FUNCTIONAL FOODS AND NUTRACEUTICALS SERIES

Phytochemicals in Citrus

Applications in Functional Foods

EDITED BY
Xingqian Ye

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FUNCTIONAL FOODS AND NUTRACEUTICALS SERIES

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Series Preface

In recent years, consumers have paid more attention to their health led by the increasing belief that the food they eat contributes directly to it. The consumption of functional foods has emerged as a major consumer-driven trend, playing an outstanding role in the prevention of nutrition-related diseases and improving the physical and mental well-being of consumers. This trend is expected to continue, which increases the need for scientific information concerning all aspects of functional foods. The aim of the "Functional Foods and Nutraceutical" series is to provide a comprehensive source of up-to-date information on the latest developments in this field. Many bioactive components present in food, from both plant and animal sources, have been shown to be effective in disease prevention and health promotion. The series covers relevant aspects of chemistry, biochemistry, epidemiology, nutrigenomics and proteomics, engineering, formulation, and processing technologies as they relate to nutraceuticals, functional foods, and dietary supplements, as well as new product developments and research progress.

Extensive studies have confirmed that diets rich in fruits and vegetables are strongly associated with numerous health benefits and a lower risk of disease. Citrus fruits, one of the most popular fruits in world market today, have long been valued as part of a nutritious and tasty diet. Citrus fruits, ranging from sweet to sour in taste, include oranges, tangerines, grapefruits, limes, and lemons. Well-known for their vitamin C content, these fruits also provide energy, fiber, folate, and potassium. In addition, they are a good source of disease-fighting antioxidants such as flavonoids. The different flavors of citrus are among the preferred in the world, and it is increasingly evident that citrus fruits not only taste good, but are good for our health too. It is well established that citrus fruits and products are a rich source of vitamins, minerals, and dietary fiber (nonstarch polysaccharides) that are essential for normal growth, development, and overall nutritional well-being. Moreover, there is an increasing awareness that some biologically active, non-nutrient compounds found in citrus and other plants (phytochemicals) can also help reduce the risk of many chronic diseases. For instance, citrus has been shown to help keep your heart healthy, specifically oranges, which have been shown to reduce the risk of heart disease and arrhythmias.

The "Functional Foods and Nutraceutical" series is appropriate for academic use, aimed at providing a solid scientific reference for faculties and students in the fields of food science and technology, nutritional science, and pharmaceutical science. This series is also meant as a reference for food science professionals in either government or industry pursuing functional food research, food ingredient development, or research and development for food companies. Herein, readers will obtain a current and sound scientific fact base of information about functional food products and their latest developments. It is our hope that the scientific community will appreciate our endeavor in preparing this series and the impact it will have on furthering the knowledge of functional foods and nutraceuticals.

John Shi, PhD
Series Editor
Senior Research Scientist
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Preface

Citrus is the largest genus in the Rutaceae family native to tropical and subtropical regions, and now it is the most traded horticultural product in the world. Taxonomic identification is difficult because there are many spontaneous and commercial hybrids, but citrus can be generally classified into the following categories: sweet oranges, mandarins (tangerines, clementines), sour/bitter oranges, lemons, limes, grapefruits, pummelos, hybrids, citrons, and so on. They are mainly characterized by a rough and bright color that ranges from yellow to orange. Citrus fruits not only contain large amounts of vitamin C, but also a variety of beneficial nutrients and vitamins such as folate, thiamin, minerals, fiber, carotenoids, flavonoids, and limonoids. Vitamin C is a powerful antioxidant that protects the body from damaging free radicals. It is also required for the synthesis of collagen, which helps wounds heal and helps hold together blood vessels, tendons, ligaments, and bone. Folate is essential for cell division and DNA synthesis. Thiamin is a B vitamin, which is important in metabolism. Citrus fruits have the advantage of containing several different antioxidants. There is considerable evidence that citrus fruits have antioxidant and antimutagenic properties and positive associations with the health of bones, the cardiovascular system, and the immune system. For example, citrus flavonoids are strong antioxidants that can neutralize free radicals and may guard against heart disease. Studies show that citrus flavonoids can improve blood flow through the coronary arteries, reduce the ability of arteries to form blood clots and prevent the oxidation of LDL cholesterol, which is an initial step in the formation of arterial plaque. Citrus fruits, as a whole, are packed with beneficial antioxidants and essential nutrients that can promote heart health and possibly reduce the risk of some chronic diseases, from cardiovascular disease and cancer to skin damage from sunlight.

Citrus fruits are valuable to human health, we should consume them daily to overcome and prevent micronutrient deficiencies. They are beneficial to the health of people suffering from obesity and diet-related chronic diseases as they contain no fat, sodium, or cholesterol. Because of the numerous nutritional and health benefits associated with the consumption of citrus fruits, they can be considered as part of a balanced diet.

This book, *Phytochemicals in Citrus*, contains 16 chapters providing a knowledge base on the chemical composition, bioactive components, biochemical properties, food use, and health benefits of citrus fruits. The information in this book will help readers to better understand the health benefits of citrus fruits, citrus products, and their dietary applications.

We thank all of the contributing authors for their cooperation in preparing this book, which we hope will serve as an excellent reference for those interested in citrus fruits, as health-promoting foods, and the science and technology of their bioactive components.

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Xingqian Ye, PhD, is a professor in the Department of Food Science and Nutrition, and the deputy dean of the College of Biosystems and Food Science at Zhejiang University in China. Prof. Ye earned a PhD degree in agriculture products storage and processing from Zhejiang Agricultural University. He has also conducted collaborative research in Bulgaria, Canada, the United States, and Greece. His research focuses on fruit and vegetable processing technology, nutraceuticals, and functional foods from fruits and vegetables. Recently, he has studied the processing and comprehensive utilization of Chinese bayberry, mandarin, and other local fruits and vegetables, especially the identification and separation of their phytochemicals. Prof. Ye has also worked on the development of mixing fruit, vegetables, nuts, and cereals to enhance their antioxidant capacity after processing. He has also studied the stability of flavonoids after ultrasonic treatment.

Dr. Ye has published more than 200 research papers in refereed scientific journals, along with 10 book chapters and has been invited to a number of presentations. He holds 35 Chinese patents and has edited *Chinese Dates: A Traditional Functional Food* (CRC Press, 2016), as well as 4 other books and a textbook on fruit and vegetable processing in Chinese (from the second edition to fourth edition). He has received several scholarly awards including the second place Award (three times) for Science and Technology from the Zhejiang Provincial Government. Prof. Ye was the guest editor of *LWT—Food Science and Technology* for the special issue on *Food Innovation in China* in 2014. He is an associate editor of *Food Quality and Safety* (Oxford University Press) and editorial board member of the *Journal of Food Engineering*, the *Journal of Chinese Institute of Food Science and Technology*, and four other Chinese journals.

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1 Citrus Fruits, Varieties, Chemical Properties, and Products in the Processing Industry

Xingqian Ye, Jianle Chen, Jianguo Xu, and Jianchu Chen

CONTENTS

1.1 CITRUS FRUITS AND THEIR BIOLOGICAL STRUCTURE

Citrus fruits, compared with other fruits, have specific characteristics. They differ botanically from berries and other fruits, and have a high nutritional value (Nagy and Shaw 1977; Ye et al. 2005).

1.1.1 The External Form of Citrus Fruits

Citrus fruit is usually globose, and its major morphological features are described in Figure 1.1 (Ye et al. 2005). The end with the pedicel is considered the base, and the opposite end is the top. A horizontal line is known as the equator. The part between the equator and the base is called the lower shoulder, and the part between equator and the top is called the upper shoulder. The part near the base is the pedicel side, and the part near the top end is the column end, where the navel is usually located. Different species vary greatly in navel size and shape. The fine points of the fruit surface are oil brittle points, with various essential oils contained in the interior (Figure 1.1).

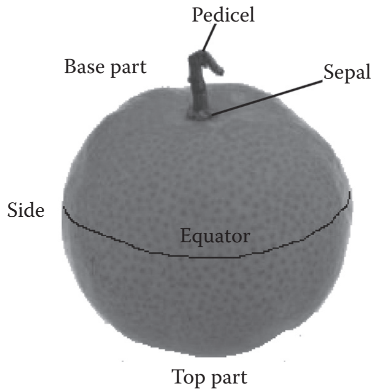


FIGURE 1.1 Citrus fruits and their nomenclature.

1.1.2 Size and Shape

Different species of citrus vary greatly in size. Generally speaking, the horizontal diameters of some common species are as follows: orange (5.7–9.5 cm), mandarin or tangerine (5.7–7.5 cm), lemon (4.4–6.4 cm), lime (3.5–5 cm), grapefruit (9.5–14.5 cm), pomelo (8–20 cm), and kumquat (1.5–3 cm). There are also great size differences between different cultivars in the same species (Ye et al. 2005; Deng et al. 2008; Citrus Pages 2014).

1.1.3 The Internal Structure of Citrus Fruits

Compared with other fruits, the internal structure of citrus fruits is more complex. From outside to inside, are peel (flavedo, oil gland, albedo, and vascular bundle),

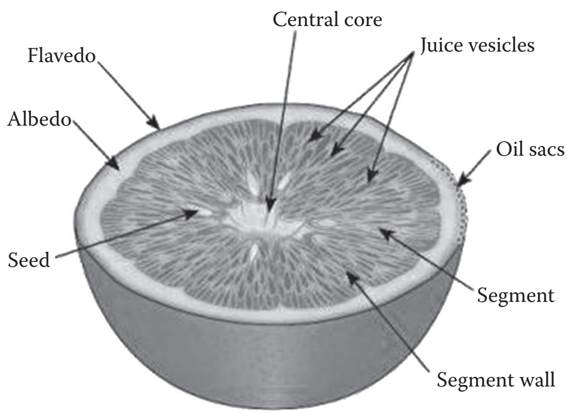


FIGURE 1.2 Structure of citrus fruits.

segments (segment membrane, juice vesicles or sac and seed), and the central core or pith (vascular bundle and parenchyma) (Figure 1.2) (Ye and Liu 2005; Kimball 1999).

1.1.3.1 Peel

Citrus peel can be divided into two layers, the epicarp (flavedo and albedo) and endocarp.

1.1.3.2 Epicarp

The epicarp is actually epidermis consisting of a wax plate of upper epicuticular wax, cuticle, and polygonal epidermic cells, and an outer wall that is horny. The exterior of epidermal cells is covered with a layer of wax that has a protective effect. The epicarp also has stomata consisting of a pair of guard cells that serves as one of the channels of fruit respiration. Generally, a citrus fruit has little or no porosity in the base, since the waxy layer is thicker at this point, and the stomata of citrus are often filled at maturity.

1.1.3.3 Mesocarp

The mesocarp includes two layers, the albedo and flavedo. The albedo contains oil sacs and pigments, while the flavedo consists of vascular tissue. Albedo cells are green, yellow, or orange, with oil sacs. The lower part of the epidermal layer consists of layers of small elongated cells, followed by layers of larger suborbicular cells, distributed before oil sacs, and finally a mix with albedo on top of the oil sacs. These cells are rich in plastids. When the fruit is ripe, when the weather turns cold, chloroplasts turn into chromoplasts. This causes the fruits to turn yellow or orange, and it can also be achieved with artificial de-greening treatments. As for the late ripening fruit, if the fruit were left on trees until the next spring, chromoplasts would turn into chloroplasts due to climate warming. Since mature citrus flavedo is rich in chromoplasts, the pigments therein are carotenoids and flavonoids, which are all beneficial to human health. In recent years, many papers have been published focused on the extraction of pigments from albedo in order to enhance or improve the color quality of citrus juice and other foods and for nutraceuticals.

