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Phenolic Compounds in Plant Foods: Chemistry and Health Benefits

– Review –

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Abstract

Phenolic compounds in food and plant materials belong to the simple phenols, phenolic acids, coumarins, flavonoids, stilbenes, tannins, lignans and lignins, all of which are considered as secondary plant metabolites. These compounds may be synthesized by plants during normal development or in response to stress conditions. Phenolics are not distributed uniformly in plants. Insoluble phenolics are components of cell walls while soluble ones are present in vacuoles. A cursory account of phenolics of cereals, beans, pulses, fruits, vegetables and oilseeds is provided in this overview. The information on the bioavailability and absorption of plant phenolics remains fragmentary and diverse. Pharmacological potentials of food phenolics are extensively evaluated. However, there are many challenges that must be overcome in order to fully understand both the function of phenolics in plant as well as their health effects.

Key words: phenolics, phenolic acids, flavonoids, anthocyanins, tannins, proanthocyanidins, crearals, legumes, oilseeds, fruit, vegetables

INTRODUCTION

Phenolics are considered as secondary metabolites that may be synthesized by plant both during normal development (1) and in response to stress conditions such as infection, wound and UV radiation, among others (2). These compounds occur ubiquitously in plants (1,3) and are a very diversified group of phytochemicals derived from phenylalanine and tyrosine (3). Plant phenolics include simple phenolics, phenolic acids, coumarins, flavonoids, stilbenes, hydrolyzable and condensed tannins, lignans, and lignins (Table 1). In plants, phenolics may act as phytoalexins, antifeedants, attractants for pollinators, contributors to the plant pigmentation, antioxidants, and protective agents against UV light, among others (3). In food, phenolics may contribute to the bitterness, astringency, color, flavor, odor, and oxidative stability of food. In addition, health-protecting capacity of some and antinutritional properties of other plant phenolics are of great importance to both consumers and producers (3).

Phenolics are not uniformly distributed in plants at the tissue, cellular and subcellular levels. Insoluble phenolics are the components of cell walls, while soluble phenolics are compartmentalized within the plant cell vacuoles (4). At the tissue level, the outer layers of plants contain higher levels of phenolics than those located in the inner part of the plants (5). Cell wall phenolics, such as lignins (the polymer of monolignol units) and hydroxycinnamic acids are linked to various cell components (6). These compounds contribute to the mechanical strength of cell walls, play a regulatory role in plant growth and morphogenesis and in the cell response to stress and pathogens (6,7). Ferulic and *p*-coumaric acids, the major phenolic acids, may be esterified to pectins and arabinoxylans or cross-linked to cell wall polysaccharides in the form of dimers such as dehydroferulates and truxillic acid (Fig. 1) (8). It has been suggested that these cross-links may play a significant role in cell-cell adhesion (9), serve as a site for formation of lignin (10) and contribute to the thermal stability of plant food texture (11). This paper provides an overview of the occurrence of phenolics in selected cereal grains, beans and pulses, oilseeds and fruits and vegetables.

PHENOLIC COMPOUNDS IN CEREALS AND LEGUMES

Phenolic acids and flavonoids are present in cereals in the free and conjugated forms. The largest concentrations of phenolic acids and flavonoids are located in the aleurone layer in cereal grains. These compounds are also found in embryos and seed coat of grains (12). Phenolic acids are found abundantly in cell walls linked to hemicelluloses in different forms such as 2-*O*-(5′-*O*-(E)-feruoyl-β-D-xylopyranosyl)-(1→4)-D-xylopyranose (13). Phenolic acids

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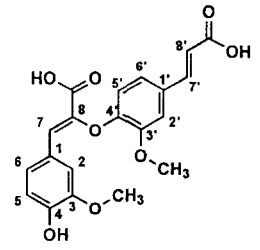
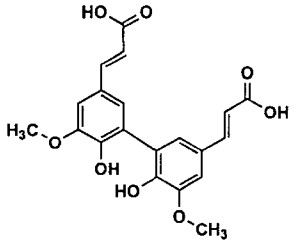
Table 1. Some dietary sources of plant phenolics

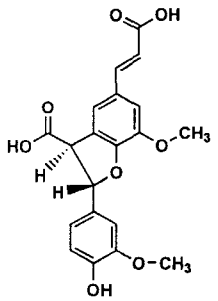
Phenolic compounds	Dietary source
Phenolic acids	
Hydroxycinnamic acids	appricots, blueberries, carrots, cereals, pears, cherries, citrus fruits, oilseeds, peaches, plums, spinach, tomatoes
Hydroxybenzoic acids	blueberries, cereals, cranberries, oilseeds,
Flavonoids	
Anthocyanins	bilberries, black and red currants, blueberries, cherries, chokecherries, grapes, strawberries
Chalcones	apples
Flavanols	apples, blueberries, grapes
Flavanonols	grapes
Flavanones	citrus fruits
Flavonols	apples, beans, blueberries, buckwheat, cranberries, endive, leeks, lettuce, onions, olive, pepper, tomatoes
Flavones	citrus fruits, celery, parsley, spinach
Isoflavones	soybeans
Tannins	
Condensed	apples, grapes, peaches, plums
Hydrolyzable	pomegranate, raspberries
Other phenolics	
Avenanthramides	oats
Capsaisinoids	pepper
Coumarins	carrots, celery, citrus fruits, parsley, parsnips
Lignans	buckwheat, flaxseed, sesame seed, rye, wheat
Secoiridoids	olives
Stilbenes	grapes



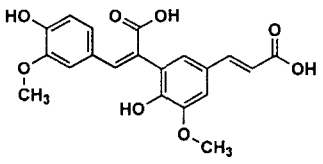
8-*O*-4'-DiFA



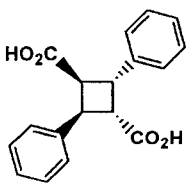
5, 5'-DiFA



8, 5'-DiFA - benzofuran form



8, 5'-DiFA - open form



Truxillic Acid

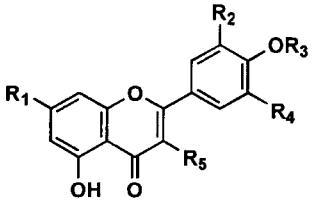
Fig. 1. Chemical structures of ferulic acid dehydrodimers and truxillic acid.

also contribute to the antioxidative potential of cereal grains (14) and are used for the prediction of end-use of cereal products (15). Cereal grains with elevated levels of phenolic acids in caryopsis exhibit greater resistance to both disease and insect herbivory (16), but have reduced extractability of endosperm (15,16). Moreover, cross-linking of arabinoxylans with phenolic acids lowers the arabinoxylan solubility and swelling in water and reduces their microbial degradation in the human colon (17).

Beans and pulses

Several flavonol derivatives have been identified as pigments in the skin of bean seeds. Kaempferol 3-*O*-β-D-glucopyranoside (astragalin) (Fig. 2) and kaempferol 3-*O*-β-D-glucopyranoside-(2→1)-*O*-β-D-xylopyranoside are responsible for the yellow color of the seed coat of 'Prim' variety of Manteca-type dry beans (18). Meanwhile astragalin, quercetin 3-*O*-β-D-glucopyranoside-(2→1)-*O*-β-D-xylopyranoside, and quercetin 3-*O*-β-D-glucopyranoside impart a red color to the seed coat of commercial dark red beans (Montcalm cv.) (19).

A number of anthocyanins were also detected in the bean seed coats. The seed coat of black-violet beans contained malvidin 3-glucoside, petunidin 3-glucoside, delphinidin 3-glucoside and 3,5-diglucoside (20), while delphinidin 3-glucoside, cyanidin 3-diglucoside and 3,5-diglucoside, and pelargonidin 3-glucoside and 3,5-diglucoside were found in beans of Canadian Wonder cultivar (21). In addition, delphinidin 3-*O*-glucoside, malvidin 3-*O*-glucoside, and petunidin 3-*O*-glucoside were iden-



Compound	R_1	R_2	R_3	R_4	R_5
Kaempferol	OH	H	H	H	OH
Rutin	OH	OH	H	H	*O*-rutinoside
Quercetin	OH	OH	H	H	OH
Quercitrin	OH	OH	H	H	*O*-rhamnoside
Isoquercitrin	OH	OH	H	H	*O*-glucoside
Hyperin	OH	OH	H	H	*O*-galactoside
Astragalin	OH	H	H	H	*O*-glucoside
Reynoutrin	OH	OH	H	H	*O*-xyloside
Avicularin	OH	OH	H	H	*O*-arabinoside
Myricetin	OH	OH	H	OH	OH
Isorhamnetin	H	OCH_3	OH	H	OH

Fig. 2. Chemical structures of some flavonol derivatives.

