SECTION A: FRUIT FLAVORS

PART I

FRUIT FLAVORS: BIOLOGY, CHEMISTRY, AND PHYSIOCHEMISTRY

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Fruits and Fruit Flavor: Classification and Biological Characterization

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Fruit has always been a part of the human diet and is an important nutritional source, with high water content (70–85%) and a relatively high amount of carbohydrates but low contents of fat (less than 0.5%) and protein (<3.5%). It usually contains many useful vitamins as well as minerals, dietary fiber, and antioxidants (Goff and Klee 2006; Knee 2002). From 2002 to 2007, there has been a steady increase in fruit production with 2.67% each year, partly in response to population growth and living standard improvement in most countries and effective encouragement by government health agencies of fruit consumption. In 2007, a total amount of 318.6 million tons of fruit was produced in the world, which is equivalent to 48.2kg per capita of production and a fruit consumption of 12kg per capita (Euromonitor 2008; http://faostat.fao.org).

In this chapter, the botanical information, characterization, importance, and production of fruits are briefly reviewed. The chapter provides general information about fruit and draws comparisons between fruit and fruit flavor. Flavor characterization is also discussed in detail.

CLASSIFICATION OF FRUITS

There are different ways to classify fruit (Table 1.1). Generally speaking, the outer, often edible layer in fleshy fruits is the pericarp, which develops from the ovary wall of the flower and surrounds the seeds. While the seeds are akin to the egg development in the ovary of a fowl, the pericarp may be assumed as the uterus. However, a small number of fruits do not fit into this description. For example, in most nuts, the edible part is the seed but not the pericarp. In addition, many edible vegetables such as cucumber and squash are common pericarp and are botanically considered as fruits. In this chapter, the use of the term "fruit" will not refer to these vegetable

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TABLE 1.1.	Types	of	Fruit
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True Berry	Pepo	Hesperidium	False Berry	Aggregate Fruit	Multiple Fruit	Other Accessory Fruit
Black currant Red currant Gooseberry Pomegranate Avocado Kiwifruit Grape	Pumpkin Cucumber Melon	Orange Lemon Lime Grapefruit	Banana Cranberry Blueberry	Blackberry Raspberry Boysenberry Hedge apple	Pineapple Fig Mulberry	Apple Peach Cherry Strawberry

fruits. In some fruits such as lychee and longan, the edible portion is actually an aril. From the botanical point, fruits can be classified into simple fruits, aggregate fruits, and multiple fruits on the basis of anatomical attributes.

Simple Fruits

Simple fruits are formed from a single ovary and may contain one to many seeds, which have developed as part of the fruit. Simple fruits can be divided into two groups: fleshy pericarp—berries, drupes, and pomes; and dry pericarp—nuts. Types of fleshy and simple fruits are berry (red currant, gooseberry, and avocado), stone fruit or drupe (plum, cherry, peach, apricot, olive), false berry—epigynous accessory fruits such as banana and cranberry, and pome—accessory fruits such as apple and pear. In contrast to fleshy and simple fruits, in nuts, it is the stony layer that surrounds the kernel of pecans and is removed when eating.

Aggregate Fruit

Aggregate fruits are formed from a single compound flower and contain many ovaries. Examples include strawberries, raspberries, and blackberries. An aggregate fruit or etaerio develops from a flower with numerous simple pistils. An example is the raspberry, whose simple fruits are termed as drupelets because each is like a small drupe attached to the receptacle. In some bramble fruits (such as blackberry), the receptacle is elongated and part of the ripe fruit, which makes the blackberry an aggregate-accessory fruit. The strawberry is also an aggregate fruit, in which the seeds are contained in achenes.

Multiple Fruit

Multiple fruits, such as pineapple, fig, and mulberry, are formed from the fused ovaries of many separate but closely clustered flowers. There are also many dry multiple fruits, for example, tulip tree (multiple of samaras), sweet gum (multiple of capsules), sycamore and teasel (multiple of achenes), and magnolia (multiple of follicles).

As described above, fruits can be summarized into eight types: (1) berry—simple fruit and seeds developed from a single ovary, (2) pepo—berries where the skin is

hardened, (3) hesperidium—berries with a rind, (4) false berries—epigynous fruit made from a part of the plant other than a single ovary, (5) compound fruit—from several ovaries in either a single flower or multiple flowers, (6) aggregate fruit—multiple fruits with seeds from different ovaries of a single flower, (7) multiple fruit—fruits of separate flowers packed closely together, and (8) other accessory fruit—where the edible part is not generated by the ovary. Another common way to classify fruits is based on growing regions such as temperate zone fruits, subtropical fruits, and tropical fruits (Kader 2002).

SPECIES, VARIETIES, AND BIOLOGICAL CHARACTERISTIC OF MAJOR FRUITS

The major fruits, such as apple, pear, grape, strawberry, citrus, banana, and mango, currently contribute the most of the total world production. About two-thirds of the major fruits produced worldwide are consumed as fresh fruit.

As discussed above, fruits are classified mainly on the basis of the ovary characteristic. In biology, fruit species can be classified by their botanical origin. In this following section, species, varieties, biological characteristic, and production of major fruits are briefly reviewed.

Apple

The genus *Malus* belongs to the Rosaceae family and forms with its closely related fruit (*Pyrus* and *Cydonia*) and ornamental (*Amelanchier*, *Aronia*, *Chaenomweles*, *Cotoneaster*, *Crateagus*, *Pyracantha*, *Sorbus*) genera, the subfamily Maloideae. Nowadays, *Malus* × *domestica* Borkh has been widely applied for apples.

