8-2022

Evaluating Flavor and Aroma Attributes of Arkansas-grown Horticultural Crops

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Evaluating Flavor and Aroma Attributes of Arkansas-grown Horticultural Crops

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Food Science

by

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Bachelor of Science in Biology, 2012

August 2022
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This thesis is approved for recommendation to the Graduate Council.

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Overall Abstract

Arkansas has a climate and geography that allows for the production of unique horticultural crops, including hops (*Humulus lupulus* L.), blackberries (*Rubus* subgenus *Rubus*), and muscadine grapes (*Vitis rotundifolia*). These crops not only have potential for growers in Arkansas but have unique flavor and aroma attributes that impact marketability. Volatile compounds present in many different agricultural plants are the primary source of biologically-derived aromas and flavors. Therefore, the volatile and other quality attributes of hops, blackberries, and muscadine grapes were evaluated at the University of Arkansas (UA System) Division of Agriculture. The quality, volatile, and sensory attributes of four hops cultivars (Cascade, Cashmere, Crystal, and Zeus) grown at the UA System Division of Agriculture Fruit Research Station in Clarksville, AR were evaluated in 2020 and 2021. In general, cultivar impacted individual and total alpha and beta acids levels with total alpha and beta levels as follows; 'Cascade' (6.0-9.2% and 5.7-9.1%, respectively), 'Cashmere' (4.9-6.9% and 5.5-8.5%. respectively), 'Crystal' (2.9-3.6% and 7.5-10.1%, respectively), and 'Zeus' (4.6-5.7% and 4.1-4.8%, respectively). In both 2020 and 2021, 'Crystal' had the highest volatile concentration (6,278 and 8,106 µg/kg, respectively) followed by 'Cashmere' (6,668 and 5,434 µg/kg, respectively) and 'Cascade' (5,829 and 4,132 µg/kg, respectively) with 'Zeus' (3,230 and 2,072 µg/kg, respectively) containing the lowest concentration. In both years, the five volatile aroma compounds with the highest levels found in Arkansas-grown hops were beta-pinene (monoterpene with herbal and pine aromas), beta-myrcene (spicy monoterpene), caryophyllene (sesquiterpene with woody aromas), beta-Selinene (herbal sesquiterpene with celery notes), and humulene (spicy/woody sesquiterpene). In both years, the descriptive sensory panelists (n=5-7) could differentiate between cultivars for aged cheese, overall citrus complex, lemon, overall

green herb complex, and overall pepper complex with overall impact as the highest rated attribute (5-7 on a 15-point scale). Since blackberry quality can vary during a harvest season, blackberries grown at the UA System Fruit Research Station were harvested on three harvest dates (early, middle, late) in 2020 (four cultivars) and 2021 (three cultivars). In general, cultivars differed for berry weight (5-13 g), soluble solids (9-13%), pH (3.3-4.2), titratable acidity (0.4-1.0%), and solids/titratable acidity ratio (9.8-31.0), but harvest date impact varied by cultivar and year. 'Sweet-Ark® Ponca' late harvest date in 2021 had the lowest concentration of volatile compounds (1,370 μg/kg), and 'Sweet-Ark Ponca' middle harvest date in 2020 had the highest (4,693 μg/kg). In 2021, six seeded and ten seeded and seedless muscadines genotypes (cultivars and breeding selections) were harvested in Arkansas and North Carolina, respectively. Muscadine grape soluble solids ranged from 14-19 %, pH ranged from 3.0-3.9, titratable acidity ranged from 0.25-1.14 %, soluble solids/titratable acidity ratio ranged from 16-70. Volatile compound levels (2,151-5,746 μg/kg) were impacted by genotype, and in the 16 cultivars harvested in both locations, there were 181-198 volatile aroma compounds identified across nine compound classes including 52 esters, 38 monoterpenes, 31 sesquiterpenes, 29 alcohols, 27 aldehydes, 16 ketones, four lactones, two aromatic hydrocarbons, and two epoxides. The three muscadine genotypes with the highest concentrations of volatiles were AM-154 (5,745 μg/kg), 'Lane' (5,285 μg/kg), and 'Hall' (5,107 μg/kg), while the three muscadine genotypes with the lowest concentration of volatiles were AM-77 (2,151 μg/kg), JB 06-30-2-20 (2,367 μg/kg), and AM-148 (2,468 μg/kg). Data generated from this project provided information on volatile and other quality attributes of hops, blackberries, and muscadine grapes that can be used to support the future growth of these industries.

Acknowledgments

I would first like to thank those at the UofA that helped me directly during my time here. First and foremost, I'd like to thank my advisor Dr. Renee Threlfall. Thank you for allowing me to work with you these past couple years, even when initially there wasn't a project for me to do, or any money to pay me with. I could not have asked for a better advisor, and I sure hope you're not too sick of me because we've got four more years together. I'd also like to think Dr. Ya-Jane Wang. Thank you for serving on my committee, for investing in me and all of the other students you've had over the years, and for believing in me enough to help fund my degree and my research. To Cindi Brownmiller, whether professionally, personally, or anything in between, you have always been a reliable source of knowledge and information, as well as fantastic personality to be around. Thank you for trusting me with all of your equipment, and for always being the troubleshooting expert when I did something silly. To the other graduate students that have worked with me during my time here, Amanda, Andrea, Cody, and James. It's amazing how quickly time has gone by and how much we've done over the past two years. Obviously, some of our projects overlapped more than others, but I've truly valued the time I have been able to spend with all of you, and I have cherished memories of each of you. And lastly, I need to acknowledge all of those behind the scenes at FDSC and at the UofA that help everything run so smoothly.

On a more personal note, I'd also like to acknowledge both of my parents. I've had a lot of highs and lows over the past few years, and I would not be where I am now without the constant love and support they have provided for me both during this program and throughout my whole life.

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Overall Introduction

Arkansas has a unique geography that allows for production of different specialty horticultural crops. Some horticultural crops of agricultural interest in Arkansas include hops (*Humulus lupulus L.*), blackberries (*Rubus* subgenus *Rubus*), and muscadine grapes (*Vitis rotundifolia*). These crops not only have potential for growers in Arkansas but have unique flavor and aroma attributes that impact marketability. The overall flavor of horticultural crops results from perception of basic tastes and volatile aroma compounds. The basic tastes include sweet, sour, salty, bitter, and umami (savory) and can result from composition attributes of the crop including sugars, acids, and phenolics. Volatile organic compounds are present in many agricultural plants and are the primary source of biologically derived aromas and flavors. Volatile organic compounds have a high volatility or vapor pressure at room temperature (Koppmann, 2007). Identifying and quantifying volatiles can provide insight to the aromatic and flavor attributes of horticultural crops.

Instrumental methods for examining flavor can provide feedback about the individual compounds associated with flavors. There are many different methods, but each is based on separation, identification, and quantification of compounds either in headspace of vials or within the actual product matrix. These methods are particularly good at identification of compounds that may result in flavor changes, and some instrumental methods can be implemented to run continually to provide immediate or near immediate information about products (Chambers and Koppel, 2013).

High Performance Liquid Chromatography (HPLC) can be used to analyze composition, such as sugars or acids, of hops, blackberries, and muscadines. Gas Chromatography-Mass Spectroscopy (GC-MS) is a solvent-free method of evaluating volatile chemicals, primarily utilizing headspace solid phase micro extraction (HS-SPME). GC-MS with flame ionization detection (FID) is one of the most widely-applied techniques in analytical chemistry, both for its large range of detection and relative cost effectiveness (Pacchiarotta et al., 2010). The FID method utilizes a helium and air flame that results in charged ions in the sample that create a small electric potential measured by the detector (Hinshaw, 2005). The detected values can be compared to standards, databases, and libraries to establish a chemical profile. Volatile extraction is typically achieved via liquid-liquid extraction, simultaneous distillation and extractions, HS-SPME, or stir bar sportive extraction techniques. SPME solvent-free technique allow the detection and isolation of trace compounds (Lee et al., 2016; Sánchez-Palomo et al., 2005).

Since the University of Arkansas System Division of Agriculture endeavors address diverse specialty horticultural crops with state, national, and world economic impacts, the volatile and other key quality attributes of hops, fresh-market blackberries, and muscadine grapes were evaluated.

Objectives

1) Evaluation of flavor and aroma attributes of Arkansas-grown hops

2) Impact of harvest date on size, composition and volatiles of Arkansas fresh-market blackberries

3) Identification of flavor and aroma attributes of fresh-market and processing muscadine grapes

Literature Review

Introduction

Arkansas has a unique geography that allows for production of different specialty horticultural crops. The University of Arkansas System Division of Agriculture (UA System) has research and outreach endeavors in many specialty horticultural crops that have state, national, and world economic impacts. Cultivar selection, production methods, harvest dates, and storage methods can impact the quality of the horticultural crops. Collaborative projects between horticulture and food science can bridge gaps between how crops are grown and impact on quality, especially marketability attributes important to consumers.

Some horticultural crops of agricultural interest in Arkansas include hops, (*Humulus lupulus L.*), blackberries (*Rubus* subgenus *Rubus*), and muscadine grapes (*Vitis rotundifolia*). Hops plants produce hops cones that are the main ingredient in beer brewing but can be used in other beverages. Hops are a new crop for growers in Arkansas, but this crop has potential in Arkansas for beginning growers and growers that would like to diversify farm operations. Another unique crop for Arkansas is fresh-market blackberries. The UA System is known worldwide for the breeding, patenting, and release of new cultivars of fresh-market blackberries. This breeding program work with cultivars and breeding selections (genotypes) to release these new cultivars. The fresh-market blackberry industry in Arkansas is expanding. Lastly, muscadine grapes are grown in Arkansas and the southeast mostly for processing (juice, wine, jams, or jellies) but also for fresh markets. Muscadine grapes have a long history of production in Arkansas, and Arkansas is one of the leading muscadine juice and wine producers in the United States. In addition, the UA System has a muscadine breeding program that is working on developing *Vitis* × *Muscadinia* hybrids to combine the disease resistance of muscadine grapes with the fruit quality of *V. vinifera*, typical table and wine grapes.

These crops not only have potential for growers in Arkansas but have unique flavor and aroma attributes that impact marketability and consumer interests. Flavor of horticultural crops arise from perception of basic tastes and volatile aroma compounds. The basic tastes include sweet, sour, salty, bitter, and umami (savory) and can result from composition attributes of the crop including sugars, acids, and phenolics. Volatile organic compounds are present in many different agricultural plants and are the primary source of biologically-derived aromas and flavors. Primarily, volatiles found in flowers and fruiting bodies are classified by their unique aromas which are used to attract or deter other biological organisms. Volatile organic compounds have a high vapor pressure at room temperature or volatility (Koppmann, 2007). Examining and analyzing volatiles can provide researchers with an objective way of identifying and quantifying aromatic and flavor attributes of horticultural crops.

Instrumental methods for examining flavor can provide feedback about the individual compounds associated with flavors. There are many different methods, but each is based on separation, identification, and quantification of compounds either in headspace of vials or within the actual product matrix. These methods are particularly good at identification of compounds that may result in flavor changes, and some instrumental methods can be implemented to run continually to provide immediate or near immediate information about products (Chambers and Koppel, 2013).

High Performance Liquid Chromatography (HPLC) can be used to analyze composition, such as sugars or acids, of hops, blackberries, and muscadines. Gas Chromatography-Mass Spectroscopy (GC-MS) is a solvent-free method of evaluating volatile chemicals, primarily utilizing headspace solid phase micro extraction (HS-SPME). GC-MS with flame ionization detection (FID) is one of the most widely-applied techniques in analytical chemistry, both for its large range of detection and relative cost effectiveness (Pacchiarotta et al., 2010). The FID method utilizes a helium and air flame that results in charged ions in the sample that create a small electric potential measured by the detector. The amount of electric potential and temperature in which the ions burn is specific to each chemical structure (Hinshaw, 2005). The detected values can be compared to standards, databases, and libraries to establish a chemical profile.

Volatile extraction is typically achieved via liquid-liquid extraction, simultaneous distillation and extractions, HS-SPME, or stir bar sportive extraction techniques. SPME solvent-free technique allow the detection and isolation of trace compounds (Lee et al., 2016; Sánchez-Palomo et al., 2005). HPLC is useful in analyzing compounds that are less volatile, or those with salts or free ions. Using both of these techniques simultaneously can be useful for analyzing samples that contain compounds with a wide range of volatility.

Gas chromatography-olfactometry (GC-O) methods are used in flavor research to determine the odor active compounds in food (Van Ruth, 2001). GC-O couples the use of traditional GC separation techniques with human assessors. The advantages of GC-O techniques are that these human assessors can determine odor activity of volatile compounds from a given sample and also assign those compounds a relative importance and intensity (Delahunty, 2006). These techniques have been applied to a wide variety of foods including meats and dairy, rice and other grains, as well as fruits and vegetables. This technology continues to advance. A research team in France utilized GC-O-associated taste (AT) to determine how certain compounds affected sweet perception (Barba et. al., 2018). GC-O and dilution analysis shows that even though some compounds are present in large concentrations, they do not necessarily have as great of an overall impact in aroma perception, and vice versa (Zellner et al., 2008).

Measurements determining the odor thresholds of volatile organic compounds have been documented as early as 1886, where researchers dispersed a weighed amount of a compound into a room of specific volume (Buttery, 1999). The introduction of GC allowed for a more objective method of determining, and most modern methods of determining aroma threshold values utilize GC-O methods. This is advantageous for numerous reasons firstly, that it is a relatively simple method, secondly, the sample is presented to the judge/panelists in a purified form after separation in the GC column, and thirdly, judges/panelists can determine the odor active volatiles of an unidentified compound (Tan et al., 2022). These values are also generally consistent, as odor thresholds identified in different laboratories, including those in Europe, Australia, and the United States, all agree within a factor of less than 10 (Buttery, 1999).

In addition to analytical methods, sensory science can be a powerful tool for analysis of horticultural crops. Sensory science is “a scientific discipline used to evoke, measure, analyze, and interpret reactions to those characteristics of food and other materials as they are perceived by the senses of sight, smell, touch, taste, and hearing” (Stone and Sidel, 2004). Descriptive sensory analyses have been conducted to determine attributes that are commercially acceptable, such as appearance, aroma, basic tastes, aromatics, and feeling factors. Descriptive sensory analysis involves a trained panel that uses a lexicon (terms to describe the product) and references to evaluate products on a line scale. In contrast, consumer sensory studies use a large number of consumers (over 75 panelists needed to ensure a representative population) to assess acceptability of a sample usually in terms of likeability or preference. Several review papers have addressed sensory-instrumental relationships or sensory interactions of food on quality.

Poinot et al. (2013) reviewed methods used to analyze aroma-related interactions, Ross (2009) reviewed the human-machine interface in sensory science examining texture, sound, aroma, and flavor, Croissant et al. (2011) reviewed sensory and instrumental volatile analyses applications of dairy products. Auvray and Spence (2008) reviewed multisensory interactions between taste, smell, and the trigeminal system.

Since UA System research and outreach endeavors address diverse specialty horticultural crops with state, national, and world economic impacts, this literature review includes an overview of hops, fresh-market blackberries, and muscadine grapes presented in separate sections.

Hops

Hops (*Humulus lupulus L.*) plants are a significant agricultural crop due to their worldwide production and have been used historically for thousands of years. Hops production in the United States began in Virginia with the first European colonists, and eventually cultivation spread from northeastern America to what is present day Washington, Oregon and California (Edwardson, 1952). Hops are part of the Cannabacea family of plants, which includes about 170 species of plants, primarily consisting of Cannabis (hemp, marijuana) Humulus (hops) and Celtis (hackberries) (Stevens, 2001). While Celtis contains the majority of the species variation, only hemp and hops are economically significant as a horticultural crop.

Hops are one of the primary ingredients used in brewing and contribute to the bitter taste and unique aroma present in beer. The hops plant is a perennial, meaning that the same plant will continue to grow and flower each year and can produce hops for 20 years (Almaguer et al., 2014). The hop female flower is called a cone and is similar in shape to a pinecone, although much smaller and more leaf-like in texture. The cones are the part of the plant used in brewing, and the crop is consistently in great demand domestically and internationally. Cones produce oils, polyphenols, and resins (lupulin) that provide the distinct aroma and flavor compounds that impact the quality of beer and other beverages (Almaguer et al., 2014).

World hops production

Optimal growth conditions for hops plants are dependent on many factors, including temperature, rainfall, soil nitrogen levels, and daylength, but the plants are mostly grown between the latitudes of 33°N and 55°N (Dodds, 2017). The best summer temperature range for hops is 5-20 □ (40-70 °F) with a wide range of precipitation levels, if irrigation is provided. Hops plants require four months of frost-free days to mature with optimal day length of 15 hours or longer prior to flower initiation. The long daylength requirement generally limits hops production to the narrow 33-55° latitude geographic area in the northern and southern hemispheres. There are over 80 cultivars of hops commercially grown in Europe and the United Kingdom (43°-54°), Asia (35°-44°), North America (38°-51°), Australia (37°- 3°S), New Zealand (41°-42°S), and South Africa at 34°S (Verzele, and De Keukeleire, 1991).

U.S. hops production

In the United States, hops are grown in the United States Department of Agriculture (USDA) plant hardiness zones 4-8 with production mainly in the Pacific Northwest (Washington, Idaho, and Oregon). In 2020, production of hops in Idaho, Oregon, and Washington totaled over 47 million kg (104 million pounds), with over 23,000 hectares (58,000 acres) of production (USDA, NASS 2020). The top five cultivars grown in Washington were 'Citra®', 'Columbus/Tomahawk/Zeus', 'Mosaic®', 'Simcoe®,' and 'Cascade', and in Idaho were 'Columbus/Tomahawk/Zeus', 'Mosaic®', 'Citra®', 'Idaho 7™', and 'Chinook', and in Oregon were 'Citra®', 'Nugget', 'Mosaic®', 'Cascade', and 'Willamette' (USDA, NASS 2020).

The 2020 value of hops production for the United States totaled $619 million (USDA, NASS 2020).

While the Pacific Northwest region of the United States accounts for over 95% of hops grown in 2020, there are many other states growing small amounts of hops commercially. California, Colorado, Michigan, Minnesota, New York, and Wisconsin had over 50 hectares (125 acres) harvested in 2020, with other states following closely behind (Hop Growers of America, 2021). North Carolina, which is on a similar latitude to Arkansas, had 10 hectares (25 acres) reported for 2020, which demonstrates that commercial hops production is possible in Arkansas (Hop Growers of America, 2021).

Hop yards and plants

Hops are herbaceous, perennial plants that utilize bines to climb. The bines are the above ground stems; one of the major components of the plant together with the roots and rhizomes, the leaves, and the flowers (hop cones). Hops bines can grow up to 6 m (20 feet) tall in a single summer but die back in the winter. Hops start to grow in late spring, with hop cone harvest occurring in August to September in the northern hemisphere. Hops are a dioecious species of plant, producing both male and female flowering plants. Only female plants are grown commercially, while male plants are used for breeding (Briggs et al., 2004). Proper hop cultivation requires some form of infrastructure, such as a trellis system, to support plant growth. The structure needs to be strong enough to support the weight of the plant, high enough to maximize bine growth and fruiting, but also allow for easy harvesting. The hops plant grows quickly, typically between 3-4 m in June and 6-10 m in July and August (Briggs et al., 2004). The hop cones typically form in 2-3 weeks beginning in July and early August in the United States, but need another three weeks to fully mature.

Harvesting hops

The growth, development, and handling of the cones produced by hops are crucial for growers since these affect hop cone qualities. Hops harvest in the United States usually occurs between mid-August through late September, and the final yield is dependent on many factors, including cultivar, age of plant, soil characteristics, growing location, and weather conditions throughout the growing season (Briggs et al., 2004; Lilley and Campbell, 1999; Morcol et al., 2020; Rodolfi et al., 2019 Santagostini et al., 2020; Sharp et al., 2014;).

While it can be difficult to determine when to harvest the cones from H. lupulus, there are several characteristics used to decide the ideal timing and method of collection. Growers typically evaluate cone maturity by assessing the tactile and aromatic qualities of the cones while still attached to the lateral branches. Immature cones have a damp, soft feel when squeezed, while mature hops have a distinctive paper-like, light texture, and the hops spring back when compressed (Verzele and De Keukeleire, 1991). Another method for determining cone maturity entails picking a hops sample and cutting the cone lengthwise down the center with a knife. When fully mature, the internal resin (lupulin sacs containing the essential oils and bitter compounds) will appear dark yellow and emit a pungent aroma reminiscent of a “hoppy” beer (Verzele and De Keukeleire, 1991). Prior to harvest, a few hop cones can be collected and dried to determine the moisture content (or dry matter) to determine harvest dates. Hops at harvest should have a moisture content of 80% (Sharp et al., 2014).

Determining when to harvest cones is important for quality purposes since overly ripe cones can brown and oxidize if left on the bines too long, while immature cones contain a smaller quantity of lupulin. In the northern hemisphere, the first traces of lupulin resin can be detected in early August, where the beta acids develop several days prior to the alpha acids, and resin synthesis is nearly complete by September (Rossini et al., 2021). Once mature, whole hop bines are cut at ground level from the trellis.

Hops can be harvested by machine or by hand depending on the size of the hop yard. Commercial hop producers with large acreage often use machines to facilitate and hasten harvesting. Growers place the bines within a trackway and, depending on the design, the mature plants enter the machine either horizontally or vertically. The hops and leaves are stripped from the bine by numerous moving wire hooks and then passed over screens to separate the hop cones from debris (Rossini et al., 2021). Debris can be composted and returned back to the hop yard as a supplement for mulch or fertilizer (Briggs et al., 2004; Turner et al., 2011). Hops can be used by brewers as a fresh product or dried for use as whole cones, ground cones, or pelletized.

Hops cones drying and storage

To ensure optimal quality for brewing, hop cones must be harvested and stored properly. Freshly harvest hops are approximately 80% water and will spoil rapidly if not treated correctly. Directly after harvesting, most of the water is removed from hop cones using kilns, oasts, or drying rooms. The final moisture content of the cones is reduced to 7-10% which reduces the rate of oxidation and spoilage (Raut et al., 2021). The drying process needs to be strictly monitored as alpha acids can be degraded at temperatures above 60 °C (140 °F) (Heřmánek et al., 2018). Once the hops are dried, the cones should be vacuum sealed or placed in other oxygen-depleted containers, then the cones are frozen (0.2 °C or 33 °F) to prolong quality. Cold storage can prevent rapid deterioration of secondary metabolites, but loss of quality can be expected after several months of storage depending on hop cultivar (Briggs et al., 2004).

Hops cones

The hop cone is considered a condensed inflorescence, similar in shape to a pinecone

(Davis, 1957). The cones contain the lupulin glands, multicellular balloon-shaped glands on the bracts and bracteoles responsible for the production of lupulin. Lupulin is a yellow resinous substance giving hops its distinctive aroma and is the primary component of commercial interest (Yedilova and Inelova, 2019). Hops cones contain several secondary metabolites, which are chemicals produced by plants that are not necessary for the survival of the plant. The secondary metabolites of hops can be divided into three main groups: acids (alpha and beta acids), essential oils, and polyphenols (De Keukeleire, 2000). Composition of the hop cones is about 30% alpha and beta acids and 3-6% polyphenols and tannins, with essential oils ranging from 0.5-5% (Clark et al., 2013; De Keukeleire et al., 2003; Eyres and Dufour, 2008; Probasco and Murphey, 1996; Van Cleemput et al., 2009).

Hops alpha and beta acids

The most substantial component of dried hops is the alpha acids, complex enolic acids that contain a six-carbon ring with several substituent groups. While there are more than seven prominent alpha acids within the lupulin glands of the hops, humulone, cohumulone, and adhumulone constitute 98-99% of the alpha-acids (Killeen et al., 2017; Rutnik et al., 2021). Humulone is the primary alpha acid found in many hop cultivars and is known to impart a soft bitter flavor during brewing. Humulone, also known for its anti-bacterial, anti-cancer, and antioxidant properties, imparts the majority of the bitter flavor that is characteristic of a beer's taste (Karabín et al., 2016). Like humulone, cohumulone is another alpha acid that imparts flavors into beer during isomerization, but cohumulone is often described by brewers as harsher in bitter flavors (Briggs et al., 2004). The remaining alpha acids, adhumulone, posthumulone, and prehumulone, also add to the overall flavor profile of beers, yet additional research is needed to ascertain the specific effects these acids have on a taste perception of a beer (Morcol et al., 2020).

The beta acids present within the hops cone are only a minor contribution to a beer's flavor, but they are a crucial component in the brewing process, especially for preservation. Beta acids are another secondary metabolite that are characteristic of hop cultivars, and the quantities vary with cultivar and maturity (Rutnik et al., 2021). While the number of analogues is the same in alpha acids, the beta acids are chemically disparate from the alpha acids due to the isopentenyl side chain in place of the second hydroxyl group at ring position six. Previous studies regarding these compounds have noted that the ratio of alpha to beta acids varies depending on the stage of development, growing location (terroir), and cultivar, but the alpha to beta acid ratio often ranges from 1:1 to 4:1 (Forteschi et al., 2019; Rodolfi et al., 2019; Rutnik et al., 2021; Santagostini et al., 2020). This ratio is often used by brewers to determine how hops will be used in beer production.

Hops polyphenolic compounds

Like alpha and beta acids, which are important to brewers because of their flavor and microbial properties, polyphenols are imperative for beer quality. Phenolic substances present in the lupulin glands can be both anti and pro-oxidants, flavor precursors with different phytochemicals that impact a few quality attributes of beer. For example, flavor, shading, colloidal, and flavor solidness of beer quality are all affected by phenolic compounds (Wannenmacher et al., 2018). While phenolic acids are probably not going to impact flavor, phenolic acids do act as flavor precursors in beer. Polyphenol extracts used in beer production influence mouthfeel, sharpness, and astringency (Jaskula-Goiris et al., 2014). Like other iso-alpha acids, phenolic compounds go through underlying changes during separation and enzymatic delivery throughout the brewing process. Eventually the phenolic compounds precipitate out of the beer along with protein and other unfermentable byproducts, and their impact declines during fermenting (Briggs et al., 2004; Wannenmacher et al., 2018). While the specific impact that hop polyphenols have on the quality, flavor, and fragrance of lager (light beer brewed at cool temperatures by slow fermentation with a slow-acting yeast) have not specifically been investigated, their antioxidant nature and effect on the shelf life of beer will continue (Briggs et al., 2004; Wannenmacher et al., 2018).

Hops volatile compounds

In hops, the primary volatile compounds are present in essential oils that are secreted in the lupulin glands of the hop cones (Brendel et al., 2020; Liu et al., 2018; Pallottino et al., 2020). The volatiles are responsible for the distinctive aroma of hops, which in turn, contribute to beer flavor. GC-FID has been used to identify over 400 different volatile compounds that can be divided into the groups, hydrocarbons, oxygenated compounds, and sulfur-containing compounds (Almaguer et al., 2014). The compounds can be aliphatic, monoterpenes, and sesquiterpenes (Rutnik et al., 2021). Yield of essential oils in dried hop cones is around 0.3% for most cultivars (Malizia et al., 1999).

The proportions of volatile oils (α-humulene, myrcene, and β-caryophyllene) fluctuate among cultivar, with the degree of oils increasing logarithmically as cones mature (Briggs et al., 2004; Danenhower et al., 2008; Killeen et al., 2017; Steenackers et al., 2015). Maintaining the proper amounts of essential oils in hops cones is especially important for brewers, as levels can decline during storage through oxidation, polymerization, or resignification and are impacted by machine harvesting, drying, and deficient baling and pelleting methods (Rutnik et al., 2021). Steinhaus and Scheiberle (2020) found that while there are hundreds of volatile compounds contained within hop cones, only 23 had a flavor dilution factor range of 16-4,096. This indicates that only a small number of volatile compounds are responsible for the overall hop aroma similar to other studies (Guadagni et al., 1966; Tressl et al., 1978).

With the rise in popularity of hoppy beer styles, craft brewers have started utilizing dry-hopping as a method of enhancing beer aroma and flavor (Lafontaine and Shellhammer, 2018a; 2018b). Dry hopping is a cold extraction of hops in fermented or partially fermented beer, which can add intense hop aroma to beer, without imparting as much bitterness as kettle hopping (Lafontaine et al., 2019). This is advantageous to many brewers, as consumers only tolerate a certain level of bitterness, but still desire a strong hoppy aroma and flavor. Oladokun et al. (2017) found that dry hopping could also increase the alpha acid levels in beer, but those results were only significant when using a hop cultivar that had high alpha acids (Oladokun et al., 2017). Craft brewers and hop growers can use this information to determine what hop cultivars are optimal for providing as much hoppy aroma and flavor as possible.

Hops and beer sensory

Trained descriptive panelists can identify and describe different sensory attributes, which can be used to create profiles for different hop cultivars. The profiles are used by brewers to emphasize and create specific flavors in beer (Hahn et al., 2018). Volatiles in hop oils induce diverse aroma and flavor sensations, ranging from floral, to fruity, to spicy (Dietz et al., 2020; Kishimoto et al., 2006; Lafontaine and Shellhammer, 2018a; Stucky and McDaniel, 2018). Bober et al. (2020) showed that small changes in hop composition will have a noticeable difference in the final taste of beer, further demonstrating the need to establish quantitative profiles for different cultivars. The profiles would allow for more objective and reproducible methods of beer production, as well as a greater degree of specificity when selecting hops cultivars, which is incredibly valuable to brewers who are looking to increase consistency in their production. While there have been many studies on the impact of hops on the sensory evaluation of beer, there are not many sensory studies on dried hops aroma.

Blackberries

Blackberry (*Rubus* subgenus *Rubus*) plants are grown both domestically and internationally and can be cultivated for both fresh-market and processing purposes. Fresh-market berries are harvested to be sold directly to the consumers, while processing berries are intended for other uses including freezing, jellies, or beverage production. The intended final destination of the fruit will have an impact on both production and harvesting methods, with fresh-market berries typically harvested by hand to preserve the integrity of the berry, while processing berries are often harvested by machine to reduce labor costs.

World blackberry production

Blackberries are native to Europe and North America, but grow wild in temperate regions all over the world, including Asia and South America (Hummer, 2018). Blackberry cultivation began over 2,000 years ago by Europeans, and the first known cultivated blackberry (*R. laciniatus*) was first mentioned in 1691 (Jennings, 1988). From 1995 to 2005, there was a 45% increase in hectares of global commercial and organic blackberry production (Hummer, 2018; Strik et al., 2007). The increased awareness of potential health benefits of blackberries, increased globalization, and faster refrigerated transportation contribute to the growing blackberry market (Safley, 2009).

U.S. blackberry production

In the United States, blackberry production in Oregon, and Washington, is predominantly grown for the processing industry. According to the National Agricultural Statistics Service

(USDA, 2017), the total blackberry acreage in the United States was around 23,500 ha (58,000 acres) for both fresh-market and processing blackberries harvested. In terms of the fresh-market industry, in 2013, Oregon ranked first for largest number of hectares of blackberry production (300 ha), California ranked second (280 ha), Texas ranked third (270 ha), Arkansas ranked fourth (240 ha), and North Carolina ranked fifth (180 ha) (Takeda et al., 2013). Blackberry production in the Southeast has been a growing part of the United States market for the past decade (Fernandez et al., 2016). Although blackberry acreage in Arkansas has lagged as other southern states across the Southeast, including Georgia, North Carolina, and Texas have expanded acreage for retail-market sales (Clark and Finn, 2014), the establishment of a new Arkansas Blackberry Growers Association has invigorated the state's industry.

Blackberry breeding

Blackberry breeders use existing cultivars and breeding selections to develop and release new cultivars. Blackberry breeding programs are important because new cultivars are needed to enhance profits obtained by growers and to meet the consumer needs for fresh-market blackberries. In the United States, blackberry breeding programs work to enhance favored traits and reduce undesirable traits in plants and fruit. The oldest currently active program is at the USDA-Agricultural Research Service at Corvallis, OR and was initiated in 1928 (Clark and Finn, 2008). Fresh-market blackberry cultivars released by USDA include 'Obsidian', 'Metolius' and the newest releases 'Eclipse', 'Galaxy' and 'Twilight' (USDA, 2020).

The UA System blackberry breeding program was initiated 1964 by Dr. James N. Moore and is currently directed by Dr. John Clark and Dr. Margaret Worthington. The UA System blackberry breeding program, based at the UA System Fruit Research Station, Clarksville, AR, prioritized development efforts focused on plant attributes including thornlessness, erect growth habit, mechanical harvesting capability, disease resistance, productivity, and environmental and geographic adaptation (Clark and Finn, 2008). The fruit improvement objectives included large fruit size, desirable flavor, firmness, and high fertility. The UA System blackberry breeding program has developed and patented 43 fresh-market blackberry cultivars and is regarded as one of the leading public blackberry breeding programs in the world. In 2020, the UA breeding program profited $1.48 million dollars from blackberry royalties from plant patents (University of Arkansas Division of Agriculture, 2021). The UA System blackberry breeding program also produced advancements in thornless plants, erect cane structures, increased fruit firmness, and the development of primocane-fruiting, which is plants that fruit on first-year primocanes, cultivars to lengthen the harvest season (Clark, 2005). 'Ouachita' and 'Osage' are two of the most widely grown cultivars released from the UA System (personal communications, Dr. John Clark). The most recent cultivars from the UA System are 'Sweet-Ark® Caddo', (Clark et al., 2019) released in 2018, 'Sweet-Ark® Ponca' released in 2019, and 'Prime-Ark® Horizon' released in 2020.

Blackberry plant morphology and physiology

Blackberries are a crown-forming perennial that produce above-ground stems called canes that are typically biennial (produce flowers and fruit then die in the second year) (Hummer, 2018). Cultivated blackberries vary in cane morphology and can be trailing, semi-erect, and erect (Finn and Clark, 2017). Trailing cultivars have canes that are typically flexible and grow along the ground, while erect cultivars have stiff, self-supporting main canes (Strik, 2017), and semi-erect cultivars have canes that are self-supporting and grow vertical but may arch towards the ground while maturing (Strik, 2017). All of these cane types can be either 'thorned' or 'thornless' (Finn and Clark, 2017).

First-year blackberry canes are called primocanes but in the second year, the canes are called floricanes and each fruiting lateral branch will have compound leaves containing three leaflets that produce inflorescences (flower cluster) at each node (Strik, 2017). A node is where the leaf petiole is attached on a main shoot or cane and is where the fruit and leaf buds are located; node numbers and complexity ultimately determine the yield or fruitfulness of the plant (Thompson et al., 2007). Blackberry buds will break during spring to produce one shoot with five to more than forty flowers depending on the cultivar or production system (Takeda, 1987). Floricane lateral length and fruitfulness and can also be influenced by position on the main floricane and by applied nitrogen fertilization rate (Strik, 2017).

Blackberry fruit structure

Blackberries are an aggregate fruit comprised of drupelets surrounding a soft tissue receptacle (torus). Each drupelet has a thin exocarp, a fleshy mesocarp, and a hard-lignified endocarp, or pyrene that encloses a single seed (Tomlik-Wyremblewska et al., 2010). As blackberries ripen, they turn from red to black. The blackberries are harvested weekly for 3-4 weeks from plants as the fruit ripens. Previous studies have shown a relationship between harvest date and different quality attributes and dependent on cultivar (Cavender et al., 2019; Jacques et al., 2014). The size (berry weight, length, and width) of a fully ripened blackberry varies among cultivars. On average, the weight of each blackberry will range from 5-15 g with length of 15-30 mm (Carvalho and Betancour, 2015). The berries can have different shapes, such as a round shape, or the berries can be long and oval shaped.

In addition, firmness, measured by the force to compress an individual blackberry can vary. Firmness is influenced by protopectin in the inter-cellular structures of blackberry drupelets, which act like cement to give blackberries a firm texture, but hydrolysis, large respiration rates, and warmer conditions during ripening decrease protopectin. Evaluation of many genotypes of blackberries showed that the average firmness was 3-8 Newtons (Salgado and Clark, 2016; Segantini et al., 2017, 2018; Threlfall et al., 2016).

Blackberry volatiles

Aromatic attributes, or volatiles perceived by the olfactory system while chewing a sample in the mouth, impact the flavor consumers experience when eating a blackberry. Volatile compounds in blackberries include acids, esters, alcohols, aldehydes, ketones, lactones, and terpenoids. Early studies focused on the volatile constituents of blackberries and blackberry products (Georgilopoulos and Gallois, 1987; Gulan et al., 1973; Scanlan et al., 1970). Compounds, such as 2-Heptanol, p-cymen-8-ol, 2-heptanone, 1-hexanol, a-terpineol, pulegone, 1-octanol, isoborneol, myrtenol, 4-terpineol, carvone, elemicine, and nonanal, have been identified as the major volatiles in blackberries. Blackberry aroma profiles are diverse, with different genotypes each having their unique aroma profile. Jacques et al. (2014) identified 45 volatile compounds in ‘Tupy’, the predominant cultivar available commercially. The majority of volatiles in blackberries were comprised of terpenoids with limonene as the predominate individual compound (Du et al., 2010).

Volatiles extracted using GC-MS with hexane, were mainly hydrocarbons and those extracted with acetone were furans and pyrans. Wang et al. (2005) reported that only 13% of the compounds were aromatic. In a similar study, Du et al. (2010) quantified volatiles of eight different genotypes of blackberries. The results showed a range of compounds, such as esters, terpenoids, aldehydes and ketones, alcohols, norisoprenoids, lactones, acids and furanones. The compounds were quantified, but the values of each compound did not distribute uniformly across all genotypes. GC-MS, along with GC-O can be used to evaluate the aroma of fresh-market blackberries. Barba et al. (2018) evaluated odorant compounds that enhanced sweet flavor in sugar-reduced juice using GC-O to isolate taste-enhancing compounds and showed that ethyl 2-methylbutonate enhanced flavor sweetness. The data could be helpful to target odorant compounds that enhance desired flavors. Limited GC-O research has been conducted on blackberries, however research conducted on other food products can help identify and isolate desired compounds in blackberries. It is possible that specific cultivar may have optimal harvest dates that differ from each other, depending on the preferred volatile composition, as is the case with grapes and other produce (Bindon et al., 2013; 2014; Jordão et al., 2017; Meyers, 2022).

Blackberry sensory

Consumers want a fresh-market blackberry that is uniform in color, fresh, has a good shelf life, fair-priced, rich in nutraceuticals, and has unique flavors and aromas (Threlfall et al., 2020, 2021). Descriptive sensory analyses have been conducted to determine attributes that are commercially acceptable, such as appearance, aroma, basic tastes, aromatics, feeling factors. Descriptive sensory analysis involves a trained panel that uses a lexicon (terms to describe the product) and references to evaluate products on a line scale. Threlfall et al. (2016) developed a fresh-market blackberry lexicon in an evaluation of UA System blackberries. In the lexicon, eight appearance, three basic tastes, two feeling factors, and eight aromatics were evaluated. Segantini et al. (2017) studied sensory attributes in postharvest storage and reported panelists could not perceive a significant difference in color, uniformity of color, glossiness, firmness or sweetness after storage, but could identify blackberries as being more astringent and less sour and bitter after storage.

Muscadine Grapes

Muscadine grapes (*Vitis rotundifolia* Michx.) are a disease-resistant specialty crop native to the southeastern United States. The black, bronze, and red grapes are traditionally used for the production of juice, wine, jelly, or jams, but have potential for increased fresh-market expansion. Advances in U.S. muscadine breeding have resulted in unique traits emerging with commercial, fresh-market potential providing opportunity to strengthen the market presence for muscadines as a southern region crop. Muscadines differ markedly from *V. vinefera* 'bunch' grapes in terms of genetics, morphology, production, and consumer experience. The genus Vitis is commonly divided into two subgenera, Euvitis Planch. (bunch grapes) and Muscadinia Planch, though some authors even consider Muscadinia a separate genus (Bailey, 1934; Reisch and Pratt, 1996). While Euvitis grapes, such as the European wine and table grapes (V. vinifera) and the American 'Concord' grape (*V. labrusca*), have 38 chromosomes, Muscadinia grapes have 40 chromosomes. Muscadinia grapes also differ from bunch grapes in that muscadines have smaller clusters, unbranched tendrils, berries that abscise (shatter) at maturity, and distinctive fruity/floral aromas and thick skins. Of the three Muscadinia species, only *V. rotundifolia* is grown commercially.

U.S. muscadine production

Muscadines are grown from Delaware to central Florida and from the Atlantic coast to eastern Texas (Lane, 1997). Native grapes have been cultivated for over 400 years and have a strong heritage in U.S. viticulture (Olien, 2019). Muscadine grape production can be a profitable enterprise for commercial growers (Noguera et al., 2005), but is dependent on availability of consumer markets. The top commercial muscadine-producing states are North Carolina (1,052 ha or 2,600 acres), Georgia (688 ha or 1,700 acres), and Florida (486 ha or 1,200 acres) (USDA NASS, 2012).

Muscadine grape breeding

There are public and private muscadine breeding programs across the southern United States in Arkansas, Florida, Georgia, and North Carolina. Previous advances in muscadine breeding include the development of perfect-flowered and self-fruitful cultivars, increased berry size and sugar content, presence of dry picking scars, and the introduction of a seedless muscadine grape (Conner, 2010). Other traits undergoing development include more cultivars with perfect flowers and large fruit, improved textures, thinner skins, a broader range of ripening dates and an expansion of the germplasm base used in muscadine breeding. Retaining the unique flavors and aromas of muscadines are a focus in creating new cultivars for the commercial fresh markets. The UA System Fruit Breeding Program began breeding muscadines in 2007 with a focus on large fruit size, crisp texture, edible skin, self-fruitful flowers, seedlessness, and improved postharvest storability (Barchenger et al., 2015a). The UA System is working on developing Vitis × Muscadinia hybrids to combine the disease resistance of muscadine grapes with the fruit quality of *V. vinifera*.

Muscadine cultivars

Over the past few decades, the muscadine industry has developed into a multimillion-dollar industry with over 100 cultivars released. The most commonly-grown muscadine cultivars for processing are ‘Noble’, a black cultivar, and ‘Carlos’, a bronze cultivar. Fresh-market cultivars have different quality requirements than processing cultivars, such as flavor, texture, color, and storability. Seedless muscadine cultivars are also of great commercial interest for commercial markets. New cultivars have been developed by crossing muscadines with *V. vinifera* cultivars. Jeff Bloodworth (Bloodworth, 2017), a private fruit breeder in North Carolina collaborated with Gardens Alive! (Lawrenceburg, IN), developing seedless muscadines, including the first seedless muscadine cultivars, ‘Oh My!®’ and ‘RazzMatazz®’. ‘RazzMatazz®’ (Gardens Alive, 2022b) was the first of the new cultivars, which is a continuously-fruiting vine producing small, red seedless berries. Another cultivar developed in 2019 was ‘Oh My!®’ (Gardens Alive, 2022a), that produces a bronze mid-size to large berry. Since these cultivars are new, neither ‘RazzMatazz®’ nor ‘OhMy! ®’ have been extensively evaluated for market potential (Hoffman et al., 2020).

Muscadine nutraceutical impacts

Muscadines grapes and products fit well in consumer-driven niche markets and local food systems trends (Brown et. al. 2016). Muscadines are a unique regional crop that can be marketed as a sustainable, locally produced table grape. Many consumers consider muscadine a nostalgic food, fondly recalling eating fresh berries from backyard vines or local farmers markets, while newer consumers are interested in the nutraceutical potential of muscadines (Perkins-Veazie et al., 2012; Striegler et al., 2005). A 10-berry serving of muscadines has 16% of the recommended daily fiber intake and 13 to 14% of vitamin C (USDA, 2011). In addition, muscadine grapes contain many health bioactives, including resveratrol, ellagic acid, anthocyanins and proanthocyanidin phenolic compounds (Ector et al., 1996; Lee et al., 2005; Pastrana-Bonilla et al., 2017; Striegler et al., 2005). Barchenger et al. (2015a) found that nutraceutical in muscadine grapes differed by grape segment and during storage.

Muscadine composition

Muscadine grapes typically have three sections: the flesh (pulp), skins, and seeds. The flesh contains primary metabolites of the grape, such as water, sugar, acids, and pectin, whereas skins and seeds contain more secondary metabolites, such as phenolic and aroma compounds (Yu 2012). Mature grapes contain water, sugar, organic acids, and pectin. Sugars (glucose and fructose) make up a majority of grape carbohydrate content with muscadine grapes having 15-23% soluble solids at harvest. In grapes, the acidity attributes measured are pH and titratable acidity (% tartaric acid). Mature muscadine grapes grown in Arkansas typically have 0.50-0.70% titratable acidity and 3.0-3.3 pH (Barchenger, et al., 2015b, Felts et al., 2020).

Muscadine volatiles

Muscadine volatiles are primarily composed of esters, alcohols, terpenes, and carbonyl compounds, which can be identified using GC-MS (Lee et al., 2016). The volatiles vary significantly by cultivar, ripening stage, and different stress factors during growth, both biotic and abiotic. Analysis of volatile compounds can be used to establish and predict consumer preferences, especially when correlated with consumer sensory data. Lamikanra (1987) determined that higher alcohols and fatty acid ethyl esters were numerically the largest classes of volatile aroma compounds in ‘Noble’ muscadine wine. Lamikanra et al. (1996) reported that 2-phenylethanol (rose and honey aroma) was predominantly synthesized during fermentation of muscadine wines but was also present in fresh muscadine grape skins. In an evaluation of ‘Noble’ wine, Mayfield (2020) reported that fruity esters were the largest class of volatile aroma compounds, followed by higher alcohols, notably 2-phenylethanol (rose and honey aroma). Baek et al. (1997) analyzed volatile aroma compounds in juice from ‘Carlos’ grapes and showed that furaneol and o-aminoacetophenone were likely responsible for characteristic candy and foxy-like aroma notes of muscadine grape juice.

Muscadine sensory

Sensory research has been done on muscadine grapes and products from grapes. Felts et al. (2018) developed a sensory lexicon for fresh-market muscadine grapes grown at the UA System Fruit Research Station and showed that panelists detected differences between genotypes in grape/overall, grape/muscadine, and fruity. Threlfall et al. (2007) identified that muscadine juices from Arkansas had cooked muscadine, apple, pear, cooked grape, green/unripe, and slightly musty aromas and flavors. In a consumer study by Brown et al. (2016), thinner skins and greater juice pH were associated with greater overall liking of muscadine grapes. Consumer acceptability of muscadines can be quantified with soluble solids analysis, texture analysis, and sensory analysis (Brown et al., 2016). An important attribute of muscadine grapes is the balance of sugars to acids in the berries at harvest. Flora et al. (1979) found the optimal titratable acidity to soluble solids ratio to be 30, including an acceptable range of 25-35, regardless if the juice is from a bronze or black cultivar. Meullenet et al. (2008) reported positive correlations between general muscadine flavor and musty flavor, general grape flavor and metallic flavor, green/unripe flavor and sourness/astringency, and sweetness and floral, apple, and pear flavors for Arkansas muscadine juice. Sensory evaluations of muscadine grapes have shown wide variation in consumer rating of flavor among muscadine genotypes (Meullenet et al., 2008), indicating that there is likely significant variation in the profiles of flavor and aroma compounds. It is important to note that few studies have paired GC-MS analysis of flavor volatiles with sensory assessments of aroma. Furthermore, no fresh-market muscadine cultivars have been analyzed for aroma volatiles.

