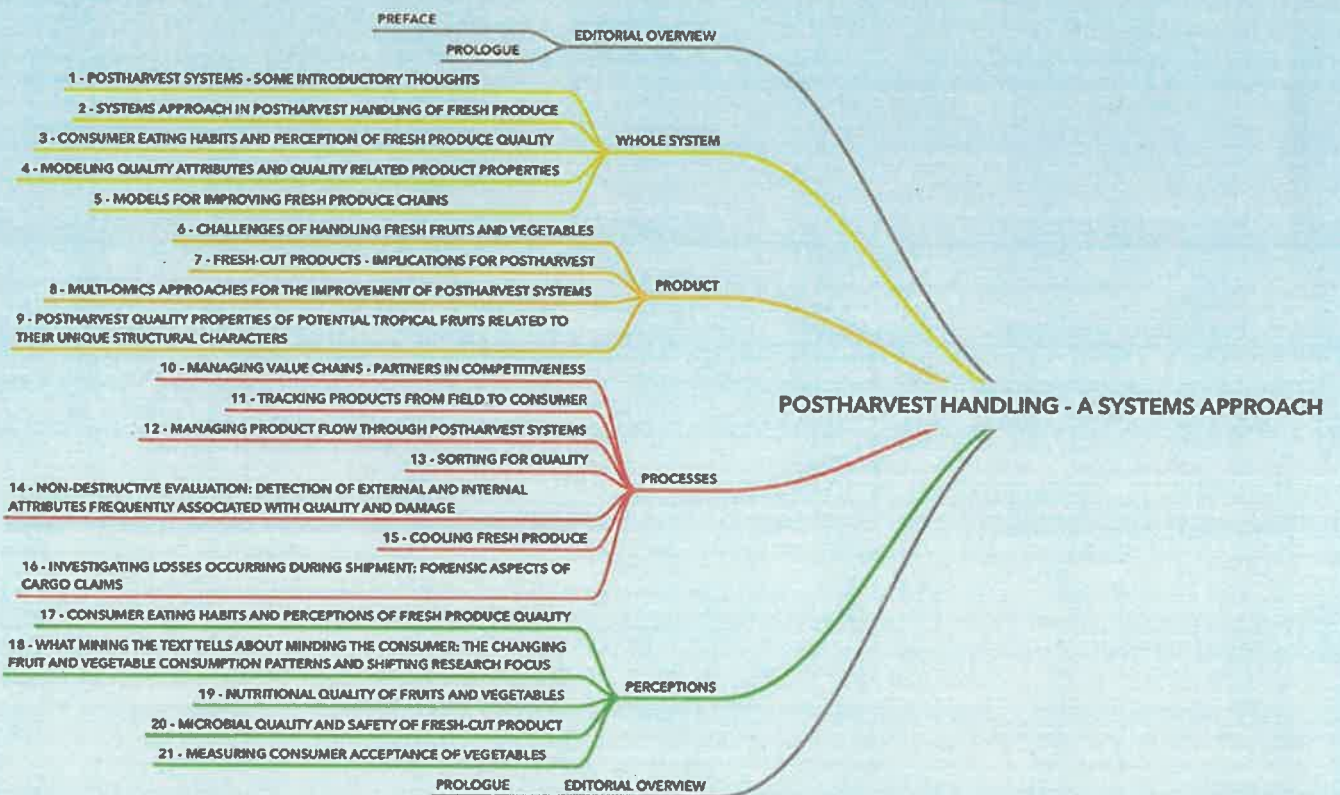


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Postharvest Handling

A Systems Approach



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Compositional determinants of fruit and vegetable quality and nutritional value

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19.1 Introduction

Chronic diseases such as heart disease, stroke, cancer, and diabetes are a leading cause of mortality (Narayan et al., 2020). Excessive weight and outright obesity are also a growing concern. These problems have been linked to lifestyle choices. A growing body of research indicates that eating fruits and vegetables reduces the risk of major diseases and delays the onset of age-related disorders, due to the contribution of nutrients and bioactive compounds and by displacing highly processed foods (Roman, Jackson, Gadhia, Roman, & Reis, 2019; Vainik, García-García, & Dagher, 2019).

The dietary constituents obtained from fruits vegetables include water, fiber, proteins (legumes), sometimes fats (olive, avocado, and nuts), minerals and digestible carbohydrates. Starch-based staples, such as potato, cassava, corn, banana, and plantain, provide a major energy source in several regions, being particularly important dietary sources in developing countries (Rinaldo, 2020). Fruits and vegetables are the main dietary source of vitamin C and a significant source of provitamin A and vitamin B₆ (Sarker, Hossain, & Oba, 2020). Compared to other food sources, they are high in potassium and low in sodium. Ascorbic acid (AsA) in horticultural commodities may enhance the bioavailability of dietary iron (Nowak, Gośliński, Wojtowicz, & Przygoński, 2018). Fruits and vegetables are low in calories (excluding staple crops) and are cholesterol-free. They also include a variety of nonnutritive bioactive phytochemicals (phytosterols, carotenoids such

as lycopene, AsA, tocopherols, glucosinolates, thiosulfonates, and phenolics) that may help to prevent disease incidence (Alasalvar, Salvadó, & Ros, 2020). This has led to the current recommendation that healthful diets include a variety of fresh horticultural commodities (www.dietaryguidelines.gov). Despite efforts made in the last decade, in the United States, only 1 in 10 adults eat enough fruits or vegetables (<https://www.cdc.gov/>). This chapter provides an overview of the composition and nutritional properties of fruits and vegetables (see also Chapter 19: Nutritional quality of fruits and vegetables).

19.2 Nutrient components

19.2.1 Water

Water is the most abundant single component of fresh fruits and vegetables. The amount varies among individual commodities due to structural differences. In leafy vegetables, water may comprise up to 97% of the mass. Water is essential for good health and though individual needs depend on environmental conditions, diet, and physical activity, an intake of 2–3 L/day is recommended.

19.2.2 Proteins and nitrogen compounds

Proteins represent <1% of the fresh mass of most fruit and vegetable tissues. Vegetables account for ~6% of protein intake in the United States, while fruits contribute with 1% (Hiza & Bente, 2007). Fruits may be also rich in simple nitrogenous substances such as free amino acids, chlorophylls, polyamines, or alkaloids. In apple, estimates range from 10% to 70%. Senescent tissues and overripe fruits may contain greater proportions of nonprotein nitrogen. Asparagine is abundant in potato and apple nonprotein nitrogen fractions. Pears and oranges are rich in proline; black and red currants, in alanine; and dates, in hydroxyproline (Maqsood, Adiamo, Ahmad, & Mudgil, 2020). The nitrogen steroidal glycoalkaloids (GLS) α -solanine and α -chacanine can induce neurological disorders. Solanin concentrations exceeding 20 mg/100 g fresh weight (FW) are unsafe for human consumption (Jamakhani, Lele, & Rekadwad, 2018). Solanin is present at highest concentration immediately under the skin of potatoes. Its concentration is 5–15 mg/100 g but may increase if tubers are light-exposed or under conditions that promote sprouting. As a rule, fluorescent light above 800-lx exposure at 20°C, for a few days, will initiate the greening process. Consequently, tubers must be stored in cool conditions and 90% relative humidity and complete darkness to prevent deterioration. Adequate and unrestricted air movement is also necessary to maintain constant temperature and humidity throughout the storage pile and to prevent excessive shrinkage from moisture loss and decay.

19.2.3 Lipids and fatty acids

Plant lipids are a large group of compounds with many functions. They could be stored as energy reserves or have structural functions such as in cellular membranes and cuticular waxes. They are present as triglycerides (esters of glycerol and three fatty acids). Yet, they include diverse chemical forms. For instance, phospholipids, in which one fatty acid

is replaced by phosphoric acid, are important membrane constituents. The lipid concentration in fruit vegetables varies with the commodity. For most commodities, besides avocado and olive, lipids account for less than 1% (e.g., 0.2% in grape, 0.1% in banana, and 0.06% in apple). Lipids comprise 35%–70% of dry mass in avocado, olive, and nuts (Maestri, Cittadini, Bodoira, & Martínez, 2020).

The physical and chemical properties of lipids are determined by their constituent fatty acids. Most fatty acids in foods are aliphatic, contain 4–26 carbons, and are monocarboxylic. They may be saturated or unsaturated to varying degrees. Oleic (18:1) and linoleic (18:2) acids are the most abundant. Lipids derived from vegetable sources tend to be richer in unsaturated fatty acids than animal fats (Table 19.1). Olive oil and other fats high in unsaturated fatty acids lower low density lipoprotein (LDL) cholesterol (so-called bad cholesterol) while protecting high density lipoprotein (HDL) cholesterol (“good” cholesterol) when consumed in moderation in place of saturated fats (Tomé-Carneiro, Crespo, López de Las Hazas, Visioli, & Dávalos, 2020). Each fatty acid double bond has either *cis* or *trans* conformation. In the *cis* geometry, the carbons next to the unsaturated site bond atoms are oriented toward the same side. In plants, unsaturated fatty acids are in the *cis* form. *Trans*-fatty acids may be present in animal fats or produced during processing (e.g., hydrogenation of vegetable oils). Excessive *trans*-fat intake has a high correlation with atherosclerosis and coronary heart disease (El-Aal, Abdel-Fattah, & Ahmed, 2019). Fatty acids are required for human body functions: to produce lipids and hormone-like substances that regulate blood pressure, blood clotting, immune, and inflammatory responses.

TABLE 19.1 Fatty acid, vitamin E, and cholesterol composition of some common dietary fats. (Kays, 1997)

	Saturated (%)	Monounsaturated (%)	Polyunsaturated (%)	Cholesterol (mg/100 g)
Animal fats				
Lard	40.8	43.8	9.6	93
Butter	54.0	19.8	2.6	230
Vegetable fats				
Coconut oil	85.2	6.6	1.7	0
Palm oil	45.3	41.6	8.3	0
Cottonseed oil	25.5	21.3	48.1	0
Wheat germ oil	18.8	15.9	60.7	0
Soya oil	14.5	23.2	56.5	0
Olive oil	14.0	69.7	11.2	0
Corn oil	12.7	24.7	57.8	0
Sunflower oil	11.9	20.2	63.0	0
Safflower oil	10.2	12.6	72.1	0
Canola oil	5.3	64.3	24.8	0

From Kays, S. J. (1997). Postharvest physiology of perishables plant products. Athens, GA: Exon Press.

Plant-derived foods do not have significant amounts of cholesterol but contain cholesterol-like steroids or phytosterols (Asl, Niazmand, & Jahani, 2020). They are absorbed only in trace amounts but inhibit absorption of intestinal cholesterol. Fat-rich fruits and nuts, cauliflower, broccoli, and carrots are good sources of phytosterols (Shahzad et al., 2017). Natural dietary intake varies from 167 to 437 mg/day, being higher in vegetarian diets (1 g/day) (Ostlund, 2002).

19.2.4 Organic acids

Organic acids (OAs), defined by the presence of carboxylic acid groups, are divided into aliphatic (straight chain) and aromatic (Chahardoli, Jalilian, Memariani, Farzaei, & Shokoohinia, 2020). Citrate, malate, and tartrate, the most abundant acids in fruits and vegetables, are aliphatic. Malate is the major acid in pome- and stone-fruit species; citrate is abundant in citrus species, soft fruits, melon, and tomato, while tartrate is predominant in grapes. Aromatic OAs occur in several fruits but at low concentrations. Benzoic acid is found in cranberry; quinic acid, in banana and kiwifruit; and chlorogenic acid, in potato and eggplant. Based on the number of carboxylic groups, acids are divided in mono-, di-, or tricarboxylic acids. Citrate is tricarboxylic, while malate and tartrate are both dicarboxylic. Lactic and acetic acids are monocarboxylic and are present in significant amounts in pickled or acidified vegetables.

Fruits are more acidic than most vegetables. Acidic foods are also most commonly spoiled by fungi, while neutral or low acid products stands as appropriate hosts for bacterial infection (see also Chapter 20). Except for lemons, acidity decreases with the progress of ripening. Opposite to apples and pears, in peaches, citrate decreases faster than malate. OA distribution within a fruit may not be uniform. For instance, the inner pulp of eggplants is less acidic than the region closer to the peel.

OAs play several different roles in fruits. They have a major effect on taste (see also Chapter 15: Cooling fresh produce). Some nutrients, such as vitamin C, are OAs. The most common fruit OAs can be a source of energy, since they can be incorporated into the tricarboxylic acid cycle, yielding ATP. Besides, OA C chains are precursors for synthesis of several important molecules, including some amino acids. Fruit OAs may stabilize some vitamins and prevent oxidation of phenolic compounds during processing.

19.2.5 Digestible carbohydrates

Carbohydrates are the second most abundant constituents in fruits and vegetables. They may account for 50%–80% of dry weight. Nonstarchy root vegetables (parsnip, beetroot, and carrot) are rich in simple sugars (8%–18%). But, most vegetables contain smaller amounts of digestible carbohydrate. Carbohydrate stores energy reserves and makes cell structural framework. Simple carbohydrates are important components of sensory quality. Carbohydrates and proteins yield 4 kCal/g while fats yield nine. In some fruits, monosaccharides are the major sugars. Glucose and fructose are the most common simple sugars in fruits. The disaccharide sucrose is the primary sugar transported in plants. These three sugars are responsible for the sweet taste of fruits and vegetables. In many fruits, (apple, pear, strawberry, figs, melon, and grape), glucose and fructose are predominant. In parsnip, beetroot, carrot, onion, sweet corn,

pea, and sweet potato, banana, pineapple, peach, and melon, sucrose is the more abundant sugar (Byeon & Lee, 2020). Mono- and disaccharide sugars (xylose, arabinose, mannose, galactose, and maltose) may also be present but in small amounts.

19.2.6 Dietary fiber

19.2.6.1 Definition and composition

Dietary fiber includes nondigestible carbohydrates (cellulose, hemicelluloses, pectins, resistant starch, and nondigestible oligosaccharides and lignin) (Saldívar & Soto, 2020). Fiber-rich products include most fruits and vegetables, seeds, and whole cereals (Canteri, Renard, Le Bourvellec, & Bureau, 2020).

19.2.6.1.1 Cellulose

Cellulose is a cell wall polymer consisting of β -1,4-linked glucose. Individual glucan chains associate through hydrogen bonds to form stable microfibrils (Carpita & McCann, 2015). The cell wall of fruits and vegetables is 1%–2% of FW and cellulose can be one-third of that. Except for avocado, in which the whole cell wall is degraded, there is little change in cellulose concentration during ripening.

19.2.6.1.2 Hemicelluloses

Hemicelluloses are alkali-soluble polymers. Primary cell walls contain 25%–35% hemicelluloses (Carpita & McCann, 2015). The most common compound within this group in dicotyledonous species is xyloglucan, characterized by a backbone of β -1,4-linked glucose with α -1,6-linked xylosyl lateral chains. The pentose residues can be further decorated with galactose, arabinose, and/or fucose. Xylans are abundant hemicellulose in monocot species, with a backbone of β -1,4-linked xylose decorated with side chains of arabinose and/or glucuronic acid. Other less abundant hemicelluloses include glucomannans, galactomannans, and galactoglucomannans

19.2.6.1.3 Pectins

Pectins are also a diverse group, with a high proportion of galacturonic acid as a common feature. Fruit tissues are particularly rich in pectins, which can be up to 40% of the cell wall polysaccharides. Extensive work has demonstrated a central role of pectin degradation in fruit softening. The most abundant cell wall polyuronide is homogalacturonan, a homopolymer of α -1,4-linked galacturonic acid with variable degree of methyl esterification at C6. The degree of polymerization and proportion of methyl esters affect pectin solubility. The degree of pectins methyl esterification decreases during ripening as well as its size for example in berries, grape, and apricot (Ayour et al., 2020; Leszczuk, Kalaitzis, Blazakis, & Zdunek, 2020; Vicente, Saladié, Rose, & Labavitch, 2007). The extent of pectin depolymerization is variable: avocado fruit undergoes a dramatic decrease in polyuronide size, while only small changes occur in peppers and some berries (Vicente et al., 2007). Rhamnogalacturonan I (RGI) and II (RGII) are also pectic polysaccharides present in plant cell walls. RGI has a backbone of alternating α -1,2-rhamnosyl and α -1,4-galacturonosyl residues with side chains rich in arabinose and galactose. Losses of side chain residues are

common during fruit ripening and affect pectin solubility and hydration potential (Uluisik & Seymour, 2020). RGII is the most complex cell wall polysaccharide and forms dimers via borate diester bonds.