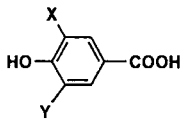
tified as the main anthocyanins responsible for the color of black and purple seed coat beans (22).

Condensed tannins are located mainly in the seed coat. The content of tannins in peas is up to 2.0% as (+)-catechin or tannic acid equivalents while the average content of tannins in faba bean was 4.3% (54). On the other hand, the level of tannins in cowpeas ranged from 0 to 0.7%, while in chickpeas it was between 0 and 0.2% (24).

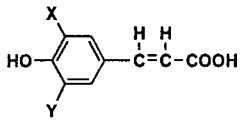
Cereals

Barley: Barley phenolics include tyrosine, tyramine and its derivatives, phenolic acids and their esters and glycosides, anthocyanins, proanthocyanidins, lignans and substances related to lignin (3). Several free phenolic acids have been found in barley grain, namely salicylic, *p*-hydroxybenzoic, vanillic, protocatechuic, *o*-, *m*- and *p*-coumaric, syringic, ferulic, chlorogenic, and sinapic acids (Fig. 3) (25). The bound-phenolic acids found in barley grains include ferulic, *p*-coumaric, vanillic, sinapic and *p*-hydroxybenzoic acids (26), as well as protocatechuic and chlorogenic acids (Fig. 3) (25). Phenolic acids are located acids in barley grains, respectively (27). Ferulic acid is mainly in the outer layers (husk, pericarp, and aleurone) of the grain (27). These layers contain 77.7~82.3 and 79.2~86.8% of the total amounts of ferulic and *p*-coumaric the predominant free phenolic acid in barley seeds and barley brans (28). The concentration of ferulic acid in 29 barley cultivars of Canadian, European and US origin ranged from 359 to 624 mg/kg of dry weight, while the level of *p*-coumaric acid was between 79 and 260 mg/kg dry weight (27). On the other hand, barley bran contained 6401 mg of ferulic acid (free and bound)/kg and 151 mg *p*-coumaric acid/kg (29). The proanthocyanidins of barley are implicated in the formation of haze in beer (30). These compounds are located in the testa of the grain and are mixtures of oligomeric prodelphinidins and procyanidins (31).

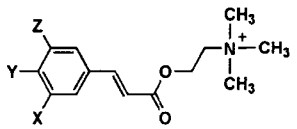
Buckwheat: The content of phenolic acids in buckwheat is low. Bran-aleurone fraction of buckwheat contains bound syringic, *p*-hydroxybenzoic, vanillic, and *p*-coumaric acids (Fig. 3) (32). The seeds and hulls of the Canadian buckwheat varieties contained, on the average, 387 and 1314 mg/100 g of flavonoids, respectively (33), while



Benzoic Acid Derivatives	X	Y
p-Hydroxybenzoic Acid	H	H
Vanillic Acid	OCH_3	H
Syringic Acid	OCH_3	OCH_3
Protocatechuic Acid	H	H
Gallic Acid	OH	OH



Cinnamic Acid Derivatives	X	Y
p-Coumaric Acid	H	H
Caffeic Acid	OH	H
Sinapic Acid	OCH_3	OCH_3
Ferulic Acid	OCH_3	H



Sinapines	X	Y	Z
p-Coumaroylcholine	H	OH	H
Feruloylcholine	H	OH	OCH_3
Isoferuloylcholine	H	OCH_3	OH
Sinapine	OCH_3	OH	OCH_3
Sinapine glucoside	OCH_3	O-Glu	OCH_3

Fig. 3. Chemical structures of phenolic acids and sinapines.

the total flavonoid contents in the seeds and hulls of Polish buckwheat variety were 18.8 and 74 mg/100 g of the dry matter, respectively (34). Rutin, quercetin, orientin, vitexin, isovitexin and isoorientin were the only flavonoids detected in buckwheat (Fig. 2 and 4) (34). Moreover, four catechins, namely (-)-epicatechin, (+)-catechin 7-*O*-β-D-glucopyranoside, (-)-epicatechin 3-*O*-*p*-hydroxybenzoate, and (-)-epicatechin 3-*O*-(3,4-di-*O*-methyl)gallate were identified in the ethanolic extracts of buckwheat groats (35).

Corn : Phenolic acids of corn are in the free, esterified and insoluble-bound forms. Of these, the insoluble bound phenolic acids are the predominant fraction constituting 69.2% of the total amount of phenolic acids (36). A number of phenolic acids are linked covalently to amine functionalities, namely feruoylputrescine, *p*-coumarylputrescine, diferuloylputrescine, di-*p*-coumarylputrescine, *p*-coumarylspermidine, diferuloylspermidine and diferuloylspermine and these are found in the embryo and aleurone of corn (37). Ferulic acid comprises 2~4% of dry matter in hulls obtained from the wet milling of corn grains (38). Three novel feruloylated disaccharides were detected in acid hydrolyzate of corn hulls, namely *O*-(2′-*O*-*trans*-feruoyl-α-L-arabinofuranosyl)-(1→3)-β-D-xylanopyronose, *O*-(2′-*O*-methoxyl-5′-*O*-*trans*-feruoyl)-α-L-arabinofuranosyl-(1→3)-β-D-xylanopyronose and *O*-(2′-*O*-methoxyl- 5′-*O*-*cis*-feruoyl)-α-L-arabinofuranosyl-(1→3)-β-D-xylan opyronose (39).

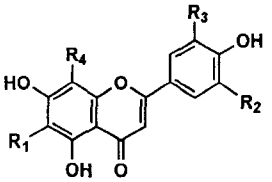
Commercial corn fiber is a richer source of steryl ferulates than rice bran as it contains 0.12% of steryl ferulates. These phenolics are located in the interior portion of the inner pericarp layer and germ, but no steryl phenolic acid ester was detected in the outer pericarp and endosperm fractions (40). A total of 16 steryl cinnamic acid derivatives were identified in corn bran (41).

Phlobaphene and anthocyanidin pigments are also found in corn (42). Presence of pelargonidin-3-glucoside and cyanidin-3-glucoside was detected in the aleurone tissue and seed coat of corn as well as cobs (43), while phlobaphene pigments were found mostly in the cob and pericarp tissues (44).

Oats : Derivatives of benzoic and cinnamic acids as well as quinones, flavones, flavonols, chalcones, flavanones, anthocyanins and amino phenolics were the major phenolics found in oat groats and hulls (3). Ferulic acid was a major phenolic acid present in the soluble bound and insoluble bound phenolic acid fractions of oats (45). Bound-phenolic acids of oat may be coupled to long-chain alcohols, glycerol, sugars, polysaccharides, lignins, amines and long chain omega-hydroxy fatty acids (46). Catechol, coniferyl alcohol, gallic acid, *p*-hydrobenzoaldehyde, salicylic acid, and vanillin were also detected in both oat groats and hulls (47). At least 25 and 20 avenanthramides and N-acylanthranilate alkaloids were identified oat in groat and hull extracts, respectively (Fig. 5). Avenanthramides are conjugates of cinnamic acid with anthranilic acids (48). Oat groats contained 54, 36 and 52 mg/kg and hulls 25, 17 and 25 mg/kg of avenanthramides A, B and C, respectively (46).

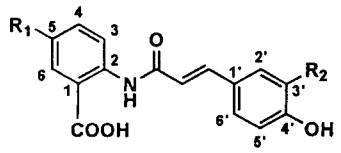
Wheats : A number of phenolic compounds, namely ferulic, vanillic, gentisic, caffeic, salicylic, syringic, *p*-coumaric and sinapic acids (Fig. 3) as well as vanillin and syringaldehyde were identified in wheat kernels (36,49). Of these, ferulic acid was the primary phenolic acid in the grain (up to 90% of total phenolic acids) during all stages of development and is present in the seeds both in the free and esterified forms (36,49) and comprised over 80% of total insoluble-bound phenolic acids (46). Ferulic acid occurs in high amounts in the aleurone cell walls of kernel and to a lesser extent in the seed coat and embryo (15). Ferulic acid in wheat grain is esterified to arabinose in the pentosan (50), stanol and sterol (51) and glucose (52). A number of steryl ferulates were identified in wheat grain and these were mainly located in the bran fraction (34 mg/100 g). Only traces of steryl ferulates were found in the endosperm fraction. Campestanyl and sitostanyl ferulates were the main steryl ferulates present in wheat grain (53).

