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Phenolic compounds in plants and agri-industrial by-products: Antioxidant activity, occurrence, and potential uses

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Abstract

Phenolic compounds, ubiquitous in plants are an essential part of the human diet, and are of considerable interest due to their antioxidant properties. These compounds posses an aromatic ring bearing one or more hydroxyl groups and their structures may range from that of a simple phenolic molecule to that of a complex high-molecular weight polymer. Flavonoids, which bear the C_6–C_3–C_6 structure, account for more than half of the over eight thousand different phenolic compounds. The antioxidant activity of phenolic compounds depends on the structure, in particular the number and positions of the hydroxyl groups and the nature of substitutions on the aromatic rings. Fruits, vegetables and beverages are the major sources of phenolic compounds in the human diet. The food and agricultural products processing industries generate substantial quantities of phenolics-rich by-products, which could be valuable natural sources of antioxidants. Some of these by-products have been the subject of investigations and have proven to be effective sources of phenolic antioxidants. When tested in edible oils, and in fish, meat and poultry products, phenolic-rich extracts have shown antioxidant activities comparable to that of synthetic antioxidants. Practical aspects of extraction and production of sufficient amounts of natural antioxidants from most of these sources remain to be elucidated.

Keywords: Phenolic compounds; Polyphenols; Flavonoids; Antioxidants

1. Introduction

Phenolic compounds are secondary metabolites that are derivatives of the pentose phosphate, shikimate, and phenylpropanoid pathways in plants (Randhir, Lin, & Shetty, 2004). These compounds, one of the most widely occurring groups of phytochemicals, are of considerable physiological and morphological importance in plants. These compounds play an important role in growth and reproduction, providing protection against pathogens and predators (Bravo, 1998), besides contributing towards the colour and sensory characteristics of fruits and vegetables (Alasalvar, Grigor, Zhang, Quantick, & Shahidi, 2001).

Phenolic compounds exhibit a wide range of physiological properties, such as anti-allergenic, anti-artherogenic, anti-inflammatory, anti-microbial, antioxidant, anti-thrombotic, cardioprotective and vasodilatory effects (Benavente-Garcia, Castillo, Marin, Ortuno, & Del Rio, 1997; Manach, Mazur, & Scalbert, 2005; Middleton, Kandaswami, & Theoharides, 2000; Puupponen-Pimiä et al., 2001; Samman, Lyons Wall, & Cook, 1998).

Phenolic compounds have been associated with the health benefits derived from consuming high levels of fruits and vegetables (Hertog, Feskens, Hollman, Katan, & Kromhout, 1993; Parr & Bolwell, 2000). The beneficial effects derived from phenolic compounds have been attributed to their antioxidant activity (Heim, Tagliaferro, & Bobilya, 2002). Phenolic compounds

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could be a major determinant of antioxidant potentials of foods (Parr & Bolwell, 2000), and could therefore be a natural source of antioxidants. This review aims to examine the chemistry of phenolic compounds in relation to their antioxidant activity, the occurrence of phenolic compounds in various food and non-food sources, the bioavailability and metabolism of phenolic compounds and also explore the potential use of these compounds as food antioxidants.

2. The chemistry of phenolic compounds

Structurally, phenolic compounds comprise an aromatic ring, bearing one or more hydroxyl substituents, and range from simple phenolic molecules to highly polymerised compounds (Bravo, 1998). Despite this structural diversity, the group of compounds are often referred to as 'polyphenols'. Most naturally occurring phenolic compounds are present as conjugates with mono- and polysaccharides, linked to one or more of the phenolic groups, and may also occur as functional derivatives such as esters and methyl esters (Harborne, 1989; Harborne, Baxter, & Moss, 1999; Shahidi & Naczk, 1995). Though such structural diversity results in the wide range of phenolic compounds that occur in nature, phenolic compounds can basically be categorised into several classes as shown in Table 1 (Harborne, 1989; Harborne et al., 1999). Of these, phenolic acids, flavonoids and tannins are regarded as the main dietary phenolic compounds (King & Young, 1999).

Table 1
Classes of phenolic compounds in plants

Class	Structure
Simple phenolics, benzoquinones	C_6
Hydroxybenzoic acids	C_6–C_1
Acethophenones, phenylacetic acids	C_6–C_2
Hydroxycinnamic acids, phenylpropanoids (coumarins, isocoumarins, chromones, chromenes)	C_6–C_3
Napthoquinones	C_6–C_4
Xanthones	C_6–C_1–C_6
Stilbenes, anthraquinones	C_6–C_2–C_6
Flavonoids, isoflavonoids	C_6–C_3–C_6
Lignans, neolignans	$(C_6–C_3)_2$
Biflavonoids	$(C_6–C_3–C_6)_2$
Lignins	$(C_6–C_3)_n$
Condensed tannins (proanthocyanidins or flavolans)	$(C_6–C_3–C_6)_n$

Phenolic acids consist of two subgroups, i.e., the hydroxybenzoic and hydroxycinnamic acids (Fig. 1). Hydroxybenzoic acids include gallic, *p*-hydroxybenzoic, protocatechuic, vanillic and syringic acids, which in common have the C_6–C_1 structure. Hydroxycinnamic acids, on the other hand, are aromatic compounds with a three-carbon side chain (C_6–C_3), with caffeic, ferulic, *p*-coumaric and sinapic acids being the most common (Bravo, 1998).

