry pomace has been investigated and proven to be effective (Vattem, et al. 2004).

The potential health effects of cranberries, cranberry products, and isolated cranberry components in humans and animals, as well as *in vitro* were reviewed by Pappas and Chaich (2009). These health benefits include prevention and treatment of urinary tract infections, prevention the formation of kidney stones, prevention cardiovascular diseases by lowering LDL, raising HDL cholesterol and inhibiting LDL oxidation, prevention and inhibition of cancer cancer (Ferguson et al., 2004; Neto, 2007; Caillet et al., 2012). Recent studies also indicate that consumption of cranberry polyphenols may improve oral health (Bonifait and Grenier, 2010) and enhance immunity against cold and influenza (Nantz et al., 2013).

CONCLUSION

The agricultural by-products discussed in this article are rich in various types of bioactive phenolics with proven health benefits. How to effectively utilize the phenolics in these by-products without causing new environmental problems is an important issue to food researchers and food industry. Although some polyphenols exhibit adverse effects, these effects were mostly observed at dosages much higher than the normal dietary intake. Controlled research data remain limited as to the safe dosages of different polyphenols for maximum benefits and minimum adverse effects. Such safe dose will also provide guidance for the fortification of food products with polyphenol extracts from agricultural by-products. Another important factor to be considered during product formulation is the stability of polyphenols and the interaction of polyphenols with other ingredients under specific food processing conditions.

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