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Chapter 3

Flavor Chemistry of Small Fruits: Blackberry, Raspberry, and Blueberry

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The increased interest in the health benefits of berry fruits has promoted research in horticulture and food science to address the fruit quality, especially in flavor quality. Flavor in fruit is largely determined by the content and variety of their particular volatile compounds. Volatiles found in fruits are diverse, consisting of hundreds of different chemical compounds, giving unique flavors to different fruits. The flavor of small fruits other than winegrapes has not been as well studied as other fruits such as tree fruits. Although the environment alters the flavor quality of fruit, genetic factors determine the flavor profile quantitatively and qualitatively. More studies are needed to understand the biogenesis of flavor compounds so that genomic tools related to flavor formation in small fruits can be developed and utilized. This type of information could be used in the future in the breeding program to develop new cultivar with desired flavor quality.

Introduction

The word 'berry' has two meanings: one, a botanical definition, the other, a common identification. Botanical berries are a simple fruit, having seeds and pulp produced from a single ovary, such as tomato, grape, lychee, loquat, lucuma, plantain, avocado, persimmon, eggplant, guava, uchuva, and chili pepper. In common language, however, berries are more broadly recognized as small, round or semi-oblong, usually brightly colored, sweet or sour fruit, such as strawberry, raspberry, blackberry, blackcurrant, blueberry, cranberry, and elderberry (*1*). In North America, commonly consumed berry fruits include blackberries (*Rubus* spp.), black raspberries (*Rubus occidentalis*), blueberries (*Vaccinium corymbosum*), cranberries (*Vaccinium macrocarpon*), red raspberries (*Rubus idaeus*) and strawberries (*Fragaria* × *ananassa*) (*2*). Although there are many types of berry fruits consumed worldwide, this chapter focuses on three of the aforementioned berries commonly consumed in North America: red raspberries, blackberries, and blueberries.

Berry fruits are consumed not only in fresh and frozen forms, but also in a variety of foods such as juice, jams and jellies. In addition, the trend of using berry extracts as ingredients in functional foods and dietary supplements is growing. The nutritional content of berries includes dietary fiber, vitamins, minerals, and high levels of phenolic compounds. The major phenolic constituents in berries include anthocyanins, flavonols, flavanols, ellagitannins, gallotannins, proanthocyanidins, and phenolic acids (*3*). These phenolic compounds have been found to have various biological properties such as antioxidant, anticarcinogenic, anti-neurodegenerative, and anti-inflammatory activities (*3*). The consumption of berries in fresh, processed, and the nutraceutical markets is expanding exponentially in the last decades.

Nutritional value aside, berry flavor is of great importance to the consumer. Studies on berry flavor have been conducted over the past fifty years. Investigations in red raspberry flavor have been extensive, while studies on blackberry and blueberry flavor are still very limited. A quick scan of these studies shows that a large number of volatile compounds have been identified in berries. So far, approximately 250 volatile compounds have been identified in raspberries and blackberries, while about 100 volatile compounds have been identified in blueberries.

Some results were discrepant, and dependant on flavor isolation and identification techniques used; some compounds were not conclusive and were only identified in a single study. Traditional isolation technique, such as distillation, liquid-liquid extraction and headspace sampling, were frequently used in those studies to isolate flavor compounds from berry samples. However, many of these traditional techniques have disadvantages of bias, artifact formation and solvent contamination. Reliable quantitative data of volatile composition in berry samples, and sensory data in berries are very limited.

The flavor composition of berries is diverse. These compounds are enzymatically produced from lipids, carbohydrates, proteins, and amino acids in the fruits. Although the metabolic pathways might be similar in berries, each berry cultivar has a unique metabolic profile, this unique metabolic profile is responsible for the generation of unique volatile profile of each species, resulting in the characteristic aroma of the fruits. This characteristic aroma is the expression of the genotype-environment interaction. Typically, genetics determine the precursors, enzyme systems, and their activity in flavor formation. It is common that varietal differences in flavor are due to quantitative differences in flavor composition, rather than qualitative differences. The quantitative differences can also arise from environmental factors such as geography, soil nutrition, weather, irrigation and many other agronomical conditions.

Reviews on the raspberry, blackberry, and blueberry flavor are available in references (*1*, *4*). Because of the growing number of studies in this field, this chapter provides an update of berry flavor research.