Wheat bran also contained 808 mg per kg of total ferulic acid dehydrodimers (DiFA). Of these, 8-*O*-4'-DiFA was the predominant etherified DiFA while 8,5'-DiFA was the most abundant esterified DiFA in wheat bran (Fig. 1) (29). According to Iiyama et al. (54), DiFA strengthen the aleurone walls during the maturation of wheat grain by formation of bridges between two arabinoxylan chains. Higher ratios of arabinoxylan to ferulic acid were detected in the anticlinal aleurone-aleurone wall of wheat grain than



Compound	R_1	R_2	R_3	R_4
Vitexin	H	H	H	C-glucosyl
Orientin	H	H	OH	C-glucosyl
Isoorientin	C-glucosyl	H	OH	H
Isovitexin	C-glucosyl	H	H	H
Tricin	H	OCH_3	OCH_3	H

Fig. 4. Chemical structures of some flavone derivatives.



	R_1	R_2
A	OH	H
B	OH	OCH_3
C	OH	OH
D	H	H

Fig. 5. Chemical structures of some avenanthramides.

in the periclinal walls (aleurone-endosperm or aleurone-pericarp wall) (55). It is believed that the cross-linking of cell walls with phenolic acids provides a physical barrier against insects and microorganisms (56). Ferulic acid residue was also found in germ-endosperm interface. Irving et al. (57) demonstrated the existence of a close association of wheat kernel hardness with the fluorescence attributed to the phenolics in the grain.

Wheat grain also contains n-alkylphenols. Several n-alkylphenols containing 17, 19, 21, 23 and 25 carbons coupled to a resorcinol ring at the 5 position were identified in wheat grain (58). Wheat brans contained up to six times more alkylresorcinols than the corresponding flours (59). A number of flavonoid pigments were also detected in both the bran and germs of hard wheat. Of these, tricin (5,7,4′-trihydroxy 3′,5′-dimethoxy flavone) (Fig. 4) was the dominant flavone pigment found in both cultivated and wild wheats (114,115). In addition, two C-glycosylflavones were isolated from wheat brans, namely 6-C-pentosyl-8-C-hexosylapigenin and 6-C-hexosyl-8-C-pentosylapigenin (60).

PHENOLIC COMPOUNDS IN FRUITS AND VEGETABLES

Consumption of fruits and vegetables has been linked to a reduction of blood pressure, lowering incidence of cancer and cardiovascular disease, among others. These health-promoting effects of fruits and vegetables have been associated with the presence of phenolics (61). On the other hand, phenolics may affect the quality of fruits and vegetables by participation in food discoloration and in off-flavor development (62). The predominat phenolics in some fruits and vegetables are provided in here.

Fruits

Apples: Hydroxycinnamic acid derivatives, flavan-3-ols (monomeric and oligomeric), flavonols and their conjugates, and dihydrochalcones are the major phenolics in apples (63,64). The total content of phenolics in most apple varieties ranged from 1000 to 6000 mg/kg fresh weight, but in some apple cultivars may be even over 10000 mg/kg fresh weight (65,66). The level of phenolic compounds varied among individual apples of the same variety (67). Chlorogenic acid (Fig. 3) was the major hydroxycinnamic acid (HCA) identified in the apple fruit accounting for 79, 76, 79, and 87% of total HCA in epidermis, parenchyma, core, and seeds, respectively (63).

Anthocyanins are found in the vacuoles of epidermal and subepidermal cells of the skin of some red apple varieties (67). Several anthocyanins, namely cyandin 3-galactoside (ideain), cyanidin 3-rutinoside, malvidin 3-glucoside, and malvidin 3,5-diglucoside were identified in Starking Delicious apple juice. Of these, ideain was the predominant anthocyanins in the apple juice and in the apple peel (68).

Phlorizidin (phloretin 2′-β-D-glucoside) and phloretin 2′-β-D-xylosyl-(1→6)-β-D-glucoside are the major dihydrochalcones found in apple fruits (69). The total content of dihydrochalcones in apple cortex and apple peel was 26～122 mg of phlorizidin equivalents/kg fresh weight and 60～500 mg/kg (63,69), respectively.

Flavonol glycosides are found predominantly in the epidermis tissue of apple fruits (63,67). Several flavonol glycosides have been identified in apple fruits, namely rutin, hyperin (quercetin-3-β-D-galactoside), isoquercitrin (quercetin-3-β-D-glucoside), reynoutrin (quercetin-3-β-D-xyloside), avicularin (quercetin-3-α-L-arabinofuranoside), and quercitrin (quercetin-3-α-L-rhamnoside) (Fig. 2) (3,63,67).

Procyanidins are found in the entire apple fruit, however, their level gradually increases from 1232 mg/kg in the seeds to 4964 mg/kg in the epidermis tissue (63). Apple procyanidins are a mixture of oligomers and polymers made of (-)-epicatechin and (+)-catechin as units (Fig. 6 and 7) (70). High-molecular-weight procyanidins represented over 26% of total procyanidins in the apple fruit and those with the highest average degree of polymerization (11.2) were located in the seeds (63). More polymerized procyanidins were found in the cortex of French apple varieties with the average degree of polymerization ranging from 4.5 (var. Judor) to 50.3 (var. Avrolles) (66) and up to 190 in the cortex of two cider apple varieties (*Malus domestica*; var. Kermerrien and Avrolles) (71).

Blueberries: Blueberries are a rich source of phenolic acids, catechins, flavonols, anthocyanins and proanthocyanidins (3,72). Phenolic acids identified in blueberries include gallic (0～2589 mg/kg), caffeic (0～63.2 mg/kg), *p*-coumaric (24～157 mg/kg), ferulic (30.2～169.7 mg/kg) and ellagic acids (2.2～66.5 mg/kg fresh weight) (Fig. 3) (72). A number of anthocyanins were isolated and identified in bluberries, namely 3-galactosides and 3-arabinosides of cyanidin, delphinidin, peonidin, petunidin and malvidin (Fig. 8), and 3-glucosides of cyanidin, delphinidin, peonidin, petunidin and malvidin (73). The total content of anthocyanins in blueberries was between 127 and 1973.4 mg cyanidin 3-glucoside equivalents/kg fresh weight (74). Lowbush blueberries contained almost 50%

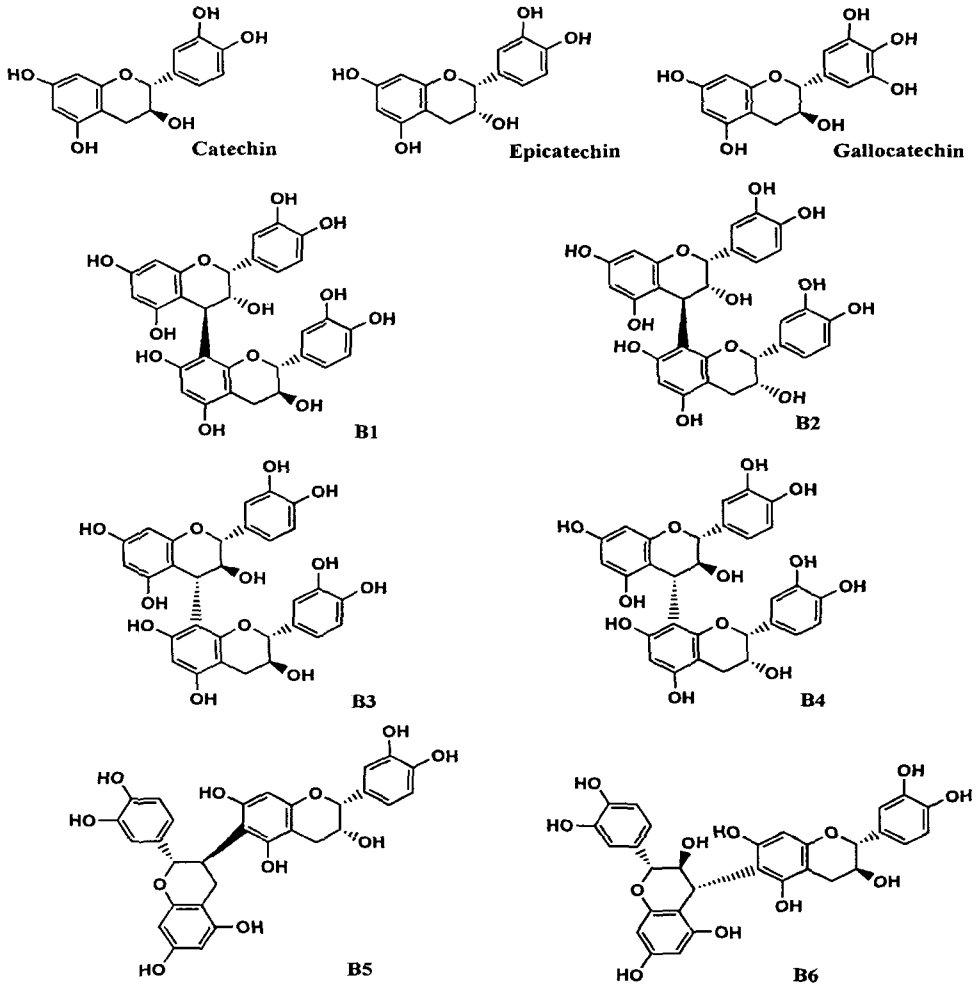


Fig. 6. Chemical structures of catechins and procyanidin dimers type B.

