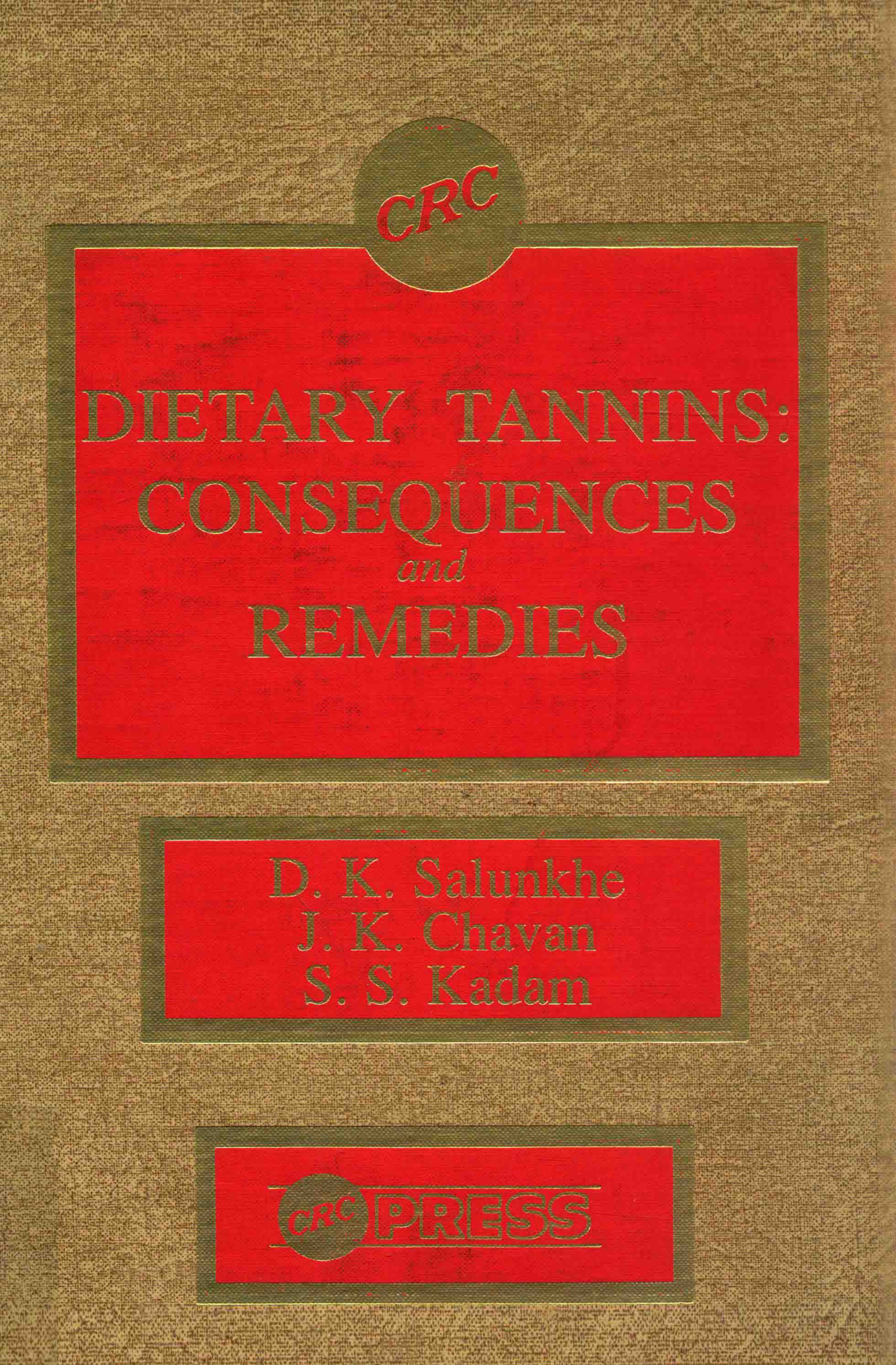

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DIETARY TANNINS: CONSEQUENCES *and* REMEDIES

D. K. Salunkhe
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Dietary Tannins: Consequences and Remedies

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PREFACE

In recent years, phenolic compounds in many food crops have been recognized as antinutrients. The antinutritional and/or toxic effects caused by natural phenolics of common plant foods consumed in normal amounts are practically nil. On the contrary, several bioflavonoids have been shown to exhibit stimulating, antibacterial, antiatherosclerolemic, antioxidant, and flavor-inducing effects. However, the occurrence of oligomeric and polymeric flavonoids (vegetable tannins) in relatively higher concentrations in certain plant foods/feeds, particularly those that are major components of the foods/feeds, seems to be of serious nutritional concern. Although the pharmacological and therapeutic properties of many bioflavonoids are well documented in the literature, the antinutritional effects of vegetable tannins in the diet are only recently recognized.