Raspberry

Wild and cultivated raspberries are in the subgenus *Idaeobatus* of the genus *Rubus*. The main types of raspberries are red raspberry and black raspberry. Others, such as yellow raspberries, result from a mutation of red raspberries that prevents the red color from forming, are grown in the same way as red raspberries. Purple raspberries are a hybrid between black and red raspberries. These species are, however, of little to no economic importance. The red raspberries are the most widely grown species.

Volatile compounds in raspberry have been studies for over fifty years, including wild selections, hybrid between different species, and multiple commercial cultivars (*5–8*). In addition, red raspberry juice, essential oils, and raspberry processed products have also been studied (*9–13*). More than 250 volatile compounds have been identified. The volatile profiles of red raspberries were dominated by norisoprenoids, lactones, carbonyl compounds, esters, and alcohols. The most abundant compounds reported in raspberries include α-ionone, β-ionone, raspberry ketone, linalool, geraniol, benzaldehyde, α-pinene, β-caryophyllene, β-myrcene, trans-β-ocimene, ethyl acetate, ethyl heptanoate, and 2-methylbutanol (*6–8*, *10*, *14*, *15*).

Gas chromatography-olfactometry (GC-O) technique has been used to determine the aroma-active compounds in raspberries. Major compounds in raspberries are summarized in Table 1. However, qualitative and quantitative studies on aroma contributing compounds are still limited. Klesk and Qian (*10*) studied the odor-active compounds in 'Meeker' raspberries from Oregon and Washington by Aroma Extract Dilution Analysis (AEDA) and GC/O-MS technique. Seventy-five aromas were identified in the red raspberry fruit. According to flavor dilution (FD) factors, furaneol, hexanal, α-ionone, β-ionone, 4-oxo-β-ionone, neo-allo-ocimene, β-pinene, β-damascenone, *cis*-3-hexenal, methional, *cis*-3-hexenol, linalool, butanoic acid, ethyl 2-methylpropanoate, *trans*-2-hexenal, 2, 3-butanedione, heptanal, thiophene, benzaldehyde, geraniol, and raspberry ketone, were considered very important to raspberry aroma. Roberts and Acree (*13*) studied the top odor-active compounds in fresh 'Heritage' raspberries using headspace analysis and solvent extraction techniques. They find that β-damascenone, diacetyl, sotolon, 1-hexen-3-one, and *cis*-3-hexenol,ethyl 2-methylbutanoate, ethyl butanoate, raspberry ketone, vanillin, *cis*-3-hexenal, and β-ionone are the most important aroma compounds in raspberry.

Table 1. Major aroma compounds identified in red raspberries

Compounds	*References*	*Compounds*	*References*
Esters		*Alcohols*	
Ethyl acetate	(*5*, *6*, *10*, *20*, *23*)	1-Hexanol	(*5*, *6*, *10*)
Ethyl butanoate	(*10*, *13*)	*trans*-3-Hexenol	(*5*)
Ethyl 2-methyl-propanoate	(*10*)	*cis*-3-Hexenol	(*5–7*, *10*, *23*)
Ethyl 2-methylbutanoate	(*10*, *13*)	trans-2-Hexenol	(*5*)
Butyl acetate	(*10*)	1-Octen-3-ol	(*10*)
Ethyl propanoate	(*10*)	1-Octanol	(*10*)
3-Methylbutyl acetate	(*10*)	2-Nonanol	(*10*)
Methyl hexanoate	(*10*, *20*)		
Ethyl hexanoate	(*10*, *20*)	*Aromatic compounds*	
Ethyl octanoate	(*10*)	Benzyl alcohol	(*5–7*, *10*)
cis-3-Hexyl acetate	(*5*, *10*, *23*)	Phenylethyl alcohol	(*5*, *6*, *10*)
		Benzaldehyde	(*5*, *6*, *10*, *20*, *23*)
Terpenoids		Eugenol	(*5*, *10*)
α-Pinene	(*5*, *10*, *20*, *23*, *24*)	Vanillin	(*5*, *10*, *13*)
β-Pinene	(*10*, *20*, *24*)	Gingerone	(*5*, *10*)
α-Phellandrene	(*5*, *10*, *23*, *24*)	Raspberry ketone	(*5*, *7*, *10*, *13*)
β-Myrcene	(*10*, *23*)		
Limonene	(*5*, *10*, *20*, *23*)	*Acids*	
trans-β-Ocimene	(*10*)	Acetic acid	(*5–7*, *10*)
Sabinene	(*5*, *10*)	Propanoic acid	(*5*, *6*)
Caryophyllene	(*5*, *10*, *24*)	Butanoic acid	(*5*, *6*, *10*)
Linalool	(*5–7*, *10*, *23*, *24*)	2-Methylbutanoic acid	(*5*, *6*, *10*)
4-Terpineol	(*5*)	Hexanoic acid	(*5–7*)
α-Terpineol	(*5*, *10*)	Octanoic acid	(*5*, *6*)
Nerol	(*5*)		
Geraniol	(*5–7*, *10*)	*Lactones*	
		γ-Hexalactone	(*5*, *6*)