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Chapter I

Evaluation of flavor and aroma attributes of Arkansas-grown hops

Abstract

Hops (*Humulus lupulus* L.) plants are a significant agricultural crop due to their worldwide production and as primary ingredients in brewing beer. Hops are herbaceous, perennial climbing plants, called bine plants that produce flowers or cones used in brewing. The hop cones produce lupulin, a yellow resinous substance, that gives hops a distinctive aroma and contains volatile compounds for brewing. The quality, volatile, and sensory attributes of four hops cultivars (Cascade, Cashmere, Crystal, and Zeus) grown at the University of Arkansas System (UA System) Division of Agriculture Fruit Research Station in Clarksville, AR were evaluated in 2020 and 2021. In general, cultivar significantly impacted the individual and total alpha and beta acids in 2020 and 2021. In both years, ‘Cascade’ (9.20 and 9.06% in 2020; 5.97 and 5.67% in 2021) and ‘Zeus’ (5.66 and 4.79% in 2020; 4.62 and 4.06% in 2021) had higher levels of alpha acids than beta acids, while ‘Cashmere’ (8.48 and 6.86% in 2020; 5.48 and 4.90% in 2021) and ‘Crystal’ (10.05 and 3.62% in 2020; 7.53 and 2.91% in 2021) had higher levels of beta acids than alpha acids. In the four cultivars harvested in both years, there were 88-127 volatile aroma compounds identified across seven compound classes including monoterpenes, alcohols, aldehydes, sesquiterpenes, esters, ketones, and aromatic hydrocarbons. In both 2020 and 2021, ‘Crystal’ had the highest volatile concentration (6,278 and 8,106 µg/kg, respectively) followed by ‘Cashmere’ (6,668 and 5,434 µg/kg, respectively) and ‘Cascade’ (5,829 and 4,132 µg/kg, respectively) with ‘Zeus’ (3,230 and 2,072 µg/kg, respectively) containing the lowest concentration. In both years, the five volatile aroma compounds with the highest levels found in Arkansas-grown hops were beta-pinene (monoterpene with herbal and pine aromas), beta-

myrcene (spicy monoterpene), caryophyllene (sesquiterpene with woody aromas), beta-Selinene (herbal sesquiterpene with celery notes), and humulene (spicy/woody sesquiterpene). The trained descriptive sensory panel (5-7) from the UA System Sensory Science Center evaluated the aroma of dried, ground hops cones from plants harvested in 2020 and 2021. In both years, the panelists could differentiate between cultivars for aged cheese, overall citrus complex, lemon, overall green herb complex, and overall pepper complex. The panelist found that the cultivars differed for more attributes in 2020 than in 2021. In both years the overall impact was the highest rated attribute (5-7 on a 15-point scale). Generally, principal component analysis showed grouping of sensory descriptive attributes with volatile compound classifications. In both years, cultivars were not grouped near each other, but sesquiterpenes, umami/savory, and white pepper were clustered together. This combination of quality, volatile, and sensory evaluation can be used to for brewing production and to evaluate which cultivars have the greatest potential for use in Arkansas.

Introduction

Hops (*Humulus lupulus* L.) plants are a significant agricultural crop due to their worldwide production and as primary ingredients in brewing beer. Hops are herbaceous, perennial climbing plants, called bine plants that produce flowers or cones used in brewing. Hops plants are mostly grown between the latitudes of 33°N and 55°N with temperature ranges of 5-20 □ and 15 hours of day length. There are over 80 cultivars of hops commercially grown worldwide.

Hops are grown in the United States Department of Agriculture (USDA) plant hardiness zones 4-8 with production mainly in the Pacific Northwest (Washington, Idaho, and Oregon). In 2020, production of hops in Idaho, Oregon, and Washington totaled over 47 million kg with over 23,000 hectares of production with a value of $619 million (USDA, NASS 2020). The top five hops cultivars grown in Washington were ‘Citra®’, ‘Columbus/Tomahawk/Zeus’, ‘Mosaic®’, ‘Simcoe®,’ and ‘Cascade’, and in Idaho were ‘Columbus/Tomahawk/Zeus’, ‘Mosaic®’, ‘Citra®’, ‘Idaho 7™’, and ‘Chinook’, and in Oregon were ‘Citra®’, ‘Nugget’, ‘Mosaic®’, ‘Cascade’, and ‘Willamette’ (USDA, NASS 2020). While the Pacific Northwest accounts for over 95% of hops grown in the United States, there are many other states growing hops commercially. California, Colorado, Michigan, Minnesota, New York, and Wisconsin harvested over 50 hectares in 2020 with other states such as North Carolina harvesting 10 hectares (Growers of America, 2021).

The bine is one of the major components of the hop plant, as well as the roots and rhizomes, the leaves, and the flowers (hop cones). Hops bines can grow up to 6 m tall in a single summer but die back to the ground in the winter. Hops start to grow in late spring, with hop cone harvest occurring in August to September in the northern hemisphere. Hops are a dioecious species of plant, producing both male and female flowers with female plants grown commercially, while male plants are used for breeding (Briggs et al., 2004). Proper hop cultivation requires some form of infrastructure, such as a trellis system, to support plant growth. The hops plant grows quickly, typically between 3-4 m in June and 6-10 m in July and August (Briggs et al., 2004). The hop cones typically form in 2-3 weeks beginning in July and early August but need another three weeks to fully mature.

The growth, development, and handling of the cones are crucial for growers since these affect hop cone qualities, as well as determining when to harvest cones. Hops harvest is dependent on many factors, including cultivar, age of plant, soil characteristics, growing location, and weather conditions (Briggs et al., 2004; Lilley and Campbell, 1999; Morcol et al., 2020; Rodolfi et al., 2019; Santagostini et al., 2020; Sharp et al., 2014). To determine when to harvest, growers can evaluate cone maturity by assessing the tactile and aromatic qualities of the cones while still attached to the plant. Immature cones have a damp, soft feel, while mature hops have a paper-like, light texture that springs back when compressed (Verzele and De Keukeleire, 1991). Cone maturity can also be evaluated by picking hops cones and cutting the cone lengthwise. When fully mature, the internal resin (lupulin sacs containing the essential oils and bitter compounds) of the cone will appear dark yellow and emit a pungent aroma reminiscent of a “hoppy” beer (Verzele and De Keukeleire, 1991). Hops cones can also be collected and dried to determine the moisture content (or dry matter) of the cones for harvest. Hops at harvest should have a moisture content of 80% (Briggs et al., 2004). Hops can be harvested by machine or by hand depending on the size of the hop yard.

To ensure optimal quality for brewing, hop cones must be harvested and stored properly. Since hops are harvested at 80% moisture, the water is removed from hop cones using kilns, oasts, or drying rooms to a final moisture content of 7-10% which reduces the rate of oxidation and spoilage. The drying temperature must not exceed 60 °C or hop cone quality will be impacted. Once the hops are dried, the cones must be stored at low temperatures in an oxygen-depleted receptacle. Growers often place harvested cones in commercial freezers once the dried product is vacuum sealed in polypropylene bags.

The hop cones contain multicellular balloon-shaped glands on the bracts and bracteoles of the cone and are responsible for the production of lupulin. Lupulin is a yellow resinous substance that gives hops its distinctive aroma and is the primary component of commercial interest for brewing (Yedilova and Inelova, 2020). Hops cones contain secondary metabolites that can be divided into three main groups: acids (alpha and beta acids), essential oils, and polyphenols (De Keukeleire, 2000). Composition of the hop cones is about 30% alpha and beta acids (Clark et al., 2013; De Keukeleire et al., 2003; Eyres and Dufour, 2008; Probasco and Murphey, 1996; Van Cleemput et al., 2009) and 3-6% polyphenols and tannins, with essential oils ranging from 0.5-5.0% (De Keukeleire et al., 2003; Van Cleemput et al., 2009).

Alpha acids are structurally complex enolic acids that contain a six-carbon ring with several substituent groups. While there are more than seven prominent alpha acids within the lupulin glands of the hops, humulone, cohumulone, and adhumulone constitute 98-99% of the alpha-acids (Killeen et al., 2017; Rutnik et al., 2021). Humulone is the primary alpha acid found that has anti-bacterial, anticancer, and antioxidant properties, and imparts the majority of the bitter flavor that is characteristic of beer (Karabín et al., 2016). Like humulone, cohumulone is another alpha acid that imparts flavors into beer during isomerization, but cohumulone is often described by brewers as much harsher in bitter flavor (Briggs et al., 2004). The remaining alpha acids, adhumulone, posthumulone, and prehumulone, also add to the overall flavor profile of beers, yet additional research is still needed to ascertain the specific effects these acids have on a consumer taste perception of a beer (Morcol et al., 2020).

Beta acids are another secondary metabolite that are characteristic of hop cultivars, and the quantities vary with cultivar and ripening age (Rutnik et al., 2021). The beta acids in the hops cone are only a minor contribution to a beer flavor but are a crucial component in the brewing process, especially for preservation. While the number of analogues is the same in alpha acids, the beta acids are chemically disparate from the alpha acids due to the isopentenyl side chain in place of the second hydroxyl group at ring position six. Previous studies regarding these compounds have noted that the ratio of alpha to beta acids varies depending on the stage of development, growing location (terroir), and the cultivar, but the alpha to beta acid ratio often ranges from 1:1 to 4:1 (Forteschi et al., 2019; Rodolfi et al., 2019; Rutnik et al., 2021; Santagostini et al., 2020). This ratio is often used by brewers to determine how hops will be used in beer production.

Phenolic substances in the lupulin glands can be both anti and pro-oxidants, flavor precursors, and respond with different phytochemicals that impact a few quality attributes of beer. For example, flavor, shading, colloidal, and flavor solidness are all affected by phenolic compounds (Wannenmacher et al., 2018). Polyphenol extracts used in beer production influence mouthfeel, sharpness, and astringency (Jaskula-Goiris et al., 2014). Like other iso-alpha acids, phenolic compounds go through underlying changes during separation and enzymatic delivery throughout the brewing process. Eventually the phenolic compounds precipitate out of the beer along with protein and other unfermentable byproducts, and their impact declines during fermenting (Wannenmacher et al., 2018). While the specific impact that hop polyphenols have on the quality, flavor, and fragrance of lager (light beer brewed at cool temperatures by slow fermentation with a slow-acting yeast) have not specifically been investigated, their antioxidant nature and effect on the shelf life of beer will continue (Wannenmacher et al., 2018).

In hops, the primary volatile compounds are present in essential oils that are secreted in the lupulin glands of the hop cones (Liu et al., 2018; Brendel et al., 2020; Pallottino et al., 2020). The volatiles are responsible for the distinctive aroma of hops, which in turn, contribute to beer flavor. Gas chromatography (GC) has been used to identify over 400 volatile compounds in hops that can be divided into the groups, hydrocarbons, oxygenated compounds, and sulfur-containing compounds (Almaguer et al., 2014). Gas chromatography coupled with a flame ionization detector (FID), quantitatively measure analytes in a gas stream. The compounds can be aliphatic, monoterpenes, and sesquiterpenes (Rutnik et al., 2021). Yield of essential oils in dried hop cones is around 0.3% for most cultivars (Malizia et al., 1999). The proportions of volatile oils (α-humulene, myrcene, and β-caryophyllene) fluctuate among cultivar, with the degree of oils increasing logarithmically as cones mature (Briggs et al., 2004; Danenhower et al., 2008; Killeen et al., 2017; Steenackers et al., 2015). Maintaining the proper amounts of essential oils in hops cones is especially important for brewers, as levels can decline during storage through oxidation, polymerization, or resignification and are impacted by machine harvesting, drying, and baling (compressing hops into large bales) and pelleting (creating pellets from dried, ground cones) methods (Rutnik et al., 2021). Steinhaus and Scheiberle (2020) found that while there were hundreds of volatile compounds contained within hop cones, only 23 had a flavor dilution factor (ratio of the concentration of the odorant in the initial extract to its concentration in the most dilute extract in which the odour is still detectable by GC-Olfactory analysis) range of 16-4,096. This indicates that only a small number of volatile compounds are responsible for the overall hop aroma which has been shown in other studies (Guadagni et al., 1966; Tressl et al., 1978).

With the rise in popularity of hoppy beer styles, craft brewers have started utilizing dry-hopping as a method of enhancing beer aroma and flavor (Lafontaine and Shellhammer, 2018a; 2018b). Dry hopping is a cold extraction of hops in fermented or partially fermented beer, which can add intense hop aroma to beer, without imparting as much bitterness as kettle hopping (Lafontaine et al., 2019). This is advantageous to many brewers, as consumers only tolerate a certain level of bitterness, but still desire a strong hoppy aroma and flavor. Oladokun et al. (2017) found that dry hopping could also increase the alpha acid levels in beer, but those results were only significant when using a hop cultivar that had high alpha acids. Craft brewers and hop growers can use this information to determine what hop cultivars are optimal for providing hoppy aroma and flavors.

The sensory and quality of hop cones and beer-derived products varies between seasons and cultivars due to the climate, cultivation method, soil conditions, cone maturity at harvest, root condition, and other abiotic factors (Lafontaine, et al., 2019; Matsui et al., 2013). While there are many attributes that impact hops plant and cone quality, the sensory profiles of beer can be fruity, herbal, floral, and citrus and result from the distinct profiles imparted from the hop cones into a beer during brewing (Missbach et al., 2017). Other research determined which descriptive sensory analysis method is optimal for the complex flavor profiles found in beer (Vázquez□Araújo et al., 2013). Volatiles in hop oils induce diverse aroma and flavor sensations, ranging from floral, to fruity, to spicy (Dietz et al., 2020 Stucky and McDaniel, 2018). Bober et al. (2020) showed that small changes in hop composition will have a noticeable difference in the final taste of beer, further demonstrating the need to establish quantitative profiles for different cultivars. Lafontaine et al. (2018a; 2018b) conducted two sensory studies to examine the impact of dry-hopping rate and mixed cultivar dry-hopping effects on the sensorial and analytical characteristics of beer indicating that the addition of more hops by dry-hopping does not lead to increased aroma intensity and it is possible to produce a beer that exhibits similar aroma profiles when dry-hopped with blends of cultivars. Although beer flavor profiles can be challenging to assess due to the variability of complex flavor attributes, sensory analysis can provide useful information to brewers to make decisions on how best to use hops.

Hops can be grown successfully in the United States outside of the Pacific Northwest, and research on hops production is currently underway in North Carolina and Florida. Since Arkansas has similar growing environments as North Carolina, there is potential for Arkansas-grown hops to support the expanding craft brewing industry in Arkansas. Thus, the objective of this research was to evaluate flavor and aroma attributes of Arkansas-grown hops.

Materials and Methods

Hopyard

The hopyard was established at the University of Arkansas System (UA System) Division of Agriculture Fruit Research Station, Clarksville, AR in September 2018 [West-Central Arkansas, lat. 35.3158°N and long. 93.2412°W; U.S. Dept of Agriculture (USDA) hardiness zone 7a; soil type Linker fine sandy loam (Typic Hapludult)]. The hopyard was composed of nine 1.2 m wide x 7.3 m long plots divided into three blocks with three replications of six hop cultivars/block (Fig. 1). Plug plants for 'Cascade', 'Cashmere', and 'Crystal' were sourced from Agristarts (Apopka, FL), and 'Centennial', 'Nugget', and 'Zeus' were sourced from Great Lakes Hops (Zeeland, MI).

The hops were grown on a 3.66 m-high trellis with equal spacing (76.2 cm) between plants. Three bines/plant were trained using three lines of bailing twine suspended to the top of the horizontal trellis wire. A shallow layer of mulch 10-15 cm deep was placed around each plant after planting to conserve soil moisture and reduce invasive grasses. One line of drip irrigation was installed with drip emitters (Rain Bird® PCEM20SPB 1.0 GPH) spaced every 76.2 cm to deliver water directly to each plant along the fertility trial row.

The hops entered dormancy during the winter months (November through March), and all above ground growth died back to the ground. Bines from all cultivars that survived dormancy emerged from the perennial crowns around mid-March through early April. Fertility treatments for the hops plants included three rates, low (32.01 g), standard (48.02 g), and high (63.87 g). The plants received four applications of 13N-13P-13K (Oakley Fertilizer, Inc., Beebe, AR) granular fertilizer that consisted of equal parts N, P, and K applied by hand broadcast methods in biweekly intervals on May 15, June 1, June 15, and June 30 in 2020 and 2021. Drip irrigation emitters were rated for 1 mm^3 per hour (1 gph) and used 6-8 hours 1-3 times/week during the peak summer months (June-August). Daily maximum and minimum temperatures at the Fruit Research Station were recorded using a Nimbus Digital Thermometer (Sensor Instrument Co. Inc., Center Point, OR). Rainfall was measured using a rain gauge.

Hop harvest

The moisture content and ripeness of the hop cones were assessed during late summer and early fall to determine the ideal time of harvest. Hops were harvested when the moisture content of the cones were 75-80%, the color and texture of the bracts were light and papery to the touch, and the internal lupulin glands were dark yellow and pungent. A sample of 30 cones per plant were picked one to two weeks prior to harvest, weighed, dried until devoid of moisture, and reweighed to determine the moisture content of the cones. All plants were harvested between mid-August through mid-September.

Drying and storing hop cones

At harvest the cones from each plant were removed, combined and placed into paper bags (17.8 cm wide x 11.4 cm long x 34.9 cm long) labeled with wet (harvest) cone weight/bag. The cones in the bags were placed in a dehydrator custom built for this site (Herrera et al., 2021). The temperature of the dehydrator was 43-49 °C, and a dehumidifier was used to remove moisture from the air. The hops were removed when the cones reached 8-10% moisture content. To ensure the cones were dried to these specifications, the individual bags were weighed every 2-4 hrs after 14-16 hrs elapsed until the intended moisture level was achieved. Additionally, other visual indicators were used to evaluate if hops were sufficiently dried. These included the presence of yellow powdery lupulin when handled and the texture of the bracts (springy, papery, and light in color).

After the cones were dried, the hops were packaged and vacuum sealed in food-grade plastic bags (UltraSource Vacuum Chamber Pouches, 4 mil, 20.3 x 30.4 cm). A Floor Model Chamber Vacuum Packaging Machine (VacPak-It VMC20FGF, Clark Associates, Lancaster, PA) was used to vacuum seal the bags with about 95% air removal from each package. This vacuum strength (removal of air from pouches) varied depending on the number of hops in the package. If the vacuum strength was too high, the cones were crushed, and the lupulin would fall from the cones and settle at the bottom of the plastic bag. The bags of hops were placed into a freezer at -2 °C for later analysis.

Dried hops analysis

Dried, frozen hops were taken to the UA System Food Science Department for analysis. For this study, the four most productive Arkansas-grown cultivars ‘Cascade’, ‘Cashmere’, ‘Crystal’, and ‘Zeus’ with the standard fertility treatment were evaluated in 2020 and 2021 with three replications. For the analysis of the dried hop cones, hops bags were removed from the freezer, samples were removed, and the unused hops were resealed with the vacuum sealer and returned to the freezer. The whole-cone hops were ground for analysis using a Magic Bullet blender (MBR - 1101, Los Angeles, CA) with cross blades in a 473-mL container. Analysis of dried hops included moisture content and alpha and beta acids by High Pressure Liquid Chromatography (HPLC) using American Society of Brewing Chemists (ASBC) methods. The extractions of alpha and beta acids were done in analytical triplicate per sample, and HPLC injections were done in duplicate. The moisture content of the hops was done in analytical duplicate per sample.

Moisture content analysis. The moisture content of the dried hops must be analyzed because the moisture content after drying can deviate from the optimal 8-10%. The hops were dried 100% to determine the moisture content for the hops cones to calculate alpha and beta acids levels using the ASBC method Hops-4C (Moisture by Routine Air Oven Method). Approximately 2.5 g of unground hops were placed in an aluminum dish. The dish was covered with aluminum foil, then the dishes with hops were weighed on a precision scale (0.001 g) and placed in a Fischer Scientific Isotemp Oven Model 655F (Houston, TX) at 103-104 °C. The dish covers were removed, the hops were dried for 1 hr, then the covers were replaced while the dish was in the oven. The dishes were transferred to a desiccator containing Drierite Absorbent (8 mesh DX2515-1, Millipore Corporation, Burlington, MA). The lid was placed on the desiccator and sealed with high vacuum silicone grease. The hops were cooled in the desiccator and reweighed. After weighing, the percent moisture of the hops was calculated using the formula:

*moisture in hops (%) = (loss in weight*100)/(weight of undried sample)*

Dry weight of the samples can also be calculated from the moisture content.

Alpha and beta acid analysis. Dried hops were analyzed by HPLC using the ASBC Hops-14 (alpha acids and beta acids in Hops and Hop Extracts by HPLC) procedure. This procedure was modified because of the limited amount of sample. A 2-g sample of dried hops were placed in 50-mL centrifuge tubes and weighed. Then, 4 mL of methanol and 20 mL of diethyl ether were added to each tube. The tube was capped and placed on a shaker for 30 min. After 30 min., flasks were opened and 8 mL of 0.1M hydrochloric acid was added. The original method for Hops-14 instructs to use 10 g of hops with 20 mL of methanol, 100 mL of diethyl ether and after shaking 40 mL of hydrochloric acid. So, for this project, the HPLC extraction was downscaled by a factor of five as compared to the original procedure. The flasks were capped and placed on the shaker for 10 min. After this, the flasks were kept in the dark for 10 min as the phases separated. After the phases separated, 1.0 mL of the supernatant phase was pipetted in a 10 mL volumetric flask and brought up to volume with methanol. The contents of the flask were sealed with parafilm and mixed. The solution was syringe filtered using a 25 mm 0.45 nylon membrane filters (VWR, Radnor, PA) before injection into the HPLC.

Samples (50 µL) were analyzed using a Waters HPLC system equipped with a model 600 pump, a model 717 Plus autosampler and a model 996 photodiode array detector. Separation was carried out using a Phenomenex (Torrance, CA) Nucleosil-5 C18 chromatographic column (250 × 4 mm, 5-µm ODS RP18). The mobile phase was a combination of methanol, water, and phosphoric acid in an 85:17:0.25 ratio (v/v) that was mixed and filtered through a 0.45-µm filter. To achieve adequate resolution, the column was conditioned with mobile phase for 1 hr prior to use. The flow rate was 0.8 mL/min, and the detection wavelength was 314 nm at an ambient temperature. Each sample was injected and analyzed in duplicate with a run time of 30 minutes. Samples were either run on the HPLC immediately or stored at 2 °C and protected from light for analysis within 24 hours. After analysis, the HPLC peak areas were converted to levels of the alpha and beta acids using the standard curves. The percentage of the fraction per gram of hops was calculated using the following formula:

*% w/w= (HPLC conc (mg/ml) *methanol volume (mL)*(mL methanol+mL ether+mL hydrochloric acid))/(mL supernatant taken*1000*starting weight of sample (g)).*

<u>Standards and Calibration.</u> The calibration curve was made using Standard hop extract ICE-4 (ASBC, Saint Paul, MN) for HPLC analysis. This is a hop extract containing a specified concentration of alpha and beta acids. ICE-4 contains cohumulone (10.98%), n+adhumulone (31.60%), colupulone (13.02%), and n+adlupulone (13.52%) with total alpha acids levels of 42.58% and total beta acids levels of 26.54%. Alpha acids can be subdivided in three main individual acids: cohumulone, n-humulone, and adhumulone. The procedure of ASBC Hops-14 that was used to separate cohumulone as an individual fraction and n-humulone and ad-humulone together as a fraction. This gives two fractions: “cohomulone” and “n+-adhumulone”. The same applies to the beta acids. Colupulone was separated from the other beta acids, n-lupulone and adlupulone. From the ICE-4 standard, 1.500 ± 0.001 g was weighed and diluted in 25 mL of toluene in a 25-mL volumetric flask. The standard was first diluted (dissolved) with toluene. The toluene dilution was then diluted by a factor of 10 volumetrically with methanol (standard A) followed by subsequent dilutions. The calibration curve of each of the standards was achieved by plotting the levels of cohumulone, n+adhumulone, colupulone, and n+adlupulone in the standard against the acquired area.

Descriptive sensory analysis

Descriptive sensory analysis was performed at the Sensory and Consumer Research Center at the UA System, Fayetteville, AR in 2020 and 2021. The descriptive sensory panelists (n=5-7) evaluated the aroma of dried, ground hops for each cultivar in triplicate. The ages of the descriptive panelists varied with four females and one male on the panel in 2020 and five females and two males on the panel in 2021. Only four cultivars (Cascade, Cashmere, Crystal, and Zeus) were evaluated due to limited availability of 'Centennial' and 'Nugget'. The samples for sensory analysis for each cultivar were from the standard fertility rate and field replications were combined for sensory analysis, but panelists evaluated the hops in triplicate. The hops were ground and served to the panelists one at a time at room temperature (25 °C) in Snap-Seal™ translucent polypropylene containers (45 mL) labeled with three-digit codes. Serving order was randomized across each replication to prevent presentation order bias. Panelists were trained to use the Sensory Spectrum method, an objective method for describing the intensity of attributes in products using references for the attributes. Intensities of the aroma were based on the Universal Scale, where a saltine cracker was equal to 2.0, applesauce was equal to 5.0, orange juice was equal to 7.5, grape juice was equal to 10.0, and Big Red Gum® (Mars, Inc., MeLean, VA) was equal to 15.0. The panelists developed a lexicon of descriptive sensory terms through consensus during orientation and practice sessions for the aroma attributes of dried, ground hops (Table 1). The descriptive panel evaluated the hops for 23 aroma attributes using a 15-point scale, where 0 = less of an attribute and 15 = more of an attribute. Panelists also listed a defining attribute to characterize each sample.

Design and statistical analysis

For this study, the four most productive Arkansas-grown cultivars 'Cascade', 'Cashmere', 'Crystal', and 'Zeus' with the standard fertility treatment were evaluated in 2020 and 2021 with three replications. The alpha and beta acid attributes were also extracted in triplicate, with HPLC injections run in duplicated. The moisture content analysis was assessed in analytical duplicate. Statistical analyses were conducted using JMP® (version 16.1.0; SAS Institute, Cary, NC). To determine if there was a significant difference among cultivars, a univariate analysis of variance (ANOVA) was used to analyze the levels of variance. Tukey's honest significant difference (HSD) test was used to detect significant differences ($p < 0.05$) among means and verify interactions at 95% significance level. For descriptive sensory evaluation, four cultivars were evaluated in triplicate using a univariate ANOVA to detect the significance of the cultivar main effect for each attribute. The panelist main effect and genotype x panelist interaction were included in the model to account for the error explained by between-panelist and within-panelist variation. Associations among all dependent variables were determined using multivariate pairwise correlation coefficients of the mean values using JMP. Principal component analysis was done using XLStat (Addinsoft Inc., New York, NY).

Results and Discussion

Average monthly temperature and rainfall at the Fruit Research Station in Clarksville, AR were recorded from January to September, the end of hops harvest (Fig. 2.) through reports generated by the Southern Regional Climate Center (Texas A&M University, 2022) and with a Nimbus Digital Thermometer (Sensor Instrument Co. Inc., Center Point, OR). While the 2020 hops season in Clarksville, AR was mild in terms of temperature and rainfall, the 2021 season had notable cold weather events in February and April. There were record cold temperatures (-5 °C) with 178 mm of snow in February of 2021 followed by a freeze in late April (-1 °C overnight). Shoots of the hops plants emerged mid-March and early April both years. The average high temperature was 22 °C and low temperature was 12 °C in both years. Average (January-September) rainfall in 2021 (103 mm) was less than rainfall in 2020 (139 mm). The total precipitation from January to September was 1,247 mm and 929 mm in 2020 and 2021, respectively. During July to September in 2021, there was less rainfall each month with 239 mm less during these months compared to 2020 (445 mm). Maximum day length for both years occurred June 20 with 14 hours and 36 minutes of daylight (1 hour and 18 minutes less than commercial regions in the Pacific Northwest). The average day length was 12 hours and 48 minutes during the measured time interval.

The alpha and beta acids were much lower in 2021 than in 2020, likely due to a number of contributing factors. When examining rainfall during peak growing months (May-August) there was a large reduction in the amount of rainfall during the end of the growing season in 2021 compared to 2020 (Fig 1). Both July and August had similar average temperatures in 2020 and 2021, but those months had much less total precipitation in 2021 than in 2020. Studies from Nakawuka et al. (2017) and Fandino et al. (2015) showed that reduced precipitation or irrigation leads to lower hops yield and cone quality, especially in hops plants that are not fully mature. Hops harvest also occurred a few weeks later in 2021 than in 2020. Darby and Bruce (2019) showed that in Vermont, hops quality slowly increased until peaking, then sharply declined. It is possible that hops harvested in 2021 experienced loss in quality from being harvested too late in the season.

Alpha and beta acids

Cultivar significantly impacted the individual and total alpha and beta acids in 2020 and 2021 (Table 2). For both years, hops had 1.1-5.1% cohumulone, 1.5-4.1% n+ adhumulone, 2.9-9.2% total alpha acids, 2.3-4.3% colupulone, 1.4-7.0% n+ adlupulone, and 4.1-10.1% total beta acids. In 2020 and 2021, ‘Crystal had the lowest total alpha acids (3.62 and 2.91%, respectively) and the highest total beta acids (10.05% and 7.53%, respectively), and ‘Zeus’ had the lowest (3.83% and 3.72%, respectively). In both years, ‘Cashmere’ and ‘Crystal’ had higher levels of beta acids than alpha acids, while ‘Cascade’ and ‘Zeus’ had higher levels of alpha acids than beta acids.

2020. ‘Crystal’ had lower cohumulone (1.43%) and total alpha acids (3.62%) than the other cultivars (Table 2). ‘Cascade’ had the highest levels of total cohumulone (5.12%), n+-adhumulone (4.07%), and total alpha acids, (9.20%), while ‘Cascade’ and ‘Crystal’ had the highest total beta acids (9.06 and 10.05% respectively). ‘Cascade’ (4.32%) had higher colupulone than all other cultivars, and ‘Crystal’ (7.00%) had a higher level of n+-adlupulone than all other cultivars.

2021. ‘Crystal’ had lower cohumulone (1.14%) and total alpha acid (2.91%) levels than any other cultivar (Table 2). ‘Crystal’ had the highest levels of n+ adlupulone (5.25%) and total beta acids (7.53%). There was no significant difference between any cultivars for colupulone, and ‘Zeus’ had the lowest levels of n+-adlupulone.

Volatile aroma attributes

In the four cultivars harvested in both years, there were 88-127 volatile aroma compounds identified across seven compound classes including monoterpenes, alcohols, aldehydes, sesquiterpenes, esters, ketones, and aromatic hydrocarbons (Table 3). Compound categories included chemical, floral, fruity, green/fat, roasted/caramelized, vegetal alcohols, floral, green/fat, vegetal, and roasted/caramelized aldehydes, fruity and vegetal aromatic hydrocarbons, fruity esters, vegetal and fruity ketones, vegetal, fruity, floral, green/fat monoterpenes, and green/fat, and fruity sesquiterpenes. Across all cultivars and both years, monoterpenes (9-49%) and sesquiterpenes (40-72%) were the major compound categories (Fig. 3). Terpenes are the largest group of natural compounds, and all terpenes are synthesized from the same two five carbon compounds: isopentenyl diphosphate and dimethylallyl diphosphate.

Enzymes called prenyltransferases synthesize linear prenyl disphosphates at the reaction site, and the active isoprene unit is repetitively added to dimethylallyl diphosphate to form various terpene skeletons (Wang et. al, 2005). Variations in the number of isoprene unit repetitions, cyclic reactions, and rearrangements are responsible for the structural and chemical diversity of terpenes. Based on the number of five-carbon isoprene units, terpenes are classified as C_5 hemiterpenes, C_{10} monoterpenes, C_{15} sesquiterpenes, C_{20} Diterpenes, C_{25} sesterterpenes, and C_{30} triterpenes. Esters, alcohols, ketones, aromatic hydrocarbons, and aldehydes were also present in low amounts. In both 2020 and 2021, 'Crystal' had the highest volatile concentration (6,279 and 8,107 µg/kg, respectively) followed by 'Cashmere' (6,668 and 5,434 µg/kg, respectively) and 'Cascade' (5,830 and 4,132 µg/kg, respectively) with 'Zeus' (3,230 and 2,073 µg/kg, respectively) containing the lowest concentration in each year (Fig. 3 and Table 4). In both years, the five volatile aroma compounds with the highest levels found in Arkansas-grown hops were beta-pinene (monoterpene with herbal and pine aromas), beta-myrcene (spicy monoterpene), caryophyllene (sesquiterpene with woody aromas), beta-selinene (herbal sesquiterpene with celery notes), and humulene (spicy/woody sesquiterpene) (Table 4).

Su and Yin (2021) investigated 'Cascade' and 'Chinook' hops grown in Virginia to determine the most impactful aromas and found 33 aroma active peaks using GC-O. They identified six esters, five monoterpenes, 11 sesquiterpenes, five terpenoids, one aldehyde and one alcohol were positively identified, with 4 other unknown compounds. Of those 29 positively identified compounds, this research found 12 of the same compounds in the four hops cultivars examined: alpha-cubebene, alpha-pinene, beta-myrcene, beta-Ocimene, beta-pinene, beta-selinene, caryophyllene, cis-beta-famesene, geraniol, humulene, linalool, and ylangene (Fig.4). Cymene was also identified in 2020, and humulene epoxide II and Caryophyllene oxide were found in 2021, but these levels were less than 10 µg/kg. In both years, 'Crystal' had the highest levels of impactful volatiles, followed by 'Cashmere', then 'Cascade', with 'Zeus' having the lowest levels in each year. Humulene (woody monoterpene) had the highest levels of the impactful volatiles in each year, followed by beta-myrcene (a spicy monoterpene), and caryophyllene (a peppery sesquiterpene). Levels of impactful volatiles were lower in 2021 than in 2020, similar to the reduction in overall volatiles identified between the two years.

Volatile levels of hops were much lower in 2021 than in 2020, in both total and impactful volatile levels. While specific harvest dates were not examined in this study, a study performed at the University of Vermont showed that hops harvested later in the season had a drastic reduction in volatile and alpha and beta acid levels (Darby and Bruce, 2019).

2020. In the four cultivars harvested, 88 volatile aroma compounds were identified across 10 compound classes including 28 esters, 22 monoterpenes, 18 sesquiterpenes, seven ketones, seven aldehydes, five alcohols, and one aromatic hydrocarbon (Table 3). In 2020, 'Crystal' had the highest volatile concentration (8,107 µg/kg) followed by 'Cashmere' (6,668 µg/kg) and 'Cascade' (5,829 µg/kg) with 'Zeus' (3,230 µg/kg) containing the lowest concentration. For all cultivars, monoterpenes and sesquiterpenes represented the largest percentage of total volatile concentration (92 and 96%, respectively) (Fig. 3). In 2020, 'Cascade' had the highest levels of beta-pinene (monoterpene with herbal notes) and beta-myrcene (spicy monoterpene) (634 and 1,293 µg/kg, respectively), 'Cashmere' (1,168 µg/kg) had the highest levels of caryophyllene (sesquiterpene with woody/citrus notes), and 'Crystal' had the highest levels of beta-selinene (herbal sesquiterpene) and humulene (woody sesquiterpene) (321 and 2,812 µg/kg, respectively).

2021. In the four cultivars harvested, there were 127 volatile aroma compounds identified across seven compound classes including 36 esters, 34 sesquiterpenes, 27, monoterpenes, 15 ketones, nine aldehydes, four alcohols, and two aromatic hydrocarbons (Table 3). In 2021, ‘Crystal’ had the highest volatile concentration (6,278 µg/kg) followed by ‘Cashmere’ (5,434 µg/kg) and ‘Cascade’ (4,132 µg/kg) with ‘Zeus’ (2,072 µg/kg) containing the lowest concentration. For all cultivars, monoterpenes and sesquiterpenes represented the largest percentage of total volatile concentration (96%) (Fig. 4). In 2021, Cascade had the highest levels of beta-pinene (monoterpene with herbal notes), caryophyllene (sesquiterpene with woody/citrus notes), and humulene (woody sesquiterpene) (475, 753, and 2,812 µg/kg respectively). Cashmere (747 µg/kg) had the highest levels of beta-selinene (herbal sesquiterpene), and ‘Crystal’ (825 µg/kg) had the highest levels of beta-myrcene (spicy monoterpene).

Descriptive sensory aroma

The descriptive sensory panel evaluated the aroma of dried, ground hops cones from plants harvested in 2020 and 2021. In both years, the panelists could differentiate between cultivars for aged cheese, overall citrus complex, lemon, overall green herb complex, and overall pepper complex. The panelist found more that the cultivars differed for more attributes in 2020 than in 2021. This could have been due to a number of contributing factors, but notably both the overall volatile level and impactful volatile levels were lower in 2021 than in 2020. Dietz et al. (2020) showed that there can be both eliminative and antagonistic effects between volatile compounds, and as there were more compounds identified in 2021 than in 2020, it is possible that some of these additional compounds had a non-synergistic effect and reduced the perception of some of these sensory attributes. In both years the overall impact was the highest rated attribute (5-7 on a 15-point scale) which is equivalent to intensities of the aroma on the Universal Scale with applesauce equal to 5.0 and orange juice equal to 7.5.

2020. In 2020, the panelists could differentiate 14 hops aroma attributes (fruity, terpenes, aged cheese, umami savory, overall citrus complex, lemon, lemongrass, citrus other, overall green herb complex, floral, mint, garlic, overall pepper complex, and overall impact (Table 5). ‘Crystal’ (6.7) and ‘Cashmere’ (6.6) had a higher overall aroma impact than ‘Cascade’ (6.1) and ‘Zeus’ (5.9). The hops cultivars differed in overall green herb complex (2.5-3.2), overall citrus complex (2.0-3.4), and overall pepper complex (1.6-2.8). ‘Cascade’ had the highest overall citrus complex, and ‘Crystal’ had the highest overall green herb and pepper complexes. Cultivars also differed for fruity, terpenes, aged cheese, umami, lemon, lemongrass, other citrus, floral, mint, and garlic, but these levels were less than 2.7. The panelists could not differentiate grass, foliage, sage, thyme, green herb other, dill, white pepper, or black pepper attributes for these cultivars. The panelists were asked to use one word to define the aroma for each cultivar, and ‘Cascade’ was “citrusy”, ‘Cashmere’ was “terpene”, ‘Crystal’ was “savory”, and ‘Zeus’ was “grass/foliage”.

2021. In 2021, the panelists could differentiate seven hops aroma attributes (aged cheese, overall citrus complex, lemon, overall green herb complex, thyme, overall pepper complex, and black pepper (Table 6). Although not significant, ‘Cascade’ (5.7) had the highest overall impact, followed by ‘Crystal’ (5.3), ‘Cashmere’ (5.2) and ‘Zeus’ (5.1). The hops cultivars differed in aged cheese (1.4-2.4), overall citrus complex (2.5-3.2), lemon (1.9-2.8), overall green herb complex (3.3-4.7), thyme (2.5-3.8), overall pepper complex (2.8-3.4), and black pepper (2.2-2.9). Cascade had the highest overall green herb complex and pepper complexes. The panelists could not differentiate grass, foliage, fruity, terpenes, umami, lemongrass, citrus other, sage, green herb other, floral, mint, garlic, dill, or white pepper attributes for these cultivars. The panelists were asked to use one word to define the aroma for each cultivar, and Cascade was “herbal”, Cashmere was “foliage”, Crystal was “herbal/citrus”, and Zeus was “herbal”.

Correlation of descriptive sensory and volatile attributes

The descriptive sensory attributes identified in the four Arkansas-grown hops were correlated with the volatile attributes. Generally, PCA analysis showed grouping of sensory descriptive attributes with compound classifications. In both years, cultivars were not grouped near each other, but sesquiterpenes, umami/savory, and white pepper were clustered together in both years.

2020. When a PCA was conducted on the compound class variables in 2020 (Fig. 5), two components explained 91% of the variation in the data. PC1 (74.00%) had positive loadings for compound categories (alcohols, monoterpenes, and aromatic hydrocarbons) and sensory attributes (grass, overall citrus complex, lemongrass, foliage, lemon, fruity, floral, dill, thyme, mint, and, other citrus). Cultivars positively loaded for PC1 included ‘Zeus’ and ‘Cascade’. Compound categories (Aldehydes, ketones, and sesquiterpenes) and sensory attributes (terpenes/off note, aged cheese, garlic, other green herb, overall green herb, overall pepper complex, black pepper, white pepper, sage, esters, and umami/savory) were all loaded negatively on PC1 along with cultivars ‘Cashmere’ and ‘Crystal’. PC2 (17.33%) had positive loadings for sensory attributes (overall green herb, other green herb, overall citrus, lemongrass, foliage, lemon, fruity, overall pepper complex, black pepper, white pepper, sage, umami/savory, thyme and other citrus) and compound categories (alcohols, aromatic hydrocarbons, ketones, sesquiterpenes, and esters) along with cultivars ‘Crystal’ and ‘Zeus’. Compound categories (aldehydes, and monoterpenes), sensory attributes (mint, dill, floral, grass, aged cheese, garlic, terpene, and overall impact), and cultivars Cashmere and Cascade.

2021. When a PCA was conducted on the compound class variables in 2021 (Fig. 6), two components explained (77.45%) of the variation in the data. PC1 (49.94%) had positive loadings for sensory attributes (white pepper, overall impact, overall pepper complex, other green herb, fruity, floral, lemon, overall citrus complex, thyme, mind, black pepper, lemongrass, overall green herb complex, sage, terpenes/off notes, and dill), compound categories (monoterpenes and aldehydes) along with cultivars Crystal Cascade and Zeus. Sensory attributes (aged cheese, umami/savory, other citrus, garlic, grass, and foliage) and compound categories (sesquiterpenes, ketones, esters, alcohols, and aromatic hydrocarbons) all loaded negatively on PC1 along with 'Cashmere'. PC2 (27.51%) had positive loadings for sensory attributes (aged cheese, umami/savory, white pepper, other green herb, overall impact, other citrus, floral, overall pepper complex, fruity, lemon, and overall citrus complex), compound categories (sesquiterpenes, ketones, esters, aldehydes, and monoterpenes) as well as cultivars Crystal and Cascade. Sensory attributes (mint, black pepper, lemongrass, overall green herb complex, sage, terpenes/off note, dill, foliage, grass, and garlic) and compound categories (alcohols, and aromatic hydrocarbons) were all negatively loaded for PC2. Cultivars negatively loaded for PC2 included 'Cashmere' and 'Zeus'.

Conclusion

The quality, volatile, and sensory attributes of four hops cultivars (Cascade, Cashmere, Crystal, and 'Zeus') grown at the UA System Fruit Research Station in Clarksville, AR were evaluated in 2020 and 2021. Although the quality, in terms of alpha and beta acid, and sensory attributes varied, the values were typical of previously reported research done on these cultivars. In both years, 'Cashmere' and 'Crystal' had higher levels of beta acids than alpha acids, while 'Cascade' and 'Zeus' had higher levels of alpha acids than beta acids. In the four cultivars harvested in both years, there were 88-127 volatile aroma compounds identified across seven compound classes including monoterpenes, alcohols, aldehydes, sesquiterpenes, esters, ketones, and aromatic hydrocarbons. In both 2020 and 2021, ‘Crystal’ had the highest volatile concentration followed by ‘Cashmere’, and ‘Cascade’ with ‘Zeus’ containing the lowest concentration in each year. In both years, the five volatile aroma compounds with the highest levels found in Arkansas-grown hops were beta-pinene, beta-myrcene, caryophyllene, beta-selinene, and humulene. In both years, the panelists could differentiate between cultivars for aged cheese, overall citrus complex, lemon, overall green herb complex, and overall pepper complex. The panelist found the cultivars differed for more attributes in 2020 than in 2021 with the overall impact the highest rated attribute (5-7 on a 15-point scale). The panelists were also asked to name a defining attribute for each cultivar and in 2020 chose “citrusy” for ‘Cascade’, “terpenes” for ‘Cashmere’, “savory” for ‘Crystal’ and “grass/foliage” for ‘Zeus’, while in 2021 the panelists chose “herbal” for ‘Cascade’, “foliage” for ‘Cashmere’, “herbal/citrus” for ‘Crystal’ and “herbal” for ‘Zeus’. When a PCA was conducted on descriptive sensory attributes, cultivars were not grouped near each other, but sesquiterpenes, umami/savory, and white pepper clustered together in both years. Volatile analysis shows that Arkansas-grown hops could offer unique aromas and attributes that would allow local brewers the opportunity to craft specialty beers made with local hops. Further analysis of OAVs would be useful in determining the key aroma compounds, however different methodologies and instrumentation would be needed to specifically identify the aroma active compounds in Arkansas-grown hops. Data generated from this project provided information on, quality, sensory, and volatile attributes of hops that can be used for developing recommendations for beer brewing, marketing, and supporting local breeding efforts.

