

Chapter 1

Phenolic Compounds in Food An Overview

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Phenolic compounds including simple phenols and phenolic acids, hydroxycinnamic acid derivatives and flavonoids are bioactive substances occurring widely in food plants. Phenolic compounds are closely associated with the sensory and nutritional quality of fresh and processed plant foods. The enzymatic browning reaction of phenolic compounds, catalyzed by polyphenoloxidase, could cause the formation of undesirable color and flavor and the loss of nutrient in fruits and vegetables. Many phenolic compounds in plants are good sources of natural antioxidants. It is a great interest in recent years that many phenolic compounds in foods have inhibitory effects on mutagenesis and carcinogenesis.

The term 'phenolic' or 'polyphenol' can be defined chemically as a substance which possesses an aromatic ring bearing one or more hydroxy substituents, including functional derivatives (esters, methyl ethers, glycosides etc.) (1). Most phenolics have two or more hydroxyl groups and are bioactive substances occurring widely in food plants that are eaten regularly by substantial numbers of people.

Occurrence of Phenolic Compounds

The phenolic compounds which occur commonly in food material may be classified into three groups, namely, simple phenols and phenolic acids, hydroxycinnamic acid derivatives and flavonoids.

The Simple Phenols and Phenolic Acids. The simple phenols include monophenols such as *p*-cresol isolated from several fruits (e.g. raspberry, blackberry) (2), 3-ethylphenol and 3,4-dimethylphenol found to be responsible for the smoky taste of certain cocoa beans (3) and diphenols such as hydroquinone which is probably the most widespread simple phenol (4).

A typical hydroquinone derivative, sesamol, is found in sesame oil (4). Several derivatives of sesamol, such as sesaminol, found in sesame oil have been evaluated to have strong antioxidant activity (Osawa, Chapter 10, Vol. II).

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Vanillin (4-hydroxy-3-methoxybenzaldehyde) is the most popular flavor. The determination of vanillin in vanilla beans is discussed by Hartman et al. (Chapter 4, Vol. I).

Gallic acid, a triphenol, is present in an esterified form in tea catechins (Balentine, Chapter 8, Vol. I). Gallic acid may occur in plants in soluble form either as quinic acid esters (5) or hydrolyzable tannins (Okuda et al., Chapter 12, Vol. II).

The Hydroxycinnamic Acid Derivatives. Hydroxycinnamic acids and their derivatives are almost exclusively derived from *p*-coumaric, caffeic, and ferulic acid, whereas sinapic acid is comparatively rare. Their occurrence in food has recently been reviewed by Herrmann (6). Hydroxycinnamic acids usually occur in various conjugated forms, more frequently as esters than glycosides.

The most important member of this group in food material is chlorogenic acid, which is the key substrate for enzymatic browning, particularly in apples and pears (7).

A number of chapters in this book discuss the occurrence of hydroxycinnamic acids in foods which include:

<i>Umbelliferous</i> vegetables	Roshdy et al. (Chapter 6, Vol. I)
Citrus fruits	Naim et al. (Chapter 14, Vol. I)
Brassica oilseed	Shahidi (Chapter 10, Vol. I)
Corn flour	Gibson and Strauss (Chapter 20, Vol. I)
Raspberry	Rommel et al. (Chapter 21, Vol. I)
Plums	Fu et al. (Chapter 22, Vol. I)

The Flavonoids. The most important single group of phenolics in food are flavonoids which consist mainly of catechins, proanthocyanins, anthocyanidins and flavons, flavonols and their glycosides.

Although catechins seem to be widely distributed in plants, they are only rich in tea leaves where catechins may constitute up to 30% of dry leaf weight. A number of chapters in Volume II of this book discuss current research on antioxidative and cancer chemopreventive properties of tea and its catechin components. Lunder (Chapter 8, Vol. II) has shown that the antioxidative activity of green tea extract could be related to the content of epigallocatechin. Osawa (Chapter 10, Vol. II) was able to demonstrate that epicatechin gallate and epigallocatechin gallate not only inhibit the free radical chain reaction of cell membrane lipids, but also inhibit mutagenicity and DNA damaging activity. Laboratory studies conducted by Ito et al. (Chapter 19, Vol. II), Conney et al. (Chapter 20, Vol. II), Wang et al. (Chapter 21, Vol. II), Chung et al. (Chapter 22, Vol. II), Laskin et al. (Chapter 23, Vol. II) and Yoshizawa et al. (Chapter 24, Vol. II) are presented. They have shown that tea and catechin components can inhibit tumorigenesis and tumor growth in animals.