1.1.3.4 Oil Sacs

Oil sacs, also called oil glands, consist of a cavity containing several aromatic oils, surrounded by a circle of cellular degradation. The outermost skin layer is the parenchyma of the albedo. These surrounding cells are the source of the oil, consisting of thin walls that are easily broken when mature. In a citrus fruit, the fruit stem has more oil glands than the top part, and the number of oil glands and the properties of the oils therein vary greatly between different *Citrus* species. Manual extraction of essential oils is efficient with lemon, orange, lime, tangerines, and others, but most mandarin oil is a low quality essential oil.

1.1.3.5 Flevedo

The flevedo is composed of a layer of loose, tubular cells with many branches. These cells are interwoven into a continuous network structure with large gaps. Cytoderm is rich in pectin, and an obvious thickening effect can be observed under the electron microscope since it is the site that has the highest pectin content within the citrus fruits. Hence, in general the raw material of artificial citrus pectin is extracted from the flavedo. The flavedo also contains flavonoids, some of which impart a bitter taste. Early on, people found that in grapefruit, oranges, lemons, and mandarin, flavonoid content in flavedo was higher than in juice, segment membrane, or albedo. The flavedo is also the main location of another bitter taste and health factor, limonoids. The thickness of flavedo varies in different *Citrus* species. Pomelos and grapefruits have the thickest, followed by oranges, natsumikans, and lemons, while mandarins and tangerines have the thinnest. In fruit juice production, the thickness of the flavedo is a major determinant of the appropriate juicer arrangement. If pressing is excessive, more flavedo is pressed into juice, making juice bitter with a content of flavonoids and limonoids substances that is too high. This is one of the causes of poor quality fruit juice by the deep-pressed method. When producing peeled mandarin segments in syrup production, the thickness of the flavedo is directly related to the ease of peeling. As for orange cake and fruit candy production, it is more related to the thickness and tenderness of the flavedo.

1.1.3.6 Citrus Segment

The interior part of the flavedo is the segment, which is thought to have developed from the endocarp. Generally, mandarin and tangerine have about 10 segments, kumquat has 3–6, while polemo has 13–25 and lemon has 7–10. The citrus segment is composed of a membrane, vesicle (sac), and seeds. The seeds of satsuma, a mandarin, degenerate because pollination does not occur. Each segment in the fruits is arranged in a ring with a central core or pith.

The orange vessels are a layer of reticulated vascular tissue that surround the segment and contain flavonoid glycosides, pectin, cellulose, and semicellulose. They may be used as a drug, but also as the material for pectin extraction. Their degree of adhesion to the segment affects the ease of peeling and processing.

There is a layer of waxy cuticle on the segment membrane consisting of six to eight layers with a relatively loose, full layer of two to three mesophyll cells between segments. The outmost layer is a mixture of mesophyll cells and flavedo. The structural components of segment membranes are very closely related with the separation of citrus segments. Generally, mandarins or tangerines are easier to peel and

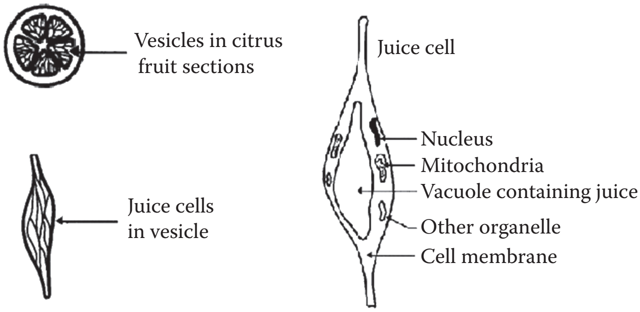


FIGURE 1.3 Citrus juice cell and vesicle (sac) cited. (From Kimball, D. A., *Citrus Processing—A Complete Guide*, 2nd ed., Aspen Publishers, Gaithersburg, MD, 1999.)

separate segments, and grapefruits are more difficult. Segment membranes also contains bitter substances, and one must be careful not to put too much pressure on the segment membrane during processing, especially in grapefruit, since they are thought to contain the highest content of limonin.

The sac is also called the juice vesicle (Figure 1.3). It is the edible part of citrus fruit located on the interior of the segment, and it is derived from independent meristems that form the sac and sac stem. The sac and sac stem surface contain wax (Kimball 1999). This is a major factor in maintaining the integrity of canned orange segments in syrup; however, in the manufacture of sac juice or drink, this can obstruct the separation of sac into a single. The sac surface also contains some pectin, and therefore treatment with calcium salt increases its hardness. The shape of the sac is related to the appearance of processed products, and canned mandarin segments in light syrup require slender sacs and short stems, firmly bonded with each other. The interior of sacs consists of thin-walled cells, characterized by large vacuoles, with lipid droplets, mitochondria, leucosomes and chromoplasts. These thin-walled cells are easily broken, thereby creating juice. Juice is mainly vacuolar sap, containing a wealth of nutrients, especially vitamins and minerals (Tisserat et al. 1990).

1.1.3.7 Citrus Seeds

Citrus seeds are often located in the interior of segments, developed from a fertilized ovule, but a fertilized ovule can also form seedless fruit. Citrus seeds contain a variety of fat, protein, and bitter substances that have a great impact on the processing and production of segments. Usually, seedless is preferred for fresh consumption. Seeds are also undesirable during juice processing, and pressure or fine filtering of crushed seed should be avoided; otherwise, it would easily make the juice bitter. On the other hand, from a comprehensive point of view, we can use seed oils and bitter substances in seeds for industrial and agricultural production services.

1.1.3.8 Central Core or Pith

The central core is also called the pith and is composed of several vascular bundles surrounded by a loose spongy group. The vasculature extends from the seed to the pedicel end. In citrus processing, the pith only affects the whole press of orange juice, and the vascular bundle and spongy tissue can increase the particle content of the fruit juice. In addition, spongy tissue is similar to flavedo in that excessive pressing will increase the glycoside extract and a mixture of other undesirable substances.

1.2 CITRUS FRUIT PRODUCTION

Citrus fruits are one of the most important agricultural products in the world, produced in more than 90 countries and regions in the world. World citrus production and consumption have experienced a strong growth period since the middle of the 1980s. The yield, total level of consumption, and consumption per capita of mandarins, tangerines, sweet oranges, pomelos, grapefruits, lemons, and limes have all experienced a rapid growth.

During the year from 1999 to 2000, annual production reached 90 million metric tons—more than grapes and bananas—the highest production among all the fruits.

International trade year volume was more than $65 billion, following wheat ($160 million) and maize ($100 billion), and a further increase in production and consumption is expected (FAO: http://www.fao.org/statistics/en/). Citrus production and export are important sources of income in many countries, while citrus are also a cheap source of vitamins, which is beneficial to nutrition, health, and food safety. With transportation and packaging costs reduced and the quality improved, the growth of citrus processing products is very fast, and is showing a strong momentum of development (Liu 2012).

TABLE 1.1
Fresh Citrus Fruit, Production, Supply, and Distribution in Selected Countries (1000 Metric Tons)

Sweet Orange	2011/2012	2012/2013	2013/2014	2014/2015	July 2016
Fresh production	53,830	49,871	52,144	48,772	45,763
Fresh domestic consumption	30,837	28,948	30,693	28,388	28,191
Processing	22,729	20,662	20,907	20,123	17,293
Export	3,932	3,889	4,002	4,051	4,309
Import	3,668	3,628	3,458	3,790	4,030
Tangerines/Mandarins					
Fresh production	23,906	24,679	26,695	28,557	28,963
Fresh domestic consumption	22,322	23,247	25,068	26,826	27,285
Processing	1,411	1,384	1,425	1,571	1,491
Export	2,389	2,165	2,483	2,337	2,322
Import	2,216	2,117	2,281	2,177	2,135
Grapefruit					
Fresh production	5,544	5,842	6,067	6,057	6,277
Fresh domestic consumption	4,602	4,818	5,087	5,260	5,540
Processing	873	954	907	732	674
Export	800	813	825	736	758
Import	731	743	752	671	695
Lemon/Lime					
Fresh production	6,524	6,512	6,216	7,301	7,001
Fresh domestic consumption	4,478	4,582	4,605	4,849	4,748
Processing	1,854	1,904	1,543	2,328	2,097
Export	1,689	1,552	1,590	1,725	1,791
Import	1,497	1,526	1,522	1,601	1,635

Source: USDA: http://www.fas.usda.gov/commodities/citrus-fruit.

TABLE 1.2
Potential Yield of Products from Citrus Fruits

Products	Orange/%	Grapefruit/%	Satsuma Mandarin/%
Juice	48%	48%	52%
Segment in light syrup			65%–70%
Dry peel			
Dry pulp w/o molasses, 10% H_2O	9.80	10.62	
Dry pulp, w/o molasses	7.11	7.25	
Molasses, 72 ^{0}Brix	3.43	3.89	
Ethanol from molasses (L, 100%)	0.49	–	
Cold pressed oil and limonene	0.74	0.26	0.76
Pulp wash solids	0.49–0.74	0.26–0.52	
Frozen pulp	4.9	7.77	
Oil-phase essence	0.0123	0.0077	
Aqueous essence at 15% alcohol	0.049	0.052	
Pectin (150 grade)	3.18	2.59	2.00
Seed oil	0.05	0.23	
Hesperidin	0.49	–	0.45
Naringin	–	0.52	
Limonoid		0.30	0.30

According to USDA statistics, the main producing countries in the world, during the years 2015 and 2016, had a total citrus production of 88 million tons, among which, oranges have 45.76 million tons, mandarins and tangerines have 28.96 million tons, grapefruits and pomelos have 6. 27 million tons, and lemons and limes have 7.00 million tons (Table 1.1). Analysis of nearly 5 years of production data has indicated that orange products are on the decline, but that mandarins or tangerines have increased the most, and that grapefruits, pomelos, lemons, and limes have had a slight rise (Table 1.2).

The leading producers of citrus are China, Brazil, the United States, Mexico, Turkey, Egypt, and so on. China has the largest production. In July 2016, it reached 31.3 million tons, accounting for 35.57% of the world's output; followed by Brazil with a production of 14.35 million tons, accounting for 16.31% of the world's output (Table 1.3).

Among *Citrus* species produced worldwide, the orange accounts for 52%, mandarin and tangerine for 33%, and lemon and pomelo for about 7% of total production. In terms of production of the total output of citrus, nearly 60% is for the fresh market consumption and about 40% is used for processing. But in Brazil, recent data show that the most abundant use is for processing of orange juice. Mandarins and tangerines are mostly used for fresh food, the main production country being China. In terms of raw materials of citrus fruit production, 80% are oranges, 8% are grapefruits, and 5% are lemons, mandarins, and tangerines (Table 1.4).