World apple production reached 66 million tons in 2007 (Euromonitor 2008). Apple production is dominated by cultivars, such as "Delicious," "Gold Delicious," "McIntosh," "Jonathan," "Cox's Orange Pippin," "Granny Smith," and "Braeburn." In Asia, these varieties often replace the local varieties selected from the native species *Malus prunifolia* and its cultivated species *Malus asiatica*. China's enormous growth in apple production is entirely due to the introduction of the "Fuji" cultivar.

Banana

Banana belongs to the genus *Musa* in the family Musaceae, order Zingiberales. The family Musaceae comprises two genera viz., *Musa* and *Ensete*. The genus *Musa* comprises all the edible bananas and plantains with over 50 species. Bananas are perennial monocotyledonous herbs that grow well in humid tropical and subtropical regions. The origin of banana is traced back to Southeast Asia in the jungles of Malaysia, Indonesia, or the Philippines. Banana originated from two wild diploid species namely, *Musa acuminate* Coll and *Musa balbisiana* Coll. *M. acuminate* is native of the Malay Peninsula and adjacent regions, while *M. balbisiana* is found in India eastward to the tropical Pacific.

Bananas are the fourth world's most important food crop after rice, wheat, and maize, with production of 73 million tons in 2007 (Euromonitor 2008). The majority

of the banana crops are grown in the tropical and subtropical zones. From a consumer perspective, bananas are nutritious with a pleasant flavor and widely consumed throughout the world. India is the world's leading producer of banana and plantain, followed by Brazil and China.

Grape

The *Vitis vinifera* L. grape is one of the oldest cultivated plants and is thought to have originated in the region between the Mediterranean and the Caspian Sea. Cultivars of the vine slowly spread eastward across southern Asia and westward around the Mediterranean Sea. The Germplasm Resources Information Network (http://www.ars-grin.gov) of the United States Department of Agriculture describes the genera and 43 species, 5 natural hybrids, and 15 varieties of species in *Vitis. V. vinifera* is the most successfully used grape species with thousands of wine, table, and raisin grape cultivars grown throughout the world's temperate zones.

Grapes are now grown in more than 90 countries of the world and become the world's largest fruit crop with a total production of 69 million tons (Euromonitor 2008). The countries with the greatest acreage are Spain, France, Italy, Turkey, China, and the United States. The leading countries for the production of table grapes consumed as fresh fruit are China, Turkey, Italy, Chile, and the United States.

Citrus Fruit

Citrus, belonging to the family Rutaceae, is one of the world's most important fruit. Citrus can be eaten as a fresh fruit, processed into juice, or added to dishes and beverages. The major types of edible citrus include citron (*Citrus medica* L.); pomelo or shaddock (*Citrus grandis*); tangerine, mandarin, or satsuma (*Citrus reticulata* Blanco); limes (*Citrus aurantifolia* L.); sour orange (*Citrus aurantium* L.); sweet oranges (*Citrus sinensis* [L.] Osbeck); lemon (*Citrus limon* L.); and grapefruit (*Citrus paradisi* Macfad.). Brazil, the United States, and China are the three largest citrus producers in the world.

Strawberry

Strawberry belongs to the genus *Fragaria*. The genus is comprised of 32 species. Historically, several *Fragaria* species and novel hybrids have been brought into cultivation in different parts of the world, including *Fragaria chiloensis* in South America, and *Fragaria moschata* and *Fragaria vesca* in Europe. However, strawberry (*Fragaria* × *ananassa* Duch) is one of the most widely grown small fruits in the world. The large modern fruit of today was developed in the early 18th century by the cross between the wild strawberry *F. chiloensis* and *Fragaria virginiana*.

Globally, a large part of the cultivated area is located in Europe, followed by Asia and North and Central America. In 2004, a total production of strawberry reached to 2.4 million tons in the world. The United States is the world's leading strawberry producer with China, Spain, and Korea. Some countries like Turkey, Morocco, and Egypt have strongly increased their production.

Peach

Peach belongs to the Prunoideae subfamily of the family Rosaceae. In temperate regions, the family ranks third place in economic importance. The genus *Prunus* is characterized by species that produce drupes known as "stone fruit." The edible portion of the fruit is a juicy mesocarp. There are three major groups of cultivars: nectarines, freestone peaches, and clingstone peaches. All commercial varieties of peach are *Prunus persica* (L.) Batsch, including nectarines differing from peach in the absence of pubescence ("fuzzless") on the fruit surface. Peaches originated in China, with a cultivation history of over 4000 years. Peach is grown in all continents except Antarctica, and world peach production has increased steadily in recent year.

Pear

Pear species belong to the genus *Pyrus*, the subfamily Maloideae (Pomoideae) in the family Rosaceae. There are about 22 primary species in the *genus*, all of which originate in either Asia or Europe. The pear has been cultivated in China for at least 3000 years. There are two major species, European pear (*Pyrus communis* L.) and Asian pear (*Pyrus pyrifolia* L.), which are commercially cultivated. The first species to be domesticated was *P. pyrifolia* (Burm.) Nakai because the wild type is edible but without selection. Later, the hardy northern Chinese type *Pyrus ussuriensis* Maxim probably became cultivated after selection from the wild type. Natural hybridization between these two wild species likely occurred in China to produce the modern "Ussuri" cultivars in northern China. In other parts of the world, cultivated pears have been derived from *P. communis* L., while *P. communis* var. pyraster and/or *P. communis* var. caucasica were probably the ancestors of the common pear of Europe, but "French" cultivars may be complex hybrids of these two.