Continued on next page.

Table 1. (Continued). Major aroma compounds identified in red raspberries

Compounds	*References*	*Compounds*	*References*
Carbonyl compounds		δ-Hexalactone	(*5*)
Hexanal	(*5*, *10*, *20*, *23*)	γ-Octalactone	(*5*, *6*)
Heptanal	(*10*, *23*)	δ-Octalactone	(*5*, *10*)
Octanal	(*10*, *13*, *20*, *23*)	δ-Decalactone	(*5*, *10*)
cis-3-Hexenal	(*10*, *13*)	δ-Dodecalactone	(*5*)
trans-2-Hexenal	(*5*, *10*, *23*)		
Diacetyl	(*6*, *10*, *13*)	*Miscellaneous*	
Acetoin	(*5–7*)	Mesifurane	(*5*)
2-Heptanone	(*10*, *20*)	Norfuraneol	(*5*)
2-Nonanone	(*10*)	Furaneol	(*5*, *10*, *13*)
2-Undecanone	(*10*)	Homofuraneol	(*10*)
		Sotolon	(*10*, *13*)
Norisoprenoids		Maple furanone	(*10*)
β-Damascenone	(*5*, *6*, *10*, *13*)		
α-Ionone	(*5–7*, *10*, *24*)	*Others*	
α-Ionol	(*10*)	Dimethyl sulfide	(*10*)
β-Ionone	(*6*, *7*, *10*, *13*, *20*, *24*)	Dimethyl disulfide	(*10*)
β-Dihydroionone	(*10*)	Methional	(*10*)

Raspberry ketone is considered to be the characteristic compound for raspberry aroma. Raspberry ketone was first isolated from raspberries by TLC and identified by Schinz & Seidel (*16*). Braun & Hieke (*17*), Gallois (*18*), and Maquin, et al, (*19*) have also examined this compound. Organoleptic evaluation of the raspberry fruits shows that increasing raspberry flavor is in agreement with increasing raspberry ketone content in the fruits. The raspberry aroma was found to depend on a relatively high raspberry ketone content (*7*, *14*, *15*).

The importance of other aroma compounds-- α-ionone, β-ionone, *cis*-3-hexenol, geraniol, linalool, benzyl alcohol, acetoin, acetic acid, and hexanoic acid--were also examined in different cultivars. Raspberry ketone, α-ionone, and β-ionone were found to be the most important aroma compounds in all raspberries regardless of the cultivar, while linalool and geraniol were found in considerable levels only in some cultivars.

The concentration of these aroma compounds are affected by genotype, fruit maturity, and many other factors. Differences in volatile composition are apparent among raspberry cultivars. Vereshchagin and Bezzubov (*11*) compared the cultivars ‘Newburgh’ and ‘Novost Kuzmina’ for volatile composition.

In Flavor and Health Benefits of Small Fruits; Qian, M., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2010.