TABLE 1.3
Fresh Citrus Production in Selected Countries (1000 Metric Tons)

	Oranges	Tangerines/ Mandarins	Grapefruits	Lemons/ Limes	Total	%
Brazil	14,350				14,350	16.31%
China	7,000	20,000	4,300		31,300	35.57%
European Union	6,055	3,035	97	1,260	10,447	11.87%
United States	5,371	876	735	847	7,829	8.90%
Mexico	3,535		430	2,270	6,235	7.08%
Egypt	2,750				2,750	3.12%
Turkey	1,700	1,040	200	670	3,610	4.10%
South Africa	1,560		330	345	2,235	2.54%
Morocco	925	1,065			1,990	2.26%
Argentina	800	350		1500	2,650	3.01%
Vietnam	520				520	0.59%
Australia	455				455	0.52%
Costa Rica	315				315	0.36%
Guatemala	155				155	0.18%
Israel	105	240	185	60	590	0.67%
Japan		1,115			1,115	1.27%
South Korea		640			640	0.73%
Thailand		375			375	0.43%
Other	167	227	0	49	443	0.50%
Total	45,763	28,963	6,277	7,001	88,004	100.00%
	52.00%	32.91%	7.13%	7.96%	100%	

Source: USDA: http://www.fas.usda.gov/commodities/citrus-fruit.

TABLE 1.4
Citrus Production and Processing (1000 Metric Tons, %)

		2011/2012	2012/2013	2013/2014	2014/2015	July 2016
Orange	Fresh production	53,830	49,871	52,144	48,772	45,763
	Processing	22,729	20,662	20,907	20,123	17,293
	% of processing	42.22	41.43	40.09	41.26	37.79
Grapefruit	Fresh production	5,544	5,842	6,067	6,057	6,277
	Processing	873	954	907	732	674
	% of processing	15.75	16.33	14.95	12.09	10.74
Lemon and lime	Fresh production	6,524	6,512	6,216	7,301	7,001
	Processing	1,854	1,904	1,543	2,328	2,097
	% of processing	28.42	29.24	24.82	31.89	29.95
Mandarin and tangerine	Fresh production	23,906	24,679	26,695	28,557	28,963
	Processing	1,411	1,384	1,425	1,571	1,491
	% of processing	5.90	5.61	5.34	5.50	5.15

1.3 MAIN *CITRUS* SPECIES AND PRODUCTION

Citrus fruits belong to *Rutaceae aurantioideae*. Since 1753, when Linneaus designated *Citrus* L. many scholars have performed a series of morphological, cytological and molecular level studies. Notably, in the work of the American taxonomist W. T. Swingle, and the Japanese scholar T. Tanaka. The former divided *Citrus* L. into 16 species, and the latter divided *Citrus* L. into 159 species. Swingle's classification is simple and clear, but many of the horticultural species cannot be determined (Swingle and Reece 1967), while Tanaka's classification is conducive to the work of the horticultural industry, but is too complex for most of the food science industry and consumers (Tanaka 1977). Since they easily hybridize between species, and due to apomixis and clonal variations, the number of species of citrus is very difficult to accurately determine. According to the views of the pomologists and food scientists, this chapter summarizes the general classification and relationship of citrus fruit from citrus fruit characteristics in the perspective of economic value. It references China's latest research from Kimball (1999) and Deng (2008), but recent advances in molecular biology are not included.

- *Citrus sinensis* (L.) Osbeck—Sweet orange
- *Citrus reticulata* Blanco—Mandarin, tangerine
- *Citrus aurantium* L.—Sour or bitter orange
- *Citrus paradisi* Macfadyen—Grapefruit
- *Citrus grandis* (L.) Osbeck or *Citrus maxima* (Burm.) Merrill—Pomelo
- *Citrus limon* L. Burm. f.—Lemon
- *Citrus aurantiifolia* (Christm.)—Lime
- *Citrus limonia*—Rangpur
- *Citrus medica* L.—Citron

Main varietal group

- *Citrus reticulata* Blanco—Mandarin, tangerine

1.3.1 Mandarins

Macroacrumen mandarins: Satsuma mandarin (*C. unshiu* Marc); Ougan (*C. suavissima* Hort. ex Tanaka); Jiaogan (*C. tankan* Hort.) (Tankan); King mandarin (*C. nobilis* Loureiro); Mediterranean mandarin (*C. deliciosu* Tenore).

Microacrumen tangerines: Ponkan (*C. reticulata* Blanco); Manju (*C. tardiferax* Hort. ex Tanaka); Hongju (red tangerine) (*C. tangerina* Hort. ex Tanaka); *Citrus paradisi* Macfadyen—Grapefruit (*Citrus paradisi* Macfadyen) (white or common, blood or pink, acidless); Pomelo [*Citrus grandis* (L.) Osbeck or *Citrus maxima* (Burm.) Merill] (white or common, blood or pink, acidless).

Dr. Mabberley, president of the IATP since 2005, deserves a special mention. He has presented the most interesting new views of citrus and the relationships between "the true citrus types." In his paper on native Australian citrus types, he introduces a new species and assigns the Swingle genera Microcitrus and Eremocitrus in the genus *Citrus*. In a classification for edible citrus, he states that there are only three *Citrus* species, citron, pomelo, and mandarin, which are then involved in several hybrids. In his more recent study on citrus linnaeus, he broadens the scope to include all the most common *Citrus* species. According to Mabberley, the following scheme provides a workable system of citrus for botanists and fruit growers alike. It is also helpful for understanding the origin of different kinds of citrus (Citrus Pages 2014).

1. *Citrus medica*, citron, is involved in: *Citrus limon* (citron × sour orange), lemon and similar hybrids like Palestine sweet lime and Volkamer lemon; *Citrus jambhiri* (citron × mandarin), rough lemon and similar hybrids like Rangpur lime, Mandarin lime, and other types like "Otaheite"; *Citrus aurantiifolia* (citron × lemon × Ichang papeda) lime (Mexican lime); and *Citrus bergamia* (citron × sour orange) bergamot, also considered a citron sour orange cross
2. *Citrus maxima*, pomelo, is involved in: *Citrus aurantium* (pomelo × mandarin) which includes three pomelo hybrids; *Citrus aurantium* (pomelo × mandarin) sour orange (the sour orange has inherited more features of the pomelo than the mandarin); *Citrus sinensis* (pomelo × mandarin) sweet orange (the sweet orange has inherited more features of the mandarin than the pomelo); this group also includes all the crosses of oranges, mandarins, and grapefruits such as tangors, ortaniques, tangelos, and their backcrosses like Page and Nova; and *Citrus paradisi* (pomelo × orange), the grapefruit

1.3.2 Mandarins and Tangerines

Mandarins (*Citrus reticulata* Blanco) are smaller and oblate rather than spherical like the common oranges (which are a mandarin hybrid). The taste is considered less sour than orange, as well as sweeter and stronger. A ripe mandarin is firm to slightly soft, heavy for its size, and pebbly-skinned. The peel is very thin, with a low bitter, white albedo, and they are usually easier to peel and split into segments. Generally mandarin and tangerine are considered part of the same group. The main species in the group are Satsumas (*Citrus unshiu* Marc.), Ponkan (*Citrus poonensis* Tanaka), and Clementines (*Citrus clementina* Tanaka). Other economically important species include Daisy, Pixie, and Changsha, among others.

Mandarins have been grown in China and Japan on a large scale since the sixteenth century. The biggest mandarin producers today are China, the European Union (mainly Spain), Japan, Morocco, and Turkey. Compared with the 2011 output, output in 2016 increased by 45.89%, 37.95%, 25%, 20.69%, and 18.86%, in Morocco, the United States, China, Argentina, and Turkey, respectively. The countries with the fastest increase in production were Morocco and the United States. The biggest mandarin exporters are China, Turkey, Morocco, the European Union (mainly Spain), and South Africa (Table 1.5).

TABLE 1.5
Fresh Fruit Production of Tangerines/Mandarins in Selected Countries (1000 Metric Tons)

	2011/2012	2012/2013	2013/2014	2014/2015	2015/2016	%
China	16,000	17,000	17,850	19,400	20,000	25.00%
European Union	3,099	2,927	3,213	3,474	3,035	–2.07%
Japan	1,001	846	1,124	1,070	1,115	11.39%
Morocco	730	662	1,160	1,003	1,065	45.89%
Turkey	875	876	880	960	1,040	18.86%
United States	635	660	700	803	876	37.95%
South Korea	586	667	672	697	640	9.22%
Thailand	360	375	375	375	375	4.17%
Argentina	290	300	370	350	350	20.69%
Israel	166	178	139	205	240	44.58%
Other	164	188	212	220	227	38.41%
Total	23,906	24,679	26,695	28,557	28,963	21.15%

Source: USDA: http://www.fas.usda.gov/commodities/citrus-fruit.

Mandarin types are grown in temperate Mediterranean-like areas, hot and humid tropical countries, and almost desert-type dry and arid environments. Additionally, some mandarin species tolerate cold and frost better than other citrus types. Certain species, for example, Satsumas, grown in China, can tolerate frost for several weeks.

Mandarins do not keep well on the tree after maturation. Due to their thin and often loose rind, they also tolerate storage and transportation less successfully than other citrus types. Mandarins are mostly eaten fresh, but a small amount of mandarin juice is produced. Canned segments in light syrup are the largest processing industry in China. They are used in fruit salads and other desserts, or as filling and decoration in cakes. Mandarin peel oil has an important position in the food industry as flavoring ingredients. It is used in sweets, gelatins, ice cream, chewing gum, pastry, and confectioneries. It is also used in soft drinks, mixers, essences, and flavorings, as well as in mandarin liqueurs and other alcohol products. Dried mandarin peels are important in traditional medicines, and serve as good material for the manufacturing of flavorings.

1.3.3 Oranges

The orange is a hybrid, between pomelos (*Citrus maxima*) and mandarins (*Citrus reticulata*). It has genes that are about 25% pomelo and about 75% mandarin. There are two kinds of oranges: one is sweet oranges (*Citrus sinensis*), and the other sour or bitter oranges (*Citrus aurantium*). The highest production is for sweet oranges, while only a very small amount of cultivation area is used for sour oranges, mainly for producing marmalades and other products. The orange fruits are round, flat round or oval, yellow to orange red, with a hard pericarp or being slightly easy to peel. Orange fruits have 9–12 segments, full or half-full cores, yellow, orange, purple or red flesh, a sweet or slightly sour taste, fewer seeds or no seeds. The flowering period is between March and May, the fruiting period from October to December, and the growing season of late maturing species extends from February to April of the following year.

The orange has a sweet and sour flavor, and is commonly peeled and eaten fresh or often used for juice production. The main production countries are Brazil, United States, Mexico, the European Union, and other countries and regions (USDA). The thick bitter rind is usually discarded, but can be processed into animal feed by desiccation, using pressure and heat. It is also used in certain recipes as a food flavoring or garnish. The outermost layer of the rind can be thinly grated with a zester to produce orange zest. The zest is popular in cooking because it contains oils and has a strong flavor similar to that of the orange pulp. The white part of the rind, including the pith, is a source of pectin and has nearly the same amount of vitamin C and other nutrients as the flesh. Over the past 5 years, the biggest producers of sweet oranges are Brazil, China, European Union, the United States, Mexico, Egypt, Turkey, and South Africa. However, during this time period, the total production volume of orange decreased by 15%, mainly in Brazil and the United States, with increases to 41% in Argentina, followed by Egypt, Australia, and other countries (Table 1.6). Oranges from Brazil and the United States are commonly used for orange juice production, the ratio of which accounts for more than 80%.