Certain cultivars of sorghum, millet, food legumes, fruits, and forages are known to contain appreciable levels of tannins. In the economically disadvantaged countries of the world, cereals and legumes form a main source of nutrients in daily diets. The total dietary intake of tannins can, therefore, be considerably higher among these people. The prevalence of protein malnutrition and undernutrition in these areas can further aggravate the tannin toxicity problem. Hence, an examination of the nature of these phenolics, their mode of synthesis, location in the plant tissue, harmful and harmless forms, methods of their determination and their pharmacological, therapeutic, physiological, and nutritional effects in mammals need continued research.

Based on the recommendations of the 36th Annual Meeting of the Institute of Food Technologists held at St. Louis, Missouri in 1979, considerable progress has been made on several aspects of dietary tannins of sorghum, millets, legumes, fruits, vegetables, wine, tea, and forages. Of particular importance are investigations on chemical characterization, methods of analysis, changes during maturation, drying, storage, and processing, nature of tannin/protein interactions and specificities, mechanisms of toxicity, effects on the functioning of certain secretory glands, agronomically desirable phenolics, development of suitable technologies to remove/inactivate tannins in foods, and elimination of their antinutritional properties. Some of the pioneering reports on these aspects of dietary tannins include the recent exhaustive reviews of E. Haslam, R. K. Gupta, J. G. Hulse, L. G. Butler, V. L. Singleton, and D. K. Salunkhe and associates.

In this book, an attempt has been made to compile, update, and critically analyze the available literature on various aspects of dietary tannins in general and that of cereals and legumes in particular. The agronomical advantages of phenolics are also added to emphasize the importance of phenolics in crop production. We hope this will serve as a useful reference book to nutritionists, biologists, plant breeders, food scientists and technologists, and agronomists who are interested in the chemistry, biochemistry, and technology of dietary tannins.

D. K. Salunkhe
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THE AUTHORS

Dr. D. K. Salunkhe, Ph.D., is a Professor Emeritus of Nutrition and Food Sciences at Utah State University, Logan, Utah. Under his guidance, 86 graduate students have received their M.S. and Ph.D. degrees. He has authored about 400 scientific papers, book chapters, and reviews. Some of his articles received recognition and awards as outstanding articles in biological journals.

He was an Alexander Humboldt Senior Fellow and a Guest Professor at the Institute für Strahlentechnologie der Bundesforschungsanstalt für Lebensmittelfrischhaltung, Karlsruhe, West Germany. He was a Guest Lecturer at the Technological Institute, Moscow, U.S.S.R., and an exchange scientist to Czechoslovakia, Rumania, and Bulgaria on behalf of the National Academy of Sciences, National Research Council, as well as an Advisor to the U.S. Army Food Research Laboratories, and many food storage, processing, and consumer organizations.

Professor Salunkhe was Sigma Xi President, Utah State University Chapter; Fellow of the Utah Academy of Sciences, Arts and Letters; Fellow of the Institute of Food Technologists; and Danforth Foundation Faculty Associate. He delivered the Utah State University 50th Faculty Honor Lecture ''Food, Nutrition, and Health: Problems and Prospects,'' on the basis of his creative activities in research and graduate teaching.

Professor Salunkhe was Vice-Chancellor of Marathwada Agricultural University, Parbhani, and Mahatma Phule Agricultural University, Rahuri, India during 1975 to 1976 and 1980 to 1986, respectively.

Professor Salunkhe was a member of the editorial boards of the *Journal of Food Biochemistry, International Journal of Plant Foods for Human Nutrition, Journal of Food Science,* and *Journal of Food Quality.*

He has authored two textbooks: *Storage, Processing and Nutritional Quality of Fruits and Vegetables* (CRC Press, 1974, Second Printing, 1976) and *Postharvest Biology and Handling of Fruits and Vegetables,* with Professor Haard (AVI Publishing Company, 1975).