Pear is the third important temperate fruit after grape and apple. Asia produces the most, followed by Europe, North and Central America, and South America. Among countries, China produced the most, followed by the United States, Italy, and Spain. Pears can be consumed as fresh fruit, fruit juice, cube for fruit salad, canned product, and dry fruit. About 80% of the total pear production is destined for fresh consumption.

Mango

The genus *Mangifera*, belonging to the dicotyledonous family "Anacardiaceae," originates in the Indo-Burma region. Almost all the edible cultivars of mango are the single species *Mangifera indica* L., which originated in the Indian subcontinent. The few other species that contribute edible fruits are *Mangifera caesia*, *Mangifera foetida*, and *Mangifera odorata*, which are confined to the Malaysian region.

Mango is a very important tropical fruit and popularly known as the "apple of the tropics." Mango is commercially grown in over 103 countries of the world. The major growing countries in the world are India, China, Mexico, Pakistan, Indonesia, Thailand, the Philippines, Brazil, Australia, Nigeria, and Egypt (http://faostat.fao.org). There are more than 1000 varieties of mango under cultivation, but only a few of them are grown on a commercial scale.

Papaya

Papaya (Carica papaya L.) belongs to family Caricaceae, which consists of six genera including Carica a monotypic genus, Jacaratia (7 species), Jarilla (3 species), Cylicomorpha (2 species), Horovitzia (1 species), and Vasconcellea (21 species). Carica is the only genus of Caricaceae containing the domesticated species papaya, which is by far the most economically important and has a wide distribution throughout the tropics and subtropics of the world. Papaya probably originated in the lowland of Central America between southern Mexico and Nicaragua, and is now cultivated in many tropical and subtropical regions.

Papaya is a major tropical fruit grown commercially in India, Brazil, Mexico, Australia, Hawaii, Thailand, South Africa, the Philippines, Indonesia, and China. In recent years, intensive improvements and selections have given rise to a large number of papaya varieties, such as "Kapoho Solo," "Sun Rise," "Sun Set," "Waimanalo," "Kamiya" (United States), "Pusa Delicious," "Pusa Nanha," "Pusa Dwarft," "Surya" (India), "Cavite Special" (the Philippines), "Sainampueng," "Kak Dum" (Thailand), and improved "Peterson," "Guinea" and "Gold and Sunnybank" (Australia).

Pineapple

Pineapple is a perennial monocot belonging to the family of Bromeliaceae, subfamily Bromelioideae. The Bromelioideae comprises 56 genera with more than 2000 species, which are classified into three subfamilies: Pitcarnioideae, Tillandsioideae, and Bromelioideae. This last subfamily shows a tendency toward the fusion of floral parts, a trait most developed in *Ananas*. Many distinctions, particularly those related to fruit size and fertility, appear to be the direct result of human selection in the course of domestication.

Pineapple is the third most important tropical fruit after bananas and mangoes and has been cultivated in South America since the 15th century. Owing to its attractive sweet flavor, pineapple is widely consumed as fresh fruit, processed juice, and canned fruit, and is used as an ingredient in exotic foods. Five countries, Thailand, the Philippines, Brazil, China, and India, contribute to the major production in the world.

Plum

Plums belong to subfamily Prunoideae of the family of Rosaceae. *Prunus* species are divided into three major subgenera: *Prunophora* (plum and apricots), *Amygdalus* (peaches and almonds), and *Cerasus* (sweet and sour cherries). The subgenus *Prunophora* is divided into two main sections: *Euprunus* groups (plum species) and *Armeniaca*, which contains the apricot species. Plum has been domesticated independently in Europe, Asia, and America. In Europe, *Prunus domestica* L. is the most important source of fruit cultivars and has been grown for over 2000 years. In Asia, the Japanese plum *Prunus salicina* L. originates from China where it has been cultivated since ancient times. In north America, the third plum domestication source, a wide range of native species, such as *Prunus americana* Marsh., *Prunus hortulana* Bailey, *Prunus angustifolia* Marsh., and *Prunus maritima* Marsh., are present. The

major production of plum is located in Europe and Asia. In Europe, Germany is the leading producer.

FRUIT FLAVOR

The consumption of fresh fruit is dependent on the fruit quality (Baldwin et al. 2007; López et al. 2007). The quality of fresh fruit includes many aspects such as appearance, color, texture, flavor, and nutritional value (Kader 2002; Song 2007). Among them, flavor is one of the most important quality traits for fresh fruit (Dirinck et al. 1989; Dull and Hulme 1971; Maarse 1991; Reineccius 2006). Fruit flavor is made up of sugars, acids, salts, bitter compounds such as alkaloids or flavonoids, and aroma volatiles (Dirinck et al. 1989; Salunkhe and Do 1976; Song and Forney 2008). The flavor of fresh fruit is determined by taste and aroma (odor-active compounds). The contribution of odor-active compounds to the fruit flavors has gained increasing attention because these compounds are important for the characteristic flavors of fruits (Baldwin 1993, 2002b; Brückner 2008). The present chapter refers specifically the term "flavor" to the volatile compounds. Volatile compounds in fruits are diverse, consisting of hundreds of different chemical compounds comprising only 10⁻⁷–10⁻⁴ of the fresh fruit weight (Berger 2007; Brückner 2008). Although these volatile compounds are produced in trace amounts, they can be detected by human olfaction. The diversity is partially responsible for the unique flavors found in different fruit species. The importance of volatile production in fruit related to its influencing factors has been intensively investigated and/or reviewed (Baldwin 2002; Dixon and Hewett 2000; Fellman et al. 2000; Forney et al. 2000; Song 2007; Song and Forney 2008).