Good sources of pectin include apple, or sugar beet, and may be used as stabilizers in jams and jellies, as fat replacers and probiotic vehicles (Khedmat, Izadi, Mofid, & Mojtahedi, 2020).

19.2.6.1.4 Lignin

Lignin, cellulose, and chitin are the most abundant biopolymers in nature. Lignin is an aromatic heteropolymer formed by the association of three hydroxycinnamyl alcohol derivatives (*p*-coumaryl, coniferyl, and sinapyl alcohols) (Vanholme, De Meester, Ralph, & Boerjan, 2019). It is a resistant polymer present in secondary cell walls and is associated with fiber sclereids, xylem vessels, seed coats, and pith of some fruits. Most fruits and vegetables have low lignin concentrations, but in some commodities, it can impair quality. Loquat fruit exhibits chilling injury (CI) symptoms after extended cold storage, evident as increased firmness and lignin content, decreased juice yield, and loss of fruit flavor (Huang, Zhu, Zhu, Wu, & Chen, 2019). Lignin deposition in asparagus spears during storage increases toughness (Lwin, Sriaong, Boonyaritthongchai, Wongs-Aree, & Pongprasert, 2020).

19.2.6.1.5 Resistant starch

Starches are polysaccharides of glucosyl residues linked by α -D-(1–4) and/or α -D-(1–6) linkages. Resistant starch and its degradation products are not digested in the small intestine. The microbiota ferments it in the large intestine (Öztür & Mutlu, 2019). Legumes are rich in resistant starch. Up to 35% of this polysaccharide could escape digestion (Marlett & Longacre, 1997). Unripe bananas, mango, and potato are also rich in resistant starch (Quintero-Castaño, Castellanos-Galeano, Álvarez-Barreto, Bello-Pérez, & Álvarez-Ramirez, 2020).

19.2.6.1.6 Nondigestible oligosaccharides

Oligosaccharides are low molecular weight carbohydrates, intermediate between simple sugars and polysaccharides. Oligosaccharides could be hydrolyzed in the digestive tract or resist digestion. Common oligosaccharides include raffinose, stachyose, and verbascose. Legumes, nuts, and blueberry are rich in NDOs (Coleman & Ferreira, 2020; Dahl & Alvarez, 2019).

19.2.6.2 Benefits of fiber intake

Dietary fiber modulates the intestinal function (see also Chapter 19: Nutritional quality of fruits and vegetables). Fiber-rich meals promote satiety earlier, have fewer calories. They also improve glycemic control and bodyweight management (Marlett, McBurney, & Slavin, 2002; Martin, Zhang, Tonelli, & Petroni, 2013). High fiber intake reduced cholesterol and blood pressure as well as the risk of coronary disease and colorectal cancer (Martin, Butelli, Petroni, & Tonelli, 2011). On the other side is rich mineral phytochemicals (Palafox-Carlos, Ayala-Zavala, & González-Aguilar, 2011). A growing body of evidence shows that fiber has a major impact in gut microbiome (Chijiwa et al., 2020; Myhrstad, Tunsjø, Charnock, & Telle-Hansen, 2020). National dietary guidelines recommend a dietary fiber intake of 38 and 25 g/day for men and women. The average fiber intake of United States adults is less than half of this (Soliman, 2019). Good examples of fiber rich

fresh fruits are mango, orange, papaya, sweet lime, and watermelon among tropical and subtropical species, apple among temperate species (Ramulu & Rao, 2003), and leafy species and gourds among vegetables (Khanum, Swamy, Krishna, Santhanam, & Viswanathan, 2000; Li, Andrews, & Pehrsson, 2002).

19.2.6.3 Sources of fiber

Whole grains, fruits, and vegetables are good sources of fiber. Fruits and vegetables provide 37% of the fiber in the diet, followed by grains (36%) and legumes (13%) (Hiza & Bente, 2007). Fruits and vegetables average 1%–3% fiber on a FW basis (Table 19.2). Fiber properties differ depending on the food source. Pectin is low in grains but makes up ~20%–35% of total fiber in fruits, vegetables, legumes, and nuts. Hemicelluloses account for about half of the total fiber in grains, but 25%–35% of total fiber in other foods. Cellulose is one-third or less of total fiber in most foods (Guillon & Champ, 2000). During storage, fruit fiber solubility increases. In contrast, it becomes more insoluble in some vegetables (artichoke, celery, and asparagus). Processing or home preparation, other than peeling, do not cause major fiber loss.

19.2.7 Vitamins

They are essential compounds required in trace amounts that cannot be produced in enough quantities. The term derives from “vital amine,” because thiamine, the first one described contained an amino group (Godswill, Somtochukwu, Ikechukwu, & Kate, 2020). They are vitamin A (retinol), B1 (thiamine), B2 (riboflavin), B3 (niacin), B5 (pantothenic acid), B6 (pyridoxine), B9 (folate/folic acid), biotin, choline, and B12 (cyanocobalamine), and vitamins C, D, E, and K (Price & Preedy, 2020).

19.2.7.1 Provitamin A

The term provitamin A refers to precursors of vitamin A, playing a crucial role in vision, bone development, and reproduction. They are carotenoids formed by eight isoprene units (2-methyl-1,3-butadiene) which contain an unsubstituted β -ring with an 11-carbon polyene chain. Around 60 carotenoids meet this structural need, the most common being α - and β -carotene and cryptoxanthin (Table 19.3). Adult daily vitamin A need is 5000 international units (1 IU = 0.3 μ g retinol or 0.6 μ g β -carotene). Vitamin A deficiency is frequent in populations having single, starch-based crop diets (Mayer, Pfeiffer, & Beyer, 2008). It can cause in severe cases blindness or even death. The problem affects about one-third of children under the age of five worldwide, especially in Africa and Asia (Watkins & Pogson, 2020). Commodities rich in provitamin A include carrot, pumpkin, peach, and mango.

19.2.7.2 Vitamin B complex

Thiamine pyrophosphate is an enzyme cofactor, present in all living systems. It is particularly important in carbohydrate metabolism. A daily intake of 1–2 mg is recommended for a normal adult. Thiamine is more heat stable than ascorbic. Yet, at cooking temperatures and low acid conditions large losses (25%–40%) may occur.

TABLE 19.2 Fiber content of selected fruits, vegetables, and nuts.
(U.S. Department of Agriculture, 2008)

Product	Dietary fiber (%)
Almond	12.2
Apple	2.4
Asparagus	2.1
Avocado	6.8
Banana	2.6
Broccoli	2.6
Carrot	2.8
Kiwifruit	3.4
Lettuce	2.1
Onion	1.7
Orange	2.4
Pea	2.6
Peach	1.5
Peanut	8.5
Pear	3.1
Pepper	2.1
Pineapple	1.4
Plum	1.4
Potato	2.2
Prune	7.1
Raisin	3.7
Spinach	2.2
Strawberry	2.0
Tomato	1.2
Walnut	6.7

From US Department of Agriculture (2008). 'Composition of foods, raw, processed, prepared' USDA national nutrient database for standard reference, release 20. Beltsville, MD: USDA-ARS, Beltsville Human Nutrition Research Center, Nutrient Data Laboratory. <http://www.ars.usda.gov/nutrientdata>. Accessed 04/2008.

Riboflavin is the central component of flavoproteins. The average human requires 1–2 mg/day. Green vegetables such as bean, beet, pepper, and spinach are good sources of riboflavin.

TABLE 19.3 Carotene concentration (mean values) of selected fruits.

Product	Carotene ($\mu\text{g}/100\text{ g}$)
Mango	1800
Cantaloupe	1000
Pawpaw	810
Guava	435
Apricot	405
Plum	295
Watermelon	230

From (Rodríguez-Amaya, 2001).

Niacin, or nicotinic acid, is a precursor to nicotinamide adenine dinucleotide (NAD) and isicotinamide adenine dinucleotide phosphate (NADP). A daily intake of 10–15-mg niacin is recommended. Almonds, avocado and cape gooseberries are good sources. It is stable but is not stored in the body more than 0–14 days. Deficiency symptoms include skin inflammation, depression and psychiatric affections (Price & Preedy, 2020).

Vitamin B5 or pantothenic acid deficiency leads to fatigue, headaches, sleep disturbances, tingling of hands, and impaired immune responses. Meats, potatoes, oat cereals, tomato products, and whole grains were among the better sources of pantothenic acid (Walsh, Wyse, & Hansen, 1981). Also, pantothenic acid is discreetly present in bananas and citrus fruits (de Assis et al., 2020).

Vitamin B6 (pyridoxal phosphate) is a common cofactor in transamination, decarboxylation, and deamination reactions. Formation of the ethylene precursor 1-Aminocyclopropane 1-Carboxylic Acid (ACC) by ACC synthase in plants requires pyridoxal phosphate. Common symptoms of vitamin B6 deficiency include dermatitis around the eyes, elbows, and mouth. It can also lead to dizziness, vomiting, weight loss, and severe nervous disturbances. Sources of vitamin B6 include bean, cabbage, cauliflower, spinach, sweet potato, grape, avocado, and banana.

Biotin deficiency leads to depression, sleeplessness, and muscle pains. It occurs in peas, beans, nuts, broccoli, mushrooms, potatoes, strawberries and sweet potatoes.

Folic acid is essential for reproduction and normal growth. Folate deficiency causes neural tube defects and anemia (García-Salinas, Ramos-Parra, & de la Garza, 2016). It is present in strawberry, tomato, avocado, spinach, cabbage and other green vegetables (Muley & Singhal, 2020). Vitamin B12 does not occur in fruits and vegetables.

19.2.7.3 Vitamin C

AsA and its first oxidation product dehydroascorbic acid are both considered vitamin C. AsA is a water-soluble, carbohydrate-derived compound with antioxidant and acidic properties due to a 2,3-enediol moiety (Fig. 19.1). Humans and a few other species cannot synthesize it (Kang et al., 2020), because the gene coding for the last enzyme in the pathway (L-gulonolactone oxidase) is not functional. AsA is involved in collagen biosynthesis. Even though nutritional deficiencies are rare in modern Western cultures, it is generally recognized that

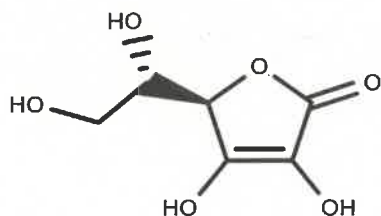


FIGURE 19.1 Structure of ascorbic acid, a primary antioxidant present in fruits and vegetables.

TABLE 19.4 Vitamin C concentration (mean values) of selected fruits. (Salunkhe, Bolin, and Reddy, 1991).

Product	Vitamin C (mg/100 g)
Guava, raw	184
Kiwi, raw	118
Litchi, raw	72
Pawpaw, raw	62
Strawberry, raw	57
Citrus fruits	31-53
Cantaloupe	42

From Salunkhe, D. K., Bolin, H. R. & Reddy, N. R. (Eds.) (1991). Storage, processing, and nutritional quality of fruits and vegetables. Volume I. Fresh fruits and vegetables. Boston, MA: CRC Press.

dietary AsA has important health benefits (Hancock & Viola, 2005). In meat-poor diets, dietary AsA can improve iron uptake. The recommended dietary allowance of vitamin C is 75 and 90 mg/day for men and young women (Levine, Wang, Padayatty, & Morrow, 2001). Plants synthesize AsA via a pathway that uses L-galactose as a precursor. A galacturonic acid pathway is also present in plants (Yuan et al., 2020). Fruits, vegetables, and juices are the main dietary sources (90%) of vitamin C (Hiza & Bente, 2007). Vitamin C concentration varies depending on the commodity from one to 150 mg/100 g (Lee & Kader, 2000). In berry fruits, AsA ranged from 14 to 103 mg/100 g (Pantelidis, Vasilakakis, Manganaris, & Diamantidis, 2007). Rosehip, jujube, guava, kiwifruit, peppers, citrus fruit, spinach, broccoli, and cabbage are rich in AsA (Table 19.4). For any given product, AsA concentrations vary due to environmental factors. Sunlight exposure is a main factor determining AsA concentration (Kang et al., 2020). In general, more sunlight received during growth increases AsA. Retention of AsA is also affected by storage and processing conditions. Potatoes lose up to 80% of the original AsA over 9 months storage. Most other fruits and vegetables also lose AsA during storage. AsA stability is reduced at high temperatures and bruising increases AsA degradation. AsA is susceptible to oxidation (Sanmartin, Pateraki, Chatzopoulou, & Kanellis, 2007). During cooking, high losses of vitamin C occur. Starchy vegetables lose 40%–80% of the vitamin C during cooking due to leaching and oxidation. Freezing does not reduce vitamin C content, but losses are found after long-term frozen storage (Leong & Oey, 2012).

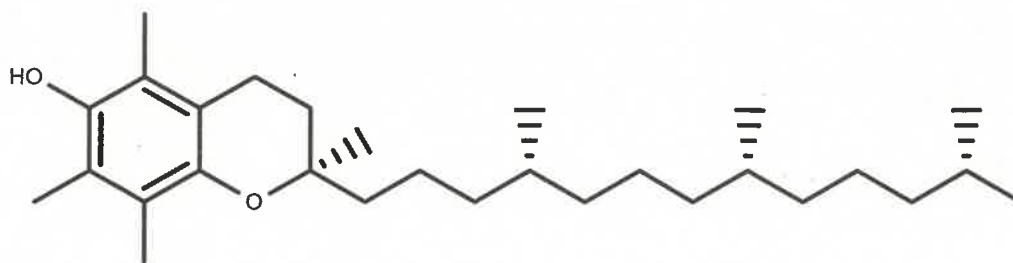


FIGURE 19.2 Structure of tocopherol.

19.2.7.4 Vitamin D

Vitamin D promotes calcium and phosphate absorption, and thus it aids bone and tooth mineralization. It also exerts a role in cell signaling and in the inhibition of autoimmune responses related to carcinogenic and cardiovascular disease (Price & Preedy, 2020). It occurs in trace amounts in fruits and vegetables. Vitamin D insufficiency affects almost 50% of the population worldwide. The major source of vitamin D for children and adults is exposure to natural sunlight. Approximately 20% of total vitamin D is obtained through the diet (Borel, Caillaud, & Cano, 2015).

19.2.7.5 Vitamin E

Vitamin E is a general term used to describe a group of eight lipophilic compounds known as tocochromanols (Mellidou et al., 2018). These compounds exist in eight forms (four tocopherols and four tocotrienols). All isomers have aromatic rings with a hydroxyl group that donates hydrogen atoms to reduce reactive oxygen species (ROS). The terms α , β , γ , and δ refer to the number and position of methyl groups on the chromanol ring. All forms have vitamin E activity, but α -tocopherol is the most active (Fig. 19.2). The biological role of vitamin E relies on its antioxidant properties (Price & Preedy, 2020). It is abundant in oily seeds, olives, nuts, peanuts, avocados, and almonds. In olives, tocochromanol levels and composition were dependent on cultivar and, to a lesser extent, on fruit developmental stage (Georgiadou et al., 2019). Broccoli and leafy vegetables have less tocopherol than fats and oils but are still a good source. Vitamin E is strong antioxidant involved in cell membrane protection during storage. Vitamin E remains relatively stable in fruits and vegetables during storage, but not many studies have characterized tocopherol metabolism during postharvest life.