Professor Salunkhe has authored the following reference books: *Postharvest Biotechnology of Fruits* (CRC Press, 1984), Vols. 1 and 2; *Postharvest Biotechnology of Vegetables* (CRC Press, 1984), Vols. 1 and 2; *Postharvest Biotechnology of Oilseeds* (CRC Press, 1986) with Dr. B. B. Desai; *Postharvest Biotechnology of Cereals* (CRC Press, 1985); *Postharvest Biotechnology of Food Legumes* (CRC Press, 1985) with Dr. J. K. Chavan and Dr. S. S. Kadam; *Modern Toxicology* (Metropolitan Press, 1984), Vols. 1, 2, and 3 with Dr. P. K. Gupta; *Nutritional and Processing Quality of Sorghum* (Oxford and IBH, 1984) with Dr. J. K. Chavan and Dr. S. J. Jadhav; *Quality of Wheat and Wheat Products* (Metropolitan Press, 1986) with Dr. S. S. Kadam and Dr. A. Austin; *Legume-Based Fermented Foods* (CRC Press, 1986) with Dr. N. R. Reddy and Dr. M. D. Pierson; *Aflatoxins in Foods and Feeds* (Metropolitan Press, 1987) with Dr. R. N. Adsule and Dr. D. N. Padule; and *Postharvest Biotechnology of Sugar Crops* (CRC Press, 1988) with Dr. B. B. Desai.

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Chapter 1

INTRODUCTION

The photosynthetic process of green plants primarily supports life on earth by converting water and carbon dioxide into a variety of organic compounds. Traditionally, processes generating plant compounds have been grouped as primary and secondary metabolism. The chemical substances that have specific indispensable roles and that are found in broadly similar patterns in most, if not all, living cells are considered primary metabolites. Compounds having no specific functions in the cell metabolism and whose distribution is sporadic are referred to as secondary metabolites. One theory propounds that such compounds are waste products or accidents of metabolism.[1] However, advances in plant physiology during the last 2 decades have clearly shown that plants do not randomly produce chemical compounds. Each metabolite is synthesized for a definite purpose, and all products are interrelated according to a complex process which conserves energy and scarce inorganic nutrients. Most secondary metabolites are now known to be essential to plant life; many of them providing a defense mechanism against bacterial, viral, and fungal attack analogous to the immune system of plants.

Phenolic compounds (phenolic acids, coumarins, and flavonoids including tannins) are one such group of secondary metabolites. These are widely distributed in the plant kingdom, being nearly ubiquitous in nature. Although the pharmacological and therapeutic properties of many bioflavonoids are well documented in the literature, the antinutritional effects of certain flavonoids, like tannins, in the diet are only recently recognized. Plants provide nearly all the phenols to higher animals since the latter cannot synthesize these compounds. The occurrence of phenolic compounds is beneficial to plants, while it may or may not be beneficial to animals, including man. Anthocyanins are responsible for different colors of flowers and leaves which aid in pollination by insects. Plant phenolics have been implicated in the resistance of plants against bird depredation,[2] insect attack,[3] preharvest seed germination,[4] and diseases caused by fungi, bacteria, and viruses.[5] The color of fruits, fruit juices, wines, beers, teas, or coffee extracts, and cooked beans or cooking liquors due to phenolic compounds gives immense aesthetic pleasure to man. Certain bioflavonoids have been implicated in stimulating antibacterial, antiatherosclerolemic, antioxidant, and flavor-inducing effects.[6]

The phenolic compounds are also known to produce certain undesirable effects in foods. The browning reactions in foods are known to take place via enzymatic and/or nonenzymatic reactions with polyphenolic substances that affect consumer acceptability. Polyphenol oxidase is responsible for browning induced by mechanical or physiological injury and needs to be inactivated during the processing of fruits and vegetables for retention of color, flavor, and nutritive value.[7] The o-quinones formed from phenolics further enhance the intensity of browning by oxidation of other substrates, complexing with amino acids and protein, and polymerization. The nonenzymatic discoloration was believed to involve metal-polyphenol complexes, as seen in the processed potato,[8] cauliflower,[9] and asparagus.[10] The conversion of leucoanthocyanidins to pink anthocyanidins in the processed broad bean,[11] green-bean puree,[12] and canned Bartlett pear[13] has been documented. Another problem related to the phenolics is their considerable reactivity towards the animal body, as exerted by gossypol (isoprenoid) in cotton seed, tangeretin (methylated flavonoid) in citrus, rhein (anthroquinone) in rhubarb,[14] isoflavones in legumes,[15] and phlorizon (dihydrochalcone glycoside) in apples.[16]

