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Review

Plant phenolic compounds for food, pharmaceutical and cosmetics production

Sytar Oksana[1,2], Brestic Marian[1,4], Rai Mahendra[3] and Shao Hong Bo[1,4,5]*

[1]Department of Plant Physiology, Slovak University of Agriculture in Nitra, Tr. A. Hlinku 2, 949 76 Nitra, Slovakia.
[2]Department of Plant Physiology and Ecology, Taras Shevchenko National University of Kyiv, Volodymyrs'ka St. 64, 01601 Kyiv, Ukraine.
[3]Department of Biotechnology, SGB Amravati University, Maharashrta, India.
[4]Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Chunhui Rd.17, Yantai 264003, China.
[5]Institute of Life Sciences Qingdao University of Science and Technology, Zhengzhou Road 53, Qingdao 266042, China.

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The biochemical features and biological function of dietary phenols, which are widespread in the plant kingdom, have been described in the present review. The ways of phenols classification, which were collected from literature based on structural and biochemical characteristics with description of source and possible effects on human, organisms and environment have been presented. The bioactivities of phenolic compounds described in literature are reviewed to illustrate their potential for the development of pharmaceutical and agricultural products.

Key words: Plant phenols, phenolic acids, flavonoids, cathecins, tannins, food industry.

INTRODUCTION

Phenolic compounds are plant secondary metabolites that constitute one of the most common and widespread groups of substances in plants (Whiting, 2001). As stated by Harborne (1989), the term "phenolic" or "polyphenol" can be precisely defined chemically as a substance which possesses an aromatic ring bearing one (phenol) or more (polyphenol) hydroxyl substituents, including functional derivatives (esters, methyl ethers, glycosides, and others): as a general rule, the terms phenolic and polyphenol refers to all secondary natural metabolites arising biogenetically from the shikimate-phenylpropanoids-flavonoids pathways, producing monomeric and polymeric phenols and polyphenols. Phenol itself is a natural product but most phenols have two or more hydroxyl groups. The structure of phenols consists of an aromatic ring carrying one (phenol) or more hydroxyl (polyphenol) moieties. Several classes of phenols have been categorized on the basis of their basic skeleton: C6 (simple phenol, benzoquinones), C6-C1 (phenolic acid), C6-C2 (acetophenone, phenylacetic acid), C6-C3 (hydroxycinnamic acids, coumarins, phenylpropanes, chromones), C6-C4 (naphthoquinones), C6-C1-C6 (xanthones), C6-C2-C6 (stilbenes, anthraquinones), C6-C3-C6 (flavonoids, isoflavonoids), (C6-C3)2 (lignans, neolignans), (C6-C3-C6)2 (bioflavonoids), (C6-C3)n (lignins), (C6)n (catechol melanins), (C6-C3-C6)n (condensed tannins) (Harborne, 1980; Aoki et al., 2000; Hättenschwiler and Vitousek, 2000; Iwashina, 2000; Lattanzio and Ruggiero, 2003). King and his colleagues in 1999 selected 3 most important groups of dietary phenols: flavonoids, phenolic acids, and polyphenols (King and Young, 1999). Several classes of phenols can be distinguished according to the number of phenol rings and to the structural elements that join these rings (Stalikas, 2007). Flavonoids are the largest group of plant phenols and the most studied. Phenolic acids form a diverse group that includes the widely distributed checked hydroxybenzoic and hydroxycinnamic acids. Two main groups of polyphenols, termed flavonoids and non-flavonoid, have been adopted in the literature (De la Rosaet al., 2010). The flavonoid

*Corresponding author. E-mail: shaohongbochu@126.com or marian.brestic@uniag.sk.

Figure 1. 3-Hydroxybenzoic acid (1) and 4-Hydroxybenzoic acid (2).

group, including flavanones, flavones, dihydroflavonols, flavonols, flavan-3-ols, isoflavones, anthocyanidins, proanthocyanidins and chalcones, comprises those compounds with a C6-C3-C6 structure.

Phenolic polymers, commonly known as tannins, are compounds of high molecular weight that are divided into 2 classes: hydrolysable and condensed tannins. Quantification of food phenols is just beginning, and preliminary results indicate high variability, even within a given food. Phenols can be important components of the human diet due to their potential antioxidant activity (Martin and Appel, 2010; Siddique et al., 2010), their capacity to diminish oxidative stress induced tissue damage resulted from chronic diseases (Bravo, 1998), and their potentially important properties such as anticancer activities (Harris et al., 2007; Huang et al., 2010).

Plants need phenolic compounds for pigmentation, growth, reproduction, resistance to pathogens and for many other functions. These compounds form one of the main classes of secondary metabolites and several thousand (among them over 8,150 flavonoids) different compounds have been identified with a large range of structures: monomeric, dimeric and polymeric phenols.

Less polar phenolic substances, such as tocopherols, lignans or resins, may be added to fats and oils increasing their stability on storage and heating. More polar phenols are advantageous for stabilization of food dispersions. Rosemary and sage resins were found efficient in frying fats. Particularly high content of phenols is found in spices, tea leaves, roasted coffee and cocoa beans, and in red wine. Attempts to increase the antioxidant levels in blood stream were not very efficient as most phenols are inactivated before or immediately after the resorption through the intestine wall (Pokorny, 2008).

Phenolic substances are mainly deposited (Yanishlieva, 2001) in leaves or bark (in case of trees or bushes), together with other waste products. Phenolic substances also serve as protectants against bacterial pathogens (*Staphylococcus areus*, *Pseudomonas aeroginosa, Bacillus cereus* and *Esherishia coli)* (Ghasemi et al., 2011; Haq et al., 2011). Phenolic compounds are potential antioxidants because there is relation between antioxidant activity and presence of phenols in common vegetables and fruits (Cai et al., 2004; Fu et al., 2011). A positive linear correlation between antioxidant capacities and total phenolic contents implied that phenolic compounds in tested 50 medicinal plants could be the main components contributing to the observed activities. The results showed that *Geranium wilfordii*, *Loranthus parasiticus*, *Polygonum aviculare, Pyrrosia sheaeri, Sinomenium acutum* and *Tripterygium wilfordii* possess the highest antioxidant capacities and total phenolic content among 50 plants tested, and could be rich potential sources of natural antioxidants (Gan et al., 2010).