Flavonoids constitute the largest group of plant phenolics, accounting for over half of the eight thousand naturally occurring phenolic compounds (Harborne et al., 1999). Flavonoids are low molecular weight compounds, consisting of fifteen carbon atoms, arranged in a C_6–C_3–C_6 configuration. Essentially the structure consists of two aromatic rings A and B, joined by a 3-carbon bridge, usually in the form of a heterocyclic ring, C (Fig. 2). The aromatic ring A is derived from the acetate/malonate pathway, while ring B is derived from phenylalanine through the shikimate pathway (Bohm, 1998; Merken & Beecher, 2000). Variations in substitution patterns to ring C result in the major flavonoid classes, i.e., flavonols, flavones, flavanones, flavanols (or

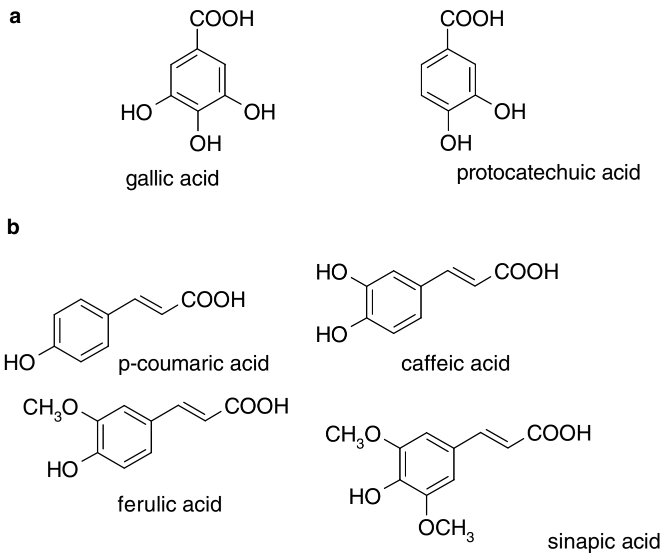

Fig. 1. Examples of hydroxybenzoic (a) and hydroxycinnamic (b) acids.

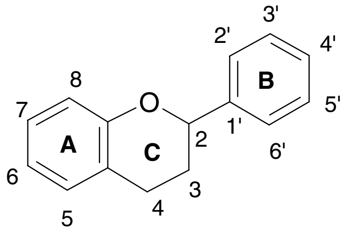

Fig. 2. Generic structure of a flavonoid molecule.

catechins), isoflavones, flavanonols, and anthocyanidins (Fig. 3) (Hollman & Katan, 1999), of which flavones and flavonols are the most widely occurring and structurally diverse (Harborne et al., 1999). Substitutions to rings A and B give rise to the different compounds within each class of flavonoids (Pietta, 2000). These substitutions may include oxygenation, alkylation, glycosylation, acylation, and sulfation (Bohm, 1998; Hollman & Katan, 1999).

Tannins, the relatively high molecular weight compounds which constitute the third important group of phenolics may be subdivided into hydrolysable and condensed tannins (Porter, 1989). The former are esters of gallic acid (gallo- and ellagi-tannins), while the latter (also known as proanthocyanidins) are polymers of polyhydroxyflavan-3-ol monomers (Porter, 1989). A third subdivision, the phlorotannins consisting entirely of phloroglucinol, has been isolated from several genera of brown algae (Porter, 1989), but these are not significant in the human diet (Bravo, 1998).

3. Structure–activity relationships

The antioxidant activity of phenolic compounds is due to their ability to scavenge free radicals, donate hydrogen atoms or electron, or chelate metal cations (Afanas'ev, Dorozhko, Brodskii, Kostyuk, & Potapovitch, 1989; Amarowicz, Pegg, Rahimi-Moghaddam, Barl, & Weil, 2004). The structure of phenolic compounds is a key determinant of their radical scavenging and metal chelating activity, and this is referred to as structure–activity relationships (SAR). In the case of phenolic acids for example, the antioxidant activity depends on the numbers and positions of the hydroxyl groups in relation to the carboxyl functional group (Rice-Evans, Miller, & Paganga, 1996; Robards, Prenzler, Tucker, Swatsitang, & Glover, 1999). Monohydroxy benzoic acids with the –OH moiety at the *ortho*- or *para*-position to the –COOH show no antioxidant activity, though the same is not true for the *m*-hydroxybenzoic acid (Rice-Evans et al., 1996). The antioxidant activity of phenolic acids increase with increasing degree of hydroxylation, as is the case of the trihydroxylated gallic acid, which shows a high antioxidant activity. However, substitution of the hydroxyl groups at the 3- and 5-position with methoxyl groups as in syringic acid reduces the activity (Rice-Evans et al., 1996).

Hydroxycinnamic acids exhibit higher antioxidant activity compared to the corresponding hydroxybenzoic acids (Andreasen, Landbo, Christensen, Hansen, & Meyer, 2001a). The higher activity of the hydroxycinnamic acid could be due to the CH=CH–COOH group, which ensures greater H-donating ability and radical stabilisation than the –COOH group in the hydroxybenzoic acids (Rice-Evans et al., 1996).