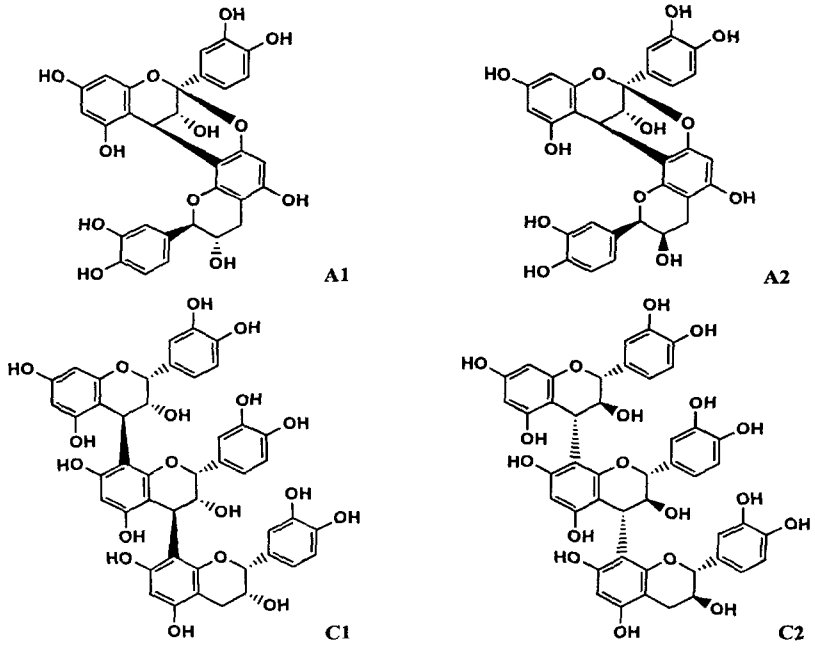
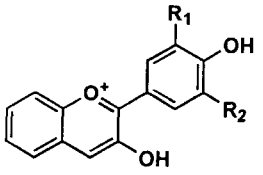


Fig. 7. Chemical structures of some procynidin dimers type A and procyanidin trimers type C.



Compound	R_1	R_2	R_3
Cyanidin	OH	H	H
Delphinidin	OH	OH	H
Pelargonidin	H	H	H
Petunidin	OCH_3	OH	H
Malvidin	OCH_3	OCH_3	H

Fig. 8. Chemical structures of some anthocyanins.

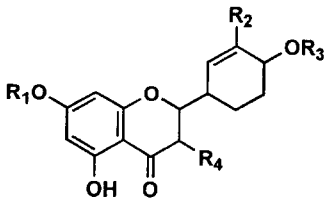
more anthocyanins than highbush blueberries (164). Catechin (145.3~3874.8 mg/kg fresh weight), myricetin (67.2~99.9 mg/kg fresh weight), quercetin (58.2~146 mg/kg fresh weight), and kaempferol (25.1~37.2 mg/kg fresh weight) were also detected in blueberries (Fig. 2 and 6). Gu et al. (75) reported that blueberry contained 19990 mg /kg dry weight of procyanidins. A number of oligomeric B-type procyanidins from dimers to octamers has been identified in blueberry (Fig. 6) (76). The polymeric procyanidins comprised over 76% of total procyanidins and were a mixture of polymers with a degree of polymerization ranging from 14.4 to 114.1 (75).

Citrus fruits : Cinnamic acid derivatives, coumarins and flavonoids (flavanones, flavones and flavonols) are the major groups of phenolic compounds occurring in citrus fruits (3). Phenolic acids are predominantly located in the flavedo of citrus fruits in the form of esters, amides and glycosides (77). Hydroxycinnamic acids have been associated with the development of off-flavor in citrus fruits and their products. Ferulic and *p*-coumaric acid esters were implicated as substrates for the formation of unpleasant compounds such as *p*-vinylguaiacol (PVG) and *p*-vinylphenol (3).

Flavanone glycosides (Fig. 9) such as naringin, neoeriocitrin and hesperidin comprise 50~80% of total flavonoids in citrus fruits (78). Naringin, naringenin 7-neohesperidoside and narirutin, naringenin 7-rutinoside are the major glycosides found in grapefruit, while narirutin, and hesperedin, hesperetin 7-rutinoside in sweet oranges. On the other hand, sour oranges contain 7-neohesperidosides, namely naringin and neohesperidin as well as hesperetin 7-neohesperidoside. (78). Hesperedin, narirutin and didymin (isosakuranetin 7-rutinoside) were the predominant flavanone glycosides in Navel (79) and blood oranges (80).

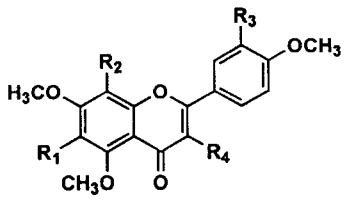
Polymethoxylated flavones (PMF) (Fig. 10) are unique phenolic compounds in citrus species, and are mostly accumulated in the peel (81). The PMF profile in the citrus fruit is fingerprint of each species (82). Nobiletin (5,6,7,8,3′,4′-hexamethoxyflavone) and sinensetin (5,6,7,3′,4′-pentamethoxyflavone) have been identified in orange peel, while tangeretin, 3,5,6,7,8,3′,4′-heptamethoxyflavone, 5,7,8,4′-tetramethoxyflavone, and 5,7,8;3′,4′-pentamethoxyflavone have been found in grapefruits (83). Edible parts of citrus fruits contained nobiletin (7~173 mg/kg dry weight), 3,5,6,7,8,3′,4′-heptamethoxyflavone (0~87 mg/kg dry weight), natsudaidain (5,6,7,8,3′,4′-hexametoxymethoxyflavone) (0~69 mg/kg dry weight) and tangeretin 98~62 (mg/kg dry weight) (84).

Glycosylated flavones have been detected in citrus fruits. Of these, diosmin (4′methoxy-5,7,3′-trihydroxyflavone-7-rutinoside) and neodiosmin (4′methoxy-5,7,3′-trihydroxyflavone-7-neohepseridoside) were the predominant glycosylated flavones identified in citrus fruits. The peel flavedo contained higher amounts of diosmin and neodiosmin than albedo of the peel, and only small quantities of these phenolics were found in the pulp (85). High levels of these two flavones were detected during the early stages of fruit development and then their levels were gradually decreased (86). The content of diosmin in immature citrus fruits was from 0 to over 30 g/kg dry



Compound	R_1	R_2	R_3	R_4
Didymin	rutinosyl	H	CH_3	H
Eriocitrin	rutinosyl	OH	H	H
Hesperidin	rutinosyl	OH	CH_3	H
Neoeriocitrin	neohesperidosyl	OH	H	H
Naringenin	H	H	H	H
Naringin	neohesperidosyl	H	H	H
Neohesperidin	neohesperidosyl	OH	CH_3	H
Narirutin	rutinosyl	H	H	H

Fig. 9. Chemical structures of some flavanone derivatives found in citrus fruits.



Compound	R_1	R_2	R_3	R_4
Sinensetin	OCH_3	H	OCH_3	H
Tetramethylscutellarein	OCH_3	H	H	H
Isosinensetin	H	OCH_3	OCH_3	H
Nobiletin	OCH_3	OCH_3	OCH_3	H
Tangeretin	OCH_3	OCH_3	H	H
Heptamethoxyflavone	OCH_3	OCH_3	OCH_3	OCH_3
Natsudaidain	OCH_3	OCH_3	OCH_3	OH

Fig. 10. Chemical structures of some polymethoxylated flavones found in citrus fruits.

weight, while in mature fruits it did not exceed 4 g/kg dry weight. On the other hand, the content of neodiosmin was 4.8～9 g/kg dry weight in immature fruits and 0.45～1.1 g/kg dry weight in mature fruits (85).