Most seeds contain large amount of polyunsaturated oils and phenolic antioxidants necessary to protect polyunsaturated fatty acids in oil against autoxidation until the next crop. During oilseed processing, less polar antioxidants are co-extracted with oil, while more polar antioxidants, insoluble in the extraction solvent, remain in the extracted meal (Pokorny et al., 2001). Plant seeds are important sources of phytochemicals for nutritional, industrial, and pharmaceutical applications (Tlili et al., 2009). For these reasons, new plant sources of antioxidant phytochemicals, especially phenols, have been investigated (Meot and magnel., 2009; Tlili et al., 2011)

PHENOLIC ACIDS

Phenolic acids have a carboxyl group attached or linked to benzene ring (Lafay and Gil-Izquierdo., 2008). Two classes of phenolic acids can be distinguished depending on their structure: benzoic acid derivatives (*i.e.* hydroxybenzoic acids, C6-C1) and cinnamic acid derivatives (that is, hydroxycinnamic acids, C6-C3) (Robbins, 2003).

3-Hydroxybenzoic acid

The compound as shown in Figure 1a is found in common plants such as grapefruit (*Citrus paradisi*), olive oil (*Olea europaea*) (Bendini et al., 2007), and medlar fruit (*Mespilus germanica*) (Gruz et al., 2011).

It has glucosylating activity (Ford and Hoj., 1998). *p*-Hydroxybenzoic acid (4-hydroxybenzoic acid, Figure 1 and 2) has been isolated from many sources including carrots (*Daucus carota*) (Sircar and Mitra ., 2009), oil palm (*Elaeis guineensis*) (Chong et al., 2009), grapes (*Vitis vinifera*), and numerous other species including east African satinwood (*Fagara macrophylla*), yellow-leaf tree (*Xanthophyllum rubescens*), peroba (*Paratecoma peroba*), taheebo (*Tabebuia impetiginosa*), red sandalwood (*Pterocarpus santalinus*), southern catalpa

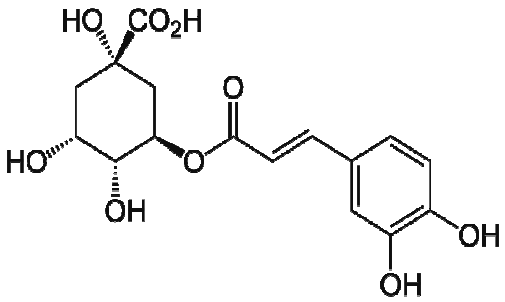


Figure 2. Chlorogenic acid.

(*Catalpa bignonioides*), Chinese chastetree (*Vitex negundo*) (Ling et al., 2005), betel palm (*Areca catechu*), Cuban royal palm (*Roystonea regia*) (Chakraborty et al., 2006), and medlar (*Mespilus germanica*) (Gruz et al., 2011). It shows antifungal, antimutagenic, antisickling, estrogenic (Pugazhendhi et al., 2005), and antimicrobial (Chong et al., 2009) activities. *p*-Hydroxybenzoic acid (Figure 1b) was detected in cell wall extracts from *Arabidopsis thaliana* roots and its concentration increased upon infection with *Pythium sylvaticum*. *p*-Hydroxybenzoic acid increases the impermeability of the cell wall, leading to increased resistance against pathogen infection (Tan et al., 2004; Horváth et al., 2007). *p*-Hydroxybenzoic and salicilic acids are synthesized de novo in stems and petioles in response to a mobile signal from the inoculated leaf by *Pseudomonas syringae* pv. *syringae* (Smith-Becker et al., 1998). *p*-Hydroxybenzoic acid has a growth stimulation effect on the freshwater green alga *Pseudokirchneriella subcapitata* (Kamaya et al., 2006).

p-Hydroxybenzoic acid may induce oxidative stress in the skin after conversion to glutathione conjugates of hydroquinone by reacting with singlet oxygen and glutathione (Nishizawa et al., 2006). Salicylic acid biosynthesis is catalyzed by benzoic acid 2-hydroxylase and connected with *p*-hydroxybenzoic acid. Therefore, induction and control of *p*-hydroxybenzoic acid under stress conditions are important for the anti-oxidative system. For example, inhibition of benzoic acid 2-hydroxylase can control the endogenous response to salt stress and prevent salycilic acid accumulation in rice seedlings under oxidative stress (Sawada et al., 2006). *p*-hydroxybenzoic acid is able to inhibit activity of both catalase isoforms (CAT1 and CAT2) in the same competitive manner. *p*-hydroxybenzoic acid was also the only phenolic compound examined that failed to induce chilling tolerance in young maize plants (Horváth et al., 2002). Exogenous *p*-hydroxybenzoic acid has been shown ability to increase abiotic stress tolerance to drought stress of the winter wheat (*Triticum aestivum* L.) cv. Cheyenne (Horváth et al., 2007).

In literature data shown that *p*-hydroxybenzoic acid increases the impermeability of the cell wall, leading to increased resistance against pathogen infection (Horváth et al., 2007). Induction and control of *p*-hydroxybenzoic acid under stress conditions are important for the anti-oxidative system because biosynthesis of salycilic acid is catalyzed by benzoic acid 2-hydroxylase and connected with P-hydroxybenzoic acid (Sawada et al., 2006). One of the role important roles of salicilic acid in inducing resistance to various environmental stresses (Matewally et al., 2003) is manifested by its ability to express genes that code for PR-proteins (Merkouropoulos et al., 1999). *p*-Hydroxybenzaldehyde might be the immediate precursor in *p*-hydroxybenzoic acid biosynthesis. At *in vitro* conversion of *p*-coumaric acid to *p*-hydroxybenzoic acid with *p*-hydroxybenzaldehyde as intermediate using cell-free extract provided an unequivocal support for CoA-independent and non-*β*-oxidative route of *p*-hydroxybenzoic acid biosynthesis (Sircar and Mitra., 2009).

Among more polar antioxidants in the extracted meal, various phenolic acids from class of cynamic acid derivatives (that is, hydroxycinnamic acids, C6-C3), such as ferulic or sinapic acids, and their esters, or chlorogenic acid are of importance. Rapeseed extracted meals are extraordinary rich source of sinapic acid, bound to choline as an ester (Schmidt and Pookorny., 2006), but it is not active as an antioxidant. Extracted meals of evening primrose seeds contain several efficient phenolic antioxidants so that their extracts are active both in oils and their emulsions (Schmidt et al., 2003).