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Table 1: Descriptive sensory lexicon used to evaluate aroma attributes from dried, ground hop cones harvested from hop plants grown at the University of Arkansas System Division of Agriculture Fruit Research Station, in Clarksville, AR (2020 and 2021)

Aroma attributes [z]	Aroma definition
Grass	Green, slightly sweet aroma associated with cut grass/dry grass/hay
Green plant (foliage)	Freshly cut leaves or weeds
Citrus complex	General impression of citrus fruits
Lemon	Lemon
Lemongrass	Lemongrass
Other	Citrus, other than lemon and lemongrass
Fruity	Mixture of nonspecific fruits: berries, apples/ pears, tropical, melons; usually not citrus fruits
Green herb complex	General impression of dried herbs
Sage	Sage
Thyme	Thyme
Other	Green herbs, other than sage and thyme
Pepper complex	General impression of pepper, peppercorns
White pepper	Freshly ground white pepper
Black pepper	Freshly ground black pepper
Terpenes/skunk/off-note	Hemp or Cannabis, also reminiscent of skunk like character
Aged cheese	Aged (ripened) cheese
Umami/savory	General impression of cooked meat
Garlic	Garlic
Dill	Dill seeds
Floral	Sweet, fragrant aroma associated with flowers
Mint	Mint family (sweet, green and menthol): peppermint, spearmint, wintergreen
Overall impact	Intensity associated with overall aroma of the sample
Defining attribute	Term that can be used to characterize the sample

[z] The Universal Aromatic Scale was used as the reference for the aroma attributes. The aroma attribute definition is aromas associated with the attribute listed.
Intensity 2.0 = Soda note of saltine cracker (Nabisco Premium Unsalted Tops Saltine Crackers, Nabisco, East Hanover, NJ)
Intensity 5.0 = Cooked apple note of applesauce (Dr. Pepper Snapple Group, Plano, TX)
Intensity 7.5 = Orange note of orange juice (Minute Maid Frozen Concentrate Orange Juice (Coca-Cola, Atlanta, GA), reconstituted with 36 oz of filtered water
Intensity 10.0 = Grape note of grape juice (Welch's, Concord, MA)
Intensity 15.0 = Big Red Gum® (Mars, Inc., MeLean, VA)

Table 2: Total alpha and beta acid levels[z] of dried, ground hop cones harvested from hop plants grown at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2020 and 2021)

Cultivar	Cohumulone (%)	n+-adhumulone[y] (%)	Total alpha-acids (%)	Colupulone (%)	n+-adlupulone (%)	Total beta-acids (%)
2020						
Cascade	5.12 a[x]	4.07 a	9.20 a	4.32 a	4.74 b	9.06 ab
Cashmere	3.54 b	3.32 b	6.86 b	3.36 b	5.13 b	8.48 b
Crystal	1.43 c	2.19 c	3.62 d	3.05 b	7.00 a	10.05 a
Zeus	3.44 b	2.22 c	5.66 c	2.88 b	1.91 c	4.79 c
P-value	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*
2021						
Cascade	2.55 a	2.35 ab	5.97 a	2.67 a	2.99 bc	5.67 ab
Cashmere	2.89 a	3.09 a	4.90 a	2.30 a	3.19 b	5.48 ab
Crystal	1.14 b	1.77 b	2.91 b	2.29 a	5.25 a	7.53 a
Zeus	3.12 a	1.50 b	4.62 a	2.63 a	1.43 c	4.06 b
P-value	*0.0002*	*0.0015*	*0.0022*	*0.4621*	*0.0005*	*0.0156*

[z] Hop cones were analyzed with high performance liquid chromatography analysis using American Society of Brewing Chemists (ASBC) methods
[y]n+adhumulone refers to the level of n-humulone and ad-humulone combined in one fraction, analogue for n+-adlupulone for n-lupulone and ad-lupulone combined
[x] Means with different letters within each year for each attribute are significantly different ($p<0.05$) according to Tukey's Honest Significant Difference (HSD) test, in each year the highest value is highlighted and lowest values is underlined

Table 3. Volatile aroma compounds [z] identified in hops cultivars grown at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2020 and 2021)

Compound Name	Retention Index 2020	Retention Index 2021	Aroma Category	Aroma Description	2020 Cascade	2020 Cashmere	2020 Crystal	2020 Zeus	2021 Cascade	2021 Cashmere	2021 Crystal	2021 Zeus
					5829.78±296.66	**6668.09±469.86**	**8106.65±964.62**	**3230.47±352.93**	**4132.45±167.48**	**5434.16±2398.94**	**6279.23±687.04**	**2072.87±430.36**
Alcohols												
3-Buten-2-ol, 2-methyl	567		Herbal	hearbal earthy oily	10.12±9.01	2.72±2.36	18.11±15.91	14±11.14	0±0	0±0	0±0	0±0
1-Butanol, 3-methyl	724		Fermented	fusel alcholic whiskey fruity banana	1.63±1.43	3.23±0.97	1.13±1.96	5.88±6.14	0±0	0±0	0±0	0±0
1-Butanol, 2 methyl	728	712	Ethereal	fusel ethereal alcoholic fatty greasy winey whiskey leathery cocoa	0.68±1.18	10±7.15	0±0	9.27±8.41	0±0	4.74±3.37	0±0	3.17±0.8
Prenol		749	Fruity	fruity green lavender fermented yeasty	0±0	0±0	0±0	0±0	0.56±0.98	0±0	5.42±0.43	0±0
3-Hexen-1-ol,	851		Green	green leafy	4.81±0.59	1.32±2.3	2.55±0.72	7.44±1.09	0±0	0±0	0±0	0±0
1-Octen-3-ol		960	Earthy	mushroom earthy green oily fungal raw chicken	0±0	0±0	0±0	0±0	2.66±2.37	0±0	0±0	6.06±1.34
Octadien-1-ol	1232		Fatty	fatty chicken creamy waxy	0±0	1.12±0.09	1.76±0.11	0±0	0±0	0±0	0±0	0±0
4-tert-Amylphenol		1386	-	-	0±0	0±0	0±0	0±0	0±0	2.17±0.39	0.33±0.58	0±0
Total Alcohols	**5**	**4**			**17.24**	**18.39**	**23.55**	**36.59**	**3.22**	**6.91**	**5.75**	**9.23**
Aldehydes												
Tiglic aldehyde		719	Green	pungent green ethereal nutty anisic fruity					0±0	2.5±1.27	0±0	0±0
2-Pentenal	746		Green	pungent green apple orange tomato	1.65±1.43	1.46±1.27	1.92±3.34	1.54±1.54				
3-Methyl-2-butenal	777	760	Aldehydic	ethereal aldehydic chocolate peach fatty	19.09±1.29	4.58±3.97	42.11±2.36	16.67±1.74	8.12±0.58	2.47±0.32	18.93±1.24	4.78±0.63
Hexanal	794	780	Green	fresh green fatty aldehydic grassy leafy sweaty	4.51±0.29	2.98±2.59	6.06±0.96	10.74±1.65	0±0	0.41±0.72	0±0	1.38±1.07
2-Hexenal	847	832	Green	sweet almond bitter fruity green leafy apple plum vegetable	30.08±2.54	38.15±6.72	15.66±2	19.69±6.6	11.48±2.67	15.01±2.18	5.89±1.06	5.13±1.97
Heptanal	899	883	Green	fresh aldehydic fatty green herbal cognac ozone	5.15±2.86	29.07±13.46	1.9±0.15	4.24±1.34	4.44±0.92	6.15±7.02	0±0	5.41±0.83
Benaldehyde	965		Fruity	sharp sweet bitter almond cherry	6.43±0.8	3.65±0.24	1.88±0.12	8.65±1.73	0±0	0±0	0±0	0.9±0.19
Octanal	1002	983	Aldehydic	aldehydic waxy citrus orange peel green herbal fresh fatty	1.56±0.43	4.5±2.9	1.66±0.18	2.56±0.79	0±0	0±0	0.28±0.49	1.86±0.53

Phenylacetaldehyde		1033	Green	green sweet floral hyacinth clover honey cocoa					0.26±0.09	0.1±0.17	0±0	0.43±0.4
Nonanal		1090	Aldehydic	waxy aldehydic rose fresh orris orange peel fatty					9.33±0.88	0±0	12±0.28	14.34±3.11
Decanal		1194	Aldehydic	sweety aldehydic waxy orange peel citrus floral					0±0	2.37±1.47	0±0	0±0
Total Aldehydes	**7**	**9**			**68.47**	**84.39**	**71.19**	**64.09**	**28.93**	**22.76**	**37.1**	**28.39**
Aromatic Hydrocarbons												
Toluene	763	742	Sweet	benzene	1.74±1.62	2.15±1.87	2.14±1.87	4.65±2.23	1.03±0.55	0.56±0.25	0.71±0.65	2.01±0.58
Styrene		875	Balsamic	sweet balsamaic floral plastic					3.45±0.54	9.82±1.46	4.42±0.85	0.51±0.89
Total Aromatic Hydrocarbons	**1**	**2**			**1.74**	**2.15**	**2.14**	**4.65**	**15.07**	**16.63**	**5.13**	**15.26**
Esters												
Isobutyl isobutyrate		894	Fruity	ethereal fruity tropical pineapple grape banana					3.78±3.27	1.2±0.55	2.19±0.25	0.43±0.38
Hexanoic acid, methyl ester		904	Fruity	ethereal pineapple fruity apricot strawberry banana bacon					0.91±0.26	0.64±0.56	1.23±1.09	0.61±0.53
Propanoic acid	912		Acidic	acidic dairy fruity	0±0	29.29±23.63	0±0	3.81±0.03				
3-Hexanoic acid	924		-	-	6.19±0.33	3.48±2.57	2.74±0.07	0.46±0.79				
Pentyl propionate		949	Fruity	sweet fruity apricot banana tropical pineapple					0±0	0±0	0±0	0.47±0.43
2-Methylbutyl propionate		950	Fruity	sweet fruity ethereal rummy					0±0	33.58±2.3	0±0	0±0
Hexanoic acid	966		Fatty	sour fatty sweaty cheesy	4.19±1.24	4.96±4.3	5.19±0.2	3.65±0.21				
Methyl 5-methylhexanoate		967	-	-					2.11±0.38	0.54±0.94	0.92±0.92	0±0
1-Butanol, 2-methyl-, propanoate	969		Fruity	sweet fruity ethereal rummy	4.48±2.54	22.9±1.77	4.34±0.65	20.73±1.24				
Isobutyl 2-methylbutyrate	976	984	Fruity	fruity citrus melon	2.34±1.06	1.87±0.56	2.52±0.56	8.4±0.73	0±0	0.93±0.83	0±0	0±0
Heptanoic acid, methyl ester	985		Fruity	sweet fruity green orris waxy floral berry	3.5±0.26	1.03±0.25	3.2±0.23	1.88±0.02				
Isobutyl isovalerate		988	Fruity	ethereal fruity tropical pineapple grape banana					1.84±0.07	5.25±4.57	1.07±0.24	5.44±0.24
Isopentyl isobutyrate		995	Fruity	fruity ethereal tropical green grape cherry banana apple cocoa					0±0	0±0	0±0	0±0
2-Methylbutyl isobutyrate		1000	Fruity	fruity ethereal tropical banana					0±0	1.57±1.36	0±0	0±0
Methyl heptanoate	1026	1005	Fruity	sweet fruity green orris waxy floral berry	5.41±0.73	9±3.16	11.33±0.18	1.86±0.27	0±0	3.44±0.47	0±0	0±0
Geranyl isovalerate	1008		Fruity	green fruity apple blueberry pineapple	1.19±0.08	2.73±1.35	1.15±0.07	1.35±0.05				

Butanoic acid, 3-methylbutyl ester	1013		Fruity	fruity green apricot pear banana	2.44±0.18	11.85±0.61	0.99±0.12	2.87±0.23				
Methyl 4-ethyl-4-pentenoate		1013	-	-					1.87±0.3	10.26±0.43	0.44±0.48	2.05±0.16
Heptanoic acid	1030		Cheesy	rancid sour cheesy sweaty	5.4±0.63	9.38±6.75	14.15±0.71	9.96±0.25				
(E)-2-Methyl-2-butenyl isobutyrate		1043	-	-					3.48±0.49	44.09±2.97	2.26±0.16	12.02±1.14
Methyl 2-methylheptanoate		1045	-	-					5.09±0.3	11.07±0.47	11.03±0.12	1.47±0.27
Methyl 6-methylheptanoate	1066	1070	-	-	0.25±0.44	1.24±0.38	0.64±0.07	0.55±0.01	5.18±0.43	5.08±0.28	13.35±0.69	7.58±0.61
3-Methylbutyl 2-methylbutanoate	1087	1087	Fruity	sweet fruity citrus cherry blueberry apple	3.78±0.44	1.71±1.03	5.76±0.29	6.85±0.73	0±0	2.88±0.48	0±0	0±0
2-Methyl-6-methylene-7-octen-3-one	1103	1106	-	-	3.76±0.22	11.06±0.99	4±0.14	6.29±1.81	4.33±0.47	2.84±0.2	6.57±0.2	6.63±0.42
Methyl octanoate	1107	1112	Waxy	waxy green sweet orange aldehydic vegetable herbal	1.4±0.1	16.17±1.27	1.04±0.08	1.84±0.1	0±0	11.06±0.89	0±0	0±0
4-Octenoic acid, methyl ester		1114	-	-					1.76±0.17	19.62±1.35	1.45±0.15	1.88±0.12
Allyl isovalerate	1124	1128	Fruity	sweet fruity banana apple pineapple cherry	4.12±0.51	4.79±0.04	12.71±1.2	2.84±0.52	0±0	0±0	0.35±0.36	0±0
Valeric acid	1149	1138	Cheesy	acidic sweaty rancid	0.64±0.05	1.07±0.51	0±0	0.34±0.3	4.82±0.27	5.66±0.26	15.69±1.18	3.49±0.89
Octanoic acid		1163	Fatty	fatty waxy rancid oily vegetable cheesy					0.04±0.07	0±0	0.54±0.15	0.1±0.18
Methyl nonanoate		1170	Fruity	sweet fruity pear waxy tropical winey					0±0	0±0	0.35±0.07	0±0
Methyl 8-methylnonanoate		1174	-	-					0±0	1.59±0.37	0±0	0±0
Nonanoic acid	1181		Waxy	waxy dirty cheesy dairy	0.75±0.18	2.76±0.46	2.39±0.31	0.88±0.26				
4-Nonenoic acid, methyl ester		1194	-	-					1.94±0.38	0±0	6.43±0.23	0±0
Methyl nonanoate		1209	Fruity	sweet fruity pear waxy tropical winey					0±0	0±0	0±0	3.03±0.48
2-Nonenoic acid	1211		Waxy	waxy dirty cheesy dairy	2.12±0.16	2.02±0.15	3.44±0.43	0.43±0.37				
Geranyl laurate		1220	Waxy	waxy floral leafy rose					2.84±0.03	2.81±0.04	4.89±0.44	0.72±0.19
Heptyl isobutyrate	1246	1229	Fruity	sweet green fruity warm floral apple cherry apricot	0±0	1.05±0.04	0±0	0±0	4.17±0.34	5.99±0.39	15.55±1.55	1.74±0.48
2-Methylbutyl hexanoate	1256	1236	Ethereal	-	4.31±0.3	1.68±0.14	3.69±0.41	1.53±0.33	0.23±0.12	0.89±0.19	1.15±0.32	0.23±0.41
Methyl 8-methylnonanoate	1282	1269	-	-	1.07±0.21	4.28±0.41	1.57±0.19	0.35±0.3	0±0	1.16±0.23	0±0	0±0
Methyl (E)-4-decenoate		1291	-	-					3.05±0.48	1.66±0.06	6.73±0.94	4.51±0.81
Methyl (E)-5-decenoate		1296	-	-					0±0	1.63±0.07	0±0	0±0
9-Decenoic acid		1301	Waxy	waxy green fruity fatty soapy					19.19±0.98	19.58±1.47	61.5±6.95	9.72±2.42
Methyl decanoate	1287	1305	Fermented	oily winey fruity floral	2.59±0.17	1.18±0.14	3.98±0.57	3.42±0.67	11.92±0.48	12.08±0.21	43.51±6.11	4.58±1.36
4-Decenoic acid	1299		Fruity	-	0.67±0.09	0.67±0.67	1.88±0.51	0.46±0.4				
Decenoic acid	1309		Waxy	waxy buttery oily creamy dairy green lactonic plum skin	13.99±0.66	14.88±0.8	51.6±8.3	7.96±1.63				
5-Hexenoic acid, 5-bromo-, methyl ester	1314		-	-	8.4±0.53	8.83±0.69	36.38±5.57	3.34±0.85				
trans-Geranic acid methyl ester	1323		Waxy	waxy green fruity floral	1.71±0.36	1.1±0.09	6.35±1.08	2.34±0.56				
Methyl 3-undecenoate		1355	-	-					2.08±0.14	1.55±0.24	8.35±1.51	3.05±0.67

Methyl undecanoate	1387	1369	Waxy	fatty waxy fruity	2.04±1.35	2.11±0.39	3.43±0.45	3.07±0.76	0±0	0±0	0.58±0.11	0±0
2-Undecenoic acid		1397	-	-					2.26±0.79	0±0	2.86±2.49	2.35±2.21
6,9,12,15-Docosatetraenoic acid	1410		-	-	1.79±0.13	0.68±0.62	2.96±0.37	0.92±0.16				
Total Esters	**28**	**36**			**91.41**	**179.07**	**199.14**	**99.77**	**83.66**	**212.23**	**209.88**	**72.6**
Ketones												
6-Methyl-5-hepten-2-one		961	Citrus	citrus green musty lemongrass apple					0±0	0.69±0.84	0±0	0±0
2-Nonanone	1091	1074	Fruity	fresh sweet green weedy earthy herbal	38.29±2.93	104.06±4.52	187.48±13.75	31.97±1.9	8.31±1.68	22.09±1.17	39.06±2.85	6.26±0.78
6-Benzyltetrahydro-2H-pyran-2-one		1076	-	-					0±0	2.68±2.4	0±0	0±0
2-Dodecanone		1145	Citrus	fruity citrus floral orange					1.11±0.29	1.78±0.7	14.84±1.27	4.53±1.04
7-Decen-2-one		1164	-	-					1.53±0.96	4.23±0.18	4.56±0.23	0.92±0.2
2-Decanone	1159	1176	Floral	orange floral fatty peach	5.14±0.58	1.59±0.13	10.94±1.03	4.17±0.55	14.52±1.26	49.77±0.24	53.17±4.79	0±0
2-Nonadecanone	1187	1179			2.64±0.37	1.2±0.26	8.32±0.78	4.37±0.55	0±0	0±0	0±0	13.17±3.12
Decanone	1193		-	-	3.01±0.14	10.84±0.52	11.16±1.34	2.71±0.33				
Undecenone	1279	1240	Fruity	-	2.15±0.23	4.86±0.33	5.41±0.72	1.08±0.14	10.45±0.62	24.31±2.06	17.62±2.72	6.92±1.03
(Z)-Undec-6-en-2-one		1262	-	-					6.5±1.07	16.4±0.62	16.39±1.87	3.32±0.48
2-Undecanone	1294	1276	Fruity	waxy fruity creamy fatty orris floral	5.84±0.22	10.47±0.48	15.39±2.38	3.51±0.64	29.51±1.78	55.74±2.4	73.21±7.79	17.11±4.23
2-Dodecanone		1342	Citrus	fruity citrus floral orange					4.59±1.67	0±0	4.32±0.51	2.36±0.5
(Z)-Tetradec-6-en-2-one		1559	-	-					2.07±1.44	3.22±0.47	4.21±1	1.17±0.24
2-Nonadecanone	1359	1580	-	-	1.21±0.86	0.23±0.39	0.83±0.08	0.66±0.23	0±0	3.39±0.75	0.35±0.61	0±0
(Z)-6-Pentadecen-2-one		1660	-	-					3.97±0.73	0±0	2.5±0.24	0±0
2-Pentadecanone		1676	-	-					0±0	3.01±2.21	0±0	0±0
Total Ketones	**7**	**15**			**58.28**	**133.25**	**239.53**	**48.47**	**82.56**	**187.31**	**230.23**	**55.76**
Monoterpenes												
.alpha.-Pinene	936	919	Herbal	fresh camphoreous sweet pine earthy woody	174.47±12.8	107.28±52.69	106.38±10.98	99.96±3.56	157.56±3.12	119.89±18.14	98.5±14.71	72.39±9.11
.beta.-Pinene	980	963	Herbal	dry woody resionous pine hay green eucalyptus camporeous	633.89±40.57	381.73±33.93	474.53±44.33	373.95±11.19	10.09±0.59	6.27±0.48	8.4±0.42	5.37±0.59
Myrcene		971	Spicy	peppery terpenic spicy balsamic plastic					1.29±0.12	0±0	1.37±0.5	0.59±0.13
beta Myrcene	991	973	Spicy	peppery terpenic spicy balsamic plastic	1292.7±68.94	836.94±55.89	627.53±28.48	825.25±65.78	517.34±10.52	387.58±13.87	314.18±5.27	336.99±21.78
alpha-Terpinene	1017	1005	Woody	woody terpenic lemon herbal medicinal citrus	7.33±0.68	94.33±4.9	5.06±0.5	31.42±2.47	3.04±0.82	1.21±1.05	3.89±0.86	1.56±0.47
Cymene	1022		Terpenic	fresh citrus terpenic woody spicy	2.25±0.19	5.04±6.34	2.84±0.17	1.9±0.1				
D-Limonene	1036	1019	Citrus	citrus orange fresh sweet	69.88±5.68	48.11±29.81	43.63±1.69	49.03±3.37	0±0	88.12±27.07	55.17±24.69	0±0
Sabinene		1020	Woody	woody terpenic citrus pine spicy					139.38±3.77	0±0	0±0	77.28±45.43
.beta.-Phellandrene		1019	Minty	minty terpenic					0±0	13.85±24	15.03±26.03	21.13±36.6

.alpha.-Phellandrene	1037	1021	Terpenic	citrus herbal terpenic green woody pepper black pepper	86.34±2.03	31.67±27.42	44±1.75	79.59±6.39	0±0	0±0	10.67±18.48	0±0
(E)-beta-ocimene	1042	1024	Floral	warm floral herbal sweet	2.22±0.17	2.37±1.46	2.42±0.13	2.09±0.07	1.71±0.09	2.65±0.17	2.08±0.6	1.44±0.3
beta-Ocimene	1053	1036	Floral	citrus tropical green terpenic woody green	10.74±0.54	53.81±4.15	7.27±0.45	4.85±0.16	8.37±0.46	44.06±0.21	5.94±0.51	3.31±0.35
gamma-Terpinene	1069	1048	Terpenic	oily woody terpenic lemon lime tropical herbal	1.22±0.25	1.46±0.3	4.9±0.29	1.19±0.15	1.07±0.23	0±0	0.67±0.6	0.45±0.55
2-Carene	1073		-	-	1.67±0.13	1.54±1.34	1.48±0.09	1.78±0.8				
Terpinolene	1094	1082	Herbal	herbal spicy chamomile green basil	3.84±0.15	5.34±0.31	6.3±0.27	3.28±0.21	0.82±1.42	0±0	4.79±0.24	1.18±1.04
Linalool	1099	1083	Floral	citrus floral sweet bois de rose green blueberry	32.13±2.57	17.17±2.33	206.59±14.6	54.96±3.1	25.22±3.87	14.61±2.25	157.28±10.12	37.7±1.23
Neo-allo-ocimene		1117	-	-					0±0	1.98±0.21	0±0	0±0
Cosmene		1118	-	-					0.23±0.39	3.99±0.23	0.29±0.26	0±0
p-Mentha-1,3,8-triene		1123	Terpenic	terpeneic camphoreous herbal woody					0.34±0.6	0±0	0.39±0.68	0.83±0.21
Octatriene	1132		Green	green plastic	1.36±2.36	12.57±1.18	5.05±1.24	4.44±0.69				
Octatetraene	1135		-	-	6.06±0.52	22.73±1.59	5.18±0.32	4.27±0.49				
Allo-ocimene	1146	1129	Floral	sweet floral nut skin pepper herbal tropical	7.93±0.47	44.99±5.32	5.62±1.72	6.27±0.81	1.2±0.41	9.09±0.25	0±0	0±0
trans-2-Pinanol		1180	-	-					0±0	1.9±0.25	0±0	0±0
(-)-alpha-Terpineol	1198	1187	Terpenic	pine terpenic lilac citrus woody floral	1.21±0.03	2.19±0.18	2.53±0.21	1.22±0.18	1.05±0.25	0±0	2.35±0.02	1±0.48
Carveol	1222.956867		Minty	minty spearmint cooling green herbal caraway spicy	2.88±0.19	4.08±0.57	10.48±1.38	1.39±0.31				
Geraniol	1259	1239			7.62±0.74	15.55±0.69	14.35±2.44	4.99±0.83	2.5±0.24	0.96±0.19	1.97±0.42	0.81±0.18
Citral		1258	Floral	sweet floral fruity rose waxy citrus					0.68±0.15	0.26±0.22	0.28±0.14	0.3±0.27
Methyl geranate	1326	1308	Waxy	waxy green fruity floral	34.97±1.16	29.22±0.51	149.34±22.69	16.84±2.08	15.11±1.1	13.33±0.62	57.98±6.73	7.35±1.79
alpha-Farnesene		1308	Woody	citrus herbal lavender bergamot myrrh neroli green					0.28±0.06	0±0	0±0	0±0
alpha-Guajene		1360	Woody	sweet woody balsamic peppery					0±0	0±0	2.07±0.34	0±0
Geranyl acetate	1383	1360	Floral	floral rose lavender green waxy	15.69±0.71	1.43±1.49	1.42±0.07	1.47±0.26	10.12±8.78	1.17±1.06	0±0	1.15±0.49
Geranyl isobutyrate	1514	1495	Floral	sweet floral fruity green peach apricot	19.77±1.45	8.05±1.55	1.11±0.96	24.02±3.27	19.62±0.72	4.95±1.21	0±0	17.07±1.69
Total Monoterpenes	**22**	**27**			**2413.29**	**1723.52**	**1717.53**	**1592.77**	**917.24**	**715.93**	**743.43**	**588.44**
Sesquiterpenes												
gamma-Elemene		1308	-	-					0±0	0±0	1.37±1.26	0±0
alpha-Cubebene	1367	1349	Herbal	herbal waxy	6.92±2.27	3.67±0.57	5.59±0.6	1.29±0.4	15.47±2.9	10.51±1.06	15.4±2.43	2.91±0.27
Aciphyllene	1377		-	-	1.11±0.04	2.76±1.22	1.09±0.1	0±0				
Ylangene	1393	1376	-	-	11.67±2.29	22.44±0.87	16.07±2.01	5.63±0.93	28.72±3.38	66±4.5	42.16±3.77	14.64±4.38

Copaene	1398	1380	Woody	woody spicy honey	30.4±2.2	71.55±2.98	44.81±6.62	13.6±2.15	73.41±3.32	182.5±8.79	111.77±13.92	33.62±7.59
(-)-cis-beta-Elemene		1387	Herbal	herbal waxy fresh					3.34±2.58	4.54±0.41	7.69±1.93	2.23±1.33
Longifolene		1401	Woody	sweet woody rose medicinal fir needle					2.5±0.45	4.63±0.85	2.71±1.48	0±0
Longifolene-(V4)		1405	Woody	sweet woody rose medicinal fir needle					0±0	4.37±1.1	0.57±0.98	0±0
Caryophyllene-(I1)		1405	Spicy	sweet woody spicy clove dry					1.36±0.67	0±0	2.21±1.93	1.94±0.36
Cis-caryophyllene		1417	Spicy	sweet woody spicy clove dry					2.8±1.34	5.76±0.82	4.24±0.4	0±0
beta-Humulene		1417	-	-					2.09±1.83	1.31±2.27	0±0	0±0
Caryophyllene	1451	1432	Spicy	sweet woody spicy clove dry	544.55±15.1	1167.47±11.24	752.78±91.34	267.68±36.88	467.74±17.18	1049.02±26.62	641.93±65.94	225.94±35.71
cis-beta-Copaene		1440	-	-					20.28±0.44	39.05±1.45	27.87±3.52	8.97±1.8
cis-.beta.-Famesene	1457	1444	Woody	woody citrus herbal sweet	49.68±1.57	88.09±1.75	66.66±8.69	22.14±2.75	527.34±6.52	69.27±5.48	24.33±3.95	42.28±12.89
trans-.beta.-Famesene	1462		Woody	woody citrus herbal sweet	538.24±16.64	64.12±11.99	20.77±1.02	34.09±3.28			8.68±0.71	
Humulene	1485	1446	Woody	woody	1244.54±37.95	2304.1±59.58	2811.92±336.78	703.21±102.25	999.96±18.68	1229.45±1056.98	2042±167.9	596.74±106.73
gamma-Elemene		1448	-	-					0±0	617.76±1069.99	193.39±27.76	0±0
gamma-Muurolene		1483	Woody	herbal woody spicy					88.44±4.07	115.98±6.89		38.81±8.6
Alloaromadendrene		1487							5.57±4.89	12.83±0.97	0±0	1.08±1.87
beta-Selinene	1501	1501	Herbal	-	130.23±3.78	165.06±3.62	320.69±45.88	55.9±8.48	269.56±3.35	238.11±6.23	746.66±80.44	118.01±27.16
.alpha.-Selinene	1505	1509	-	amber	13.46±0.28	19.05±1.62	3.16±0.07	7.04±2.17	222.01±2.4	115.9±5.99	717.64±79.64	99.22±25
gamma-Cadinene	1520	1524	-	-	218.85±10.39	182.88±2.08	741.63±108.89	103.08±3.18	62.64±0.97	116.42±5.46	110.85±13.32	27.19±5.62
delta-cadinene	1527	1528	Herbal	thyme herbal woody dry	202.1±8.73	90.27±5.23	709.78±106.4	87.01±3.8	106.65±3.48	213.95±12.31	189.35±17.75	48.62±9.92
Guaiol		1534	-	-					25.34±4.54	64.26±5	59.31±5.65	13.83±5.63
Cubenene		1541	Spicy	spicy fruity mango					8.85±0.54	14.85±1.71	13.54±1.9	2.42±1.18
gamma.-Elemene	1542				51.21±2.67	88.58±2.98	93.11±13.21	21.4±3.34				
alpha-Muurolene		1546	-	-					12.34±0.6	23.06±1.31	21.61±2.61	5.71±1.98
beta.-Cadinene	1547		Woody	green woody	81.26±3.06	160.69±5.85	154.9±20.85	33.25±5.25				
.alpha.-Calacorene		1555	-	woody					14.38±0.45	18.71±0.92	16.2±1.8	6.18±0.64
cis-Calamenene	1550		-	-	19.03±0.94	49.25±11.94	55.03±7.46	13.81±6.5				
alpha.-Cadinene	1565		Woody	woody dry	10.88±2.67	16.42±0.35	16.43±2.15	4.3±0.76				
alpha.-Calacorene	1573		-	woody	9.37±0.2	12.81±1.4	10.48±1.54	3.32±0.75				
Caryophyllene oxide		1606	Woody	sweet fresh dry woody spicy					1.17±1.45	0.91±0.32	0±0	0±0
Humulenol-II		1620	-	-					0±0	0±0	0±0	0.6±0.09
Humulene epoxide I		1620	Herbal	-					0±0	0±0	1.63±0.14	0±0
Humulene epoxide II		1632	-	-					6.03±3.77	10.49±1	24.23±5.35	0±0
Humulenol-II	1651	1641	-	-	7.24±1.2	9.84±3.55	21.31±2.43	3.17±0.64	1.75±0.46	5±1.38	1.58±1.9	2.06±0.24
1,3-Cyclododecadiene, (E,Z)-		1653	-	-					16.81±2.14	13±11.46	0±0	5.74±0.4
T-Muurolol		1669	Herbal	herbal spicy honey					0±0	3.97±6.88	3.01±5.22	0±0
(-)-alpha-Cadinol		1669	Herbal	herbal woody					6.23±0.6	0±0	0±0	0±0
Cadalene		1690	-	-					7.58±3.93	19.58±2.65	13.74±4.34	3.47±3.19
Total Sesquiterpenes	**18**	**34**			**3178.91**	**4526.96**	**5853.13**	**1383.72**	**3001.29**	**4271.92**	**5047.23**	**1302.73**

[z] Relative peak area percent compounds were identified by comparison of mass spectra with NIST14 (National Institute of Standards and Technology, Gaithersburg, MD, USA), Flavors and Fragrances of Natural and Synthetic Compounds (FFNSC3, John Wiley & Sons, Inc., Hoboken, NJ, USA), and Adams Essential Oils (Adams 2007) mass spectral libraries and comparison of calculated Kovats retention indices (Kováts 1958) with previously reported values; yellow highlighted compounds were the same in both years and cultivars.

Table 4. Highest volatile aroma compounds[z] (µg/kg) of dried, ground hop cones harvested from hop plants grown at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2020 and 2021)

	Compound				
	Beta-pinene	Beta-myrcene	Caryophyllene	Beta-selinene	Humulene
	Compound class				
	Monoterpene	Monoterpene	Sesquiterpene	Sesquiterpene	Sesquiterpene
	Aroma category				
	Herbal	Spicy	Spicy	Herbal	Woody
	Aroma descriptors				
Cultivar	Pine, woody, spicy, balsamic	Peppery, woody, herbaceous	Woody, citrus, peppery	Green, herbal, Celery	Woody, oceanic, spicy-clove
2020					
Cascade	633.89±40.57	1292.7±68.94	544.55±15.10	130.23±3.78	1244.54±37.95
Cashmere	381.73±33.93	836.94±55.89	1167.47±11.24	165.06±3.62	2304.10±59.58
Crystal	474.53±44.33	627.53±28.48	752.78±91.34	320.69±45.88	2811.92±336.78
Zeus	373.95±11.19	825.25±65.78	267.68±36.88	55.90±8.48	703.21±102.25
2021					
Cascade	474.53±44.33	627.53±28.48	752.78±91.34	320.69±45.88	2811.92±336.78
Cashmere	98.5±14.71	314.18±5.27	641.93±65.94	746.66±80.44	2042.00±167.9
Crystal	373.95±11.19	825.25±65.78	267.68±36.88	55.90±8.48	703.21±102.25
Zeus	72.39±9.11	336.99±21.78	225.94±35.71	118.01±27.16	596.74±106.73

[z] Means and standard deviations

Table 5. Descriptive sensory evaluation [z] (n=5) of dried, ground hop cones from cultivars of hop grown at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2020).

Attributes [z]	**Cascade**	**Cashmere**	**Crystal**	**Zeus**	*P-value*
Grass	2.0 a [y]	1.9 a	1.5 a	2.4 a	*0.145*
Foliage	1.9 a	1.2 a	1.4 a	1.9 a	*0.451*
Fruity*	**1.1 ab**	**0.1 c**	**0.3 bc**	**1.5 a**	***0.005***
Terpenes off note skunk*	**0.5 c**	**3.2 a**	**1.4 b**	**0.3 c**	***<0.0001***
Aged cheese*	**0.3 b**	**1.4 a**	**1.0 a**	**0.2 b**	***<0.0001***
Umami savory*	**0.6 bc**	**1.1 ab**	**1.3 a**	**0.3 c**	***0.001***
Overall citrus complex*	**3.4 a**	**2.0 b**	**2.7 ab**	**2.7 ab**	***0.013***
Lemon*	**1.8 a**	**1.0 b**	**1.3 ab**	**1.5 a**	***<0.0001***
Lemongrass*	**2.7 a**	**0.9 b**	**1.6 b**	**1.6 b**	***0.002***
Other*	**0.3 ab**	**0.0 b**	**0.0 b**	**0.8 a**	***0.016***
Overall green herb complex*	**2.7 b**	**2.6 b**	**3.2 a**	**2.5 b**	***0.034***
Sage	1.5 a	2.0 a	2.3 a	1.5 a	*0.076*
Thyme	1.6 a	1.1 a	1.0 a	0.8 a	*0.255*
Other	0.2 a	0.1 a	0.5 a	0.7 a	*0.053*
Floral*	**0.6 b**	**0.5 b**	**0.4 b**	**1.5 a**	***0.001***
Mint*	**0.4 a**	**0.1 bc**	**0.0 c**	**0.2 ab**	***0.005***
Garlic*	**0.3 c**	**1.9 a**	**1.2 b**	**0.3 c**	***<0.0001***
Dill	0.5 a	0.4 a	0.2 a	0.5 a	*0.466*
Overall pepper complex*	**2.2 b**	**2.3 ab**	**2.8 a**	**1.6 c**	***0.001***

White pepper	1.1 a	1.4 a	1.7 a	1.0 a	*0.096*
Black pepper	1.3 a	1.4 a	1.5 a	0.7 a	*0.105*
Overall impact*	**6.1 b**	**6.6 a**	**6.7 a**	**5.9 b**	***0.001***
Defining attribute [x]	**Citrusy**	**Terpenes/off-note**	**Savory**	**Grass/foliage**	

[z] The Universal Aromatic Scale (0 to 15 points) was used as the reference for the aroma attributes. The aroma attribute definition is aromas associated with the attribute listed as Intensity 2.0 = Soda note of saltine cracker; Intensity 5.0 = Cooked apple note of applesauce; Intensity 7.5 = Orange note of orange juice; Intensity 10.0 = Grape note of grape juice; Intensity 15.0 = Big Red Gum®

[y] Means with different letters for each attribute are significantly different ($p<0.05$) according to Tukey's Honest Significant Difference (HSD) test, highlighted row are significant attributes

[x] Defining attribute is the term used to characterize the sample

Table 6. Descriptive sensory evaluation ^{z} (n=7) of dried, ground hop cones from cultivars of hop grown at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2021)

Attributes	Cascade	Cashmere	Crystal	Zeus	*P-value*
Grass	2.7 a	3.1 a	2.6 a	3.0 a	*0.179*
Foliage	3.7 a	4.1 a	3.4 a	3.5 a	*0.099*
Fruity	1.2 a	1.2 a	1.5 a	1.5 a	*0.47*
Terpenes off note skunk	2.5 a	2.1 a	2.4 a	2.6 a	*0.585*
Aged cheese*	**2.3 a**	**2.0 ab**	**2.4 a**	**1.4 b**	***0.030***
Umami savory	1.8 a	2.0 a	1.9 a	1.5 a	*0.111*
Overall citrus complex*	**3.2 a**	**2.5 b**	**3.2 a**	**3.2 a**	***0.006***
Lemon*	**2.7 a**	**1.9 b**	**2.8 a**	**2.8 a**	***0.026***
Lemongrass	2.0 a	1.5 a	1.8 a	1.9 a	*0.134*
Other	0.6 a	0.7 a	0.6 a	0.5 a	*0.734*
Overall green herb complex*	**4.7 a**	**3.3 b**	**4.1 a**	**4.5 a**	***0.001***
Sage	3.3 a	2.4 a	3.0 a	3.2 a	*0.062*
Thyme*	**3.8 a**	**2.5 b**	**3.5 a**	**3.7 a**	***0.001***
Other	1.3 a	1.4 a	1.7 a	1.5 a	*0.051*
Floral	1.9 a	1.6 a	2.2 a	2.1 a	*0.08*
Mint	1.9 a	1.5 a	1.9 a	2.0 a	*0.097*
Garlic	1.0 a	1.2 a	0.8 a	1.2 a	*0.391*
Dill	2.0 a	1.7 a	2.0 a	2.1 a	*0.204*
Overall pepper complex*	**3.4 a**	**2.8 b**	**2.9 b**	**2.8 b**	***0.019***

White Pepper	2.7 a	2.3 a	2.4 a	2.0 a	*0.067*
Black Pepper*	**2.9 a**	**2.2 b**	**2.5 ab**	**2.6 ab**	***0.042***
Overall Impact	5.7 a	5.2 a	5.3 a	5.1 a	*0.236*
Defining attribute	**Herbal**	**Foliage**	**Herbal/citrus**	**Herbal**	

[z] The Universal Aromatic Scale (0 to 15 points) was used as the reference for the aroma attributes. The aroma attribute definition is aromas associated with the attribute listed as Intensity 2.0 = Soda note of saltine cracker; Intensity 5.0 = Cooked apple note of applesauce; Intensity 7.5 = Orange note of orange juice; Intensity 10.0 = Grape note of grape juice; Intensity 15.0 = Big Red Gum®

[y] Means with different letters for each attribute are significantly different ($p<0.05$) according to Tukey's Honest Significant Difference (HSD) test, highlighted row are significant attributes

[x] Defining attribute is the term used to characterize the sample

Table 7. Principal components (PC) analysis of volatile aroma compounds and sensory aroma descriptors dried, ground hop cones harvested from hop plants grown at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2020) *Percent of variation in data explained by each component.*
Compound class variables represent the sum of the total ion chromatogram (TIC) relative peak areas (%) of positively identified compounds within each compound class (Table 3) and the descriptive sensory attributes (Table 5)

		Principal Component 1 (74.00%) Overall impact → Mint	**Principal Component 2 (17.33%)** Aldehydes → Overall green herb complex
Positive loadings	*Compound classifications*	Alcohols	Esters
		Monoterpenes	Sesquiterpenes
		Aromatic Hydrocarbons	Aromatic Hydrocarbons
			Ketones
			Alcohols
	Sensory Attributes	Grass	Thyme
		Overall citrus complex	Umami savory
		Lemongrass	Other citrus
		Lemon	Sage
		Foliage	Fruity
		Floral	White Pepper
		Dill	Foliage
		Fruity	Lemon
		Other citrus	Black Pepper
		Thyme	Lemongrass
		Mint	Overall pepper complex
			Overall citrus complex
			Other green herb
			Overall green herb complex
	Cultivar	Cascade	Zeus
		Zeus	Crystal
Negative loadings	*Compound classifications*	Esters	Monoterpene
		Ketones	Aldehyde

	Sesquiterpenes	
	Aldehydes	
Sensory Attributes	Overall green herb complex	Dill
	Other green herb	Floral
	Terpenes/off note skunk	Aged cheese
	Overall pepper complex	Garlic
	Garlic	Grass
	Aged cheese	Terpenes/off note skunk
	Black pepper	
	White pepper	
	Sage	
	Umami savory	
	Overall impact	
Cultivar	Cashmere	Cascade
	Crystal	Cashmere

Table 8. Principal components (PC) analysis of volatile aroma compounds and sensory aroma descriptors dried, ground hop cones harvested from hop plants grown at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2021) *Percent of variation in data explained by each component.*
Compound class variables represent the sum of the total ion chromatogram (TIC) relative peak areas (%) of positively identified compounds within each compound class (Table 3) and the descriptive sensory attributes (Table 6)

		Principal Component 1 (49.94%) Other citrus → Thyme	**Principal Component 2 (27.51%)** Garlic → Aged cheese
	Compound classifications	Monoterpenes	Esters
		Aldehydes	Aldehydes
			Ketones
			Monoterpenes
			Sesquiterpenes
	Sensory Attributes	White pepper	Thyme
		Overall impact	Lemongrass
		Other green herb	Lemon
		Fruity	Overall citrus complex
		Overall pepper complex	Floral
Positive loadings		Black pepper	Black pepper
		Floral	Other green herb
		Overall green herb complex	Other citrus
		Dill	Overall pepper complex
		Mint	Overall impact
		Lemon	Umami savory
		Lemongrass	White pepper
		Sage	Aged cheese
		Terpenes/off note skunk	
		Overall citrus complex	
		Thyme	
		Crystal	Cascade
	Cultivar	Zeus	Crystal

		Cascade	
	Compound classifications	Alcohols	Aromatic hydrocarbons
		Aromatic hydrocarbons	Alcohols
		Sesquiterpenes	
		Ketones	
		Esters	
	Sensory Attributes		
		Aged cheese	Sage
Negative loadings		Garlic	Foliage
		Grass	Overall green herb complex
		Umami savory	Fruity
		Foliage	Mint
		Other citrus	Terpenes/off note skunk
			Dill
			Grass
			Garlic
	Cultivar	Cashmere	Cashmere
			Zeus

plot number	cultivar	block
1	1	block 1
2	2	
3	3	
4	4	
5	5	
6	6	
7	3	
8	2	
9	1	
10	4	
11	6	
12	5	
13	5	
14	2	
15	4	
16	3	
17	1	
18	6	
19	1	block 2
20	6	
21	3	
22	2	
23	5	
24	4	
25	3	
26	6	
27	2	
28	4	
29	5	
30	1	
31	5	
32	2	
33	6	
34	1	
35	4	
36	3	
37	2	block 3
38	5	
39	3	
40	4	
41	1	
42	6	
43	6	
44	3	
45	4	
46	5	
47	2	
48	1	
49	1	
50	5	
51	6	
52	4	
53	3	
54	2	

<u>Cultivars</u>

1=Cascade

2=Nugget

3=Zeus

4=Cashmere

5=Centennial

6=Crystal

Fig. 1. Plot map of hop cultivars grown at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR divided in three blocks with three replicates of each cultivar planted in a completely randomized block design (2020 and 2021)

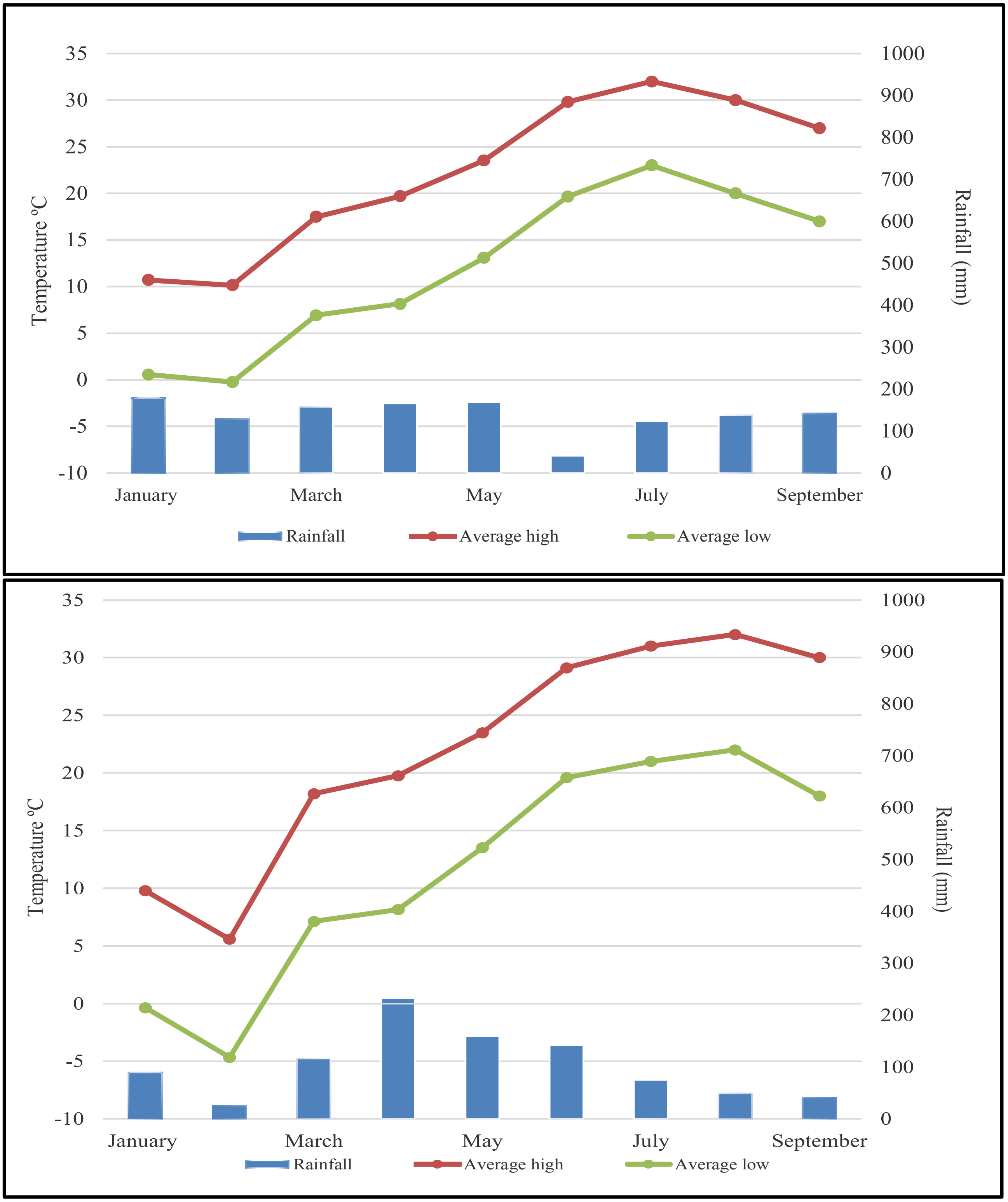

Fig. 2. Temperature and rain conditions from January to September at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2020 top and 2021 bottom)