Classification of Volatile Compounds in Fruit Flavor

Chemical Structure Various types of fresh fruits produce distinct volatile profiles. Volatile compounds, which are produced by fresh fruits, are mainly comprised of diverse classes of chemicals, including esters, alcohols, aldehydes, ketones, lactones, and terpenoids (Table 1.2). However, some sulfur compounds, such as *S*-methyl thiobutanoate, 3-(methylthio) propanal, ethyl 2-(methylthio) acetate, ethyl 3-(methylthio) propanoate, and 3-(methylthio) propyl acetate, also contribute to the flavor of fruit such as melons (Song and Forney 2008). Although an overwhelming number of chemical compounds have been identified as volatile compounds in fresh fruit, only a fraction of these compounds have been identified as impact compounds of fruit flavor based on their quantitative abundance and olfactory thresholds (Cunningham and Barry 1986; Schieberle et al. 1990; Wyllie et al. 1995).

Biogenesis Volatile compounds forming the fruit flavor are produced through many metabolic pathways during fruit ripening and postharvest storage, and depend on many factors related to the species, variety, climate, production, maturity, and pre- and postharvest handling. For most fruits, volatile production is closely related to fruit ripening. As direct products of a metabolic pathway or as a result of interactions between pathways or end products, volatile compounds can be classified by the biogenesis: fatty acids (FAs), amino acids, glucosinolates, terpenoid, phenol, and related compounds (Berger 2007). However, from the point of chemical

TABLE 1.2. Volatile Compounds Present in Fruit Flavor

Esters	Alcohols	Aldehydes	Ketones	Lactones	Terpenoids
Butyl acetate Butyl butanoate	Benzyl alcohol Butan-1-ol	Acetaldehyde Benzaldehyde	2,3-Butanedione β-Damsenone	γ-Butyrolactone γ-Decalactone	β-Caryophyllene 1,8-Cineole
Butyl hexanoate	(E)-cinnamyl	(E)-	Eugenol	8-Decalactone	Citral
Butyl-2-methyl butanoate	1-Hexanol	(E,E)-2,4-decadienal	2-Heptanone	γ -Dodecalactone	β-Damascenone
Butyl propanoate	(E)-2-hexenol	Hexanal	4-(<i>p</i> -Hydroxyphenyl)- 2-butanone	δ-Dodecalactone	Dihydroedulan
Ethyl acetate	(Z)-3-hexenol	(E)-2-hexenal	3-Hydroxy-2- butanone	γ -Jasmolactone	Farnesyl acetate
Ethyl butanoate	1-Octanol	(Z)-3-hexenal	β-Ionone	γ-Octalactone	Geraniol
Ethyl hexanoate	Hexan-1-ol	Nonanal	6-Methyl-5-heptene-		α-Ionone
Ethyl 2-methylbutanoate	(Z,Z)-3,6-nonadienol	(Z)-6-nonenal	2-one Nerolidol		β-Ionone
Ethyl 3-methylbutanoate	1-Phenylethanol	(E,Z)-2,6-nonadienal	1-Octen-3-one		Limonene
Ethyl 2-methylpropanoate Ethyl 2-methylbutanoate	2-Phenylethanol	(E)-2-nonenal Phenylacetaldehyde	2-Pentanone (Z) -1,5-octadien-3-		Linalool Myrtenol
Ethyl propanoate Ethyl 2-methylpropanoate			Terpenes		Nerol $lpha$ -Phellandrene
Ethyl nonanoate (E)-2-hexenyl acetate					α -Pinene β -Pinene

(E)-3-hexenyl acetate	Terpinen-4-o
Hexyl acetate	α-Terpineol
Hexyl butanoate	Terpinolene
Hexyl propanoate	α-Farensene
Hexyl-2-methyl butanoate	
Methyl acetate	
Methyl cinnamate	
Methyl butanoate	
Methyl hexanoate	
Methyl nonanoate	
Methyl octanoate	
Methyl-2-	
methylbutanoate	
Methyl-3-	
methylbutanoate	
2-Methylbutyl acetate	
3-Methylbutyl acetate	
2-Methylpropyl acetate	
(Z)-6-nonenyl acetate	
(Z,Z)-3,6-nonadienyl	
acetate	
Pentyl acetate	
Benzyl acetate	
Propyl acetate	
Propyl-2-methyl	
butanoate	

characterization, volatiles can be classified as esters, alcohols, aldehydes, ketones, lactones, and terpenoids (Table 1.2).