Chlorogenic acid

Chlorogenic acid is a hydroxycinnamic acid, a member of a family of naturally occurring organic compounds (Figure 2). These are esters of polyphenolic caffeic acid and cyclitol (-)-quinic acid (Clifford et al., 2003). It is an important biosynthetic intermediate (Wout et al., 2003). Coffee is a major source of chlorogenic acid in the human diet; daily intake in coffee drinkers is 0.5 to 1 g; coffee abstainers will usually ingest, 100 mg/day. Chlorogenic acid could be partly responsible for the higher homocysteine concentrations observed in coffee drinkers (Margreet et al., 2001). Other dietary sources of chlorogenic acid include apples, pears, berries, artichoke and aubergines (Clifford, 1999). It is also one of the phenols found in black tea (Margreet et al., 2001), bamboo *Phyllostachys edulis* (Kweon et al., 2001), buckwheat plants (Alvares-Jubete et al., 2010), as well as many other plants.

Previous studies have confirmed that chlorogenic acid has the same biosynthesis pathway as quercetin-3-O-rutinoside and cyanidin-3-galactoside (Lancaster, 1992). Mohamed et al. (2001) suggested that the accumulation of chlorogenic acid is apparently not affected by the synthesis of quercetin-3-O-rutinoside and cyanidin-3-galactoside (Mohamed et al.,

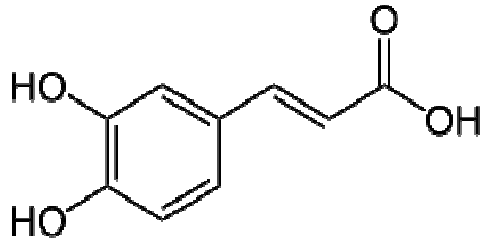


Figure 3. Caffeic acid.

2011). Venkataramaiah et al. (2007) has indicated that the biosynthesis of chlorogenic acid can be catalyzed by a cytochrome P450 enzyme, CYP98A3 from Arabidopsis (Venkataramaiah et al., 2007). Hydroxycinnamoyl CoA quinate transferase (HQT) is the key enzyme catalysing chlorogenic acid biosynthesis in tomato and relationship between phenolic accumulation and UV-susceptibility in transgenic tomato plants with altered HQT expression. The capability of the phenolic compounds to protect against potentially harmful UV radiation is determined both by the total levels of phenols that accumulate in leaves as well as by the specific composition of the phenolic profile (Carla Cle et al., 2008).

Chlorogenic acid and many other polyphenol compounds are extensively used in medicine and industries such as in consumer chemicals and food industries (Kweon et al., 2001). Chlorogenic acid is used as various additives in beverage, cosmetics, tea products and foods as well as medical substances (Jin et al., 2005). Chlorogenic acid has antibacterial and antiviral properties (Jiang et al., 2001). Chlorogenic acid, the most potent functional inhibitor of the microsomal glucose-6-phosphate translocase (G6PT), is thought to possess cancer chemopreventive properties (Herling et al., 1998). It is also a promising precursor compound for the development of medicine that can resist AIDS virus HIV (Ma et al., 2003).

Chlorogenic acid is an extremely widespread plant metabolite that appears to provide protection against certain forms of stress (Grace et al., 2000). Although the reduced form of chlorogenic acid exhibits antioxidant activity (Rice-Evans et al., 1997), its oxidized form has been shown to initiate lipid peroxidation of soybean liposomes that can be detected by the formation of 4-hydroxynonenal, a decomposition product of lipid peroxide (Sakihama and Yamasaki, 2002). Al enhances lipid peroxidation induced by the oxidized form of chlorogenic acid (Sakihama et al., 2002). Enhancement of the prooxidant nature of chlorogenic acid by Al can be accounted for by stabilization of the radical. In fact, other spin-stabilizing metals produce effects similar to Al. Zn, Cd, Mg and Ca, all of which have been reported to have the spin-stabilizing effects, stimulate lipid peroxidation induced by the oxidized form of chlorogenic acid (Sakihama et al., 2002). Because these metals without chlorogenic acid radicals are do not induce significant *in vitro* lipid peroxidation (Sakihama et al., 2002). In this case direct interactions between metals and lipids can be considered negligible in the stimulation mechanism.

Caffeic acid

Caffeic acid is occurs in foods mainly as an ester with quinic acid called chlorogenic acid (5-caffeoylquinic acid), and found at extremely high levels in coffee, but also at more modest levels in other plant foods (Figure 3) (Clifford, 1999). Caffeic acid (3,4-dihydroxycinnamic acid) is among the major hydroxycinnamic acids present in wine (Ilhami, 2006).

Potential health effects of caffeic acids have been demonstrated in many animal models and *in vitro* assays (Clifford, 1999). Caffeic acid is an effective antioxidant in different i*n vitro* antioxidant assays including total antioxidant activity by ferric thiocyanate method, reducing power, ABTS•+ scavenging, DPPH• scavenging, superoxide anion radical scavenging and metal chelating activitiy when it is compared to standard antioxidant compounds such as butylated hydroxyanisole, α-tocopherol, a natural antioxidant, and trolox which is a water-soluble analogue of tocopherol (Ilhami, 2006). Chlorogenic acid and caffeic acid are antioxidants *in vitro* (Rice-Evans et al., 1996), and they might inhibit the formation of mutagenic and carcinogenic N-nitroso compounds because they are inhibitors of the *N*-nitrosation reaction *in vitro* (Margreet et al., 2001). Caffeic acid esters are *in vitro* inhibitors of plant pathogenic bacteria and fungi too (Helle et al., 1989). Caffeic acid and its derivatives are good substrates of polyphenol oxidases, and under certain conditions may undergo oxidation in plant tissues or products of plant origin (Bassil et al., 2005).

In the Rancimat test, the addition of test compounds in lard significantly extended the induction time of lipid oxidation, and the activities in decreasing order were caffeic acid ≈α-tocopherol > caffeic acid phenethyl ester ≈ rosmarinic acid > chlorogenic acid > ferulic acid ≈ ferulic acid phenethyl ester. When the lipid substrate was changed to corn oil, the effectiveness of antioxidants on the induction time was obviously decreased, and the potency order of antioxidants was changed to rosmarinic acid > caffeic acid ≈ caffeic acid phenethyl ester ≈ chlorogenic acid > α-tocopherol > ferulic acid and ferulic acid phenethyl ester had no significant antioxidative effect in the corn oil system (Jiang Hong Chen et al.,1997).