Cranberries: Cranberry fruits serve as an excellent source of anthocyanins (73), flavonol glycosides, proanthocyanidins (87) and phenolic acids (88). Cranberries contain about 1 g/kg fresh weight of phenolic acids, predominantly as glycosides and esters (88,89). Sinapic, caffeic and *p*-coumaric acids were the most abundant bound phenolic acids while *p*-coumaric, 2,4-dihydroxybenzoic and vanillic acids were the predominant free phenolic acids found in cranberry (Fig. 3) (88). The predominant anthocyanins in American cranberries were 3-*O*-galactosides and 3-*O*-arabinosides of cyanidin and peonidin, while 3-*O*-glucosides of cyanidin and peonidin in European cranberries (73). The total content of anthocyanins in cranberry fruits ranged from 180 to 656 mg/kg fresh weight (90) and these were located under the fruit skin (73). Whole cranberries contained approximately 17 mg/kg of total proanthocyanidin (76) and the polymeric proanthocyanidins comprised 63% of total proanthocyanidins in cranberries (75).

Grapes: Grape seeds and skins are an excellent source of health-promoting flavonoids such as proanthocyanidins, flavonols and flavan-3-ols (91). Of these, proanthocyanidins are the major polyphenols present. Procyanidins are the predominant proanthocyanidins in grape seeds, while procyanidins and prodelphinidins are dominant in grape skins and stems (91). The mean degree of polymerization for proanthocyanidins isolated from the seed and skin of grapes (cv. Cabernet franc) ranged from 4.7 to 17.4 and from 9.3 to 73.8, respectively (91,92).

Whole grape berries and skins also contain phenolic acids such as caftaric acid (*trans*-caffeoyltartaric acid), coutaric acid (*p*-coumaryltartaric acid), and *trans*-fertaric acid (91), flavonols such as quercetin 3-glucuronide, quercetin 3-glucoside, myricetin 3-glucuronide, and myricetin 3-glucoside (93), and flavanonols, such as astilbin (dihydroquercetin 3-rhamnoside) and engeletin (dihydrokaempferol 3-rhamnoside) (91).

Stilbenes are phytoalexins detected in grape leaves and berries (Fig. 11). These include *trans*- and *cis*- resveratrols (3,5,4′-trihydroxystilbene), *trans*- and *cis*-piceids (3-*O*-β-D-glucosides of resveratrol), *trans*- and *cis*-astringins (3-*O*-β-D-glucosides of 3′-hydroxyresveratrol), *trans*- and *cis*-resveratrolosides (4′-*O*-β-D-glucosides of resveratrol), and pterostilbene (a dimethylated derivative of stilbene). In berries stilbenes are mostly located in the grape skin (94). *cis*-Piceid was the predominant stilbene found in berry skins during fruit ripening (39.5 mg/kg fresh weight at 60 days after véraison), while resveratrol was the main stilbene in wilting berries (28 mg/kg at day 74) (94).

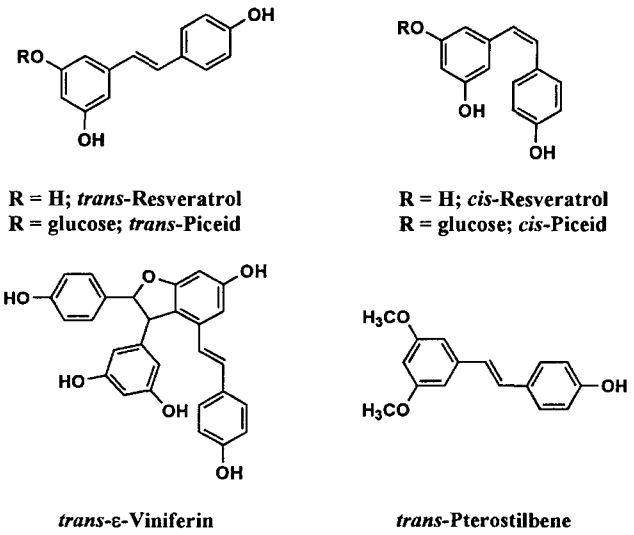


Fig. 11. Chemical structures of some stilbens.

Pomegranates: Pomegranates are a rich source of hydrolyzable tannins and anthocyanins. The total content of anthocyanins and hydrolyzable tannins ranged from 161.9 to 387.4 mg/L and from 417.3 to 556.6 mg/L, respectively (95). Several anthocyanins were detected in pomegranate juice, namely cyanidin 3-glucoside (59.5～128.3 mg/L), delphinidin 3-glucoside (23.6～95.2 mg/L), cyanidin 3,5-diglucoside (31.4～71.4 mg/L), delphinidin 3,5-diglucoside (21.1～61.1 mg/L) and pelargonidin 3-glucoside (3.9～8.5 mg/L) (95). Furthermore, the presence gallotannins, ellagic acid tannins and gallagyl esters such as punicalagin and punicalin in pomegranates were also reported. Of these, gallagyl type tannins were the major tannins in commercial pomegranate juice which contained 1500～1900 mg/L of punicalagin (95).

Vegetables

Carrots: The total content of soluble phenolics in carrots ranged from 5088 to 7699 mg/kg dry weight (96). Phenolic acids and isocoumarins were the predominant phenolics in carrots (97). The total content of phenolic acids in fresh carrots ranged from 77.2 mg/kg fresh weight for yellow varieties to 746.4 mg/kg fresh weight for purple varieties (98). Major phenolic acids in carrots included *p*-hydroxybenzoic acid, syringic acid and 3′-caffeoylquinic acid (neochlorogenic acid), 5′-caffeoylquinic acid (chlorogenic acid), 3′-, 4′- and 5′-feruoylquinic acids, 3′- and 5′-*p*-coumaroylquinic acids, 3′,4′- and 3′,5′-dicaffeoylquinic acids and 3′,4′- and 3′,5′-diferuoylquinic acids (Fig. 3) (96-98). The total content of phenolic acids esterified to cell wall material of carrots was between 324.8 mg/kg of cell wall carbohydrate in mature and 661.1 mg/kg in stored carrots (99). Over 30% of total ferulic acid existed in the dehydrodimer form (Fig. 1) (99). Cell wall material also contained small amounts of vanillic, *p*-

coumaric, *trans*- and *cis*-ferulic acids as well as vanillin and *p*-hydroxybenzaldehyde (99). Moreover, the presence of coumarins, namely 6-methoxymellein and 6-hydroxymellein was also reported in carrot tissues (Fig. 12) (100).

These compounds were predominantly accumulated in the periderm tissue of carrot root and their concentrations decreased incrementally from the peel to vascular tissues (101). The reported levels of 6-methoxymellein in whole carrots ranged from 0 to 400 mg/kg dry weight (96).

Lettuce: Several phenolic acids, namely caffeoyltartaric, chlorogenic, dicaffeoyltartaric and 3′,5′-dicaffeoylquinic acids have been identified in red lettuce (cv. Lollo Rosso) (102), as well as iceberg and romaine lettuce (103). The total content of phenolic acids in whole red lettuce ranged from 65 to 270 mg/kg fresh weight (104). On the other hand, whole romaine, iceberg and butter leaf lettuce contained only between 2.83 and 45 mg phenolic acids/kg fresh weight (103).

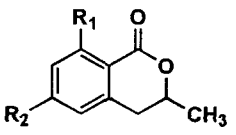
Lettuce is also a good source of flavonoids. Several quercetin conjugates were detected in both red pigmented and green leaf lettuce, namely quercetin 3-(6-malonylglucoside), quercetin 3-glucoside, quercetin 3-glucuronide, quercetin 3-rhamnoside, quercetin 3-galactoside, and quercetin 3-(6-malonylglucoside)-7-glucoside (102). Red lettuce varieties contained higher levels of flavonoids than did green lettuce varieties. Green leaf and head lettuce varieties contained 2～54 and 1～28 mg quercetin/kg fresh weight, respectively (105). On the other hand, the outer and inner leaves of "Lollo Rosso" red lettuce contained 911 and 450 mg quercetin/kg fresh weight, respectively. In addition, the red tissues of "Lollo Rosso" lettuce contained 3～8 times more phenolics and 5～30 times more flavonoids than the white and green tissues (106,107).

