

# FOOD PHENOLICS

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SOURCES

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CHEMISTRY

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EFFECTS

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APPLICATIONS

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Fereidoon Shahidi  
Marian Naczk

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INTEREST in food phenolics has reached a new high in recent years. Apart from the usual academic interest in the biology and chemistry of phenolic compounds in nature, the scientific and commercial interest in food phenolics has been accentuated by reports on beneficial health effects of such compounds. Many food phenolics have been reported to possess antimutagenic and anticarcinogenic activity in test animals. Furthermore, there has been a renewed interest on natural sources of antioxidants and these generally belong to the phenolic group of compounds. Our daily intake of phenolics from dietary sources exceeds one gram. The effect of these compounds on our health status and prevention of deterioration of processed foods as well as their nutritional and sensory quality needs to be addressed. The present monograph reports the occurrence and chemistry of phenolics in different food commodities, their nutritional and health effects, and their role as antioxidants in food processing. In addition, methods of analysis and quantification of food phenolics are covered. The book is intended for senior undergraduate and graduate students and scientists in academia, government and industry. Food scientists, chemists, biochemists, nutritionists, food processors and commercial organizations will find it of interest. An extensive bibliography is also provided for further reading of the original reports.

FEREIDOON SHAHIDI  
MARIAN NACZK

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## *Food Phenolics: An Overview*

### **INTRODUCTION**

PHENOLIC compounds in foods originate from one of the main classes of secondary metabolites in plants (Van Sumere, 1989). Chemically, phenolics can be defined as substances possessing an aromatic ring bearing one or more hydroxy substituents, including their functional derivatives. Their occurrence in animal tissues and non-plant materials is due to ingestion of plant foods. The most ubiquitous phenols are polymeric and insoluble lignins that are found in all vascular plants. Many of the food phenolics are soluble in water or organic solvents. Most plants, if not all, contain polyphenols which differentiate them from one another. Phenolics found in foods generally belong to phenolic acids, flavonoids, lignans, stilbenes, coumarins and tannins (Harborne, 1993a).

Phenolic compounds are essential for growth and reproduction of plants and also act as antifeedant and antipathogens (Butler, 1992). Their contribution to pigmentation of plant foods is also well recognized. Injured plants may secrete phenolics to defend them against pathogens. The antifeedant activity of phenolics is greater for those containing oxidized phenolics with quinoidal structures. Recognition of symbionts may also be related to the presence of polyphenols in plants.

Many properties of plant products are associated with the presence and content of their polyphenolic compounds. The astringency of foods (Clifford, 1992), the beneficial health-related effects of certain phenolics (Huang and Ferraro, 1992; Mergens, 1992; Tanaka et al., 1992) or their potential antinutritional properties (Butler, 1992), when present in large quantities in plant foods, are of importance to consumers. Furthermore, polyphenolic anthocyanins are responsible for the orange, red, blue, violet and purple color of most plant species and their products. Colorants produced from the skins of grapes, after their

extraction with water and concentration or other processes, are used by the food industry (Francis, 1993).

Many plant foods contain polyphenol oxidases which catalyse reactions with phenols in the presence of molecular oxygen (McEvily et al., 1992). Initial oxidation of phenols to quinones followed by the formation of colored pigments results in enzymatic browning of products. In most cases, enzymatic browning is undesirable. Inhibition of enzymatic browning is therefore achieved by changes in the pH, temperature or application of procedures which inhibit the enzymes, substrates or their reaction products. The most widely used antibrowning agents are sulfites. The 4-substituted resorcinols have also been shown to be potent polyphenol oxidase inhibitors.

Presence of phenolics in foods may have an important effect on the oxidative stability and microbial safety of products. In addition, many phenolics in foods possess important biological activity related to their inhibitory effects on metagenesis and carcinogenesis. Many plant foods such as grains, oilseeds, legumes, as well as herbs, spices and tea contain phenolics with potent antioxidant activity (Shahidi and Wanasundara, 1992). Therefore, there has been an increasing interest in the extraction and use of antioxidants from natural plant sources in food processing.