'Novost Kuzmina' had greater quantities of alcohols and carbonyl compounds, whereas 'Newburgh' had more terpenoid compounds. The variation in raspberry ketone, α-ionone and β-ionone concentration among ten raspberry cultivars: 'Andenken an Paul Camenzind', 'Chilcotin', 'Glen Clova', 'Glen Moy', 'Glen Prosen', 'Meeker', 'Rutrago', 'Skeena', 'Veten', and 'Zenith', has been reported. Although the raspberry ketone concentration varied from 1 ppm to 4 ppm, minimal variation was observed for other compounds (*7*). Borejsza-Wysocki, et al (*15*), also reported variation of raspberry ketone among different cultivars. Cultivars such as 'Canby' and 'Royalty' contained less than 30 ppb of raspberry ketone, while 'Willamette' contained over 170 ppb. The content of raspberry ketone was also investigated on other cultivars. 'Chilliwack', 'Comox', 'Malahat', 'Meeker', 'Tulameen', and 'Willamette' had raspberry ketone concentrations varying from 0.01-0.05 mg/mL (*20*). More recently, Malowicki and Qian (*21*) quantified 29 volatile aroma compounds in 'Chilliwack', 'Tulameen', 'Willamette', 'Yellow Meeker', and 'Meeker' and find that volatile variation depends on specific compounds and cultivars. Large variations for α-ionone, β-ionone, geraniol, linalool, and *cis*-3-hexenol were observed in different raspberry cultivars.

Growing conditions will also cause flavor variations. Significant year-to-year differences in raspberry ketone, alcohol, aldehyde, ester, ketone, and terpene concentrations have been noticed in raspberries grown on the same plot, as studied by Moore (*20*). These variations were also witnessed between plots of raspberries, although the reported differences were generally smaller than the differences reported from year-to-year. Malowicki and Qian (*21*) also reported that the volatile composition of 'Meeker' raspberries grown in different locations varied. Raspberries grown in Oregon appeared to have higher concentration of δ-octalactone, δ-decalactone, geraniol, and linalool than the berries grown in Washington. It is not clear what agronomical parameter(s) causes these differences.

Flavor composition in fruits is dramatically influenced by the degree of ripening. Aroma volatiles generally change at the final stages of ripening. Guichard (*22*) reported dramatic increases in terpenoids during ripening and some increases in esters, although specific compounds in different cultivars responded differently in the overripe phase. A clear difference was shown between maturity stages for green-pink stage, pink stage and ripe/overripe stages; however, the flavor changes occurring as fruit reaches the overripe stage are not as evident as those that occur before the ripe stage. During the ripening of 'Glen Prosen' raspberries, the abundances of several monoterpenes including camphene, β-myrcene, and limonene rise steadily, as do the compounds α-phellandrene, α-pinene, α-ionone, β-ionone, methyl acetate, ethyl acetate, 2-methyl-1-butanol, and *cis*-3-hexenol. In addition, the concentration of volatiles associated with green leafy aromas declined (*23*).

The volatile aroma composition changes during the freezing process and long-term frozen storage are minimal. A significant increase was observed only for α-ionone and caryophyllene in some cultivars during long term (12 months) of storage (*24*).

Blackberry

Blackberries, like raspberries, belong in the family *Rosaceae*, genus *Rubus*. Blackberry cultivars can be classified according to their growth habit: trailing, semi-erect, or erect. Blackberries are grown all over the world, and the Pacific Northwest of America is a leading production region. The major blackberries in this region are trailing types blackberries such as 'Thornless Evergreen', 'Marion', and 'Black Diamond'. Historically 'Marion' has been the most appreciated blackberry due to its unique aroma and flavor. However, with more acreage of new cultivars such as 'Black Diamond' being harvested this may change.

More than 250 volatile compounds have been identified in blackberry whole fruit, essence, juice, and other products (*25–28*). Volatile profiles of blackberry are diverse, including esters, aldehydes, ketones, lactones, terpenoids, norisoprenoids, alcohols, phenolics, furanone, and acids. The major volatiles identified in blackberry are summarized in Table 2.

Table 2. Major aroma compounds identified in blackberries

Compounds	*References*	*Compounds*	*References*
Esters		*trans*-2-Hexenol	(*27*, *31*)
Ethyl acetate	(*27*, *30*, *31*, *33*)	2-Heptanol	(*27*, *30*, *31*, *33*)
Ethyl 2-methyl-propanoate	(*30*, *33*)	1-Octen-3-ol	(*27*, *30*)
Methyl butanoate	(*27*, *30*, *33*)	1-Octanol	(*27*, *30*, *31*, *33*)
Ethyl butanoate	(*27*, *30*, *33*)		
Ethyl 2/3-methylbutanoate	(*27*, *30*, *31*, *33*)	*Aromatic compounds*	
Butyl acetate	(*27*, *30*, *31*, *33*)	Methyl salicylate	(*31*)
Methyl hexanoate	(*27*, *30*, *33*)	Benzyl alcohol	(*27*, *30*, *33*)
Ethyl hexanoate	(*27*, *30*, *31*)	Phenylethyl alcohol	(*27*, *30*, *33*)
Hexyl acetate	(*27*, *31*)	Cinnamaldehyde	(*27*, *30*)
		Eugenol	(*27*, *31*, *33*)
Terpenoids		Isoeugenol	(*27*)
α-Phellandrene	(*31*)	Vanillin	(*27*, *33*)
Myrcenene	(*30*, *33*)	Methyl vanillate	Unpublished
Limonene	(*30*, *31*, *33*)	Zingerone	Unpublished
Linalool	(*27*, *30*, *31*, *33*)	Raspberry ketone	Unpublished
4-Terpineol	(*27*, *31*, *33*)		
Borneol	(*27*, *31*)	*Acids*	