The SAR of flavonoids is generally more complicated than that of hydroxybenzoic and hydroxycinnamic acids due to the relative complexity of the flavonoid molecules. Some of the structural features and nature of substitutions on rings B and C which determine the antioxidant activity of flavonoids include the following:

(i) The degree of hydroxylation and the positions of the –OH groups in the B ring, in particular an *ortho*-dihydroxyl structure of ring B (catechol group) results in higher activity as it confers higher

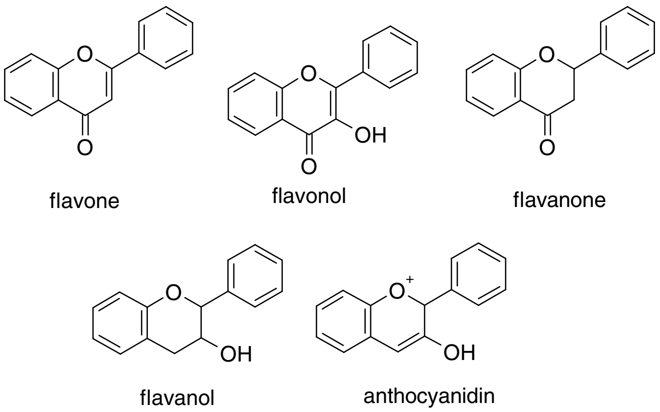

Fig. 3. Generic structure of major classes of flavonoids.

stability to the aroxyl radical by electron delocalisation (van Acker et al., 1996), or acts as the preferred binding site for trace metals (Pietta, 2000).

(ii) The presence of hydroxyl groups at the 3′-, 4′-, and 5′-positions of ring B (a pyrogallol group) has been reported to enhance the antioxidant activity of flavonoids compared to those that have a single hydroxyl group (van Acker et al., 1996). However, under some conditions, such compounds may act as pro-oxidants, thus counteracting the antioxidant effect (van Acker et al., 1996). This is consistent with the observation of Seeram and Nair (2002), who reported that the conversion of the 3′,4′-dihydroxyphenyl to 3′,4′,5′-trihydroxylphenyl increases the antioxidant activity for anthocyanidins but decreases the activity for catechins.

(iii) A double bond between C-2 and C-3, conjugated with the 4-oxo group in ring C enhances the radical scavenging capacity of flavonoids (Pietta, 2000).

(iv) A double bond between C-2 and C-3, combined with a 3-OH, in ring C, also enhances the active radical scavenging capacity of flavonoids, as seen in the case of kaempferol (van Acker et al., 1996). Substitution of the 3-OH results in increase in torsion angle and loss of coplanarity, and subsequently reduced antioxidant activity (Seeram & Nair, 2002).

(v) Substitution of hydroxyl groups in ring B by methoxyl groups alters the redox potential, which affects the radical scavenging capacity of flavonoids (Pietta, 2000; Seeram & Nair, 2002).

4. Bioavailability and metabolism of phenolic compounds

The possible health benefits derived from dietary phenolic compounds depend on their absorption and metabolism (Parr & Bolwell, 2000), which in turn are determined by their structure including their conjugation with other phenolics, degree of glycosilation/acylation, molecular size and solubility (Bravo, 1998). It had been initially believed that the absence of glycosidic-cleaving enzymes in the gut meant that only aglycones could pass through these walls (Kuhnau, 1976). However, Hollman, de Vries, van Leeuven, Mengelers, and Katan (1995), working on healthy ileostomy volunteers found that absorption of glycosides does occur in humans. They even found that absorption of quercetin glucoside from fried onions (52%) was higher than that of its orally administered aglycon (24%). It has been suggested that the bioavailability of quercetin glycosides depends on the sugar moiety attached to the phenolic structure, for example conjugation with glucose enhances bioavailability (Hollman & Katan, 1999). The bioavailability of phenolic compounds can also be affected by differences in cell wall structures, location of glycosides in cells and binding of phenolic compounds within the food matrix (Hollman et al., 1997).

Much of the earlier studies on bioavailability of phenolic compounds had concentrated on the most common dietary flavonol, quercetin. However, major advances have been achieved in recent years in understanding the absorption and metabolism of most other classes of phenolic compounds. These studies have focused on anthocyanins, flavanones, catechins, proanthocyanidins, and the hydroxybenzoic and hydroxycinnamic acids and have been extensively reviewed by Manach, Williamson, Morand, Scalbert, and Rémésy (2005) and Williamson and Manach (2005).

The precise mechanism by which some phenolic glycosides are absorbed from the gastrointestinal tract is yet to be fully elucidated, but the involvement of lactase phlorizin hydrolase (LPH), active sugar transporter (SGlT1), carrier-mediated transport process and the possible role of multidrug-resistant associated proteins (MRP) has been postulated (Clifford, 2004; Hollman et al., 1997; Murota & Terao, 2003; Yang, Landau, Huang, & Newmark, 2001). Andreasen, Kroon, Williamson, and Garcia-Conesa (2001b) have shown that esterified diferulates found in cereal brans released by intestinal esterases, can cross the gastrointestinal barrier and enter peripheral circulation. It is estimated that relative to total intake of phenolic compounds, about 5–10% is absorbed in the small intestines.

Phenolic compounds that are unabsorbed in the small intestines, as well as compounds absorbed and metabolised in the liver and excreted in bile enter the colon (Scalbert & Williamson, 2000; Yang et al., 2001). Enzymes secreted by colonic microflora hydrolyse the unabsorbed glycosides, strip the conjugates of their attached moieties, break the larger phenolic compounds to simpler molecules such as phenolic acids, or split the heterocyclic oxygen-containing ring (Hollman, 2001; Scalbert & Williamson, 2000).