19.2.7.6 Vitamin K

Vitamin K is essential for bone metabolism, the antiinflammatory response, and blood coagulation. With a recommended daily intake of 120 μg , vitamin K deficiency is uncommon (Johnson, 2020). It is abundant in lettuce, spinach, cauliflower, and cabbage. Also, it can be produced by gut microbiota.

19.2.8 Minerals

Mineral nutrition is of interest to plant postharvest biologists because of the many processes it is involved in, its effect on internal and external quality traits of fruits and vegetables that affect consumer behavior, and the benefits of an adequate and balanced intake for human health. The level of minerals in fruit and vegetables at harvest can be affected by soil nutrient availability, fertilization practices, and prevailing growing conditions. The mineral contents in fruit and vegetable tissues can also show variations due to losses of water and respirable substrates. Postharvest deliberate supplementations would also alter the level of the minerals applied.

Although there is no universally accepted definition or classification, the dietary "minerals" support the biosynthetic apparatus with required elemental components other than carbon (C), hydrogen (H), and oxygen (O). Seventeen nutrient elements are essential in plants. The three elements most abundant in plant tissues, C, H, and O, are not minerals. The remaining 14 mineral elements are required by plants for successful completion of their life cycle, as components of essential plant components or metabolites. Minerals are classified as macrominerals or microminerals, based on the relative concentrations of each nutrient considered adequate for normal tissue function. Plant macrominerals include nitrogen (N), potassium (K), calcium (Ca), magnesium (Mg), phosphorus (P), and sulfur (S). Their concentrations in plant tissues range from 1000 to 15,000 $\mu\text{g/g}$ dry weight. Macrominerals can also be classified into those that maintain their identity as ions within plant tissues (K^+ , Ca^{2+} , and Mg^{2+}) and those that are assimilated into organic compounds (N, P, and S). Plant essential microminerals include chlorine (Cl), boron (B), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), molybdenum (Mo) and nickel (Ni), and their concentrations are 100- to 10,000-fold less than those of macrominerals. Other microminerals such as sodium (Na), silicon (Si), and cobalt (Co) may be beneficial over a certain concentration range. Fluorine and iodine are essential for animal and human health but not for plant growth.

Minerals in food items are defined as the total ash content. The classification of many elements as essential minerals for human nutrition is not definitive and there is still debate over the natural biological roles of vanadium, chromium, aluminum, and silicon in human health.

Macrominerals required for good human health include Ca, Mg, P, K, Na, Cl, and S, all essential in amounts >50 mg/day. Essential microminerals (Fe, I, Fl, Zn, Se, Cu, Mn, Cr, Mo, Co, Ni, and B) are required in trace concentrations (<50 mg/day). In general, vegetables are considered as richer sources of minerals than fruits (Table 19.5).

Minerals have both direct and indirect effects on human health. The direct effects of minerals are the consequences of their consumption by humans; while indirect effects include impact on fruit and vegetable quality and subsequent consumer acceptance. From a direct nutrition standpoint, potassium is the most abundant in both fruits and vegetables, but nitrogen and calcium also have major impacts on food quality. Nutrition research has focused on single-mineral effects on human health, generally with incongruent results (Aaron & Sanders, 2013). Epidemiological surveys suggest that total diet has more influence on health than specific components. It is increasingly clear that it is not only an excess or deficiency of a single mineral that affects health, but also effects of multiple nutrients in combination that affect dietary health.

TABLE 19.5 Fruit and vegetable sources of potassium, ranked by potassium/standard amount, also showing calories in the standard amount^a.

Fruits and vegetables, standard amount	Potassium (mg)	Calories
Sweet potato, baked, 1 potato (146 g)	694	131
Tomato paste, 1/4 cup	664	54
Beet greens, cooked, 1/2 cup	655	19
Potato, baked, flesh, 1 potato (156 g)	610	145
White beans, canned, 1/2 cup	595	153
Tomato puree, 1/2 cup	549	48
Prune juice, 3/4 cup	530	136
Carrot juice, 3/4 cup	517	71
Lima beans, cooked, 1/2 cup	484	104
Winter squash, cooked, 1/2 cup	448	40
Banana, 1 medium	422	105
Spinach, cooked, 1/2 cup	419	21
Tomato juice, 3/4 cup	417	31
Tomato sauce, 1/2 cup	405	39
Peaches, dried, uncooked, 1/4 cup	398	96
Prunes, stewed, 1/2 cup	398	133
Apricots, dried, uncooked, 1/4 cup	378	78
Cantaloupe, 1/4 medium	368	47
Honeydew melon, 1/8 medium	365	58
Plantains, cooked, 1/2 cup slices	358	90
Kidney beans, cooked, 1/2 cup	358	112
Orange juice, 3/4 cup	355	85
Split peas, cooked, 1/2 cup	355	116

^aU.S. Department of Health and Human Services and U.S. Department of Agriculture (2005). The dietary reference intake (DRI) for potassium for adults and adolescents is 4700 mg/day.

Fruits and vegetables are not recognized as primary sources of mineral nutrients but hold a place in dietary advice because of mineral content, especially electrolytes (Slavin & Lloyd, 2012). The Dietary Approaches to Stop Hypertension (DASH) emphasizes fruits, vegetables, and low-fat dairy products as sources of minerals. In the DASH dietary pattern, vegetables contribute 14.3%, 15.5%, 16.2%, and 10.4% of required calcium, magnesium, potassium, and zinc, respectively (Lin et al., 2003). Vegetable contribution of potassium, phosphorus, magnesium, calcium, copper, iron, and zinc to the United States

TABLE 19.6 Minerals (%) contributed from fruits and vegetables to the US food supply in selected years. (Hiza and Bente, 2007).

Mineral	Fruits			Vegetables		
	Year/s			Year/s		
	1909–19	1960–69	2004	1909–19	1960–69	2004
Potassium	8.0	8.7	11.2	36.7	27.1	26.6
Calcium	2.6	2.2	2.6	8.7	6.0	7.0
Phosphorus	1.5	1.5	1.8	10.4	7.7	7.7
Magnesium	4.5	5.6	6.1	18.2	15.9	13.9
Copper	5.2	6.1	6.1	30.2	22.8	17.2
Iron	3.3	3.1	2.5	18.4	13.5	10.1
Zinc	1.2	1.3	1.2	9.1	7.4	6.4
Sodium	0.8	1.3	2.0	10.4	23.4	28.9
Selenium	0.5	0.6	0.4	1.2	2.4	2.3

From Hiza, H. A. B. & Bente, L. (2007). Nutrient content of the U.S. food supply, 1909–2004: A summary report. Home economics research report number 57. Washington, DC: U.S. Department of Agriculture, Center for Nutrition Policy and Promotion.

food supply decreased significantly during the last century, while the fruit contribution of potassium, phosphorus, magnesium, and copper increased (Table 19.6). Strategies for improving mineral intake from fruits and vegetables have been implemented. These comprise increasing the consumption of fruits and vegetables and increasing concentrations of essential nutrients through fortification. Alternative approaches include improving nutrient bioavailability and retention.

19.2.8.1 Potassium (K)

Adequate intake of potassium for adult males and females is 4700 mg/ day (Davison, 2017). A potassium-rich diet helps lower blood pressure, blunting the effects of NaCl. Inadequate potassium intake has long been associated with increased mortality (Wang et al., 2014) and higher blood pressure (McCarron & Reusser, 2001). Potassium regulates heartbeat, assists in muscle contraction, and is needed to send nerve impulses and to release energy from fat, carbohydrates, and protein. Different nutrients and phytochemicals in fruits and vegetables, including potassium, may independently or jointly reduce cardiovascular disease risk (Ignarro, Balestrieri, & Napoli, 2007). Hypertension is rapidly increasing in sub-Saharan Africa, an area where such health problems did not exist a couple of decades ago. It is now the fastest growing health problem there and increased consumption of fresh fruit as a source to alleviate the problem.

Potassium is a systemic electrolyte that coregulates ATP with sodium. Potassium affects acid–base metabolism favorably, which may reduce the risk of developing kidney stones (Zerwekh, Odvina, Wuermser, & Pak, 2007), and possibly decreases bone loss with age. Potassium is the most abundant individual mineral element in fruits and vegetables, at

concentrations ranging between 60 and 600 mg/100 g FW. The commodities accumulation higher levels of potassium are those presenting lower water contents such as potato, pumpkin plantain, and banana. It is active in many cellular and whole plant functions. It balances the charges of anions, activates ~60 plant enzymes, maintains cytoplasmic pH homeostasis and is involved in key metabolic processes, including protein synthesis. Other roles are linked to potassium high mobility. Potassium movement is the driving force for osmotic changes, since it serves as an osmotic for cellular growth and stomata function, translocation of assimilation products and light-driven and seismonastic movements of organs. Also, it provides a charge-balancing counter-flux that supports the movement of other ions. Growth requires directed movement of potassium (Amtmann, Armengaud, & Volkov, 2004). In fruits and vegetables, potassium occurs mainly in combination with OAs. Examples of potassium-rich fruits and vegetables include bananas and plantains, leafy green vegetables, many dried fruits, oranges and orange juice, cantaloupes, honeydew melons, tomatoes, and root vegetables (Tables 19.5 and 19.7). Notably, potatoes provide >10% of the potassium intake in the United States and United Kingdom populations (Lanham-New, Lambert, & Frassetto, 2012).

19.2.8.2 Calcium (Ca)

Adequate intake of calcium is 1 g/day for adults aged 19–50 years and 1.2 g for adults over 50 years (Davison, 2017). Additional amounts are recommended to meet the needs of pregnancy, infancy, childhood, adolescence, and lactation, since calcium is essential for bone and tooth formation. Calcium is very important during later adulthood from a public health perspective, because inadequate calcium intake may increase the risk of osteoporosis, a condition in which bone mass decreases (Cohen & Roe, 2000). Nearly half of American women over 50 have low mineral bone density or osteoporosis (Debar et al., 2004). In the United States, annual osteoporosis-related fractures are projected to increase from 1.9 to 3.2 million (68%), from 2018 to 2040, with annual direct medical costs associated with fractures estimated at \$48.8 billion in 2018 (Lewiecki et al., 2019), so osteoporosis prevention is a major public health target.

Calcium fluxes are important mediators of hormonal effects on target organs through the phosphoinositol system and are closely linked with cyclic adenosine monophosphate (AMP) systems. In plants, calcium plays a dual role, both as a structural component of cell walls and membranes and as a ubiquitous second messenger involved in a wide range of physiological processes and responses. Calcium is primarily associated with pectins: it has a major influence on the rheological properties of the cell wall and, consequently, in the texture and storage life of fruits and vegetables. Ca^{2+} can interact with anionic pectic polysaccharides, coordinating with the oxygen functions of two adjacent pectin chains to form the so-called eggbox structure and cross-linking the chains. Also, intracellular Ca^{2+} occupies a pivotal role in cell signal transduction. Plant signals associated with Ca^{2+} signatures include wounding, temperature stress, fungal elicitors, oxidative stress, anaerobiosis, abscisic acid, osmotic stress, red or blue light or ultraviolet-B (UV-B) signaling, and mineral nutrition (Bailey et al., 2010). Transient increases in intracellular Ca^{2+} are often associated with initiation of responses. Thus Ca^{2+} is a prominent intracellular second messenger for a variety of processes and must be maintained in the cytoplasm at concentrations many orders of magnitude lower than in the cell wall (Thor, 2019).

TABLE 19.7 Mineral composition of some fruits in mg/100 g fresh weight.

Fruit	Mineral									
	K	Ca	Mg	P	Mn	Cu	Fe	Zn	Na	Se
Apple, with skin	107	6	5	11	0.035	0.027	0.12	0.04	1	0.0
Apricot	259	13	10	23	0.077	0.078	0.39	0.2	1	0.1
Avocado (California)	507	13	29	54	0.149	0.170	0.61	0.68	8	0.4
Avocado (Florida)	351	10	24	40	0.095	0.311	0.17	0.4	2	—
Banana	358	5	27	22	0.270	0.078	0.26	0.15	1	1.0
Blackberries, raw	162	29	20	22	0.646	0.165	0.62	0.53	1	0.4
Blueberries, raw	77	6	6	12	0.336	0.057	0.28	0.16	1	0.1
Cherries, sweet, raw	222	13	11	21	0.070	0.060	0.36	0.07	0	0.0
Figs, raw	232	35	17	14	0.128	0.070	0.37	0.15	1	0.2
Grapefruit, raw, pink, and red pi re3u (California and Arizona)	147	11	9	12	0.020	0.032	0.08	0.07	1	—
Grapefruit, raw, pink and red (Florida)	127	15	8	9	0.010	0.044	0.12	0.07	0	1.4
Grapes, red, or green (European type, e.g., "Thompson Seedless"), raw	191	10	7	20	0.071	0.127	0.36	0.07	2	0.1
Kiwifruit, fresh, raw	312	34	17	34	0.098	0.130	0.31	0.14	3	0.2
Lemons, raw, without peel	138	26	8	16	0.030	0.037	0.60	0.06	2	0.4
Mangos, raw	156	10	9	11	0.027	0.110	0.13	0.04	2	0.6
Melons, Cantaloupe, raw	267	9	12	15	0.041	0.041	0.21	0.18	16	0.4
Oranges, raw, California, 'Valencia'	179	40	10	17	0.023	0.037	0.09	0.06	0	—
Papayas, raw	257	24	10	5	0.011	0.016	0.10	0.07	3	0.6
Peaches, raw	190	6	9	20	0.061	0.068	0.25	0.17	0	0.1
Pears, raw	119	9	7	11	0.049	0.082	0.17	0.10	1	0.1
Pineapples, raw, all varieties	109	13	12	8	0.927	0.110	0.29	0.12	1	0.1
Plums, raw	157	6	7	16	0.052	0.057	0.17	0.10	0	0.0
Pomegranates, raw	259	3	3	8	—	0.070	0.30	0.12	3	0.6
Raspberries, raw	151	25	22	29	0.670	0.090	0.69	0.42	1	0.2
Strawberries, raw	153	16	13	24	0.386	0.048	0.41	0.14	1	0.4
Watermelon, raw	112	7	10	11	0.038	0.042	0.24	0.10	1	0.4

From US Department of Agriculture (2008). 'Composition of foods, raw, processed, prepared' USDA national nutrient database for standard reference, release 20. Beltsville, MD: USDA-ARS, Beltsville Human Nutrition Research Center, Nutrient Data Laboratory. <http://www.ars.usda.gov/nutrientdata>. Accessed 04/2008.

TABLE 19.8 Fruits and vegetables particularly rich in specific antioxidant groups.

Ascorbic acid	Vitamin E	Carotenoids	Phenolics
Strawberry	Almond	Pineapple	Blueberry
Pepper	Corn	Plum	Plum
Kiwifruit	Broccoli	Peach	Raspberry
Orange	Spinach	Pepper	Strawberry
Pepper	Peanut	Mango	Apple
Broccoli	Avocado	Melon	Blackberry
Guava		Tomato	
Rosehip		Carrot	
Persimmon			

Horticultural crops are a secondary source of calcium to dairy products, but fruits and vegetables account for ~10% of the calcium in the United States food supply (Table 19.7). Dark green, leafy cabbage family vegetables and turnip greens are good calcium sources and most green leafy vegetables are potential sources of absorbable calcium (Titchenal & Dobbs, 2007). Projects designed to test the efficacy of a health plan-based lifestyle intervention for increasing bone mineral density propose not only increased consumption of high-calcium dairy products but also of fruits and vegetables (Debar et al., 2004) (Table 19.8).

Bioavailability of calcium can be reduced in the presence of antinutrient components, mainly oxalates and phytates. Soluble oxalate is found mostly in vegetables such as spinach and green amaranth and in seeds, while fruit and green tea contain moderate amounts of oxalate (Lo, Wang, Wu, & Yang, 2018). Almost no calcium is absorbed from spinach, while low-oxalate vegetables such as broccoli and kale show high calcium bioavailability. Domestic processing such as blanching or boiling can leach soluble oxalate into the cooking water and it is a recommended way to reduce soluble oxalate (Gharibzahedi & Mahdijafari, 2017). Phytates are present in beans, nuts, cereals, and, to a lesser extent, in fruits, leafy vegetables and tubers (Lo et al., 2018). They can form nonabsorbable complexes with calcium impairing its absorption: a phytate/calcium molar ratio >0.24 impairs bioavailability of calcium (Lo et al., 2018).