Although many low molecular weight phenols are readily metabolized in the bodies of higher animals, especially in the kidney, heart, and liver,[16] the metabolic fate of phenolic compounds of flavonoid origin is not yet clearly known. The sheer number of naturally occurring flavonoid compounds in plant foods further complicates the problem in human

TABLE 1
World Production of Sorghum, Millet, and Pulses

Region	Production (million t) Sorghum	Millets	Pulses
World	77.5	31.6	49.2
Africa	13.5	11.6	5.9
North-Central America	35.6	—	3.4
South America	7.8	0.1	3.4
Asia	18.6	17.5	23.1
Europe	0.4	—	4.7
Oceania	1.4	—	0.9
U.S.S.R.	0.2	2.2	7.9

From Food and Agricultural Organization, Production Yearbook, Food and Agricultural Organization, Rome, Italy, 1985.

nutrition. Common dietary plant phenols are not considered toxicants under normal amounts and conditions. The polymeric phenols, often called vegetable tannins, is one possible exception. By definition, vegetable tannins are polyphenols of 500 to 3000 mol wt and possess the ability to complex and precipitate proteins from aqueous solution. This property of polyphenols and their occurrence in certain foods has attracted the attention of nutritionists due to their possible antinutritional influence in animal and human diets.

On the basis of their structure, vegetable tannins are grouped into two classes, namely hydrolyzable and nonhydrolyzable or condensed tannins.[17,18] The hydrolyzable tannins consist of polyhydric alcohol (glucose) surrounded by phenolic acids, usually gallic or ellagic acid. They are readily hydrolyzed by acids, bases, and certain enzymes. The condensed tannins are oligomers of flavan-3-ols and flavan-3,4-diols.[19] These are resistant to hydrolysis. The acid treatment promotes condensation of polyphenols as well as hydrolysis.[20] Both types of vegetable tannins exhibit the ability to complex and precipitate proteins. Thus, both are nutritionally hazardous. Most of the reports related to the antinutritional effects of tannins before 1970 are based on tannic acid and other hydrolyzable tannins. However, now most agree that hydrolyzable tannins, if present, are only in traces, and the condensed tannins are the major polyphenols of commonly consumed foods.

The condensed tannins are widespread in fruits, vegetables, forage plants, cocoa, red wine, and certain food grains such as sorghum, finger millet, and legumes.[20] The dietary intake of tannin will vary among people depending on their dietary habits and sources of foods. Dietary tannins may not be a nutritional problem for those whose diets include animal foods and cereals, such as rice, wheat, corn, or barley. However, tannins may be of concern where diets are based on sorghum, millets, and pulses. Rao and Prabhavati[21] reported a range of 1.5 to 2.5 g daily intake of dietary tannins in different regions of India. Tannin intake may be considerably higher for the people of certain parts of Africa where high-tannin sorghum cultivars are grown and used for human consumption. The daily intake of tannin through tannin-containing foods like red wine, fruit juices, beetle quid, or arecanut can be lowered to a minimum by consuming lesser quantities of such food items. However, tannins cannot be avoided when they are present in foods which are important components of a daily diet.

Sorghum, millets, and food legumes (pulses) are important food crops of several countries in semiarid regions of Asia and Africa (Table 1). In certain countries of Asia, Africa, the Near East and the Middle East, almost the entire production of sorghum, millet, and pulses goes for human consumption and forms a major source of dietary energy and protein to people, particularly in rural areas and farming communities.[23] Certain genotypes of sorghum, millet, and legumes are known to contain appreciable levels of condensed tannins which can be nutritionally harmful.[24,25] Tannins are reported to be responsible for decreases in feed intake, growth rate, feed efficiency, net and metabolizable energy, and protein digestibility.[24-26] Such effects are exerted through the formation of complexes with proteins, starch, and digestive enzymes. Sorghum tannins have been reported to cause leg abnormalities in hens, and delays in physical or sexual maturity or even death in hamsters.[27] Dietary tannins have been linked to the incidence of cancer of the esophagus.[28,29]

Attempts have also been made to remove or inactivate tannins in foods and feeds. The technologies developed for this purpose involve the identification of low tannin cultivars in cereals and legumes; pearling or dehusking the grains; soaking of grains in water and various chemical solutions; supplementation of high tannin diets with nutritional and/or nonnutritional tannin-binding proteins like gelatin and methyl group donors like methionine or its analogues; and cooking, sprouting and drying of grains.[26] However, every method has certain limitations in commercial applications.