Investigation of structure−activity relationships of synthetic caffeic acid amide and ester analogues as potential antioxidants and free radical scavengers has been established that the radical scavenging activity of the compounds increased with increasing numbers of

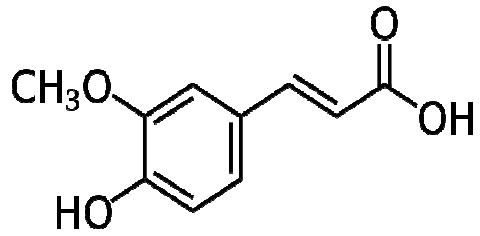


Figure 4. Ferulic acid.

hydroxyl groups or catechol moieties and also with the presence of other hydrogen-donating groups (−NH, −SH) (Sopheak Son and Betty ., 2002). The 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) scavenging activity of the test compounds was *N-trans*-caffeoyl-L-cysteine methyl ester > *N-trans*-caffeoyldopamine > *N-trans*-caffeoyltyramine > *N-trans*-caffeoyl-β-phenethylamine > Trolox C > caffeic acid phenethyl ester > caffeic acid > ferulic acid. Dietary hydroxycinnamates consist predominantly of ferulic acid and caffeic acid.

Ferulic acid

Ferulic acid (4-hydroxy-3-methoxycinnamic acid) is representative of hydroxycinnamates group (Paul A Kroon et al., 1999) (Figure 4), an effective component of Chinese medicine herbs such as *Angelica sinensis, Cimicifuga heracleifolia* and *Lignsticum chuangxiong*, is a ubiquitous phenolic acid in the plant kingdom. Ferulic acid is covalently linked to plant cell walls and is especially abundant in an insoluble form in cereal brans. It is mainly conjugated with mono- and oligosaccharides, polyamines, lipids and polysaccharides and seldom occurs in a free state in plants (Shiyi and Ou Kin-Chor., 2004). Ferulic acid is a ubiquitous plant constituent that arises from the general phenylpropanoid pathway in plants. This pathway originates from phenyalanine and tyrosine and is responsible for the biosynthesis of a very large number of diverse secondary metabolites such as lignin and lignin precursors, including feruloyl CoA and *p*-coumaroyl CoA (Boudet, 1998). Fang et al. (2006) suggested model for monolignol and ferulate biosynthesis which appears to be an over-simplification, at least in alfalfa, and additional enzymes may be needed for the 3-*O*-methylation reactions of S lignin and ferulate biosynthesis (Fang et al., 2006).

Ferulic acid is a phenolic acid of low toxicity; it can be absorbed and easily metabolized in the human body. Due to its phenolic nucleus and an extended side chain conjugation, it readily forms a resonance stabilized phenoxy radical which accounts for its potent antioxidant potential. UV absorption by ferulic acid catalyzes stable phenoxy radical formation and thereby potentiates its ability to terminate free radical chain reactions. By virtue of effectively scavenging deleterious radicals and suppressing radiation-induced oxidative reactions, ferulic acid may serve an important antioxidant function in preserving physiological integrity of cells exposed to both air and impinging UV radiation (Ernst, 1992).

The high fluorescence yield of ferulic acid containing cell walls is also documented by fluorescence excitation spectra of isolated, dried cell walls before and after alkaline hydrolysis of ferulic acid. Members of the Poaceae (monocotyledonous plants), e.g. maize (*Zea mays* L.), wheat (*Triticum aestivum* L.) or oat (*Avena sativa* L.), possessed a much higher blue-green fluorescence and content of ferulic acid in cell wall. Plants which do not possess ferulic acid in their cell walls, such as sunflower, pumpkin (*Cucurbita ficifolia* L.) or tobacco, exhibit only a very faint blue-green fluorescence emission (Lichtenthaler and Schweiger, 1998). Ferulic acid has been reported to have many physiological functions, including protection against coronary disease, lowers cholesterol and increases sperm viability (Shiyi and Kin-Chor., 2004). In same time because of photoprotective properties and low toxicity, ferulic acid is now widely used in the food and cosmetic industries. The photoprotective properties are afforded to skin by ferulic acid dissolved in cosmetic lotions. Its incorporation into a topical solution of 15% L-ascorbic acid and 1% α-tocopherol improved chemical stability of the vitamins (C+E) and doubled photoprotection to solar-simulated irradiation of skin from 4-fold to approximately 8-fold as measured by both erythema and sunburn cell formation. Inhibition of apoptosis was associated with reduced induction of caspase-3 and caspase-7 (Fu-Hsiung et al., 2005). This antioxidant formulation efficiently reduced thymine dimer formation. This combination of pure natural low molecular weight antioxidants provides meaningful synergistic protection against oxidative stress in skin and should be useful for protection against photoaging and skin cancer. Ferulic acid is addition to foods inhibits lipid peroxidation and subsequent oxidaive spoilage. By the same mechanism ferulic acid may protect against various inflammatory diseases like other representatives of hydroxycinnamates group. The interest in hydroxycinnamates as bioactive components of the diet, as structural and functional components of plant cell walls, and as precursors for favours in the food industry has expanded rapidly in the last 5-10 years. There were also striking increases (10- to 20-fold) in the number of publications on related hydroxycinnamates (caffeic, *p*-coumaric and sinapic acid).

p-Coumaric acid

P-Coumaric acid (4-hydroxycinnamic acid) is a hydroxy derivative of cinnamic acid. There are three isomers, *o*-coumaric acid, *m*-coumaric acid, and *p*-coumaric acid, which differ by the position of the hydroxy substitution of

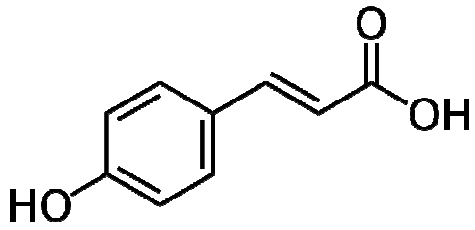


Figure 5. *p*-Coumaric acid.