19.2.8.3 Magnesium (Mg)

The recommended dietary allowance for magnesium is 420 mg/day for adult males and 320 for adult females over 31 years old (Davison, 2017). Magnesium is important in protein synthesis and acts as a controlling factor in skeletal and smooth muscle contraction, release of energy from muscle storage, cardiac excitability, body temperature regulation, immune system health and nerve impulse transmission. It is critical for proper heart function and bone formation as described previously. Magnesium activates over 100 enzymes.

In plants, Ca^{2+} and Mg^{2+} are the most abundant divalent cations and appear to have antagonistic cellular interactions. A homeostatic balance between Ca^{2+} and Mg^{2+} is necessary in plants for optimal growth and development (Tang & Luan, 2017). The porphyrin-like ring structure of chlorophyll contains a central magnesium atom coordinated to the four pyrrole rings. Magnesium is also involved in energy metabolism, as a constituent of the Mg-ATP or Mg-ADP complex. The Calvin cycle pathway that produces a three-carbon compound as the first stable product in the multistep conversion of CO_2 into carbohydrates is regulated partially via stromal Mg^{2+} concentration.

The vegetable contribution to total magnesium in the United States food supply was 14% (Table 19.6). Mixed users, who are more likely to consume grains, fruit, and dairy products, have greater magnesium densities than high-fat users, who consumed more meat (Sigman-Grant, Warland, & Hsieh, 2003). Generally, magnesium is significantly more abundant in vegetables than in fruits, while nuts are good sources of this nutrient. Overall, dry fruits, legumes, pumpkin seeds, nuts (Brazil nuts), artichokes, and spinach are high in magnesium (Gharibzahedi & Jafari, 2017). As for calcium, oxalic acid can form poorly soluble magnesium oxalate and phytate can produce complexes with magnesium, making this macromineral nonabsorbable.

19.2.8.4 Phosphorus (P)

The recommended dietary allowance for phosphorus is 700 mg/day for adults over 19 years old (Davison, 2017). Inorganic phosphate is essential for skeletal mineralization and for multiple cellular functions, including glycolysis, gluconeogenesis, DNA synthesis, RNA synthesis, cellular protein phosphorylation, phospholipid synthesis, and intracellular regulatory roles (Dimeglio, White, & Econs, 2000). Phosphorus is a primary bone-forming mineral. Because most Westerners eat high-phosphate diets, isolated dietary phosphate deficiency is exceedingly rare, except for occasional metabolic disorders such as hyperphosphatemia.

Phosphorus exists in plants as both inorganic phosphate anions and organophosphate compounds. Unlike sulfate and nitrate, phosphate is not reduced during assimilation, but remains in its oxidized state, forming phosphate esters with a variety of organic compounds. Inorganic phosphorus is a primary structural component of nucleic acids and phospholipids, plays a central role in energy conversion in the form of high-energy phosphoester and diphosphate bonds, is important as a substrate and a regulatory factor in oxidative metabolism and photosynthesis, participates in signal transduction and regulates the activities of an assortment of proteins through covalent phosphorylation/dephosphorylation reactions.

Fruit and vegetable contribution to total phosphorus in 2004 was 9.5% (Table 19.6). According to the National Health and Nutrition Examination Survey (2001–14), grains are the largest dietary phosphorus source, followed by meats and milk products, while the contributions of vegetables and fruits (excluding nuts) to phosphorus intake are 6.7% and 2%, respectively. Legumes, nuts, and seeds are also significant sources (4.8%) (McClure, Chang, Selvin, Rebholz, & Appel, 2017). Pumpkin seeds and Brazil nuts are rich in phosphorus (Gharibzahedi & Jafari, 2017).

19.2.8.5 Nitrogen (N)

Nitrogen is a chemical element essential to life. It is considered a “mineral” for plants, as it is often included in fertilizers. It is one of the four major structural elements in the human body by weight (together with oxygen, hydrogen, and carbon), but it is not included in lists of major nutrient minerals. The largest requirement for nitrogen in eukaryotic organisms is for amino acid biosynthesis, building blocks of proteins and precursors of many other compounds. Proteins represent a large percentage of the human body and carry out many different cell functions. Therefore, protein synthesis is central to cell growth, differentiation, and reproduction. Nitrogen is also an essential component of nucleic acids, cofactors, and other metabolites. Several plant hormones (indole-3-acetic acid, zeatine, spermidine) contain nitrogen or are derived from nitrogenous precursors. Alkaloids and other secondary compounds contain nitrogen and various phenolics derived from the amino acid phenylalanine. Nitrogen is also a major constituent of chlorophyll. The characteristic preharvest yellow color of nitrogen-starved vegetables—a physiological disorder called chlorosis—reflects their inability to synthesize adequate amounts of green chlorophyll under nitrogen-limiting conditions.

19.2.8.6 Sulfur (S)

Sulfur is an essential nutrient for growth, used primarily to synthesize cysteine and methionine. Most dietary sulfur is provided by these sulfur-containing amino acids, with a daily sulfur amino acid requirement of 13 mg/kg body weight for healthy adults (Van de Poll, Dejong, & Soeters, 2006). Methionine is the only essential sulfur amino acid and can provide sulfur for cysteine and taurine synthesis. These amino acids are pivotal for structural and catalytic functions of proteins and are used to form numerous essential and secondary metabolites. Oxidized thiol groups of two cysteine residues form disulfide bonds: covalent linkages that establish tertiary and sometimes quaternary protein structures. The dithiol ↔ disulfide interchange can be a regulatory mechanism that mediates redox reactions.

Sulfur nutrition is important for species in the order Brassicales (e.g., white cabbage, broccoli, cauliflower, kale, Brussels sprouts, capers) to synthesize anticarcinogenic glucosinolate compounds (reviewed in Sozzi, 2001). In caper (*Capparis spinosa* L.), 160 flavor components were identified, including elemental sulfur (S₈) and >40 sulfur-containing compounds, among them thiocyanates and isothiocyanates. *Allium* vegetables (garlic, onions, leeks, chives) are also rich in sulfur compounds (Gharibzadeh & Jafari, 2017). Although essential for human and plant life, sulfur is a minor component compared to nitrogen. Generally, it is not a growth-limiting nutrient, since sulfate, the oxidized anion, is abundant in the environment.

19.2.8.7 Manganese (Mn)

Recommended dietary intakes of manganese differ considerably among countries, ranging from 1.4 mg/day in the United Kingdom to 5.5 mg/day in Australia and New Zealand (Freeland-Graves, Mousa, & Kim, 2016). In humans, manganese is involved in a variety of processes and functions including bone and connective tissue growth (bone stores the most Mn in the human body: ~40%–50% total body Mn), reproduction, brain function, blood sugar regulation, protein and energy metabolism, and cellular protection (Chen, Bornhorst, & Aschner, 2018). It serves as a cofactor for several critical enzymes: the mitochondrial manganese superoxide dismutase 2 (involved in antioxidant protection),

arginase (the rate-limiting enzyme in urea synthesis), acetyl-Co A carboxylase (first and rate-limiting enzyme in de novo fatty acid synthesis), phosphoenolpyruvate carboxykinase and pyruvate carboxylase (metabolic enzymes in the gluconeogenesis pathway), and the astrocyte-specific glutamine synthetase (crucial for brain ammonia metabolism). In plants, manganese atoms undergo successive oxidations to yield a strongly oxidizing complex that can oxidize water during photosynthesis. Like magnesium, manganese is required in enzyme reactions involving carbon assimilation. Chloroplasts are most sensitive to manganese deficiency. Among horticultural crops, nuts (hazelnuts, pecans, and almonds), pumpkin seeds, green leafy vegetables (spinach), fruits, and fruit juices are good sources of manganese (Gharibzahedi & Jafari, 2017).

19.2.8.8 Copper (Cu)

The recommended dietary allowance for copper is 900 µg/day for adults over 19 years old (Davison, 2017). Copper is a cofactor for over 30 proteins, including superoxide dismutases 1 and 3 (with a key role in antioxidant defense), ceruloplasmin (the major copper-carrying ferroxidase in the blood, it plays a role in iron metabolism) and hephaestin (a ferroxidase involved in intestinal iron absorption), lysyl oxidase (that catalyzes formation of aldehydes from lysine residues in collagen and elastin precursors), mitochondrial cytochrome *c* oxidase (the last enzyme in the respiratory electron transport chain of cells located in the membrane), tyrosinase (the rate-limiting enzyme of melanin production, plays an important role in enzymatic browning) and dopamine-β-hydroxylase (an essential neurotransmitter-synthesizing enzyme that primarily contributes to catecholamine and trace amine biosynthesis), peptidylglycine alpha-amidating monooxygenase (involved in the alpha-amidation of neuropeptides), and amine, monoamine, and diamine oxidases (Collins, 2017). Also, many copper-binding proteins have been identified (Collins, 2017). Copper, a redox-active metal, is critical for the oxidative defense system; oxidative stress is a characteristic of copper deficiency (Uriu-Adams & Keen, 2005). Copper is required for brain development and supports the functions of the central nervous system. It is involved in neuropeptide synthesis and immune function and is necessary to form hemoglobin and connective and bone tissue (Collins, 2017). Deficits in this nutrient during pregnancy can cause gross structural malformations in the fetus and persistent neurological and immunological abnormalities in the offspring (Uriu-Adams & Keen, 2005).

In plants, copper is required for chlorophyll synthesis and several copper-containing enzymes that reduce molecular oxygen. As with other trace minerals, the availability of copper to plants decreases as the pH rises above seven. At high pH, copper is strongly adsorbed to clays, iron and aluminum oxides, and organic matter. Of the micronutrients required by plants, copper often has the lowest total concentration in soil. Grains (21%), legumes, nuts, and soy (20%) are the leading sources of dietary copper, followed by vegetables (17%) (Table 19.7; Hiza & Bente, 2007). Among horticultural crops, nuts (cashew nuts in particular), raw kale, dried fruit (prunes), and avocados are good sources of copper (Gharibzahedi & Jafari, 2017).

19.2.8.9 Iron (Fe)

The recommended dietary allowance for iron is 8 mg/day for adult males over 19 years old and adult females over 50 years old, and 18 mg/day for adult females between 19 and

50 years (Davison, 2017). The metabolic fates of copper and iron are intimately related. Their essential role resides in their capacity to participate in one-electron exchange reactions. Systemic copper deficiency generates cellular iron deficiency, which in humans results in reduced intellectual capacity, stunted growth, altered bone mineralization, and compromised immune responses. Iron is required in heme-containing proteins involved in binding and/or transporting oxygen: hemoglobin, myoglobin, neuroglobin, and cytoglobin. Some hemoproteins are enzymes: cytochrome P450s, cytochrome *c* oxidase, catalase, and peroxidases. Other hemoproteins enable electron transfer, as they form part of the electron transport chain (cytochrome *a*, cytochrome *b*, and cytochrome *c*) and microsomal electron transport. Iron is also required for deoxyribonucleotide synthesis (ribonucleotide reductase) and for other nonheme iron enzymes (phenylalaninehydroxylase, tyrosine hydroxylase) and iron–sulfur enzymes (aconitase) (Abbaspour, Hurrell, & Kelishadi, 2014). Almost 70% of the body's iron is found in the hemoglobin present in circulating erythrocytes, another 5% helps form myoglobin, 5% is distributed across body cells as an enzyme cofactor, a minor percentage circulates in the plasma bound to transferrin, and ~20% of the iron in the body is stored as ferritin or held as hemosiderin.

In plants, iron is required for chlorophyll synthesis and photosynthesis. In vegetable green leaves, there is good correlation between iron and chlorophyll concentrations. Inadequate iron nutrition results in abnormal chlorophyll development: deficiency begins as interveinal chlorosis on younger leaves, resulting in prominently green veins. The resultant reduced photosynthetic capability also reduces the weight and area of affected leaves. The plant plastid stroma may contain deposits of phytoferritin, an iron storage form similar to the ferritin of animal cells. Phytoferritin occurs almost exclusively in plastids, especially those of storage organs (Briat & Lobreaux, 1997).

Plant sources supply only nonheme iron, tightly bound to organic compounds. It has low bioavailability (<10%, Saini, Nile, & Keum, 2016) and is strongly influenced by the presence of other food constituents. Adult users of lower fat foods consume more nutrient-dense diets and more iron (Sigman-Grant et al., 2003). The predominant source of iron in the American food supply is grain products, followed by meat, poultry, and fish. Between 1909 and 1919, vegetables furnished 18% of the iron in the food supply, but in 2004, that share dropped to 10% (Table 19.6), partially due to reduced consumption of white potatoes after 1920. Although potatoes are not a good source of iron, their contribution increases when eaten in large quantities (Hiza & Bente, 2007), particularly if the skin is consumed: baked potato skin has 20-fold more iron than the flesh. Spices and herbs are very good sources of iron (Saini et al., 2016). Nuts (cashew, hazelnut, pistachio, almonds, walnuts, and pecans), pumpkin seeds, green vegetables (parsley, spinach, Swiss chard, broccoli, kale, and collards), and legumes (green peas and beans) are also good sources of iron (Gharibzahedi & Jafari, 2017).

19.2.8.10 Zinc (Zn)

The recommended dietary allowance for zinc is 11 mg/day for men and 8 mg/day for women (Davison, 2017). Zinc is a pervasive and versatile microelement that plays a catalytic or structural role in over 300 enzymes involved in digestion (carboxypeptidase, liver alcohol dehydrogenase, carbonic anhydrase), metabolism, reproduction, and wound healing (Prasad, 2017). Over 2000 transcription factors require zinc to conserve their structures

and to bind to DNA. Zn^{2+} is a cation with various coordination possibilities and several potential geometries. Thus it easily adapts to different ligands. The primary role of structural Zn^{2+} in proteins is to stabilize tertiary structures. Zinc has also a critical role in the immune response and is an important antioxidant and antiinflammatory agent (Prasad, 2017).

Zinc activates many plant cell enzymes, but only a few (alcohol dehydrogenase, superoxide dismutase, carbonic anhydrase, and RNA polymerase) contain the micronutrient. Zinc affects carbohydrate metabolism because Zn-dependent enzymes participate in biochemical reactions of sugars (Sozzi, Greve, Prody, & Labavitch, 2002). Zinc also plays a role in maintaining cell membrane integrity, protecting from O_2^- damage and synthesizing RNA and tryptophan, a precursor of indole-3-acetic acid. Several mechanisms involve zinc in plant defense against pathogens and herbivores (Cabot et al., 2019). Fruits and vegetables account for only 1.2% and 6.4%, respectively, of the zinc in the American food supply (Hiza & Bente, 2007). As with magnesium, zinc intakes may be insufficient in both adults and children (Sigman-Grant et al., 2003). Fruits are poor in zinc, but nuts (cashew, pecan, Brazil nut, almond, hazelnut, pistachio, and walnut) and squash seeds are good sources (Gharibzahedi & Jafari, 2017). As with calcium and iron, oxalates and phytates bind zinc and form insoluble precipitates, decreasing its availability for absorption.

19.2.8.11 Boron (B)

No estimated average requirements or dietary reference intakes have been set for boron, only a tolerable upper intake level of 20 mg/day for individuals aged ≥ 19 years (Białek, Czauderna, Krajewska, & Przybylski, 2019). In humans, boron plays important roles in growth and maintenance of bone tissue, improvement of wound healing, and calcium metabolism (enhanced gut absorption of calcium, calcification). Boron acts together with vitamin D, calcium, and magnesium in bone metabolism. Boron has antiinflammatory effects, influences central nervous system functions, and helps regulate the hormones testosterone, estrogen, insulin, triiodothyronine, and thyroxine. It increases biological half-life and bioavailability of estradiol and vitamin D. Boron raises the abundance of antioxidant enzymes, such as superoxide dismutase, catalase, glutathione peroxidase, glutathione-S-transferase, and glucose-6-phosphate dehydrogenase. It also detoxifies reactive oxygen and nitrogen species and reduces lipid peroxidation and DNA damage (Białek et al., 2019).