TABLE 1.6
Fresh Fruit Orange Production in Selected Countries (1000 Metric Tons)

	2011/2012	2012/2013	2013/2014	2014/2015	2015/2015	%
Brazil	20,482	16,361	17,870	16,716	14,350	−29.94%
China	6,900	7,000	7,600	6,900	7,000	1.45%
European Union	6,023	5,890	6,550	5,954	6,055	0.53%
United States	8,166	7,501	6,140	5,778	5,371	−34.23%
Mexico	3,666	4,400	4,533	4,158	3,535	−3.57%
Egypt	2,350	2,450	2,570	2,630	2,750	17.02%
Turkey	1,650	1,600	1,700	1,650	1,700	3.03%
South Africa	1,466	1,659	1,723	1,645	1,560	6.41%
Morocco	850	784	1,001	868	925	8.82%
Argentina	565	550	800	800	800	41.59%
Vietnam	530	520	520	520	520	−1.89%
Australia	390	435	430	430	455	16.67%
Costa Rica	370	325	315	315	315	−14.86%
Guatemala	150	155	155	155	155	3.33%
Israel	116	73	69	86	105	−9.48%
Other	156	168	168	167	167	7.05%
Total	53,830	49,871	52,144	48,772	45,763	−14.99%

Source: USDA: http://www.fas.usda.gov/commodities/citrus-fruit.

Main sweet orange cultivars can be divided into the following categories:

1. *Early sweet and common oranges*: Ambersweet, Hamlin, Rotuma Island, Berna, Jaffa (Florida Jaffa), Salustiana, Cadenera, Jincheng, Shamouti (Palestine Jaffa), Castellana, Marss, Trovita, Comuna, Parson Brown, Pineapple
2. *Valencia oranges*: Valencia, Delta Valencia, Midknight Valencia, and so on
3. *Navel oranges*
   a. Early navel oranges: Atwood, Navelina, Fisher, Skagg's bonanza, Thomson Zimmerman
   b. Mid-season navels: Cara Cara, Fukumoto, New Hall, Spring, Washington navel
   c. Late navel oranges: Autumn Gold, Lane Late, Ricalate, Barnfield, Navelate, Rohde Navel, and so on
4. *Blood oranges*: Rhode Red Valencia, Washington Sanguine, Ruby, Full blood oranges

1.3.4 Grapefruits

The grapefruit (*Citrus* × *paradisi*) is a subtropical citrus tree known for its sour to semisweet fruit. Grapefruits are a hybrid originating in the Barbados as an accidental cross between two introduced species, sweet oranges (*C. sinesis*) and pomelos, or shaddocks (*C. maxima*), both of which were introduced from Asia in the seventeenth century. When found, it was named the "forbidden fruit" (Morton 1987) and it has been misidentified with pomelos (Li et al. 2010). The fruit flesh is segmented and acidic, varying in color depending on the cultivars, which include white, pink and red pulps of varying sweetness (generally, the redder species are sweeter).

In many parts of the world, grapefruits are the customary breakfast fruits. Most grapefruits are chilled, cut in half, loosened from the peel and skin membranes with a special curved grapefruit knife and served fresh with perhaps a touch of sugar or honey. Grapefruit juice has increased in popularity, especially after its promotion as a diet drink started. Many weight loss diets include grapefruit juice. The pulp left over after commercial juice extraction is an important source of grapefruit oil, which is used as a flavoring in many soft drinks. The inner peel is a source of pectin and citric acid. Both are used by the food industry in the preservation of other fruits and in making jams and marmalades. Naringins, also extracted from grapefruit peels, gives tonic water its distinctive bitter flavor (Table 1.7).

1.3.5 Lemons and Limes

The lemon (*Citrus* × *limon*) is a species of small evergreen tree native to Asia. A study of the genetic origin of the lemons reported it to be a hybrid between bitter oranges (sour orange) and citrons. The tree's ellipsoidal yellow fruits are used for culinary and nonculinary purposes throughout the world, primarily for its juice, which has both culinary and cleaning uses (Citrus Pages 2014). The pulp and rind (zest) are also used in cooking and baking. The juice of the lemons is about 5% to 6% citric acid, which gives a sour taste. The distinctive sour taste of lemon juice makes it a key

TABLE 1.7
Fresh Grapefruit Production in Selected Countries (1000 Metric Tons)

	2011/2012	2012/2013	2013/2014	2014/2015	2015/2015	%
China	3200	3370	3717	3900	4300	34.38%
United States	1047	1092	950	807	735	–29.80%
Mexico	415	425	424	430	430	3.61%
South Africa	305	437	413	387	330	8.20%
Turkey	230	200	235	238	200	–13.04%
Israel	245	208	236	186	185	–24.49%
European Union	102	110	92	109	97	–4.90%
Other	0	0	0	0	0	0.00%
Total	5544	5842	6067	6057	6277	13.22%

Source: USDA: http://www.fas.usda.gov/commodities/citrus-fruit.

TABLE 1.8
Fresh Lemon and Lime Production in Selected Countries (1000 Metric Tons)

	2011/2012	2012/2013	2013/2014	2014/2015	2015/2015	%
Mexico	2055	2120	2187	2260	2270	10.46%
Argentina	1300	1350	780	1450	1500	15.38%
European Union	1264	1179	1308	1598	1260	–0.32%
United States	771	827	748	820	847	9.86%
Turkey	750	680	760	725	670	–10.67%
South Africa	260	245	312	339	345	32.69%
Israel	53	51	64	65	60	13.21%
Other	71	60	57	44	49	–30.99%
Total	6524	6512	6216	7301	7001	7.31%

Source: USDA: http://www.fas.usda.gov/commodities/citrus-fruit.

ingredient in drinks and foods such as lemonade and lemon meringue pie. The pulp, left over after commercial juice extraction, is an important source of citrus oil, pectin, and citric acid. These are used by the food, cosmetics, and pharmaceutical industries. Mexico, Argentina, and the European Union are the most important production countries of lemons and limes. The production has risen slightly in the past 5 years (Table 1.8).

1.4 SOME BIOACTIVE COMPONENTS IN CITRUS FRUITS

Citrus varieties such as oranges, grapefruits, mandarins, limes, and lemons, possess unique sensory properties and high nutritional value, and are among the most widely produced fruits in the world. Citrus originated in China where it is a highly profitable agricultural product. Citrus has a large cultivation area and long cultivation history.

TABLE 1.9
Major Events of Citrus Processing and Comprehensive Utilization

1950s	Successful development and commercialization of FMC citrus juice extractor and Brown juice extractor, enabling a large increase in the production of citrus fruits
1960s	Popularized frozen concentrated fruit juice as a food product
1970s	Studies on the comprehensive utilization of citrus; citrus essential oil recycling; application of citrus peel processing feed; selection of specific cultivars for canning in China
1977	*Citrus Science and Technology* published in the United States, which summarized global advances in research
1980s	Brazil becomes the largest producer of orange and orange juice; China promotes the spread of cultivars for canning, start of the promotion of low-temperature sterilization
1990s	China becomes the largest producer of canned citrus segments in light syrup, using a large number of low-temperature sterilization methods, and establishes a citrus juice production line
2000s	NFC chilly juice becomes popular; citrus polymethoxylated flavones, beta cryptoxanthin, zeaxanthin, coumarin, limonin are used as functional health factors; limonene application is used in the electronics industry as a cleaning agent

Among the 18 provinces and their cities in the southern part of the Yangtze River, the cultivation area has reached 1.5 million hm^2. Citrus production is abundant, which provides an incentive for the development and utilization of citrus resources. This has great potential, as citrus fruits are rich in nutrition, with not only high levels of pectin, oligosaccharide, organic acid, a variety of amino acids and other nutrients, but also a variety of nonnutritive physiologically active components such as limonin, alkaloid, volatile oils, phenolics, and other elements. These promote human health and have been associated with the prevention and treatment of some diseases. These trace elements give citrus fruits their unique flavor and nutritional value (Table 1.9).

Recently, phytochemicals in citrus fruits received attention in the literature, including phenolics (Abeysinghe et al. 2007; Kelebek et al. 2007), limonoids (Lam et al. 1994; Yu et al. 2005; Sun et al. 2005), coumarins (Ito et al. 2005; Widmer and Haun 2005), and alkaloids. Research has not been restricted to the edible parts of citrus fruits, but also byproducts created during processing. Phytochemicals in peels and seeds have attracted a wide attention from researchers. In addition, the scope of study has been extended to the immature fruits of citrus. The study found that the amount of these compounds in citrus peels and seeds are higher than that in the edible parts. For example, the content of flavonoids and other substances in immature citrus fruits is significantly higher than that in mature fruits. Hence, extracting these substances from citrus peels, seeds, and immature fruits might not only increase the value of citrus waste, but it will also provide a useful source of health-promoting food additives.

1.4.1 Flavonoid Compounds

1.4.1.1 Classification and Structural Characteristics of Citrus Flavonoids

Flavonoids are a class of phenolic compounds with the structure of C6–C3–C6, and are derivatives of chromone or chromane. Flavonoids are the most important active substances in citrus, and are found in fruit, bark, leaves and flowers of all species of sweet oranges, sour oranges, lemons, mandarins, and grapefruits. Based on the presence of the double bond between the C2 and C3 atoms in the carbon ring of its molecular structure, the presence of the hydroxyl group, the different connection sites of B ring in the C ring, and whether C ring is open, natural flavonoids can be divided into six categories. These are the flavones, flavanones, flavonols, isoflavones, anthocyanidins, and flavanols (or catechins) (Peterson and Dwyer 1998) (Figure 1.4). Thus far, more than 60 kinds of flavonoids have been identified in citrus, and they all belong to the first five categories listed above. Anthocyanidins, served as pigments of flowers and fruits, are very important in other plants, but are not as important in citrus—only as a substance existing in blood orange. Moreover, flavanones are found almost exclusively in citrus. Flavonoids are in the form of glycosides or aglycones, in the vast majority of varieties of citrus fruits. Those in the form of aglycones, can be divided into three categories: flavanone aglycones, flavone aglycones, and flavonol aglycones; those in the form of glycosides can be divided into two categories: Neohesperidosides and rutinosides (Macheix et al. 1990) (Figure 1.5).

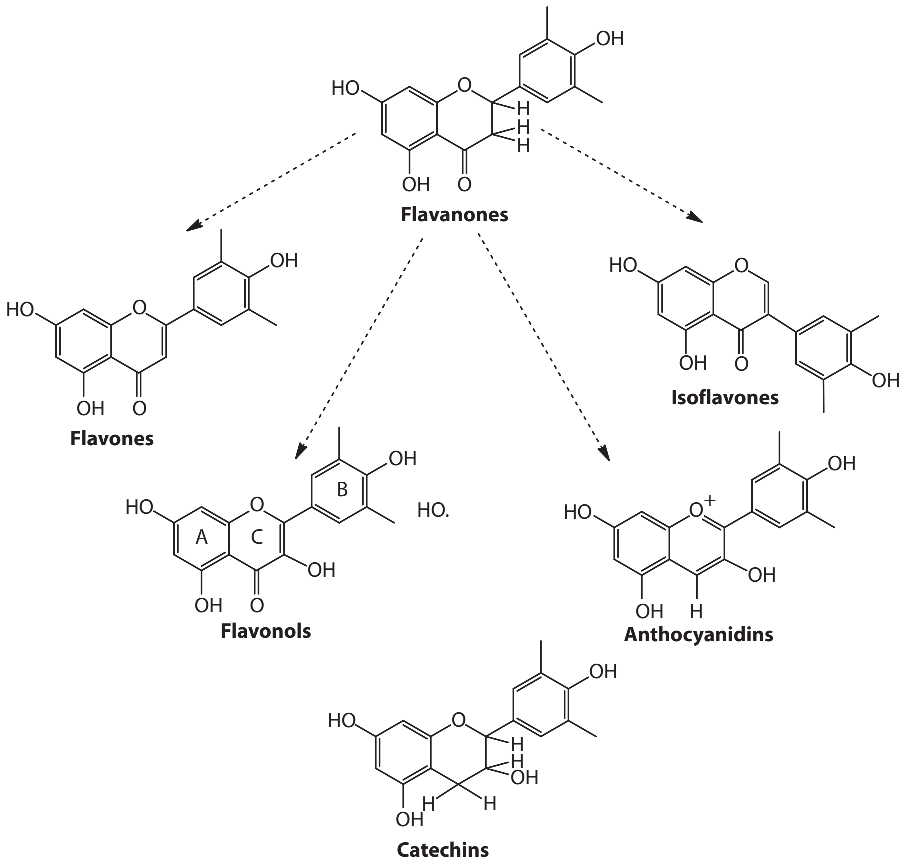


FIGURE 1.4 Molecular structures of flavonoids (arrows indicate biosynthetic paths).