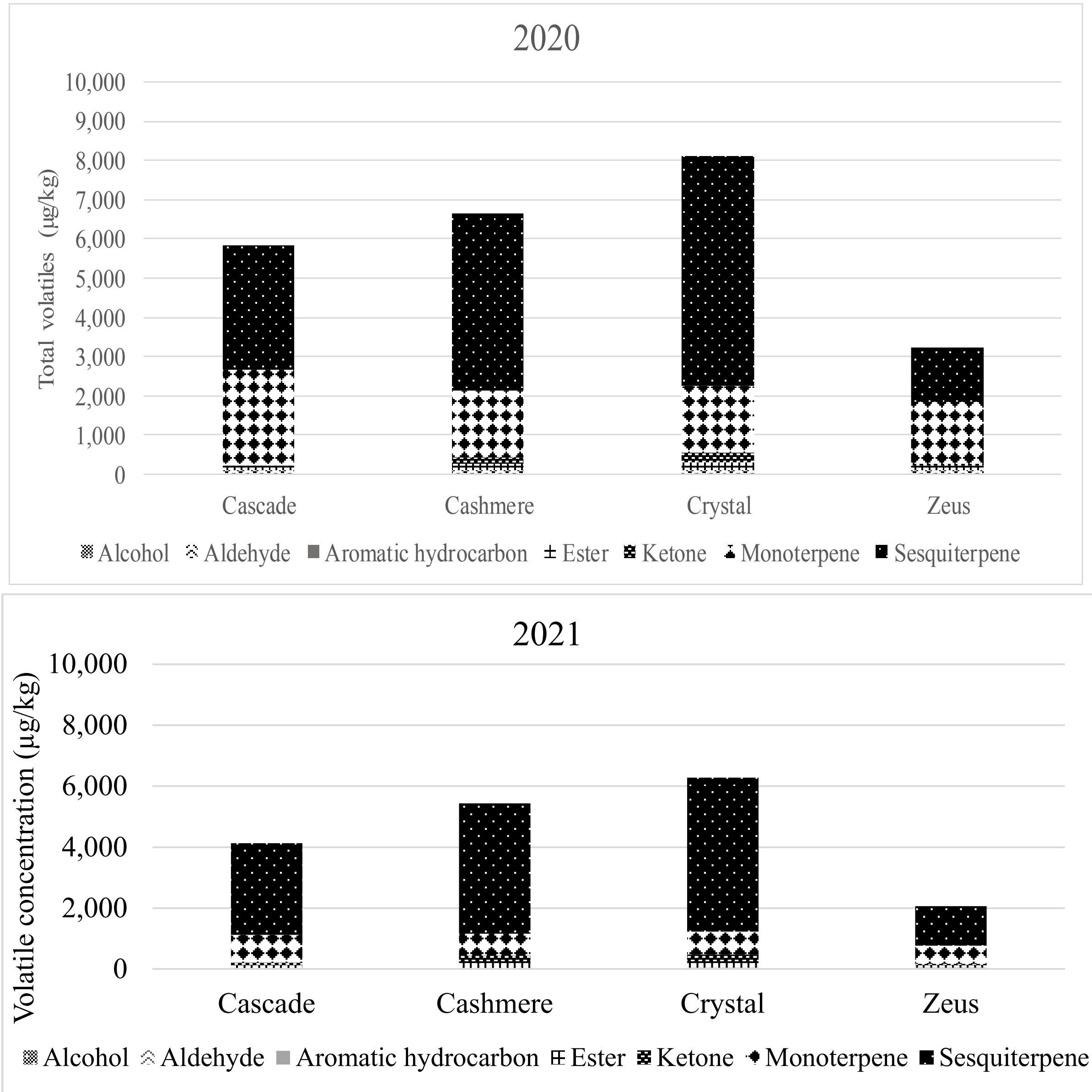

Fig. 3. Total concentrations of volatile aroma compounds identified in dried, ground hop cones harvested from hop plants grown at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2020 and 2021)

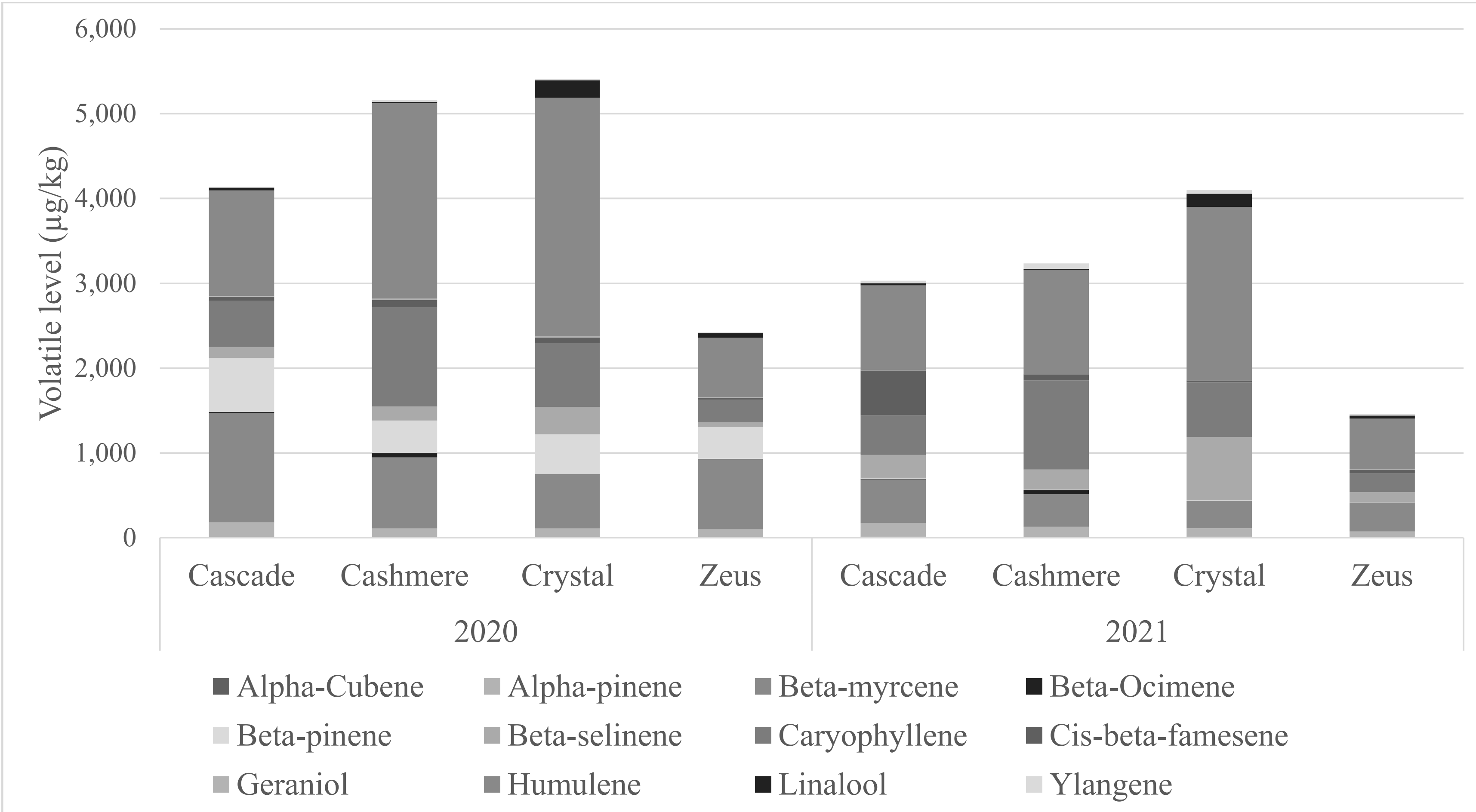

Fig. 4. Total concentrations of impactful volatile aroma compounds identified (µg/kg) in hops cultivars grown at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2020 and 2021).

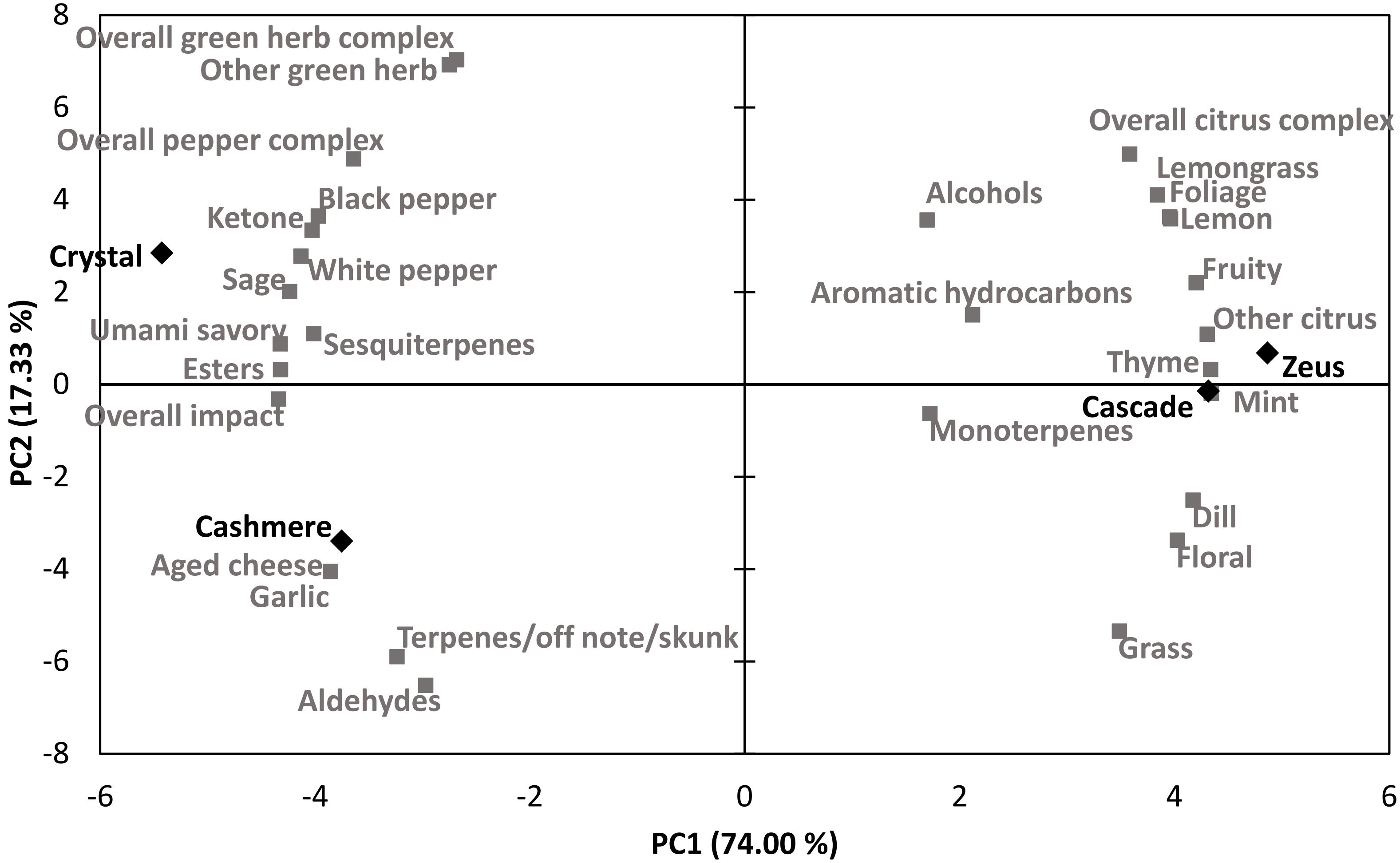

Fig 5. Principal components (PC) analysis of volatile aroma compounds and sensory aroma descriptors dried, ground hop cones harvested from hop plants grown at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2020) *Percent of variation in data explained by each component.*
Compound class variables represent the sum of the total ion chromatogram (TIC) relative peak areas (%) of positively identified compounds within each compound class (Table 3) and the descriptive sensory attributes (Table 5)

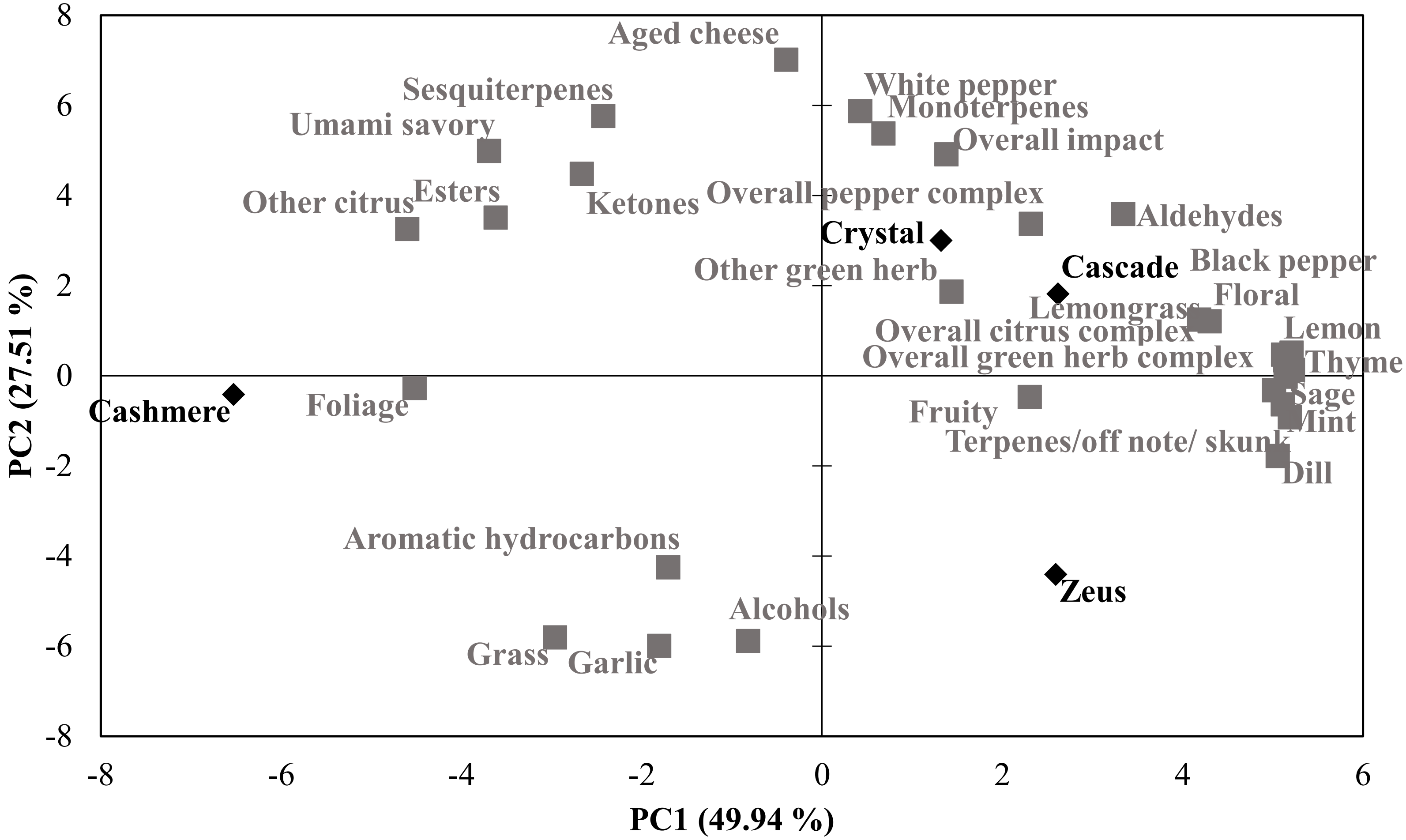

Fig 6. Principal components (PC) analysis of volatile aroma compounds and sensory aroma descriptors in dried, ground hop cones harvested from hop plants grown at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2021) *Percent of variation in data explained by each component.*
Compound class variables represent the sum of the total ion chromatogram (TIC) relative peak areas (%) of positively identified compounds within each compound class (Table 3) and the descriptive sensory attributes (Table 6)

Chapter II

Impact of Harvest Date on Size, Composition and Volatiles of Arkansas Fresh-market Blackberries

Abstract

As demand for fresh-market blackberries (*Rubus* subgenus *Rubus* Watson) increases, new cultivars with unique attributes are being released. These robust flavors of blackberries are influenced by basic tastes and volatile aroma compounds. However, within a blackberry cultivar, fruit quality can vary during a harvest season. The impact of harvest date (early, middle, and late) on four fresh-market blackberry cultivars ('Natchez', 'Prime-Ark® Horizon', 'Prime-Ark® Traveler', and 'Sweet-Ark® Ponca') in 2020 and three cultivars ('Natchez', 'Prime-Ark® Traveler', and 'Sweet-Ark® Ponca') in 2021 grown at the University of Arkansas System (UA System) Division of Agriculture Fruit Research Station in Clarksville, AR were evaluated. The blackberries were hand-harvested on three dates one week apart and frozen (-10 °C) for evaluation of berry weight, composition, and volatile aroma attributes. In general, cultivars differed for berry weight (5-13 g), soluble solids (9-13%), pH (3.3-4.2), titratable acidity (0.4-1.0%), and solids/titratable acidity ratio (9.8-31.0), but harvest date impact varied by cultivar and year. In the cultivars harvested on three dates for both years, there were 139-165 volatile aroma compounds identified across 9-10 compound classes including monoterpenes, alcohols, aldehydes, sesquiterpenes, esters, ketones, fatty acids, aromatic hydrocarbons, furans, and lactones. Sweet-Ark® Ponca' late harvest date in 2021 had the lowest cumulative concentration of volatile compounds (1,369.96 µg/kg), and 'Sweet-Ark Ponca' middle harvest date in 2020 had the highest (4,692.89 µg/kg). In both years, six impactful volatiles, ethyl butanoate (2.84-38.49 µg/kg) (fruity, apple-like), linalool (38.30-61.79 µg/kg) (floral, perfume), ethyl 2-

methylbutanoate (2.59-19.24 µg/kg) (fruity), 2-hexenal (45.14-286.25 µg/kg) (green, leafy), geraniol (28.48-55.44 µg/kg)(sweet, rose-like), and *allo*-ocimene (0.57-2.57 µg/kg) (floral, citrus) were identified in Arkansas-grown fresh-market blackberries with 2-hexenal and linalool in the highest concentrations. Generally, principal component analysis showed clustering around both harvest dates and cultivar, and the two primary components covered 63.9%-63.3% in 2020 and 2021, respectively. This research provided a critical data berry attributes that impact the aroma and flavor of blackberries and can be used by blackberry breeders to help southern U.S. growers market blackberries.

Introduction

Blackberry (*Rubus* subgenus *Rubus* Watson) plants are grown domestically and internationally and can be cultivated for both fresh-market and processing. Fresh-market berries are harvested and sold directly to the consumers, while processing berries are intended for other uses including freezing, jellies, or beverages. Fresh-market berries are typically harvested by hand to preserve the berry integrity, while processing berries are harvested mechanically to increase harvest volume. The increased awareness of potential health benefits of blackberries, expanded globalization, and expedited refrigerated transportation methods contributed to the growing blackberry market (Safley, 2009).

In the United States, blackberry production in Oregon, Washington, and California is predominantly for the processing industry. According to the National Agricultural Statistics Service (USDA NASS, 2017), the total blackberry acreage in the United States was around 23,500 ha (58,000 acres) for both fresh-market and processing blackberries. In terms of the fresh-market industry in 2013, Oregon ranked first for the largest blackberry production (300 ha), California ranked second (280 ha), Texas ranked third (270 ha), Arkansas ranked fourth (240 ha), and North Carolina ranked fifth (180 ha) (Takeda et al., 2013). Fresh-market blackberry production in the Southeast has been a growing part of the United States market for the past decade (Fernandez et al., 2016).

Blackberries are a crown-forming perennial that produce above-ground stems called canes that are typically biennial (produce flowers and fruit then die in the second year) (Hummer, 2018). First-year blackberry canes are primocanes, but the second-year canes are floricanes. Blackberries produced by the plant are an aggregate fruit comprised of drupelets surrounding a soft tissue receptacle (torus). Each drupelet has a thin exocarp, a fleshy mesocarp, and a hard-lignified endocarp, or pyrene that encloses a single seed (Tomlik-Wyremblewska et al., 2010). As blackberries ripen, the drupelets on the blackberries turn from red to black. The blackberries are harvested weekly for 3-4 weeks from plants as the fruit ripens. Previous studies have shown a relationship between harvest date and quality attributes but was dependent on cultivar (Cavender et al., 2019; Jacques et al., 2014). The size (berry weight, length, and width) and shape of a fully ripened blackberry varies among cultivars. The weight of each blackberry will range from 5-15 g with length of 15-30 mm (Carvalho and Betancour, 2015). The berries can have different shapes, such as a round shape, or the berries can be long and oval shaped.

The U.S. blackberry breeding programs play a critical role in global blackberry production, using current cultivars and breeding selections (genotypes) to develop and release new cultivars. In the United States, the United States Department of Agriculture (USDA)-Agricultural Research Service at Corvallis, OR (Clark and Finn, 2008) is the oldest currently active blackberry breeding program. Fresh-market blackberry cultivars released by USDA include 'Obsidian', 'Metolius' and the newest releases 'Eclipse', 'Galaxy' and 'Twilight' (USDA, 2020). The University of Arkansas System Division of Agriculture (UA System) Blackberry Breeding Program located at the UA System Fruit Research Station, Clarksville, AR, has developed and patented 43 fresh-market blackberry cultivars. The UA System blackberry breeding program also produced advancements in thornless plants, erect cane structures, increased fruit firmness, and primocane-fruiting (plants fruit on first year primocanes), and cultivars to lengthen the harvest season (Clark, 2005). 'Ouachita' and 'Osage' are two of the most widely-grown cultivars released from the UA System (*personal communications, Dr. John Clark*). The most recent cultivars from the UA System are 'Sweet-Ark® Caddo' (Clark et al., 2019) released in 2018, 'Sweet-Ark® Ponca' released in 2019, and 'Prime-Ark® Horizon' released in 2020. Although blackberry acreage in Arkansas has lagged as other southern states across the Southeast, including Georgia, North Carolina, and Texas, have expanded acreage for retail-market sales (Clark and Finn, 2014), this breeding program and the establishment of a new Arkansas Blackberry Growers Association has invigorated the state's industry.

The aroma, appearance, flavor, and texture of blackberries varies by cultivar. Although the basic tastes (sweetness, sourness, and bitterness) impact the flavor of blackberries, volatile aroma compounds (substances in fruit which vaporize easily at ambient temperature) are also responsible for typical aromas and aromatic flavors of blackberries. Sugars (mostly glucose and fructose) are the major soluble solids in blackberries that impact the sweetness and sourness (Mikulic-Petkovsek et al., 2012). The soluble solids of commercially acceptable fresh-market blackberry ranges from 8-11% (Threlfall et al., 2016). The titratable acidity is a measure of the predominant acid (usually citric) in the fruit and is inversely related to the pH. The pH of a commercially-acceptable fresh-market blackberry ranges from 3.0-3.6 and titratable acidity ranges from 0.7-1.4% (Threlfall et al., 2016). Segantini et al. (2018) determined important attributes for quality, demonstrating fresh-market blackberries had a good balance of acidity and sugar content, as noted by descriptive sensory panelists. The balance of sugars and acids are important attributes for fresh-market blackberries, especially to target consumer markets.

Volatile organic compounds are also impact consumer perceptions and preferences of blackberry flavor. Unlike the basic tastes which are perceived by taste receptors on the tongue, volatiles are perceived through smell detected by olfactory receptors in the nose and mouth (Klee and Tieman, 2018). The olfactory system and odor thresholds of individuals vary widely, making olfactory perception a difficult trait to quantify (Hasin-Brumshtein et al., 2009). While many different volatiles affect blackberry flavor, specific compounds that drive consumer preferences vary (Klee and Tieman, 2018). Volatiles are extracted using gas chromatography mass spectrometry (GC-MS) then quantified using flame ionization detector (FID). Solid Phase Micro Extraction (SPME) fibers can capture analytes in the headspace of a sample for analysis. Gas chromatography-Olfactometry (GC-O) can also be used to evaluate the aroma of fresh-market blackberries. The GC-O separates compounds using GC, and as a peak is detected, that odor is separated and delivered to a trained panelist to evaluate the intensity of the aroma detected (Wang et al., 2005).

Volatile compounds in blackberries include acids, esters, alcohols, aldehydes, ketones, lactones, and terpenoids. Early studies focused on the volatile constituents of blackberries and blackberry products (Georgilopoulos and Gallois, 1987; Gulan et al., 1973; Scanlan et al., 1970). Compounds, such as 2-heptanol, p-cymen-8-ol, 2-heptanone, 1-hexanol, a-terpineol, pulegone, 1-octanol, isoborneol, myrtenol, 4-terpineol, carvone, elemicine, and nonanal were identified as major volatiles in blackberries. Blackberry aroma profiles are diverse, with different genotypes having unique aroma profiles. Jacques et al. (2014) identified 45 volatile compounds in 'Tupy', the predominant cultivar available commercially. The majority of volatiles in blackberries were comprised of terpenoids with limonene as the predominate compound (Du et al., 2010).

Wang et al. (2005) examined volatiles in 'Chickasaw' blackberries, a UA System cultivar, grown in Oregon and Arkansas. While the number volatiles and the aroma compositions of the samples from the two locations were similar, there were differences in aroma impact of the blackberries between the two regions. The flavor and aroma of the fruit were strongly influenced by the local growing environment within the same cultivar. The berries grown in Oregon had cut grass, green, fruity, citrus, and watermelon aromas, while the Arkansas berries had cinnamon, piney, floral, sweet, and caramel aromas. The most potent aroma compounds in Oregon-grown

‘Chickasaw’ were ethyl butanoate (fruity, apple-like), linalool (floral, perfume), methional (cooked potato), trans,cis2,6-nonadienal (green, cucumber), cis-1,5-octadien-3-one (green, grass), and 2,5-dimethyl-4-hydroxy-3(2H)-furanone (sweet, strawberry-like), while in Arkansas-grown ‘Chickasaw’ were ethyl butanoate, linalool, methional, ethyl 2-methylbutanoate (fruity), beta-damascenone (rose-like, berry), and geraniol (sweet, rose-like).

In a similar study, Du et al. (2010) quantified volatiles of eight Oregon-grown genotypes of blackberries identified a range of compounds, such as esters, terpenoids, aldehydes, ketones, alcohols, norisoprenoids, lactones, acids, and furanones. The compounds were quantified, but the values of each compound did not distribute uniformly across genotypes. Barba et al. (2018) evaluated odorant compounds that enhanced sweet flavor in sugar-reduced juice using GC-O to isolate taste-enhancing compounds and showed that ethyl 2-methylbutonate enhanced flavor sweetness. The data help target odorant compounds that enhance desired flavors. It is possible that specific cultivars may have optimal harvest dates that differ from each other, depending on the preferred volatile composition, as is the case with grapes and other produce (Bindon et al., 2013; 2014; Jordão et al., 2017; Meyers, 2022).

Flavor dilution (FD) is the ratio of the concentration of the odorant in an initial extract to the concentration in the most dilute extract, but the odor is still detachable by GC-O. The compounds with the most impactful aromas found by Wang et al. (2005) in Arkansas-grown ‘Chickasaw’ determined by their FD were ethyl butanoate, linalool, methional, ethyl 2-methylbutanoate, β-damascenone, geraniol, allo-ocimene, trans-2-hexenal, and 2,5-dimethyl-4-hydroxy-3(2H)-furanone; all with a FD = 512. Whereas, the odor activity value (OAV) estimates odor potency as a ratio of the volatile concentration to its odor detection threshold (Patton, 1957). Du et al., 2010) calculated OAVs and found furaneol, linalool, β-ionone, 2-heptanol, and carvone that contributed to the major aroma compounds in blackberries grown in the Pacific Northwest. The volatile concentrations are calculated based on comparing volatile peak areas from GC response to the internal standard and external databases. In contrast to Wang et al. (2005), methional, β-damascenone, allo-ocimene, ethyl 2-methylbutanoate, and 2,5-dimethyl-4-hydroxy-3(2H)-furanone were not detected in Arkansas-grown blackberries by Morin nor Meyers (Meyers, 2021; Morin 2021) who also investigated volatiles in Arkansas-grown blackberries.

Consumers want a fresh-market blackberry that is uniform in color, fresh, has a good shelf life, fair-priced, rich in nutraceuticals, and has unique flavors and aromas (Threlfall et al., 2020, 2021). A study conducted on blueberries showed lipid-derived volatiles explained 15% of overall liking scores in a sensory panel, and the carotenoid/terpene compound group explained 21% of the overall liking score (Colantonio et al., 2020). Descriptive sensory analyses have been conducted to determine attributes that are commercially acceptable for fresh-market blackberries, such as appearance, aroma, basic tastes, aromatics, feeling factors. Threlfall et al. (2016) developed a fresh-market blackberry lexicon to evaluate UA System blackberries. In the lexicon, eight appearance, three basic tastes, two feeling factors, and eight aromatics were evaluated. Segantini et al. (2017) studied sensory attributes in postharvest storage and reported panelists could not perceive a difference in color, uniformity of color, glossiness, firmness or sweetness after storage, but could identify blackberries as more astringent and less sour and bitter after storage. Gilbert et al. (2015) identified breeding priorities for blueberry flavor using biochemical, sensory, and genotype by environment analyses and found many of the compounds affecting flavor including β-caryophyllene oxide and 2-heptanone were genetically controlled.

There is a critical need to determine the key volatile attributes that that impact the aroma and flavor of blackberries and can be used by blackberry breeders to help southern U.S. growers market blackberries. Since the UA System Blackberry Breeding Program contributes to the global blackberry industry, the objectives of the research were to evaluate the impact of harvest date on size, composition, and volatiles of Arkansas fresh-market blackberries.

Materials and Methods

Blackberry plants and culture

The blackberry plants were grown at the UA System Fruit Research Station in Clarksville, AR (West Central Arkansas, lat. 35 °31'58" N and long. 93 °24'12" W). Four blackberry cultivars (Natchez, Prime-Ark® Horizon, Prime-Ark® Traveler, and Sweet-Ark® Ponca) were evaluated in 2020, and three cultivars (Natchez, Prime-Ark® Traveler, and Sweet-Ark® Ponca) were evaluated in 2021. Plants were trained to a T-trellis with two lower wires ~0.5 m from the soil surface spaced 0.5 m apart and two upper wires ~1.0 m high spaced 0.8 m apart. The blackberry plants that were harvested for this project were in three plots with five plants per plot, and the plots were established in 2017, 2018, and 2019. Standard cultural practices for erect blackberry production were used including annual spring nitrogen fertilization (56 kg/ha N) using ammonium nitrate. The plants were irrigated as needed using trickle irrigation. Dormant pruning consisted of removing dead floricanes and removing primocane tissue to a point below the flowering area on the primocanes. The plants received a single application of liquid lime sulfur (94 L/ha) at budbreak for control of anthracnose (*Elsinoë veneta* [Burkholder] Jenk.). Raspberry crown borer (*Pennisetia marginata* [Harris]) was controlled by a single application of a labeled insecticide with bifenthrin as the active ingredient in October of each year. Insecticides labeled for commercial use in Arkansas were used for spotted wing drosophila (*Drosophila* *suzukii* Matsumura) control. Average monthly temperature and rainfall at the Fruit Research Station in Clarksville, AR were tracked, recorded, and reported from January to June each year (Fig 1).

Blackberry harvest

Blackberries were hand harvested from the floricanes from 7:00$_{AM}$ to 10:00$_{AM}$. The fruit was harvested at the shiny-black stage of ripeness and were free of major blemishes, flaws, or damage. About 2 kg of blackberries were harvested three consecutive weeks in June 2020 and 2021 for each cultivar and placed directly into 312 g (11oz) vented clamshells. After harvest, the clamshells of blackberries were placed in chilled coolers and transported to the UA System Department of Food Science, Fayetteville and frozen (-10 °). After the blackberries were frozen, the blackberries were divided into three replications (10 berries/replication) for each of the evaluations for berry weight, composition attributes, and volatile attributes.

Berry weight analysis

Ten berries per cultivar, harvest date, and replication were used for berry weight. Each berry was weighed (g) using a precision digital scale (PA224 Analytic Balance, Ohaus Corporation, Parsippany, NJ). These berries were also used for composition.

Composition attribute analysis

Composition of the juice from ten berries per cultivar, harvest date, and replication were measured for soluble solids, pH, and titratable acidity. The ten berries were thawed at room temperature (21 °C) and squeezed through cheesecloth to extract the juice for analysis.

<u>Soluble solids.</u> Soluble solids of the juice were measured and expressed as percent (%) using an Abbe Mark II refractometer (Bausch and Lomb, Scientific Instrument, Keene, NH).

<u>pH</u>**.** The pH of juice was measured using a pH700 Benchtop pH meter (APERNA Instruments,

Columbus, OH).

Titratable acidity. The titratable acidity of the juice was measured using a Metrohm 862 Compact Titrosampler (Metrohm AG, Herisau, Switzerland) fitted with a pH meter. Three grams of sample was added to 50 mL degassed, deionized water and titrated with 0.1 N sodium hydroxide to an endpoint of pH 8.2. The titratable acidity of juice was expressed as % w/v (g/100 mL) citric acid.

Soluble solids/titratable acidity ratio. The soluble solids/titratable acidity ratio was calculated as the soluble solids divided by the titratable acidity.

Volatile aroma attribute analysis

Ten berries per cultivar, harvest date, and replication were used for volatile aroma attribute analysis. Gas chromatography analysis was performed using a Shimadzu GC-2010 Plus Gas Chromatograph equipped with a Flame Ionization Detector (GC-FID) and a GCMS-QP2010 SE Mass Spectrometer (GC-MS). The analysis includes identification and quantitation of odor-active compounds. For the analysis of blackberry volatiles, frozen blackberries (10 g), deionized water (10 mL), and NaCl (3 g) were mixed using a ratio of 1:1:0.3 (w/v/w). Two samples (one for GC-MS and one for FID) of 4 mL berry/deionized water/NaCl solution were placed in 20 ml headspace vials. The vials were incubated for 20 minutes with agitation and heat at 65 °C, and then the volatiles were absorbed using an 85 µm DVB/CAR/PDMS Solid Phase Microextraction (SPME) fiber was placed in the headspace above the sample for an additional 30 minutes. The SPME fiber was removed from the vial and placed into GC injection ports.

Samples were analyzed on both GC-FID and GC-MS and separation was performed on each using a HP-5 (30 m × 0.25 mm inner diameter, 5% phenyl-methylpolysiloxane, 1.0 µm film thickness) capillary column. For both GC-MS and GC-FID analysis, the injector temperature was

250 °C. Helium was used as the carrier gas and column flow rate was 1.92 mL/min for GC-FID and 1.20 mL/min for GC-MS. The oven temperature was programmed for a 4 min hold at 30 °C, then 30 °C to 180 °C at 6 °C/min, then from 180 °C to 280 °C at 8 °C/min, and with a 3 min hold at 280 °C. The GC-FID detector temperature was 280 °C, and the interface temperature for the GC-MS had an ion source temperature of 230 °C and an interface temperature of 250 °C. GC-MS was performed in full scan mode, with a scan range of 20-300 *m/z*. The volatiles were identified by comparison of their mass spectra with the spectral library, literature data, and retention indices, and expressed as µg/kg.

Statistical design and analysis

For berry weight, composition, and volatiles cultivars and harvest dates were evaluated in triplicate by year. In both years, three harvest dates were evaluated (early, middle, and late). Four cultivars (Natchez, Prime-Ark® Horizon, Prime-Ark® Traveler, and Sweet-Ark® Ponca) were evaluated in 2020, and three cultivars (Natchez, Prime-Ark® Traveler, and Sweet-Ark® Ponca) were evaluated in 2021. The data was analyzed by analysis of variance (ANOVA) using JMP® (version 16.0.0; SAS Institute Inc., Cary, NC). Tukey's Honestly Significant Difference was used for mean separations ($p = 0.05$). Associations among all dependent variables were determined using multivariate pairwise correlation coefficients of the mean values using JMP (version 16.0.0; SAS Institute Inc., Cary, NC). Principal component analysis was done using XLStat (Addinsoft Inc., New York, NY).

Results and Discussion

Average monthly temperature and rainfall were reported from January to June, the end of blackberry harvest at the Fruit Research Station in Clarksville (Fig. 1.) The 2020 blackberry season in Clarksville, AR was typical in terms of temperature and rainfall. However, the 2021 season had notable weather events in February and April. In both years the high temperatures in June were 33 °C. The low temperatures in 2020 were 14 °C, and the low temperatures in 2021 were 11 °C. There was record cold temperatures (-5 °C) with 178 mm of snow in February of 2021 at the Fruit Research Station followed by a freeze after budbreak in late April (-1 °C overnight). The cultivars available for harvest were impacted by both low temperature events in 2021. Total rainfall in 2021 (765 mm) was less than rainfall in 2020 (843 mm). Rainfall in June 2021 (142 mm) was triple the rainfall in June 2020 (41 mm). There was rainfall the day before the early harvest date (23 mm) and late harvest date (7 mm), but no precipitation prior to the middle harvest date.

Berry weight attributes

The cultivar x harvest date interaction was significant for berry weight in 2020 but not 2021 (Table 1 and 2). In general, 'Sweet-Ark® Ponca' had the smallest berries in both years, and harvest date had minimal impact on berry weight. For both years, berries were 5-13 g, which falls within ranges established by previous research on Arkansas-grown fresh-market blackberries (Felts et al., 2020; Threlfall et al., 2016, 2020, 2021). Felts et al. (2020) harvested nine Arkansas genotypes in 2017 with berry weights 4-9 g. Carvalho and Betancur (2015) found the average weight of blackberries grown in Colombia ranged from 5-15 g and 15-30 mm in length. Berries harvested in 2021 were larger than berries in 2020. This is likely due to the April freeze which occurred during flowering, and greatly reduced the total number of berries per plant. Ciobotari et al. (2013) also found that both 'Thornfree' and 'Lochness' blackberries increased fruit yield under optimal sunlight and irrigation conditions, but berry size differed between cultivars when the plant was given reduced sunlight and irrigation. 'Thornfree' berries were generally smaller in low water conditions, while 'Lochness' berries were generally larger.

This indicates that cultivars handle water and nutrient stressors differently, and further research is necessary to determine how each cultivar responds to different environmental factors.

2020. 'Prime-Ark® Horizon' from the middle harvest (11.26 g) had the largest berry weight, and 'Prime-Ark® Traveler' regardless of harvest date (4.74-4.86 g) had the smallest (Table 1). There were not any differences among the harvest dates within the cultivars except in 'Prime-Ark® Horizon' where the berries from the middle harvest had higher berry weight than the early harvest (8.10).

2021. Cultivar impacted berry weight with 'Natchez' (13.02 g) higher than 'Sweet-Ark® Ponca' (5.89 g) and 'Prime-Ark® Traveler' (5.39 g). Harvest date did not impact berry weight but had an average berry weight of 8.1 g.

Composition attributes

The cultivar x harvest date interaction was significant for soluble solids and soluble solids/titratable acidity ratio in both years (Figs. 2 and 3). In general, cultivars differed for the composition attributes, but harvest date impact on composition attributes varied by cultivar and year. For both years, berries had 9-13% soluble solids, 3.3-4.2 pH, 0.4-1.0% titratable acidity, and 9.8-31.0 soluble solids/titratable acidity ratio. Cavender et al. (2019) found that harvest date affected berry weight, soluble solids, pH, and titratable acidity, but that the values for pH and titratable acidity followed fewer trends. The same study also showed that different fertilizers affected berry production and composition, indicating that nitrogen availability throughout the harvest period has an effect on fruit yield and quality. This relationship between nitrogen and fruit quality has been previously established (Al-Kharusi, 2009; Beckles, 2012; Christensen et al., 1994; Skupien and Oszmianski, 2007; Wang and Lin, 2002)

The composition attributes were within ranges established by previous research on Arkansas-grown fresh-market blackberries. Segantini et al. (2017) harvested 11 Arkansas-grown genotypes in 2015 with soluble solids 4.7-19.5%, pH 3.0-3.4, and titratable acidity 0.5-1.5%. In a consumer sensory study on Arkansas-grown fresh market blackberries, Threlfall et al. (2016) concluded that for a majority of the consumers the fresh-market blackberries should have soluble solids of 9-11%, titratable acidity of 0.9-1.0%, and a soluble solids/titratable acidity ratio of 10-13.

2020. Cultivar and harvest date impacted titratable acidity (Table 1). The titratable acidity for 'Natchez', 'Prime-Ark® Traveler' and 'Sweet-Ark® Ponca' was 0.93%, 0.77%, 0.73%, and 0.38%, respectively. The titratable acidity for the early harvest date (0.82%) was higher than the middle (0.65%) and late (0.64%). 'Sweet-Ark® Ponca' early harvest date (13.80%) had the highest soluble solids, and 'Natchez' late harvest date (7.67%) had the lowest (Table 1, Fig. 2). Harvest date did not impact the soluble solids within each cultivar, however, while not significant, the early harvest date had slightly higher soluble solids than the late harvest date in all the cultivars. The cultivar x harvest date was also significant for pH (Fig. 2). In terms of pH, 'Prime-Ark® Traveler' late harvest date had the highest pH (4.54), and harvest date did not impact the pH of 'Natchez', 'Sweet-Ark® Ponca" or 'Prime-Ark® Horizon', but pH increased as harvest date increased in 'Prime-Ark® Traveler'. 'Prime-Ark® Traveler' last harvest (41.08) had the highest solids/titratable acidity ratio and 'Natchez' early harvest (7.76) had the lowest. Harvest date impacted soluble solids/titratable acidity ratio of 'Prime-Ark® Traveler' with the middle and late harvest dates having a higher than the early harvest date.

2021. Cultivar impacted the pH but not the harvest date. 'Sweet-Ark® Ponca' (3.71) had a higher pH than Natchez (3.35) and 'Prime-Ark® Traveler' (3.48), but harvest date did not impact pH

(Table 2). 'Sweet-Ark® Ponca' early harvest date (14.63%) had the highest soluble solids, and 'Prime-Ark® Traveler' late harvest date (9.33%) had the lowest (Table 2). Harvest date impacted the soluble solids of 'Natchez' and 'Sweet-Ark® Ponca' with the early harvest date higher in soluble solids than the late harvest date. The cultivar x harvest date was significant for titratable acidity (Table 2). Natchez late harvest date had the highest titratable acidity and lowest soluble solids/titratable acidity ratio (1.14% and 8.83, respectively), and 'Prime-Ark® Traveler' middle harvest date had the highest titratable acidity and lowest soluble solids/titratable acidity ratio (24.03 and 0.44%, respectively). Harvest date did not impact titratable acidity or soluble solids/titratable acidity ratio for any cultivar.

Volatile aroma attributes

In the four cultivars harvested on three dates for both years, there were 139-165 volatile aroma compounds identified across 9-10 compound classes including monoterpenes, alcohols, aldehydes, sesquiterpenes, esters, ketones, fatty acids, aromatic hydrocarbons, furans, and lactones (Tables 3 and 4). Across all cultivar/harvest date combinations and both years, alcohols (14-37%), aldehydes (7-41%), esters (15-44%), and monoterpenes (7-40%) were the major compound categories (Figs. 4 and 5). Monoterpenes are a class of terpenes that contain two isoprene molecules and are predominantly the product of secondary metabolism of plants known for their biological activities such as antimicrobial, anti-inflammatory, and anti-plasmodial properties and have been used in flavorings and fragrances (Tchimene et al., 2013). Esters with a fruity aroma were the second largest class of compounds in all blackberries. Sesquiterpenes, ketones, aromatic hydrocarbons, norisoprenoids, acids, and lactones were also present in low amounts.

These results varied from Du et al. (2010a) and Qian and Wang (2005) for blackberries grown in the Pacific Northwest who found that acids, alcohols, and monoterpenes (32, 32, and 24%, respectively) were the major classes. In a study performed on Spanish and Italian blackberries (*Rubus* ulmifolius *Schott*), D'Agostino et al. (2015) found that esters and alcohols were the predominant class of volatiles followed by monoterpenes, aldehydes, and ketones. Discrepancies between other studies and our results is to some degree expected, as variations in genetics, ripening stage, harvest, storage conditions, and sample preparation and gas chromatography procedures affect the volatile composition of blackberries (El Hadi et al., 2013; Qian & Wang, 2005).

While extraction method can impact volatile identification and quantification when comparing values from different research, our study conditions were optimized to achieve ideal results. All samples were prepared the same using a DVB/CAR/PDMS SPME fiber (preferable for berry volatiles), 4 mL-sample amount, 20 min pre-equilibrium time, 30 min extraction time, and 65 °C extraction temperature.

Wang et al. (2005) investigated 'Chickasaw', an Arkansas bred and grown cultivar, to determine the most impactful aromas in 'using flavor dilution (FD) factors and found that the impactful aromas were ethyl butanoate, linalool, methional, ethyl 2-methylbutanoate, *β*-damascenone, geraniol, *allo*-ocimene, trans-2-hexenal, and 2,5-dimethyl-4-hydroxy-3(2H)-furanone; all of which had a FD ≥ 512. Figures 6-7 show the total concentration of the impactful volatile aroma compounds in 2020 and 2021. Six of the nine impactful volatiles found in Wang et al. (2005) were identified in Arkansas-grown fresh-market blackberries in both 2020 and 2021. The compounds found were ethyl butanoate, linalool, ethyl 2-methylbutanoate, geraniol, allo-ocimene, and trans-2-hexenal, but compounds not found in our research were methional, beta-damascenone, and 2,5-dimethyl-4-hydroxy-3(2H)-furanone. The 2-hexenal (a floral aldehyde) and linalool (a floral monoterpene) had the highest levels of the six impactful compounds in the Arkansas-grown blackberries in both years, followed by ethyl 2-methylbutanoate, an ester with a fruity aroma. Levels of the six impactful compounds was much less (almost 50% less) in 2021 than in 2020, with levels of 2-hexenal seeing the largest reduction in total concentration. 'Sweet-Ark® Ponca', regardless of harvest date, had the highest levels of linalool in both 2020 and 2021, and 'Sweet-Ark® Ponca' middle harvest date had the highest level of impactful volatiles in both 2020 and 2021.

Du et al. (2010a) used OAVs to identify the impactful aroma contributing compounds in blackberries grown in the Pacific Northwest and found furaneol, linalool, *β*-ionone, 2-heptanol, and carvone as the most impactful aromas. In contrast to Wang et al. (2005), methional, *β*-damascenone, ethyl 2-methylbutanoate, and 2,5-dimethyl-4-hydroxy-3(2H)-furanone were not detected in our Arkansas-grown blackberries. This indicated measuring impactful volatiles rather than evaluating the entire volatile profile is a better approach for screening blackberries for aroma.

In general, overall volatiles were similar levels in 2020 and 2021, but impactful volatiles were much lower, most notably 2-hexenal was recorded at much higher levels in 2020 in all cultivars than in 2021. Other impactful volatiles were found at similar levels in both years, for example, 'Sweet-Ark® Ponca' had higher levels of linalool and 'Natchez' had relatively high levels of geraniol when compared to other cultivars. This reinforces previous research indicating that individual cultivars have unique volatile profiles (El Hadi et al., 2013; Qian and Wang, 2006). To clearly determine which of the identified odor-active volatiles contribute to the distinctive aromas of blackberries, including those volatiles that add subtle background aromas required for a "natural, complete" blackberry aroma, further studies are required. In addition, volatile composition may change during the storage as well as during the freezing and thawing process.