In vascular plants, boron forms strong complexes with different molecules carrying *cis*-diol groups in appropriate spatial configurations and is essential for correct formation and stabilization of primary cell walls. Most authors consider the formation of borate diester cross links with two chains of rhamnogalacturonan-II is an essential function for growth, development, and reproduction in vascular plants (Wimmer et al., 2020). Animals lack the capacity to metabolize inorganic boron compounds (like boric acid or borates) into mono- or di-sugar-borate esters (e.g., glucose and fructose borate esters), bis-sucrose borate esters, sugar alcohol borate esters (sorbitol, mannitol), or pectic polysaccharide borate esters. In contrast, plants can convert inorganic boron into dietary sugar-borate ester complexes, which are the best chemical form for assimilation into cells. In general, plants have higher boron concentrations (from 0.1 to 0.6 mg B/100 g) than animal-based foods (from 0.01 to 0.06 mg/100 g) (Białek et al., 2019). Fresh fruits (e.g., avocado, apple, banana, and red grape), leafy vegetables, flowering heads (broccoli), dried fruits (plums, apricots, and raisins), seeds, and nuts (pecans, almonds, and hazelnuts) are primary natural dietary

sources of fructoborate esters, mainly calcium fructoborate complex—an excellent source of soluble boron with many beneficial physiological properties (Gharibzahedi & Jafari, 2017).

19.2.8.12 Selenium (Se)

The recommended dietary allowance for selenium is 55 µg/day (Davison, 2017). In humans, this trace mineral is associated with the endocrine system, the antioxidant defense, and the immune function. Iodothyronine deiodinases are selenium-dependent enzymes that convert inactive thyroxine to active thyroid hormone, triiodothyronine. Glutathione peroxidases are antioxidant seleno enzymes that protect against reactive oxygen and nitrogen species. The antioxidative effects of selenium and vitamin E may act together to protect from oxidative damage. At adequate doses, selenium protects plants from different abiotic stresses. It works as an antioxidant: it scavenges ROS by their dismutation and reduces metal-induced oxidative stress (Shahid et al., 2018). Fruits and vegetables typically contain small amounts of selenium. But, certain species, such as onions, garlic, broccoli, and cabbage, can accumulate selenium when grown on selenium-rich soils (Gharibzahedi & Jafari, 2017) (see also Chapter 7: Fresh-cut products—implications for postharvest).

19.2.8.13 Silicon (Si)

Silicon is suggested as an essential element for human health (Michalak & Chojnacka, 2018). Its essentiality is difficult to prove because silicon is very common (it is the second-most abundant element in the Earth's crust by mass, after oxygen); hence, deficiency symptoms are difficult to reproduce. In the human body, this mineral is associated with connective tissue formation in general: bone health (silicon can increase bone volume and density in patients with osteoporosis), elastin and collagen synthesis, and skin aging prevention. It is one of the nutrients sustaining good condition of nails and hair and is also involved in cardiovascular health (Michalak & Chojnacka, 2018).

In plants, silicon is useful for the healthy growth of many species, since it plays multiple roles to alleviate a wide variety of biotic and abiotic stresses. In fruit trees, it promotes root growth and development, prevents root rot and premature aging, improves photosynthesis, and regulates fruit absorption of different minerals (Etesami & Jeong, 2020). Plant-based foods are the major contributors to dietary silicon. Fruits (banana in particular) and vegetables (e.g., beetroot, carrot, potato, green beans, and spinach) are good sources of silicon (Farooq & Dietz, 2015). Little silicon was bioavailable from bananas (5.8%) and spinach (4.9%), despite their high silicon content (Robberecht, Van Dyck, Bosscher, & Van Cauwenbergh, 2008).

19.2.8.14 Sodium (Na)

In general, fruits are poor in sodium and are recommended for low-sodium diets. Low sodium is defined as 140 mg of sodium per serving and an ideal maximum intake of sodium for low sodium diet is 1500 mg/day (Davison, 2017). Sodium is important for electrolyte balance and blood pressure. Along with potassium, it coregulates ATP and is important in neuromuscular function. Table salt (NaCl) in the diet also provides chloride, which is part of gastric acid, the human digestive fluid required for proper digestion. Sodium intake from vegetables increased during the past few decades (Table 19.6) due to

increased consumption of processed vegetables, largely tomatoes and white potatoes. Except for canned vegetables, food supply sodium estimates do not include sodium added in processing. Thus the relative contribution of vegetables to sodium in the food supply is likely overstated (Hiza & Bente, 2007). Olives and spinach are horticultural sources of sodium.

19.2.8.15 Molybdenum (Mo)

The recommended dietary allowance for molybdenum is set at 45 $\mu\text{g}/\text{day}$ for adults. In both humans and plants, molybdenum must be complexed by a special cofactor to gain catalytic activity: it is bound to a pterin, forming molybdenum cofactor (Moco), the active compound at the catalytic site of molybdenum-containing enzymes. In the human body, there are four molybdenum-dependent enzymes (two mitochondrial and two cytosolic enzymes), each harboring a pterin-based molybdenum cofactor in the active site (Schwarz, 2016). In plants, different enzymes are molybdenum-dependent, including nitrate reductase. Molybdenum concentrations in plant foodstuffs are dependent on the soil content. In general, fruits and vegetables are poor sources, but nuts are rich in molybdenum (Novotny, 2011).

19.2.8.16 Nickel (Ni)

Nickel is an essential nutrient for plants, but there is no evidence that nickel is of nutritional value in humans (Genchi, Carocci, Lauria, Sinicropi, & Catalano, 2020). In plants, it plays roles in both primary and secondary metabolism. It is a key component of enzymes involved in nitrogen metabolism, among them, urease (Wood, 2015). High mean concentrations of nickel have been measured in nuts (e.g., walnuts, 3.6 mg/kg); moderately high concentrations were found in vegetables (742–753 $\mu\text{g}/\text{kg}$). Fruits are poorer sources of nickel (Mania, Rebeniak, & Postupolski, 2019).

19.2.8.17 Fluorine (F)

Most fruits and vegetables have low concentrations of fluorine (Mahmoud, Mutchnick, Svider, McLeod, & Fribley, 2020). Adequate intake of fluorine (which occurs naturally as the monoatomic anion fluoride, F^-) is 4 mg/day for adult males and 3 mg/day for females (Davison, 2017). Fluorine is important for the health of bones and teeth in humans but may be a toxic pollutant for plant metabolism. The main sources of human fluorine are treated drinking water, tea and other beverages, fish, and dental products.

19.2.8.18 Iodine (I)

The recommended dietary allowance for iodine is 150 $\mu\text{g}/\text{day}$ (Davison, 2017). The thyroid gland concentrates 70%–80% of the human body's iodine and uses about 80 $\mu\text{g}/\text{day}$ to synthesize thyroid hormones (triiodothyronine and thyroxine). These hormones are primarily responsible for regulation of metabolism, normal growth, neurological development, and reproduction. Some horticultural crops (cassava, sweet potatoes, turnips, and vegetables from the genus *Brassica* such as broccoli, Brussels sprouts, cabbage, and cauliflower) contain substances called goitrogens that interfere with iodine uptake or use by the thyroid gland (Langer, 2018). Most of these goitrogens can be inactivated by heat. They are of clinical importance only if consumed in large amounts and/or iodine supply is deficient. Fruits and vegetables are poor sources of iodine, but leafy vegetables such as

lettuce are richer in iodine than other horticultural crops (Fuge & Johnson, 2015). Bananas, cranberries, dried prunes, and strawberries are good fruit sources of iodine (Gharibzahedi & Jafari, 2017). The use of iodine-biofortified vegetables such as *Brassica* genotypes may be a healthier alternative than iodine-fortified salt for preventing iodine deficiency and related human disorders (Gonnella, Renna, D'Imperio, Santamaria, & Serio, 2019).

19.2.8.19 Factors influencing mineral content of fruits and vegetables

19.2.8.19.1 Species and cultivar

Mineral composition varies widely in raw fruits (Table 19.7) and vegetables. Leafy vegetables have higher concentrations of nutrients that are less mobile in the plant (e.g., calcium) and depend on direct water flow rather than recycling from older leaves. Mineral concentrations may vary widely among cultivars. For example, both "Dwarf Brazilian" (Santa Catarina Prata, *Musa* sp. AAB) and "Williams" (Cavendish subgroup, *Musa* sp. AAA) bananas are considered good sources of potassium. Nevertheless, "Dwarf Brazilian" bananas have more P, Ca, Mg, Mn, and Zn than "Williams" bananas (Wall, 2006). As a result of the distribution of vascular tissue, sink characteristics, and metabolic rates, higher mineral concentrations are found in the skin and seeds than in the flesh of fruits. In "Rocha" pears, nitrogen, calcium, magnesium, manganese, iron, copper, zinc, and boron show radially decreasing concentrations from the fruit skin to the inner flesh tissues (Saquet, Streif, & Almeida, 2019). Tissues with higher metabolic rates (epicarp, core) may accumulate more nitrogen. Rapidly expanding or large-celled tissues are unlikely to have high calcium concentrations. Distal fruit tissue contains the least calcium and the greatest susceptibility to calcium deficiency disorders (Tonetto de Freitas & Mitcham, 2012).

19.2.8.19.2 Preharvest factors

Orchard location has important effects on fruit and vegetable mineral composition (Table 19.7). For example, potassium in bananas differs among locations/microclimates (Wall, 2006). Similar fluctuations in potassium among growing areas are seen in "Rainbow" papaya fruits (Wall, 2006). Mineral composition fluctuates widely in raw fruits and vegetables due to preharvest factors (soil fertility, including both pH and concentrations of nutrients, soil moisture, temperature) and cultural practices (amount and timing of fertilization and irrigation, application of plant growth regulators, pruning, and thinning of tree fruit species) (see also Chapter 7: Fresh-cut products—implications for postharvest). Most agricultural practices are established primarily to increase productivity, not to improve human health, horticultural crop postharvest life, or flavor (Crisosto & Mitchell, 2002). Most fertilizers are applied directly to the soil to raise nutrient concentrations that are inadequate for successful crop growth and to maintain soil fertility, which will decline if nutrient removal from the soil via crop uptake, leaching, volatilization, or denitrification exceeds nutrients added via weathering of minerals and mineralization of organic matter.

Nitrogen is the most frequently deficient element and most common fertilizer in orchards, while phosphorus and potassium are added when soil test results, plant response, or tissue analysis indicate a need. N–P–K addition with irrigation water has several advantages, including the ability to transport soluble nutrients directly to the root zone

whenever water is applied to the plant. Calcium additions can be large when lime is applied to increase soil pH. Most micronutrients are rarely applied to soil but instead are sprayed directly on the canopy in dilute concentrations. In fruits, the quantity of nutrients absorbed through the waxy cuticle is often small, relative to nutrient demand, but can ameliorate deficiency symptoms and improve fruit quality.

An excessive supply of nutrients relative to photosynthesis develops when the rate of nutrient assimilation is high relative to net photosynthesis. When this happens, nutrients can accumulate in fruits and vegetables to concentrations that are toxic for the plant or consumers. Excessive nitrogen leads to potentially harmful accumulations of nitrate in leafy greens and potatoes (Pavlou, Ehaliotis, & Kavvadias, 2007). Such nutrient imbalances also affect crop quality. Nutrient transport and source–sink relations also affect nutrient accumulation. For example, altered water economy affects calcium uptake, since calcium is transported in the soil toward the roots and translocated to the shoots with the mass flow of water driven by transpiration and growth. Bagging fruit may decrease calcium concentrations and increase calcium-related disorders (Li, Han et al., 2020; Li, Cheng, Zhang, Wang, & Yang, 2020). Canopy position and crop load also influence calcium uptake. Fruit calcium uptake is determined by the calcium concentration in the xylem sap, and xylem/phloem ratio of fruit sap uptake, which is affected by the rates of leaf and fruit transpiration and growth (Tonetto de Freitas & Mitcham, 2012). Fruit from upper parts of the canopy tend to have less calcium (Ferguson & Triggs, 1990) and heavily cropped trees have fruit with more calcium and less potassium (Ferguson & Watkins, 1992). Gibberellins, auxins, abscisic acid, and cytokinins may help regulate calcium uptake and translocation to fruit tissues. Gibberellins affect cellular calcium partitioning and distribution, which increase fruit susceptibility to calcium deficiency disorders (Tonetto de Freitas & Mitcham, 2012). Treatment of tomato plants and apple trees with prohexadione-calcium, a gibberellin biosynthesis inhibitor, increases the total calcium in fruits (do Amarante et al., 2020). Pre- and postharvest treatments with different calcium sources have been used to maintain quality, extend shelf-life, and enhance the nutritional value of fresh fruits and vegetables (Martín-Diana et al., 2007).

Tree size, spacing, row orientation, canopy shape, and training system influence light distribution within fruit trees, which affects fruit mineral composition. In grapes, improving light penetration into the canopy increased anthocyanins and soluble phenols but reduced potassium (Prange & DeEll, 1997). In kiwifruit, light promoted calcium accumulation (Montanaro, Dichio, Xiloyannis, & Celano, 2006). This finding was not fully explained by fruit transpiration: regulation by phytohormones could help determine calcium concentrations. The effect of sunlight is not universal: avocado fruit from the sunny side of trees had the same calcium concentration as fruit from the shaded side (Witney, Hofman, & Wolstenholme, 1990). The mineral concentrations in some horticultural species are affected by intensive culture systems (glasshouse) or organic conditions. Tomato fruit contained more calcium and less potassium, magnesium, and sodium when grown in an organic compost/soil mix than in hydroponic substrates (Premuzic, Bargiela, García, Rendina, & Iorio, 1998).

Organic cultivation did not affect strawberry mineral concentrations consistently (Bedbabis, Ferrara, Rouina, & Boukhris, 2010; Hakala, Lapveteläinen, Huopalahti, Kallio, & Tahvonon, 2003). Organic crops overall contained 21.1% more iron, 29.3% more magnesium, and 13.6% more phosphorus than their conventional counterparts (Rembiałkowska, 2007).

There were higher concentrations of nitrogen, phosphorus, potassium, sulfur, calcium, magnesium, and boron in organically grown kiwifruits than in those grown under a conventional production system (Amodio, Colelli, Hasey, & Kader, 2007). In contrast, another study found no consistent differences in concentrations of nitrogen, phosphorus, potassium, and magnesium in kiwifruit grown under organic or conventional production systems and only calcium was more abundant in fruit from organic orchards (Benge, Banks, Tillman, & De Silva, 2000). Organic cropping systems may promote mineral content, but there are instances where differences are small or nonexistent (Mditshwa, Magwaza, Tesfay, & Mbili, 2017).

19.2.8.19.3 Harvest and postharvest practices

Mineral composition of some horticultural crops can be modified by harvest practices. In broccoli florets, changes in mineral content (floret:stalk ratio) may be dependent on stalk length (Guo et al., 2018). Postharvest treatments with minerals, primarily calcium, can increase the storage life and quality of some fruits and vegetables. In the last decade, the industry has been encouraged to fortify food and beverages with calcium. Increasing the calcium concentration of horticultural crops gives consumers' new ways to enhance calcium intake without supplements. Also, phosphorous-free sources of calcium can help provide a good balance of dietary calcium and phosphorus (Martín-Diana et al., 2007).

There are two primary ways to apply postharvest calcium to horticultural crops: (1) dipping-washing and (2) impregnation (Martín-Diana et al., 2007). Immersion treatments are used for fresh, sensitive products like leafy vegetables. Impregnation modifies the composition of food through partial water removal and replacement with solutes, without damaging integrity. The driving forces can be an osmotic gradient between sample and solution, application of vacuum followed by normal atmospheric pressure, or both. CaCl_2 is widely used as a firming agent for whole and fresh-cut fruits and vegetables. Mineral concentrations were similar in fresh, canned, and frozen fruit and vegetable products; this is expected, since these nutrients are inert and thus not sensitive to degradation by the thermal processes used in food preservation.