A symposium on polyphenols in cereals and legumes was held during the 36th Annual Meeting of the Institute of Food Technologists at St. Louis, MO, in 1979.[24] On the basis of the recommendations of this symposium, several investigators have attempted to study different aspects of polyphenols in sorghum, millets, legumes, and forages. These include the nature of phenolics in these grains; methods of analyses; changes during grain development, germination, cooking, drying, and storage; mechanism and specificities of tannin-protein binding; identification of agronomically beneficial and nutritionally harmless forms of phenolics in these grains; and physiological effects of tannin consumption on the functioning of certain salivary glands. Attempts have also been made to develop simple and economical methods to remove or inactivate tannins in these grains before consumption. During the past decade, several reports and critical reviews have been published on these aspects of dietary tannins.[26,27,29-32] In this book, an attempt has been made to update and summerize the available literature on chemical nature, occurrence, composition of tannins in various foods and forages, methods of analyses, dietary consequences, and technologies developed to remove and/or inactivate them. The agronomical advantages of plant phenolics in crop growth are also reviewed, and future research needs are addressed.

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Chapter 2

PLANT PHENOLICS: STRUCTURE, CLASSIFICATION, AND BIOSYNTHESIS

I. INTRODUCTION

Phenolic compounds include a large group of chemical substances containing at least one aromatic ring with one or more hydroxyl groups, in addition to a number of other substituents. Numerous reports are available on the structure, classification, and possible biosynthetic pathways of phenolic compounds.[1-36] However, the precise structure of polymeric phenols such as condensed tannins are not yet completely elucidated due to problems associated with their isolation and purification. The biosynthetic pathways reported in the literature are often speculative. The use of word "tannin" for polyphenols in food grains has been recently questioned.[34] The precise nomenclature for the phenolic substances in seeds of important food grains, such as sorghum, millets, and grain legumes, is yet to be developed. This section briefly discusses the structure, classification, and biosynthesis of plant phenolics in foods and feeds.