2020. In the four cultivars harvested on three dates, there were 165 volatile aroma compounds identified across 10 compound classes including 45 monoterpenes, 31 alcohols, 28 aldehydes, 18 sesquiterpenes, 15 esters, nine ketones, nine fatty acids, six aromatic hydrocarbons, three furans, and one lactone (Table 3). Compound categories included chemical, floral, fruity, green/fat, roasted/caramelized, vegetal alcohols, floral, green/fat, vegetal, and roasted/caramelized aldehydes, fruity and vegetal aromatic hydrocarbons, fruity esters, vegetal and fruity ketones, vegetal, fruity, floral, green/fat monoterpenes, and green/fat, and fruity sesquiterpenes. 'Natchez' Early harvest date had the lowest cumulative concentration of volatile compounds (1,257.72 µg/kg), and 'Sweet-Ark® Ponca' Middle harvest date had the highest (3,777.34 µg/kg).

Figure 4 shows the total volatile concentration for each cultivar and harvest date with different compound categories. For every cultivar except for 'Prime-Ark® Traveler' late harvest had a higher overall volatile concentration than did the early harvest date. In addition, 'Natchez' and 'Sweet-Ark® Ponca' middle harvest had a higher overall volatile levels than did the early harvest date. The four volatile aroma compounds with the highest levels found in Arkansas-grown blackberries were 2-methylbutanoic acid (fatty acid with fruity aromas), 5-hexenal, 4-methylene (aldehyde with fruit and cocoa aromas), hexanal (aldehyde with grassy and fruity notes), and 2-phenylethanol (alcohol with floral and honey notes) (Table 4). In 'Natchez' and 'Sweet-Ark® Ponca', 2-methylbutanoic acid and hexanal all increased in level as the harvest dates progressed. Natchez' also showed the same trend 2-phenylethanol, however, 'Sweet-Ark® Ponca' also increased in 5-Hexenal, 4-methylene as the harvest dates progressed.

The impactful volatile aroma compounds with the highest levels in 2020 were 2-hexenal (33.70 – 589.09 µg/kg), a floral aldehyde, and linalool (0 - 281.57 µg/kg), a floral monoterpene (Fig. 6). The next highest impactful compound was geraniol (7.32 - 69.88 µg/kg), a monoterpene with floral and fruity aromas.

When a PCA was conducted on the compound class variables in 2020 (Fig. 8), two components explained 64% of the variation in the data. PC1 (42.9%) had positive loadings for ketones, acids, sesquiterpenes, esters, aromatic hydrocarbons, and lactones. Cultivar/harvest date combinations positively loaded for PC1 included 'Prime-Ark® Traveler' late, 'Natchez' early, 'Natchez' middle, and 'Natchez' late. Monoterpenes, alcohols, furans, and aldehydes were all loaded negatively on PC1 along with cultivar/harvest date combinations 'Prime-Ark® Horizon' middle, 'Prime-Ark® Horizon' late, 'Prime-Ark® Traveler' middle, 'Sweet-Ark® Ponca' late, 'Sweet-Ark® Ponca' middle, 'Prime-Ark® Horizon' early, 'Prime-Ark® 'Traveler' early, and 'Sweet-Ark® Ponca' early. PC2 (21.0%) had positive loadings for furans, aromatic hydrocarbons, lactones, esters, aldehydes, monoterpenes, acids, ketones, and alcohols. Cultivar/harvest date combinations 'Sweet-Ark® Ponca' late, 'Prime-Ark® Horizon' early, 'Prime-Ark® Traveler' early, 'Prime-Ark® Horizon' late, 'Prime-Ark® Traveler' late, 'Natchez' late, and 'Sweet-Ark® Ponca' middle. Sesquiterpenes and the cultivar/harvest date combinations 'Sweet-Ark® Ponca' early, 'Prime-Ark® Traveler' middle, 'Prime-Ark® Horizon' middle, and 'Natchez' early were all negatively loaded for PC2.

Berry weight was negatively correlated (r^2= -0.58, *p=0.0462*) with aldehydes and positively correlated with aromatic hydrocarbons (r^2= 0.82, *p=0.0012*), esters (r^2= 0.77, *p= 0.0035*), lactones (r^2=0.89, *p=0.0001*), and sesquiterpenes (r^2= 0.78, *p=0.0029*). The pH was negatively correlated with sesquiterpenes (r^2= -0.58, *p=0.0471*). Titratable acidity was negatively correlated with aldehydes (r^2= -0.60, *p=0.0381*), while soluble solid/titratable acidity ratio was positively correlated with aldehydes (r^2= 0.60, *p=0.0383*) and negatively correlated with sesquiterpenes (r^2=-0.60, *p= 0.0407*).

2021. In the three cultivars harvested on three dates, there were 139 volatile aroma compounds identified across 9 compound classes including 31 monoterpenes, 23 esters 23 alcohols, 23 aldehydes, 17 sesquiterpenes, 7 acids, 7 ketones, 5 aromatic hydrocarbons, 3 lactones (Table 4). Compound categories included chemical, floral, fruity, green/fat, roasted/caramelized, vegetal alcohols, floral, green/fat, vegetal, and roasted/caramelized aldehydes, fruity and vegetal aromatic hydrocarbons, fruity esters, vegetal and fruity ketones, vegetal, fruity, floral, green/fat monoterpenes, and green/fat, and fruity sesquiterpenes. 'Sweet-Ark® Ponca' Late harvest date had the lowest cumulative concentration of volatile compounds (1,369.27 µg/kg), and 'Prime-Ark® Traveler' middle harvest date had the highest (3,665.85 µg/kg).

Figure 5 shows the total volatile concentration for each cultivar and harvest date with different compound categories. For each cultivar, the middle harvest date had a higher overall volatile level than did the early harvest date. The four volatile aroma compounds with the highest levels found in Arkansas-grown blackberries were 2-butanol (alcohol with fruity apricot aromas), ethyl acetate (ester with ethereal grape-like notes), 2-hexen-1-ol (alcohol with fruity, green and banana aromas), and methyl octanoate (ester with waxy orange and vegetable notes) (Table 6).

The impactful volatile aroma compounds with the highest concentrations in 2021 were geraniol (0 - 107.47 µg/kg), a fruity monoterpene, and linalool (2.11 - 170.16 µg/kg), a floral monoterpene (Fig. 5). The next highest impactful compounds were 2-hexenal (1.28- 145.13 µg/kg), an aldehyde with fruity aromas, and ethyl 2-methylbutanoate, an ester with fruity aromas.

When a PCA was conducted on the compound class variables in 2021 (Fig. 9), two components explained (63.3%) of the variation in the data. PC1 (35.6%) had positive loadings for aromatic hydrocarbons, esters, aldehydes, alcohols, sesquiterpenes, monoterpenes, lactones, and acids. Cultivar/harvest date combinations positively loaded for PC1 included 'Sweet-Ark® Ponca' middle, 'Prime-Ark® Traveler' early, 'Natchez' late, 'Natchez' middle, and 'Prime-Ark® Traveler' middle. Ketones loaded negatively on PC1 along with cultivar/harvest date combinations 'Prime-Ark® Traveler' late, 'Natchez' early, 'Sweet-Ark® Ponca' early, and 'Sweet-Ark® Ponca' late. PC2 (27.7%) had positive loadings for sesquiterpenes, alcohols, acids, monoterpenes, ketones, and aromatic hydrocarbons. Cultivars/harvest date positively loaded for PC2 included 'Natchez' late, 'Natchez' middle, and 'Natchez' early. Aldehydes, lactones, and esters were all negatively loaded for PC2. Cultivars/harvest date negatively loaded for PC2 included 'Sweet-Ark® Ponca' middle and 'Sweet-Ark® Ponca' late. In addition, berry weight was positively correlated with aromatic hydrocarbons (r^2= 0.63, *p=0.0006*), and pH was positively correlated with esters (r^2= 0.69, *p=0.0411*).

Conclusion

The physical, composition, and volatile attributes of Arkansas-grown fresh-market blackberries were evaluated. Four cultivars were harvested on three harvest dates (early, middle, and late) from the UA System Fruit Research Station in Clarksville, AR in 2020, and three cultivars were harvested on three harvest dates in 2021. Although the physical and composition attributes varied, the values were typical of previously-reported values from other research done on these cultivars. 'Sweet-Ark® Ponca' early had highest soluble solids in both years (13.80-14.63%). There were 165 volatile aroma compounds identified in Arkansas-grown blackberry cultivars in 2020 and 139 in 2021, mainly monoterpenes, esters, aldehydes, and alcohols. Total volatiles levels in 2020 were higher than values in 2021. ‘Sweet-Ark® Ponca’ middle (4,692.89 µg/kg) had the highest total volatiles in 2020 and ‘Prime-Ark® Traveler’ (3,666.48 µg/kg) had highest in 2021. In both years, six impactful volatiles were identified in Arkansas-grown fresh-market blackberries including ethyl butanoate, linalool, ethyl 2-methylbutanoate, geraniol, allo-ocimene, and trans-2-hexenal. Levels of the six impactful compounds was much less (almost 50% less) in 2021 than in 2020, with levels of 2-hexenal seeing the largest reduction in total concentration. Generally, principal component analysis showed clustering around both harvest dates and cultivar, and the two primary components covered 63.9%-63.3% in 2020 and 2021 respectively. In both years, berry weight was positively correlated with aromatic hydrocarbons, grassy-vegetal aromas. The combination of physical, composition, and volatile attribute information can be a useful tool to steer breeding decisions, help southern U.S. growers market blackberries better, and determine commercial potential of Arkansas-grown, fresh-market blackberries.

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Table 1. Main effect and interactions on berry weight and composition of fresh-market blackberry cultivars grown at the University of Arkansas System Division of Agriculture Fruit Research Station and harvested on three dates, Clarksville, AR (2020).

Effect [z]	Berry weight (g)	Soluble solids (%)	pH	Titratable acidity (%)[y]	Soluble solids/titratable acidity ratio
Cultivar					
Natchez	8.97 a	8.78 d	3.55 bc	0.93 a	9.84 c
Prime-Ark® Horizon	9.71 a	11.40 b	3.42 c	0.77 b	18.69 b
Prime-Ark® Traveler	4.81 b	10.30 c	4.15 a	0.73 b	14.84 b
Sweet-Ark® Ponca	5.50 b	13.19 a	3.66 b	0.38 c	31.02 a
P-value	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*
Harvest date					
Early	6.81 b	11.40 a	3.56 b	0.82 a	15.13 b
Middle	7.51 a	11.25 a	3.71 a	0.65 b	19.84 a
Late	7.42 ab	10.10 b	3.56 b	0.64 b	20.83 a
P-value	*0.0301*	*<0.0001*	*<0.0001*	*0.0003*	*0.0009*
Cultivar x Harvest date (*P-value*)	*0.0100*	*0.0115*	*<0.0001*	*0.0584*	*0.0001*

[z] Cultivars and harvest dates were evaluated in triplicate. Means with different letters for each attribute are significantly different ($p<0.05$) using Tukey's Honestly Significant Difference test.
[y] Titratable acidity expressed as % citric acid.

Table 2. Main effect and interactions on berry weight and composition of fresh-market blackberry cultivars grown at the University of Arkansas System Division of Agriculture Fruit Research Station and harvested on three dates, Clarksville, AR (2021).

Effect [z]	**Berry weight (g)**	**Soluble solids (%)**	**pH**	**Titratable acidity (%)**[y]	**Soluble solids/titratable acidity ratio**
Cultivar					
Natchez	13.02 a	9.79 b	3.35 b	1.01 a	10.92 b
Prime-Ark® Traveler	5.39 b	12.72 a	3.48 b	0.78 b	19.37 a
Sweet-Ark® Ponca	5.89 b	10.84 c	3.71 a	0.56 c	17.22 a
P-value	*<0.0001*	*<0.0001*	*0.0004*	*<0.0001*	*0.0006*
Harvest date					
Early	8.27 a	12.05 a	3.54 a	0.80 ab	15.86 ab
Middle	8.26 a	11.27 b	3.58 a	0.68 b	18.24 a
Late	7.77 a	10.03 c	3.42 a	0.86 a	13.40 b
P-value	*0.3453*	*<0.0001*	*0.0997*	*0.0070*	*0.0499*
Cultivar x Harvest date (*P-value*)	*0.1316*	*<0.0001*	*0.1910*	*0.0076*	*0.0170*

[z] Cultivars and harvest dates were evaluated in triplicate. Means with different letters for each attribute are significantly different ($p<0.05$) using Tukey's Honestly Significant Difference test.
[y] Titratable acidity expressed as % citric acid.

Table 3. Volatile aroma compounds [z] identified in fresh-market blackberry cultivars grown at the University of Arkansas System Division of Agriculture Fruit Research Station and harvested on three dates (early, middle, and late), Clarksville, AR (2020).

Compound	Retention index	Aroma category	Aroma description	Natchez Early	Natchez Middle	Natchez Late	Prime-Ark® Horizon Early	Prime-Ark® Horizon Middle	Prime-Ark® Horizon Late	Prime-Ark® Traveler Early	Prime-Ark® Traveler Middle	Prime-Ark® Traveler Late	Sweet-Ark® Ponca Early	Sweet-Ark® Ponca Middle	Sweet-Ark® Ponca Late
Total				**1257.72±761.07**	**2920.86±2596.64**	**3519.66±1546.94**	**2544.32±517.93**	**1881.85±1425.22**	**2736.5±556.11**	**3321.62±1524.25**	**2190.6±516.45**	**2931.32±3193.94**	**2596.97±1102.17**	**3777.34±1080.04**	**3317.35±2568.81**
Acids															
Butanoic acid, 3-methyl	832	Fruity	apple fruity pineapple	2.49±4.31	1.13±0.57	0.65±0.15	0.97±0.18	1.35±2.35	1.22±1.35	1.22±0.21	0.56±0.15	36.24±47	6.06±9.57	0.59±0.53	0±0
Butanoic acid, 2-methyl	845	Fruity	fruity pear apricot apple tropical gooseberry spicy rummy	0±0	0±0	0±0	0±0	0.8±0.91	0.64±1.12	0.43±0.75	0±0	0±0	0±0	0±0	0±0
2-Methylvaleric acid	931	Cheesy	sour cheesy	0±0	0±0	0±0	2.53±0.57	2.76±3.78	2.4±0.54	11.66±7.19	5.1±2.11	13.65±17	0±0	0±0	0±0
4-Methylpentanoic acid	940	Cheesy	pungent cheesy	4.39±5.95	23.16±24.14	41.26±26.98	73.4±39.32	65.36±87.81	96.71±59.65	0±0	0±0	0±0	57.33±59.45	47.87±9.72	45.35±42.48
2-Butenoic acid, 2-methyl-	940	-	-	5.24±9.08	18.12±18.92	89.45±80.31	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
Hexanoic acid	979	Fatty	sour fatty sweaty cheesy	112.02±170.85	345.28±134.98	188.31±51.62	82.36±22.75	38.25±34.9	94.83±49.89	331.11±294.64	157.36±174.41	815.04±1139.75	36.68±33.89	200.99±252.22	171.13±296.4
2-Methylbutanoic acid	993	Acidic	pungent acidic cheesy roquefort cheese	0±0	0±0	0±0	12.67±11.05	29.55±31.18	29.58±17.64	2.51±4.35	7.24±6.28	0±0	0±0	0±0	0±0
Octanoic acid	1165	Fatty	fatty waxy rancid oily vegetable	24.01±14.86	53.87±66.35	65.86±30.73	8.8±3.79	13.99±8.58	11.92±3.66	24.14±10.44	23.62±17.1	17.7±18.9	6.95±4.74	49.11±68.99	12.62±8.05
Decanoic acid	1361	Fatty	rancid sour fatty citrus	1.6±1.3	3.89±5.71	3.45±1.88	0.76±0.31	1.11±0.71	1±0.5	1.35±0.48	1.89±1.55	4.95±3.95	0.49±0.42	3.57±5	2.66±3.75
Total Acids	**9**			**149.76±206.37**	**445.47±250.7**	**389.01±191.69**	**181.52±77.99**	**153.2±170.26**	**238.33±134.38**	**372.43±318.09**	**195.79±201.62**	**887.61±1226.63**	**107.54±108.09**	**302.15±336.48**	**231.77±350.7**
Alcohols															
2-Butanol, 2-methyl-	644	Ethereal	fusel ethereal alcoholic fatty greasy winey whiskey leathery cocoa	0±0	0.15±0.27	1.38±1.22	18.42±16.01	0±0	34.05±25.57	0±0	0±0	0±0	0±0	0±0	0±0
1-Butanol	644	Fermented	fusel oily sweet balsamic whiskey	0±0	0±0	0±0	1.86±3.22	0±0	0±0	0±0	2.4±0.11	0±0	0±0	0±0	0±0
Butanal, 2-methyl-	645	Ethereal	fusel ethereal alcoholic fatty greasy winey whiskey leathery cocoa	5.16±8.95	0.17±0.3	0±0	8.03±13.91	5.22±9.05	0±0	9.7±8.43	10.15±5.22	22.91±22.19	4.48±7.76	4.73±6.01	3.91±5.58
1-Butanol	663	Fermented	fusel oily sweet balsamic whiskey	0±0	0.5±0.86	1.06±0.94	14.44±16.09	37.8±65.47	3.33±0.36	2.3±3.98	48.19±4.02	3.83±5.05	7.58±6.64	2.19±0.86	2.02±1.84
1-Penten-3-ol	679	Green	ethereal horseradish green radish chrysanthemum vegetable tropical fruity	1.02±0.79	3.31±2.3	0.33±0.35	7.66±13.28	1.54±2.68	19.12±1.25	41.29±52.95	17.31±16.34	0±0	13.59±12.04	7.79±7.29	6.78±6.01
1-Butanol, 3-methyl-	720	Fruity	sweet fruity banana solvent	5.75±4.1	9.54±14.2	4.8±1.03	24.78±42.93	39.57±46.06	4.08±5.41	108.76±93.49	13.68±12.26	101.08±118.88	3.64±6.31	3.48±6.03	0±0
Isobutenylcarbinol	732	Fruity	sweet fruity	0±0	0.38±0.44	6.93±6.08	70.43±53.3	0±0	105.19±42.23	26.32±32	0.72±1.24	59.26±81.69	27.26±23.7	11.08±11.4	17.76±18.58
1-Butanol, 2-methyl-	739	Ethereal	ethereal fusel alcoholic fatty greasy winey	5.54±9.6	0.6±1.05	0±0	17.77±6.63	7±12.12	16.11±2.37	1.62±2.81	1.93±0.67	6.13±8.68	4.43±5.58	2.6±1.05	3.36±3.03
1-Butanol, 3-methyl	767	Fruity	sweet fruity banana solvent	0±0	4.1±4.6	8.27±7.16	72.33±19.85	0±0	58.92±4.31	11.88±20.58	14.18±1.26	40.53±24.54	36.96±21.53	23.88±15.79	26.3±21.02
2-Penten-1-ol, (Z)	771	Green	green phenolic ethereal cherry metallic	0±0	0.97±0.64	0±0	10.23±3.57	4.2±5.1	9.71±3.79	3.49±3.39	2.68±0.45	3.2±4.52	7.04±4.23	4.68±3.12	4.46±4.08
Prenol	778	Fruity	fruity green lavender	0.36±0.63	0.23±0.2	0±0	1.68±2.92	5.24±7.81	0±0	0.84±1.45	3.47±0.44	0±0	0±0	0±0	0±0
2-Hexen-4-ol	785	Spicy	-	0.55±0.95	0.04±0.06	0.42±0.73	0.81±1.4	2.49±2.43	3.68±0.63	1.97±3.41	0.22±0.39	0±0	1.28±2.23	0.49±0.86	0±0
2-Hexen-1-ol	836	Fruity	fresh green leafy fruity banana	66.62±59.3	3.69±4.3	4.66±1.56	10.03±3.44	8.76±9.05	11.44±7.38	29.46±36.73	3.24±2.83	13.11±14.68	3.9±3.68	1.17±1.08	0.52±0.91
3-Hexen-1-ol	855	Green	green leafy	0±0	3.02±1.47	0.46±0.45	3.89±3.56	51.82±72.41	0±0	0±0	0±0	0±0	0±0	0±0	0±0
2 Heptanol	862	Citrus	fresh lemongrass herbal sweet fruity green	31.59±54.72	44.04±21.34	46.07±25.23	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
1-Hexanol	871	Herbal	ethereal fusel oily fruity alcoholic sweet green	0.34±0.45	0±0	0.48±0.83	144.83±33.5	132.96±97.21	148.95±35.97	178.43±66.62	104.87±24.72	77.02±100.46	191.07±41.97	195.55±92.04	145.96±100.75
3-Heptanol	880	Herbal	herbal bitter pungent	0.05±0.09	0.35±0.35	1.63±1.04	3.29±1.52	3.05±3.43	2.65±0.55	3.34±2.13	0.4±0.32	3.83±1.32	20.31±26.51	34.71±19.79	31.87±23.83
4-Heptyn-2-ol	895	-	-	2.26±3.11	2.36±0.14	0.78±1.35	10.9±2.38	8.32±9.19	15±3.24	11.88±7.26	4.36±0.89	7.37±10.43	5±4.94	6.27±3.67	5.65±4.79
2-Heptanol	904	Citrus	fresh lemongrass herbal sweet fruity green	18.5±29.58	162.28±23.74	219.03±118.44	98.32±14.73	56.46±58.45	123.29±8.08	23.27±12.37	10.04±1.61	12.51±9.37	104.83±57.64	155.8±29.69	113.84±86.65
2-Methyl-6-hepten-3-ol	919			0.25±0.44	0.59±0.68	1.17±0.88	6.59±2.61	6.48±8.55	6.49±1.58	9.08±6.11	3.95±1.68	8.5±0.97	4.96±5.26	4.4±3.81	1.64±2.84
2-Heptanol, 2-methyl-	933	-	-	0±0	0±0	0±0	0.64±0.19	0.63±0.87	0.84±0.03	0±0	0±0	0±0	0±0	0±0	0±0
1- Heptanol	973	Green	musty leafy violet herbal green sweet woody peony	0±0	0±0	18.35±31.79	0±0	25.89±44.85	0±0	184.31±175.7	136.4±92.61	22.24±31.46	40.18±37.64	56.75±31.02	66.46±43.83
1-Octen-3-ol	984	Earthy	mushroom earthy green oily fungal raw chicken	3.74±1.62	5.15±2.47	5.96±3.22	8.34±2.49	9.55±5.03	7.4±6.79	35.63±30.04	12.4±7.12	6.17±0.35	20.69±14.18	22.06±13.41	15.06±10.73
3-Ethyl-4-methylpentan-1-ol	1027	-	-	0.35±0.47	0.27±0.15	0.65±0.4	2.29±0.18	1.57±1.38	2.92±0.12	2.54±1.31	1.1±0.05	1.13±1.51	0.37±0.29	0.58±0.18	0±0
2-Ethylhexanol	1034	Citrus	citrus fresh floral oily sweet	0.24±0.15	0.05±0.09	2.29±0.98	1.15±0.3	1.07±0.49	1.73±0.26	1.67±1.01	0.69±0.13	0.95±1.33	1.69±0.98	2.45±1.01	2.28±2.11
1-Octanol	1073	Waxy	waxy green rose mushroom	30.78±21.99	71.12±88.9	107.79±45.38	18.97±5.82	18.64±8.68	22.88±6.28	31.8±14.68	21.96±11.72	28.71±34.37	27.01±9.11	90.17±67.6	38.95±22.84
2-Phenylethanol	1128	Floral	fresh sweet almond gardenia hyacinth	100.21±173.58	419.49±441.91	531.62±251.78	233.02±54.72	110.33±123.36	275.54±131.16	250.72±144.09	311.77±147.97	404.59±422.49	179.83±131.75	524.65±314.08	343.84±66.5
1-Nonanol	1176	Floral	fresh clean fatty floral rose orange dusty wet oily	2.96±1.39	7.7±8.19	9.07±4.09	4.72±1.63	5.15±2.02	6.03±1.38	9.1±3.98	5.42±2.11	5.66±6.77	2.8±1.15	9.32±6.35	4.7±0.97
1-Decanol	1276	Fatty	fatty waxy floral orange sweet clean watery	6.22±5.57	18.28±26.72	25.09±12.76	1.3±0.71	2.99±2.13	1.74±0.83	2.34±0.94	5.04±4.47	9.72±7.29	0.06±0.12	0.38±0.66	0.81±0.7
1-Dodecanol	1480	Waxy	earthy soapy waxy fatty honey coconut	0.57±0.29	0.72±0.73	0.66±0.08	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
1-Hexadecanol	1887	Waxy	waxy clean greasy floral oily	0.55±0.16	0.56±0.28	0.57±0.1	1.91±0.98	0.67±0.59	1.03±0.1	0±0	0±0	0±0	0±0	0±0	0±0
Total Alcohols	**31**			**284.85±379.94**	**762.19±647.61**	**1002±518.72**	**835.39±385.47**	**687.37±801.63**	**882.24±289.77**	**981.86±725.6**	**786.21±353.81**	**838.55±908.43**	**709.07±425.35**	**1165.29±636.9**	**836.26±427.69**
Aldehydes															
Butanal, 3-methyl-	643	Aldehydic	ethereal aldehydic chocolate peach fatty	0±0	0±0	0±0	6.78±11.74	3.78±6.55	1.65±2.87	4.89±8.48	3.99±6.92	0±0	0±0	0±0	0±0
2-Butenal, (E)-	654	-	-	0±0	2.19±3.79	3.77±3.43	4±3.51	27.85±45.7	2.66±2.32	17.58±15.98	0±0	7.03±9.94	7.25±7.7	5.12±1.21	3.39±3.5
Butanal, 3-methyl-	657	Cocoa	musty cocoa phenolic coffee nutty malty fermented fatty alcoholic	0.78±1.36	16.82±10.09	3.23±2.87	5.57±4.82	26.14±18.85	12.85±0.35	10.77±15.06	0±0	15.21±21.51	5.54±9.6	9.9±5.89	10.25±9.38
Butanal, 2-methyl-	670	Fermented	fermented bready fruity nutty berry	1.95±2.45	5.4±1.85	4.39±2.28	76.96±121.5	12.77±15.75	18.48±2.84	27.26±24.28	11.28±11.5	14.85±21	4.3±7.45	6.6±2.54	5.91±5.23
Butanal, 2-methyl-	698	Green	pungent green ethereal nutty anisic fruity	0.67±0.62	2.04±1.08	2.51±0.49	73.15±5.81	1.09±1.9	53.67±47.06	0±0	0±0	0±0	23.26±33.18	13.45±14.99	29.7±26.62
Pentanal	701	-	-	0.32±0.56	3.6±5.75	8.32±6.69	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
2-Pentenal, (E)-	731	Green	pungent green apple orange tomato	0±0	0±0	0±0	0±0	7.79±7.99	0±0	20.89±36.19	0±0	0±0	0±0	0±0	0±0
2-Butenal, 2-methyl, (E)	746	Fruity	sweet fruity pungent brown nutty almond cherry	0±0	0.22±0.38	0.51±0.44	0±0	0±0	0.36±0.63	4.04±6.16	0±0	0.5±0.71	0±0	0.54±0.1	0.88±1
2-Pentenal, (E)-	750	Green	fresh green fatty aldehydic grassy leafy sweaty	0±0	1.53±0.38	2.36±1.72	8.69±1.45	4.32±7.49	0.38±0.66	5.16±5.85	2.5±0.21	2.18±0.49	5.46±1.06	5.06±3.54	3.13±2.72
2-Butenal, 3-methyl	787	Bready	sweet woody almond bread baked caramellike phenolic	0.18±0.32	1.07±1.86	3.53±3.06	8.56±2.13	5.76±7.11	8.05±2.43	8.51±4.35	5.52±1.64	8.97±12.39	3.46±2.74	3±0.56	5.45±5.3
Hexanal	804	Green	sweet almond bitter fruity green leafy apple plum vegetable	8.57±11.67	42.12±42.72	86.46±78.04	365.79±139.88	203.27±134.94	325.77±69.81	272.2±128.86	130.09±10.02	203±279.71	231.34±74.78	198.27±100.04	177.12±132.96
Furfural	840	Green	fresh aldehydic fatty green herbal cognac ozone	0±0	10.45±9.82	1.96±0.83	21.33±2.23	16.24±21.98	21.15±5.27	0±0	0±0	0±0	7.37±6.44	0±0	0±0
2-Hexenal, €	850	Green	green fatty	0±0	0±0	0±0	0±0	0±0	0±0	10.96±7.02	4.76±0.8	0±0	7.69±2.27	9.1±9.02	41±51.85
2-Hexenal	859	Fruity	sharp sweet bitter almond cherry	33.7±54.75	118.44±76.95	104.03±59.45	250.4±162.94	125.93±199.48	239.1±82.67	540.76±203.79	321.56±120.6	141.89±124.03	511.35±136.85	579.99±349.89	394.43±341.7
Heptanal	907	Aldehydic	aldehydic waxy citrus orange peel green herbal fresh fatty	0.26±0.29	1.37±0.09	1.64±0.69	3.14±0.72	1.75±1.57	3.4±0.14	3.8±1.98	1.48±0.04	1.38±1.36	2.19±0.27	2.59±1.25	1.75±1.52
2-Heptenal, (E)-	963	Green	green sweet floral hyacinth clover honey cocoa	3.09±1.89	0.91±0.52	0.92±0.54	1.39±0.9	0.46±0.8	1.31±0.61	5.21±5.99	0.82±0.24	0.49±0.37	2.9±2.06	2.11±0.66	1.13±0.76
Benzaldehyde	975	Fatty	fatty green herbal	0±0	58.8±101.85	114.3±104.24	288.12±114.14	144.87±234.44	336.8±54.12	0±0	0±0	0±0	19.03±32.96	173.29±0.48	131.17±87.57
Octanal	1008	Fruity	sweety fruity cherry almond bitter phenolic	5.94±5.72	5.16±3.21	5.74±2.38	9.54±2.23	8.15±3.05	9.06±1.14	16.68±9.59	4.55±1.45	1.85±1.03	10.38±3.65	16.9±8.16	13.51±8.21
Phenylacetaldehyde	1059	Fruity	fruity cherry phenolic	0±0	10.55±10.06	12.36±11.67	0±0	6.21±6.19	13.46±2.42	63.87±29.47	31.45±13.35	35.24±27.2	6.78±6.78	28.51±13.89	2.51±4.35
2-Octenal	1066	Aldehydic	waxy aldehydic rose fresh orris orange peel fatty	5.3±0.96	8.97±6.38	12.95±7.18	5.92±2.14	4.62±4.38	8.75±0.75	12.37±5.38	7.26±1.63	5.41±6.35	6.05±0.9	11.73±3.65	7.09±3.81
3-Methylbenzaldehyde	1090	Herbal	herbal green woody amber leafy	0.04±0.08	0.29±0.07	0.37±0.17	0±0	0±0	0±0	0±0	0.04±0.07	0±0	0±0	0±0	0±0
4-Methylbenzaldehyde	1100	Fatty	fatty green waxy cucumber melon	2.66±1.46	5±2.33	7.2±2.67	11.75±4.2	12.32±3.61	14.99±2.4	13.34±4	8.81±4.54	10.8±6.66	2.76±4.79	11.6±3.59	10.4±3.52
Nonanal	1110	Aldehydic	sweety aldehydic waxy orange peel citrus floral	9.48±3.45	12.5±9.68	16.11±4.37	19.54±3.41	20.66±7.82	22.37±2.46	46.67±24.38	19.62±6.7	10.78±15.24	15.21±4.58	27.77±5.25	15.43±13.51
2-Nonenal	1170	Fatty	fatty orange rose aldehydic floral green	0.8±1.39	1.83±1.62	0±0	2.35±0.56	1.54±1.43	3.18±0.48	7.13±2.54	3.21±2.78	2.46±2.61	2.2±1.2	2.51±2.21	5.15±2.98
Decanal	1212	Citrus	sharp lemon sweet	3.5±0.72	2.91±2.56	3.25±3.1	4.11±3.49	4.52±1.33	4.01±0.53	8.15±3.48	4.89±2.26	2.68±3.17	11.97±9.52	45.2±10.09	17.15±5.95
2-Decenal	1270	Aldehydic	soapy waxy aldehydic citrus green floral	5.84±1.87	7.54±5.74	7.64±3.01	5.74±2.16	5.01±1.5	5.8±1.2	9.56±6.16	5.45±1.88	2.7±2.51	4.69±3.17	41.01±54.18	3.42±0.68
Undecanal	1285	Waxy	fresh waxy	0.9±0.29	2.26±2.11	2.87±1.08	1.37±0.21	0.69±0.24	0.97±0.54	0.96±1.66	0.98±0.89	1.02±1.44	0±0	0±0	0±0
Dodecanal	1420	Aldehydic	soapy waxy aldehydic citrus green floral	0.47±0.19	0.98±1	0.92±0.38	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
Total Aldehydes	**28**			**84.55±90.13**	**323.06±302.01**	**407.46±300.93**	**1174.31±590.28**	**645.85±734.21**	**1108.34±283.82**	**1110.86±550.74**	**568.35±187.62**	**468.53±537.8**	**891.27±352.06**	**1194.36±591.27**	**880.08±713.23**
Aromatic Hydrocarbons															

4-tert-Butylphenyl acetate	1412	-	-	2.74±2.46	5.38±5.63	2.55±4.42	13.57±6.51	9.23±4.69	10.76±2.37	21.46±15.45	4.57±1.11	3.88±4.99	20.61±8.91	15.26±5.69	2.84±3.32
Toluene	776	Sweet	benzene	0±0	4.49±3.7	7.65±4.23	7.8±0.7	3.37±3.22	9.13±1.71	10.2±5.43	3.71±0.77	5.09±7.2	7.94±4.89	8.4±1.02	9.72±8.1
Hexyl acetate	1017	Fruity	fruity green apple banana	0.08±0.13	0.13±0.13	0.21±0.09	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0.08±0.14	0.36±0.59
Benzothiazole	1255	Herbal	-	1.49±2.59	6.22±7.68	8.27±2.29	0±0	0±0	0±0	0.39±0.68	2.73±3.12	1.64±1.4	4.31±2.24	10.76±3.58	5.18±1.45
Hexadecane	1508	-	-	87.16±65.54	86.17±77.09	103.41±40.57	0±0	28.78±26.76	38.04±33.17	0±0	0±0	0±0	0±0	0±0	0±0
Heptadecane	1707	-	-	2.71±0.28	3.95±2.38	0.94±1.64	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
Total Aromatic Hydrocarbons	**6**			**94.2±71.02**	**106.36±96.64**	**123.07±53.26**	**21.38±7.21**	**41.39±34.68**	**57.94±37.26**	**32.06±21.58**	**11.02±5.01**	**10.62±13.59**	**32.87±16.04**	**34.52±10.45**	**18.11±13.49**
Esters															
Butanoic acid, methyl ester	707	Fruity	ethereal fruity tropical pineapple grape banana	0±0	0.03±0.06	0.04±0.07	4.26±1.42	23.88±20.73	2.97±0.9	0±0	2.93±1.44	0±0	0±0	0±0	0±0
Propanoic acid, ethyl ester	714	Fruity	ethereal pineapple fruity apricot strawberry banana bacon	0±0	0.95±1.65	4.06±3.53	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
Methyl butyrate	724	Acidic	acidic dairy fruity	0.03±0.05	0.37±0.51	1.33±1.03	5.65±2.69	4.65±5.62	7.95±3.17	2.95±5.12	0±0	17.58±24.87	0.86±1.5	0.65±0.26	1.27±1.36
Methyl 2-methylbutyrate	782	-	-	0.15±0.26	0.26±0.23	0.06±0.11	1.5±1.53	1.38±2.13	1.55±1.1	0±0	0±0	3.5±1.21	0±0	0±0	0±0
Ethyl (Z)-2-butenoate	847	Fruity	sweet fruity apricot banana tropical pineapple	12.76±4.57	7.26±11.48	22.51±20.95	7.76±6.64	3.98±6.89	5.87±3.05	4.63±4.88	2.17±1.38	16.28±18.09	5.58±5.85	7.67±10.2	2.67±3.54
Ethyl 2-methylbutyrate	855	Fruity	sweet fruity ethereal rummy	0±0	0±0	0.47±0.55	1.49±1.39	2.59±3.76	4.84±3.09	1.31±1.68	0.78±0.17	9.83±1.9	4.21±2.2	3.41±2.28	2.2±1.91
Methyl hexanoate	929	Fatty	sour fatty sweaty cheesy	1.16±1.24	4.8±3.4	7.28±4.64	2.95±2.01	2.97±4	6.33±2.18	19.97±9.64	13.89±7.95	31.22±41.76	3.34±2.73	5.85±1.62	4.49±3.66
Ethyl hexanoate	1000	-	-	18.44±16.63	33.82±41.18	63.74±43.16	44.37±34.89	18.88±17.58	48.3±23.62	15.76±9.82	16.85±10.88	48.49±68.58	11.04±7.35	33.47±40.85	13.34±11.24
Propyl pivalate	1005	Fruity	sweet fruity ethereal rummy	0±0	0±0	0±0	0.91±1.58	3.87±4.84	5.5±4.76	6.61±2.19	0±0	0.13±0.19	11.09±5.5	4.86±4.35	0.9±1.57
Ethyl 3-hydroxyhexanoate	1131	Fruity	fruity citrus melon	0.39±0.68	0.76±0.98	1.28±0.55	1.34±1.7	0.65±0.68	1.28±1.17	1.14±1.77	0.52±0.9	1.06±1.5	0.36±0.4	1.23±1.15	0±0
Ethyl octanoate	1199	Fruity	sweet fruity green orris waxy floral berry	59.81±60.09	78.39±135.79	154.34±135.14	1.45±2.51	1.57±1.24	3.92±1.37	0±0	0±0	0±0	0±0	0±0	0±0
Methyl decanoate	1327	Fruity	ethereal fruity tropical pineapple grape banana	0.17±0.29	0.74±0.98	0.59±0.45	0±0	0±0	0±0	0.28±0.24	0.2±0.35	1.73±0.84	0±0	0±0	0±0
Ethyl decanoate	1397	Fruity	fruity ethereal tropical green grape cherry banana apple cocoa	4.16±6.27	7.33±11.52	10.25±5.63	0.67±0.63	1.03±0.57	0.97±0.07	0.11±0.19	0.69±0.41	4.03±2.89	0±0	0±0	0±0
Hexyl octanoate	1589	Fruity	fruity ethereal tropical banana	0.22±0.18	0.33±0.35	0.3±0.06	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
Ethyl dodecanoate	1595	Fruity	sweet fruity green orris waxy floral berry	2.1±3.16	3.73±4.5	4.74±1.92	0.12±0.11	0.18±0.16	0.1±0.18	0±0	0.24±0.21	1.1±0.74	0±0	0±0	0±0
Total Esters	**15**			**99.43±93.47**	**138.84±212.68**	**271.06±217.85**	**72.51±57.16**	**65.69±68.26**	**89.62±44.7**	**52.79±35.56**	**38.3±23.73**	**135.01±162.62**	**36.52±25.56**	**57.16±60.75**	**24.9±23.31**
Furans															
Furan, 2-ethyl-	706	Chemical	beany ethereal cocoa bready malty	1.27±2.09	0.23±0.4	0.5±0.43	1.25±0.14	0±0	0.93±0.87	1.54±2.01	0±0	0.75±1.07	2.47±2.16	1.19±1.17	0.4±0.7
Furan, 2-methyl-	716	Chocolate	ethereal cocoa acetone	0±0	0.07±0.12	0.16±0.14	0±0	0±0	1.22±1.32	0.63±0.55	0±0	0±0	0±0	0±0	0±0
2-Ethylfuran	918	Chemical	ethereal cocoa bready coffee nutty	0.32±0.29	0.72±0.68	0.42±0.26	0.64±0.52	0.58±0.25	0.56±0.67	2.51±1.07	1.26±0.38	1.37±0.57	5.25±4.67	2.36±1.84	2.73±1.25
Total Furans	**3**			**1.59±2.38**	**1.03±1.21**	**1.09±0.84**	**1.9±0.67**	**0.58±0.25**	**2.73±2.87**	**4.7±3.64**	**1.26±0.38**	**2.13±1.64**	**7.73±6.83**	**3.55±3.02**	**3.14±1.95**
Ketones															
1-Penten-3-one	684	Citrus	citrus green musty lemongrass apple	2.03±2.57	19.67±31.15	4.3±6.83	0±0	0±0	0±0	0±0	0±0	0±0	4.69±4.12	7.76±13.45	14.27±14.82
Methyl Isobutyl Ketone	712	Fruity	fresh sweet green weedy earthy herbal	0±0	0±0	0±0	36.44±37.52	0±0	44.26±15.89	9.56±8.52	0±0	14.92±21.1	7.08±7.49	2.63±4.57	2.1±3.64
2-Hexanone	793	-	-	0.1±0.05	4.15±7	3±4.82	2.29±1.07	1.64±1.92	1.72±0.75	1.22±1.76	0.2±0.36	1.18±1.31	0.3±0.52	0.25±0.31	0.36±0.41
2-Heptanone	892	Citrus	fruity citrus floral orange	4.36±4.73	14.92±13.81	21.2±13.73	5.41±1.75	4.42±4.32	7.65±1.23	0.98±0.97	1±0.11	6.94±5.73	4.67±1.84	13.78±14.36	5.5±5.46
4-Methyl-2-heptanone	945	-	-	0±0	0±0	0±0	2.87±1.54	1.75±2.03	3.84±1.16	3.5±2.21	0.82±0.51	8.41±10.67	2.31±2.27	2.55±1.13	1.25±1.13
6-Methylheptan-2-one	959	Floral	orange floral fatty peach	0.41±0.56	0.22±0.07	0.44±0.43	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
6-Methyl-5-hepten-2-one	989	Floral	-	1.29±0.83	0±0	0±0	2.21±1.93	2.9±2.33	2.85±2.47	0.68±1.18	0.71±1.24	0.71±1.01	4.92±2.87	0.35±0.61	1.49±2.58
6-Methyl-6-hepten-2-one	996	Floral	-	0±0	2.39±2.27	3.46±3	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
Acetophenone	1083	Floral	sweet pungent mimosa almond	1.47±0.98	1.31±0.93	0.69±0.15	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
Total Ketones	**9**			**9.68±9.74**	**42.67±55.25**	**33.11±28.98**	**49.23±43.82**	**10.72±10.62**	**60.34±21.53**	**15.95±14.64**	**2.76±2.23**	**32.18±39.83**	**24±19.15**	**27.36±34.45**	**24.99±28.08**
Lactones															
gamma-Decalactone	1488	Fruity	freshy oily waxy	27.82±19.55	38.67±42.4	45.23±12.98	0±0	1.32±2.29	0±0	5.36±4.65	4.3±7.45	9.25±0.62	0±0	0±0	0±0
Total Lactones	**1**			**27.82±19.55**	**38.67±42.4**	**45.23±12.98**	**0±0**	**1.32±2.29**	**0±0**	**5.36±4.65**	**4.3±7.45**	**9.25±0.62**	**0±0**	**0±0**	**0±0**
Monoterpenes															
.alpha.-Pinene	947	Terpenic	oily woody terpenic lemon lime tropical herbal	25.19±30.43	81.47±117.68	136.18±94.2	13.65±6.52	35.18±49.37	10.55±1.9	57.12±50.91	95.19±57.13	205.98±72.26	85.26±46.09	96.39±100.11	140.35±140.13
Camphene	968	-	-	1.18±0.63	3.05±4.48	5.59±3.94	0±0	0±0	0±0	7.14±6.19	2.94±1.27	5.34±4.3	0±0	0±0	0±0
.beta.-Phellandren-8-ol	986	Herbal	herbal spicy chamomile green basil	0.74±1.29	2.61±2.64	4.2±2.46	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
beta-Myrcene	998	Floral	citrus floral sweet bois de rose green blueberry	25.61±10.15	56.74±62.22	90.29±49.31	46.67±14.39	49.07±30.85	81.02±4.29	97.83±41.48	60±24.42	60.9±54.9	109.51±69.46	159.3±29.69	192.55±138.47
gamma.-Terpinene	1020	-	-	0±0	14.3±9.56	17.91±10.94	0±0	0±0	0±0	0±0	0±0	0±0	41.26±20.41	47.01±19.73	10.87±5.41
Verbenol	1022	-	-	43.35±11.55	106.84±76.11	130.41±62.08	4.64±1.32	5.49±2.65	5.67±0.5	188.69±103.35	127.06±48.95	52.74±74.59	78.65±110.08	113.2±66.49	199.84±174.21
alpha-Terpinene	1029	Terpenic	terpeneic camphoreous herbal woody	8.38±1.33	18.6±18.03	0±0	0±0	0±0	0±0	2.09±2.12	6.01±2.71	0.09±0.13	0±0	0±0	0±0
O-Cymene	1039	Green	green plastic	1.91±0.68	3.45±3.48	5.21±2.35	0.87±0.18	0.74±0.86	1.42±0.07	3.38±1.83	2.55±1.07	1.71±2.41	3.27±2.38	4.42±2.54	5.84±4.66
D-Limonene	1042	-	-	13.41±11.73	27.37±38.88	40.61±23.14	6.08±2.02	5.8±5.27	8.31±2.84	20.29±12.32	16.69±7.84	10.19±14.14	27.99±20	51.86±23.06	55.93±46.6
beta-Phellandrene	1046	Floral	sweet floral nut skin pepper herbal tropical	0±0	2.89±2.63	3.89±3.39	0.29±0.28	0.17±0.15	1.57±2.34	0±0	0±0	0±0	0±0	0±0	0±0
(E)-beta-ocimene	1056	-	-	1.59±0.44	2.79±3.26	3.69±1.04	1.53±0.67	1.95±1.1	2.03±0.78	1.21±1.2	0.71±0.31	0.8±1.1	4.41±4.53	9.65±3.59	19.11±17.65
trans-Linalool oxide	1085	Terpenic	pine terpenic lilac citrus woody floral	0±0	0±0	0±0	5.2±1.71	3.02±2.91	6.28±1.2	0±0	0±0	0±0	6.37±3.37	9.7±5.86	7.37±3.5
cis-Verbenol	1088	Minty	minty spearmint cooling green herbal caraway spicy	0±0	0±0	0±0	0±0	0±0	0±0	8.29±3.84	2.8±0.85	3.79±0.04	0±0	0±0	0±0
beta-Terpineol	1095			0±0	0±0	0±0	1.15±0.81	1.63±1.6	1.77±0.79	2.41±1.95	0±0	0±0	42.58±43.4	3.58±2.57	4.36±3.16
Dehydro-p-cymene	1105	Floral	sweet floral fruity rose waxy citrus	90.27±45.1	155.26±138.27	218.8±52.88	0±0	0±0	0±0	53.19±15.08	53.41±22.74	20.23±28.61	34.5±21.97	129.78±157.75	122.54±94.19
Linalool	1108	Waxy	waxy green fruity floral	6.59±11.42	2.85±4.94	0±0	35.46±19.52	51.02±28.1	40.71±8.34	13.89±12.11	0±0	0±0	107.46±96.2	201.89±175.61	281.57±209.24
Camphenone, 6-	1133	-	-	1.27±0.57	3.51±1.17	1.61±2.79	0±0	0±0	0±0	5.14±4.3	3.3±0.68	1.4±1.75	0±0	0±0	0±0
Allocimene	1139	-	-	0.97±0.3	0.4±0.7	2.69±2.65	1.55±0.82	1.01±1.75	3.34±0.56	0±0	0±0	0±0	5.04±3.82	6.86±3.23	8.94±4.37
.alpha.-Campholenal	1144	Woody	woody citrus herbal sweet	1.08±0.35	1.92±1.36	1.84±1.19	1.03±0.82	0.55±0.5	3.39±1.69	2.23±3.36	0±0	0.05±0.07	7.96±6.46	10.03±5.62	11.9±5.43
Neo-allo-ocimene	1151	Woody	woody citrus herbal sweet	0.25±0.44	1.88±2.02	2.52±0.85	0±0	0±0	0±0	0±0	0±0	0.6±0.85	4.23±3.74	5.54±1.77	10.94±4.75
Verbenol	1163	Woody	woody	2.6±0.98	5.75±4.92	7.08±1.61	0±0	0±0	0±0	3.34±3.25	0.85±1.48	9.68±13.69	0.82±1.42	5.48±4.21	3.05±2.75
Camphenol, 6-	1185	-	-	4.08±2.48	1.62±2.33	2.35±1.16	1.22±1.57	0.87±0.76	1.99±1.25	12.14±6.36	7.08±1.91	3.34±2.72	4.15±4.83	14.22±3.25	16.37±13.88
Menthol	1188	Woody	herbal woody spicy	2.63±4.55	10.7±7.43	14.51±4.42	2.72±0.7	1.63±0.59	3.46±0.74	0±0	0±0	0±0	0±0	0±0	0±0
(-)-Borneol	1191			1.95±0.58	3.42±2.14	4.84±1.87	0±0	0±0	0±0	6.34±3.23	3.8±1.1	4.6±4.33	3.33±2.36	5.32±0.37	3.75±1.68
1-Myrcenol	1196	Herbal	-	3.33±5.78	20.47±23.57	16.72±17.94	10.83±3.49	6.8±3.65	11.07±3.47	0±0	0±0	0±0	0±0	15.52±26.89	13.22±8.89
p-Cymen-8-ol	1202	-	amber	8.8±11.05	76.13±49.67	43.81±75.88	1.07±0.51	0.65±0.61	1.19±0.46	6.57±3.07	4.54±2.31	1.54±1.34	3.73±2.33	46.46±73.44	9.98±8.55
Myrtenol	1218	-	-	8.39±2.16	23.81±26.81	30.05±15.56	1.98±1.77	2.12±3.67	1.28±2.22	4.09±7.08	6.67±2.72	8.82±12.47	0±0	0±0	0±0
Myrtenal	1221	Herbal	thyme herbal woody dry	0±0	0±0	0±0	0.81±0.17	0.99±0.93	0.35±0.53	0±0	0±0	0±0	0±0	0±0	0±0
gamma-Geraniol	1224	-	-	0±0	0±0	0±0	1.87±0.73	1.2±1.32	1.81±0.48	5.85±2.97	5.87±2.44	6.86±9.4	2.33±2.38	11.35±12.32	7.09±4.36
Verbenone	1230	Spicy	spicy fruity mango	3.4±1.68	10.44±11.27	13.48±7.01	0±0	0±0	0±0	4.33±2.79	2.26±1.7	2.43±3.12	0±0	0±0	0±0
Citronellol	1236			3.76±0.91	10.05±11.48	15.94±7.95	1.15±0.35	0.98±0.76	1.51±0.59	0±0	0±0	0±0	0.53±0.93	8.3±12.24	2.7±1.62
P-Menth-1-en-9-al	1239	-	-	12.17±7.01	27.38±19.59	38.35±12.59	8.76±7.76	11.81±3.79	14.04±2.59	27.54±14.38	13.49±4.83	9.09±8.18	20.57±7.94	48.81±4.73	49.93±32.19
Carveol	1245	Woody	green woody	0.72±0.78	2.77±4.81	0±0	0±0	0±0	0±0	1.03±1.78	1.38±0.65	0.47±0.66	1.44±0.77	6.8±3.31	0±0
beta-Cyclocitral	1248	-	woody	0±0	1.5±2.6	3.15±3.08	1.82±0.89	0.79±0.87	1.36±0.24	2.89±1.74	0.2±0.35	0.31±0.44	0±0	0±0	0±0
2-Carene	1252	-	-	8.17±1.17	8.16±1.57	9.89±5.17	9.42±4.2	8.21±3.64	8.42±3.28	11.75±8.54	0±0	0±0	0±0	0±0	0±0
Geraniol	1261	Woody	woody dry	18.97±4.46	53.12±56.04	69.88±26.11	12.28±4.21	13.59±6.33	16.28±4.54	18.94±7.99	14.29±3.87	7.32±8.34	10.99±3.55	66.2±42.74	39.95±27.32
d-Carvone	1267	-	woody	3.39±2.94	0±0	0±0	0±0	0±0	0±0	26.56±11.54	22.28±1.25	9.63±10.45	3.74±1.42	7.39±9.11	5.97±3.94
Citral	1282	Woody	sweet fresh dry woody spicy	3.22±1.18	7.75±8.38	9.38±3.76	1.04±1.81	0.58±1	0.83±0.77	2.36±1.51	2.54±1.03	1.52±2.15	1.09±0.99	15.23±5.23	6.55±4.51
Perillaldehyde	1298	-	-	1.7±0.82	2.47±3.99	3.37±1.67	0.55±0.96	0.84±1	0.81±0.74	1.59±1.42	0.47±0.82	1.12±1.15	0±0	0±0	0±0
Perillyl alcohol	1301	Herbal	-	7.76±2.24	22.53±27.74	23.58±11.9	0±0	0±0	0±0	7.57±4.55	2.9±1.12	2.65±1.77	0±0	0±0	0±0
Perillyl acetate	1317	-	-	9.39±4.61	24.92±33.07	27.68±14.23	1.17±2.03	0.52±0.45	2.7±1.13	3.61±1.54	4.25±2.44	4±2.2	0±0	0±0	0±0
Damascenone	1391	-	-	8.51±3.85	8.34±7.48	10.58±5.76	3.46±6	5.22±5.31	9.44±1.73	2.17±3.77	5.34±1.88	6.27±5.99	7.46±4.38	10.64±6.15	10.38±9.78
Ylangene	1404	-	-	5.02±6.51	3.46±4.31	4.99±4.21	1.16±1.61	1.06±1.12	1.31±0.39	0.33±0.58	0.38±0.66	1.37±1.59	2.5±2.24	3.22±3.19	5.01±6.91
Geranylacetone	1465	Herbal	herbal spicy honey	5.41±2.13	7.89±4.93	8.61±5.33	0.79±1.38	4.43±2.66	4.68±0.79	5.28±4.58	0±0	0±0	0±0	9.02±3.94	4.53±1.55
.alpha.-Muurolene	1535	Herbal	herbal woody	4.06±5.11	3.55±2.27	3.83±2.42	0±0	0.48±0.84	0±0	2.97±5.14	0.97±1.68	7.04±2.14	8.3±12.9	4.35±0.25	2.24±2.36
Total Monoterpenes	**45**			**382.46±208.66**	**955.42±981.48**	**1138.56±612.36**	**201.4±99.06**	**242.06±175.04**	**273.03±55.68**	**739.72±412.77**	**579.42±247.76**	**541.45±462.06**	**759.17±593.48**	**1843.02±1376.4**	**1695.26±1352.59**
Sesquiterpenes															
alpha-Cubebene	1377	Herbal	thyme herbal woody dry	5.21±4.24	3.89±3.25	4.7±2.27	1.03±0.48	1±0.64	1.61±0.21	1.1±0.42	0.7±0.78	1.06±1.2	1.68±0.56	3.27±2.88	1.93±2.1
Copaene	1408	-	-	8.68±12.31	5.23±6.68	7.89±7.58	1.88±2.09	3.22±2.15	3.78±0.21	2.85±2.02	0.84±1.46	1.77±2.51	4.71±3.28	7.93±3.76	9.9±13.57
epsilon-Muurolene	1423	Spicy	spicy fruity mango	0.56±0.16	0.54±0.87	0.86±0.41	0.76±0.15	0.45±0.48	0.6±0.25	0±0	0±0	0±0	0±0	0±0	0±0
beta-Panasinsene	1439			6.65±9.8	4.29±5.88	5.41±6.49	1.39±2.08	1.58±1.67	1.57±0.5	0.45±0.4	0.63±1.09	1.11±1.58	3.61±2.73	5.69±4.48	8.41±12.29
.alpha.-Ionone	1454	-	-	0.41±0.28	0.8±1.15	1.03±0.53	0.07±0.12	0.45±0.47	0.4±0.42	0±0	0±0	0±0	0±0	0±0	0±0