19.2.8.20 Incidence of minerals on fruit and vegetable quality and consumer acceptance

Many of these qualities are affected by mineral concentrations and are part of many factors leading to fruit and vegetable acceptability. Acceptability determines the consumption of many essential nutrients: vitamins, antioxidants, and fiber. Thus the effect of minerals on crop quality and consumer acceptance should be considered. The effect of minerals on color, flavor, firmness, and other attributes of specific horticultural commodities is described below.

Consumers buy certain products as good sources of specific minerals: potato and sweet potato for potassium, banana for magnesium and potassium, spinach for iron, potassium, magnesium, and as a nondairy source of calcium (see also Chapter 19: Nutritional quality of fruits and vegetables). Minerals are credence attributes because they cannot be detected by visual inspection or consumption. Thus there is no incentive to measure minerals in a quality control program unless specific nutritional claims can be made. To judge quality, consumers use purchase attributes (size, color, firmness, aroma, and absence of defects) and consumption attributes (flavor and mouth feel).

19.2.8.20.1 Effect of minerals on color

In apples and pears, both leaf and fruit nitrogen correlate positively with fruit green background color (Marsh, Volz, Cashmore, & Reay, 1996). Manganese is also associated with green ground color in apples (Deckers, Daemen, Lemmens, Missotten, & Val, 1997). Excessive nitrogen inhibits background color change from green to yellow, inhibits reddish blush development, and decreases edibility in peaches (Crisosto, Johnson, DeJong, & Day, 1997). In apples, correcting potassium deficiency can increase fruit red color, but applications in excess of need have no effect (Nielsen & Nielsen, 2003). In tomato, potassium deficiency is associated with less lycopene and increased β -carotene (Trudel & Ozbun, 1971), while selenium application to hydroponically grown plants decreased ethylene production and β -carotene accumulation (Pezzarossa, Rosellini, Borghesi, Tonutti, & Malorgio, 2014). In broccoli, foliar sprays of calcium, iron, zinc, or manganese during plant growth increase total chlorophyll content and reduce yellowing of harvested heads; moreover, calcium and manganese applications may enhance chlorophyll retention during postharvest cold storage (El-Mogy, Mahmoud, El-Sawy, & Parmar, 2019). In grapes, sprayings with calcium chloride throughout the fruiting season reduced anthocyanin content (pigments responsible for their red color) but increased total phenolic acids and flavonol (Martins, Billet, Garcia, Lanoue, & Gerós, 2020).

19.2.8.20.2 Effect of minerals on flavor

Nitrogen content shows negative correlation with soluble solids in apples (Dris, Bennett, & Bash, 1999). In contrast, soluble solids increased with increased nitrogen in tomatoes (Barringer, Bennett, & Bash, 1999). In mango, total soluble solids increased when zinc sulfate fertilizer was applied to the soil (Bahadur, Malhi, & Singh, 1998). In "Fino 49" lemon, salinity reduced juice percentage and impaired juice quality by decreasing soluble solid sugars and acidity (García-Sánchez, Carvajal, Porras, Botía, & Martínez, 2003) (see also Chapter 7: Fresh-cut products—implications for postharvest).

Preharvest calcium chloride sprays increase synthesis of key volatile compounds that contribute to overall flavor in ripe Ussurian pear (*Pyrus ussuriensis*), both at harvest and after a five-day storage. Calcium treatment promotes glucosidase activity that releases bound aroma compounds into free forms. Applied calcium also increases lipoxygenase, pyruvate decarboxylase, and alcohol dehydrogenase activities that boost synthesis of ethanol and acetaldehyde in fruit and also the amounts of metabolic unsaturated fatty acids that promote biosynthesis of ester compounds (Wei et al., 2017).

Minerals also affect production of several classes of volatile compounds in pomme fruit (reviewed in Mattheis & Fellman, 1999). In fresh onions, increased sulfur availability enhances pungency and total sulfur flavor, but decreases the concentrations of precursors for synthesis of volatiles, imparting "green" and "cabbage" notes (Randle, 1997). Selenite treatment improves postharvest quality of broccoli through changes in the volatile compound profile, particularly alcohols and sulfides (Lv et al., 2017) (see also Chapter 23).

19.2.8.20.3 Effect of minerals on firmness

Excess nitrogen can decrease tissue firmness (Prange & DeEll, 1997). The relationship between calcium and fruit firmness has been studied and reviewed extensively. Greater

firmness and/or slower softening after harvest/storage are associated with higher calcium concentrations or calcium applications (Angeletti et al., 2010; Dong, Zhi, & Wang, 2019). Calcium foliar sprays on peaches and nectarines increased calcium (Manganaris, Vasilakakis, Mignani, Diamantidis, & Tzavella-Klonari, 2005; Manganaris, Vasilakakis, Diamantidis, & Mignani, 2006), while papaya fruit peel and pulp showed quadratic increases in calcium after foliar and fruit calcium chloride applications (Madani, Wall, Mirshekari, Bah, & Mohamed, 2015). In California, no consistent effect on the quality of mid- or late-season peaches and nectarines was found (reviewed in Crisosto et al., 1997).

Postharvest calcium treatments can retain fruit firmness in peaches (Manganaris, Vasilakakis, Diamantidis, & Mignani, 2005; Manganaris, Vasilakakis, Diamantidis, & Mignani, 2007) and lemons (Martínez-Romero, Valero, Serrano, & Riquelme, 1999), among other fruits. Calcium effects on fruit firmness are attributable to calcium's ability to cross-link with pectic polysaccharides by ionic association. Calcium binding may reduce the accessibility of cell wall-degrading enzymes to their substrates. Calcium applications are frequently combined with other physical or chemical treatments (Dong et al., 2019; Nguyen, Nguyen, & Nguyen, 2020).

Preharvest foliar and fruit application of selenium increases selenium concentrations in "Suncrest" peaches and "Conference" pears and enhances flesh firmness both at harvest and after a 14-day storage at 2°C (Pezzarossa, Remorini, Gentile, & Massai, 2012). In "Starking Delicious" apples, foliar application of selenium increases both leaf and fruit selenium concentration, enhances flesh fruit firmness, and lowers ethylene production throughout 6-month storage at 0°C (Babalar, Mohebbi, Zamani, & Askari, 2019). Postharvest applications of different sources of silicon can improve fruit keeping quality and delay softening in banana (Nikagolla, Udugala-Ganehenegge, & Daundasekera, 2019) and apples (Ge et al., 2019). Sodium silicate treatment partially counteracted the increased total activity of the cell wall enzymes polygalacturonic acid transeliminase, pectin methyltranseliminase, pectin methylgalacturonase, polygalacturonase, cellulase, and β -galactosidase, which are involved in apple cell wall degradation and subsequent softening (Ge et al., 2019).

19.2.8.20.4 Effect of minerals on rots, physiological disorders, and nutritional value

Calcium-treated fruit has increased firmness and reduced rot incidence. Calcium may affect both processes through its role in strengthening plant cell walls (Manganaris, Vasilakakis, Mignani et al., 2005). High nitrogen increases susceptibility to decay caused by *Monilinia fructicola* (brown rot) in nectarines (Daane et al., 1995). Wounded and inoculated "Fantasia" and "Flavortop" nectarines from trees with >2.6% leaf nitrogen were more susceptible to *M. fructicola* than fruit from trees with less leaf nitrogen (Michailides, Ramirez, Morgan, Crisosto, & Johnson, 1993). Low phosphorus and nitrogen fruit concentrations increase the intensity and incidence of fruit flesh browning in "Grand Pearl" nectarines during cold storage (Olivos, Johnson, Xiaoqiong, & Crisosto, 2012).

Silicon alleviates biotic and abiotic stresses and increases plant resistance to pathogenic fungi. The efficacy of silicon in reducing the severity of several fungal diseases in fruit crops has been studied (Etesami & Jeong, 2020). Silicon, like calcium, plays a role in forming physical resistance barriers that make plant cells less susceptible to fungal pathogen invasion and subsequent enzymatic degradation. Additionally, silicon promotes defense-related enzyme activities in plant-pathogen interactions, which are connected to disease

resistance. Silicon-treated muskmelons showed various defense responses (regulation of energy metabolism and ROS production) against *Trichothecium roseum* (Lyu et al., 2019). In sweet cherry fruit, silicon reduces decay and lesion diameter of blue mold and brown rot caused by *Penicillium expansum* and *Monilinia fructicola*, respectively (Qin & Tian, 2005). It also decreases the incidence and severity of postharvest carrot rot caused by *Sclerotinia sclerotiorum* (Elsherbiny & Taher, 2018). In banana, a postharvest silicon dip treatment delayed the time required for diseases (stalk end rot and anthracnose caused by *Lasiodiplodia* sp. and *Colletotichum* sp.) to cover 5% of total fruit area (Nikagolla et al., 2019).

Consumers consider that fruits have less predictable quality than manufactured snacks. The effect of nutrients on the final quality of horticultural products may not become evident until harvest, distribution, or consumption. The expression "latent damage" describes damage incurred at one step, but not apparent until a later step. Physiological disorders are a type of latent damage. Some physiological disorders are related to nutrient imbalance. Calcium deficiency is associated with postharvest disorders. Calcium deficiency is an important preharvest factor for fruit and vegetable physiological disorders such as bitter pit in pomme fruit, blossom-end rot in tomato, pepper, and watermelon, blackheart in celery, cracking and cavity spot in carrot, and tipburn in lettuce and cabbage (Ferguson, Volz, & Woolf, 1999), although total fruit tissue calcium content may not be the only cause of development of these disorders (Tonetto de Freitas & Mitcham, 2012). Apples and pears with low calcium concentrations develop more superficial scald than those with high concentrations (Li, Han et al., 2020; Li, Cheng et al., 2020). Preharvest applications of calcium, alone or in combination with other chemicals, can mitigate sweet cherry rain cracking, a major cause of crop loss worldwide (Correia, Schouten, Silva, & Gonçalves, 2018; Dong et al., 2019). Cracking, a physiological failure of the fruit peel caused by cell wall swelling, also manifests as fractures in the peel or cuticle of different susceptible fruits such as apple, grape, persimmon, avocado, pistachio, *Citrus*, and banana. Foliar calcium fertilization alleviated this disorder in species other than sweet cherry and preharvest applications of calcium decrease cracking in pomegranate (Davarpanah et al., 2018) and some plum cultivars (Vangdal, Lunde Knutsen, & Kvamm-Lichtenfeld, 2018). Other calcium-related disorders are associated with long-term cold storage, such as CI in muskmelon (Combrink, Jacobs, & Maree, 1995). Postharvest calcium applications limited the incidence of CI in peach fruit, expressed as flesh browning, after 4 weeks cold storage at 5°C and additional ripening at room temperature for 5 days (Manganaris et al., 2007). Nevertheless, preharvest calcium applications did not affect the onset of CI in peaches and nectarines (reviewed in Lurie & Crisosto, 2005). In apples, interaction of elements such as K/Ca, N/Ca, and Mg/Ca was more closely associated with bitter pit than those elements individually. Magnesium and potassium are part of an index to predict bitter pit (Autio, Bramlage, & Weis, 1986). "Rocha" pear fruits that developed disorders after a 22-week storage had been harvested mostly from orchards with lower Ca concentrations and higher K/Ca ratios; also, the (K + Mg)/Ca ratios were higher in fruit with internal disorders (Saquet et al., 2019).

Minerals can influence the concentrations of other nutrients in horticultural crops. In a field trial of mature papaya trees, preharvest applications of calcium chloride decreased magnesium concentrations in fruit peel and pulp (Madani et al., 2015). Nitrogen fertilizers applied at high rates decreased the concentration of vitamin C in fruits (citrus juices) and

vegetables (potatoes, cauliflower, white cabbage, and crisphead lettuce), while increased potassium fertilization increases AsA (reviewed in Lee & Kader, 2000). Foliar applied calcium lactate enhanced sweet pepper quality attributes: vitamin C, fruit firmness, total soluble solids, carotenoids, total phenols, flavonoids, and antioxidant activity (Barzegar, Fateh, & Razavi, 2018). In persimmon, postharvest combined treatments with calcium lactate and hot water maintained fruit quality and antioxidant capacity and increased soluble tannins and AsA during cold storage (Naser, Rabiei, Razavi, & Khademi, 2018). In grapes, sprayings with calcium chloride throughout the fruiting season stimulated synthesis of stilbenoids (Martins et al., 2020).

19.3 Antioxidants

19.3.1 Oxidative damage and antioxidants

ROS are reduced forms of oxygen such as singlet oxygen, hydrogen peroxide (H_2O_2), superoxide ($O_2^{\cdot-}$), or hydroxyl radical (OH^{\cdot}). ROS cause deleterious modifications in proteins, lipids, and nucleic acids by altering normal metabolism in living organisms (Waris & Ahsan, 2006). The protective effects of fruit and vegetables against ROS are linked to the presence of antioxidants. Such compounds, able to prevent uncontrolled cellular oxidation (Dragsted, 2003) are present in all plant organs and include diverse metabolites including AsA, carotenoids, vitamin E, phenolics, glucosinolates, and thiosulfates (Fig. 19.3, Table 19.8).

19.3.2 Carotenoids, ascorbic acid, tocopherols and tocotrienols

Besides on their role as vitamins these compounds play a key role in the regulation of cell redox status (Järvinen, Knekt, Hakulinen, Rissanen, & Heliövaara, 2001; Rao & Rao, 2007; Tan et al., 2010). The general properties of these compounds were described in Section 19.2.7.

19.3.3 Phenolic compounds

Phenolics are diverse compounds derived from aromatic amino acids. Many phenolic compounds have been identified in plants. They are grouped into subclasses such as phenolic acids, flavonoids, lignans, stilbenes, tannins, coumarins, and lignin (Vuolo, Lima, & Junior, 2019). Their distinctive feature is the presence of aromatic rings with variable degrees of hydroxylation. Phenolics contribute to fruit pigmentation and act as predator deterrents and antimicrobials. They may provide astringency or bitter taste to some products (Zhang et al., 2020). During processing or storage many phenolics are readily oxidized by plant peroxidases (PODs) and polyphenol oxidases (PPOs), leading to undesirable tissue browning.

Phenolic compounds are generally present at low concentrations but in blueberry can be over 0.1%. Phenolics accumulate preferentially in the peel, but this varies depending on species and chemical group. Eggplant anthocyanins are concentrated in the peel, while chlorogenic acid, the primary antioxidant, predominates in the pulp, surrounding the

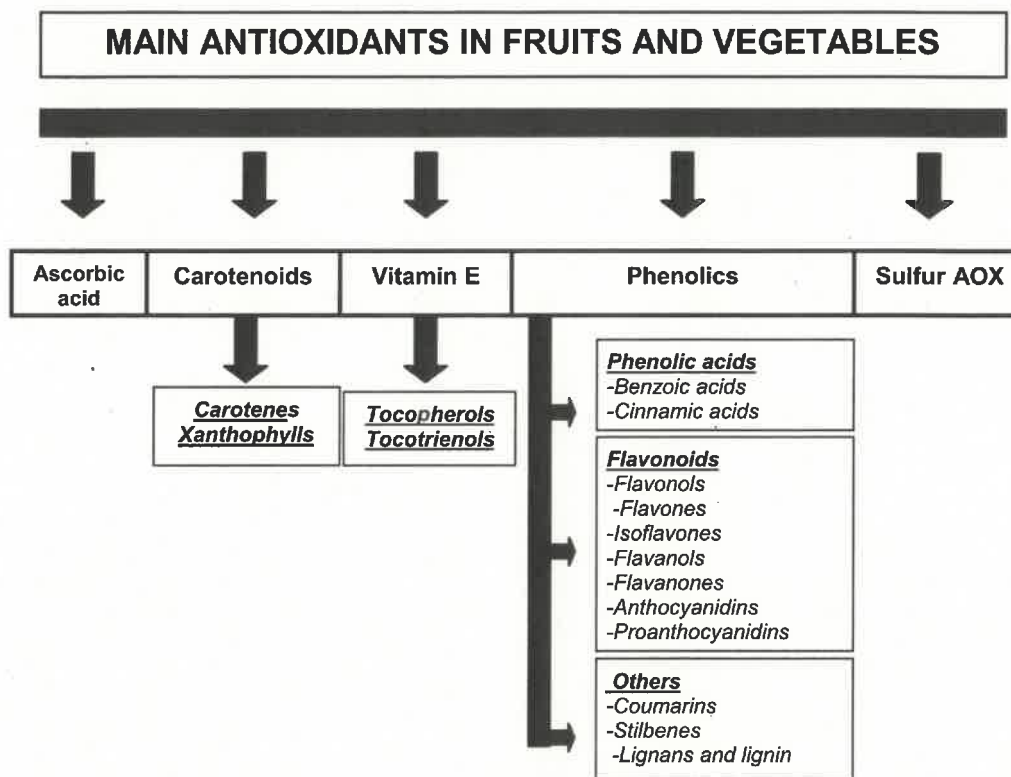


FIGURE 19.3 Main dietary antioxidants present in fruits and vegetables.