Volatile Compounds Formed from FAs FAs are precursors for a large number of volatile compounds. Many of them are important character-impacted aroma compounds that are responsible for fresh fruit flavors. Those compounds are usually having straight-chain carbons ranged from C₁ to C₂₀. Degradation of FAs occurs mainly by the three different oxidative routes: (1) α - and β -oxidation, (2) oxidation by the lipoxygenase pathway, and (3) autoxidation. The formation of flavors via βoxidation is exemplified by considering flavor formation in pears (Jennings 1967). The widest variety of flavor compounds formed from lipids arises via lipoxygenase activity. Many of the aliphatic esters, alcohols, acids, and carbonyls found in fruits are derived from the oxidative degradation of linoleic and linolenic acids (Reineccius 2006). In addition, some of the volatile compounds derived from enzyme-catalyzed oxidative breakdown of unsaturated FAs may also be produced by autoxidation (Chan 1987). Autoxidation of linoleic acid produces the 9- and 13-hydroperoxides, whereas linolenic acid also produces 12- and 16-hydroperoxides (Berger 2007). Hexanal and 2,4-decadienal are the primary oxidation products of linoleic acid, while autoxidation of linolenic acid produces 2,4-heptadienal as the major product. Further autoxidation of these aldehydes leads to the formation of other volatile products (Chan 1987). As an alternative to the membrane catabolism, a hypothesis of low rate of de novo FA biosynthesis (free FA hypothesis) was proposed as the limiting factor for the aroma biosynthesis in fruit harvested too early (Song and Bangerth 2003). This hypothesis is also supported by the evidence that a close relationship between low aroma volatile production, low free FA, and low ATP content in apple fruit (Song and Bangerth 2003; Tan and Bangerth 2001). Either oxidative degradation of FAs or newly biosynthesized free FAs are precursors responsible for the formation of straight-chain esters in many fruits, but their role in flavor formation needs to be clarified.

Volatile Compounds Formed from Amino Acid Metabolism Amino acid metabolism generates aromatic, aliphatic, and branched-chain alcohols, acids, carbonyls, and esters that are important to fruit flavor (Reineccius 2006). Some volatile compounds can be produced by the action of enzymatic systems on amino acids. The major types of volatile compounds formed from the interaction of amino acids and sugars include aldehydes, alkyl pyrazines, alkyl thiazolines and thiazoles, and other heterocycles from the Strecker degradation (Maarse 1991). Amino acids are precursors for some branched aliphatic compounds such as 2-methyl-1-butanol and 3-methyl-1-butanol that are formed during the amino acid catabolism. These compounds can be further synthesized to form esters, which are important volatile compounds in many fruits with distinct "fruity" odor. As they share the same precursor pyruvate, which is generated from glycolysis, the interaction between FAs and branched amino acids is another important factor in the volatile biosynthesis of fruits. As apple fruits ripen, there is a great production of volatile compounds from branched amino acid pathway (Song 1994).

Volatile Compounds Formed from Carbohydrate Metabolism A large variety of volatile flavors can be traced to carbohydrate metabolism (Berger 2007). As the

photosynthetic pathways involve turning CO₂ into sugars that are metabolized into other plant needs, for example, lipids and amino acids, nearly all plant flavors come indirectly from carbohydrate metabolism. However, there are few flavor constituents that come directly from carbohydrate metabolism (Reineccius 2006).

Volatile Compounds Derived from Terpenoid Terpenoids are widely distributed among fruits. There are two main types of terpenoids that may contribute significantly to the fruit flavor: (1) monoterpenes and sesquiterpenes and (2) irregular terpenes mainly produced by catabolistic pathways and/or autoxidation (Berger 2007). The monoterpenes and sesquiterpenes are mainly formed by anabolic processes and, therefore, are present in intact plant tissue. However, the formation of some irregular terpenes cannot be explained by anabolic pathways in some fruits. These terpenoids are primarily oxidation-degraded products of the carotenoids.

Phenols and Related Compounds A large number of volatile phenols and related compounds occur in fruits, some of which are potent aroma compounds (Berger 2007). The majority of volatile phenols and related compounds are formed mainly through the shikimic acid pathway and are present either as free aglycones or bound glycosides that can be liberated by enzymatic hydrolysis. Generally, the volatile phenols and related compounds are benzene-substituted derivatives with methoxy and phenolic groups, often with an allyl, a vinyl, or an aldehyde group. Common flavor compounds of this group are eugenol, vanillin, myristicin, apiole, elemicin, and benzaldehyde.

VOLATILE COMPOUNDS AND THEIR BIOLOGICAL CHARACTERISTIC OF MAJOR FRUITS

As described above, lipids, carbohydrates, proteins, and amino acids are enzymatically converted to volatile compounds. The characterization of fruit volatiles can be very complicated due to various influencing factors such as cultivars, fruit maturity, postharvest treatment, fruit sample (either intact fruit, slices, or homogenized samples), and analytic techniques (Berger 2007; Brückner 2008; Cunningham and Barry 1986). Volatiles can be classified as "primary" or "secondary" compounds, indicating whether they were present in intact fruit tissue or produced as a result of tissue disruption (Drawert et al. 1969). It should be pointed out that analysis of volatiles from either intact or disrupted fruit tissues will influence the aroma profiles and final aroma interpretation. This following section reviews overall flavor characterization of volatile compounds reported for some major fruits published in the past few years. The listed volatile compounds are those that are produced by fruit at a full ripe or close to consumption stage and summarized from different methodologies. In the following section, volatile compounds of major fruits are summarized in Table 1.3.