Phenolic compounds may undergo methylation (catalysed by catechol-*O*-methyl transferase, COMT), sulfation (catalysed by sulfotransferases, SULT) or glucuronidation (catalysed by UDP glucuronosyl transferase, UGT), or a combination of these processes in the small intestines, liver or kidney (Yang et al., 2001). The primary site of metabolism depends on the dose, smaller doses being metabolised in the intestinal mucosa with the liver playing a secondary role, while larger doses are metabolised in the liver (Scalbert & Williamson, 2000). These enzymatic biotransformations, which result in conjugation of hydroxyl groups generally, produce metabolites that have reduced antioxidant activity (Hollman, 2001; Manach, Scalbert, Morand, Rémésy, & Jiménez, 2004).

A major concern expressed with regards to phenolic compounds has been in relation to the perceived role as 'antinutrients', particularly due to their ability to reduce digestibility of proteins, either by direct precipitation or by inhibition of enzyme activity (Ferguson, 2001). Tannins, for example form complexes with dietary proteins and carbohydrates, as well as with enzymes (Naczk, Oickle, Pink, & Shahidi, 1996; Naurato, Wong, Lu, Wroblewski, & Bennick, 1999). Besides, tannins have also been shown to reduce the absorption of minerals such as iron and copper (Reddy & Cook, 1991; Samman et al., 2001). However, chelation of these metals could sometimes be beneficial as this is one of the mechanisms by which phenolic compounds exert their antioxidant activity (Bravo, 1998).

Concerns of potential adverse effects due to excessive consumption of phenolic compounds have been expressed as there is yet limited information in this area. Several studies which suggest that some phenolic compounds, when ingested at high concentrations may be exhibit possible roles in carcinogenicity, genotoxicity, thyroid toxicity, interaction with pharmaceuticals, and estrogenic activity (for isoflavones), have been reviewed by Mennen, Walker, Bennetau-Pelissero, and Scalbert (2005).

5. Food sources of phenolic compounds

Though phenolic compounds are present in almost all foods of plant origin, fruits, vegetables, and beverages are the major sources of these compounds in the human diet (Hertog, Hollman, Katan, & Kromhout, 1993).

5.1. Fruits and vegetables

There are wide variations between the total phenolics contents of the different fruits or vegetables, or even for the same fruits or vegetables reported by different authors (Tables 2 and 3). These differences may be due to the complexity of these groups of compounds, and the methods of extraction and analysis (Bravo, 1998; Kalt et al., 2001). For example, phenolic compounds present in fruits are found in both free and bound forms (mainly as β-glycosides), but as the latter are often excluded from analyses, the total phenolics contents of fruits are often underestimated (Sun, Chu, Wu, & Liu, 2002). Besides, phenolics contents of plant foods depend on a number of intrinsic (genus, species, cultivars) and extrinsic (agronomic, environmental, handling and storage) factors (Tomás-Barberán & Espín, 2001; Rapisarda et al., 1999). Species differences are also pronounced, as observed from the data in Table 2, which suggests that the phenolics content of some fruits, i.e., banana, litchi (lichee), mango, and persimmon is considerably lower than that of berries and grapes. Asami, Hong, Barrett, and Mitchell (2003) reported that organically grown strawberries were found to have higher phenolics content than conventionally grown crops, though another study could not establish such a correlation (Häkkinen & Törrönen, 2000). Processing and storage may have varying impacts on different phenolic compounds, as seen in berry processing where myricetin and kaempferol were found to be more prone to losses than quercetin (Häkkinen, Kärenlampi, Mykkänen, & Törrönen, 2000).

Table 2
Phenolics content of selected fruits

Fruit	Total phenolics content	Reference
Apple	296.3 ± 6.4[a]	Sun et al. (2002)
Banana	90.4 ± 3.2[a]	Sun et al. (2002)
Banana	11.8 ± 0.4[a]	Luximon-Ramma et al. (2003)
Black plum	143.5 ± 40.6[b]	Karakaya et al. (2001).
Blackberry	417–555[a]	Sellappan et al. (2002)
Blackberry (*Rubus* species)	26.7–452.7[a]	Deighton et al. (2000).
Blueberry (rabbiteye)	270–930[a]	Sellappan et al. (2002)
Blueberry (Southern highbush)	261–585[a]	Sellappan et al. (2002)
Blueberry (*Vaccinium species*)	171–961[a]	Moyer et al. (2002)
Cherry	105.4 ± 27.0[b]	Karakaya et al. (2001).
Cranberry	527.2 ± 21.5[a]	Sun et al. (2002)
Guava (pink)	126.4 ± 6.0[a]	Luximon-Ramma et al. (2003)
Guava (white)	247.3 ± 4.5[a]	Luximon-Ramma et al. (2003)
Litchi (lichee)	3.35 ± 0.05[c]	Gorinstein et al. (1999)
Litchi (lichee)	28.8 ± 1.7[a]	Luximon-Ramma et al. (2003)
Mango	6.25 ± 0.05[c]	Gorinstein et al. (1999)
Mango	56.0 ± 2.1[a]	Luximon-Ramma et al. (2003)
Peach	84.6 ± 0.7[a]	Sun et al. (2002)
Papaya	57.6 ± 4.1[a]	Luximon-Ramma et al. (2003)
Persimmon	1.45[c]	Gorinstein et al. (1999)
Pineapple	94.3 ± 1.5[a]	Sun et al. (2002)
Pineapple	2.58 ± 0.05[c]	Gorinstein et al. (1999)
Plums	174–375[a]	Kim et al. (2003)
Prunes (pitted)	184.0 ± 85.5[a]	Donovan et al. (1998)
Raisins	399.4 ± 57.6[b]	Karakaya et al. (2001).
Rambutan	1.64 ± 0.04[c]	Gorinstein et al. (1999)
Raspberry	114–178[a]	de Ancos et al. (2000)
Red grape	220.6 ± 61.2[c]	Karakaya et al. (2001).
Red grape	201.0 ± 2.9[a]	Sun et al. (2002)
Starfruit (acidic)	142.9 ± 7.1[a]	Luximon-Ramma et al. (2003)
Starfruit (sweet)	209.9 ± 10.4[a]	Luximon-Ramma et al. (2003)
Strawberry	161–290[a]	Heinonen et al. (1998)
Strawberry	160 ± 1.2[a]	Sun et al. (2002)