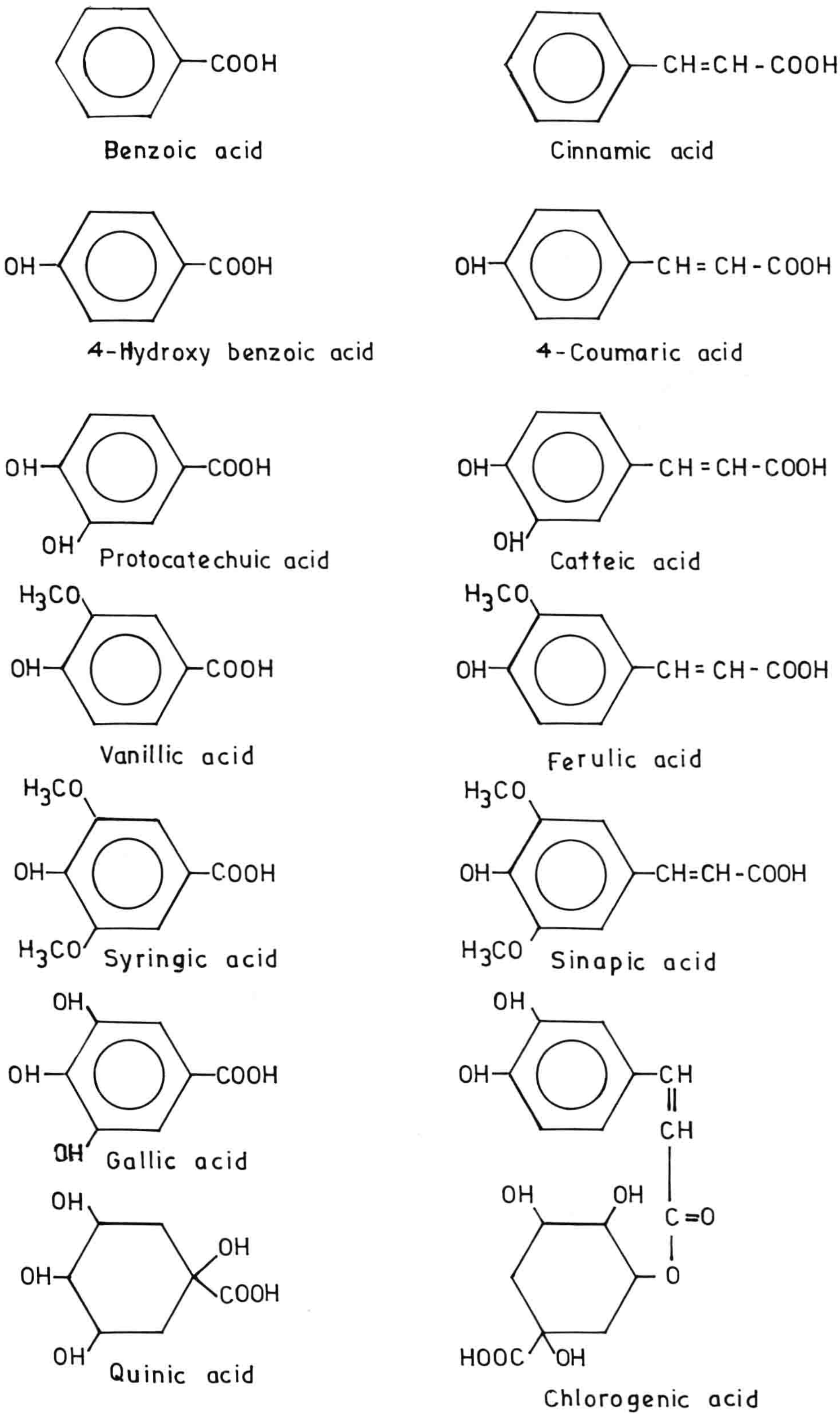
II. STRUCTURE AND CLASSIFICATION

Harborne and Simmonds[6] have classified plant phenolics into 15 major groups. However, the major or most common phenolic constituents of plants can be divided broadly into two main groups: phenolic acids and coumarins (C_6–C_1 and C_6–C_3 structures), and flavonoids, including anthocyanidins (C_6–C_3–C_6 types).

A. PHENOLIC ACIDS

Two families of phenolic acids are widely distributed in plants — a range of substituted benzoic acid (C_6–C_1) derivatives and those derived from cinnamic acid (C_6–C_3). Both types of phenolic acids usually occur in conjugated or esterified form. The simpler type of benzoic acid derivatives include 4-hydrobenzoic, protocatechuic, vanillic, gallic, and syringic acids, and the o-hydroxy salicylic and gentisic acids (Figure 1). The cinnamic acids — 4-coumaric, caffeic, ferulic, and sinapic — are found in most oilseeds and occur frequently in the form of esters with quinic acid or sugars. The chlorogenic acid, which commonly occurs in sunflowers, coffee beans, and cooked potatoes, is an ester of caffeic and quinic acid, and is found in several isomeric and derivatized forms. The phenolic acids such as caffeic and protocatechuic, commonly present in mushrooms, potatoes, sweet potatoes, tobacco leaves, apples, tomatoes, bananas, and tea leaves, play an important role in the development of enzymatic browning reactions. These acids have appropriate configurations for the phenolase activity. The quinones formed polymerize into red-brown polymers, often called melanins, which appear at a point of mechanical injury in a potato tuber or at the surface of an apple. Chlorogenic acid is often responsible for the postcooking blackening sometimes observed in potatoes.

Aromatic amino acids like tyrosine and phenylalanine are the most commonly observed C_6–C_3-type phenolic acids in all living cells and are vital components of cell proteins. They are also involved in the biosynthesis of a number of other phenolic compounds. Glycosides of dihydroxyphenylalanine (DOPA) occur in bean plants. DOPA is also a precursor of the melanin pigments of animals. The cinnamic acid derivatives (R–CH=CH–COOH) which exist not as free acids but in bound form, such as esters, are of widespread occurrence. Ferulic acid and 4-coumaric acid esters are widely distributed in vascular plants. Common esters are chlorogenic acid, p-coumaryl-D-glucose ester, and the corresponding ferulic acid glucose ester. Cinnamic acids also occur as amides such as subaphylline or egelin. The ferulic acid has also been reported to form esters in wheat flour with xylan of glycoprotein.[37]



Benzoic acid

Cinnamic acid

4-Hydroxy benzoic acid

4-Coumaric acid

Protocatechuic acid

Caffeic acid

Vanillic acid

Ferulic acid

Syringic acid

Sinapic acid

Gallic acid

Chlorogenic acid

Quinic acid

FIGURE 1. Structures of common phenolic acids found in plants.