Apple

More than 300 volatile compounds have been identified in apple fruit (Dirinck et al. 1989). Only a few of these volatiles have been identified as important active

TABLE 1.3. Volatile Compounds of Major Fruits

Fruit Name	Volatile Compounds	Reference
Apple	Alcohols, aldehydes, 1-butyl acetate, butyl 2-methylbutanoate, β-damascenone, ethyl butanoate, ethyl butanoate, ethyl 2-methylbutanoate, ethyl 2-methylbutanoate, ethyl acetate, <i>n</i> -hexanal, 1-hexanol, hexen-1-ol, hexyl acetate, hexyl butanoate, hexyl 2-methylbutanoate, hexyl propanoate, ketone, 2-methylbutanoate, methyl 2-methylbutanoate, propyl 2-methylbutanoate, pentyl acetate, 1-propyl propionate, <i>trans</i> -2-hexenal, and <i>trans</i> -2-hexen-1-ol	Dixon and Hewett (2000), Flath and others (1969), Cunningham (1985)
Banana	Alcohols, amyl butanaote, butyl butanaote, esters, and isoamyl acetate	Jayanty and others (2002), Maciel and others (1986)
Citrus fruit	Acetaldehyde, acetoin, carvone, β-damascenone, (<i>E,E</i>)-2,4-decadienal, decanal, diacetyl, dodecanal, elinalool, ethanol, ethyl acetate, ethyl butanoate, ethyl propanoate, ethyl-2-methyl propanoate, ethyl-2-methyl butanoate, ethyl hexanoate, ethyl-3-hydroxy hexanoate, ethyl octanoate, ethyl decanoate, geranial citronellal, hexanal, (<i>E</i>)-2-hexenaln, (<i>E</i>)-2-hexen-1-ol, (<i>Z</i>)-3-hexenal, (<i>Z</i>)-3-hexen-1-ol, limonene, methyl butanoate, 3-methyl butanol, neral, nonanal, (<i>E</i>)-2-nonenal, (<i>Z</i>)-2-nonenal, 1-penten-3-one, 1-octanol, octanal, 1-octen-3-one, β-sinensal, α-terpincol, and terpinen-4-ol	Berger (2007), Berry and others (1983)
Strawberry	Butyrates, butyl acetate, 2,5-dimethyl-4-hydroxy-3(2H)-furanone, dimethyl-4-methoxy-3(2H)-furanone, γ-decalactone, γ-dodecalactone, ethyl butanoate, ethyl cinnamates, ethyl hexanoate, ethyl 3-methylbutanoate, ethyl propanoate, farnesyl acetate, furaneol, furaneol-β-glucoside, geraniol, 2-heptanone, hexanal, (<i>E</i>)-2-hexenal, hexyl acetate, linalool, methyl cinnamates, methyl and ethyl acetates, methyl anthranilate, methyl butanoate, methyl 2-methylbutanoate, methyl hexanoate, mesifurane, methional, propionates, and 1-octen-3-one	Forney and others (2000), Hakala and others (2002), Sanz and others (1994), Whitaker and Evans (1987)

TABLE 1.3. Continued

Fruit Name	Volatile Compounds	Reference
Peach	Benzaldehyde, benzyl alcohol, γ - caprolactone, cis -3-hexenyl acetate, β -damascenone, γ -decalactone, (E,E) - 2,4-decadienal, δ -decalactone, γ - decalactone, dimethyl disulfide, γ -dodecalactone, δ -dodecalactone, ethyl acetate, ethyl butanoate, ethyl octanoate, γ -decalactone, hexanal, (Z) -3-hexen-1-yl acetate, (E) -2-hexen-1-ol, (Z) -3-hexenal, γ -jasmolactone, linalool, methyl octanoate, γ -octalactone, δ -octalactone, 6-pentyl α -pyrone, and terpinolene	Aubert and Milhet (2007), Berger (2007), Horvat and others (1992), Narain and others (1990), Visai and Vanoli (1997)
Pear	Butyl acetate, butyl butanoate, hexyl acetate, ethyl hexanoate, ethyl octanoate, ethyl (E) -2-octenoate, ethyl (E,Z) -2,4-decadienoate, methyl (E,Z) -2,4-decadienoate, and pentyl acetate	Argenta and others (2003), Kahle and others (2005), Rapparini and Predieri (2003), Rizzolo and others (1991)
Grape	Methyl anthranilate	Rosillo and others (1999), Whitaker and Evans (1987)
Mango	Camphene, butan-1-ol, car-3-ene, β-caryophyllene, <i>p</i> -cymene, <i>cis</i> -hex-3-en-1-ol, α-copanene, cyclohexane, dimethylcyclohexane, 1,1-diethoxyethane, ethanol, ethylcyclohexane, ethyl butenoate, ethyl dodecanoate, ehyl decanoate, ethyl octanoate, α-fenchene, 2-furfural, hexanal, α-humulene, hydrocarbon, limonene, 1-methylpropan-1-ol, methylcyclohexane, 3-methylbutan-1-ol, myrcene, α-phellandrene, β-phellandrene, α-pinene, β-pinene, sabinene, sabinyl acetate, toluene, γ-terpinene, α-terpinolene, and xylene	MacLeod and Snyder (1985), Macleod and Troconis (1982), Malundo and others (2001), Pino and Mesa (2006)
Papaya	Linalool, ethyl acetate, phenylacetonitrile, benzyl isothiocynate, methyl butanoate, ethyl butanoate, 3-methylbutanol, benzyl alcohol, α-terpineol, and butanol	Almora and others (2004), Flath and others (1990), Heidlas and others (1984), Pino and others (2003)
Pineapple	Acetoxyacetone, p -allyl phenol, γ -butyrolactone, β -hydroxyhexanoic acids, 4-methoxy-2,5-dimethyl-2(H)-furan-3-one, methyl esters of β -hydroxybutyric, γ -octalactone, 2-propenyl hexanoate, sesquiterpene, 1-(E , Z)-3,5-undecatriene, and 1-(E , Z , Z)3,5,8-undecatetraene	Berger and others (1983, 1985), Takeoka and others (1991), Tokitomo and others (2005)
Plum	Benzaldehyde, (E,E) -2,4-decadienal, δ -decalactone, γ -decalactone, ethyl nonanoate, (Z) -3-hexenal, linalool, methyl cinnamate, and δ -octalactone	Maarse (1991), Horvat (1992)