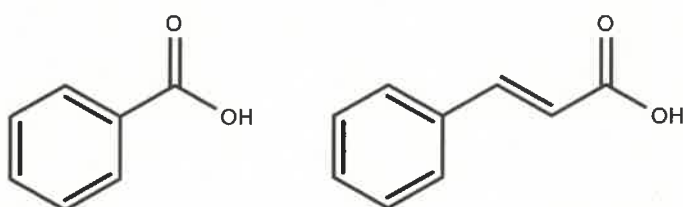


FIGURE 19.4 Structure of benzoic acid (left) and cinnamic acid (right), precursors of the two main classes of phenolic acids present in fruits and vegetables.

seeds (Zaro, Chaves, Vicente, & Concellón, 2014). As with other compounds, the health-promoting effects of phenolics depend on their bioavailability, but their concentration in plasma is very low (Konic-Ristic et al., 2011).

19.3.3.1 Phenolic acids

Phenolic acids are derivatives of benzoic and cinnamic acids (Benbrook, 2005) (Fig. 19.4). The most abundant benzoic acid derivatives are *p*-hydroxybenzoic, vanillic, syringic, and gallic acids. Common cinnamic acid derivatives include *p*-coumaric, caffeic, ferulic, and sinapic acids. The derivatives differ in the degree of hydroxylation and methoxylation of the aromatic

ring. Caffeic acid is the most abundant in berry fruits (Mattila, Hellstrom, & Torronen, 2006), while coumaric is present at lower concentrations. Ferulic acid is 90% of total phenolic acids in cereals. Frying and roasting readily degrade phenolic acids (Rashmi & Negi, 2020). Improved retention is observed under frozen storage.

19.3.3.2 Flavonoids

They are a large group of phenolic compounds with two aromatic rings associated by a C3-oxygenated heterocycle. Flavonoids are further divided in subclasses: flavones and flavonols, flavanones and flavanols, isoflavones, proanthocyanidins, and anthocyanidins (Thakur et al., 2020).

19.3.3.2.1 Flavones and flavonols

Flavonols have a central 3-hydroxypyran-4-one ring. Flavones lack the OH in position 3 (Fig. 19.5). Rutin, luteolin, and apigenin are common flavones, while the most abundant flavonols are quercetin and kampferol (Manach, Scalbert, Morand, Remesy, & Jimenez, 2004). Onions are rich in quercetin. Blueberry also has high concentrations, especially in peel, because their biosynthesis is stimulated by light exposure. Celery is a good source of flavones. In citrus, they are also abundant, in the peel and high concentrations are also present in herbs (Sljimestad, Fossen, & Brede, 2020).

19.3.3.2.2 Flavanones and flavanols

Flavanones have no double bond in position 2,3 of the central ring, while flavanols lack a carbonyl group at position 4 (Fig. 19.6). The genus *Citrus* accumulates flavanone glycosides. Orange juice contains the flavanone glycoside hesperidin (Tripoli, La Guardia, Giammanco, Di Majo, & Giammanco, 2007). The flavanols catechin and epicatechin are common in grape, capers, and parsley (Faggio et al., 2017).

19.3.3.2.3 Proanthocyanidins

Proanthocyanidins are oligomeric flavonoids (oligomers of catechin and epicatechin). They are common in grape peel, seeds, and wine, in which they are related to astringency (Basalekou et al., 2019). Sources of proanthocyanidins include apple, almond, and blueberry (Bodoira & Maestri, 2020; Li, Han et al., 2020; Li, Cheng et al., 2020).

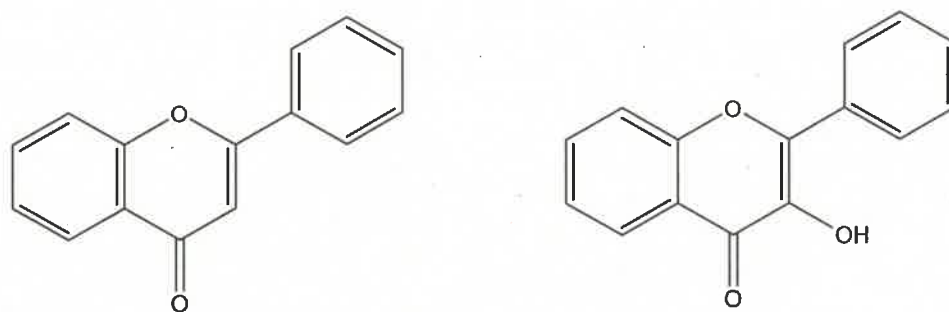


FIGURE 19.5 General structure of flavones (left) and flavonols (right).

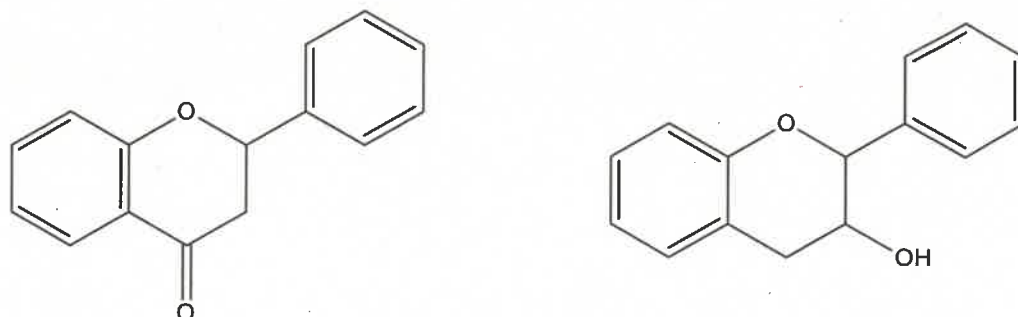


FIGURE 19.6 General structure of flavanones (left) and flavanols (right).

19.3.3.2.4 Anthocyanidins

The term anthocyanin derives from the Greek words *anthos* and *cyan*, meaning flower and blue. They provide characteristic red or purple colors to some fruits (Faggio et al., 2017). Yet, some forms are uncolored. Anthocyanidins contribute to the antioxidant capacity of fruits and vegetables. Because of their widespread distribution, anthocyanins are common antioxidants in the human diet. The antioxidant capacity of anthocyanins relies on their ability to donate H from aromatic hydroxyls to free radicals and to delocalize unpaired electrons. The basic structure of anthocyanidins derives from the flavilium cation (2-phenyl-benzopyril). Owing to their polarity, anthocyanins are water soluble. Six anthocyanidins are found in fruits and vegetables: pelargonidin, cyanidin, delphinidin, peonidin, petunidin, and malvidin. They differ in the substituents (OH, H, or OCH₃) associated with the phenolic rings. Their distribution in fruits is iscyanidin: 30%; delphinidin: 22%; pelargonidin: 18%; peonidin: 7.5%; malvidin: 7.5%; and petunidin: 5% (Andersen & Jordheim, 2006). Hydroxyl distribution influences both the hue and antioxidant capacity of anthocyanidins. As a general rule, hydroxylation induces a shift of the visible max toward longer wavelengths (bathochromic effect, also known as blueing effect) (Gómez-Míguez, González-Manzano, Escribano-Bailón, Heredia, & Santos-Buelga, 2006). Methylation of hydroxyl groups causes the reverse trend. Consequently, the anthocyanidins with more hydroxyls are bluish, while those with methoxyl groups are red (Delgado-Vargas & Paredes-López, 2003). They are glycosylated or acylated, which increases or reduces solubility, respectively. Sugars may be present as mono-, di-, or trisaccharides. A major form of anthocyanins in most fruits is the monoglycoside (70%–100% of the total). Glucose, galactose, rhamnose, and arabinose are the most common sugars in anthocyanins. Acylating agents include caffeic, *p*-coumaric, ferulic, and sinapic acids (Castañeda-Ovando, Pacheco-Hernandez, Paez-Hernandez, Rodríguez, & Galan-Vidal, 2009). Anthocyanins form copigments with some metallic ions or colorless organic compounds in complex associations. Such interaction may change pigment hues and increase intensity (Boulton, 2001). Anthocyanin color is affected by pH. At low pH, the flavylum cation contributes purple and red colors. At higher pH, the quinoidal blue species predominate. Anthocyanin concentrations range from undetectable up to 611 mg/100 g FW in bilberry (Table 19.9) (Faggio et al., 2017).

TABLE 19.9 Anthocyanidin concentrations in common fruits. (Bhagwat, Haytowitz, and Holden, 2011).

Fruit	Content (mg/100 g FW)
Acai	53.6
Acerola	22.6
Apple, Fuji	0.7
Apple, Gala	1.1
Apple, Red Delicious	3.8
Avocado	0.3
Blackberry	90.6
Blueberry	141.0
Cherry	27.7
Cranberry	85.5
Currant, black	154.8
Currant, red	75.0
Eldberry	485.3
Grape, Concord	65.6
Grape, red	44.0
Nectarine and peach	1.8
Pear	12.2
Plum red	7.0
Plum black	39.7
Plum yellow	0.3
Raspberry	40.9
Strawberry	23.8

Adapted from Bhagwat, S., Haytowitz, D. B. & Holden, J. M. (2011). 'USDA database for the flavonoid content of selected foods', Release 3. Nutrient Data Laboratory, Beltsville Human Nutrition Research Center, Agricultural Research Service, U.S. Department of Agriculture.

19.3.3.3 Others

Lignans are diphenolic structures formed by the association of two cinnamic acid derivatives. They are present in linseed, cereals, and legumes, but not significantly in fruits and vegetables. The main dietary sources of lignans are linseed, soybean, and whole cereals and berries among fruits (Durazzo et al., 2019). Stilbenes have received great attention due to their suggested anticarcinogenic properties (Fig. 19.7). Resveratrol belongs to this group; it accumulates in response to pathogens and other stresses in grapes (González-

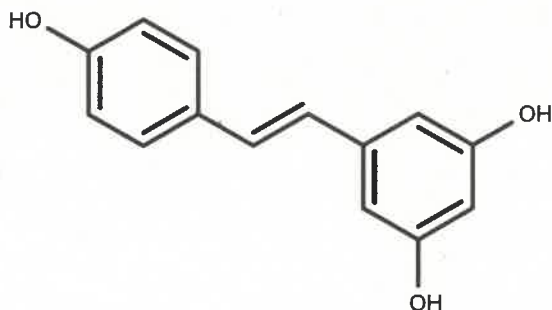


FIGURE 19.7 Structure of resveratrol. This compound has been studied in detail in grapes and may have anticarcinogenic properties.

Barrio et al., 2006). Stilbenes are present at high concentrations in grape, almond, bean, blueberry, bilberry, peanut, cranberry, plum, and wine (El Khawand, Courtois, Valls, Richard, & Krisa, 2018). It has also been identified in other fruits, such as blueberry. Lignin was described in Section 19.2.6.1. Due to its very low solubility and digestibility, its contribution to antioxidant activity is negligible.

19.3.3.4 Association between phenolic structures and antioxidant capacity

The structure of phenolic compounds is directly related to their antioxidant properties. A higher degree of hydroxylation of the aromatic rings increases antioxidant activity of hydroxycinnamic acids (Fan et al., 2009). More hydroxyls in the B ring also increases antioxidant activity of anthocyanins (Cao, Sofic, & Prior, 1997). Hydroxyls in *ortho* configuration enhance antioxidant activity (Zheng & Wang, 2003). The antioxidant activity of phenolic acids is enhanced by other electron-donating groups associated with the rings (Jing et al., 2012).

Glycosylation has variable effects on the antioxidant capacity of phenolic compounds. Often anthocyanins have similar antioxidant activity than the corresponding anthocyanidin. Cyanidin, delphinidin, and malvidin have similar antioxidant (AOX) capacity to their glycosylated derivatives. Yet, arabinose and rutoside glycosides and diglucosides have less antioxidant capacity than monoglucosides (Zheng & Wang, 2003). Flavonols are more potent antioxidants than anthocyanins, due to a 2,3 double bond associated with a 4-oxo function (Melidou, Riganakos, & Galaris, 2005).

19.3.4 Sulfur antioxidants

Sulfoxides and glucosinolates are among the most important sulfur antioxidants present in vegetables. Sulfoxides are common in vegetables of the genus *Allium*, particularly garlic (*Allium sativum*), one of the oldest medicinal plants. The major sulfur compounds in intact garlic are δ -glutamyl-S-allyl-L-cysteine and S-allyl-L-cysteine sulfoxide (alliin) (Butt, Sultan, Butt, & Iqbal, 2009). When raw garlic is chopped, the sulfoxides are converted to unstable thiosulfinates like allicin. Other thiosulfinates include allylmethyl-, methylallyl-, and trans-1-propenyl-thiosulfinate. Glucosinolates are present in plants of the order Brassicales. They have received great attention because their degradation products are powerful anticarcinogenic compounds. They consist of a β -D-thioglucose group, a sulfonated oxime moiety and a side chain derived from methionine, an aromatic, or a branched

amino acid. In broccoli, the most abundant is glucoraphanin (80%), followed by glucobras-sicin. Sinigrin is predominant in Brussels sprouts and mustard seeds (Bischoff, 2016).

19.3.5 Factors regulating the concentrations of antioxidants in fruits and vegetables

Several factors influence the accumulation of antioxidants in fruits and vegetables. Changes in composition from harvest to consumption depend on the compound, commodity, cultural practices, postharvest handling, processing, and home cooking conditions (Fig. 19.8).

19.3.5.1 Genetic factors

19.3.5.1.1 Species

The species determines the prevalence of specific antioxidants. With some exceptions, most fruits accumulate typical antioxidants (Table 19.6). Berries and artichokes are rich in phenolics (Avio et al., 2020; Bouali et al., 2020; Zheng & Wang, 2003). In ripe blueberry, AsA contributes only 0.4%–9.0% of total antioxidant capacity (Kalt, Forney, Martin, & Prior, 1999). The distribution of antioxidants varies among the tissues of a fruit. Water-soluble polyphenolic compounds are found primarily in skins of peaches, pears, and apples (Ain, Saeed, Barrow, Dunshea, & Suleria, 2020).