## EFFECT OF PHENOLIC COMPOUNDS ON FOOD QUALITY

Phenolic compounds are closely associated with nutritional and sensory quality of foods derived from plant sources. While at low concentrations, phenolics may protect the food from oxidative deterioration, at high concentrations they, or their oxidation products, may participate in discoloration of foods, interactions with proteins, carbohydrates and minerals. In addition, the astringency and bitterness of foods depends on their concentration of phenolic compounds. Recently, Ha and Lindsay (1991) reported that highly characteristic mutton aroma of ovine was due to *p*-cresol, 2-, 3- and 4-isopropylphenol, 3,4-dimethylphenol, thymol and carvacrol. They also noted that cresols, especially *m*-cresol, contributed to beef flavor. The role of wood components, especially lignin, in production of smoke phenolics and smoke flavor is quite important in processed meat and certain cheese products. Many of the phenolics in foods occur as their glycoside and may modify the quality characteristics of foods. In general, the leaves, flowers, fruits and other living tissues of the plants contain glycosides while woody tissues contain aglycones. The seeds may contain phenolics in either form.

## PHENOLIC COMPOUNDS IN CANCER PREVENTION

Phenolic compounds, especially flavonoids, occur widely in plants. At least 5000 phenolics, including over 2000 different naturally occurring flavonoids have been identified (Harborne, 1993b). Among the most widely found flavonoids are quercetin and rutin which occur in tea, coffee, grains and a variety of fruits and vegetables. A variety of dietary plant flavonoids has been found to inhibit tumor development. This inhibitory effect of flavonoids may be exerted by (a) inhibition of metabolic activation of carcinogens by modulation of cytochrome p-450 isoenzymes; (b) inactivation of ultimate carcinogens; (c) inhibition of generation of active oxygen species and action as scavengers of active oxygen species; (d) inhibition of metabolism of arachidonic acid; (e) inhibition of activity of protein kinase C and other kinases; and (f) reducing the bioavailability of carcinogens. Although several flavonoids are reported to have mutagenic activity, these results have not been confirmed by other investigations. In addition, quercetin, a major suspect, is neither an initiator nor a promoter of mouse skin tumors.

Table 1.1 summarizes the relative concentration of flavonoids and related compounds in plant tissues. On the average, our daily consumption of food phenolics, especially flavonoids, is about 1 g on a daily basis. The inhibitory effect of flavonoids against the mutagenic activity of the diol epoxide ( $\pm$ )-7 $\beta$ ,8 $\alpha$ -dihydroxy-9 $\alpha$ ,10 $\alpha$ -epoxy-7,8,9-10-tetrahydrobenzo[a]pyrene in *S. typhimurium* TA 100 is summarized in Table 1.2. Flavonoids with free phenolic groups were found to be most active. Several flavonoids, including quercetin and rutin, were able to suppress mutagenesis induced by the direct-acting carcinogen *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine.

*Table 1.1. Relative Content of Flavonoids and Related Compounds in Plant Tissues.<sup>a</sup>*

| Tissue        | Relative Content  |
|---------------|---|
| Fruit         | Cinnamic acid > catechin $\approx$ leucoanthocyanidins > flavonols                      |
| Leaf          | Flavonols $\approx$ cinnamic acid > catechins $\approx$ leucoanthocyanidins > flavonols |
| Bark and wood | Catechins $\approx$ leucoanthocyanidins > flavonols > cinnamic acid                     |

<sup>a</sup>Adapted from Pratt (1992).

*Table 1.2. Inhibition of the Mutagenic Activity of ( $\pm$ )-7 $\beta$ ,8 $\alpha$ -Dihydroxy-9 $\alpha$ ,10 $\alpha$ -epoxy-7,8,9,10-tetrahydrobenzo[a]pyrene by Selected Flavonoids.<sup>a</sup>*

| Flavonoid  | Inhibition <sup>b</sup> |
|------------|-------------------------|
| Myricetin  | excellent               |
| Robinetin  | excellent               |
| Luteolin   | excellent               |
| Quercetin  | excellent               |
| Rutin      | excellent               |
| Quercetrin | excellent               |
| Morin      | very good               |
| Myricitrin | very good               |
| Kaempferol | very good               |
| Diosmetin  | very good               |
| Fisetin    | very good               |
| Apigenin   | very good               |
| Naringenin | good                    |
| Robinin    | good                    |
| D-Catechin | good                    |
| Genistein  | good                    |
| Chrysin    | none                    |

<sup>a</sup>Adapted from Huang and Ferraro (1992).