Onions: Onions are rich in flavonoids and serve as one of the major sources of flavonols such as quercetin, isorhamnetin, myricetin (Fig. 2) and kaempferol conjugates in the diet (107). Of these, the quercetin and its conjugates are the predominant flavonols in onions (108). The content of quercetin conjugates in bulbs of red onion cultivars ranged from 110 to 295 mg quercetin equivalents per kg, between 119 and 286 mg quercetin equivalents per kg in bulbs of yellow onion cultivars (107,108) and varied from 185 to 634 mg quercetin equivalents per kg in bulbs of white onion cultivars (107).

The flavonols are mostly concentrated in the skin which contained from 5.3 to 34.15 g quercetin equivalents per kg fresh weight. In the scales, abaxial epidermis of scales contained a higher level of flavonols than did the mesophyll. In addition, approximately 50% of flavonols present in onions were accumulated in the top quarter part of the scales. Anthocyanins are mostly concentrated in the red onion skin and the outer fleshy layer (3,107). A number of anthocyanins were identified in red onions, namely peonidin 3-glucoside, cyanidin 3-glucoside and cyanidin 3-arabinoside and their malonylated derivatives, cyanidin 3-laminariobioside, and delphinidin and petunidin derivatives (109).

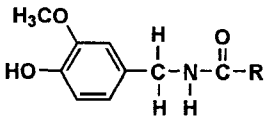
Peppers: Total content of soluble phenolics in green pepper ranged from 1180 to 3849 mg chlorogenic acid equivalents/kg fresh weight (110). Flavonoids and capsaicinoids were the predominant phenolics found in pepper. Capsaicinoids are responsible for the development of pungency in pepper (111). The total content of capsaicinoids in the fruits of pepper was between 189 and 778 mg/kg fresh weight (111). The apical pepper fruits contained higher levels of caspaicinoids (1090 mg/ kg dry weight) compared to those harvested from the middle and basal (780 mg/kg dry weight) segments of the plant (112).

Capsaicinoids are acid amides of vanillylamine and C_8 and C_{13} branched fatty acids (Fig. 13) (113). Over 15 capsaicinoids have been isolated and identified (113). Of these, capsaicin (8-methyl-N-vanillyl-6-nonenamide) and dihydrocapsaicin contribute about 90% to the total pungency. Nordihydrocapsaicin is considered to be a third major pungent principle in the pepper fruit (114). These



Compound	R_1	R_2
6-Methoxymellein	OH	OCH_3
Mellein	OH	OH
6,8-Dimethoxymellein	OCH_3	OCH_3

Fig. 12. Chemical structures of some coumarins.



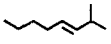
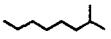
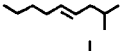
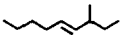
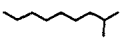
Compounds	R
Capsaicin	
Dihydrocapsaicin	
Nordihydrocapsaicin	
Homocapsaicin I	
Homocapsaicin II	
Homodihydrocapsaicin I	
Homodihydrocapsaicin II	

Fig. 13. Chemical structures of some capsaicinoids.

compounds are accumulated predominantly in the epidermal tissue of the placenta (114).

Small amounts of phenolic acids such as protocatechuic, chlorogenic, coumaric and ferulic acids (Fig. 3) as well as their glycoside were also detected (115). Moreover, quercetin and luteolin, two major flavonoids, were found in pepper fruits (*Capsicum* species) in the form of glycosidic conjugates (116). The total content of flavonoids in pepper cultivars was 1.75~851.53 mg/kg fresh weight (110).

Spinach: Total content of phenolics in fresh spinach (*Spinacia oleracea*) leaves ranged from 1629 to 4835 mg chlorogenic acid equivalents/kg of fresh weight. Furthermore, spinach harvested in the spring contained higher levels of total phenols than that grown in the fall (117). Moreover, the total content of flavonoids in fresh-cut spinach was between 807 and 2241 mg of flavonoids/kg fresh weight (117). Spinach flavonoids such as patuletin (quercetagetin 6-methyl ether), jaceidin, and spinacetin (quercetagetin 6,3′-dimethyl ether) conjugates (Fig. 14) (118) and methoxyflavones accounted for 21.8, 32.4, 6.3, and 39.5% of the total flavonoids in spinach leaves, respectively (117).

Tomatoes: Flavonols, the predominant phenolics, are located mostly in the tomato skin and only small quantities are found in the flesh and seeds (119). Cherry tomatoes contained a much higher level of flavonols (17~203 mg/kg fresh weight) than larger size tomato cultivars (2.2 and 11.2 mg/kg freash weight) (107). These compounds are a mixture of quercetin 3-rhamnosylglucoside (rutin), quercetin 3-rhamnosyldiglucoside, kaempferol 3-rhamnosylglucoside and kaempferol 3-rhamnosyldiglucoside. Of these, rutin was the major flavonol in tomatoes (Fig. 2) (119).

PHENOLIC COMPOUNDS IN OILSEEDS

The predominant phenolic compounds of oilseed products belong to the phenolic acid, coumarin, flavonoid, tannin and lignin group of compounds (3). Major phenolic compounds present in the seeds of borage, canola/rapeseed, evening primrose, flax, sesame, as well as in soybeans and olive fruits are discussed here.

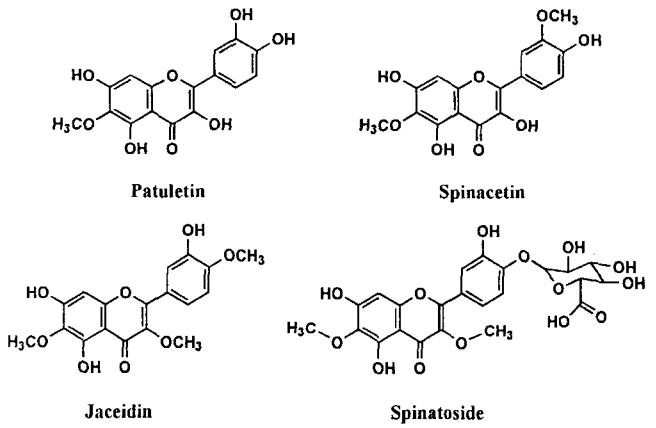


Fig. 14. Chemical structures of some phenolic compounds found in spinach.

Borage seeds

Wettasinghe et al. (120) positively identified rosmarinic, syringic and sinapic acids in the ethanolic extract of borage meal. Subsequently, Zadernowski et al. (121) found 185 mg of total phenolic acids/kg of defatted borage meal. Free phenolics were the predominant form of phenolic acids and comprised 69.3% of the total phenolic acids in borage meal. Ferulic acid accounted for 50.2% of the total free phenolic acids, while protocatechuic, *p*-hydroxybenzoic, and *p*-hydroxyphenyllactic acids contributed 40.5% to the total free phenolic acids.

Canola/rapeseed

The total content of phenolic acids in rapeseed protein products ranged from 13248 to 18370 mg/kg of defatted meal and from 6235 to 12809 mg/kg of flour, on a dry weight basis. On the other hand, rapeseed and canola hulls contain only 600 to 2400 mg of sinapine/kg sample (122). Phenolic acids of rapeseed occur in the free, esterified, glycosidic and insoluble-bound forms. Esterified phenolic acids comprised up to 90% of phenolic acids present in rapeseed and canola (123). Sinapine, the choline ester of sinapic acid, was the predominant phenolic ester in rapeseed (124) while sinapic acid constituted over 73% of free phenolic acids and about 99% of the phenolic acids released from esters and glycosides (Fig. 3) (125). Minor phenolic acids were *p*-hydroxybenzoic, vanillic, gentisic, protocatechuic, syringic, *p*-coumaric, ferulic and caffeic acids (Fig. 3) (125).

The total content of condensed tannins in canola and rapeseed hulls, calculated as the sum of soluble and insoluble tannin contents, ranged from 19130 to 62130 mg/kg of oil-free hulls (126). The content of soluble condensed tannins in hulls of canola and rapeseed varieties ranged from 234 to 27190 mg/kg of hulls (122). The insoluble tannins may comprise 70.0~95.8% of the total condensed tannins in canola and rapeseed hulls (126).

Flaxseed

Flaxseed contains 8000~10000 mg total phenolic acids/kg of seeds. The content of esterified and etherified phenolic acids was up to 5000 mg/kg and 3000~5000 mg/kg, respectively (127). *Trans*-ferulic and *trans*-sinapic acids were the major, while *trans*-caffeic, *p*-coumaric and *p*-hydroxybenzoic the minor phenolic acids found in dehulled, defatted flaxseed meal (Fig. 3) (128). Flavonoids and lignans were the predominant phenolics in flaxseed. The total content of flavonoids in the seeds ranged from

350 to 710 mg/kg (129). Flavone C- and O-glycosides were the major flavonoids present in flaxseed cotyledons (130). Secoisolariciresinol diglucoside (SDG) was identified as a major lignan of flaxseed (131) while isolariciresinol, pinoresinol, and matairesinol were identified as minor lignan components (132). The content of secoisolariciresinerol and matairesinol in flaxseed was 3700 and 10870 mg/kg, respectively (131).