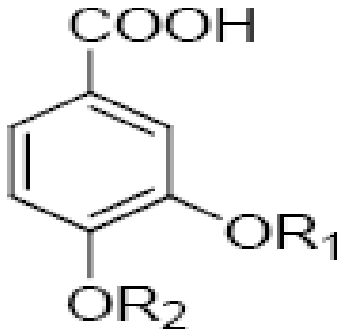


Figure 6. Vanillic acid (1), and Isovanillic acid (2).1. Vanillic acid (R1=CH3, R2=H)2. Isovanillic acid (R1=H, R2=CH3).

the phenyl group. *p*-coumaric acid is the most abundant isomer of the three in nature (Figure 5). Together with sinapyl alcohol and coniferyl alcohols, *p*-coumaric acid is a major component of lignocellulose. It is biosynthesized from cinnamic acid by the action of the P450-dependent enzyme 4-cinnamic acid hydroxylase.

P-Coumaric acid (4- hydroxycinnamic acid) is a ubiquitous plant phenolic acid that is typically esterified to arabinoxylan residues of hemicellulose or to lignin in graminaceous plants, including maize, oats (Xing and Pamela., 1997), and wheat (Pan et al., 1998). It is also presented as an ester conjugate and as the free acid in fruits and vegetables such as apples (Geoffrey et al., 1996), grapefruits, oranges, tomatoes, potatoes, and spinach (Clifford , 1999). In respect of maize, *p*-coumaric acid has been reported to account for up to 4% of the dry weight including the stalk, root, and cob (Janelle et al., 2001).

Bryngelsson et al. (2002) reported that common commercial processing such as steaming and autoclaving increased the levels of *p*-coumaric acid and ferulic acid in dehhuled oat groats, while the levels of caffeic acid and tocotrienols were not increased. The daily consumtion of cereals, vegetables, fruits in the ingestion of a large amount of p-coumaric acid sentence imcomplete. *P*-coumaric acid inhibited morpholine nitrosation (Li et al., 1994), and reacted with peroxynitrite to reduce 3-nitrotyrosine formation *in vitro* (Niwaa et al., 1999), suggesting that p-coumaric acid would exhibit its physiological effects through regular intake.

P-coumaric acid has antioxidant properties and is believed to reduce the risk of stomach cancer (Ferguson et al., 2005) by reducing the formation of carcinogenic nitrosamines (Kikugawa et al., 1983).

In same time the dietary phenolic acids thus showed diversified characteristics in their intestinal absorption. The transepithelial transport of such common dietary phenolic acids as *p*-coumaric acid and gallic acid across Caco-2 cell monolayers was examined. *P*-coumaric acid transport was dependent on pH, and in a vectorial manner in the apical-basolateral direction. The permeation was concentration-dependent and saturable, the Michaelis constant and maximum velocity being 17.5 mM and 82.7 nmol min^{-1} (mg of protein)$^{-1}$, respectively. Benzoic acid and acetic acid inhibited the permeation of *p*-coumaric acid. These results indicate that the transepithelial transport of *p*-coumaric acid was via the monocarboxylic acid transporter (Konishi et al., 2003).

Yan et al. (2009) has shown that a plant phenolic compound, *p*-coumaric acid, represses the expression of T3SS genes of the plant pathogen *Dickeya dadantii*, suggesting that plants can also defend against bacterial pathogens by manipulating the expression of the type III secretion system. A further analysis of several *p*-coumaric acid analogs suggests that the *para* positioning of the hydroxyl group in the phenyl ring and the double bond of *p*-coumaric acid may be important for its biological activity (Yan et al., 2009).

Vanillic acid

4-hydroxy-3-methoxybenzoic acid (Figure 6) occurs in many plants such as prickly ash (*Fagara* spp.), Japanese alder (*Alnus japonica*), spiny oleaster (*Elaeagnus pungens*), Spanish heath (*Erica australis*), upland cotton (*Gossypium mexicanum*), Chinaberry (*Melia azedarach*), oriental ginseng (*Panax ginseng*), Korean peroba (*Paratecoma koraiensis*), red sandalwood (*Pterocarpus santalinus*), dog rose (*Rosa canina*), shensi (*Picrorhiza kurrooa*), luo shi (*Trachelospermum asiaticum*), ishpingo (*Amburana cearensis*), Shiitake mushroom (*Lentinula edodes*) and Eggplant (*Solanum melongena* L.) (Shaoli Chen et al., 2011).

Besides antisickling and anthelmintic activities, vanillic acid could suppress hepatic fibrosis in chronic liver injury (Itoh et al., 2009, 2010). It is also found to be an inhibitor of snake venom 5'-nucleotidase (Dhananjaya, et al., 2009). Sathyaneson and Booblaan (2010) has shown the potential protective role of vanillic acid as one of the major phenolic derivatives from edible plants and fruits was evaluated against the acetaminophen, which is a widely used analgesic and antipyretic drug and in

overdose can cause life-threatening hepatotoxicity and nephrotoxicity in humans (Sathyaneson and Boolaan., 2010).

Isovanillic acid

(3-hydroxy-4-methoxybenzoic acid) is a methyl ether derivative of protocatechuic acid. It is found in hortensia (*Hydrangea macrophylla*), Chinese endospermum tree (*Endospermum chinense*) (Li et al., 2007), the orange relative *Citrus changshan-huyou* (Zhao et al., 2009), Chinese banyan (*Ficus microcarpa*) (Lai and Zhou., 2008), the chamomile relative *Anthemis melanolepis* (Saroglou et al., 2008), poonspar (*Calophyllum polyanthum*) (Zhong et al., 2010), sanchi ginseng (*Panax notoginseng*) (Komakine et al., 2006), Formosa koa (*Acacia confusa*) (Tung et al., 2007), the breadfruit relative *Treculia obovoidea* (Kuete et al., 2007), and saffron (*Crocus sativus*). Isovanillic acid has antibacterial (Kuete et al., 2007) and antioxidant activities (Tung et al., 2007).