alpha-Elemene	1458	Woody	green woody	0±0	0±0	0±0	0±0	0±0	0±0	0.31±0.29	0±0	0±0	0.08±0.14	0.2±0.18	0.43±0.75
beta-Caryophyllene	1461	-	woody	0.42±0.49	0.36±0.3	0.41±0.3	0±0	0±0	0.21±0.37	0±0	0.03±0.06	0±0	0±0	0±0	0±0
beta-Farnesene	1469	-	-	0.19±0.34	0.15±0.27	0.35±0.17	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
Dihydro-.beta.-ionol	1473	Woody	woody dry	0.23±0.13	0.24±0.23	0.31±0.1	0±0	0.16±0.14	0.17±0.17	0±0	0±0	0±0	0±0	0±0	0±0
beta-Ionone	1515	-	woody	0.56±0.5	0.8±0.86	1.05±0.82	0.2±0.18	0.56±0.19	0.66±0.13	0.16±0.14	0±0	0±0	0.27±0.34	0.86±0.35	0.94±1.33
.beta.-Longipinene	1525	Woody	sweet fresh dry woody spicy	1.14±1.43	0.97±1.19	0.94±0.58	0.36±0.1	0.22±0.19	0.2±0.17	0.62±0.66	0.14±0.17	0.06±0.09	0±0	0±0	0±0
(-)-cis-beta-Elemene	1548	-	-	0.34±0.37	0.29±0.28	0.2±0.29	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
(+)-delta-Cadinene	1555	Herbal	-	2.7±4.09	2.36±2.8	2.66±2.03	0.16±0.28	0.76±0.57	0.61±0.19	0±0	0.18±0.31	0.39±0.56	0.42±0.45	2.06±2.89	1.87±2.67
trans-Calamenene	1565	-	-	1.47±1.43	1.51±1.59	1.6±0.86	0.75±0.11	0.87±0.53	0.78±0.26	0.32±0.56	0.6±0.6	1.51±0.61	1.36±0.63	2±0.92	1.83±2.1
Cadina-1,4-diene	1572	-	-	11.21±19.42	15.13±17.28	13.95±12.07	0±0	0±0	0±0	0±0	0±0	0±0	11.68±4.29	9.85±17.07	14.18±17.78
.alpha.-Calacorene	1582	-	-	28.68±30.94	24.67±26.05	26.97±14.13	0±0	4.64±8.04	0±0	0±0	0±0	0±0	0±0	0±0	0±0
T-Muurolol	1688	Herbal	herbal spicy honey	33.03±39.95	22.08±19.28	23.65±15.69	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
Cadalene	1719	Herbal	herbal woody	21.74±17.49	23.7±11.78	16.99±3.61	0±0	19.67±3.63	13.26±11.72	0±0	0±0	0±0	4.9±8.5	33.53±6.6	5.74±9.94
Total Sesquiterpenes	**18**			**123.32±143.44**	**107.09±99.82**	**109.03±68.01**	**6.63±5.62**	**33.63±18.75**	**23.89±14.66**	**5.85±4.52**	**3.15±4.49**	**5.93±6.56**	**28.76±20.94**	**65.43±39.17**	**45.27±62.58**

[z] Relative peak area percent compounds were identified by comparison of mass spectra with NIST14 (National Institute of Standards and Technology, Gaithersburg, MD, USA), Flavors and Fragrances of Natural and Synthetic Compounds (FFNSC3, John Wiley & Sons, Inc., Hoboken, NJ, USA), and Adams Essential Oils (Adams 2007) mass spectral libraries and comparison of calculated Kovats retention indices (Kováts 1958) with previously reported values

Table 4. Volatile aroma compounds [z] identified in fresh-market blackberries grown at the University of Arkansas System Division of Agriculture Fruit Research Station and harvested on three dates (early, middle, and late), Clarksville, AR (2021).

				Natchez			Prime-Ark® Traveler			Sweet-Ark® Ponca		
Compound	Retention index	Aroma category	Aroma description	Early	Middle	Late	Early	Middle	Late	Early	Middle	Late
				2391.68±524.92	**2965.99±909.89**	**3336.69±974.61**	**2636.25±923.16**	**3665.85±1222.6**	**2300.84±665.73**	**1687.32±470.93**	**2556.32±881.43**	**1369.27±328.29**
Acids												
Butanoic Acid	774	Cheesy	sharp acetic cheesy buttery fruity	1.79±0.87	12.2±6.84	0±0	0±0	1.02±0.7	2.81±1.58	2.24±0.83	0.28±0.17	0.33±0.2
Pentanoic acid, 4-methyl-	931	Cheesy	pungent cheesy	3.99±0.12	2.44±0.55	3.77±0.93	5.31±1.57	8.7±0.84	4.73±0.69	2.16±0.45	1.44±0.87	1.24±0.37
Hexanoic acid	964	Fatty	sour fatty sweaty cheesy	0±0	0±19.71	28.46±0	0±0	0±0	0±30.6	36.07±0	0±27.52	39.72±0
Octanoic acid	1155	Fatty	fatty waxy rancid oily vegetable	16.17±11.2	0±3	25.78±0.92	10.78±4.71	1.62±0.52	0±0	2.2±1.52	0±0	2.54±2.15
Decanoic acid	1351	Fatty	rancid sour fatty citrus	59.16±0.88	138.61±41.92	126.11±9.93	57.66±81.18	226.95±9.39	100.45±12.97	28.3±9.54	73.77±16.13	40.99±4.51
Dodecanoic acid	1556	Fatty	fatty coconut bay	5.13±0.83	26.48±14.82	11.8±5.38	12.71±1.03	6.32±0.84	6.73±0.37	5.49±1.02	15.8±4.97	3.1±1.3
Total Acids	**6**			**90.23±15.27**	**180.25±88.32**	**198.23±17.3**	**92.6±90.05**	**265.78±18.82**	**123.52±50.12**	**80.07±14.48**	**94.35±50.72**	**88.95±8.63**
Alcohols												
2-Butanol	610	Fruity	sweet apricot	312.31±103.18	305.22±17.3	759.72±353.72	77.96±81.14	308.15±48.78	370.8±94.06	98.58±22.14	90.36±12.55	66.77±9.07
1-Butanol	666	Fermented	fusel oily sweet balsamic whiskey	3.99±1.37	0.52±1.48	2.31±0.14	6.14±1.56	21.17±6.53	8.8±3.91	3.61±1.12	3.06±1.06	1.03±0.1
1-Penten-3-ol	683	Green	ethereal horseradish green radish chrysanthemum vegetable tropical fruity	4.62±2.53	0±0.3	4.8±3.69	18.38±7.57	12.44±3.66	36.42±17.72	13.89±0.53	14.68±4.43	6.4±0.81
3-Buten-1-ol, 3-methyl-	731	Fruity	sweet fruity	5.39±2.05	3.81±0.79	11.73±7.42	69.93±15.53	40.75±15.33	15.41±0.29	68.93±24.93	15.26±7.03	22.38±7.68
1-Butanol, 3-methyl-	738	Fruity	sweety fruity banana solvent	4.25±0.83	2.67±0.91	2.71±1.12	4.69±1.52	4.93±1.3	1.94±0.29	2.95±25.13	39.63±0.71	2.32±0.53
1-Butanol, 2-methyl	743	Ethereal	fusel ethereal alcoholic fatty greasy winey whiskey leathery cocoa	4.03±1.12	3.82±0.6	1.6±0.43	1.89±0.24	4.01±3.39	14.07±2.26	1.32±8.97	14.99±1.48	3.73±0.3
1-Pentanol	763	Fermented	fusel oily sweet balsamic	3.18±1.11	0.53±2.29	5.25±0.65	9.45±1.85	3.94±0.91	5.05±0.4	5.26±1.48	4.01±1.35	3.08±0.31
2-Penten-1-ol	767	Green	-	0.66±0.32	0.45±3.09	8.31±2.3	9.89±2.79	11.35±1.46	9.48±0.81	5.38±0.88	2.17±0.1	4.08±0.75
3-Hexen-1-ol	779	Green	green leafy	40.58±1.9	15.2±10.07	3.54±2.26	6.63±5.14	16.75±5.32	10.75±0.95	4±0.59	4.03±2.79	1.9±0.96
5-Methyl-1-heptanol	900	-	-	0±0	0.04±0.03	0±0	1.49±0.09	1.03±0.22	0.53±0.2	1.01±0.23	0.92±0.24	0.8±0.02
1-Heptanol	966	Green	musty leafy violet herbal green sweet woody peony	48.9±2.09	39.38±14.51	35.87±4.01	104.04±3.8	99.34±19.8	107.56±16.41	63.87±5.67	62.84±8.17	51.28±13.49
1-Octen-3-ol	977	Earthy	mushroom earthy green oily fungal raw chicken	1.53±0.8	2.28±0.42	1.59±0.79	32.83±4.71	45.58±12.91	53.97±20.09	3.46±0.75	18.34±11.13	2.54±0.67
1-Hexanol, 2-ethyl-	1026	Citrus	citrus fresh floral oily sweet	7.46±3.6	6.64±4.34	5.81±0	2.97±0.09	8.64±3.95	0±0.55	1.62±1.21	4.75±0.45	1.6±0.67
1-Octanol	1075	Waxy	waxy green orange aldehydic rose mushroom	1.63±0.27	0.84±0.06	1.4±0.15	0.51±0.12	1.72±0.93	0.33±0.51	1.58±2.36	6.91±1.07	2.43±0.23
Sabinol	1089	-	-	2.68±0.26	3.66±2.3	0.56±0.07	2.55±0.53	5.61±3.05	2.17±0.25	0.87±0.18	0.68±0.15	0.75±0.07
Phenylethyl alcohol	1127	Floral	floral rose dried rose	24.39±1.15	24.49±8.38	13.86±8.59	54.53±13.67	74.75±6.82	45.51±3.93	15.84±8.48	66.63±34.4	15.48±7.8
1-Nonanol	1167	Floral	fresh clean fatty floral rose orange	20.39±12.7	3.47±0.36	3.92±0.23	2.14±0.99	4.01±0.69	3.51±0.33	2.19±0.29	3.28±0.11	2.57±0.15
Verbenol	1177	Balsamic	fresh pine ozone herbal	7.56±1.92	1.57±0.88	9.87±1.94	2.76±0.18	3.84±0.51	2.4±0.22	1.67±0.17	2.33±0.12	2.13±0.14
1-Decanol	1268	Fatty	fatty waxy floral orange sweet clean watery	7.82±0.67	28.84±9.16	18.48±1.35	2.33±1.54	5.99±0.24	3.09±0.51	1.05±0.2	3.36±1.2	1.74±0.58
2-Decen-1-ol	1278	Fatty	waxy fresh ozone citrus rose	0.49±0.04	0.51±0.04	0.45±0.02	0.7±0.07	0.83±0.06	0.5±0.06	0.3±0.03	0.26±0.09	0.24±0.01
1-Nonanol, 4,8-dimethyl-	1289	-	-	0.46±0.01	0.71±0.06	0.56±0.3	0.16±0.11	0±0.06	0.19±0.08	0.16±0.02	0±0.01	0.09±0.01
Perilla alcohol	1300	Green	green cumin spicy aromatic woody	0.3±0	0.39±0.05	1.92±0.35	0.44±0.04	0.51±0.05	0.34±0.06	0.26±0.01	0.38±0.09	0.17±0.02
Perilla alcohol	1311	Green	green cumin spicy aromatic woody	1.8±0.1	1.49±0.44	1.71±0.9	1.4±0.45	1.63±0.23	1.95±0.13	1.73±0.02	2.6±0.39	1.85±0.25
Di-epi-1,10-cubenol	1664	-	-	0.88±0.45	7.24±3.8	3.44±1.82	1.03±0.62	1.52±0.19	2.69±0.78	0.69±0.34	2.53±0.76	0.71±0.08
Total Alcohols	**24**			**501.31±137.1**	**453.25±80.18**	**897.1±392.11**	**408.7±142.79**	**657.32±129.86**	**688.66±160.89**	**296.61±104.61**	**360.94±88.82**	**195.04±44.6**
Aldehydes												
Butanal, 3-methyl-	597	Aldehydic	ethereal aldehydic chocolate peach fatty	132.62±51.69	127.86±60.76	60.18±17.6	185.84±38.72	95.87±3.68	17.73±53.29	86.96±3.11	73.89±27.12	101.73±62.64
Butanal, 3-methyl-	660	-	-	4.62±0.26	7.86±2.49	31.49±24.68	29.19±6.76	4.24±1.88	7.07±0.85	17.23±3.73	10.75±5.81	15.06±0.27
Butanal, 2-methyl	669	Cocoa	musty cocoa phenolic coffee nutty malty fermented fatty alcoholic	3.35±0.98	0±1.01	2.04±0.49	18.57±3.04	2.94±4.13	17.59±4.6	5.88±2.04	11.36±5.68	7.25±4.84
Pentanal	698	Fermented	fermented bready fruity nutty berry	23.52±9.34	4.27±0.53	14.55±7.44	64.11±18.6	19.67±3.96	5.08±0.03	30.91±10.28	14.65±7.06	19.47±4.36
2-Pentenal	754	Green	pungent green ethereal nutty anisic fruity	0.38±0.2	1.62±0.48	1.45±0.16	6.93±1.32	2.8±1.08	6.28±1.32	1.69±0.61	3.3±1.06	2.58±0.06

Hexanal	789	-	-	40.19±2.4	22.8±3.97	36.47±6.35	55.58±0.66	116.27±69.06	81±0.04	0.7±0.09	0.73±0.12	2.47±1.74
2-Hexenal,	845	Green	pungent green apple orange tomato	2.48±0.07	1.25±0.74	0.51±0.02	0.99±3.16	28.86±12.81	0.48±0.19	0.58±1.64	3.84±6.96	11.04±0.29
Heptanal	906	Fruity	sweet fruity pungent brown nutty almond cherry	0.09±0	0.1±0.05	0.02±0	1.09±0.18	0.49±0.08	0.21±0.58	1.28±0.2	1.12±0.35	0.68±0.22
2,4-Hexadienal	911	Green	fresh green fatty aldehydic grassy leafy sweaty	0.13±0.02	0.08±0.03	0.06±0.02	0.34±0.02	0.34±0.08	0.52±0	0.23±0.02	0.21±0.01	0.23±0.03
2-Heptenal	957	Bready	sweet woody almond bread baked caramellike phenolic	2.12±2.11	6.7±0.99	2.75±0.46	9.22±0.73	7.21±0.66	4.25±1.61	3.75±9.04	17.23±1.14	2.67±0.02
Benzaldehyde	968	Green	sweet almond bitter fruity green leafy apple plum vegetable	73.63±5.97	75.3±32.41	54.67±0.84	59.08±2.53	31.22±11.66	45.38±4.52	18.06±3.62	18.22±10.97	42.78±8.71
Octanal	1002	Green	fresh aldehydic fatty green herbal cognac ozone	2.06±0.27	3.08±0.38	4.32±0	5.21±1.45	12.13±3.05	3.17±0.54	2.93±0.63	5.2±1.25	2.34±0.28
Phenylacetaldehyde	1051	Green	green fatty	4.3±0.82	3.31±1.67	7.08±0.07	13.82±4.21	25.6±7.87	7±0.58	5.98±0.71	4.61±2.59	4.95±0.79
2-Octenal,	1059	Fruity	sharp sweet bitter almond cherry	2.6±0.57	6.98±1.24	4.49±0.6	2.03±0.78	3.97±1.14	0.89±1.32	2.85±1.58	4.61±0.13	2.55±1.2
Benzaldehyde, 4-methyl-	1093	Aldehydic	aldehydic waxy citrus orange peel green herbal fresh fatty	9.29±0.23	25.2±5.12	18±3.13	0±0	0.26±0.18	0±0	0±0	0±0.29	0.42±0
Nonanal	1103	Green	green sweet floral hyacinth clover honey cocoa	1.47±0.5	0.64±0	1.29±0.22	11.02±4.27	14.6±2.07	6.9±1.14	6.23±0.83	3.71±2.03	9.03±0.67
2,4-Octadienal, (E,E)-	1111	Fatty	fatty green herbal	1.29±0.37	0.03±0.15	0.5±0.23	1.25±0.29	0.88±0.21	1.09±0.05	0.87±0.09	0.45±0.15	0.98±0.11
2-Nonenal,	1161	Fruity	sweety fruity cherry almond bitter phenolic	7.74±8.86	39.14±9.07	0±0	7.6±5.84	21.23±4.93	25.45±3.97	9.75±3.17	17.9±1.84	12.57±5.5
Decanal	1205	Fruity	fruity cherry phenolic	4.86±0.72	2.76±0.37	1.71±0.88	1±2.85	5.59±0.59	1.55±0.05	1.04±0.41	3.93±0.6	2.49±0.02
2-Decenal,	1263	Aldehydic	waxy aldehydic rose fresh orris orange peel fatty	0±0	0±0	0±0	1.93±2.22	4.95±0.64	1.79±1.04	2.74±0.19	1.68±0.7	2.32±0.04
Geranial	1273	Herbal	herbal green woody amber leafy	9.32±0.38	14.6±1.63	11.52±0.92	3.97±0.63	6.79±0.6	3.41±0.64	2.78±0.48	13.97±6.54	3.96±0.07
Dodecanal	1408	Fatty	fatty green waxy cucumber melon	0.66±0.13	0.19±0.05	0.17±0.09	1.17±0.3	0.69±0.05	0.26±0.04	0.18±0.06	1.03±0.31	0.28±0
Pentadecanal	1721	Aldehydic	sweety aldehydic waxy orange peel citrus floral	2.86±0.24	9.15±3.77	3.22±0.26	5.96±0.35	6.15±0.38	3.72±0.02	3.19±0.36	13.77±4.46	3.49±0.17
Total Aldehydes	**23**			**329.58±86.13**	**352.92±126.91**	**256.49±64.46**	**485.9±98.91**	**412.75±130.79**	**240.82±76.42**	**205.81±42.89**	**226.16±87.17**	**251.34±92.03**
Aromatic hydrocarbons												
Toluene	771	Sweet	benzene	1.2±0.65	1±0.69	1.45±1.23	5.85±1.5	2.98±1.22	1.04±0.23	0.53±0.16	2.46±0.76	1.07±0.04
Styrene	896	Balsamic	sweet balsamaic floral plastic	60.19±3.78	43.2±5.77	36.7±16.22	2.16±0.12	2.1±0.37	2.02±6.55	19.71±4.61	16.31±5.37	11.46±2.75
Benzofuran, 4,7-dimethyl-	1240	-	-	4.86±0.29	5.43±0.7	4.78±0.25	3.18±0.92	6.22±0.66	3.54±0.15	1.87±0.36	7.56±3.2	2.38±0.66
Eugenol	1372	Spicy	sweet spicy clove woody	7.51±0.7	7.02±0.74	6.68±0.42	3.37±1.12	6.55±0.72	4.86±0.09	2.27±0.31	5.55±1.17	1.9±0.2
Copaene	1399	Woody	woody spicy honey	0.35±0.24	7.67±4.79	1.9±1.2	0.59±0.34	0.92±0.03	0.19±0.03	0.13±0.07	0.74±0.22	0.2±0.06
Total Aromatic hydrocarbons	**5**			**74.11±5.66**	**64.32±12.69**	**51.51±19.32**	**15.15±4**	**18.77±3**	**11.65±7.05**	**24.51±5.51**	**32.62±10.72**	**17.01±3.71**
Esters												
Ethyl Acetate	619	Fruity	ethereal fruity tropical pineapple grape banana	236.64±87.28	71.02±38.87	3.58±3.04	454.84±172.83	201.92±137.28	477.42±55.26	161.92±49.96	156.71±44.55	102.03±53.81
Methyl butanoate	621	Fruity	ethereal pineapple fruity apricot strawberry banana bacon	0±0	1.51±0.55	13.12±10.99	2.49±1.37	6.54±4.53	2.46±1.01	0.63±0.06	0.6±0.4	4.52±0.21
Ethyl propionate	711	Acidic	acidic dairy fruity	1.29±0.19	0.72±0.07	0.94±0.29	3.97±2.18	9.28±2.47	5.61±0.95	1.19±0.21	2.09±0.29	1.21±0.32
Methyl butanoate	721	-	-	4.63±2.5	2.55±0.25	0.47±0.06	13.55±5.56	10.87±7.66	34.76±6.48	3.46±0.28	1.63±0.36	1.55±0.18
Ethyl butanoate	799	Fruity	sweet fruity apricot banana tropical pineapple	0.24±0	0.22±0.15	0±0	84.54±19.35	69.61±0.02	0±27.8	76.26±16.69	48.42±16.85	39.31±6.65
Butyl acetate	805	Fruity	sweet fruity ethereal rummy	0.51±0.03	0.38±0.06	0.9±0.34	0.18±0.11	0.13±0.05	0.17±0.05	0±0.23	0.41±0.07	0.19±0.06
Ethyl (2E)-2-butenoate	841	Fatty	sour fatty sweaty cheesy	4.21±0.19	6.73±2.42	0.97±0.82	1.68±3.6	9.55±2.04	1.11±0.13	0.93±0.26	1.3±0.53	1.04±0.48
Ethyl 2-methylbutanoate	850	-	-	9.52±1.14	4.28±30.38	51.65±5.92	22.8±13.86	16.01±12.03	39.58±11.75	23.26±0.13	1.08±0.5	5.02±4.26
3-Hexen-1-ol, (E)-	853	Fruity	sweet fruity ethereal rummy	105.5±39.96	52.07±20.15	28.85±24.48	135.95±58.9	84.98±31.26	41.48±23.46	72.23±24.67	123.15±31.7	45.69±15.64
2-Hexen-1-ol, (E)	865	Fruity	fruity citrus melon	13.12±1.8	23.52±12.99	274.08±102.06	270.21±28.63	104.33±44.71	126.46±85.83	256.9±49.07	179.26±59	50.16±5.16
Methyl hexanoate	922	Fruity	sweet fruity green orris waxy floral berry	0.92±0.1	1.16±0.46	1.25±0.2	2.52±2.32	9.19±0.93	3.52±0.02	1.16±0.1	1.34±0.24	1.19±0.01
Ethyl Butyrate	940	Fruity	ethereal fruity tropical pineapple grape banana	0.45±0.12	2.57±1.56	3.1±2.35	0.64±2.64	7±0.9	1.01±0.25	1.04±0.28	1.53±0.8	1.32±0.1
Ethyl hexanoate	995	Fruity	fruity ethereal tropical green grape cherry banana apple cocoa	1.13±0.74	0.13±0	0±0	4.15±6.11	18.13±4.96	2.17±0	1.16±0.26	2.98±1.11	1.7±0.44
Hexyl acetate $$ Hexyl ethanoate	1008	Fruity	fruity ethereal tropical banana	0.24±0.03	0.2±0.31	0.8±0.02	0.79±0.08	0.44±0.17	0.63±0.01	0.41±0.1	0.26±0.09	0.27±0.06
Methyl octanoate	1121	Fruity	sweet fruity green orris waxy floral berry	110.89±4.31	190.14±34.23	156.95±5.17	103.65±42.49	195.43±41.94	150.25±11.09	91.67±19.01	48.97±5.69	90.51±2.23
Ethyl hydroxy-3-hexanoate	1130	Fruity	green fruity apple blueberry pineapple	69.9±3.99	92.03±16.86	55.55±14.57	55.78±4.41	55.55±11.78	32.58±3.45	35.3±6.28	46.86±4.88	48.42±4.39
Hexyl butanoate	1189	Fruity	fruity green apricot pear banana	5.25±1.11	1.73±0.78	8.95±1.38	1.08±0.33	0±0.26	0.95±1.35	2.11±0.29	1.72±0.3	0.55±0.1
Hexyl 2-methylbutanoate	1244	-	-	0.11±0	0.09±0	0.11±0.03	0.05±0.01	0.04±0	0.05±0	0.04±0	0.06±0	0.03±0
Hexyl hexoate	1382	Cheesy	rancid sour cheesy sweaty	0.94±0.18	0.31±0.15	1.15±0.13	0±0	0±0	0±0	0±0	0.5±0.21	0.16±0.1
2-Hexenyl hexanoate	1385			0±0	0±0	0±0	1.6±0.57	0.31±0.13	0.29±0.24	0.61±0.02	1.05±0.3	0.29±0.24
Ethyl decanoate	1389	Fermented	oily winey fruity floral	0.3±0.01	1.1±0.2	1±0.1	0.21±0.4	1.03±0.05	0.42±0.35	0.76±0.32	1.41±0.25	0.19±0.02

hexyl hexanoate	1517	Fruity	-	2.08±0.51	0.84±0.39	1.57±0.69	0.79±0.43	1.17±0.03	0.29±0.51	2.17±0.35	3.44±0.78	0.25±0.04
Methyl dodecanoate	1526	Waxy	waxy buttery oily creamy dairy green lactonic plum skin	0.07±0.01	0.04±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
Total Esters	**23**			**567.94±144.2**	**453.34±160.83**	**604.99±172.64**	**1161.47±366.18**	**801.51±303.2**	**921.21±229.99**	**733.21±168.57**	**624.77±168.35**	**395.6±94.5**
Ketones												
3-Buten-2-one, 3-methyl-	677	Citrus	citrus green musty lemongrass apple	4.99±2.46	5.5±2.08	0.45±0	10.22±4.76	13.53±9.19	23.3±1.3	3.16±0.28	3.99±1.78	10.97±4.69
2-Heptanone	889	Fruity	fresh sweet green weedy earthy herbal	70.76±2.86	10.92±1.5	9.97±1.45	1.7±0.33	2.81±0.91	0.5±1.08	3.05±0.49	8.33±4.29	15.34±2.33
5-Hepten-2-one, 6-methyl-	985	-	-	1.95±0.08	3.97±1.57	3.94±0	4.65±0.48	1.74±0.68	2.29±0.16	0.91±0.52	2.56±0.61	1.23±0.13
2-Undecanone	1291	Citrus	fruity citrus floral orange	0±0	0.49±0.07	0.63±0.02	0.3±0.07	0.61±0.08	0.17±0.02	0.04±0.06	0.46±0.13	0.11±0.01
2-undecanone	1302	-	-	2.69±0.09	3.97±0.38	2.89±0.53	1.51±0.5	1±0.08	0.66±0.01	0.44±0.07	0.85±0.19	0.35±0.03
2-Undecanone, 6,10-dimethyl-	1402	Floral	orange floral fatty peach	0.42±0.08	0.43±0.1	0.22±0.12	0.56±0.04	0.65±0.08	0.47±0.01	0.23±0.01	2.37±1.32	0.33±0.07
Beta Ionone	1505	Floral	floral woody sweet fruity tropical	0.38±0.03	1.02±0.45	0.59±0.32	0.98±0.2	0.66±0.08	0.54±0.04	0.26±0.07	0.93±0.3	0.27±0.03
Total Ketones	**7**			**81.19±5.6**	**26.3±6.15**	**18.69±2.44**	**19.92±6.38**	**21±11.1**	**27.93±2.62**	**8.09±1.5**	**19.49±8.62**	**28.6±7.29**
Lactones												
gamma-Hexalactone	1055	Tonka	herbal coconut sweet coumarinic	1.6±1.32	7.98±2.31	9.78±0.68	8.62±1.95	13.03±5.22	4.79±0.18	4.88±1.5	10.91±3.06	3.76±0.97
Geranylacetone	1455	Floral	fresh green fruity waxy rose	0.33±0.02	0.28±0.1	0.66±0.09	3.67±0.51	2.12±0.02	1.17±0.15	0.27±0.05	1.04±0.39	0.29±0.01
gamma decalactone	1481	Fruity	fresh oily waxy peach coconut buttery	0.05±0.03	2.4±1.42	0.69±0.4	3.36±0.75	2.17±0.29	2.06±0.05	1.23±0.04	3.32±1.01	2.83±1.26
Total Lactones	**3**			**1.98±1.37**	**10.66±3.83**	**11.13±1.17**	**15.65±3.21**	**17.32±5.53**	**8.02±0.38**	**6.38±1.59**	**15.27±4.46**	**6.88±2.24**
Monoterpenes												
.alpha.-Thujene	933	-	-	15.95±1.42	23.88±11.25	14.78±2.93	24.29±50.77	152.05±40.44	16.99±0.65	21.67±11.17	21.96±9.68	19.19±8.63
alpha.-Pinene	943	Herbal	herbal waxy	2.37±1.01	0.44±7.88	27.97±11.85	11.42±3.68	0±1.43	6.33±0.31	3.72±3.93	11.57±1.95	2.99±0.52
Camphene	962	-	-	3.22±0.07	0.38±0.1	0.37±0.31	0±0.91	1.32±0	0±0	0±0	0±0	0±0
beta.-Myrcene	991	-	-	13.1±2.38	39.51±11.22	32.56±7.29	0±6.01	18.84±4.17	0±0	4.65±1.26	15.3±1.99	15.03±0.11
alpha.-Phellandrene	1012	Woody	woody spicy honey	173.89±6.25	171.6±32.59	129.24±26.74	0±18.44	30.25±2.52	0±0	0±1.03	1.49±7.88	11.37±0
delta 3-Carene	1018	Herbal	herbal waxy fresh	0.2±0	0.07±0.11	0.61±0.05	2.67±0.78	3.71±2.09	2.93±1.42	5.22±1.68	6.13±2.01	2.15±0.08
.alpha.-Terpinene	1024	Woody	sweet woody rose medicinal fir needle	3.69±0.68	3.07±0.73	4.55±0.05	6.88±1.42	5.22±1.84	2.76±0.33	1±0.76	2.38±0.11	1.75±0.26
Cymene	1032	Woody	sweet woody rose medicinal fir needle	0.56±0.28	3.07±0.31	2.4±0.33	0.41±0.25	0.83±0.18	0.29±0.03	0.21±0.05	0.38±0.04	0.34±0.01
D-Limonene	1037	Spicy	sweet woody spicy clove dry	2.54±0.5	12.73±7.63	14.15±5.14	3.78±5.21	12.9±2.44	2.36±0.22	1.89±0.3	4.02±1.47	1.83±0.17
(Z)-beta-Ocimene	1039	Spicy	sweet woody spicy clove dry	1.2±0.05	0.65±0	0.7±0.6	0±0	0±0.33	0.73±0	0.21±0.14	0±0	0.3±0.25
beta.-Phellandrene	1044	-	-	0.16±0.03	0±0	0±0	0.38±0.1	0.51±0.21	0.22±0.02	0.16±0.3	0.48±0.27	0.45±0.05
trans-.beta.-Ocimene	1048	Spicy	sweet woody spicy clove dry	0.52±0.27	1.99±0.26	1.48±0.03	0.31±0.22	0.64±0.08	0.29±0.18	0.47±0.07	2.28±0.91	0.68±0.14
Cymene	1063	-	-	7.08±1.1	1.13±0	0±0	3.79±1.33	1.43±0.86	6.43±1.71	1.41±0.19	3.92±1.04	4.79±1.56
gamma.-Terpinene	1066	Woody	woody citrus herbal sweet	8.03±1.6	29.09±4.12	53.4±15.4	4.96±2.88	8.35±1.09	3.89±1.51	5.71±1.14	4.13±1.43	4.43±0.56
Linalool oxide	1097	Woody	woody citrus herbal sweet	10.09±0.3	3.75±1.39	52.49±30.62	3.18±3.91	14.51±1.72	3.82±0.8	4.11±25.2	48±4.05	3.78±0.4
Linalool	1100	Woody	woody	12.77±0.8	10.91±3.51	9.09±0.52	6.16±0.57	3.26±1.13	2.11±24.31	53.99±10.19	170.16±45.39	76.26±8.89
4,6-Allocimene	1145	-	-	0.95±0.29	0.95±0.28	0.8±0.08	0.16±0.14	0.6±0.06	0.41±0.02	0.15±0.08	0.65±0.11	0.47±0.01
Carveol	1149	Woody	herbal woody spicy	57.09±39.71	179.8±22.3	194.93±26.69	73.02±22.84	850.41±495.68	0±23.28	56.26±25.78	484.76±257.55	49.89±7.5
endo-Borneol	1183			2.68±1.3	6.6±0.95	2.59±0.08	2.87±0.11	6.02±2.01	1.91±0.1	1.08±0.13	1.72±0.09	1.44±0.18
Terpinen-4-ol	1190	Herbal	-	53.24±9.43	31.13±6.24	86.93±6.32	13.55±13.51	49.63±6.24	9.16±6.68	12.99±0.75	12.75±2.91	4.47±0.43
p-Cymene-8-ol	1193	-	amber	156.1±27.38	306.69±89.79	269.79±57.54	2.73±13.19	36.51±7.77	7.09±1.9	8.71±5.12	46.21±9.09	14.99±2.58
L-.alpha.-Terpineol	1201	-	-	27.86±1.12	45.87±1.44	85.4±29.28	19.05±1.29	10.26±1.33	4.87±5.34	14.19±1.94	48.8±7.97	32.28±0.23
Myrtenol	1213	Herbal	thyme herbal woody dry	0±0	0±0	0±0	1.06±0	0±0	0±1.72	3.59±1.07	3.64±1.26	0±0
Myrtenal	1220	-	-	5.65±0.3	7.54±0.69	6.5±0.68	1.98±0.52	3.73±0.33	1.89±0.28	1.74±0.17	1.76±0.32	1.4±0.2
Verbenone	1226	Spicy	spicy fruity mango	3.33±0.46	8.68±1.25	6.87±0	1.96±0.32	2.74±0.29	1.62±0.02	1.15±0.11	13.36±8.26	1.47±0.3
Citronellol	1231			4.09±0.12	5.63±0.2	6.92±1.23	1.56±0.14	2.12±0.16	1.1±0.38	1.6±0.26	4.75±0.8	2.38±0.07
Benzothiazole	1247	-	-	0±0	5.76±0.72	24.48±12.84	3.54±1.98	5.46±0.51	1.34±0	0.99±0.39	4.82±1.37	2.92±0.15
methyl carvacrol	1249	Woody	green woody	0±0	0±0	0±0	0.15±0	0±0	0±0	0±0	0±0	0±0
Geraniol	1254	-	woody	80.48±3.82	88.11±6.81	107.47±21.04	13.38±0	0±19.89	43.08±28.47	76.39±15.51	66.85±23.88	23.21±19.69
Carvone	1257	-	-	33.23±7.72	28.28±6.46	12.06±10.23	31.97±2.54	62.09±15.11	37.25±21.07	0±11.19	33.51±12.86	39.97±17.29
Ylangene	1395	Woody	woody dry	0.19±0.06	2.43±1.48	0.5±0.26	0.25±0.11	0.38±0.01	0.14±0.02	0.1±0.03	0.45±0.12	0.13±0.01

Total Monoterpenes	**31**			**680.26±108.45**	**1019.74±219.71**	**1149.03±268.13**	**235.46±153.17**	**1283.77±609.92**	**159.01±120.77**	**283.36±119.94**	**1016.23±404.81**	**320.36±70.27**
Sesquiterpenes		Woody	sweet fresh dry woody spicy									
alpha.-Cubebene	1368	-	-	17.57±1.55	28±8.72	21.81±6.46	15.25±7.16	19.11±1.14	12.1±2.98	5.41±1.37	14.69±2.14	5.81±1.29
Beta Caryophyllene	1425	Herbal	-	0.02±0.01	0.17±0.08	0.01±0.01	0.19±0.02	0.13±0.02	0.1±0	0.04±0.04	0.14±0.02	0±0
.beta.-Panasinsene	1430	-	-	0.15±0.23	6.76±4.22	1.56±1.04	0.42±0.4	0.85±0.02	0.16±0.04	0.1±0	0.84±0.43	0.12±0.05
gamma.-Elemene	1517	-	-	1.19±0.29	0.48±0.22	0.9±0.39	0.45±0.24	0.67±0.02	0.18±0.28	1.24±0.2	1.96±0.44	0.14±0.02
.beta.-Longipinene	1521	Woody	green woody	0.11±0.02	1.16±0.67	0.33±0.1	0.83±0.1	0.49±0	0.28±0.01	0.1±0.03	0.39±0.1	0.11±0.01
delta.-Cadinene	1523	-	woody	0±0	1.2±0.76	0.04±0	0±0	0±0	0±0	0±0	0±0	0±0
alpha.-Muurolene	1525	-	-	0.29±0.02	0.09±0	0±0	0±0	0±0	0±0.01	0.01±0.01	0.02±0	0±0
.beta.-Guaiene	1528	Woody	woody dry	0±0	37.09±22.34	15.07±3.49	56.9±6.71	29.25±2.37	25.31±0.68	14.55±1.24	26.17±7.22	11.29±1.46
delta.-Cadinene,	1551	-	woody	23.21±14	253.97±136.31	75.61±13.52	41.57±26.24	94.63±3.63	51.67±8.43	13.25±5.2	52.27±14.71	28.71±0.49
trans-Calamenene	1556	Woody	sweet fresh dry woody spicy	4.73±2.56	11.06±6.48	5.24±1.77	24.84±6.73	17.49±0.77	13.05±2.27	6.99±1.46	7.84±0.31	5.25±0.12
alpha.-Calacorene	1574	-	-	5.05±0.92	41.12±23.11	15.26±6.15	42.75±7.83	14.52±0.91	10.87±1.74	2.2±0.94	15.17±7.37	4.51±0.92
Ethyl dodecanoate	1593	Herbal	-	8.03±0.8	13.43±3.7	7.87±1.89	5.97±0.43	5.98±0.61	4.18±0.33	4.45±1.14	41.4±22.75	6.67±0.14
.tau.-Muurolol	1676	-	-	1.01±0.24	7.22±3.89	3.21±1.46	3.43±0.83	2.12±0.13	0.58±0.09	0.59±0.07	2.2±0.81	0.78±0.18
alpha.-Cadinol	1676	-	-	1.4±0.09	1.04±0.32	0.1±0.08	4.46±0.59	0.77±0.53	0.17±0.09	0±0	0.44±0.3	0.2±0.17
Muurolol	1680	-	-	1.25±0.31	1.02±0.19	1.51±0.59	3.34±1.05	0.51±0.12	0.77±0.43	0±0	0.17±0.18	0.31±0
Cadalene	1711	Herbal	herbal spicy honey	0.16±0.04	0.69±0.19	0.4±0.08	0.42±0.01	0.37±0.06	0.13±0	0.12±0.01	0.35±0.07	0.16±0
Epicubenol	1747	Herbal	herbal woody	0.91±0.06	0.71±0.07	0.6±0.01	0.58±0.13	0.74±0.05	0.47±0.11	0.23±0.13	2.44±0.91	1.43±0.17
Total Sesquiterpenes	**17**			**65.08±21.14**	**405.21±211.27**	**149.52±37.04**	**201.4±58.47**	**187.63±10.38**	**120.02±17.49**	**49.28±11.84**	**166.49±57.76**	**65.49±5.02**