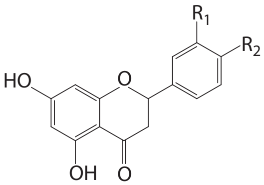
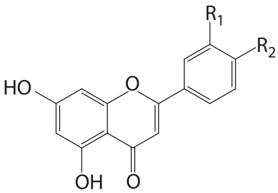
Compound	Chemical name	Structural formula	Molecular formula
Flavanone aglycone forms:			
			
	Naringenin	R_1=H; R_2=OH	$C_{15}H_{12}O_5$
	Hesperetin	R_1=OH; R_2=OCH$_3$	$C_{16}H_{14}O_6$
	Isosakuranetin	R_1=H; R_2=OCH$_3$	$C_{16}H_{14}O_5$
	Eriodictyol	R_1=OH; R_2=OH	$C_{15}H_{12}O_6$
Flavone aglycone forms:			
			
	Apigenin	R_1=H; R_2=OH	$C_{15}H_{10}O_5$
	Luteolin	R_1=OH; R_2=OH	$C_{15}H_{10}O_6$
	Diosmetin	R_1=OH; R_2=OCH$_3$	$C_{16}H_{12}O_6$

FIGURE 1.5 Structural characteristics of main citrus flavonoids in the aglycone and glycoside forms. (*Continued*)

1.4.1.2 Flavanones

Among all species of citrus fruits, flavanone is the most abundant flavonoid compound, and naringenin and hesperetin are the most abundant flavanones. They are commonly found in the form of glycosides, rarely in the form of aglycones, and they can be found in various parts of citrus fruits. Based on the difference of glycoside, they can then be divided into two categories: neohesperidosides and rutinosides. Flavanone neohesperidosides are mainly containing naringin, neohesperidin, and neoeriocitrin, and so on, which have a bitter taste. Flavanone rutinosides are mainly hesperidin, narirutin, and didymin, and so on, with no bitter taste (Figure 1.5). In citrus fruits, flavanones usually exist in the form of diglycosides, which are associated with the typical flavor of citrus fruits. Peterson made a comprehensive overview and summary of the content, distribution and composition of flavanones in mandarins, sweet oranges, sour oranges, lemons, and grapefruits (Peterson et al. 2006a,b). Naringin and neohesperidin can be hydrolyzed to dihydrochalcone, which are 300

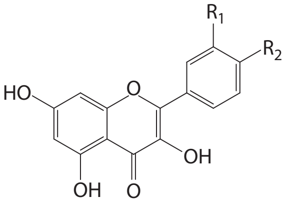
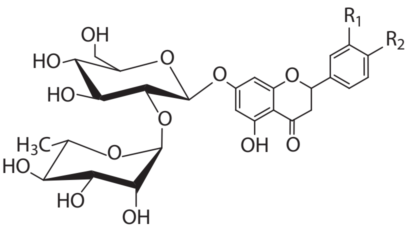
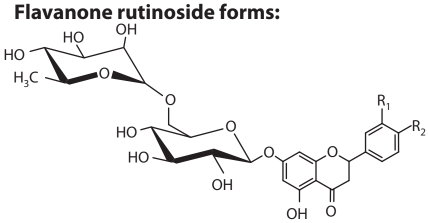
Compound	Chemical name	Structural formula	Molecular formula
Flavonol aglycone forms:			
			
	Quercetin	R_1=OH; R_2=OH	$C_{15}H_{10}O_7$
	Kaempferol	R_1=H; R_2=OH	$C_{15}H_{10}O_6$
Flavanone neohesperidoside forms:			
			
	Naringin	R_1=H; R_2=OH	$C_{27}H_{32}O_{14}$
	Neohesperidin	R_1=OH; R_2=OCH_3	$C_{28}H_{34}O_{15}$
	Poncirin	R_1=H; R_2=OCH_3	$C_{28}H_{34}O_{14}$
	Neoeriocitrin	R_1=OH; R_2=OH	$C_{27}H_{32}O_{15}$
Flavanone rutinoside forms:			
			
	Narirutin	R_1=H; R_2=OH	$C_{27}H_{32}O_{14}$
	Hesperidin	R_1=OH; R_2=OCH_3	$C_{28}H_{34}O_{15}$
	Didymin	R_1=H; R_2=OCH_3	$C_{28}H_{34}O_{14}$
	Eriocitrin	R_1=OH; R_2=OH	$C_{27}H_{32}O_{15}$

FIGURE 1.5 (CONTINUED) Structural characteristics of main citrus flavonoids in the aglycone and glycoside forms.

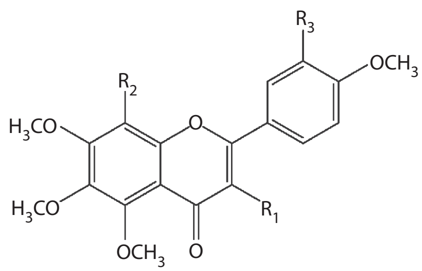
and 1000 times sweeter than sucrose, respectively (Del Río et al. 1997; Horowitz and Gentili 1969).

1.4.1.3 Polymethoxylated Flavonoids

Like other flavonoids, the parent nucleus of polymethoxylated flavones (PMFs) is a 2-benzene chromone with a skeleton of C6–C3–C6, but the benzene rings, especially the A ring, are replaced by a lot of methoxy, (sometimes hydroxy) groups, having a weaker polarity compared to flavanone glycosides. Polymethoxylated flavones are widely found in various species of citrus fruits, and almost only found in the citrus genus (Ye et al. 2005; Tang et al. 2006). In addition, each species is unique, although the content is small. It has many special effects and can be used as a commercial maker for citrus juice adulteration (Marini and Balestrieri 1995; Ooghe and Detavernier 1997) and in identification of citrus classification. Flavonoids are usually detected by HPLC-MS. Mouly et al. (1998) divided these compounds into two groups based on the different elution time: flavanone glycoside is the first eluted compound and polymethoxylated flavones are the last, which are less polar (PMFs). More than 20 kinds of flavonoids have been isolated and identified from citrus plants, among which the most common ones are nobiletin, tangeretin, and sinensetin; their chemical structures are shown in Figure 1.6.

1.4.1.4 Distribution and Determination of Flavonoids in the *Citrus* Genus

Flavonoids are widely found in citrus plants. Present in the largest amounts in citrus fruits we find neohesperidin and naringin in flavanone neohesperidoside forms, narirutin and hesperidin in flavanone rutinoside forms, and naringin and



Polymethoxylated flavonoids	**R1**	**R2**	**R3**
Scutellarein	H	H	H
Sinensetin	H	H	OCH_3
Tangeretin	H	OCH_3	H
Hexamethoxyflavone	OCH_3	H	OCH_3
Nobiletin	H	OCH_3	OCH_3
Heptamethoxyflavone	OCH_3	OCH_3	OCH_3

FIGURE 1.6 Structural characteristics of common citrus polymethoxylated flavones.

polymethoxylated flavones in flavone aglycone forms—Nobiletin, Tangeretin, and Sinensetin. Flavanones with 7-*O*-glycosyl are the most abundant flavonoid compounds in all citrus fruits (Benavente-García et al. 1995). For example, lemon peels are rich in glycosidic flavonoids (Park et al. 1983). The distribution of flavonoids varies in the different varieties of citrus fruits. Naringin, neohesperidin and poncirin in flavanone neohesperidoside forms are mainly found in bergamot, grapefruit, and bitter orange juice, while hesperidin, narirutin, and didymin, in flavanone rutinoside forms, are mainly found in bergamot, oranges, tangerines, and lemon juice (Horowitz 1986). Bitter orange is an important source of neohesperidin and naringin. These compounds may be used to produce sweeteners. Lemons are rich in neoeriocitrin and hesperidin. The predominant flavonoid compounds in pummelo are naringin, hesperidin, neohesperidin, narirutin, and other flavanone glycosides, among which, naringin accounts for more than 80% of the total content (Russell et al. 1987).

The composition of flavonoids differs across different fruit tissues, and as such flavanone glycosides have a different composition whether in the seeds and peels, or in the juice. For example, in lemon peels and seeds, as well as *Citrus reticulata* seeds, there exists naringin; however, it is not present in their juice (Ooghe and Detavernier 1997). On the other hand, the compositions of flavanone compounds are different in citrus seeds and peels. For example, lemon seeds mainly contain neoeriocitrin and hesperidin, while peels are rich in neoeriocitrin, naringin, and neohesperidin (Tripoli et al. 2007). Also flavanone glycoside contents are quite different. In lemon peels, neoeriocitrin and naringin have similar content, but in lemon seeds, the content of neoeriocitrin is 40 times higher than that of naringin (Bocco et al. 1998).

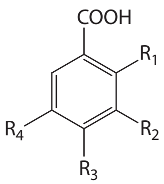
Kelebek et al. (2008) determined, using HPLC-DAD, the content of five flavanones in two blood orange varieties (Moro and Sanguinello) and found that they mainly contained narirutin, naringin, hesperidin, neohesperidin, and didymin, and that Moro juice had a higher content of these five compounds than Sanguinello juice. Wang et al. (2007) determined the content of three flavanones (naringin, hesperidin, and neohesperidin), two flavone aglycones (diosmetin and luteolin), two flavonol aglycones (quercetin and kaempferol), one flavonol glycosides (rutin), and one polymethoxylated flavone (sinensetin) in the edible parts of eight citrus fruits from Taiwan using the method of RP-HPLC, and documented the differences in flavonoid composition and content between the peels and edible parts.