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Table 2. (Continued). Major aroma compounds identified in blackberries

Compounds	*References*	*Compounds*	*References*
α-Terpineol	(*27*, *31*)	Acetic acid	(*27*, *30*, *31*, *33*)
Carvone	(*27*, *30*, *33*)	Butanoic acid	(*30*, *31*, *33*)
Myrtenol	(*27*, *31*, *33*)	2-methylbutanoic acid	(*30*, *31*, *33*)
Nopol	(*31*)	Hexanoic acid	(*27*, *30*, *31*, *33*)
Citronellol	(*31*, *33*)		
Nerol	(*33*)	*Lactones*	
Geraniol	(*27*, *33*)	γ-Octalactone	(*27*)
Perillyl alcohol	(*27*, *31*)	δ-Octalactone	(*27*)
		γ-Decalactone	(*27*)(*33*)
Carbonyl compounds		δ-Decalactone	(*27*)
3-Methylbutanal	(*27*, *30*, *31*)	γ-Undecalactone	(*27*)
Hexanal	(*27*, *30*, *31*, *33*)		
trans-2-Hexenal	(*27*, *31*, *33*)	*Miscellaneous*	
trans,*trans*-2,4-Heptadienal	(*27*, *31*)	*cis* / *trans*-Linalool oxide	(*30*, *31*)
Diacetyl	(*27*, *30*, *33*)	Theaspirane A / B	(*27*, *30*, *31*, *33*)
2-Heptanone	(*27*, *30*, *31*, *33*)	Mesifurane	(*27*)
1-Octen-3-one	(*30*)	Furaneol	(*30*, *33*, *45*)
2-Undecanone	(*27*, *30*, *31*, *33*)	Homofuraneol	(*30*, *33*)
		Sotolon	(*30*)
Norisoprenoids		Maple furanone	(*30*)
Damascenone	(*27*, *30*, *33*)		
α-Ionone	(*31*)	*Others*	
β-Ionone	(*27*, *31*, *33*)	Dimethyl sulfide	(*30*, *33*)
		Thiophene	(*30*)
Alcohols		2-Methylthiophene	(*30*)
1-Hexanol	(*27*, *30*, *31*)	Dimethyl disulfide	(*30*)
cis-3-Hexenol	(*27*, *31*, *33*)	Methional	(*30*, *33*)

The essence of 'Thornless Evergreen' blackberry was first investigated in the 1970s (*25*, *26*). Out of twenty-three volatile compounds identified, only 3, 4-dimethoxyallylbenzene was identified to contribute to the characteristic 'Thornless Evergreen' flavor. More intensive studies (*27*) of fresh 'Thornless

Evergreen' by fractionation and gas chromatography-olfactometry identified more than 200 compounds. The major aroma compounds were identified as 2-heptanol, *p*-cymen-8-ol, 2-heptanone, 1-hexanol, α-terpineol, pulegone, 1-octanol, isoborneol, myrtenol, 4-terpineol, carvone, elemicine, and nonanal. Mixing appropriate amounts of these compounds resulted in an odor somewhat reminiscent of blackberries, but lacking the delicate aroma of the natural extract.