Evening primrose

Lu and Foo (133) identified a procyanidin gallate oligomer in evening primrose seeds. Later, Shahidi et al. (134) reported that evening primrose seeds contained both catechins as well as dimers and trimers of proanthocyanidins. Subsequently, Wettasinghe et al. (135) detected (+)-catechin, (-)-epicatechin and gallic acid in acetone extracts from evening primrose seed. Recently, Hamburger et al. (136) discovered three triterpenoid caffeates in cold-pressed, non-raffinated evening primrose oil, namely 3-*O*-*trans*-caffeoyl derivatives of betulinic, morolic, and oleanolic acids. Evening primrose seeds contained also small quantities of phenolic acids (124 mg of total phenolic acids/kg defatted meal). Free phenolic acids comprised 69% of total phenolic acids content. Protocatechuic acid was the predominant phenolic acid and constituted 58.5% of the total free phenolic acids present (121).

Olives

Secoiridoids, oleuropein, demethyloleuropein, and ligstroside were the main phenolic glucosides, while verbascoside (caffeoylrhamnosylglucoside of hydroxytyrosol) was the main hydroxycinnamic acid derivative of olive fruit (137). Oleuropein is the major phenolic compound responsible for the development of bitterness in olive fruits (138). Phenolic acids, namely hydroxycinnamic, hydroxybenzoic, hydroxycaffeic, and hydroxyphenylacetic acids were also reported in olive fruits (139). Flavonoids, including quercetin, rutin (Fig. 2), luteolin 7-glucoside and apigenin glucosides (73) as well as hydroxy-isochromans, namely 1-phenyl-6,7-dihydroxy-isochroman and 1-(3′-methoxy-4′-hydroxy)phenyl-6,7-dihydroxy-isoc hroman (140) were also identified in olive fruits. The concentration of hydroxytyrosol and hydroxytyrosol derivatives in table olive fruits ranged from 100 to 430 mg/kg and from 3670 to 5610 mg/kg, respectively (139), while the content of verbascosides in olive fruits from Italian cultivars was 160～3200 mg/kg (141). On the other hand, the contents of rutin and luteolin 7-glucoside, two main flavonoids in olive fruits (142), ranged from 110 to 660 and from 5 to 600 mg/kg, respectively (138).

Sesame

Sesame seeds contain carboxyphenols and lignophenols (143). The major lignans of sesame seed are sesamin (200～500 mg per 100 g) and sesamolin (200～300 mg per 100 g). Furthermore, sesamolinol and sesaminol were found in both seeds and oil (Fig. 15) (144). Several pinoresinol glucosides were also detected in sesame seed, namely pinoresinol 4′-*O*-β-D-glucopyranosyl (1→6)-β-D-glucopyranoside, pinoresinol 4′-*O*-β-D-glucopyranosyl (1→2)-β-D-glucopyranoside and pinoresinol 4'-*O*-β-D-glucopyranosyl (1→2)-β-D-glucopyranosyl (1→2)-β-D-glucopyranoside (145). In addition, *trans*-caffeic, *trans*-*p*-coumaric and *trans*-ferulic acids and traces of *p*-hydroxybenzoic acid were found in sesame flour (Fig. 3) (128).

Soybeans

Soybeans contain anthocyanins, flavonols, flavones, isoflavones and chalcones as well as their derivatives with acetic, *p*-hydroxybenzoic, caffeic, coumaric, ferulic, gallic, malonic, hydroxycinnamic, oxalic and sinapic acids (146). Of these, the isoflavones (Fig. 16) are of much interest because of their health-promoting effects (147). Several isoflavones, namely daidzein (7,4′-dihydroxyisoflavone), glycitein (7,4′-dihydroxy-6-methylisoflavone) and genistein (6,7,4′-trihydroxyisoflavone) have been identified in soybean protein products. These compounds occur in soybean and soy foods in the form of glucosides (daidzin, glycitin, genistin), malonylglucosides (6"-*O*-manoyldaidzin, 6"-*O*-manoylglycitin, 6"-*O*-manoylgenistin), acetylglucosides (6"-*O*-acetyldaidzin, 6"-*O*-acetylglycitin, 6"-*O*-acetylgenistin) and also in the free form (146). The total content of isoflavones in soybeans ranged from 472 to 4200 mg/kg (148). Presence of phytoalexins such as coumestrol (7,12-dihydroxy-coumestan), a coumestan isoflavone, and glyceollins I, II and III indicates exposure of soybean to microorganisms (149).

FACTORS AFFECTING THE LEVEL AND BIOAVAILABILITY OF PHENOLICS IN PLANTS

The level of phenolics in food derived from plant sour-

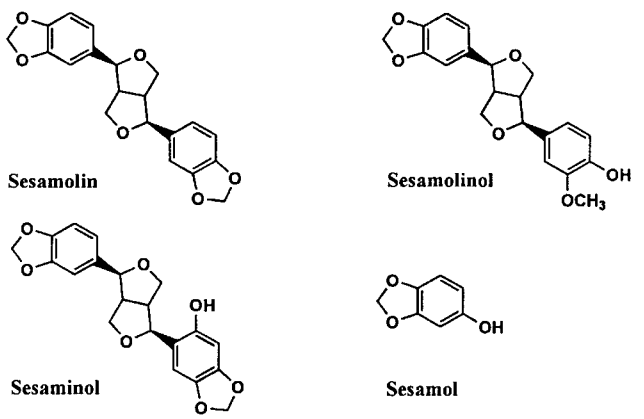
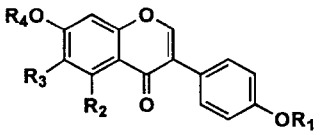


Fig. 15. Chemical structure of some phenolic compounds found in sesame seeds.



Compound	R_1	R_2	R_3	R_4
Daidzein	H	H	H	H
Formononetin	CH_3	H	H	H
Genistein	H	OH	H	H
Glycitein	H	H	OCH_3	H
Daidzin	H	H	H	glucose
Genistin	H	OH	H	glucose
Glycitin	H	H	OCH_3	glucose
6"-*O*-Acetyldaidzin	H	H	H	6"-*O*-acetylglucose
6"-*O*-Acetylgenistin	H	OH	H	6"-*O*-acetylglucose
6"-*O*-Acetylglycitin	H	H	OCH_3	6"-*O*-acetylglucose
6"-*O*-Malonyldaidzin	H	H	H	6"-*O*-malonylglucose
6"-*O*-Malonylgenistin	H	OH	H	6"-*O*-malonylglucose
6"-*O*-Malonylglycitin	H	H	OCH_3	6"-*O*-malonyldglucose

Fig. 16. Chemical structures of some isoflavones found in soybean.

ces depends on such factors as cultivation techniques employed, cultivar, growing conditions, ripening process, as well as processing and storage conditions, among others. For example, peeling, chopping, boiling, microwaving, and frying onions lowers their total content of quercetin conjugates from 1% in case of chopping to up to 75% in case of boiling onions in water (150). On the other hand, storage of whole parsnips at +4°C for 7 days brought about an increase in furanocoumarins from 1 mg/kg fresh weight to 33 mg/kg fresh weight, while storage of parsnips at -18°C up to 50 days did not markedly affect the content of furanocoumarins (151).

The content of some phenolics may increase under stress conditions such as UV radiation, infection by pathogens and parasites, wounding, air polution, and exposure to extreme temperatures (152). In grapes, the synthesis of stilbenes (Fig. 11), namely *trans*- and *cis*-resveratrols, *trans*- and *cis*-piceids (3-*O*-β-D-glucosides of resveratrol), *trans*- and *cis*-astringins (3-*O*-β-D-glucosides of 3′-hydroxyresveratrol), *trans*- and *cis*-resveratrolosides (4′-*O*-β-D-glucosides of resveratrol) and pterostilbene (a dimethylated derivative of stilbene) is induced by fungal infection (*Botris cinerea*), injury, UV radiation, and wilting as well as such factors as grape cultivar, developmental stage of the berry, and soil cultivation practices (153). In carrots, the synthesis of 6-methoxymellein (isocoumarin) (Fig. 12) is stimulated by their exposure to ethylene (154) and to UV radiation (3,154), by microbial infection by wounding (101) and storage at elevated temperatures (154).