[z] Relative peak area percent compounds were identified by comparison of mass spectra with NIST14 (National Institute of Standards and Technology, Gaithersburg, MD, USA), Flavors and Fragrances of Natural and Synthetic Compounds (FFNSC3, John Wiley & Sons, Inc., Hoboken, NJ, USA), and Adams Essential Oils (Adams 2007) mass spectral libraries and comparison of calculated Kovats retention indices (Kováts 1958) with previously reported values

Table 5. Four volatile aroma compounds (µg/kg) with the highest levels in fresh-market blackberry cultivars harvested on three dates from the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2020)

	Compound			
	2-Methylbutanoic Acid	5-Hexenal, 4-methylene	Hexanal	2-phenylethanol
	Compound class			
	Ester	Aldehyde	Aldehyde	Alcohol
	Aroma category			
	Fruity	Fruity/Cocoa	Green/Fat	Floral
	Aroma descriptors			
Cultivar [z]	Fruity, pineapple, anise	Cocoa, honey, coffee	Green, herbal tea, spearmint	Floral, rose, honey
Natchez				
Early	3.64 ± 2.81	14.20 ± 24.60	3.64 ± 2.81	12.39 ± 14.76
Middle	30.56 ± 32.53	235.02±205.86	17.88 ± 14.10	55.76 ± 17.77
Late	51.82 ± 21.41	65.21±110.90	21.95 ± 9.17	77.38 ± 12.78
Prime-Ark® Horizon				
Early	15.52 ± 10.51	17.14 ± 27.09	52.72 ± 33.79	20.05 ± 1.07
Middle	20.84 ± 17.95	36.47 ± 39.83	0.03 ± 0.06	16.51 ± 7.24
Late	32.36 ± 15.50	4.47 ± 1.75	51.38 ± 27.05	21.37 ± 10.68
Prime-Ark® Traveler				
Early	38.81 ± 29.92	3.74 ± 4.44	56.84 ± 46.61	36.72 ± 5.36
Middle	19.57 ± 4.71	.90 ± 1.62	9.11 ± 0.23	29.06 ± 6.07
Late	46.38 ± 2.62	2.80 ± 0.21	83.11 ± 1.06	57.17 ± 23.48
Sweet-Ark® Ponca				
Early	77.60 ± 25.41	0.53 ± 0.91	47.80 ± 41.26	24.11 ± 7.01
Middle	139.07 ± 74.90	49.76 ± 52.71	48.17 ± 6.55	51.03 ± 32.13
Late	167.24 ± 85.10	110.78 ± 6.07	51.39 ± 10.33	40.97 ± 17.44

Table 6. Four volatile aroma compounds (µg/kg) with the highest levels in fresh-market blackberry cultivars harvested on three dates from the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2021)

	Compound			
	2-Butanol	Ethyl acetate	2-Hexen-1-ol	Methyl octanoate
	Compound class			
	Alcohol	Ester	Alcohol	Ester
	Aroma category			
	Fruity	Ethereal	Fruity	Waxy
	Aroma descriptors			
Cultivar [z]	Sweet apricot	Ethereal, fruity, sweet, grape and rum-like	Sharp, green, leafy, fruity, unripe banana	Waxy, green, orange, vegetable, herbal
Natchez				
Early	312.31±103.18	236.64±87.28	13.12±1.80	110.89±4.31
Middle	305.22±17.30	71.02±38.87	23.52±12.99	190.14±34.23
Late	759.72±353.72	3.58±3.04	274.08±102.06	156.95±5.17
Prime-Ark® Traveler				
Early	77.96±81.14	454.84±172.83	270.21±28.63	103.65±42.49
Middle	308.15±48.78	201.92±137.28	104.33±44.71	195.43±41.94
Late	370.8±94.06	477.42±55.26	126.46±85.83	150.25±11.09
Sweet-Ark® Ponca				
Early	98.58±22.14	161.92±49.96	256.9±49.07	91.67±19.01
Middle	90.36±12.55	156.71±44.55	179.26±59.01	48.97±5.69
Late	66.77±9.07	102.03±53.81	50.16±5.16	90.51±2.23

Table 7. Principal components (PC) analysis of volatile aroma compounds in fresh-market blackberry cultivars grown at the University of Arkansas System Division of Agriculture Fruit Research Station and harvested on three dates, Clarksville, AR (2020).
Percent of variation in data explained by each component.
Compound class variables represent the sum of the total ion chromatogram (TIC) relative peak areas (%) of positively identified compounds within each compound class (Table 3)

		Principal Component 1 (42.94%) Aldehydes → Lactones	**Principal Component 2 (21.00%)** Alcohols → Sesquiterpenes
Positive loadings	*Compound classifications*	Ketones Acids Esters Sesquiterpenes Aromatic hydrocarbons Lactones	Furans Aromatic hydrocarbons Lactones Esters Aldehydes Monoterpenes Acids Ketones Alcohols
	Cultivar / Harvest Date	Prime-Ark® Traveler Late Natchez Early Natchez Middle Natchez Late	Sweet-Ark® Ponca Late Prime-Ark® Horizon Early Prime-Ark® Traveler Early Natchez Middle Prime-Ark® Horizon Late Prime-Ark® Traveler Late Natchez Late Sweet-Ark® Ponca Middle
Negative loadings	*Compound classifications*	Monoterpenes Alcohols Furans Aldehydes	Sesquiterpenes
	Cultivar / Harvest Date	Sweet-Ark® Ponca Early Prime-Ark® Traveler Early Prime-Ark® Horizon Early Sweet-Ark® Ponca Middle Sweet-Ark® Ponca Late Prime-Ark® Traveler Middle Prime-Ark® Horizon Late Prime-Ark® Horizon Middle	Sweet-Ark® Ponca Early Prime-Ark® Traveler Middle Prime-Ark® Horizon Middle Natchez Early

Table 8. Principal components (PC) analysis of volatile aroma compounds in fresh-market blackberry cultivars grown at the University of Arkansas System Division of Agriculture Fruit Research Station and harvested on three dates, Clarksville, AR (2021).
Percent of variation in data explained by each component.
Compound class variables represent the sum of the total ion chromatogram (TIC) relative peak areas (%) of positively identified compounds within each compound class (Table 3)

		Principal Component 1 (35.56%) Acids → Ketones	**Principal Component 2 (27.68%)** Aromatic hydrocarbons → Esters
Positive loadings	*Compound classifications*	Aromatic hydrocarbons	Sesquiterpenes
		Esters	Acids
		Aldehydes	Alcohols
		Alcohols	Monoterpenes
		Sesquiterpenes	Ketones
		Monoterpenes	Aromatic hydrocarbons
		Lactones	
		Acids	
	Cultivar / Harvest Date	Sweet-Ark® Ponca Middle	Natchez Late
		Prime-Ark® Traveler Early	Natchez Middle
		Natchez Late	Natchez Early
		Natchez Middle	
		Prime-Ark® Traveler Middle	
Negative loadings	*Compound classifications*	Ketones	Aldehydes
			Lactones
			Esters
	Cultivar / Harvest Date	Prime-Ark® Traveler Late	Sweet-Ark® Ponca Middle
		Natchez Early	Sweet-Ark® Ponca Late
		Sweet-Ark® Ponca Early	Prime-Ark® Traveler Middle
		Sweet-Ark® Ponca Late	Sweet-Ark® Ponca Early
			Prime-Ark® Traveler Late
			Prime-Ark® Traveler Early

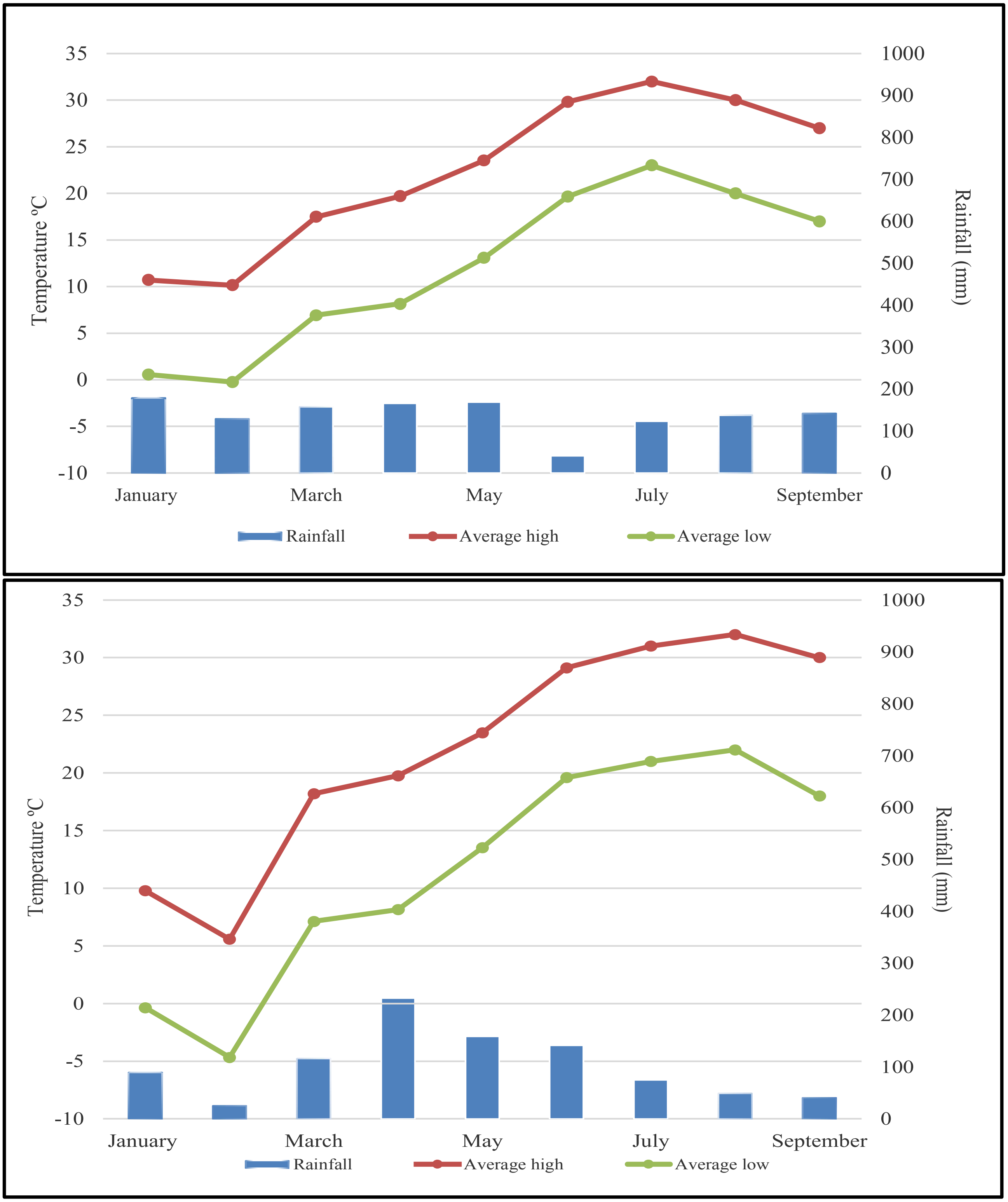

Fig. 1. Temperature and rain conditions from January to September at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2020 top and 2021 bottom)

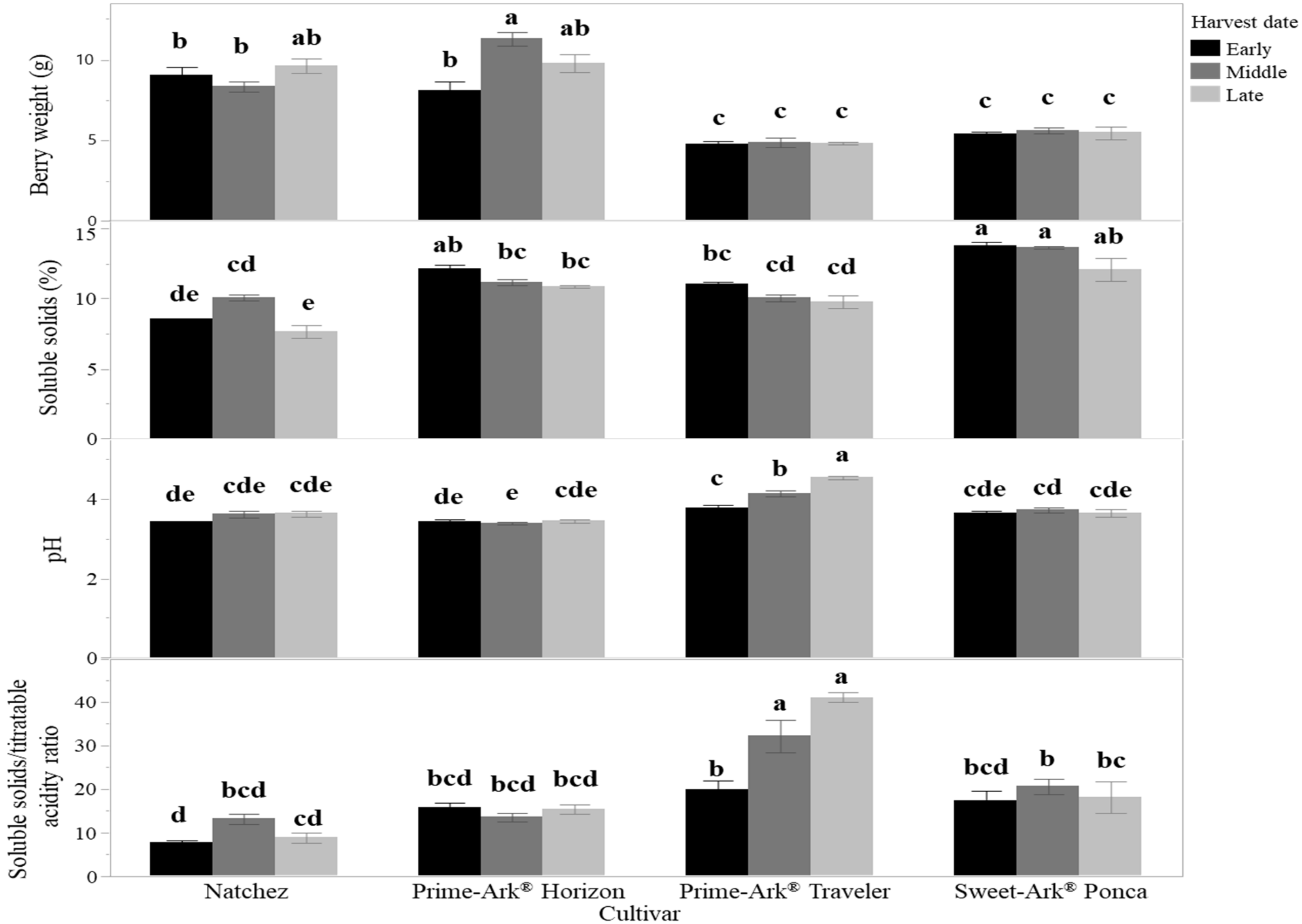

Fig. 2. Interaction of cultivar x harvest date on berry size, soluble solids, pH, and soluble solids/titratable acidity ratio of fresh-market blackberries harvested from the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2020)

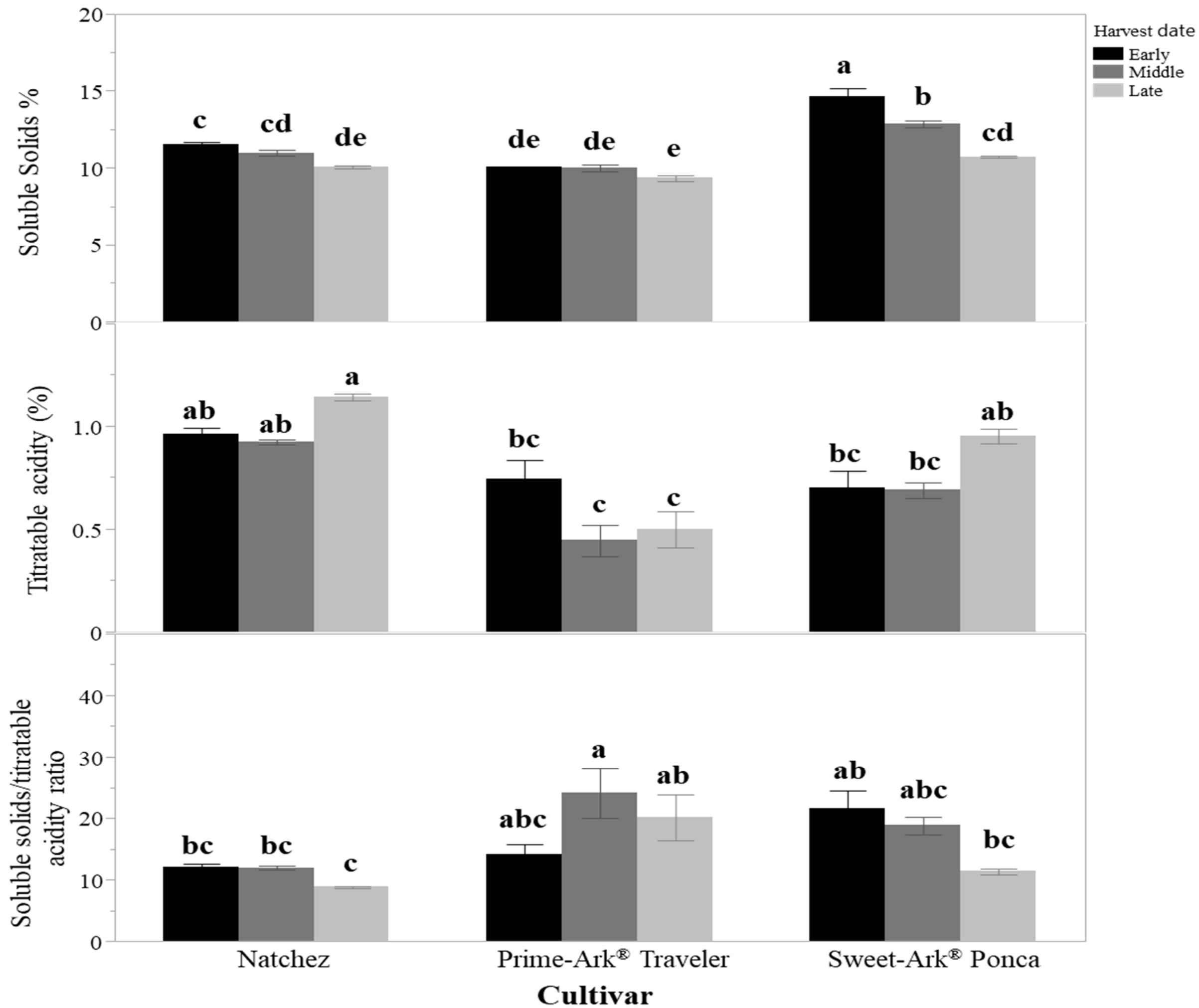

Fig. 3. Interaction of cultivar x harvest date on berry size, soluble solids, pH, and soluble solids/titratable acidity ratio of fresh-market blackberries harvested from the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2021)

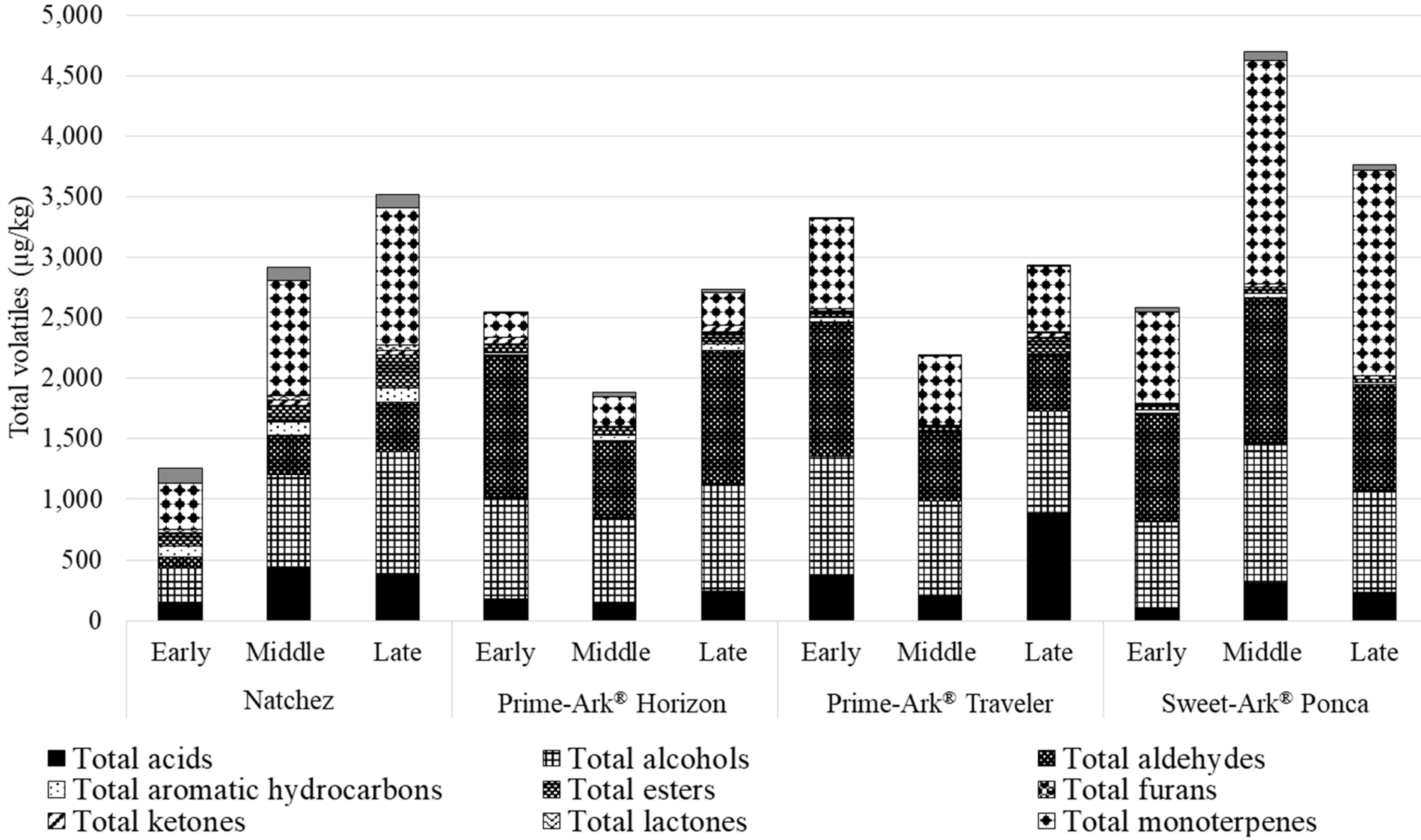

Fig. 4. Total concentrations of volatile aroma compounds identified in fresh-market blackberry cultivars grown at the University of Arkansas System Division of Agriculture Fruit Research Station and harvested on three dates, Clarksville, AR (2020).

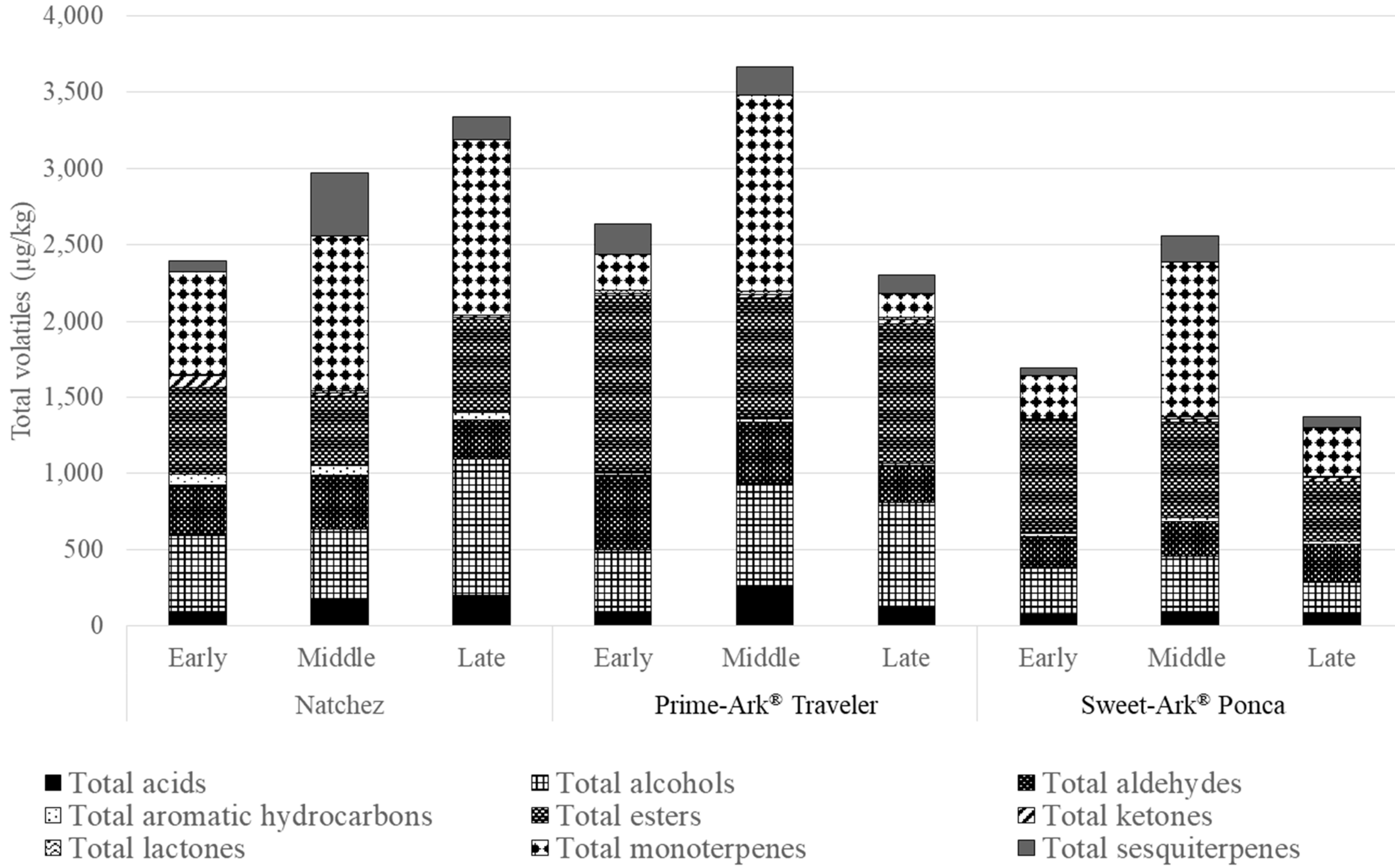

Fig. 5. Total concentrations of volatile aroma compounds identified in fresh-market blackberry cultivars grown at the University of Arkansas System Division of Agriculture Fruit Research Station and harvested on three dates, Clarksville, AR (2021).

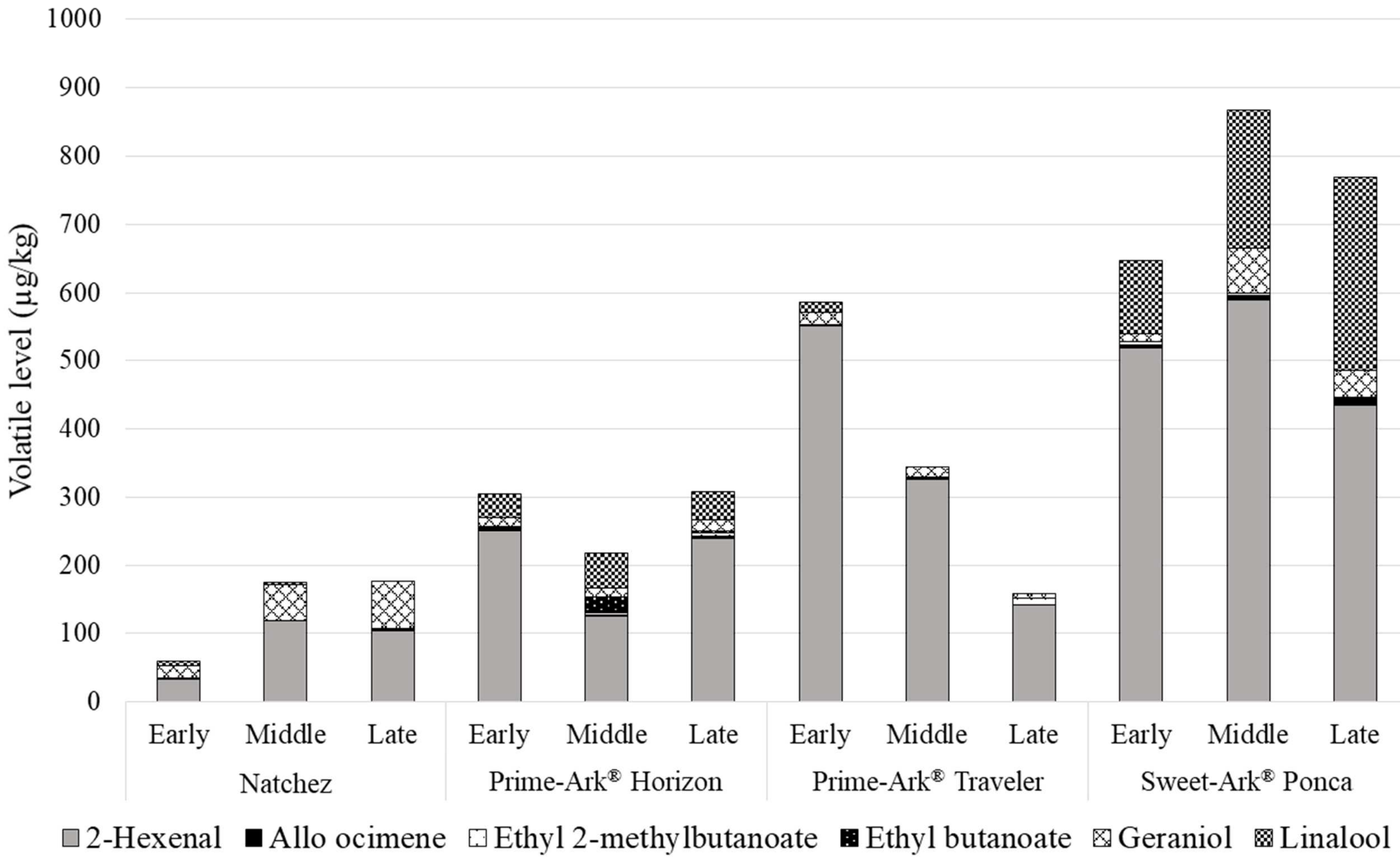

Fig. 6. Total concentrations of impactful volatile aroma compounds identified (µg/kg) in fresh-market blackberry cultivars grown at the University of Arkansas System Division of Agriculture Fruit Research Station and harvested on three dates, Clarksville, AR (2020).

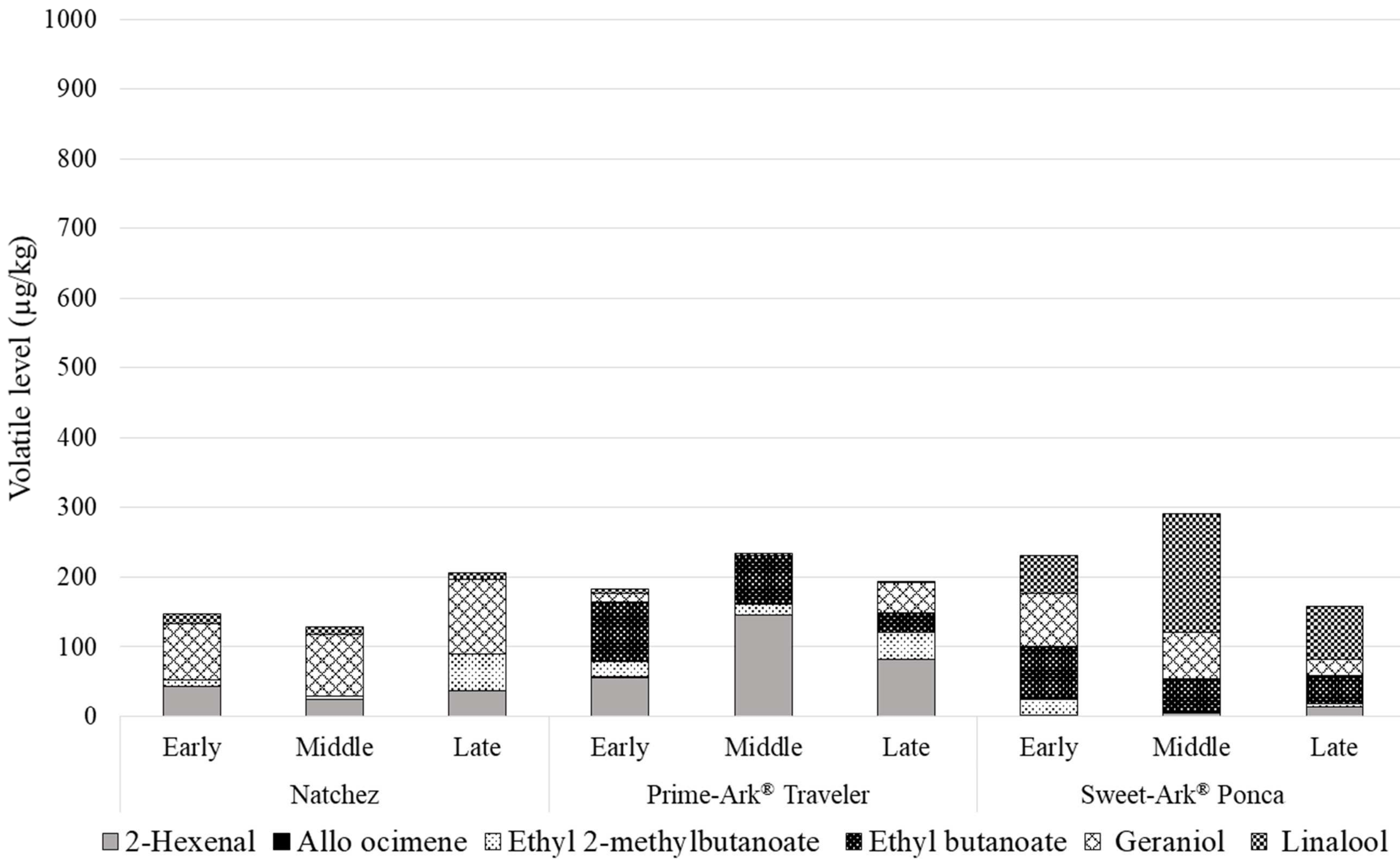

Fig. 7. Total concentrations of impactful volatile aroma compounds identified (µg/kg) in fresh-market blackberry cultivars grown at the University of Arkansas System Division of Agriculture Fruit Research Station and harvested on three dates, Clarksville, AR (2021).

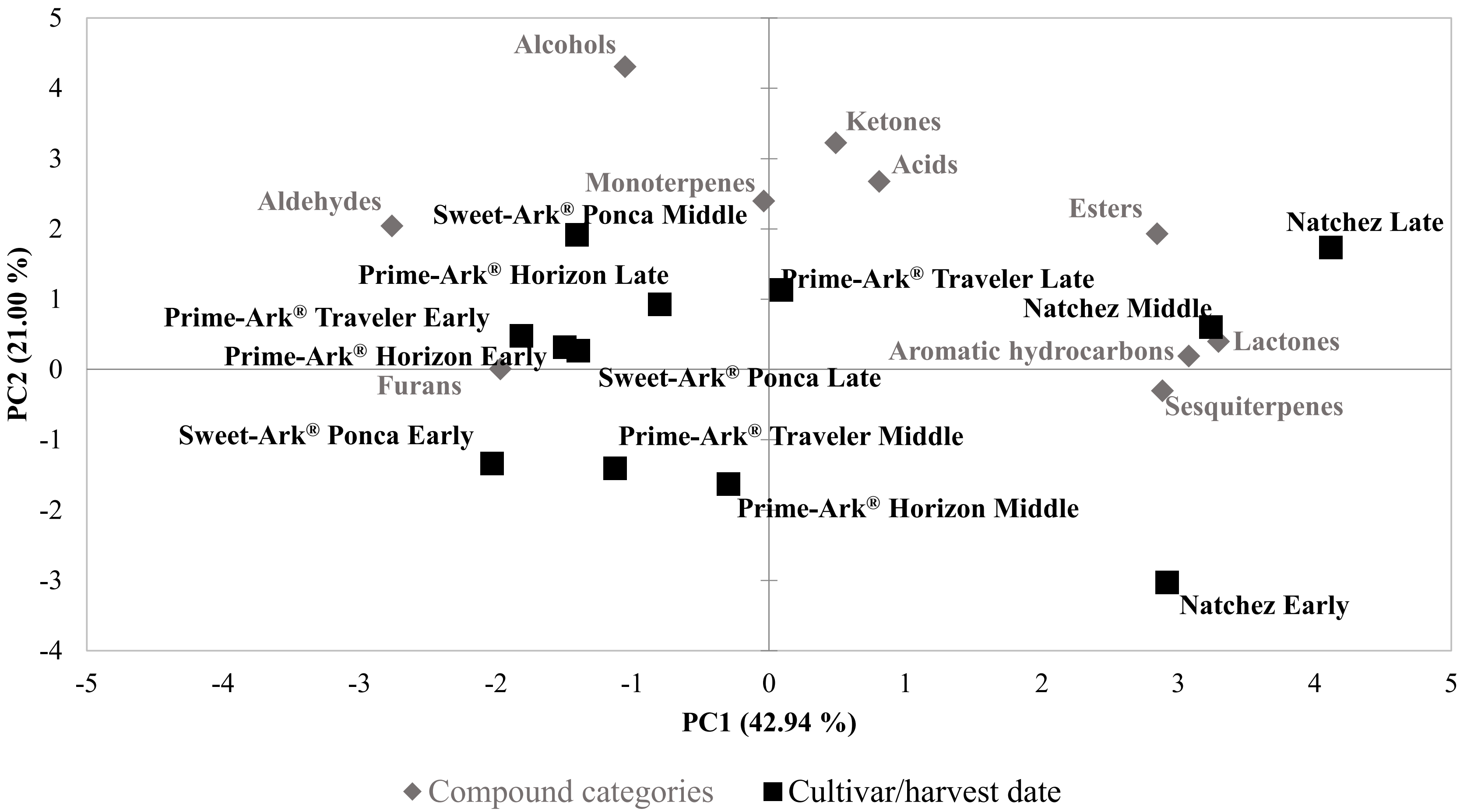

Fig. 8. Principal components (PC) analysis of volatile aroma compounds in fresh-market blackberry cultivars grown at the University of Arkansas System Division of Agriculture Fruit Research Station and harvested on three dates, Clarksville, AR (2020).
Percent of variation in data explained by each component.
Compound class variables represent the sum of the total ion chromatogram (TIC) relative peak areas (%) of positively identified compounds within each compound class (Table 3)

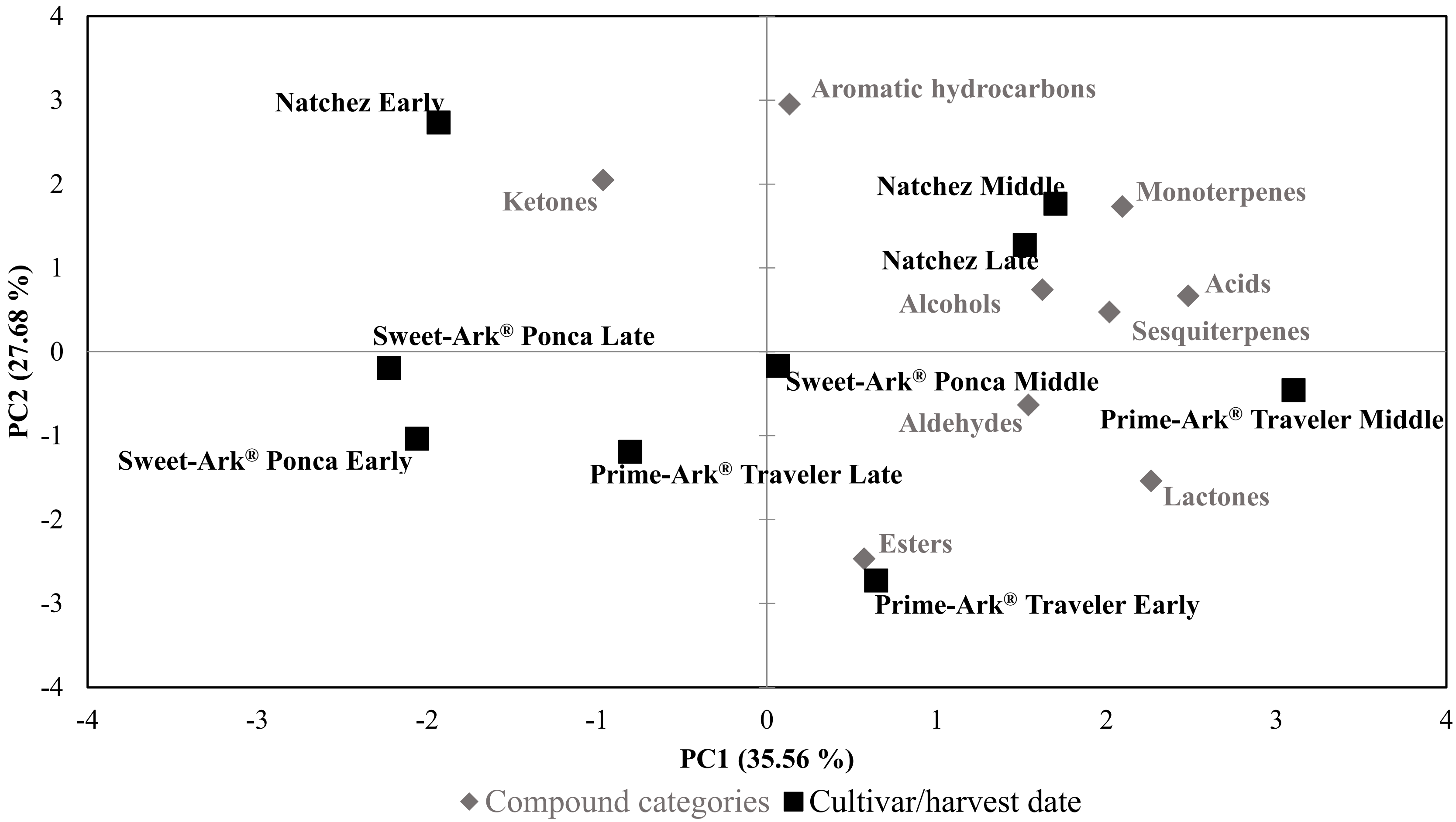

Fig. 9. Principal components (PC) analysis on volatile aroma compounds in fresh-market blackberry cultivars grown at the University of Arkansas System Division of Agriculture Fruit Research Station and harvested on three dates, Clarksville, AR (2021).
Percent of variation in data explained by each component.
Compound class variables represent the sum of the total ion chromatogram (TIC) relative peak areas (%) of positively identified compounds within each compound class (Table 4).

Chapter III

Identification of Flavor and Aroma Attributes of Fresh-market and Processing Muscadine Grapes

Abstract

Muscadine grapes (*Vitis rotundifolia* Michx.), a disease-resistant specialty crop native to the southeastern United States has had major advances in U.S. muscadine breeding efforts resulting in unique traits, including new seedless cultivars to expand commercial, fresh-market potential. Retaining the unique flavors and aromas of muscadines are a focus in creating new cultivars for the commercial fresh markets. In 2021, muscadine genotypes (cultivars and advanced breeding selections) were evaluated at the University of Arkansas (UA) System Division of Agriculture. The genotypes were harvested from the UA System Fruit Research Station in Clarksville, AR and a private grower in Kings Mountain, NC. Six seeded and ten seeded and seedless genotypes were harvested in Arkansas and North Carolina, respectively. Fruit was harvested from both locations, and fruit was from North Carolina was shipped in clamshells to Arkansas for evaluation. Physical, compositional, and volatile attributes of the muscadines were evaluated at the UA System Food Science Department, and each of these attributes were significantly impacted by genotype. Regardless of location, the berry weight (1-14 g), soluble solids (14-19%), pH (3-4), titratability acidity (0.3-1.1%), and soluble solids/titratable acidity ratio (16-70) were impacted by genotype. In the 16 genotypes harvested in both locations, volatile compounds ranged from 2,151-5,746 µg/kg with 201 volatile aroma compounds identified across nine compound classes including 52 esters, 38 monoterpenes, 31 sesquiterpenes, 29 alcohols, 27 aldehydes, 16 ketones, four lactones, two aromatic hydrocarbons, and two epoxides. The three muscadine genotypes with the highest concentrations of volatiles

were AM-154 (5,746 µg/kg), ‘Lane’ (5,285 µg/kg), and ‘Hall’ (5,108 µg/kg), while the three muscadine genotypes with the lowest concentration of volatiles were AM-77 (2,151 µg/kg), JB 06-30-2-20 (2,367 µg/kg) and AM-148 (2,468 µg/kg). Seven compounds with a high aromatic impact were also identified of which geraniol (monoterpene with floral and fruity aromas) had the highest level in most genotypes (3-638 µg/kg). Principal component analysis of the volatile aroma compound classes and genotype indicated that in addition to genotype, growing location and seedlessness may have an impact on volatile attribute profiles. Data generated from this project provided information on physical, composition, and volatile attributes of muscadine grapes that can be used to support future muscadine breeding efforts.

Introduction

Muscadine grapes (*Vitis rotundifolia* Michx.) are a disease-resistant specialty crop native to the southeastern United States. The black, bronze, and red grapes are traditionally used for the production of juice, wine, jelly, or jams, but have potential for increased fresh-market expansion. Advances in U.S. muscadine breeding have resulted in unique traits emerging with commercial, fresh-market potential providing opportunity to strengthen the market presence for muscadines as a southern region crop. Due to the high humidity and incidence of disease in the southern region of the United States, grapes grown for commercial production need an increased disease tolerance, such as muscadines and other native grapevine species. In the South, muscadines are better adapted than *V. vinifera*, which makes cultivation easier for muscadines (Morris and Brady, 2004). Muscadines are resistant to many diseases and pests such as Pierce's disease (*Xylella fastidiosa*), grape fan leaf virus (*Nepovirus* spp.), and anthracnose (*Elsinoë ampelina Shear*) as compared to *V. vinifera* grapevines (Bouquet, 1981; Hopkins, 1974; Ren and Lu, 2002). Muscadines differ markedly from *V. vinifera* 'bunch' grapes in terms of genetics, morphology, production, and consumer experience. Muscadines have smaller clusters, unbranched tendrils, berries that abscise (shatter) at maturity, and distinctive fruity/floral aromas and thick skins. Muscadines are grown from Delaware to central Florida and from the Atlantic coast to eastern Texas and can be a profitable enterprise for commercial growers (Lane, 1997; Noguera et al., 2005). The top commercial muscadine-producing states are North Carolina (1,052 ha), Georgia (688 ha), and Florida (486 ha or 1,200 acres) (USDA NASS, 2012).