The aroma compounds in 'Thornless Evergreen' and 'Marion' blackberries were investigated using Aroma Extract Dilution Analysis as well as odor-activity values (ratio of the concentration of a compound in the sample to its threshold) (*29–31*). According to flavor dilution factor (FD values), 2,5-dimethyl-4-hydroxy-3-(2H)-furanone, 2-ethyl-4-hydroxy-5-methyl-3-(2H)-furanone, 4-hydroxy-5-methyl-3-(2H)-furanone, 4,5-dimethyl-3-hydroxy-2-(5H)-furanone, and 5-ethyl-3-hydroxy-4-methyl-2-(5H)-furanone are prominent aromas in 'Thornless Evergreen' and 'Marion', however, the ratio is different for the two cultivars. Furaneol is very important to the aroma of both cultivars, however, 'Marion' has 16 times more furaneol than 'Thornless Evergreen' (*32*). Other major odorants in 'Thornless Evergreen' are ethyl hexanoate, 2-heptanone, ethyl 2-methylbutanoate, 2-heptanol, 3-methylbutanal, α-pinene, limonene, *p*-cymene, linalool, *trans*-2-hexenal, myrtenal, hexanal, 2-methylbutanal, and sabinene, while the other major aroma compounds in 'Marion' are ethyl hexanoate, ß-ionone, linalool, 2-heptanone, α-ionone, and hexanal (*31*).

As with many other fruits, blackberry flavor is affected by environmental factors. Seasonal variations always exist for agricultural products. Qian and Wang (*31*) analyzed the volatile compositions of 'Marion' and 'Thornless Evergreen' blackberries from three growing seasons. Seasonal variations were present for both cultivars, however, the variation and magnitude of change is highly dependent on the aroma compounds, and the cultivar difference is the determining factor for the difference in aroma composition.

Growing regions have a major impact on aroma composition. Wang *et al.* (*33*) compared the aroma profile of 'Chickasaw' blackberry growing in Oregon and Arkansas. The major aroma compounds in 'Chickasaw' blackberry grown in Oregon are ethyl butanoate, linalool, methional, *trans*, *cis*-2, 6-nonadienal, *cis*-1, 5-octadien-3-one, and 2, 5-dimethyl-4-hydroxy-3(2H)-furanone. In comparison, the major aroma compounds in Arkansas-grown berries were ethyl butanoate, linalool, methional, ethyl 2-methylbutanoate, β-damascenone, and geraniol. The higher level of *trans*, *cis*-2, 6-nonadienal and *cis*-1, 5-octadien-3-one is probably caused by lower mean growing temperature in Oregon during the ripening season of June and July. The ripening conditions in Oregon give fruit more "green" and "fruity" notes than berries grown in Arkansas.

Heating blackberry juice can dramatically alter the flavor profile (*28*, *34*). It has been found that the concentrations of aldehydes, lactones, and furan compounds increased significantly upon heating, and furfural, 3-methylbutanal, 3-methylbutanol, phenylacetaldehyde, and *trans*-furan linalool oxide dominate the aroma of concentrated blackberry juice (*28*, *34*).

Blackberry research has switched to develop thornless cultivars with attributes of high yield, machine-harvestable, cold tolerance and superior flavor.

ome thornless blackberries with very good flavor such as ‘Black Diamond’, ‘Black Pearl’ and ‘Nightfall’ have been recently released to the industry.

Blueberry

Blueberries are in the genus *Vaccinium*, section *Cyanococcus*. The species from which the cultivated types were developed are native only to North America. The genus consists of 24 blueberry species, including 7 diploid, 14 tetraploid, and 3 hexaploid species (*35*). Three predominant types of blueberry are cultivated commercially including the tetraploid highbush (*Vaccinium corymbosum*) and lowbush (*V. angustifolium*) blueberries, and the hexaploid rabbiteye (*V. virgatum*; formerly *V. ashei*) blueberries. Highbush blueberries are native to much of the eastern and northeastern U.S., from the Appalachian Mountains to the Atlantic Ocean; Lowbush blueberries are native from Minnesota to Virginia and to the northeastern U.S. and the Maritime Provinces of Canada; ‘Rabbiteye’ blueberries are native to the southeastern U.S.

Compared to raspberries, the blueberry flavor research is limited. Overall, fewer volatile compounds have been identified in blueberries than in raspberries and blackberries (Table 3). The flavor profiles in these species are similar and are dominated by terpenoids, C6 alcohols, and esters.