Proanthocyanidins, or condensed tannins, are polyflavonoid in nature, consisting of chains of flavan-3-ol units. They are widely distributed in food such as apple, grape, strawberry, plum, sorghum and barley (8). Proanthocyanidins have relatively high molecular weights and have the ability to complex strongly with carbohydrates and proteins. Comprehensive treatment of polyphenol complexation is given by Haslam et al. in this book (Chapter 2, Vol. I). Hagerman (Chapter 19, Vol. I) and Butler and Rogler (Chapter 23, Vol. I) also present overviews on these topics.

Anthocyanins are almost universal plant colorants and are largely responsible for the brilliant orange, pink, scarlet, red, mauve, violet and blue colors of flower

petals and fruits of higher plants (9). Anthocyanins as food colorants have recently been reviewed (10).

Flavones, flavonols and their glycosides also occur widely in the plant kingdom. Their structural variations and distribution have been the subjects of several comprehensive reviews in recent years (11-13). It has been estimated that humans consuming high fruit and vegetable diets ingest up to 1 g of these compounds daily (Leighton et al., Chapter 15, Vol. II). The most common and biologically active dietary flavonol is quercetin. A number of presentations in Volume II of this book discuss current research on the effect of quercetin on mutagenesis and carcinogenesis. Quercetin was found by Verma (Chapter 17, Vol. II) to inhibit both initiation with 7,12-dimethylbenz[*a*]anthracene (DMBA) and tumor promotion with 12-*O*-tetradecanoylphorbol-13-acetate (TPA) of mouse skin tumor formation. Starvic et al. (Chapter 16, Vol. II) suggest that quercetin and other polyphenols such as ellagic acid and chlorogenic acid may play a dual protective role in carcinogenesis by reducing bioavailability of carcinogens, and by interfering with their biotransformation in the liver. By using an experimental model of colon cancer, Deschner (Chapter 18, Vol. II) was able to demonstrate that under conditions of low dietary fat intake, quercetin and rutin have displayed considerable activity in suppressing the hyperproliferation of colonic epithelial cells, thereby reducing focal areas of dysplasia and ultimately colon tumor incidence.

Effect of Phenolic Compounds on Food Quality

Phenolic compounds are closely associated with the sensory and nutritional quality of fresh and processed plant foods (14). The enzymatic browning reaction of phenolic compounds, catalyzed by polyphenoloxidase, is of vital importance to fruit and vegetable processing due to the formation of undesirable color and flavor and the loss of nutrients. For examples, polyphenoloxidase was found to be responsible for the browning of grapes (15), and catechin, polyphenoloxidase and oxygen were reported to be required for the browning of yams (16). The enzymatic browning reaction in fruits often has been considered to be a linear function of the phenolic content and polyphenoloxidase activity. In this book, however, Lee (Chapter 24, Vol. I) show that the rate of browning in fruit products is not a linear function of the total phenolic content and that browning of fruits depends on the concentration and nature of polyphenol compounds that are co-present.

A common approach for the prevention of the browning of food and beverages has been the use of antibrowning agents. The most widespread antibrowning agents used in the food and beverage industries are sulfites. Due to the health risks of sulfiting agents (17), the Food and Drug Administration has banned or limited the use of sulfites in certain foods (18). McEvily et al. (Chapter 25, Vol. I) discuss the isolation and characterization of several 4-substituted resorcinols from figs. These novel 4-substituted resorcinols were shown to be potent polyphenoloxidase inhibitors.

Oxidative changes of polyphenols during processing are important for the development of color and flavor in certain foods. Browning of polyphenols is a natural process of cocoa fermentation (19). For the manufacture of black tea, the tea leaves are crushed, causing polyphenoloxidase-dependent oxidative polymerization and leading to the formation of theaflavins and thearubigins, the orange and red pigments of black tea. This subject is reviewed in the chapter by Balentine.

Phenolic compounds may contribute directly to desirable and undesirable aromas and tastes of food. Recently, Ha and Lindsay (20) reported that highly characterized sheep-mutton aromas in ovine fats were contributed by *p*-cresol, 2-isopropylphenol, 3,4-dimethylphenol, thymol, carvacrol, 3-isopropylphenol and 4-isopropylphenol. They also observed that cresols, especially *m*-cresol, appeared to contribute to beef flavors. Several discussions of flavor characteristics of phenolic compounds are included in this book. Maga (Chapter 13, Vol. I) reviews the roles of hemicellulose, cellulose and lignin thermal degradation on the formation of phenolic compounds which are the major contributors to wood smoke aroma. Fisher (Chapter 9, Vol. I) and Omar (Chapter 12, Vol. I) present overviews on the contribution of phenolic compounds to the aroma and taste of certain spices and plant extracts. Naim et al. (Chapter 14, Vol. I) report that 4-vinylguaiacol is one of the major detrimental off-flavors that form under typical processing and storage of citrus products. Their studies reveal that 4-vinylguaiacol is formed from ferulic acid following the release of ferulic acid from bound forms.