odor compounds being responsible for the characteristic aroma in most apple cultivars, such as β -damascenone, butyl, isoamyl, and hexyl hexanoate, along with ethyl, propyl, and hexyl butanoates (Cunningham 1985). The most abundant volatile components are esters, alcohols, aldehydes, ketones, and ethers, while esters are the principal compounds responsible for fruity odor (Fellman et al. 2000; Plotto et al. 2000). For example, ethyl 2-methylbutanoate, 2-methylbutyl acetate, and hexyl acetate contribute mostly to the characteristic aroma of "Fuji" apples, while ethyl butanoate and ethyl 2-methylbutanoate are the active odor compounds in "Elstar" apples, and ethyl butanoate, acetaldehyde, 2-methyl-1-butanol, and ethyl methylpropanoate in "Cox Orange" (Acree et al. 1984; Berger 2007; Echeverria et al. 2004). Ethyl 2-methylbutanoate also has a direct impact on "Granny Smith" apple flavor (Lavilla et al. 1999).

Banana

The major volatile compounds in banana fruit are identified as alcohols and esters, including amyl acetate, isoamyl acetate, butyl butyrate, and amyl butyrate. Esters predominate in the volatile fraction of banana fruit. Based on the combined analytic chemistry with sensory analysis, penten-2-one, 3-methylbutyl, and 2-methylpropyl esters of acetate and butyrate have been identified as the most important banana fruit aroma (Berger et al. 1986). Isopentyl acetate and isobutyl acetate are also known as the most important impact compounds of banana aroma. The concentrations of acetates and butanoates increased during ripening of banana fruit (Jayanty et al. 2002). In addition, isoamyl alcohol, isoamyl acetate, butyl acetate, and elemicine were detected by olfactometric analyses as characteristics of banana odor (Boudhrioua et al. 2003).

Citrus

Citrus volatiles have been extensively examined over the past several decades. As the most foods of commercial interest, the volatile components of citrus juice have been known for some time. Table 1.2 lists the volatile compounds present in citrus juice, which were detected by gas chromatography (GC)–olfactometry. Esters are important as they are responsible for the flavor characteristic (Berger 2007), while the major esters are ethyl esters of C₃ to C₄ organic acids. Linalool is by far the most important alcohol. However, ketones, carvone, diacetyl, and acetoin are off-flavors. Thus, the key flavor compounds in fresh citrus fruit still need to be identified.

Strawberry

Over 360 different volatile compounds have been identified in strawberry fruit (Maarse 1991). Strawberry aroma is composed predominately of esters with alcohols, ketones, lactones, and aldehydes being present in smaller quantities (Forney et al. 2000). Strawberries contain primarily straight esters, which comprise primarily of methyl, and ethyl acetates, butanoates, and hexanoates. Esters provide an aroma characteristic to the fruit (Gomes da Silav and Chavees das Neves 1999). Terpenoids and sulfur compounds may also have a significant impact on the characteristic

aroma of strawberry fruit (Dirinck et al. 1981). The most important aroma compounds in strawberry fruit include ethyl cinnamates, methyl cinnamates, 2,5-dimethyl-4-hydroxy-3(2H)-furanone,furaneol,furaneol-beta-glucoside,dimethyl-4-methoxy-3(2H)-furanone (mesifurane), methyl and ethyl acetates, propionates, and butyrates, which are responsible for fruity flavor. A number of terpenes also contribute to the flavor of strawberry fruit.

Peach

Approximately 100 volatile compounds have been identified in peaches, including alcohols, aldehydes, alkanes, esters, ketones, lactones, and terpenes (Aubert et al. 2003; Visai and Vanoli 1997). The major volatile compounds are identified as ethyl acetate, *cis*-3-hexenyl acetate, methyl octanoate, ethyl octanoate, γ -decalactone, benzyl alcohol, γ -caprolactone, and δ -decalactone. Among them, lactones, particularly γ -decalactone and δ -decalactone, have been reported as character-impacted compounds in peaches and are associated with C6-aldehydes, aliphatic alcohols, and terpenes, which are responsible for fruity characteristics (Derail et al. 1999; Engel et al. 1988; Horvat et al. 1990; Narain et al. 1990). Nectarines produce less volatiles in total but more esters, linalol, and terpinolene and have more fruity and floral aroma notes than peaches (Visai and Vanoli 1997).

Pear

More than 300 volatile compounds have been identified in pear, including aldehydes, alcohols, esters, ketones, and sulfur compounds (Rapparini and Predieri 2003). The most important character-impacted compounds of pears are listed in Table 1.3. Methyl and hexyl esters of decadienoate are the character-impacted compounds of the European pear (Argenta et al. 2003; Kahle et al. 2005; Rapparini and Predieri 2003). Other volatile esters, for example, hexyl acetate, 2-methylpropyl acetate, butyl acetate, butyl butanoate, pentyl acetate, and ethyl hexanoate possess strong pear-like aroma (Rapparini and Predieri 2003). Ethyl octanoate and ethyl (*E*)-2-octenoate contribute to sweet or fruity odors in pears, while a high concentration of 2,4-decadienoates in fruit flesh is accepted by consumers (Rizzolo et al. 1991). In addition, hexanal, 2-methylpropyl acetate, ethyl acetate, hexyl acetate, 3-methylbutyl 2-methylbutanoate, ethyl butanoate, and butanol are identified as impact volatiles in "Conference" pears (Rizzolo et al. 2005).