[a] Gallic acid equivalents/100 g fresh weight.
[b] Catechin equivalents/100 g fresh weight.
[c] Chlorogenic acid equivalents/100 g fresh weight.

5.2. Beverages

Beverages such as fruit juices, tea and wines are important sources of phenolics in the human diet. Most of the data available on phenolics contents of commonly consumed juices are for commercial samples (Table 4). Reductions or losses of phenolic compounds have been reported in commercial juices, and these have been attributed to commercial processing procedures (Spanos,

Table 3
Phenolics content of selected vegetables

Vegetable	Total phenolics content	Reference
Broccoli	101.6 ± 1.24[a]	Chu et al. (2002)
	87.5 ± 8.1[b]	Kaur and Kapoor (2002)
Brussel sprouts	68.8 ± 1.3[b]	Kaur and Kapoor (2002)
Cabbage	54.6 ± 7.0[a]	Chu et al. (2002)
	92.5 ± 2.4[b]	Kaur and Kapoor (2002)
Carrot	56.4 ± 5.1[a]	Chu et al. (2002)
	55.0 ± 0.9[b]	Kaur and Kapoor (2002)
Cucumber	19.5 ± 1.6[a]	Chu et al. (2002)
	48.0 ± 0.9[b]	Kaur and Kapoor (2002)
Mint	399.8 ± 3.2[b]	Kaur and Kapoor (2002)
Spinach	91.0 ± 8.5[a]	Chu et al. (2002)
Tomato	25.9 – 50.0[c]	Martínez-Valverde et al. (2002)
	68.0 ± 1.6[b]	Kaur and Kapoor (2002)
Vidalia onion varieties	73.3–180.8[a]	Sellappan and Akoh (2002)
Yellow onion	76.3 ± 1.9[a]	Chu et al. (2002)

[a] Gallic acid equivalents/100 g fresh weight.
[b] Catechin equivalents/100 g fresh weight.
[c] Ferulic acid equivalents/100 g fresh weight.

Table 4
Phenolic content of some fruit juices

Juice	Total phenolics content	Reference
Commercial juices		
Apple	339 ± 43[a]	Gardner et al. (2000)
Grapefruit	535 ± 11[a]	Gardner et al. (2000)
Orange	755 ± 18[a]	Gardner et al. (2000)
Pineapple	358 ± 3[a]	Gardner et al., 2000
Prune	441 ± 59[b]	Donovan et al. (1998)
Fresh juices		
Grape (red)	1728[a]	Sánchez-Moreno et al. (1999)
Grape (white)	519[a]	Sánchez-Moreno et al. (1999)
Orange	382–1147[b]	Rapisarda et al. (1999)

[a] mg gallic acid equivalents/ L.
[b] mg ferulic acid equivalents/L.

Wrolstad, & Heatherbell, 1990). Arts, van de Putte, and Hollman (2000) reported that low levels of catechins were detected in commercial grape juice, and none in commercial apple juice, while van der Sluis, Dekker, Skrede, and Jongen (2002) reported that the chlorogenic acid content of apple juice was only 50% of that of fresh apples. On the other hand, Gerard and Roberts (2004) reported that processes such as microwave heat treatment of apple mash increased total phenolics content in the juice up to 65 mg/100 mL. In general, the phenolics content of juices are quite stable during storage, particularly at low temperatures. It was found that apple juice stored at 4 °C or at 20 °C for up to 1 month showed no significant changes in phenolics content (van der Sluis, Dekker, & van Boekel, 2005).

Catechins (flavan-3-ols), predominantly (−)-epicatechin (EC), (−)-epicatechin gallate (ECG), (−)-epigallocatechin (EGC), (−)-epigallocatechin gallate (EGCG), (+)-catechin (C), and (+)-gallocatechin (GC) are the major phenolic compounds in green tea (Dufresne & Farnworth, 2000; Heijnen, Haenen, Wiseman, Tijburg, & Bast, 2000). The production of black tea via fermentation (enzyme-catalysed oxidation reaction) results in the formation of more complex substances such as theaflavins and thearubigins (Richelle, Tavazzi, & Offord, 2001), as the catechin content is reduced to 20% of that in green tea (Heijnen et al., 2000). Hydroxycinnamic acids such as chlorogenic acid, caffeic acid, ferulic acid and *p*-coumaric acid are present in coffee (Nardini, Cirillo, Natella, & Scaccini, 2002). The phenolics content of black and green teas and coffee are as shown in Table 5.