He et al. (1997) used HPLC-MS to isolate and identify eight flavonoids in *Citrus aurantium* extract, including isonaringin, naringin, hesperidin, neohesperidin, naringenin, nobiletin, and naringenin. Ortuno et al. (1997) used the RP-HPLC method to compare these flavonoids and found that citrus (including *Citrus aurantium*) had the highest content of hesperidin, naringin, and neohesperidin. The most important flavonoids components are naringin, rhoifolin, poncirin, and neohesperidin in the epicarp of the immature fruit of *Citrus grandis* (exocarpium citri grandis [Hua Ju Hong] or Rutaceae citrus *Citrus grandis* "Tomentosa") (Su and Lin 2001; Lei et al. 2000). Weber et al. (2006) used a combination of HPLC-MS (LC-MS) and HPLC-NMR-PDA (MS liquid NMR) methods to isolate and identify polymethoxylated flavones in molecular distillation cold pressed orange peel oil, and they detected sinensetin, nobiletin, tangeretin, quercetogetin, heptamethoxyflavone, and others. Wang and Chen (1995) used HPLC to determine the naringin content in *Citrus aurantium* L. and also compared the naringin content in different parts of the fruits and noted the changes of the naringin contents during different harvest seasons.

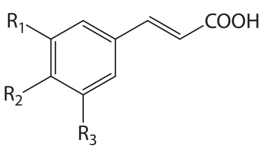
1.4.2 Phenolic Acids

1.4.2.1 Types and Structural Characteristics of Phenolic Acids

Phenolic acids are a class of substances characterized by a benzene ring with a hydroxyl group; they account for about one-third of plant-derived phenolic compounds in foods. According to their structure, they can be divided into hydroxybenzoic and hydroxycinnamic acids. Common hydroxylated cinnamic acid derivatives include coumaric acid, caffeic acid, and ferulic acid, which are usually esterified with quinic acid or glucose. The hydroxylated benzoic acid derivatives of the most common phenolic acids are hydroxybenzoic acid, vanillic acid, protocatechuic, and so on, mainly in the glycoside form (Herrmann 1989). The structures and classification of common phenolic acids are shown in Figure 1.7. Citrus phenolic acids mainly exist in free and bound forms. Bound phenolic acids are typically bonded with an ester bond or an ether bond with a number of compounds (Xu et al. 2007). Phenolic acids, as a potential protective factor against cancer and heart disease, have received much attention in recent years partly because of their potential antioxidant and anti-inflammatory activity, their effects on chronic diseases, and their widespread



	R_1	R_2	R_3	R_4
Benzoric acid	H	H	H	H
Salicylic acid	OH	H	H	H
Gentisic acid	OH	H	H	OH
Vanillic acid	H	OH	OMe	H
Gallic acid	H	OH	OH	OH
Syringic acid	H	OMe	OH	OMe



	R_1	R_2	R_3
Cinnamic acid	H	H	H
Coumaric acid	H	OH	H
Caffeic acid	OH	OH	H
Ferulic acid	OMe	OH	H
Sinapic acid	OMe	OH	OMe

FIGURE 1.7 Molecular structures of phenolic acids.

existence in plant-derived foods (Morton et al. 2000; Mattila and Kumpulainen 2002; Lodovici et al. 2001).

1.4.2.2 Distribution and Determination of Phenolic Acids in Citrus Fruits

Kelebek et al. (2008) used HPLC-DAD to determine the content of two kinds of benzoic phenolic acids (gallic acid and protocatechuic acid) and five cinnamic acids (caffeic acid, chlorogenic acid, *p*-coumaric acid, ferulic acid, and sinapic acid) in two blood oranges, Moro and Sanguinello. The results showed that Moro juice has a total of 9.25 mg/L of benzoic phenolic acids and 74.35 mg/L of cinnamic phenolic acids, which is more than in Sanguinello juice. Gorinstein et al. (2004) conducted a study on the composition and content of phenolic acids in the pulp and peel of Jaffa White and its variant, Jaffa Sweeties. Experimental results showed that the content of gallic acid, protocatechuic acid, 4-hydroxybenzoic acid, vanillic acid, *p*-coumaric acid, salicylic acid, ferulic acid, anisic acid, and erucic acid in the peel of Jaffa White and its variant is significantly higher than that in the pulp. The total content of these four hydroxylated cinnamic acids (caffeic acid, *p*-coumaric acid, ferulic acid, and erucic acid) is higher in Jaffa White pulp (362 nmol/g) and peel (1513 nmol/g), compared to the content in its variant (272 and 1277 nmol/g, respectively; Figure 1.9). Bocco et al. (1998) determined the content of esterified phenolic acids (four kinds of cinnamic acid: caffeic acid, *p*-coumaric acid, ferulic acid, and erucic acid) in citrus fruit peel and seeds of *Citrus reticulata*, *Citrus sinensis* (L.) Osbeck, lemon, *Citrus maxima*, and *Citrus aurantium* L. originated from South Africa and Italy. They found a significantly higher content of phenolic acids in the seeds than in the peel. Rapisarda et al. (2003) conducted a study on the change, of four cinnamic phenolic acids (caffeic acid, *p*-coumaric acid, ferulic acid, and erucic acid) present in the citrus juices of blood oranges, tangerines and their hybrids; with different maturity they found that the trend in change has a significant relationship with citrus varieties. Peleg et al. (1991) also reported the composition and content of cinnamic phenolic acids of oranges and grapefruits at different stages of maturity. They found that with the increase in maturity, the content of erucic acid in orange juices increased, while the content of other three phenolic acids dropped.

1.4.3 Limonoid Substances

1.4.3.1 Types and Structural Characteristics of Limonoids

Limonoids are also called limonins, and they are a class of highly oxidized secondary metabolites of tetracyclic triterpenoids found in plants, mainly present in the rutaceae and meliaceae families. Citrus limonin compound is one of the main bitter flavor components (Cai and Hashinaga 1996). So far, about 300 kinds of lemon bitter analogues have been isolated. About 38 kinds of aglycone limonoids and 20 kinds of limonoid glycosides have been isolated from citrus plants (Sawabe et al. 1999; Saipetch et al. 2004).

In citrus plants, limonoid compounds exist in two forms: one form is limonoids aglycone, the structural features of which are that, on D ring C-17 is connected with a pyran ring, C-3, C-4, C-7, C-16, and C-17 are connected with the oxygen-containing functional groups. Except for deoxy limonin, epoxy structures exist on the site of both C-14 and C-15 (Liu et al. 2007). Aglycone limonoid compounds can be divided into two parts: limonene A ring lactone and limonene D ring lactone. Complete fruits contain large amounts of limonene A ring lactone (LARL) (without bitterness), which under acidic conditions are soon transformed into limonene D ring lactone (with bitterness). This reaction is accelerated by the presence of limonene D ring lactone hydrolase, which is the reason why citrus juice produces a bitter aftertaste (Hasegawa et al. 1991). The main citrus aglycones have limonin, nomilin, and knock Obama ketone (structures shown in Figure 1.8).

The other form is limonoid glycoside without bitterness (Ohta et al. 1992) and are constituted of a pentose in form of glycosidic bond synthetic by limonoids aglycone molecule D ring after ring opening at the position C-17, which experienced a series of very complex biochemical processes in the plant body. At present, only 19 kinds of glycosides have been identified in the *Citrus* genus. The common types of limonoid glycosides are: limonin 17-β-glucopyranoiside, nomilin acid 17-β-D-glucopyranoside, ichchangin 17-β-D-glucopyranoiside, isolimonic acid 17-β-D-glucopyranoside, deactylnomilic acid 17-β-D-glucopyranosied, obacunone 17-β-D-glucopynoside, and so on. Figure 1.9 shows the structure of limonin glucoside and nomilin glucoside (Bennett et al. 1989).

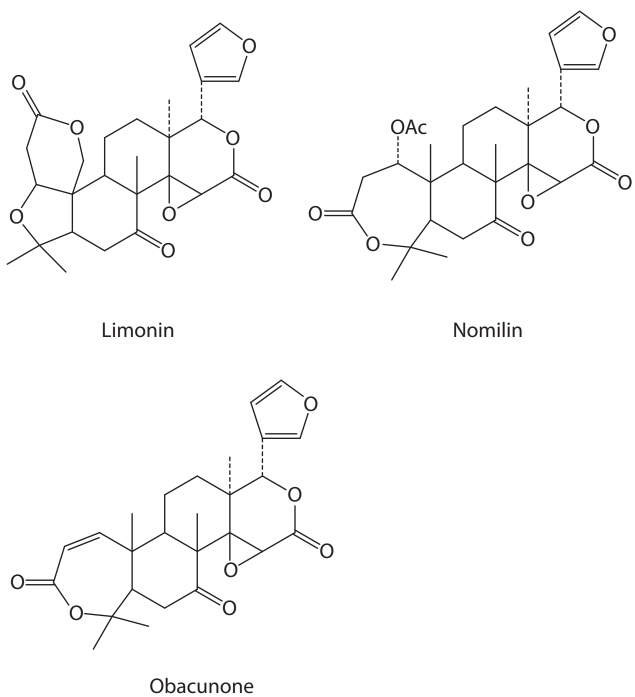


FIGURE 1.8 Structures of the main aglycone of limonoids.

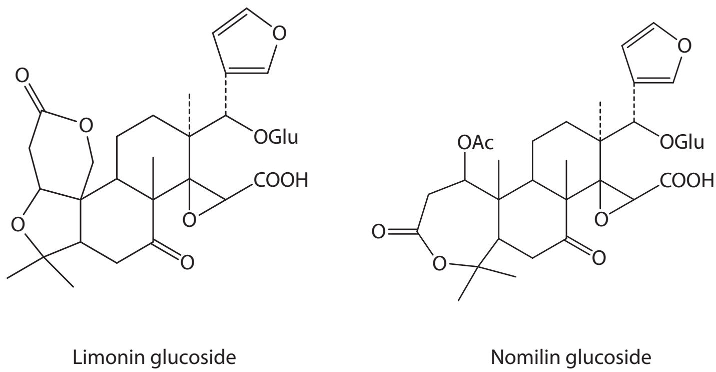


FIGURE 1.9 Structures of limonin and nomilin glucosides.

1.4.3.2 Distribution and Determination of Limonoids Glycoside Compounds in *Citrus* Genus Plants

Limonoids are widely distributed in a variety of species in the *Citrus* genus, and the total fruit content and composition of limonoids differs between varieties. Ohta and Hasegawa (1995) conducted a study on the composition of limonoids on 16 species of mature pomelo fruits and found that pummelo juice contains 18 ppm limonin and 29 ppm limonin glycoside (LG). Seeds contained limonene, nomilin, obama knock one, and a trace amount of deacetylation nomilin and its glycosides. In seeds, the content of limonoid aglycone is between 773 and 9900 ppm, and its glycoside has a content of 130 to 1912 ppm. Chen et al. (2006) used HPLC method to determine limonin and naringin in citrus juice from three different places, and compared the content differences.

Different parts of citrus fruits have different limonoids content. Seeds have the highest, followed by peels, while pulp has the lowest (Luo and Pan 2008); and with the content of limonene, nomilin, obama knock ketone from high to low (Hashinaga et al. 1983). But there are exceptions, such as citrons where nomilin content is greatest in all parts except the seeds, followed by limonin, which suggests citron bitterness is mainly due to nomilin content (Cai et al. 1992, 1993). In addition, grapefruit seeds are a major source of limonoid substances, in a proportion of about 1.5% of the fresh weight of seeds (Brano et al. 2000). Sun et al. (2004) determined the content of limonin and nomilin in different tissues of ripe Zhoushan Gaoxie pomelo fruits. In the epicarp, no limonin and nomilin were detected, while the coat had a higher content of limonin and nomilin than the peel. Zeng et al. (2003) determined the content of limonoids and limonin from different parts (peel, seed, juice) of different varieties of citrus, and found that limonoid content in the seed was higher than in peels, but lower in the juice. Limonoids content in seeds is highest in Guanximiyou (208.4 mg/kg), followed by Dengken Grapfruit (182.4 mg/kg), Nanchung sweet oranges (165.2 mg/kg), Jin oranges (34.2 mg/kg), and finally, Da-Huang-Bao red oranges (26.2 mg/kg). Moreover, limonins content in citrus fruits is also related to fruit maturity. For Huyou, pomelo, Wenzhoumigan, and Penggan, during growth and maturation, the contents of Limonin and Nomilin increase from May to September, and diminish afterwards until the end of October when the contents stabilize at a lower level (Sun et al. 2005).