Phenolic Compounds as Natural Antioxidants

Antioxidants are added to fats and oils or foods containing fats to prevent the formation of various off-flavors and other objectionable compounds that result from the oxidation of lipids. BHA and BHT, the most widely used synthetic antioxidants, have unsurpassed efficacy in various food systems besides their high stability, low cost, and other practical advantages. However, their use in food has been falling off due to their suspected action as promoters of carcinogenesis as well as being due to a general rejection of synthetic food additives (21).

The most important natural antioxidants which are commercially exploited are tocopherols. Tocopherols have a potent ability to inhibit lipid peroxidation *in vivo* by trapping peroxy radicals. Their antioxidative mechanism and structure-activity relationship are discussed by Hughes et al. (Chapter 13, Vol. II). Unfortunately, tocopherols are much less effective as food antioxidants. The search and development of other antioxidants of natural origins is highly desirable. Such new antioxidants would also be welcome in combatting carcinogenesis as well as the aging process.

Most natural antioxidants are phenolic in nature. Some of the food materials containing phenolic antioxidants studied and reported herein include:

Chili pepper	Nakatani (Chapter 5, Vol. II)
Ginger	Nakatani (Chapter 5, Vol. II)
Green tea	Lunder (Chapter 8, Vol. II), Osawa (Chapter 10, Vol. II)
Pepper	Nakatani (Chapter 5, Vol. II)
Oregano	Nakatani (Chapter 5, Vol. II)
<i>Osbeckia chinensis</i>	Osawa (Chapter 10, Vol. II)
Rice hull	Osawa et al. (Chapter 9, Vol. II)
Rosemary	Nakatani (Chapter 5, Vol. II)
Sesame seeds	Osawa (Chapter 10, Vol. II)
Soybean	Fleury et al. (Chapter 7, Vol. II)
Thyme	Nakatani (Chapter 5, Vol. II)

Phenolic antioxidants not only inhibit the autoxidation of lipids, but sometimes, they also have the ability to retard lipid oxidation by inhibiting lipoxygenase activity. It is believed that the metabolism of arachidonic acid to lipid peroxides and various other oxidative products is significant in carcinogenesis (22). It appears to play an important role in tumor promotion because inhibitors of arachidonic acid metabolism have been observed to inhibit this promotion (23). Four green tea catechin components having strong antioxidant activity also exhibited various degrees of lipoxygenase-inhibitory activities (Ho, C.-T.; Shi, H., unpublished data). (-)-Epigallocatechin gallate, (-)-epicatechin gallate and epigallocatechin displayed IC_{50} values toward soybean 15-lipoxygenase enzyme ranging from 10-21 μ M (Table I). (-)-Epicatechin is, on the other hand, relatively inactive. It is also interesting to note that two of the oxidative dimers of tea catechins, the theaflavin monogallate B and theaflavin digallate, which are important polyphenols of black tea, have even stronger lipoxygenase-inhibitory activities than the catechin monomers. The other two structurally closely-related theaflavins, theaflavin and theaflavin monogallate A, have no activity at all (Table I). The detailed chemical structures of these tea polyphenols can be found in the chapter by Balentine (Chapter 8, Vol. I).

Table I. Inhibition of Soybean Lipoxygenase by Tea Polyphenols

Compound	IC_{50} (μ M)
(-)-Epicatechin (EC)	140
(-)-Epicatechin gallate (ECG)	18
(-)-Epigallocatechin (EGC)	21
(-)-Epigallocatechin gallate (EGCG)	10
Theaflavin	3604
Theaflavin monogallate A	366
Theaflavin monogallate B	0.62
Theaflavin digallate	0.25

Conclusion

Phenolic compounds are ubiquitous in plant foods, and therefore, a significant quantity is consumed in our daily diet. They are closely associated with the sensory and nutritional quality of fresh and processed plant foods. The antioxidant activities of phenolic compounds have been recognized for decades, and research and development on the use of natural substances or food ingredients containing phenolic antioxidants will continue to be of great interest to the food industry.

Biological activities of phenolic compounds have become well known in recent years. The most important biological activity of phenolic compounds is probably their many observed inhibitory effects on mutagenesis and carcinogenesis. This topic is covered in great depth in the overview chapter by Huang and Ferraro (Chapter 1, Vol. II) and many chapters in Volume II of this book.

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