FLAVONOIDS

The role of flavonoids as the major red, blue, and purple pigments in plants has gained these secondary products a great deal of attention over the years. Flavonoids constitute a relatively diverse family of aromatic molecules that are derived from Phe and malonyl-coenzyme A (CoA; via the fatty acid pathway). These compounds include six major subgroups that are found in higher plants: the chalcones, flavones, flavonols, flavandiols, anthocyanins, and condensed tannins (or proanthocyanidins); a seventh group, the aurones, is widespread, but not ubiquitous. Some plant species also synthesize specialized forms of flavonoids, such as the isoflavonoids that are found in legumes and a small number of nonlegume plants.

Similarly, sorghum (*Sorghum bicolor*), maize (*Zea mays*), and gloxinia (*Sinningia cardinalis*) are among the few species known to synthesize 3-deoxyanthocyanins (or phlobaphenes in the polymerized form). The stilbenes, which are closely related to flavonoids, are synthesized by yet another group of unrelated species that includes grape (*V. vinifera*), peanut (*Arachis hypogaea*), and pine (*Pinus sylvestris*). Thus, it appears that branches in this pathway have evolved multiple times or been lost from specific plant lineages over the course of evolution (Winkel-Shirley, 2001).

All plant leaves contain phenolic substances, sometimes in high amounts. e. g. in tea leaves. Most phenolic antioxidants are flavonoids, such as catechins, of different structures and antioxidant activities (Pokorný, 2000). Natural antioxidants from herbs and spices were recently reviewed (Yanishlieva et al., 2006). Many among them are well known because of their phenols content. On contrary, less familiar materials, such as sweetgrass (*Hierochloe odorata* Walhl.), used for flavouring certain types of vodka, was also found very effective as an antioxidant (Zainuddin et al., 2002). Some plant leaves are applied to food, and are widely used. Perhaps the best known antioxidants from plant leaves are leaves from green and black (fermented) tea. Content of catechins is particularly high in green tea, but its infusions are less concentrated. During the tea fermentation, about 50% phenolic substances are converted into black tea pigments – theaflavins and thearubigins – nevertheless, they have some residual activity, too, and black tes, prepared at higher concentrations, is a very good source of antioxidants in Europe (Pokorný, 2007). A few cups of strong tea would supply nearly the daily portion of antioxidants. Extracts from tea wastes are commerically available. Herbal teas also contain phenolic substances, but in smaller amounts.

CATHECINS

There are several polyphenolic catechins in green tea, viz. (−) epicatechin (EC), (−) epicatechin-3-gallate (ECG), (−) epigallocatechin (EGC), (−) epigallocatechin-3-gallate (EGCG), (+) catechin, and (+) gallocatechin (GC) (Figure 7). EGCG, the most abundant catechin in green tea, accounts for 65% of the total catechin content. A cup of green tea may contain 100–200 mg of EGCG. Catechin and gallocatechin are present in trace amounts (Chu and junejal., 1997).

These catechins are present in higher quantities in green tea than in black or oolong tea, because of differences in the processing of tea leaves after harvest. For green tea, fresh tea leaves from the plant *Camellia sinensis* are steamed and dried to inactivate the polyphenol oxidase enzyme, a process that essentially maintains the polyphenols in their monomeric forms. Black tea, on the other hand, is produced by extended fermentation of tea leaves which results in the polymeric compounds, thearubigins and theaflavins. Oolong tea is a partially fermented product and contains a mixture of the monomeric polyphenols and higher molecular weight theaflavins (Graham, 1992). All three varieties of tea contain significant amounts of caffeine (3 to 6%) which is unaffected by the different processing methods (Chu, 1997).

Monomeric flavonoids (flavan 3-ols or tea catechins) present in *Camellia sinensis* leaf are transformed to polymeric theaflavin and thearubigin by oxidation occurring during tea fermentation. The distinctive colour, decreased bitterness and astringency, and characteristic flavour are derived from the fermentation process giving fermented teas a marked distinction from non-fermented green tea. Even though teas are available in many different fermentation levels from green to black, the