The major phenolic constituents of wines include hydroxybenzoic and hydroxycinnamic acid derivatives, as well as flavonols (quercetin and myricetin), flavan-3-ols (catechin and epicatechin) (Minussi et al., 2003). The phenolic contents and composition in wines vary widely and are determined by several factors, such as the variety of grapes used, conditions under which they were grown, wine making techniques, maturity, and processing parameters (Goldberg, Karumanchiri, Tsang, & Soleas, 1998; Mazza, Fukumoto, Delaquis, Girard, & Ewert, 1999).

The phenolics content of different wines are shown in Table 6. Red wines contain more than 1000 mg gallic acid equivalents (GAE)/L of total phenolics, compared to less than 500 mg GAE/L for most white wines. Anthocyanins from grape skins are the major component responsible for the colour and the higher phenolics content of red wines compared to white wines (Mazza et al., 1999). In general, wines made from fruits or berries other than grapes were found to have lower total phenolics content than red wines (Heinonen, Lehtonen,

Table 5
Phenolic content of teas and coffee

Beverage, type	Total phenolics content[a]	Reference
Tea		
Black tea	80.5–134.9	Khokhar and Magnusdottir (2002)
Black tea	154.9–162.9	Lakenbrink et al. (2000)
Black tea	62–107	Luximon-Ramma et al. (2005)
Green tea	65.8–106.2	Khokhar and Magnusdottir (2002)
Green tea	117.3	Samman et al. (2001)
Green tea	61–200	Schulz et al. (1999)
Coffee		
Instant coffee	146–151	Lakenbrink et al. (2000)
Ground coffee	52.5–57.0	Lakenbrink et al. (2000)

[a] mg gallic acid equivalents/g dry matter.

Table 6
Phenolic content of different wines

Colour, region, country	Total phenolics content[a]	Reference
Red wines		
Argentine	1593–1637	Sánchez-Moreno et al. (2003)
Brazilian	1947–1984	Minussi et al. (2003)
Californian	1800–4059	Frankel et al. (1995)
Chilean	2133	Minussi et al. (2003)
French	1847–2600	Teissedre and Landrault (2000)
French	1018–3545	Landrault et al. (2001)
Greek	1217–3722	Arnous et al. (2001)
Italian	3314–4177	Minussi et al. (2003)
Japanese	1810–2151	Sato et al. (1996)
Portuguese	1615	Minussi et al. (2003)
Spanish	1869	Sánchez-Moreno et al. (1999)
White wines		
Argentine	216	Minussi et al. (2003)
Brazilian	256–353	Minussi et al. (2003)
Californian	165–331	Frankel et al. (1995)
Californian	220–306	Sánchez-Moreno et al. (2003)
French	245	Teissedre and Landrault (2000)
French	262–1425	Landrault et al. (2001)
Italian	439–854	Minussi et al. (2003)
Italian	191–296	Sánchez-Moreno et al. (2003)
Japanese	295–556	Sato et al. (1996)
Spanish	292	Sánchez-Moreno et al. (1999)
Rose wines		
Italian	1304	Minussi et al. (2003)
Japanese	340	Sato et al. (1996)

[a] mg gallic acid equivalents/L.

& Hopia, 1998). Sánchez-Moreno, Cao, Ou, and Prior (2003), however reported that wines made from blueberries have higher total phenolics content (600–1860 mg GAE/L) than that of white wines (191–306 mg GAE/L).

6. Phenolic compounds from agro-industrial by-products

The processing of plant foods results in the production of by-products that are rich sources of bioactive compounds, including phenolic compounds (Schieber, Stintzing, & Carle, 2001). The availability of phenolic compounds from agricultural and industrial residues, their extraction and antioxidant activity have been the subject of a review by Moure et al. (2001).

Phenolic compounds with antioxidant activity have been identified in several agricultural by-products, such as rice hulls (Ramarathnam, Osawa, Namiki, & Kawakishi, 1989), buckwheat hulls (Watanabe, Ohshita, & Tsushida, 1997) and almond hulls (Takeoka & Dao, 2002). Bryngelsson, Mannerstedt-Fogelfors, Kamal-Eldin, Andersson, and Dimberg (2002) reported that the total cinnamic acid content of the hulls of Swedish oats (*Avena sativa* L) was higher than that of the groats (23.6 compared to 3.6 mg/kg dry matter). Pistachio hulls are another source of phenolic antioxidants, and may contain up to 34 mg tannic acid equivalents phenolics/g dry weight (Goli, Barzegar, & Sahari, 2005).

The citrus industry produces large quantities of peels and seed residue, which may account for up to 50% of the total fruit weight (Bocco, Cuvelier, Richard, & Berset, 1998). Citrus industry by-products, if utilised optimally could be major sources of phenolic compounds as the peels, in particular, have been found to contain higher amounts of total phenolics compared to the edible portions. Gorinstein et al. (2001) found that the total phenolics content in peels of lemons, oranges, and grapefruit were 15% higher than those in the peeled fruits.