<sup>b</sup>Symbols refer to inhibition of mutagenicity by 50% at: 2 – 5 nmole, excellent; 10 – 40 nmole, very good; 50 – 100 nmol, good; and > 100 nmole, none.

## RESEARCH PROGRESS

The progress of research on food phenolics has been rapid in recent years. The present monograph reports on food phenolics with respect to their occurrence, chemistry, properties and methods of analysis. After an overview (Chapter 1), eight other chapters summarize these topics in three parts under occurrence and chemistry (Part One—Chapters 2 to 5), characteristics, effects and properties (Part Two—Chapters 6 to 8) and methods of analysis and quantification (Part Three—Chapter 9). Extensive bibliography and key references are provided in each chapter for further consultation.

## REFERENCES

- Butler, L. G. 1992. Protein-polyphenol interactions: nutritional aspects. In *Proceedings of the 16th International Conference of Grape Polyphenols*, Volume 16, Part II, p. 11.

- Clifford, M. N. 1992. Sensory and dietary properties of phenols. In *Proceedings of the 16th International Conference of Grape Polyphenols*, Volume 16, Part II, p. 19.
- Francis, F. J. 1993. Polyphenols as natural food colorants. In *Polyphenolic Phenomena*, Scalbert, A., Ed., Institut National de la Recherche Agronomique, Paris, p. 209.
- Ha, J. K. and Lindsay, R. C. 1991. Volatile alkylphenols and thiophenol in species-related characterizing flavors of red meats. *J. Food Sci.*, 56:1197–1202.
- Harborne, J. B. 1993a. New naturally occurring plant polyphenols. In *Polyphenolic Phenomena*, Scalbert, A., Ed., Institut National de la Recherche Agronomique, Paris, p. 19.
- Harborne, J. B. 1993b. *The Flavonoids: Advances in Research Since 1986*. Chapman and Hall, London.
- Huang, M.-T. and Ferraro, T. 1992. Phenolic compounds in food and cancer prevention. In *Phenolic Compounds in Food and Their Effects on Health. II. Antioxidants and Cancer Prevention*. Huang, M.-T., Ho, C.-T. and Lee, C. Y., Eds., ACS Symposium Series 507, American Chemical Society, Washington, DC, p. 8.
- McEvily, A. J., Iyenger, R. and Gross, A. T. 1992. Inhibition of polyphenol oxidase by phenolics compounds. In *Phenolic Compounds in Food and Their Effects on Health I: Analysis, Occurrence and Chemistry*, Ho, C.-T., Lee, C. T. and Huang, M.-T., Eds., ACS Symposium Series 506, American Chemical Society, Washington, DC, p. 318.
- Mergens, W. J. 1992. Tocophenol: Natural phenolic inhibitor of nitrosation. In *Phenolic Compounds in Food and Their Effects on Health II. Antioxidants and Cancer Prevention*, Huang, M.-T., Ho, C.-T. and Lee, C. Y., Eds., ACS Symposium Series 507, American Chemical Society, Washington, DC, p. 350.
- Pratt, D. E. 1992. Natural antioxidants from plant material. In *Phenolic Compounds in Food and Their Effects on Health II. Antioxidants and Cancer Prevention*, Huang, M.-T., Ho, C.-T. and Lee, C. Y., Eds., ACS Symposium Series 507, American Chemical Society, Washington, DC, p. 54.
- Shahidi, F. and Wanasundara, P. K. J. P. D. 1992. Phenolic antioxidants. *CRC Crit. Rev. Food Sci. Nutr.*, 32:67.
- Tanaka, T., Yoshima, N., Sugie, S. and Mori, H. 1992. Protective effects against liver, colon, and tongue carcinogenesis by plant phenols. In *Phenolic Compounds in Food and Their Effects on Health II. Antioxidants and Cancer Prevention*, Huang, M.-T., Ho, C.-T. and Lee, C. Y., Eds., ACS Symposium Series 507, American Chemical Society, Washington, DC, p. 326.
- Van Sumere, C. F. 1989. Phenols and phenolic acids. In *Methods in Plant Biochemistry. Vol. I. Plant Phenolics*, Harborne, J.B., Ed., Academic Press, London, p. 29.



PART ONE

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# OCCURRENCE AND CHEMISTRY