Table 3. Compounds identified in highbush, lowbush, Rabbiteye, and wild diploid blueberries

Compounds	*Highbush*	*Lowbush*	*Rabbiteye*	*Wild Diploid*
Esters				
Methyl acetate		(*40*)		(*35*)
Ethyl acetate	(*36*)	(*40, 41*)	(*42*)	(*35*)
Ethyl propanoate		(*41*)		(*35*)
Methyl 2-methylpropanoate		(*41*)		
Ethyl 2-methylpropanoate		(*41*)		(*35*)
Methyl butyrate		(*41*)		(*35*)
Methyl 2-methylbutanoate		(*4*)		
Methyl 3-methylbutanoate		(*4, 41*)		(*35*)
Ethyl butyrate		(*4, 41*)		(*35*)
Methyl 3-methyl-2-butenoate		(*41*)		
Ethyl 2 / 3-methylbutanoate		(*4, 41*)		(*35*)
Ethyl 3-methyl-2-butenoate		(*41*)		(*35*)

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Table 3. (Continued). Compounds identified in highbush, lowbush, Rabbiteye, and wild diploid blueberries

Compounds	*Highbush*	*Lowbush*	*Rabbiteye*	*Wild Diploid*
Ethyl hexanoate				(*35*)
Hexyl acetate	(*38*)			
Farnesyl acetate	(*38*, *39*)			
Geranyl formate			(*42*, *43*)	
Linalool acetate			(*42*)	
Terpinyl acetate			(*43*)	
Terpenoids				
α-Pinene	(*38*)			(*35*)
β-Pinene				(*35*)
Myrcene	(*38*)		(*43*)	(*35*)
Limonene	(*36*, *38*)	(*41*)	(*42*, *43*)	(*35*)
Eucalyptol	(*38*)		(*43*)	(*35*)
α-Terpinolene			(*43*)	(*35*)
Caryophyllene	(*38*)			
Allocimene			(*43*)	
Linalool	(*4*, *36–39*)	(*4*)	(*42*, *43*)	(*35*)
4-Terpieneol			(*42*, *43*)	
α-Terpineol	(*4*, *36*, *38*, *39*)		(*42*, *43*)	
Citronellol	(*38*, *39*)			
Nerol	(*36*, *38*, *39*)		(*42*, *43*)	
Geraniol	(*36*, *38*, *39*)		(*42*, *43*)	
Pulegone			(*43*)	
Carveol			(*42*)	
Hydroxycitronellol	(*38*, *39*)			
cis-Caren-3-ol			(*42*, *43*)	
Farnesol	(*38*, *39*)			
Cineralone			(*42*)	
Carbonyl compounds				

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Table 3. (Continued). Compounds identified in highbush, lowbush, Rabbiteye, and wild diploid blueberries

Compounds	*Highbush*	*Lowbush*	*Rabbiteye*	*Wild Diploid*
2 / 3-Methylbutanal				(*35*)
Hexanal	(*36*, *38*)		(*42*, *43*)	(*35*)
trans-2-Hexenal	(*36*, *38*, *39*)		(*42*, *43*)	(*35*)
Decanal				(*35*)
Diacetyl				(*35*)
2-Pentanone			(*42*, *43*)	
2-Heptanone		(*41*)		
2-Nonanone		(*41*)		(*35*)
2-Undecanone			(*42*)	
Norisoprenoids				
β-Ionone			(*42*, *43*)	
Alcohols				
3-Methylbutanol				(*35*)
1-Penten-3-ol	(*36*, *38*)		(*42*, *43*)	
1-Hexanol	(*36*, *38*, *39*)		(*42*, *43*)	(*35*)
cis-3-Hexenol	(*36–39*)		(*43*)	
trans-2-Hexenol	(*36*, *38*, *39*)		(*43*)	
Heptanol	(*36*)		(*42*)	
1-Octanol	(*38*)			
1-Nonanol	(*36*, *38*)			
Aromatic compounds				
p-Cymene		(*41*)	(*42*, *43*)	(*35*)
Benzyl alcohol	(*38*, *39*)	(*41*)	(*42*)	
Phenylethyl alcohol	(*38*, *39*)			
Cinnamyl alcohol	(*38*, *39*)			
Phenol	(*38*, *39*)			
Thymol	(*38*)		(*42*, *43*)	

Continued on next page.