The peels of several other fruits have also been found to contain higher amounts of phenolics than the edible fleshy parts. For instance, peels from apples, peaches and pears were found to contain twice the amount of total phenolics as found in the peeled fruits (Gorinstein et al., 2002). Similarly, peels of yellow- and white flesh nectarines were reported to contain at least twice as much phenolics as the flesh (Gil, Tomás-Barberán, Hess-Pierce, & Kader, 2002). Chang, Tan, Frankel, and Barrett (2000) studied eight selected clingstone peach cultivars, and reported that the peels contain 2–2.5 times the amount of total phenolics as that contained in the edible flesh. While the edible pulp of banana (*Musa cavendish*) contains 232 mg/100 g dry weight phenolics, this amount is about 25% of that present in the peel (Someya, Yoshiki, & Okubo, 2002). Similarly, Li et al. (2005) have reported that pomegranate peels contain 249.4 mg/g phenolics compared to just 24.4 mg/g phenolics in the pulp. Apple peels were found to contain up to 3300 mg/100 g dry weight of phenolics (Wolfe & Liu, 2003), while the lypholisate recovered from apple pomace was found to contain about 118 mg/g of phenolics (Schieber et al., 2003).

The by-products of the olive industry have attracted considerable interest as a source of phenolic compounds, with much attention focused on the olive mill wastes. The phenolic compounds present in the olive fruits are distributed into the olive oil, the aqueous-phase wastewater, or the solid phase pomace, with only 1–2% partitioning into the former (Rodis, Karathanos, & Mantzavinou, 2002). The olive mill wastes are therefore a major potential source of phenolics, particularly in consideration that annual production exceeds 7 million tonnes (Ranalli, Lucera, & Contento, 2003). The phenolic content of the olive mill waste water (OMWW) is reported to fluctuate between 1.0% and 1.8% (Visioli & Galli, 2003) depending on varietal factors and processing effects. The major components in OMWW include hydroxytyrosol, tyrosol, oleuropein, and a variety of hydroxycinnamic acids (Obied et al., 2005). Besides OMWW, olive leaves are another by-product of the olive industry that has been explored as a source of phenolics, albeit to a lesser extent. Benavente-Garcia, Castillo, Lorente, Ortuňo, and Del Rio (2000) found that oleuropein was the major phenolic compound in olive leaves, followed by hydroxytyrosol, luteolin-7-glucoside, apigenin-7-glucoside, and verbascoside.

Grape seeds and skin, by-products of grape juice and white wine production are also sources of several phenolic compounds, particularly mono-, oligo-, and polymeric proanthocyanidins (Shrikhande, 2000; Torres & Bobet, 2001). Soong and Barlow (2004) have reported that the total phenolics content of seeds of several fruits, i.e., mango, longan, avocado, and jackfruit were higher than that of the edible flesh, as such these seeds could be a valuable source of antioxidant phenolics. The peels and seeds of tomatoes have been found to be richer sources of phenolic compounds than the fleshy pulp. George, Kaur, Khurdiya, and Kapoor (2004) studied 12 genotypes of tomatoes, and found that the free phenolic content (expressed as mg catechin/100 g, fresh weight) in pulps ranged from 9.2 to 27.0 mg/100 g, compared to 10.4 to 40.0 mg/100 g in peels, and also that for each genotype, the phenolic content in peel was higher than in pulp. A similar observation has been made by Toor and Savage (2005), who reported that the total phenolics content (expressed as mg gallic acid equivalents/100 g) of skin and seeds of tomatoes were, respectively, 29.1 and 22.0, compared to 12.7 mg /100 g in the pulp. The phenolic compounds content of several other agro-industrial by-products are as illustrated in Table 7.

Some bioprocesses can enhance recovery of phenolic compounds from agri-industrial wastes. One such process reported by Correia, McCue, Magalhães, Macêdo, and Shetty (2004) describes use of the fungus *Rhizopus oligosporus* to produce phenolic compounds from pineapple waste (residual pulp, peels and skin)-soybean flour mixture. These authors found a 2-fold increase in total phenolics content of a 1:1 pineapple:soybean flour mixture 12 days after incubation with the fungus. Thermal processing has also been found to enhance the recovery of phenolic compounds, as described by Garrote, Cruz, Domínguez, and Parajó (2003) for autohydrolysis of corn cobs, where increasing reaction temperatures resulted in higher phenolics yields, but with lower specific activity. In another study, Jeong et al. (2004) too have reported that heat treatment at 150 °C for 40 min liberated bound phenolics in citrus peels, as a result of which the total phenolic content increased significantly from 71.8 to 171.0 μM after treatment. Other bioprocesses for the production of phenolics from agro-industrial by-products include the sequential treatments of dewaxed sugarcane baggase with water, alkali and alkaline peroxide which resulted in estherified ferulic and coumaric acids (Sun, Sun, Sun, Fowler, & Baird, 2003).