Grape

The flavor of grapes is made up of volatile alcohols, aldehydes, esters, acids, terpenols, and carbonyl compounds. Grape may be divided into aromatic and non-aromatic varieties. Free terpenols, for example, linalool and geraniol, have been identified as major aroma compounds in both red and white grapes (Rosilllo et al. 1999). Octanoic acid and alcohols, particularly 2-phenylethanol, are recognized after crushing (Rosilllo et al. 1999). In addition, esters and aldehydes were also reported in "Aleatico" grapes (Bellincontro et al. 2009). Fruit flavor is highly correlated with consumer likings in table grapes.

Mango

Mango possesses a very attractive flavor characteristic. About 270 volatile compounds from mango fruit were identified. However, application of distillation extraction in combination with active odor value (aroma threshold) technologies exhibits that monoterpenes such as α -pinene, myrecene, α -phelladrene, σ -3-carene, p-cymene, limone and terpinolene, esters including ethyl-2-methylpropanaote, ethyle-butanoate, as well as (E,Z)-2,6-nonadienal, (E)-2-nonenal, methyl benzoate, (E)- β -ionone, decanal, and 2,5,-dimethyl-4-methoxy-3(2H)-furanone are the most important compounds contributing to mango flavor (Pino and Mesa 2006). The acids, esters, and lactones found were considered to be produced by the lipid metabolism in the flavor development of mango fruit during ripening.

Papaya

Papaya possesses a characteristic aroma, which is due to several volatile components such as alcohols, esters, aldehydes, and sulfur compounds (Chan et al. 1973). Fiftyone volatile compounds from intact "Hawaiian" papaya at different ripening stages were detected. Linalool, followed by linalool oxide A, linalool oxide B, ethyl acetate, phenylacetonitrile, and benzyl isothiocynate, was the major compound in the fully ripe fruits (Flath et al. 1990). Other work indicated the esters as the predominant compounds among the volatiles of papayas from Sri Lanka and Colombia (Heidlas et al. 1984; Macleod and Pieris 1984). In addition, methyl butanoate, ethyl butanoate, 3-methylbutanol, benzyl alcohol, α-terpineol, and butanol are found to be important volatiles in papaya fruit (Almora et al. 2004; Pino et al. 2003).

Pineapple

More than 280 volatile compounds have been found in pineapple fruit (Tokitomo et al. 2005). The major volatile compounds are identified as 4-methoxy-2,5-dimethyl-2(H)-furan-3-one, 2-propenyl hexanoate, sesquiterpene hydrocarbons, 1-(E,Z)-3,5-undecatriene, 1-(E,Z,Z)3,5,8-undecatetraene, 2-propenyl n-hexanoate ethyl, para-allyl phenol, γ-butyrolactone, γ-octalactone, acetoxyacetone, methyl esters of β-hydroxybutyric, and β-hydroxyhexanoic acids. Monoterpene alcohols (linalool, α-terpineol, and terpinen-4-ol) and sesquiterpenes were also identified (Berger et al. 1985; Flath and Forry 1970). In addition, the sulfur compounds such as methyl 3-(methylthio)-(E)-2-propenoate, methyl 3-(methylthio)-(Z)-2-propenoate, ethyl 3-(methylthio)-(Z)-2-propenoate, methyl 5-hexenoate, methyl (E)-4-hexenoate, methyl 4-(methylthio)-butanoate, nonanol, and ethyl 4-methylthiobutanoate, were reported as impact-flavor compounds in fresh "Hawaiian" pineapple (Takeoka et al. 1991).

Plum

Approximately 75 volatile compounds have been identified in plum juices (Maarse 1991). Lactones from C_6 to C_{12} are major classes of volatile compounds in plums (Horvat 1992), but the key flavor compounds in fresh plum fruit are not yet identified.

CONCLUDING REMARKS

The diversity of varieties of fruit for today's human consumption has resulted from a long history of natural development, selection, and scientific breeding. Fruits play important roles in human nutrition and diet. However, they are perishable due to natural ripening, senescence, and pathological decay. Fruit quality attributes, such as texture, appearance, flavor, and nutrition, significantly change during ripening, but they have not been understood fully. Thus, the further development of modern technologies of breeding, production, and postharvest handling will enable consumers to enjoy fruits and their products without limitations of seasons and geographic locations.

Fruit flavor is an important aspect of quality. Many compounds are responsible for the fruit aromas that have strong penetration odors with low threshold values. Advances in identifying and quantifying volatile compounds by improved analysis techniques in various fruits have greatly increased our knowledge about fruit flavor (Brückner 2008; Song 2007; Song and Forney 2008; Tholl et al. 2006; Tzortzakis 2007). Advances in the biogenesis of volatile compounds in fresh fruits have also improved our current understanding; however, knowledge of the biochemical pathways and key regulating steps of the synthesis of these volatile compounds is still incomplete. A fuller understanding of the flavor chemistry and biology of volatile compounds of fruits is important to improve the flavor quality of fresh fruit that complies with the consumer needs for better quality. Furthermore, employing state-of-the-art genomic, proteomic, and microscopy tools to study fundamental metabolism, and combining these results with direct measurement of chemical and sensory properties (Baldwin 2002a; Bood and Zabetakis 2002; Raab et al. 2006; Song and Forney 2008) will lead to a better understanding of how to optimize and retain fruit flavor quality in the market places for the benefit of both consumers and fruit industry.

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