Table 3. (Continued). Compounds identified in highbush, lowbush, Rabbiteye, and wild diploid blueberries

Compounds	*Highbush*	*Lowbush*	*Rabbiteye*	*Wild Diploid*
Carvacrol			(*43*)	
Eugenol	(*38*, *39*)		(*42*, *43*)	
Isoeugenol	(*38*)			
Benzaldehyde	(*4*, *38*, *39*)	(*41*)	(*43*)	
Cinnamaldehyde	(*38*)			
Vanillin	(*38*, *39*)			
Acids				
Acetic acid	(*38*)			
Butanoic acid	(*38*)			
2-Methylbutanoic acid	(*38*)			
Pentanoic acid	(*38*)			
Hexanoic acid	(*38*)			
Others				
γ-Butyrolactone	(*4*)			
Dimethyl sulfide				(*35*)
6-ethyl-2, 6-decadiene-4, 5-diol	(*4*)			
2-furfural			(*42*, *43*)	
5-methylfurfural			(*42*, *43*)	
acetylfuran				

Highbush cultivars have large berries and pleasant aromas. Parliment and Kolor (*36*) first reported the major volatile compounds in highbush blueberries were ethyl acetate, *trans*-2-hexenal, *trans*-2-hexenol, hexanal, *cis*-3-hexenol, linalool, and geraniol. An aroma recombination study demonstrates that the combination of *trans*-2-hexenal, *trans*-2-hexenol, *cis*-3-hexenol and linalool gives the characteristic blueberry flavor (*36*, *37*). However, more recent studies (*4*, *38*, *39*) show that there are more compounds contributing to the aroma of highbush blueberries. GC-olfactometry and OAV studies suggest that *trans*-2-hexenal, geraniol, *cis*-3-hexen-1-ol, linalool, citronellol, a-terpineol, 2-phenylethanol and vanillin may contribute to the typical aroma of blueberries.

Only a few studies reported the aroma composition of lowbush blueberries (*4*, *40*, *41*). These studies identified the aroma-active compounds in lowbush blueberry as acetaldehyde, methyl acetate, ethyl acetate, methyl 2-methylbutanoate, methyl 3-methylbutanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, methyl butanoate and linalool. Apparently, more esters were reported in lowbush than in highbush blueberries.

Studies on the flavor of rabbiteye blueberries are also limited, and the literature comes from only one group. Horvat et al.(*42*, *43*) studied the volatile composition of rabbiteye blueberries using distillation, followed with pentane extraction, and gas chromatographic and mass spectrometric identification. The major components identified are ethyl acetate, *p*-cymene, hexanol, *cis*-2-hexenol, heptanol, cinerolone, β-ionone, terpene-4-ol, 2-undecanone, α-terpineol, carveol, nerol, and eugenol. A mixture of *cis*-3-hexenol, *trans*-2-hexenol, *trans*-2-hexenal, linalool, and geraniol produced a typical fruity aroma reminiscent of fresh rabbiteye blueberry flavor, as determined by informal sensory evaluations (*43*).

Little research has examined the effect of environmental factors on the volatile composition of blueberries. A comparison of the volatile constituents in rabbiteye (*43*, *44*) revealed that during ripening, concentrations of low molecular weight volatiles tend to decrease while higher molecular weight compounds increase. The compounds *trans*-2-hexenal, *trans*-2-hexenol, *cis*-3-hexenol, α-terpienol, and β-caryophyllene all decreased in concentration as the fruit progressed from green to midripe to fully ripe. However, linalool and geraniol concentrations were equal or greater in midripe and ripe fruit, than in green fruit.

Wild diploid blueberries have also been studied (*35*). Acetaldehyde, dimethyl sulfide, diacetyl, ethyl acetate, hexanal, ethyl 2-methylbutanoate, *trans*-2-hexenal, eucalyptol, and linalool have been identified.

Conclusion and Perspective

A large number of volatile aroma compounds have been identified in raspberries, blackberries, and blueberries through qualitative, quantitative, and sensory evaluation. The investigation in raspberry flavor has been relatively extensive, while studies are still very limited for blackberry and blueberry flavor. Volatile aroma composition varies among cultivars and is affected by environmental factors such as geographical location, soil nutrition, weather, and irrigation.

A better understanding of the volatile chemicals responsible for berry flavor is needed. New methodologies must be developed to further identify and quantify aroma compounds in fresh berry crops. For instance, some polar aroma compounds have berry flavor, but are hard to analyze with common methods. Efforts need to continue combining sensory evaluation and chemical analysis to develop a complete picture of the chemical basis of aroma and flavor.

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