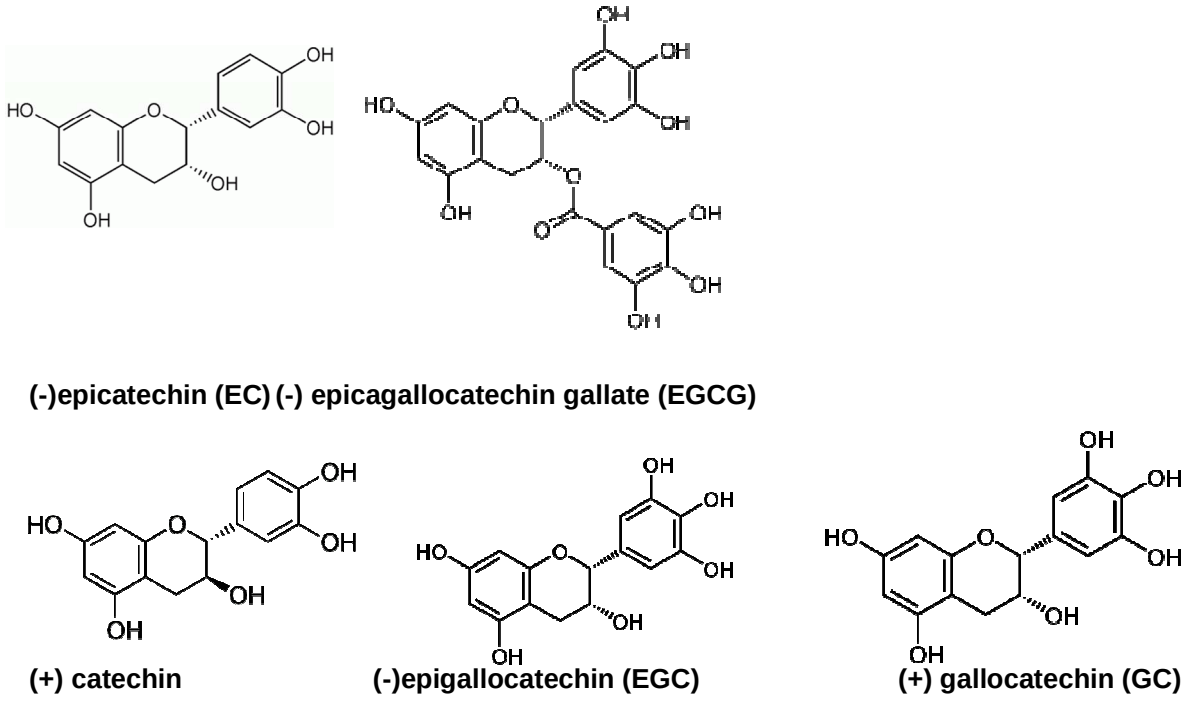


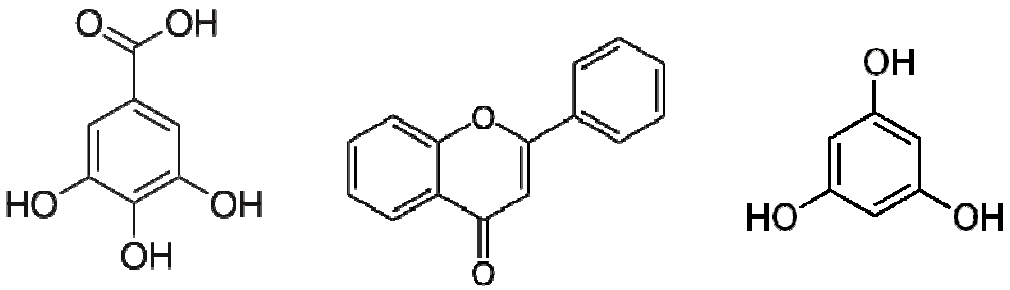
Figure 7. Structure of major polyphenolic cathechins.

difference in phytochemicals and volatile compounds in teas with different degrees of fermentation has not been fully investigated yet within the same tea leaf. Kim et al. (2001) in their research work with strict processing control and evaluation the degree of fermentation for the maximum antioxidant capacity of same tea material has been observed that fermentation diminished antioxidant capacity of tea and could result in lowering potential health benefits from flavonoid (Kim et al., 2011).

Most of the medicinal properties of green tea are associated with the 'epi'catechins rather than the catechins. The green tea catechins have been shown to be more effective antioxidants than vitamins C and E (Rice-Evanset al., 1995), and their order of effectiveness as radical scavengers is ECG-EGCG-EGC-EC-catechin.

The cancer chemopreventive properties, green tea and epigallocatechin gallate (EGCG) have been shown to be anti-angiogenic (prevention of tumor blood vessel growth) (Pfeffer et al., 2003) and anti-mutagenic (Han, 1997). The antioxidant properties and the ability of its polyphenolic catechins to scavenge reactive oxygen species are due to the presence of the phenolic hydroxy groups on the B-ring in ungalloylated catechins (epicatechin and epigallocatechin) (Figure 7) and in the B- and D-rings of the galloylated catechins (epigallocatechin and epigallocatechin gallate) (Salah et al., 1995). The presence of the 3,4,5-trihydroxy B-ring has been shown to be important for antioxidant and radical scavenging activity (Valcic et al., 1999). The metal-chelating properties of green tea catechins are also important contributors to their antioxidative activity (Kumamoto et al., 2001). Recent studies have shown that misregulated iron metabolism may be a central pathological feature in Parkinson's disease and that the iron-chelating properties of epigallocatechin gallate are important for its protective effects in neurodegenerative diseases (Mandel et al., 2004a). In well-established animal models of Parkinson's disease, neurotoxins 1-methyl-4- phenyl-1,2,3,4-tetrahydropyridine (MPTP) and 6-hydroxydopamine (6-OHDA) induce dopaminergic cell death and accumulation of Lewy bodies, mediated through several mechanisms involving oxidative stress. Various studies have shown that green tea and epigallocatechin gallate significantly prevent these pathologies in animal models (Levites et al., 2001). Epigallocatechin gallate administered orally in doses as low as 25 mg/kg, prevented loss of dopaminergic neurons in the substantia nigra and preserved striatal levels of dopamine (Choi et al., 2002).

In addition to antioxidant effects, green tea catechins have effects on several cellular and molecular targets in signal transduction pathways associated with cell death and cell survival. These effects have been demonstrated in both neuronal cells and in tumor epithelial/endothelial cells (Mandel et al., 2004b; Gouni-Berthold and Sachinidis, 2004). However, it is still unclear whether these effects on molecular endpoints in signal transduction pathways are downstream events of the modulation of pro-oxidant/antioxidant balance in cells or



Gallic acid **Flavone** **Phloroglucinol**

Figure 8. Tannins.

due to the direct action of epigallocatechin gallate and other catechins on the various molecular targets, independent of antioxidant activities. Furthermore, most of the putative molecular mechanisms that have been proposed are based on *in vitro* studies at epigallocatechin gallate concentrations far in excess of those achievable *in vivo*. Whether these molecular are targets affected *in vivo* after green tea consumption still remains to be shown.

PHENOLIC POLYMERS, TANNINS

Tannins are phenolic compounds found in many plant species. Tannins deter against animal consumption due to a bitter taste and/or toxic consequences upon injestion. The important biochemical property of tannins is their ability to bind to protein and form insoluble complexes. Tannins are generally poorly defined chemically and are found in complex mixtures in many plants. All tannins are polyphenolic compounds, although not all polyphenols have the protein binding properties of tannins. Tannin–protein binding is usually reversible: acid or alkaline pH, treatment with detergents (surfactants) or phenol or other organic solvents can result in the dissociation of the complexes (Waterman, 1999).

Tannins in plants are mainly physically located in the vacuoles or surface wax of plants. Tannins are found in leaf, bud, seed, root, and stem tissues. An example of the location of the tannins in stem tissue is that they are often found in the growth areas of trees, such as the secondary phloem and xylem and the layer between the cortex and epidermis. Tannins may help regulate the growth of these tissues. There may be a loss in the bio-availability of still other tannins in plants due to birds, pests, and other pathogens (Kadam et al., 1990).

Tannins can be categorized on the basis of their structure into two major groups: hydrolyzable and condensed tannins (proanthocyanidins) (Bruneton, 1999; Reed, 1995). In 2004 as addition to these two groups of tannins was found phloroglucinol (phlorotanins) which present in brown algae (Toshiyuki et al., 2004; Yoshihito et al., 2004) (Figure 8).

Hydrolyzable tannins are Gallic or Ellagic acid esters of sugars. When they are consumed by ruminants, they can be degraded into gallic acid and be absorbed in the digestive tract (Bruneton, 1999). Because they are readily absorbed, they have been considered responsible for causing toxic effects in herbivores.