Information on the bioavailability and absorption of plant phenolics is still fragmentary and controversial. Bioavailability and absorption of plant phenolics in the small intestine of human body is influenced by such factors as molecular size, lipophilicity, solubility, and pK_a as well as gastric and intestinal transit time, membrane permeability, and pH of the lumen (155).

TOXICANT ACTIVITY

The published data on the toxicity of food phenolics are still fragmentary. Phenols may become toxic if natural barriers or detoxification mechanisms are overloaded by the amount of ingested phenols, but the toxicity level of phenols depends also on the manner of their administration and is affected by the presence of substances containing di-ether or isopropenoid structures (156). Low- and high-molecular- weight phenolics may bring about nutritional implications by consuming the metabolized energy in their detoxification process or by lowering the contribution of methyls or glucuronic acid to more useful metabolisms (157). Daily intake of flavonoids, from common foodstuffs, produce very low toxicities because of their low absorption, rapid metabolism, as well as the presence of an efficient defence mechanism in mammals. Excessive intake of flavonoids, above that obtained from a typical vegetarian diet may, however, pose a serious health risk for humans. At higher doses, flavonoids may inhibit key enzymes involved in hormone metabolism, generate free radicals as well as may act as potent mutagens (158-160).

Singleton and Kratzer (156) reported that the LD_{50} values for a single dose of tannins orally administered to rats, mice and rabbits ranged from 2.25 to 6.00 g per kg of body weight. Isocoumarins, 6-hydroxymellein and 6-methoxymellein found in carrots, also displayed toxic effects on the animal cells, microorganisms and plant cells. The toxic effects exerted by 6-methoxymellein on Chinese hamster cells (EC_{50}=0.46 mM) were much lower than that exerted on microorganisms and plant cells (EC_{50}=0.04 ~ 0.05 mM) (161). On the other hand, Wren et al. (162) did

not detect any significant toxicological effects in rats consuming grape extract containing less than 5.5% catechin monomers. The rats used in this study were fed for 90 days with a diet containing 0, 0.5, 1.0, and 2.0% of grape extract. Furthermore, Lake (163) suggested that coumarins do not cause any health risk to humans at the maximum human daily intake estimated to be 0.02 mg/kg/day.

Several flavonoids, namely quercetin, rhamnetin, rutin, kaempferol as well as some extracts from citrus displayed mutagenicity in bacterial cells (164). Furthermore, Buening et al. (165) reported that nobiletin, tangeretin and 7,8-benzoflavone increased metabolic activation of benzo[*a*] pyrene and aflatoxin B_1 to mutagens. Subsequently, Delaney et al. (166) demonstrated that standardized polymethoxylated flavones from citrus did not exhibit any mutagenicity in both bacterial cell and mammalian cell lines.

HEALTH EFFECTS

Health potentials of food phenolics have been extensively reviewed (8,167) Therefore, only some aspects of pharmacological potentials of food phenolics will be discussed here.

Gibson et al. (168) and Howell (169) demonstrated that cranberry proanthocyanidins may be responsible for the inhibition of cellular adherence of uropathogenic strains of P-type (mannose-resistant) *Escherichia coli* to mucosal cells in the urinary tract. It has been suggested that these compounds competitively inhibit the adhesion of *Escherichia coli* to mucosal cells through receptor-ligand interactions (169). Subsequently, Foo et al. (170) reported that cranberry proanthocyanidins with A-type linkage displayed greater antiadhesion activities than those with B-type linkage.

Plant flavonoids also exhibited a significant antiviral activity. Quercetin, a flavonol aglycone, found in a number of fruits such as apple, apricot, fig, plum, strawberry, and tomato, among others, displayed antiviral activities against herpes simplex virus type 1, parainfluenza virus type 3 and polio virus type 1 both in the *in-vivo* and *in-vitro* studies (171). On the other hand, hesperetin inhibited the infectivity of herpes simplex type viruses, polio viruses, and parainfluenza viruses (172), while tannins from pericarp of pomegranate displayed antiviral activity against the genital herpes virus (173).

Grape seed procyanidins suppressed the stomach mucosal injury caused by acidified ethanol (174). It has been suggested that the antiulcer property of grape procyanidins may be due to both their radical scavenging activity and their ability to bind to proteins (174). Other reported biological activities of grape seed extracts include antiatherosclerotic (175), antidiabetic (176), and anticarcinogenic activities (177).

Isoflavones not only exhibit estrogenic activities, but also protect against several chronic diseases. Consumption of soybean isoflavones lowers the incidence of breast, prostate, urinary tract and colon cancers as well as provides protection against coronary heart diseases and osteoporosis (178). In addition, isoflavones exhibit marked inhibitory activity against oxidation of lipoprotein in serum (179).

Biological activities of citrus flavonoids has been extensively studied (180). Auraptene (7-geranyloxycoumarin) found in citrus fruit peel was an effective inhibitor in rat colon (180). Flavanones also suppress carcinogenesis (181) and in addition showed antiallergic and anti-inflammatory properties (182). On the other hand, polymethoxylated flavones inhibited the formation of tumor necrosis factor-α in culture of human monocytes (183). Diosmin is an active component of some drugs used for the treatment of circulatory system illnesses (184) and severe hemorroidal disease (185).

Quercetin and rutin found in vegetables and fruits suppressed the colonic neoplasia induced by azoxymethanol (186). Quercetin also displays vasoactive properties (187), gastroprotective effect (188), as well as an inhibitory effect on the mutagenic activity of heterocyclic amines (HCA). The suppression of the HCA activity is due to the inhibition of metabolic activation of HCA in the liver (189).

FUTURE TRENDS

In spite of significant progress in research on plant phenolics during the last 25 years, the published data on the content, composition and bioactivity of plant phenolics are still incomplete and often restricted to few cultivars. In addition, data on the effect of different steps in the food production on the bioactive phenolics is very limited. Therefore, there is still a need to expand research to greater variety of cultivars and include plants of great economical significance such as palm kernel, banana, pineapple, rye, rice, evening primrose, and borage, among others, as well as to determine the effect of processing on bioactive phenolics. In addition, not all bioactive phytochemicals have been identified and/or their health-promoting properties documented fully. Thus, there is also a need to continue research efforts leading to the discovery of novel potent bioactive phytochemicals and to ascribe their role in promoting health.

Epidemiological studies have provided evidence on the existence of correlation between consumption of some foods of plant origin and the prevention of certain chronic diseases such as coronary heart diseases and cancer (190).

Therefore, there is a growing demand by consumers for food products containing high levels of health-promoting phytochemicals. These demands can be met by extracting bioactive components from by-products such as citrus peels and grape seeds and using them as such or adding them to foods, selecting cultivars high in bioactive components or formulating-health promoting supplements. On the other hand, potential adverse effects of excessive intake of flavonoids should not be overlooked, as at high intakes plant phenolics may act as mutagens, prooxidants and inhibitors of key enzymes (160). Thus, more research is still needed to establish possible toxicological effects associated with high intake of phenolics.

The biosynthesis, localization within the cell, and specific function of phenolics in plants has been studied extensively and considerable progress made. However, there are still, according to Harborne (191), many challenges that must be overcome in order to fully understand the physiological function of phenolics at different stages of plant development, and the mechanisms responsible for the diversity of phenolics in plants and accumulation of phenolics at cellular, subcellular and tissue levels. Metabolism of phenolics and identification of their metabolites also deserves further studies.

SOURCES OF FURTHER INFORMATION AND ADVICE

This review paper provides only an overview of plant phenolics found in some cereals, fruits, vegetables and oilseeds. A number of excellent books and reviews on various aspects of the chemistry, biological properties and health effects of plant phenolics have recently been published. In this section only some sources of information were highlighted. Biological role of phenolics in plant is discribed in books edited by Cosgrove and Knievel (192), Macheix et al. (193), Scalbert (7) and Tomás-Barberán and Robins (194). More comprehensive reviews of the chemistry of plant phenolics are provided in books published by Haslam (195), Macheix et al. (193), Mazza (196), Mazza and Miniati (73), Mazza and Oomah (197), Scalbert (7), and Shahidi and Naczk (3). Excellent reviews on dietary intake and absorption and metabolism of phenolics were recently published by Scalbert and Williams (198). Health effects are thoroughly discussed in books published by Bidlack et al. (167, 190), Ho et al. (199), Huang et al. (200), Mazza (196), Mazza and Oomah (197), and Scalbert (7).

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