1.4.4 Alkaloids

1.4.4.1 Structural Characteristics of the Main Alkaloids in Citrus

Alkaloids (alkaloids) generally refer to alkaline nitrogenous compounds found in plants, most of which are heterocyclic with optical rotation and obvious physiological effect. Alkaloids in citrus include octopamine, synephrine, tyramine, *N*-methyltyramine, hordenine, and other phenethylamine alkaloids. Among these, synephrine is the most important (Fumiyo et al. 1992), and its structure is as shown in Figure 1.10. It is reported that synephrine can affect the body's metabolism, help obese people lose weight by a mechanism in which stimulated lipolysis leads to a metabolic rate and fat oxidation acceleration (Carpéné et al. 1999; Tang et al. 2006). Synephrine and *N*-methyltyramine are two identified essential ingredients in *Citrus aurantium*, which strengthen the heart, increase cardiac output, contract blood vessels and enhance total peripheral vascular resistance to raise left ventricular pressure and arterial blood pressure, and can be used for the treatment of bronchial asthma and anesthesia hypotension, orthostatic hypotension, shock, and collapse after surgery.

1.4.4.2 Distribution and Determination of Alkaloids in Citrus

Synephrine alkaloids are widely distributed in many plants belonging to the Rutaceae citrus family, with various contents in each variety, which decrease with fruit maturity. In China, citrus plant alkaloid research is mainly aimed at young citrus fruits and traditional Chinese herbal medicine *Citrus aurantium* and its alkaloid

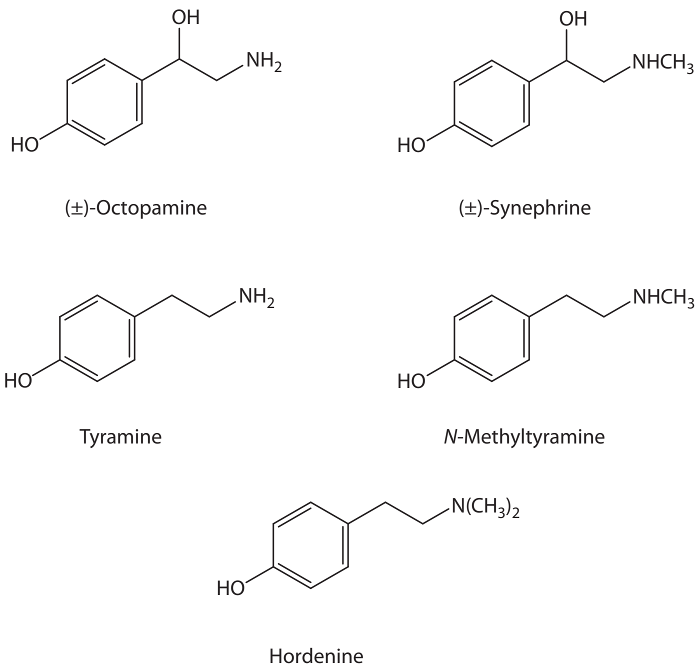


FIGURE 1.10 Chemical structures of phenethylamine alkaloids isolated from citrus.

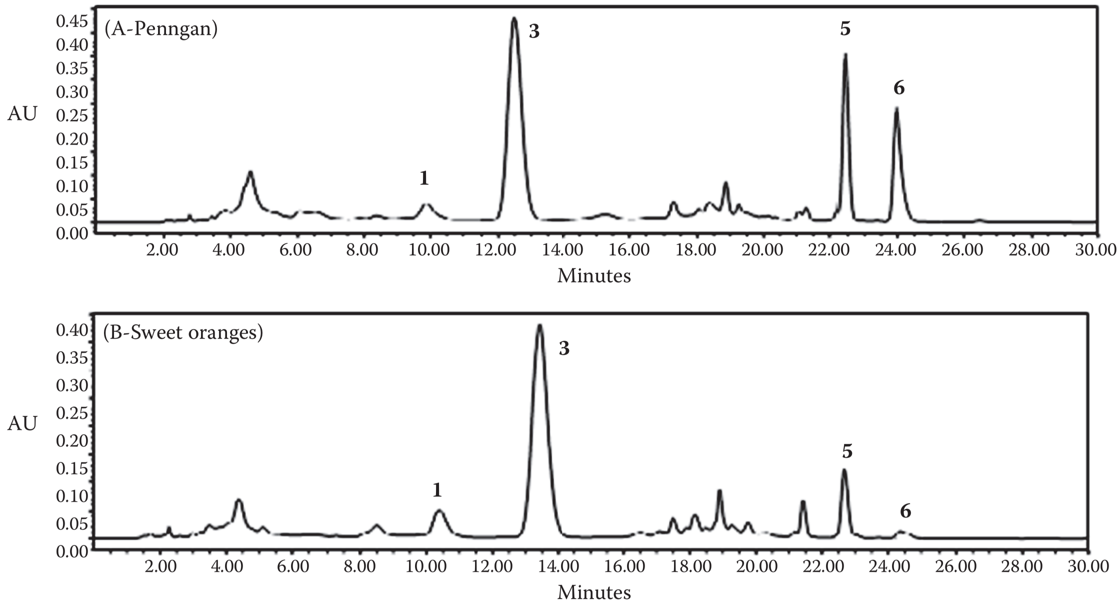


FIGURE 1.11 HPLC profile of the PGs and PMFs of the sample at 330 nm (*1*: narirutin, *2*: naringin, *3*: hesperidin, *4*: neohesperidin, *5*: nobiletin, *6*: tangeretin). (*Continued*)

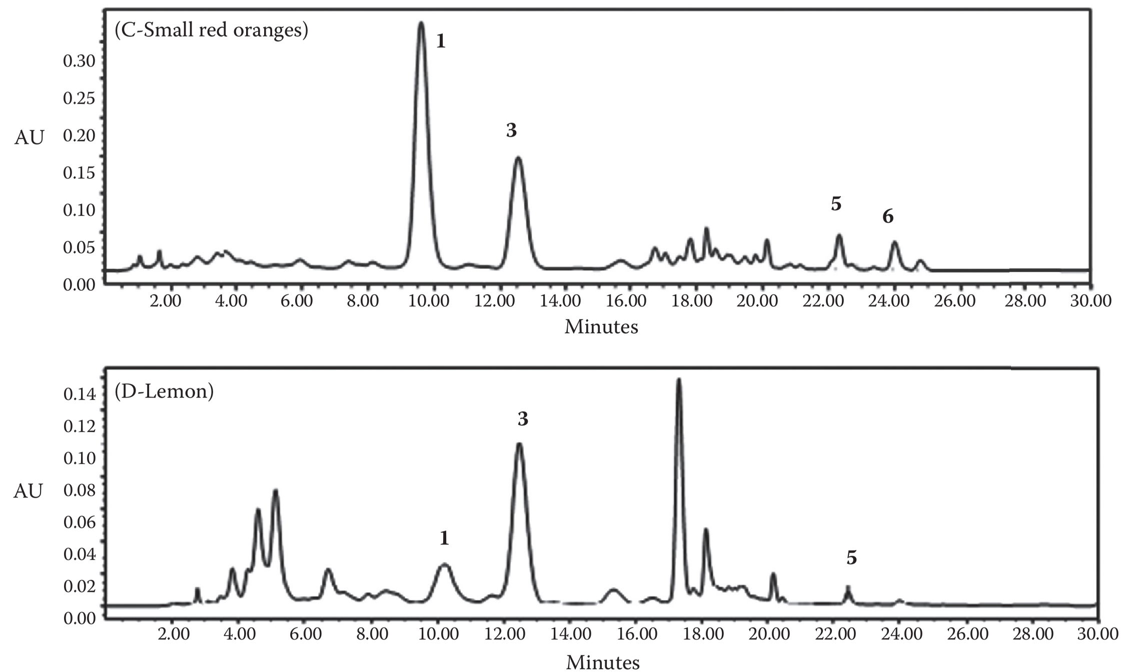


FIGURE 1.11 (CONTINUED) HPLC profile of the PGs and PMFs of the sample at 330 nm (*1*: narirutin, *2*: naringin, *3*: hesperidin, *4*: neohesperidin, *5*: nobiletin, *6*: tangeretin). (*Continued*)

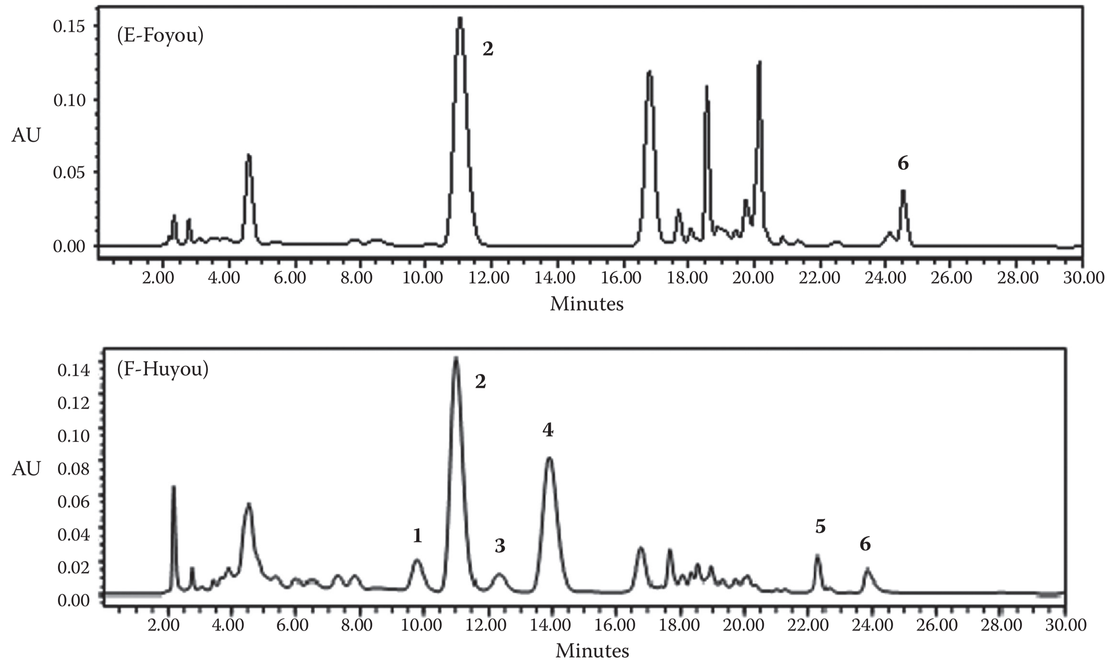


FIGURE 1.11 (CONTINUED) HPLC profile of the PGs and PMFs of the sample at 330 nm (*1*: narirutin, *2*: naringin, *3*: hesperidin, *4*: neohesperidin, 5: nobiletin, 6: tangeretin). (*Continued*)

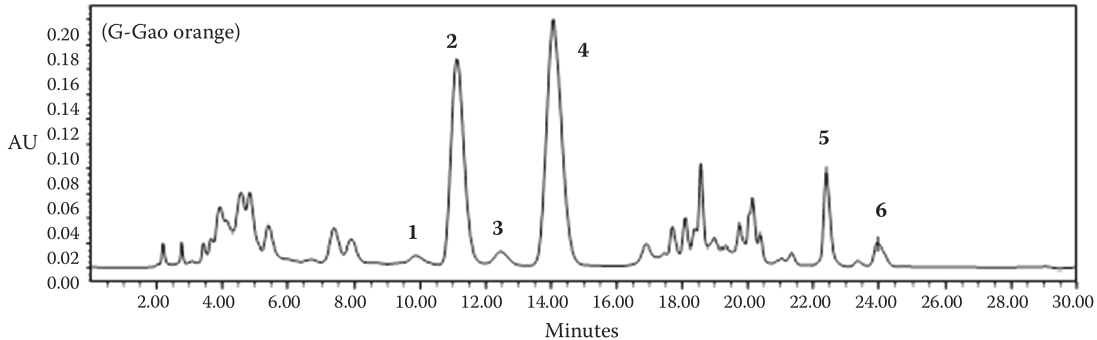


FIGURE 1.11 (CONTINUED) HPLC profile of the PGs and PMFs of the sample at 330 nm (*1*: narirutin, *2*: naringin, *3*: hesperidin, *4*: neohesperidin, *5*: nobiletin, *6*: tangeretin). (From Ye, X. Q., and D. H. Liu, *Citrus Processing and Utilization*, Beijing, Light Industry Publishing House, 2005.)