7. Phenolic compounds as food antioxidants

Synthetic antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and *tert*-butylhydroquinone (TBHQ) have been used widely as

Table 7
Phenolic compounds from agricultural by-products

By-product	Phenolic compounds	Levels[a]	Reference
Almond [*Prunus dulcis* (Mill.) D.A. Webb] hulls	Chlorogenic acid	42.52 ± 4.50 mg/100 g fw	Takeoka and Dao (2002)
	4-*O*-Caffeoylquinic acid	7.90 mg/100 g fw	
	3-*O*-Caffeoylquinic acid	3.04 mg/100 g fw	
Apple peels	Flavonoids	2299 mg CE/100 g dw	Wolfe and Liu (2003)
	Anthocyanin	169 mg CGE/100 g dw	
Artichoke blanching waters	Neochlorogenic acid Cryptochlorogenic acid Chlorogenic acid Cynarin Caffeic acid derivatives	11.3 g phenolics/100 mL	Llorach et al. (2002)
Buckwheat (*Fagopyrum esculentum* Möench) hulls	Protocatechuic acid	13.4 mg/100 mg dw	Watanabe et al. (1997)
	3,4-Dihydroxybenzaldehyde	6.1 mg/100 g dw	
	Hyperin	5.0 mg/100 g dw	
	Rutin	4.3 mg/100 g dw	
	Quercetin	2.5 mg/100 g dw	
Dried apple pomace	Flavonols	673 mg/kg dw	Schieber et al. (2003)
	Flavanols	318 mg/kg dw	
	Dihydrochalcones	861 mg/kg dw	
	Hydroxycinnamates	562 mg/kg dw	
Dried coconut husk	4-Hydroxybenzoic acid ferulic acid	13.0 mg phenolics/g dry weight	Dey et al. (2003)

[a] Expressed on fresh weight (fw) or dry weight (dw) basis.

antioxidants in foods, but concerns over the safety of use have led towards interests in natural antioxidants (Wanasundara & Shahidi, 1998). These synthetic antioxidants are substituted phenolic compounds, and subsequently much of the research on natural antioxidants has also focused on phenolic compounds, in particular the flavonoids and hydroxycinnamic acids (Martínez-Valverde, Periago, Provan, & Chesson, 2002). The antioxidant activities of phenolic compounds extracted from different sources have been studied in several foods and food model systems.

Frankel, Huang, Prior, and Aeschbach (1996) reported that rosemary extracts (carnosol and carnosic acid) were effective antioxidants in corn, soybean, peanut and fish oils tested in bulk systems, but were either ineffective or acted as prooxidants in the corresponding vegetable oil-in-water emulsion systems. This was attributed to the interfacial phenomena, where the hydrophilic rosemary antioxidants remained oriented in the air-oil interphase, thus affording better protection against oxidation. Rosemary extracts, used in combination with the synthetic antioxidant BHT, in mixtures of 75:25, 50:50, or 25:75 provided more effective protection against oxidation of soybean oil than when either was used alone (Basaga, Tekkaya, & Acikel, 1997). Wanasundara and Shahidi (1998) found that green tea extract had a prooxidant effect on the oxidation of marine oils examined under Schaal oven conditions at 65 °C, and this was attributed to the presence of chlorophyll. Subsequent work using dechlorophyllised green tea extract (DGTE) indicated that DGTE at $\geqslant$200 ppm exhibited an antioxidant activity higher than BHA, BHT and α-tocopherol, but less than that of TBHQ. Phenolic compounds extracted from mango seed kernel powder was found to extend the shelf life of buffalo ghee (Puravankara, Boghra, & Sharma, 2000). Yu, Haley, Perret, and Harris (2002) demonstrated that extracts from the hard winter wheat (*Triticum aestivum)* variety Trego was able to suppress the oxidation of fish oils, and its capacity was comparable to tocopherol. Phenolic compounds from extra virgin olive oil (EVOO) at 400 ppm showed comparable antioxidant effect as 100 ppm 1:1 mixture of BHT:BHA during thermal oxidation of tuna lipids at 40 and 100 °C (Medina, Satué-Gracia, German, & Frankel, 1999). Yanishlieva and Marinova (2001) have reviewed the use of phenolic compounds from plant sources as natural antioxidants in a number of edible oils, such as corn, cottonseed, fish, olive, peanut, rapeseed, soybean, and sunflower oils. Goli et al. (2005) reported that pistachio hull extracts used at a concentration of 0.06% (w/w), was as effective as BHA and BHT at 0.02% in inhibiting oxidation of soybean oil at 60 °C.

Methanolic extracts of wild rice hulls were shown to inhibit lipid oxidation in ground beef as measured by the thiobarbituric acid reactive substances (TBARS) (Asamarai, Addis, Epley, & Krick, 1996). Tea catechins were found to be more efficient than α-tocopherol (both applied at 300 mg/kg level) in inhibiting minced muscle lipid oxidation in fresh meats, poultry and fish (Tang, Sheehan, Buckley, Morrissey, & Kerry, 2001). Lau and King (2003) reported that the addition of grape seed extract to dark poultry meat patties at 1.0% and 2.0% effectively inhibited the development of TBARS, with treated samples having 10-fold lower TBARS values compared to untreated control. The addition of 2% orange fibre to bologna sausages was found to significantly retard the development of TBARs over 28-days of storage at 4 °C when compared to untreated sausages (Fernández-López et al., 2004). Pazos, Gallardo, Torres, and Medina (2005) reported that phenolics from grape pomace were as effective an antioxidant as propyl gallate in fish oil-in-water emulsions.

8. Conclusion

Phenolic compounds are ubiquitous in plants, and when plant foods are consumed, these phytochemicals contribute to the intake of natural antioxidants in the human diets. Agro-industrial by-products are good sources of phenolic compounds, and have been explored as source of natural antioxidants. While the use of naturally occurring phenolic compounds as food antioxidants is particularly interesting, practical aspects that need to be considered include extraction efficiency, availability of sufficient raw material, and toxicity or safety considerations. The very complexity in the phenolic compounds profile of these by-products has to be resolved to obtain the optimum antioxidant efficiency.

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