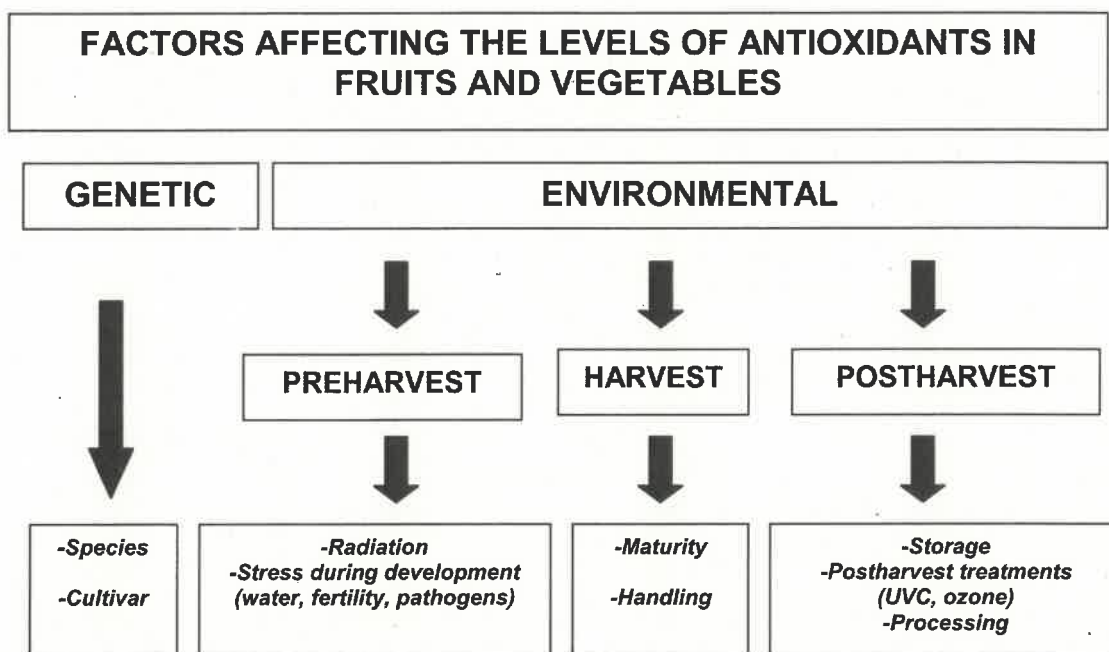


FIGURE 19.8 Factors affecting the concentrations of antioxidants in fruits and vegetables.

19.3.5.1.2 Cultivar

For a given species, antioxidant concentrations vary by cultivar (Wang & Lin, 2000). The identification of lines or mutants that accumulate antioxidants might be useful in breeding programs to improve the nutritional value of fruits and vegetables. Overexpression of high-pigment (*hp*) in tomato increased carotenoid accumulation (Liu et al., 2004). Also, in tomato, overexpression of phytoene synthase and lycopene cyclase increased β -carotene and lycopene (D'Ambrosio et al., 2004). In carrot, overexpression of β -carotene ketolase from *Haematococcus pluvialis* led to accumulation of the ketocarotenoid astaxanthin (Jayaraj, Devlin, & Punja, 2007). Transgenic approaches have increased the concentrations of phenolic compounds. Transformation of tomato with a *Petunia* gene for chalcone isomerase increased the flavonol concentration in the peel 80-fold (Muir et al., 2001). While the biosynthetic pathway for AsA is established and most of its genes have been cloned and expressed in various plant species, these strategies have had limited success (Tripodi et al., 2018).

19.3.5.2 Environmental factors

19.3.5.2.1 Radiation

Modifications in the concentrations of phenolic compounds, AsA, and carotenoids are associated with changes in sunlight exposure. Fruit location within the canopy and thus sun exposure can affect the concentrations of bioactive compounds (Ali, Ejaz, Anjum, Nawaz, & Ahmad, 2020). Sun-exposed fruit sides have more phenolics and vitamin C than shaded regions (Olale, Walyambillah, Mohammed, Sila, & Shepherd, 2019). In leafy vegetables, there are 10 times more flavonols in surface leaves than in internal leaves. Total phenolics doubled in tomato plants exposed to more light. These plants also accumulated more carotenoids and AsA (Gautier et al., 2008). Thus radiation interception is important to obtain commodities with increased antioxidants. But, the optimal irradiance to maximize accumulation of different antioxidants in fruits and vegetables is not established.

19.3.5.2.2 Cultivation practices

Several works analyzed the effect of cultural practices on antioxidants. Strawberries grown with plastic mulch had greater antioxidant capacity than fruits from uncovered beds (Wang, Zheng, & Galletta, 2002). High nitrogen is associated with reduced AsA (Lee & Kader, 2000). Adding compost as a soil supplement significantly enhanced AsA (Wang & Lin, 2003). Vitamin C accumulation is inversely correlated with rainfall (Toivonen, Zebarth, & Bowen, 1994). Some studies found that organic products accumulated more antioxidants and vitamins than conventionally grown commodities (Asami, Hong, Barrett, & Mitchell, 2003; Chassy, Bui, Renaud, Van Horn, & Mitchell, 2006). Other studies found no differences or opposite results (Barrett, Weakley, Diaz, & Watnik, 2007). It is not possible to conclude that organically grown products are nutritionally superior to conventional commodities (see also Chapter 19: Nutritional quality of fruits and vegetables). Antioxidant accumulation is also dependent on plant nutritional status (Sonntag et al., 2020). The roostock/cultivar combination also modulates antioxidant accumulation in plums (Radović et al., 2020).

19.3.5.2.3 Maturity at harvest

Fruit developmental stage has a large impact on total antioxidant capacity. These changes depended on the commodity. In tomato and pepper, total antioxidant capacity increases as carotenoids and vitamin C accumulate during ripening. Total anthocyanin increases during ripening in all berries (Wang & Lin, 2000). Yet, the antioxidant capacity peaks in other species early in development. During berry ripening, anthocyanins accumulate while phenolic acids decrease (Lin et al., 2020; Wang & Lin, 2000). Carotenoids increase during development in pepper, tomato, mango, and *Prunus* species (Kim et al., 2020). In products in which anthocyanins or chlorophylls dominate, carotenoids decrease during development. In cherry, AsA accumulates during ripening (Xu et al., 2020).

19.3.5.2.4 Wounding

Tissue damage greatly affects total antioxidant concentration. Cell disruption exacerbates turnover of AsA and phenolic compounds. Eliminating cellular compartmentalization triggers oxidation of preexisting phenolics by PPOs and increases hydrogen peroxide, providing the cosubstrate for POD-mediated degradation. Wounding also alters phenolic biosynthesis (Hussein, Fawole, & Opara, 2020). In lettuce, cutting induced phenylalanine ammonia lyase and led to accumulation of chlorogenic acid (Choi, Tomás-Barberán, & Saltveit, 2005). Carotenoid turnover is also accelerated by oxygen, but they are more stable than other AOX groups. Careful handling reduces antioxidant losses (Erkan & Dogan, 2019).

19.3.5.2.5 Storage

Refrigeration slows deterioration of vitamin C. Except for broccoli and banana; most commodities lose visual quality before significant loss of antioxidant capacity occurs (Kevers et al., 2007). Improper temperature management significantly reduces visual quality and thus, consumer acceptance. Ethylene induces accumulation of the bitter compound iso-coumarin 6-methoxymellein. After extended storage, both membrane disruption causing loss of cell compartmentation and the increase in ROS have been linked to antioxidant degradation (Tao, Wang, Zhang, Jiang, & Lv, 2019).

19.3.5.2.6 Other treatments

Biosynthesis of phenolics is triggered by elicitors like ultraviolet radiation or ozone. In grape, postharvest UV-C and ozone increased accumulation of resveratrol (González-Barrio et al., 2006). In strawberry, UV-C also increased phenolic compounds and antioxidant potency (Li et al., 2019). UV-B exposure increased accumulation of glucosinolates in broccoli, with the changes dependent on the combination of radiation intensity and dose applied (Darré et al., 2017; Duarte-Sierra, Hasan, Angers, & Arul, 2020).

19.3.5.2.7 Processing

Processing operations greatly affect antioxidant concentrations of fruits and vegetables (Nayak, Liu, & Tang, 2015). Effects of processing on the amount and bioavailability of antioxidants depend on treatment intensity and the specific compound (Bernhardt & Schlich, 2006). Washing and peeling may result in loss of water-soluble AOXs. In general, freezing does not reduce antioxidants, but these responses may be cultivar-dependent. Four raspberry cultivars

showed contradictory results during 1 year of frozen storage, from no change to a 12% increase and decreases of 21% and 28%, respectively (Rickman, Barrett, & Bruhn, 2007). Fat-soluble nutrients such as carotenoids and vitamin E may be released from their cellular matrices by thermal, freezing, high-pressure, or other preservation treatments. In carrot and spinach, vapor cooking increases carotenoid bioaccessibility by disrupting its complexes with proteins. Similarly, the bioavailability of lycopene increases in heat-treated tomato (Nayak et al., 2015). But, cooking can isomerize β -carotene to *cis* forms with less provitamin A activity (Deming, Baker, & Erdman, 2002; Deming, Teixeira, & Erdman, 2002). Heat, light, and oxygen accelerate carotenoid degradation (Von Elbe & Schwartz, 1996). AsA is one of the most labile antioxidants (Lee & Kader, 2000). Heat treatments degrade vitamin C and may cause leaching into the liquid medium. Blanching or even freezing and thawing can cause losses of up to 25%. More drastic treatments destroy 90% of AsA. Factors affecting AsA loss include the severity of heating, the exposed surface (which affects leaching in the cooking medium), oxygen availability, and pH (Eitenmiller & Landen, 1999). AsA is more stable at acidic pH, under reduced oxygen, in darkness, and in the presence of chelating agents. Consumption of fresh foods is the best way to minimize AsA losses. Processing can decrease phenolic antioxidants (Tiwari & Cummins, 2013). Peeling or cutting reduces quercetin by only 1%, but water cooking might destroy 75%. Strawberry processing into jams decreased ellagic acid and flavonols by 20% (Häkkinen, Heinonen et al., 1999; Häkkinen, Karenlampi, Heinonen, Mykkanen, & Torronen, 1999). During drying, anthocyanins were more readily degraded than other phenolics. Anthocyanin losses in processed berries are reduced by blanching, indicating enzymatic degradation (Sablani et al., 2010).

Although processing does not increase the concentration of antioxidants, it may make them more easily extracted and bioavailable. Increased free ellagic acid was found in heated raspberry pulp. This was likely released from insoluble ellagitannins. After canning, total anthocyanins decreased up to 44%, but phenolic concentrations and antioxidant activity increased by 50% and 53%, respectively (Sablani et al., 2010). AOXs is present in foods mostly as esters, glycosides, or polymers, which are not absorbed directly. Hydrolysis of aglycones may increase their bioavailability (Hollman & Katan, 1997).

19.4 Allergens

Allergies are exaggerated immune reactions to substances that are then known as allergens (Remington et al., 2020). The first stage of allergic responses, sensitization, involves the production of immunoglobulin E antibodies as a defense response. Subsequent episodes result in the release of other substances such as histamine, leukotrienes, and cytokines that can induce observable responses. Symptoms appear immediately or after a short term of ingestion or contact. Food allergies may be induced either by consumption or contact. Consumption allergies are associated with a variety of symptoms, including but not limited to oral or general pruritus (itching), sneezing, tearing or redness of the skin, digestive symptoms (abdominal pain, vomiting, or diarrhea), urticaria, choking, dizziness, and hypotension (Skypala, 2019). Contact allergies more often lead to urticaria, contact dermatitis, conjunctivitis, or respiratory symptoms such as rhinitis or asthma. Sometimes, lip erythema swelling of the lips and tongue (angioedema) may also appear

(Muluk & Cingi, 2018). In severe cases, allergies may lead to systemic disease (anaphylaxis) and death (Remington et al., 2020). Food allergenicity depends on several factors, including the individual susceptibility, the type of allergenic substance and its concentration (Skypala, 2019). The threshold dose is dependent on age (Turner et al., 2016). Exercise, alcohol, or certain nonsteroidal antiinflammatory drugs can often be cofactors of the allergic reaction (Skypala, 2019). This has been seldom addressed with regard to fresh fruit and vegetables. Many different foods, including fruits and vegetables may contain allergenic substances (Skypala, 2019).

19.4.1 Allergens in fruits

One important source of allergic reaction in fruit is in latex-containing species. Such responses are linked to chitinases (Righetti et al., 2015; Sompornrattanaphan et al., 2019). Banana has one of the highest allergenic capacities (Nikolić et al., 2018). Kiwifruit has the most allergens identified, with 13 proteins (Le et al., 2013). Fruits belonging to the *Rosaceae* family have identified allergens. Apple is the fruit most implicated in exercise-induced anaphylaxis (Skypala, 2019). It has four identified allergens: Mal d 1 (pathogenesis-related protein), Mal d 2 (thaumatin-like protein), Mal d 3 (nonspecific lipid transfer protein), and Mal d 4 (profilin) (www.allergen.org). Apple processing, including heat treatment and its combination with reducing agents such as sulfur, may reduce allergenicity (Marzban et al., 2014). Sweet cherry (*Prunus avium*) has five identified allergens. Cherry cultivation under cover favored antioxidant accumulation without increasing the allergen Pru av 1 (Schmitz-Eiberger & Blanke, 2012). Peach fruit contains six identified allergens, but two of them (Pru p 3, nonspecific lipid transfer protein and Pru p 7, gibberellin-regulated protein) are more frequently linked to allergic episodes. Allergen concentrations change depending on the variety and maturity stage (Jin et al., 2020). Pru p 3 is more problematic, since it is the most resistant to the gastrointestinal tract and heat treatment (Tuppo et al., 2014). Peach packaging in opaque bags reduced the amount of allergens (Ma et al., 2018). The application of high hydrostatic pressures and pulsed electric fields treatments has been evaluated as a method to reduce allergenicity in processed peach (Tobajas et al., 2020).

19.4.2 Allergens in vegetables

One of the most frequent causes of adverse allergenic events is celery, for which six allergens have been identified (www.allergen.org). The concentration of allergens, as in fruit, varies depending on cultivar (Dölle et al., 2018). Celery allergies have been linked to exercise-induced anaphylaxis. Some technological factors can decrease the reactivity of allergens in celery, such as pH and heat treatment (Rib-Schmidt et al., 2018). Tomato plant and fruit can cause contact dermatitis and allergic reactions upon consumption (Martín-Pedraza et al., 2016). Seven allergenic proteins have been identified in this species. (Kurze, Lo Scalzo, Campanelli, & Schwab, 2018). Particularly, Sola l 4 is sensitive to heat treatment and can be reduced by drying (Kurze et al., 2018). An eggplant 17 kDa protein (Sola m 1) has been identified as a proteic allergen (Maity, Bhakta, Bhowmik, Sircar, & Bhattacharya, 2020). Also, this fruit is rich in histamine, which can eventually cause contact dermatitis,

followed by systemic manifestations in the digestive or respiratory tracts (Kiran Kumar, Harish Babu, & Venkatesh, 2009). In lettuce, lipid transfer protein allergen (Lac s 1) has been identified (Bascones, Rodríguez-Pérez, Juste, Moneo, & Caballero, 2009). Food allergy is the most frequent allergic reaction to lettuce (Paulsen & Andersen, 2015). Chicory may cause contact dermatitis (Herman & Baeck, 2017).

19.5 Conclusion

In this chapter, we reviewed the main components present in fruits and vegetables in relation to their nutritional and quality value in postharvest systems. Fruit and vegetable consumption makes a major contribution of nutritionally relevant components such as water, fiber, some minerals, and vitamins (especially C and provitamin A). In addition, they are an important source of dietary antioxidants and bioactive molecules. Major advances have been made in the characterization of the isolated metabolites. However, the interaction between the different components is far from being understood. Both the level and bioavailability of fruit and vegetable components show wide variation depending on the commodity, production, and postharvest processing conditions considered. Growing evidence supports the central role of fruits and vegetables in the protection against several chronic and degenerative diseases as well as in the prevention of some types of cancer. Recent works also point out several other relevant benefits, such as the modulating the immune system and regulating the gut microbiota. All such findings increasingly stress the relevance of promoting fruit and vegetable consumption, especially considering that fruit and vegetable intake is still well below the current WHO recommendation. Efficient postharvest systems must also have a key role preventing losses of the large set of highly valuable compounds present in fruits and vegetables.

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