Condensed tannins are polyphenols of higher molecular weight and consist mainly of oligomers or polymers of catechin (flavan-3-ols) (Bruneton, 1999; Waterman, 1999). When condensed tannins get depolymerized, they produce mainly cyanidin or delphinidin, and therefore have been further classified as procyanidins or prodelphinidins (Bruneton, 1999). Only a low degree of absorption of condensed tannins by the digestive tract of herbivores has been reported. One of their most important chemical properties is the ability to form soluble and insoluble complexes with macromolecules, such as protein, fiber and starch.

Their content in foods is affected by many factors that influence phenolic stability, biosynthesis and degradation. In terms of their biosynthesis the key enzyme phenylalanine ammonia-lyase (PAL) is especially relevant, as it can be induced by different stress (environmental) conditions. In addition, polyphenol oxidases (PPO) and peroxidases (POD) are the main enzymes responsible for quality loss due to phenolic degradation (Francisco et al., 2001). It was found that two of the major types of tannins in plants (ellagitannins and condensed tannins) can be oxidized by the plant enzyme horseradish peroxidase (POD). Therefore, the large amounts of tannins in many tree leaves, and not just the smaller amounts of low molecular weight phenols, are substrates.

The most abundant polyphenols are the condensed tannins, found in virtually all families of plants, and

comprising up to 50% of the dry weight of leaves. Tannins were not found in any coffee bean sample. The presence of soluble condensed tannins in Coffea arabica pulp was confirmed at approximately 1% (Clifford and Ramirez-Martinez, 1991). The hydrolysable tannins as ellagic acid esters of glucose, known as ellagitannins, are found in different type of fruits and in legumes (Okuda et al., 2011). Fruits like persimmons and mostly berries, such as cranberries (Vattem et al., 2005), strawberries and blueberries (Puupponen-Pimiä et al., 2001), contain both hydrolyzable and condensed tannins.

Pomegranates contain a diverse array of hydrolyzable tannins, in particular hydrolysable tannins. The most abundant of pomegranate tannins are called punicalagins. Punicalagins have a molecular weight of 1038 and are the largest molecule found intact in rat plasma after oral ingestion (Scalbert et al., 2002) and were found to show no toxic effects in rats who were given a 6% diet of punicalagins for 37 days (Cerdá et al., 2003). Punicalagins are also found to be the major component responsible for pomegranate juice's antioxidant and health benefits (Gil et al., 2000). It is generally accepted that the beneficial effects observed following the consumption of condensed tannins are mainly due to their protein-binding ability, which protects dietary protein from degradation in the rumen and thus increases protein availability in the lower digestive tract (Min et al., 2003; Min and Hart, 2003; Waghorn and McNabb al., 2003). Interestingly, the protein-binding capacity of tannins has been also considered responsible for causing adverse effects on livestock production.

The concentration and the structure of the condensed tannins present in the different plant species seem to be two major factors modulating efficacy against nematode. An overview of *in vivo* studies in sheep, goats and deer involving plants containing condensed tannins suggests that a threshold of at least 30 to 40 g of condensed tannins per kg dry matter (DM) (3 to 4% DM) has to be reached to observe antiparasitic activity (Herve´ et al., 2006).

Results obtained from the various studies conducted with tannin-rich or other bioactive plants suggest that the effects of the active compounds on essential nematode biological processes could vary with the parasite species (Herve´ et al., 2006). This is also illustrated by studies using quebracho as a source of tannins for sheep (Athanasiadou et al., 2000, 2001) and for goats (Paolini et al., 2003, 2005).

Two main hypotheses have been proposed to explain the effect of tannins against gastrointestinal nematodes in ruminants. First, tannins could act indirectly, by improving the response of the host to parasites. Because of their protein-binding ability, tannins can protect proteins from degradation in the rumen and increase protein flow to, and amino acid absorption by, the small intestine (Min et al., 2003; Waghorn and McNabb, 2003). As any increase in intestinal protein supply is known to improve host homeostasis and its immune response against worms (Coop and Kyriazakis, 2001), the improved utilization of nutrients by hosts receiving moderate amounts of dietary tannins could thus contribute to the improvement in resilience usually observed in infected animals (Min et al., 2003; Waghorn and McNabb, 2003), and it could also modulate host resistance. Few studies have addressed this indirect hypothesis by measuring specifically local or general parameters related to host immunity, and the results remain largely inconclusive (Paolini et al., 2003; Tzamaloukas et al., 2005). However, the possibility of indirect mechanisms contributing to the anthelmintic properties of condensed tannins cannot be discarded. Second, the direct hypothesis, tannins could have anthelmintic properties in themselves that affect several key biological processes, has been the subject of a number of investigations. This hypothesis is supported by results from multiple in vitro assays and, importantly, from *in vivo* studies in sheep and goats in which the short-term experimental design did not permit the development and expression of effective host immune responses (Athanasiadou et al., 2001; Paolini et al., 2003). However, the exact mechanisms of action remain obscure and could differ depending on the parasite, its stage of development and possibly the biochemical characteristics of the forage species (Min et al., 2003).

CONCLUSION

The biochemical features and biological function of dietary phenols which widespread in plant kingdom are described in this review. The structural features of representatives of 3 most important groups of phenols (flavonoids, phenolic acids, and polyphenols) are based on the presence of benzoic and phenolic functional groups on a core monocyclic carbon skeleton. In the review a few ways of phenols classification which were collected from literature data are presented. By providing detailed descriptions of the source organisms for these monocyclic phenolic acids, we have endeavoured to demonstrate that unlike many secondary metabolites, which have a very restricted distribution in the bacterial, algal, fungal, and plant (and to a much lesser and generally secondary extent, animal) kingdoms, many of the compounds discussed here are found in a wide diversity of unrelated plant, algal, fungal, and bacterial species. Despite different source and various biosynthetic origins of phenolic compounds, many of these molecules have been shown in experimental studies to have similar biological functions. Phenols have antioxidant, antimutagenic, antibacterial (bactericidal, bacteriostatic), phytotoxic, antifungal, nematicidal, insecticidal, cytotoxic, neurotoxic and other activities. Thus, this review of the structures, occurrence and activities of main widespread phenolic compounds can provide new knowledge for development of natural and derivative pharmaceutical

and agricultural chemicals with implications for significant benefits to human health and nutrition.

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