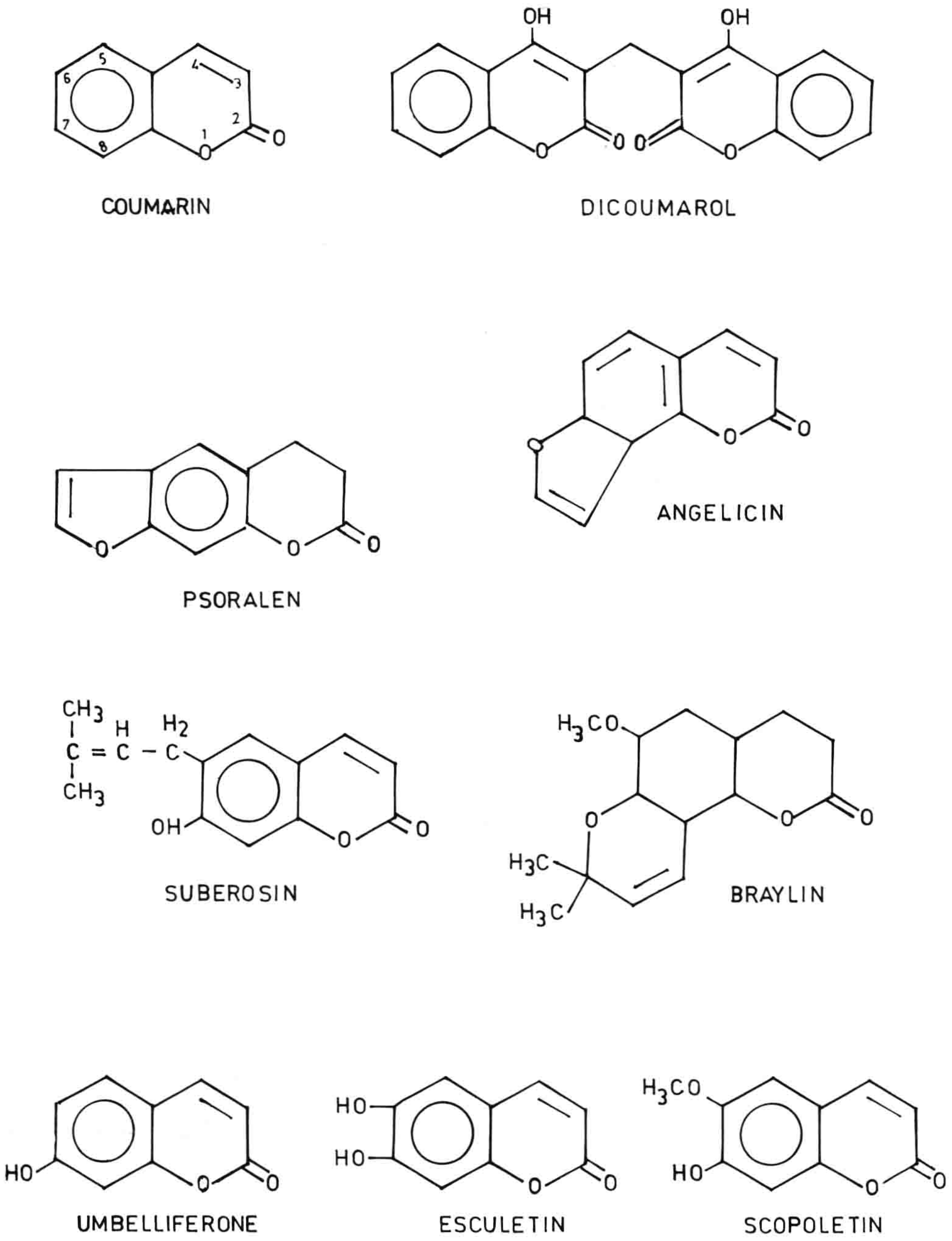


FIGURE 2. Structures of some natural coumarins.

B. COUMARINS

Coumarins are lactones of *cis*-o-hydroxy cinnamic acid derivatives (Figure 2). They are of widespread occurrence in vascular plants. Neish[38] has listed over 30 naturally occurring coumarins. In addition to the usual hydroxyl and methoxyl substitutes, furocoumarins such as psoralen and angelicin are also found. The suberosin and braylin appear to have been alkylated by an isoprenoid group. Dicoumarol is a hermorraegic factor found in spoiled sweet clover hay. Coumarins are less widely distributed in seeds and occur primarily as glucosides. They exhibit limited chemical reactivity and have little effect on the organoleptic or nutritive value of food.