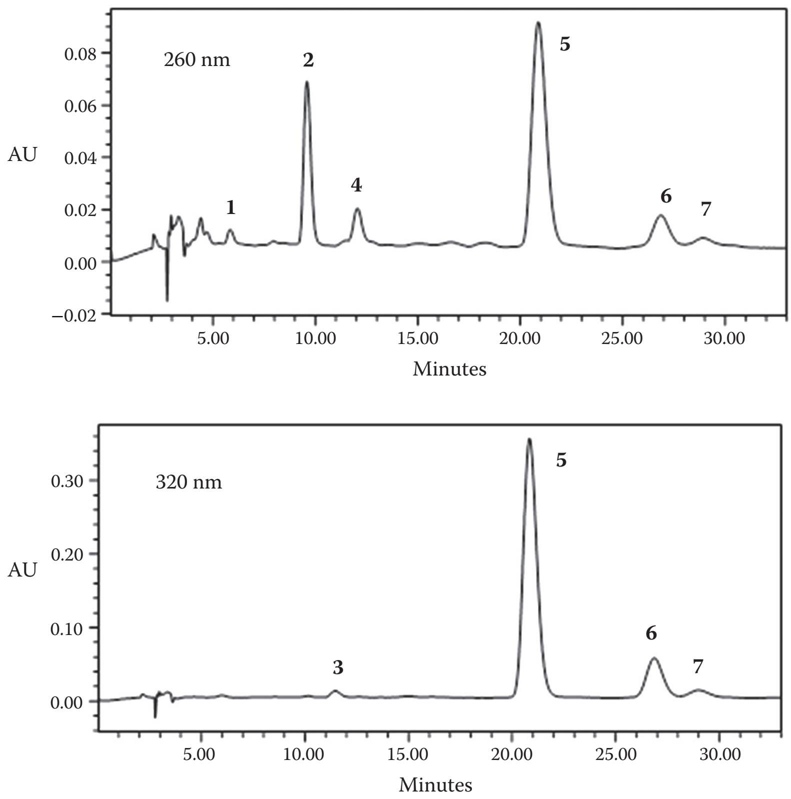


FIGURE 1.12 HPLC graphs of the phenolic acids of young lemon fruits at 260 nm and 320 nm (*1*: protochatechuic; *2*: *p*-hydroxybenzoic; *3*: caffeic; *4*: vanillic; *5*: *p*-coumaric; *6*: ferulic; *7*: sinapic). (From Ye, X. Q., and D. H. Liu, *Citrus Processing and Utilization*, Beijing, Light Industry Publishing House, 2005.)

types, content and their physiological functions. Pellati and Benvenuti (2002) used RP-HPLC to determine the content of *N*-methyltyramine, synephrine, and tyramine in fresh *Citrus aurantium*, *Citrus aurantium* dry goods and a commercial *Citrus aurantium* extract, and at the same time, performed quantitative separation of DL-synephrine in all *Citrus aurantium* samples using chiral columns with beta cyclodextrin as the stationary phase. The researchers found that D-synephrine content in dry *Citrus aurantium* samples was significantly higher than that of L-synephrine. Li et al. (2004) determined the synephrine and *N*-methyltyramine content of Qingpi and Sihua Qingpi from three and four places of origin respectively, and their different growth periods. Some chemical compositions by HPLC profiles of the PGs and PMFs of the orange samples, and some phenolic acids from lemon young fruits are shown in Figures 1.11 and 1.12, respectively (Ye and Lui 2005).

Chen (2005) summed up the synephrine and *N*-methyltyramine content of *Citrus aurantium* from 21 different places of origin. As shown in the results by species, the content of synephrine in *Citrus aurantium* from highest to lowest was: *Citrus* *reticulate* > sweet orange > sour orange > *Citrus sinensis* > citron (Chen 2005). Different storage periods also had an impact on synephrine content. Zhou and Gui (1997) conducted a study of bran fried *Citrus aurantium* quality during different storage periods, and found that along with the extended storage, bran fried *Citrus aurantium* synephrine levels decreased significantly. Synephrine decreased by 56.7% when comparing a 4-year sample with one that had not been stored at all.

1.4.5 Research Progress of Antioxidant Ability of Some Bioactive Components on Citrus Fruits

1.4.5.1 Antioxidant Ability of Flavonoids in Citrus Fruits

The antioxidant property of flavonoids (such as naringin, and so on) is mainly caused by the removal of peroxide, hydroxyl radical scavenging, and the antilipid peroxidation (LPO) activity (Mohamad-Reza et al. 2003). Wilmsen et al. (2005) used the DPPH radical scavenging test and reported the antioxidant activity of hesperidin, compared with that of Trolox, and found they are at the same level of antioxidant activity. Yu et al. (2005) used the β-carotene bleaching method, DPPH free radical scavenging experiment, superoxide free radical scavenging experiment, and the LDL oxidation experiment to evaluate the antioxidant activity of limonoids, flavonoids (flavanone aglycone, flavanone glycoside, flavonols) and coumarin. They found that the majority of flavonoids had strong antioxidant activities, while limonoids and coumarin, which have less hydroxyl groups, had relatively weak antioxidant activities. Majo et al. (2005) studied the antioxidant activity of nine flavanones (aglycone, and glucoside, and so on), and found that antioxidant ability of flavanone was related to the sites, number and *O*-methylated degree of free hydroxyl groups in the flavanone molecule.

Based on the hydroxyl sites and the total number of hydroxyl group antioxidant mechanisms, flavanone aglycones' *O*-methylation has nearly no impact on antioxidant ability; however, as for flavanone glycosides, *O*-methylation can decrease antioxidant ability significantly. Kim and Lee (2004) also found that the number of free hydroxyl group and the antioxidant ability of flavonoids was significantly positively correlated. The antioxidant ability of polyphenol is generally stronger than that of monophenol, but glycosylation reduces the flavanones antioxidant ability. In recent years, there have been many papers reporting flavanones and their glycosides antioxidant ability, but antioxidant capacity of polymethoxylated flavonoid *in vitro* has rarely been reported.

1.4.5.2 Antioxidant Ability of Phenolic Acids in Citrus Fruits

Literature on the evaluation of the antioxidant ability of phenolic acids stems mostly from *in vitro* studies. Kikuzaki et al. (2002) used multiple antioxidant methods and determined the antioxidant ability of 30 kinds of phenolic acids. The DPPH free radical scavenging ability was, from highest to lowest: caffeic acid > sinapic acid > ferulic acid > ferulic acid ester > coumaric acid. The results also showed that under the system of linoleic acid, esterification enhances the antioxidant ability of ferulic acid. According to reports, cinnamic acid can effectively prevent the oxidation of low-density lipoprotein (LDL), and the antioxidant ability is, from strongest to lowest: caffeic acid > ferulic acid > coumaric acid (Castelluccio 1996). Gulcin (2006) conducted a comprehensive assessment of the *in vitro* antioxidant capacity of caffeic acid. The methods used were: ABTS radical scavenging experiment, DPPH radical scavenging test, reducing power test, ferric thiocynanate method (FTC), superoxide anion radical scavenging experiments, and experimental metal chelate; the results showed that caffeic acid has a good antioxidant activity *in vitro*.

1.4.5.3 Antioxidant Ability of Limonin in Citrus Fruits

Opinions on the antioxidant ability of limonoids substances are also different. Sun et al. (2005) conducted a study using β-carotene bleaching assay and showed that the antioxidant ability of limonin and nomilin varied across different tissues and citrus varieties, and that the antioxidant ability of limonin and nomilin was about 2.9 to 8.3 times of that of ascorbic acid. Yu et al. (2005) evaluated the antioxidant ability of 11 active substances in citrus and found that, at 10 μM concentration, the inhibition rate of limonin glycoside to β-carotene-linoleic acid system free radical is less than 7%, while the inhibition rate of flavonoids could be as high as 51.3%. In the DPPH system, the free radical scavenging rate of limonene and limonene glycoside was only 0.5% and 0.25% respectively, which was significantly lower than rutin, baicalin, and other flavonoids. The peroxide radical scavenging rate of limonene, limonene glycosides, and coumarin was 2.5–10%, while flavonoids had the highest peroxide radical scavenging rate at 64.1%. Breksa and Manners (2006) used four *in vitro* antioxidation systems, ORAC (the oxygen radical absorbance capacity), TEAC (Trolox equivalent antioxidant capacity), DPPH and β-carotene-linoleic acid bleaching to study the antioxidant activity of limonin and nomolin, and claimed that pure limonin and nomilin had no antioxidant capacity, because they did not have the basic molecular structure to exhibit an antioxidant ability.

1.5 CITRUS FRUIT PROCESSING AND UTILIZATION

1.5.1 Citrus Product Development

Due to its complex structure, citrus is one of the most difficult fruits to process. Before the breakthrough technology of citrus juice in the 1950s, there was not much processing of citrus juice. However, after the 1950s, there was a rapid increase in the production of fruit juice, such that citrus juice became the first major juice considered to be a daily fruit juice drink. The United States and Brazil are the main countries processing citrus juice. Brazil began mass production since the 1960s, and has since maintained its position as the top producer in the world.

Large quantities of mandarins and tangerines are processed in Asia and the Mediterranean region. From the perspective of processing characteristics, mandarins are suitable for processing into segments. Spain is an important manufacturer of canned products in Europe. Japan used to be the main producer and exporter of canned citrus, and the major country for importations; however, since the middle of the 1980s, it has gradually been replaced by China. Since the 1960s, canned citrus segments in light syrup are still one of the main agricultural exports from China.

From a technical point of view, the citrus processing industrialization process has been helped by some significant advances in technology. For example, as for orange juice processing, special juice extractors were invented by FMC Corporation in 1946.