C. FLAVONOID COMPOUNDS

Flavonoids include the largest and most diverse range of plant phenolics.[13,27,28] They consist of scarlet, crimson, and purple anthocyanin pigments of flowers; ivory or pale yellow flavones, flavonols, flavanols; less commonly found yellow chalcones; and aurones and colorless flavonones and isoflavones. All flavonoids share a basic C_6–C_3–C_6 or the C_{15} skeleton of flavone (Figure 3A), the ring A being derived from three acetate units condensed head-to-tail, while ring B and the three carbon atoms of the central ring are derived from cinnamic acid. Although more than one hundred different flavonoid aglycones have been isolated from plants, only 11 of these are most common (Figure 3B). The anthocyanidins are very widely present in colored flowers and fruits. Flavonols usually accompany anthocyanidins in flowers and also occur with great frequency in leaves.

Depending upon the presence or absence of an OH group in the side chain of the C_9 unit of the C_{15} skeleton, two branches of flavonoid families are generated. If an OH group is absent (as in the case of cinnamic, p-coumaric, or caffeic acid), the condensation of C_9 and C_6 units results in the formation of 3-desoxyflavonoids (Figure 4), whereas the presence of OH in the side chain of the C_9 unit (as in the case of the enol form of phenylpyruvate or after the reaction of water with the quinoid radical of cinnamic acid) results in the formation of 3-hydroxyflavonoids (Figure 5). In both flavonoid families, accessory hydroxyl and methyl groups, as well as different sugar residues in O- and C-glycosidic linkages, can be introduced at different positions of the molecule. The positions, number, and combinations of these substituents contribute to the enormous complexity of the flavonoid spectrum. Both families are independent from each other in their origin as well as in occurrence, while flavanones and flavones are often found together. They are connected with each other and chalcones by specific enzymes, yet there is a certain mutual exclusion between flavones and flavonols in many plant families. Anthocyanins are almost absent in flavanone-rich plants.[16] On the other hand, the production of flavonols and anthocyanins is under a common and specific gene control. The interactions of the idividual flavonoid subgroups are shown in Figure 6.

Most flavonoids occur as glycosides in which the C_6–C_3–C_6 aglycone part of the molecule is linked with a number of different sugars. Depending on whether the linkage of sugar to flavonoid aglycone is through an OH group or through a carbon-carbon bond, they are called O-glycosylflavonoids or C-glycosylflavonoids, respectively. The binding of sugars imparts sap solubility, stability to light, and resistance to enzymic degradation of flavonoids. The types of sugars and position of attachment vary greatly. The glycosidic linkage is usually β except in rhamnosides and arabinosides. The linkages are usually $1 \rightarrow 2$ or $1 \rightarrow 6$ types, and the sugar at the reducing end is always glucose. Anthocyanins always have a sugar at the 3-hydroxyl group, although 3, 5-diglycosides are also common. Flavonols usually have a sugar at the 3-position, but also carry sugars at 7-, 3′-, and 4′ as monoglucosides, and 3, 7-, 3, 4′, and 7-4′-diglucosides.

Some flavonoids among the flavones, isoflavones, and flavonones are C–C-linked glycosides. The number of sugars may be one (mono) or two (di-C-glycosylflavonoids). Among the mono-C-glycosylflavonoids, C-glycosylflavones, C-glycosylflavonols, C-glycosylflavonones, C-glycosylisoflavones, and C-glycosyldihydro-chalcones are well defined, and only C-glycosylflavones are the most important group.[39] The well-characterized C-glycosylflavones are vitexin, isovitexin, glucosylvitexin, orientin, isoorientin, and glucosylorientin (Figure 7). The vitexin, glucosylvitexin, and glucosylorientin are principal flavonoids of pearl millet grain.

Flavanones and dihydroflavonols are the simple reduction products of flavones and flavonols, and serve as precursors of the more highly oxidized flavonoids in plants. Isoflavones are isomeric with flavones and are produced from the same C_{15} skeleton by aryl migration. Flavanols are unique in that they do not occur as glycosides, but show reactivity through polymerization into ''condensed tannins.''