There are public and private muscadine breeding programs across the southern United States in Arkansas, Florida, Georgia, and North Carolina. Previous advances in muscadine breeding include the development of perfect-flowered and self-fruitful cultivars, increased berry size and sugar content, presence of dry picking scars, and the introduction of a seedless muscadine grape (Conner, 2010). Other traits undergoing development include more cultivars with perfect flowers and large fruit, improved textures, thinner skins, a broader range of ripening dates and an expansion of the germplasm base used in muscadine breeding. Retaining the unique flavors and aromas of muscadines are a focus in creating new cultivars for the commercial fresh markets. The University of Arkansas (UA) System Division of Agriculture Fruit Breeding Program began breeding muscadines in 2007 with a focus on large fruit size, crisp texture, edible skin, self-fruitful flowers, seedlessness, and improved postharvest storability (Barchenger et al., 2015a). The UA System is working on developing *Vitis* × *Muscadinia* hybrids to combine the disease resistance of muscadine grapes with the fruit quality of *V. vinifera*. Muscadine genotypes (cultivars and breeding selections) are evaluated for potential as a commercial crop.

Over the past few decades, the muscadine industry has developed into a multimillion-dollar industry with over 100 cultivars released. The most commonly-grown muscadine cultivars for processing are ‘Noble’, a black cultivar, and ‘Carlos’, a bronze cultivar. Fresh-market cultivars have different quality requirements than processing cultivars, such as flavor, texture, color, and postharvest storability. Seedless muscadine cultivars are also of great commercial interest for commercial markets. New cultivars have been developed by crossing muscadines with *V. vinifera* cultivars. Jeff Bloodworth (Bloodworth, 2017), a private fruit breeder in North Carolina collaborated with Gardens Alive! (Lawrenceburg, IN), developing seedless muscadines, including the first seedless muscadine cultivars, ‘Oh My!®’ and ‘RazzMatazz®’. ‘RazzMatazz®’ (Gardens Alive, 2022b) was the first of the new cultivars, which is a continuously-fruiting vine producing small, red seedless berries. Another cultivar developed in 2019 was ‘Oh My!®’ (Gardens Alive, 2022a), that produces a bronze mid-size to large berry. Since these cultivars are new, neither 'RazzMatazz®' nor 'OhMy! ®' have been extensively evaluated for market potential (Hoffman et al., 2020).

Muscadines grapes and products fit well in consumer-driven niche markets and local food systems trends (Brown et. al., 2016). Muscadines are a unique regional crop that can be marketed as a sustainable, locally produced table grape. Many consumers consider muscadine a nostalgic food, while newer consumers are interested in the nutraceutical potential of muscadines (Perkins-Veazie et al., 2012; Striegler et al., 2005). A 10-berry serving of muscadines has 16% of the recommended daily fiber intake and 13 to 14% of vitamin C (USDA, 2011). In addition, muscadine grapes contain many different health bioactives, including resveratrol, ellagic acid, anthocyanins, and proanthocyanidin phenolic compounds (Ector et al., 1996; Lee et al., 2005; Pastrana-Bonilla et al., 2017; Striegler et al., 2005). Barchenger et al. (2015a) found that the nutraceutical in muscadine grapes differed by grape segment and during storage.

Muscadine grapes typically have three sections: the flesh (pulp), skins, and seeds. The flesh contains primary metabolites of the grape, such as water, sugar, acids, and pectin, whereas skins and seeds contain more secondary metabolites, such as phenolic and aroma compounds (Yu and Ahmedna, 2013). Mature grapes contain water, sugar, organic acids, and pectin. Sugars (glucose and fructose) make up a majority of grape carbohydrate content with muscadine grapes having 15-23% soluble solids at harvest. In grapes, the acidity attributes measured are pH and titratable acidity (% tartaric acid). Mature muscadine grapes grown in Arkansas typically have 0.50-0.70% titratable acidity and 3.0-3.3 pH (Barchenger et al., 2015b; Felts et al., 2020).

Muscadine volatiles are primarily composed of esters, alcohols, terpenes, and carbonyl compounds, which can be identified using gas chromatography-mass spectroscopy (GC-MS) (Lee et al., 2016). The volatiles of muscadines vary by genotype, ripening stage, and different stress factors during growth, both biotic and abiotic. Analysis of volatile compounds can be used to establish and predict consumer preferences, especially when correlated with consumer sensory evaluations. Lamikanra (1987) determined that higher alcohols and fatty acid ethyl esters were numerically the largest classes of volatile aroma compounds in 'Noble' muscadine wine. Lamikanra et al. (1996) reported that 2-phenylethanol (rose and honey aroma) was predominantly synthesized during fermentation of muscadine wines but was also present in fresh muscadine grape skins. In an evaluation of 'Noble' wine, Mayfield (2020) reported that fruity esters were the largest class of volatile aroma compounds, followed by higher alcohols, notably 2-phenylethanol (rose and honey aroma). Baek et al. (1997) analyzed volatile aroma compounds in juice from 'Carlos' grapes and showed that furaneol and o-aminoacetophenone were likely responsible for characteristic candy and foxy-like aroma notes of muscadine grape juice. Baek et. al. (1997) examined aroma compounds in muscadine juice and found 33 aroma active compounds of which 21 were positively identified and comprised of six esters, four alcohols, four aldehydes, four ketones, two acids, and one phenol. With volatiles compounds, large qualities do not necessarily mean more flavor or aroma, rather the odor activity value (OAV) estimates odor potency as a ratio of the volatile concentration to its odor detection threshold (Patton, 1957)

Sensory research has been done on muscadine grapes and products from grapes. Felts et al. (2018) developed a sensory lexicon for fresh-market muscadine grapes grown at the UA System Fruit Research Station and showed that panelists detected differences between genotypes in grape/overall, grape/muscadine, and fruity. Threlfall et al. (2007) identified that muscadine juices from Arkansas had cooked muscadine, apple, pear, cooked grape, green/unripe, and slightly musty aromas and flavors. In a consumer study by Brown et al. (2016), thinner skins and greater juice pH were associated with greater overall liking of muscadine grapes. Consumer acceptability of muscadines can be quantified with soluble solids analysis, texture analysis, and sensory analysis (Brown et al., 2016). An important attribute of muscadine grapes is the balance of sugars to acids in the berries at harvest. Flora et al. (1979) found the optimal titratable acidity to soluble solids ratio to be 30, including an acceptable range of 25-35, regardless of whether or not the juice is from a bronze or black cultivar. Meullenet et al. (2008) reported positive correlations between general muscadine flavor and musty flavor, general grape flavor and metallic flavor, green/unripe flavor and sourness/astringency, and sweetness and floral, apple, and pear flavors for Arkansas muscadine juice. Sensory evaluations of muscadine grapes have shown wide variation in consumer rating of flavor among muscadine genotypes (Meullenet et al., 2008), indicating that there is likely significant variation in the profiles of flavor and aroma compounds.

The unique color, flavor, and aroma attributes of muscadine grapes are important, especially for breeding considerations. Since there is limited information about volatiles of fresh-market genotypes the berry weight, composition, and volatiles of muscadine grapes grown in Arkansas and North Carolina were evaluated.

Materials and Methods

Plants and culture

The muscadine genotypes for this study included both seedless and seeded muscadine grapes grown in Arkansas and North Carolina in 2021 (Table 1).

Arkansas. Muscadine were harvested from vines grown at the UA System Fruit Research Station, Clarksville AR [west-central Arkansas, 35.533798404565445, -93.40583345945807; U.S. Dept of Agriculture (USDA) hardiness zone 7a; soil type Linker fine sandy loam (Typic

Hapludult)]. Vines are spaced 6.1 m apart and rows are spaced 3.0 m apart. The vines are trained to a bi-lateral, high-cordon/curtain training system and pruned to three- to four-bud spurs annually. Weeds are controlled by applications of preemergence and postemergence herbicides applied annually. Vines are fertilized annually in March or April with nitrogen or complete fertilizers. Fungicides are applied similar to a commercial requirement to control macrophoma rot (*Botryosphaeria dothidea*), bitter rot (*Greeneria uvicola*), and ripe rot (*Colletotrichum spp*.). The last application of any fungicide is usually done near the end of June to early July. On average, five fungicide sprays and two insecticide sprays are applied to the grapes.

North Carolina. Muscadines were harvested from a commercial vineyard in King Mountain North Carolina. The commercial vineyard was formally Lineberger's Killdeer Farms, now owned by Gardens Alive! [West-central North Carolina, 35.288541278322555, -81.37195264596885; U.S. Dept of Agriculture (USDA) hardiness zone 7a; Madison-Bethlehem complex soil type sandy clay loam)]. Pest and weed management of muscadines were followed using the Muscadine Grape Production Guide for the Southeast (Hofmann et al., 2020).

Harvest

Fruit was harvested from both the UA System Fruit Research Station, Clarksville, AR and a private commercial grower in Kings Mountain, NC in 2021. The muscadines were hand harvested September-October at optimal ripeness and free of major visible blemishes, flaws, or damage. Approximately 1.8 kg of berries were harvested into 846 g (1-quart) vented clamshells for each genotype at each site. In Arkansas, the clamshells of grapes were placed in an ice chest chilled with ice packs and transported to the UA System Department of Food Science in Fayetteville, AR. The clamshells of grapes from North Carolina were placed in a walk-in cooler (4 °C) after harvest for 24 hrs prior to shipping to Arkansas. After harvest (and upon arrival of the North Carolina fruit), the grapes were sorted into 470 g (1-pint) vented clamshells in triplicate for each genotype and storage date. For muscadines that shipped from North Carolina, fruit without any shipping damage was used for this study. The genotypes from each location were evaluated in triplicate.

Arkansas. Six seeded genotypes (AM-26, AM-70, AM-77, AM-135, AM-148, and AM-154) were harvested. There were two bronze (AM-26 and AM-135), three dark/black (AM-70, AM-77, and AM-148), and one pink/red (AM-154) genotype.

North Carolina. Ten genotypes (‘Hall’, JB-06-30-2-20, JB 08-38-1-10, JB-09-15-3-09, ‘Lane’, ‘Oh My!®’, ‘Paulk’, ‘RazzMatazz®’, ‘Summit’, and ‘Supreme’) were harvested. There were five seedless (JB-06-30-2-20, JB 08-38-1-10, JB-09-15-3-09, ‘Oh My!®’, and ‘RazzMatazz®’) and five seeded (‘Hall’, ‘Lane’, ‘Paulk’, ‘Summit’ and ‘Supreme’) genotypes. There were four bronze (‘Hall’, JB-06-30-2-20, ‘Oh My!®’, and ‘Summit’), four dark/black (JB 08-38-1-10, ‘Lane’, ‘Paulk’, and ‘Supreme’), and two pink/red (JB-09-15-3-09 and ‘RazzMatazz®’) genotypes. The clamshells of muscadine from North Carolina were shipped overnight to UA System Food Science Department, Fayetteville, AR. A shipping container with appropriate packaging was used to minimize muscadine fruit bruising and keep temperatures below 10 °C. There were 2-4 clamshells for small-sized genotypes and 4-6 clamshells for large-sized genotypes. The clamshells of muscadines were packed in cardboard/Styrofoam shipping containers with ice packs. Each clamshell was secured with a rubber band and placed in cardboard trays. A moisture resistant foam or bubble wrap was used inside the container to protect the fruit during shipping. The temperature of the container was monitored with DeltaTrak FlashLink® In-Transit BLE Temperature and Humidity Logger (Model 40910, Pleasanton, CA). The maximum temperature during shipping did not exceed 12.8 °C in 2021.

Berry weight

The berry weight of five berries per genotype and replication were evaluated at the UA System Food Science Department at harvest (day 0 or upon arrival after shipping). After berry weights were measured, the samples for composition and volatile attributes were placed in zip-type bags and stored at -10 °C until analysis.

Composition attribute analysis

Five to twenty-five berries (depending on the size of the berries) per genotype and replication were evaluated for composition attributes. Berries were thawed placed in cheesecloth, and the berries were squeezed to extract the juice from the berries. The juice from the berry samples was used to determine composition attributes. The composition (soluble solids, pH, and titratable acidity) attributes of each of the fresh-market muscadines grown in Arkansas and North Carolina were evaluated at harvest (day 0 or upon arrival after shipping).

<u>Soluble solids.</u> Soluble solids (expressed as percent) of the juice were measured using an Abbe Mark II refractometer (Bausch and Lomb, Scientific Instrument, Keene, NH).

<u>pH.</u> The pH of juice was measured using a PH700 pH meter (Apera Instruments, Columbus, Ohio). The pH was measured after the probe has been in the sample for 2 min.

<u>Titratable acidity.</u> The titratable acidity of the juice was measured using a Metrohm 862 Compact Titrosampler (Metrohm AG, Herisau, Switzerland) fitted with a pH meter. Titratable acidity was determined using 6 mL of juice diluted with 50 mL of deionized, degassed water by titration with 0.1 N sodium hydroxide (NaOH) to an endpoint of pH 8.2; results was expressed as g/L tartaric acid.

<u>Soluble solids/titratable acidity ratio.</u> The soluble solids/titratable acidity ratio was calculated as the soluble solids divided by the titratable acidity.

Volatile analysis

Five berries per genotype and replication were used for volatile aroma attribute analysis. The seeds were removed from the seeded-muscadine berries before analysis. Gas chromatography analysis was performed using a Shimadzu GC-2010 Plus Gas Chromatograph equipped with a Flame Ionization Detector (GC-FID) and a GCMS-QP2010 SE Mass Spectrometer (GC-MS). The analysis includes identification and quantitation of odor-active compounds. For the analysis of muscadine volatiles, frozen berries (5 g), deionized water (10 mL), and NaCl (3 g) were mixed using a ratio of 1:1:0.3 (w/v/w). Two samples (one for GC-MS and one for FID) of 4 mL berry/deionized water/NaCl solution were placed in 20 ml headspace vials. The vials were incubated for 20 minutes with agitation and heat at 65 °C, and then the volatiles were absorbed using an 85 µm DVB/CAR/PDMS Solid Phase Microextraction (SPME) fiber was placed in the headspace above the sample for an additional 30 minutes. The SPME fiber was removed from the vial and placed into GC injection ports.

Samples were analyzed on both GC-FID and GC-MS and separation was performed on each using a HP-5 (30 m × 0.25 mm inner diameter, 5% phenyl-methylpolysiloxane, 1.0 µm film thickness) capillary column. For both GC-MS and GC-FID analysis, the injector temperature was 250 °C. Helium was used as the carrier gas and column flow rate was 1.92 mL/min for GC-FID and 1.20 mL/min for GC-MS. The oven temperature was programmed for a 4 min hold at 30 °C, then 30 °C to 180 °C at 6 °C/min, then from 180 °C to 280 °C at 8 °C/min, and with a 3 min hold at 280 °C. The GC-FID detector temperature was 280 °C, and the interface temperature for the GC-MS had an ion source temperature of 230 °C and an interface temperature of 250 °C. GC-MS was performed in full scan mode, with a scan range of 20-300 *m/z*. The volatiles were identified by comparison of their mass spectra with the spectral library, literature data, and retention indices, standards, and expressed as µg/kg.

Statistical design and analysis

For berry weight and composition attributes, all genotypes were evaluated in triplicate. The data was analyzed by analysis of variance (ANOVA) using JMP® (version 16.1.0; SAS Institute Inc., Cary, NC). Tukey's Honestly Significant Difference was used for mean separations ($p \leq 0.05$). Data for volatiles was presented as means and standard deviations of the three replicates. Associations among all dependent variables were determined using multivariate pairwise correlation coefficients of the mean values using JMP. Principal component analysis (PCA) was done using XLStat (Addinsoft Inc., New York, NY).

Results and Discussion

Berry weight

Genotype significantly impacted berry weight in both Arkansas and North Carolina-grown muscadines. In general, Arkansas-grown muscadines were larger than North Carolina grown muscadines (10.9 g and 7.0 g, respectively) (Table 2). Regardless of location, Supreme (14.41 g) from North Carolina had the largest berry weight, and 'RazzMatazz®' (1.12 g) from North Carolina had the smallest. The range of berry sizes was smaller in Arkansas-grown muscadines (5.67-13.88 g) than in North Carolina-grown muscadines (1.12-14.41 g).

Arkansas. AM-77 (5.67 g) had a significantly lower berry weight than the other Arkansas-grown genotypes. AM-135 (13.88 g) had the highest berry weight and was larger than AM-26 (11.08 g), AM-77 (5.67 g), AM-148 (11.86 g), or AM-154 (9.61 g) but not AM-70 (13.50 g). While many of the examined muscadine genotypes do not have established composition values, the berry sizes were similar to previous studies of Arkansas-grown muscadines (Barchenger et al., 2015; Felts et al., 2018; Threlfall et al., 2007). Xu et al. (2017) found that muscadines range from 3-23 g, however, consumers prefer a muscadine that is slightly larger than other grapes. All of the Arkansas-grown berries (5.67-13.88 g) examined in this study were within established commercial ranges in Arkansas (9-14 g) (Brown et al., 2016; Felts et al., 2018). As more cultivars are developed, fruit breeders can use berry weight to make breeding decisions regarding parentage and crossing.

North Carolina. ‘Supreme’ (14.41 g) had a higher berry weight than the other North Carolina-grown muscadines, with ‘RazzMatazz®’ (1.12 g) having the lowest berry weight (Table 2). Seedless muscadines (JB-06-30-2-20, JB 08-38-1-10, JB-09-15-3-09, ‘Oh My!®’, and ‘RazzMatazz®’) (3.55 g, 2.72 g, 4.29 g, 5.87 g, and 1.12 g, respectively) weighed significantly less than the seeded muscadines (‘Hall’, ‘Lane’, ‘Paulk’, ‘Summit’ and ‘Supreme’) (10.07 g, 9.35 g, 8.96 g, 9.85 g, and 14.41, g respectively).

Composition attributes

Genotype significantly impacted all of the composition attributes in both Arkansas and North Carolina-grown muscadines. In Arkansas-grown muscadines soluble solids ranged from 14.00 to 19.47%, pH ranged from 3.04 to 3.89, titratable acidity ranged from 0.25 to 0.88%, soluble solids/titratable acidity ratio ranged from 16.06 to 70.34. Muscadines from North Carolina had a range of soluble solids from 14.40 to 18.60%, a pH range of 2.95 to 3.55, a range of titratable acidity from 0.47 to 1.14, and soluble solids/titratable acidity ratio ranged from 16.16 to 37.16. Walker et al. (2001), Threlfall et al. (2007), and Felts et al. (2018) indicated a preferred soluble solids/titratable acidity ratio of muscadine grapes and juice of 20-35. While the majority of the muscadines examined in this study were within this range, both AM-77 and

'RazzMatazz®' had values below this range (16.06 and 16.16, respectively), while AM-135 (70.31), AM-70 (66.06), and AM-154 (68.92) were above this range.

Arkansas. In the muscadines from Arkansas, AM-135 had the highest soluble solids (19.47%) and soluble solids/titratable acidity ratio (70.31). AM-70 had the highest pH (3.89). AM-77 had the highest titratable acidity (0.88%) and the lowest pH (3.04), soluble solids (14.00%), and soluble solids/titratable acidity ratio (16.06).

North Carolina. For the muscadines from North Carolina, 'Summit' had the highest soluble solids (18.60%) and soluble solids/titratable acidity ratio (37.66). JB-08-38-1-10 had the lowest soluble solids (14.40%). 'Lane' had the highest pH (3.55) and lowest titratable acidity (0.47%). RazzMatazz® had the highest titratable acidity (1.14%) and lowest soluble solids/titratable acidity ratio (16.16).

Volatile attributes

In the 16 genotypes harvested in both locations, there were 181-198 volatile aroma compounds were identified across nine compound classes including esters, monoterpenes, sesquiterpenes, alcohols, aldehydes, ketones, lactones, aromatic hydrocarbons, and epoxides (Fig. 2 and Tables 3 and 4). The three muscadine genotypes with the highest volatiles were AM-154 (5,746 μg/kg), 'Lane' (5,285 μg/kg), and 'Hall' (5,108 μg/kg), while the three muscadine genotypes with the lowest volatiles were AM-77 (2,151 μg/kg), JB 06-30-2-20 (2,367 μg/kg), and AM-148 (2,468 μg/kg). We found that this chemical classification agreed with the major constituents for grape volatiles that have been previously reported (Deng, 2021; Golombek et al., 2021; Ju et al., 2021; Lee et al., 2016; Lin et al., 2019; Mencarelli and Bellincontro, 2018; Wu et al., 2020)

Looking at the total volatile concentration alone does not give the most accurate representation of a sample's aroma profile. Compounds have different organoleptic response threshold than each other, meaning that some compounds have a larger overall effect on the perceived aroma than others. Compounds that are particularly impactful are said to have a high odor active value (OAV), and closely examining these compounds can give a better representation of how consumers will perceive muscadines. Baek et. al. (1997) examined aroma compounds in muscadine juice and found 33 aroma active compounds of which 21 were positively identified. These 21 compounds comprised of six esters (ethyl acetate, ethyl butanoate, ethyl 2-methylbutanoate, ethyl hexanoate, ethyl 3-hydroxybutanoate, and phenethyl acetate), four alcohols (3-methyl-1-butanol, (E,Z)-2,6-Nonadien-ol, (E)-Geraniol, and 2-phenylethanol), four aldehydes (hexanal, 3-(methylthio)propanal, (E,Z)-2,6-nonadienal, and phenylacetaldehyde), four ketones (2,3-butanedione, 1-octen-3-one, 2,5-dimethyl-4-hydroxy-3 (2H)-furanone, o-Aminoacetophenone), two acids (acetic acid and 3-methyl butanoic acid), and one phenol (p-vinylguaiacol). In the Arkansas and North Carolina muscadines, seven of these impactful compounds were identified (ethyl butanoate (fruity ester), ethyl 2-methylbutanoate (ester with fruity, green apple notes), hexanal (aldehyde with grassy and fruity aromas), ethyl hexanoate (ester with tropical fruit notes), phenylacetaldehyde (aldehyde with green and floral aromas), geraniol (alcohol with fruity and floral aromas), and 2-phenylethanol (alcohol with rosy aromas) (Fig 3.). AM-154 had the highest levels of impactful volatiles, followed by 'Lane' 'Hall' and 'Summit'. AM-148 had the lowest levels of impactful volatiles, followed by AM-77, JB 06-30-2-20, and 'Oh My!®'. Geraniol (floral monoterpene) had the highest level of these impactful volatiles found in most muscadine genotypes, followed by ethyl 2-methylbutanoate (fruity ester) and ethyl butanoate (fruity ester). El Hadi et al. (2013) also indicated that some compounds are more impactful in certain cultivars of grapes due to synergistic effects between different volatile compounds. This could explain why certain genotypes reported low levels of impactful volatile compared to other genotypes. Further research is necessary to determine specific aroma profiles of muscadine grapes.

Arkansas. In the six genotypes harvested in Arkansas 181 volatile aroma compounds were identified across nine compound classes including 47 esters, 37 monoterpenes, 27 alcohols, 24 sesquiterpenes, 24 aldehydes, 15 ketones, four lactones, two aromatic hydrocarbons, and one epoxide (Table 3). In Arkansas, AM-154 (5,746 µg/kg) had the highest volatile concentration, followed by AM-70 (4,361 µg/kg), AM-135 (4,217 µg/kg), AM-26 (3,732 µg/kg), and AM-148 (2,438 µg/kg) with AM-77 (2,151 µg/kg) containing the lowest. AM-154 had the highest levels of geraniol (floral monoterpene) (1,276 µg/kg) and was the only genotype grown in Arkansas to contain 2-phenylethanol (floral alcohol) (312 µg/kg) and phenylacetaldehyde (green/floral aldehyde) (89 µg/kg).

North Carolina. In the 10 genotypes harvested in North Carolina 198 volatile aroma compounds were identified across nine compound classes including 52 esters, 38 monoterpenes, 31 sesquiterpenes, 28 alcohols, 26 aldehydes, 16 ketones, three lactones, two aromatic hydrocarbons, and two epoxides (Table 4). In North Carolina ‘Lane’ (5,235 µg/kg) had the highest level of volatiles, followed by ‘Hall’ (5,108 µg/kg), ‘Paulk’ (5,091 µg/kg), ‘Supreme’ (4,182 µg/kg), ‘Summit’ (4,061 µg/kg), ‘Oh My!®’ (3,804 µg/kg), JB 09-15-3-09 (3,741 µg/kg), ‘RazzMatazz®’ (3,368 µg/kg), and JB 08-38-1-10 (2,541 µg/kg) with JB 06-30-2-20 (2,356 µg/kg) containing the lowest. The five seeded muscadines (‘Hall’, ‘Lane’, ‘Paulk’, ‘Supreme’, and ‘Summit’) had higher volatile levels than the seedless muscadine. ‘Lane’ also had the highest levels of impactful volatiles, followed by ‘Hall’, ‘Summit’ and JB 08-38-1-10. ‘Lane’ had the highest levels of geraniol (floral monoterpene) and 2-phenylethanol (floral alcohol), while ‘Supreme’ had the highest levels of hexanal (green aldehyde).

Principal component analysis

Principal component analysis was used to separate compound categories and genotypes into different groups for muscadines grown at each location. In Arkansas-grown muscadines, two components explained 79.93% (Table 5) of the data, however for North Carolina-grown muscadines three components explained 66.39% of the data (Table 6). Because an additional component was required to explain a lower amount of the variation, it can be inferred that North Carolina-grown muscadines have a greater variability between genotypes than do Arkansas-grown muscadines. (Xu et al., 2017). Wu et al. (2016) examined table grapes in China and found that ‘Kyoho’ (*V. vinifera* and *V. labrusca* hybrid) had high levels of esters, while muscat grapes had higher levels of monoterpenes. Wu et al. (2016) also postulated that grouping aroma compounds into similar descriptors is useful for determining organoleptic profiles.

Arkansas. When PCA was conducted on Arkansas-grown muscadines, two components explained 79.93% of the variation in the data (Table 5). PC1 (52.56%) had positive loadings for the following compound classifications: lactones, alcohols, monoterpenes, aldehydes, ketones, sesquiterpenes, and epoxides, and also for genotypes AM-135, AM-26, AM-154, and AM-70. PC1 had negative loadings for esters and aromatic hydrocarbons, as well as AM-148 and AM-77 genotypes. PC2 (27.37%) had positive loadings for alcohols, ketones, and lactones, as well as genotypes AM-148 AM-26, AM-77, AM-135, and AM-70. Sesquiterpenes, epoxides, esters, monoterpenes, aldehydes and the AM-154 genotype were negatively associated with PC2. Clustering indicated that AM-135, AM-26, and AM-70 were positively correlated with ketones, lactones, and alcohols, but negatively correlated with esters and aromatic hydrocarbons, while

AM-154 was positively correlated with monoterpenes, sesquiterpenes, epoxides, and aldehydes. AM-148 and AM-77 were not positively correlated with any compound classifications, however, they were both negatively correlated with aldehydes, monoterpenes, sesquiterpenes and epoxides.

North Carolina. When PCA was conducted on North Carolina-grown muscadines, three components explained 66.39% of the variation (Table 6). The positive loadings in PC1 (28.42%) were compound classifications aldehydes, epoxides, esters, lactones, and sesquiterpenes and genotypes 'Paulk' 'Supreme', JB 08-38-1-10, JB-06-30-2-20, JB-09-15-3-09, and 'Oh My!®'. The negative loadings were alcohols, aromatic hydrocarbons, ketones, monoterpenes, 'Summit', 'Lane', 'Hall' and 'RazzMatazz®'. The positive loadings in PC2 (21.24%) were alcohols, aromatic hydrocarbons, esters, and lactones, as well as genotypes 'Summit', 'Hall' 'Supreme' JB-09-15-3-09, and 'RazzMatazz®'. The negative loadings for PC2 were aldehydes, epoxides, ketones, monoterpenes, sesquiterpenes, 'Paulk' 'Lane', JB 08-38-1-10, JB-06-30-2-20, and 'Oh My!®'. The positive loadings for PC3 (16.73%) were aromatic hydrocarbons, monoterpenes, epoxides, ketones, esters, alcohols, aldehydes, lactones, 'Paulk', 'Lane', 'Hall', 'Supreme', JB-09-15-3-09, and 'Oh My!®', while negative loadings were sesquiterpenes, 'Summit' JB 08-38-1-10, JB-06-30-2-20, and 'RazzMatazz®'. Additional PCAs could be completed on both the seeded and unseeded genotypes independently to see how that affects the grouping of certain variables.

Conclusion

Physical, compositional, and volatile attributes of muscadines grown in Arkansas and North Carolina were significantly impacted by genotype. Regardless of location, the berry weight (1-21 g), soluble solids (14-19%), pH (3-4), titratability acidity (0.3-1.2%), and soluble solids/titratable acidity ratio (16-70) were significantly impacted by genotype. Genotype impacted total volatiles (2,140-5,739 μg/kg) and impactful volatile (100-1,000 μg/kg) levels. The PCA indicated that more factors affect the volatile concentrations in North Carolina berries than Arkansas berries, but additional inferences about what those factors may be could not be ascertained without further testing. There was much greater variation between genotypes in impactful volatiles than in total volatiles. As new muscadine breeding selections like AM-148 and JB 06-30-2-20 had lower total volatiles and AM-154 had higher total volatiles, it is important to identify these unique aspects and apply to breeding decisions. Because these genotypes have such unique profiles, additional research to better establish what the impactful volatiles are in some of these novel genotypes would be greatly beneficial for future breeding efforts. Data generated from this project provided information on physical, composition, and volatile attributes of muscadine grapes grown in Arkansas and North Carolina that can be used to support breeding efforts.

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Table 1. Muscadine grapes grown in Arkansas (Clarksville, AR) and North Carolina (Kings Mountain, NC) and evaluated at the University of Arkansas System Division of Agriculture (2021).

Location	Genotype	Skin color	Seeds
Arkansas	AM-26	Bronze	Seeded
	AM-70	Dark/black	Seeded
	AM-77	Dark/black	Seeded
	AM-135	Bronze	Seeded
	AM-148	Dark/black	Seeded
	AM-154	Pink/Red	Seeded
North Carolina	Hall	Bronze	Seeded
	JB-06-30-2-20	Bronze	Seedless
	JB 08-38-1-10	Dark/black	Seedless
	JB-09-15-3-09	Pink/red	Seedless
	Lane	Dark/Black	Seeded
	Oh My!®	Bronze	Seedless
	Paulk	Dark/black	Seeded
	RazzMatazz®	Pink/red	Seedless
	Summit	Bronze	Seeded
	Supreme	Dark/black	Seeded

Table 2. Berry weight and composition attributes at harvest of muscadine grapes grown in Arkansas (Clarksville, AR) and North Carolina (Kings Mountain, NC) and evaluated at the University of Arkansas System Division of Agriculture (2021).

Location and genotype [z]	Berry weight (g)	Soluble solids (%)	pH	Titratable acidity (%)[y]	Soluble solids/titratable acidity ratio
Arkansas					
AM-26	11.08 b	16.23 b	3.62 b	0.50 b	32.65 b
AM-70	13.50 a	18.90 a	3.89 a	0.29 c	66.06 a
AM-77	5.67 d	14.00 c	3.04 c	0.88 a	16.06 c
AM-135	13.88 a	19.47 a	3.89 a	0.28 c	70.31 a
AM-148	11.86 b	16.30 b	3.67 b	0.54 b	30.53 b
AM-154	9.61 c	16.93 b	3.58 b	0.25 c	68.92 a
P-value	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*
North Carolina					
Hall	10.07 b	15.23 c	3.40 ab	0.48 bc	31.67 ab
JB-06-30-2-20	3.55 cd	17.63 a	2.95 d	0.56 bc	31.50 ab
JB 08-38-1-10	2.72 d	14.40 c	3.01 d	0.56 bc	25.76 bc
JB-09-15-3-09	4.29 cd	17.30 ab	3.24 bc	0.61 bc	28.53 b
Lane	9.35 b	14.87 c	3.55 a	0.47 c	32.12 ab
Oh My!®	5.87 c	15.00 bc	3.09 cd	0.78 b	20.18 cd
Paulk	8.96 b	15.47 c	3.32 b	0.58 bc	25.94 bc
RazzMatazz®	1.12 e	17.40 ab	2.98 d	1.14 a	16.16 d
Summit	9.85 b	18.60 a	3.29 b	0.50 bc	37.66 a
Supreme	14.41 a	15.77 c	3.27 b	0.56 bc	27.77 bc
P-value	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*

[z] Genotypes were evaluated in triplicate. Means highlighted are highest value and means underlined are lowest in each location. Means with different letters for each attribute by location are significantly different ($p<0.05$) within each location using Tukey's Honestly Significant Difference test.
[y] Titratable acidity expressed as % tartaric acid.

Table 3. Volatile aroma compounds[z] identified in muscadine genotypes grown at the University of Arkansas System Division of Agriculture Fruit Research Station, Clarksville, AR (2021)

Compound Name	Retention Index	Aroma Category	Aroma Descriptor	AM-26	AM-70	AM-77	AM-135	AM-148	AM-154
Totals	**181**			**3732.14±309.46**	**4360.6±634.62**	**2150.66±1899.88**	**4217.32±1922.96**	**2468.38±407.58**	**5745.62±317.42**
Alcohols									
2-Butanol	610	Fruity	sweet apricot	3.46±2.36	2.52±3.34	18.1±23.82	18.68±13.2	8.98±9.94	27.5±23.12
1-Butanol	644	Fermented	fusel oily sweet balsamic whiskey	5.16±6.68	7.52±6.52	0.68±1.2	12.88±8.8	7.2±6.8	3.08±2.68
1-Penten-3-ol	683	Green	ethereal horseradish green radish chrysanthemum vegetable tropical fruity	27±37.32	19.12±26.28	29.72±42.6	10.28±8.2	12.2±10.56	44.64±64.72
2-Methyl-1-butanol	735	Ethereal	fusel ethereal alcoholic fatty greasy winey whiskey leathery cocoa	0±0	0±0	0±0	0±0	8.04±7	11.64±8.36
3-Methyl-3-buten-1-ol	739	Fruity	sweet fruity	0±0	20.56±27.36	27.28±40.64	28.08±45.48	40.68±34.36	13.32±23.08
1-Pentanol	763	Fermented	pungent fermented bready yeasty fusel winey solvent	26.44±23.60	71.00±104.00	8.56±8.4	125.28±189.88	4.04±3.56	10.96±9.72
3-Methyl-1-butanol	767	Fermented	fusel alcoholic pungent ethereal cognac fruity banana molasses	0±0	0±0	0±0	12.32±21.32	12.64±10.04	50.72±7.44
2-Penten-1-ol	769	Green	green	0±0	0±0	0±0	1.8±3.16	0±0	2.2±3.8
3-Hexen-1-ol	781	Green	leafy	0±0	15.08±14.96	37.08±32.8	49.44±51.28	0±0	0±0
2-Hexen-1-ol	836	Fruity	fruity green leafy	635.2±418.04	515.52±571.6	6±5.2	326.12±290.12	162.64±162.28	5.4±1.2
2 Heptanol	861	Citrus	fresh lemongrass herbal sweet floral fruity green	42.68±72.36	116.08±200.36	348.48±305.72	232.52±401.84	72.08±67.72	294.4±29.64
1-Hexanol	871	Herbal	ethereal fusel oily fruity alcoholic sweet green	130.52±223.8	2.08±3.6	1.72±1.52	0.48±0.4	0±0	3.96±6.4
5-Methyl-1-heptanol	894	-	-	1.2±1.04	7.76±5.08	2±1.8	2.88±2.04	8.12±3.96	2.48±2.72
2-Methyl-1-heptanol	900	-	-	9.6±4.32	15.24±11.48	26±22.84	8.84±13.84	12.64±11.8	18.76±0.12
2-Methyl-6-hepten-3-ol	919	-	-	0±0	0±0	0.92±1.64	0.84±1.2	1±0.16	1.88±0.32
2-methyl-2-heptanol	933	-	-	0.44±0.4	1.08±1.4	27.24±26.88	0.52±0.48	2.8±1.2	1.24±0
1-Octen-3-ol	960	Earthy	mushroom earthy green oily fungal raw chicken	1.52±2.2	1.36±2.36	1.92±1.68	5.44±9.44	46.56±15.44	0±0
1- Heptanol	973	Green	musty leafy violet herbal green sweet woody peony	4.16±3.8	11.4±19.8	0±0	0±0	7.8±13.52	0±0
2-Ethylhexanol	1034	Citrus	citrus fresh floral oily sweet	5.96±1.44	11.72±4.88	16.76±25.76	16.68±6.6	5.64±2.12	0±0
1-Octanol	1074	Waxy	waxy green orange aldehydic rose mushroom	0±0	0±0	0±0	2.68±1.08	2.52±1.24	2.64±0.16
1-Phenylethanol	1127	Floral	fresh sweet almond gardenia hyacinth	170.44±80.72	958.72±300.12	127.48±134.32	1207.84±690.8	610.4±408.6	624.48±16.72
1-Nonanol	1176	Floral	fresh clean fatty floral rose orange dusty wet oily	2.2±1.12	3.92±1.2	6.16±9.52	2.16±0.76	2.24±1.64	4±0.96
1-Decanol	1277	Fatty	fatty waxy floral orange sweet clean watery	0±0	5.68±2.16	4.4±4.16	0.28±0.24	1.96±0.52	0±0
4,8-Dimethylnonan-1-ol	1289	-	-	113.04±32.88	80.76±27.8	46.8±52.2	115.16±119.92	76.72±25.64	179±19.8
Eugenol	1371	Spicy	sweet spicy clove woody	0±0	1.84±1.6	0.88±1.56	1.08±0.96	1.8±1.56	0.96±1.28
1-Dodecanol	1480	Waxy	earthy soapy waxy fatty honey coconut	1.56±0.84	2.44±0.96	2.04±1.92	1±0.8	1±0.04	1.6±0.4
1-Hexadecanol	1887	Waxy	waxy clean greasy floral oily	4.68±3.76	3.16±1.16	2.52±2.88	1.4±0.6	0.8±0.04	1.52±0.24
Totals	**27**			**1188.72±919.04**	**1877.08±1341.36**	**760.84±772.88**	**2203.36±1895.64**	**1119.48±809.68**	**1333.88±246**
Aldehydes									
3-Methylbutanal	643	Aldehydic	ethereal aldehydic chocolate peach fatty	11.54±10.22	12.5±19.9	0±0	0±0	6.74±9.92	1.06±1.86
2-Butenal	654	-	-	3.3±4.72	4.5±6.94	7.44±6.44	4.56±7.18	7.74±7.66	3.6±2.78
2-Methylbutanal	669	Cocoa	musty cocoa phenolic coffee nutty malty fermented fatty alcoholic	0.98±1.2	3.24±0.92	0.54±0.46	1.12±1.6	5.52±4.26	2.48±2.6
Pentanal	701	Fermented	fermented bready fruity nutty berry	16.4±3.7	9.84±4.34	11.46±10.12	4.4±1.2	7.42±2.94	1.46±0.14
Tiglic aldehyde	728	Green	pungent green ethereal nutty anisic fruity	23.26±12.54	4.66±6.74	2.9±2.54	17.66±2.22	2.62±0.92	5.16±4.46
3-Methylpentanal	746	-	-	90.64±153.32	2.56±3.08	0.32±0.3	2.66±3.38	1.76±1.04	0.32±0.28
2-Pentenal	754	Green	pungent green apple orange tomato	3.86±4.16	3.18±1.86	2.78±2.52	6.82±3.14	3.6±2.46	2.38±0.4
2-Butenal, 3-methyl	787	Fruity	sweet fruity pungent brown nutty almond cherry	1.4±2.44	4.02±2.54	6.46±5.78	3.28±0.16	3.04±5.28	3.28±2.66
Hexanal	804	Green	fresh green fatty aldehydic grassy leafy sweaty	0.58±0.64	5.34±5.1	1.5±2.62	11.52±14.76	15.16±20.72	82.26±142.06
2-Hexenal	845	Green	sweet almond bitter fruity green leafy apple plum vegetable	159.04±155.88	197.88±245.08	110.5±107.8	141.6±35.32	50.14±26.66	266.72±39.34
Heptanal	892	Green	fresh aldehydic fatty green herbal cognac ozone	0.42±0.36	0.18±0.08	0.08±0.06	0.06±0.1	0.7±0.22	0.06±0.06
2-Heptenal	957	Green	green fatty	1.44±2.52	3.86±5.22	1.46±1.72	3.94±1.9	1.2±0.86	1.7±0.14
Benzaldehyde	966	Fruity	sharp sweet bitter almond cherry	49.16±21.72	60.98±53.08	60.54±53.74	24.4±32.26	13.96±13.8	51.56±49.82
Octanal	1002	Aldehydic	aldehydic waxy citrus orange peel green herbal fresh fatty	17.12±23.74	29.44±25.94	19.42±16.98	10.52±12.68	4.52±3.94	22±3.08
Phenylacetaldehyde	1059	Green	green sweet floral hyacinth clover honey cocoa	0±0	0±0	0±0	0±0	0±0	88.9±10.64
2-Octenal	1066	Fatty	fatty green herbal	0±0	0±0	0±0	27.12±43.2	0.04±0.1	56.84±9.74
4-Methylbenzaldehyde	1093	Fruity	fruity cherry phenolic	0.46±0.36	0.46±0.34	0.18±0.18	1.44±0.76	0.38±0.66	0.86±0.08
Nonanal	1103	Aldehydic	waxy aldehydic rose fresh orris orange peel fatty	6.2±10.76	10.44±18.08	22.06±19.14	9.22±16	0±0	19.84±5.1
Alpha-campholenal	1144	Herbal	herbal green woody amber leafy	2.82±0.4	7.7±4.62	3.5±3.78	6.64±2.22	4.98±1.86	3.32±0.64
2-Nonenal	1170	Fatty	fatty green waxy cucumber melon	2.14±3.5	0.16±0.28	0±0	0.32±0.28	0±0	0±0
Decanal	1212	Aldehydic	sweety aldehydic waxy orange peel citrus floral	4.1±1.02	3.46±0.88	0.4±0.7	5.78±2.96	1.56±1.36	1.88±2.18
Citral	1282	Citrus	sharp lemon sweet	55.28±12.08	92.32±18.4	50.52±45.62	41.86±42.94	55.96±10.84	57.92±9.16
Dodecanal	1419	Aldehydic	soapy waxy aldehydic citrus green floral	0.22±0.2	0.54±0.58	0.82±1.04	0.36±0.22	0.4±0.12	0.34±0.18

Pentadecanal	1721	Waxy	fresh waxy	2.58±1.82	1.16±0.66	0.82±0.88	1.54±1.8	0.6±0.1	0.5±0.1
Totals	**24**			**452.94±427.3**	**458.42±424.66**	**303.7±282.42**	**326.82±226.28**	**188.04±115.72**	**674.44±287.5**
Aromatic Hydrocarbons									
Toluene	777	Sweet	benzene	0±0	0±0	0±0	0.08±0.14	21.6±36.96	0.9±1.56
1,3-Cyclododecadiene, (E,Z)-	1653	-	-	0.22±0.22	0±0	0±0	0±0	0±0	0±0
Totals	**2**			**0.22±0.22**	**0±0**	**0±1**	**0.08±0.14**	**21.6±36.96**	**0.9±1.56**
Epoxides									
Humulene epoxide I	1620	Herbal	-	0.28±0.08	0.42±0.18	0.26±0.24	0.26±0.1	0.16±0	0.38±0.24
Totals	**1**			**0.28±0.08**	**0.42±0.18**	**0.26±0.24**	**0.26±0.1**	**0.16±0**	**0.38±0.24**
Esters									
Butanoic acid, methyl ester	709	Fruity	fruity apple sweet banana pineapple	0±0	0±0	4.16±7.2	0.54±0.64	0±0	0±0
Ethyl propionate	713	Fruity	sweet fruity rummy juice fruity grape pineapple	1.22±1.06	1.12±0.98	5.56±9.06	2.74±2.92	1.18±1.14	1.98±3.42
Propanoic acid, ethyl ester	721	Fruity	sweet fruity rummy juice fruity grape pineapple	3±4.74	3.5±3.28	0.28±0.5	2.74±2.56	0.74±0.8	0.5±0.88
Methyl butanoate	731	Fruity	pungent ethereal fruity fusel fermented creamy	6±1.84	2.38±3.14	2.62±3.76	1.26±2.18	1.86±0.76	0±0
Butanoic Acid	771	Cheesy	sharp acetic cheesy buttery fruity	110.52±187.5	7.76±7.38	7.66±6.82	36.46±53.56	37.7±62.74	7.72±0.86
Methyl 2-methylbutanoate	783	Fruity	ethereal estery fruity tutti frutti apple green apple lily of the valley powdery fatty	0±0	0±0	0±0	5.96±5.68	20.24±34.82	2.12±2.72
Ethyl butanoate	799	Fruity	fruity juicy fruit pineapple cognac	0.3±0.28	24.22±39.06	78.24±68.14	0.78±0.34	14.52±9.58	99.68±84.26
Butyl acetate	809	Ethereal	ethereal solvent fruity banana	12.84±15.96	5.2±6.04	62.34±55.48	3.36±2.94	2.86±3.1	7.14±6.2
Methyl 3-methylbutanoate	814	Fruity	apple fruity pineapple	76.88±129.4	5.24±2.52	4.42±4.78	52.64±43.26	6.08±2.46	7.04±2.62
Ethyl 2-methylbutanoate	850	Fruity	sharp sweet green apple fruity	134.46±118.76	97.98±34.74	97.52±85.18	125.18±3.46	131.58±65.4	140.4±18.46
Ethyl 2-methylbutyrate	857	Fruity	sharp sweet green apple fruity	0±0	0±0	2.88±4.98	0±0	44.46±77.02	0±0
Isobutyl isobutyrate	886	Fruity	ethereal fruity tropical pineapple grape banana	1.22±0.84	2.64±2.98	2.6±3.34	3.46±2.34	0.84±1.26	1.66±2.88
Hexanoic acid, methyl ester	904	Fruity	ethereal pineapple fruity apricot strawberry banana bacon	0±0	0±0	4.38±7.58	1.46±1.16	3±1.9	1.24±0.3
Propanoic acid	911	Acidic	acidic dairy fruity	3.14±2.1	0.68±0.04	2.76±2.4	1.54±1.42	2.44±1.62	2.94±0.72
Methyl hexanoate	923	Fruity	ethereal fruity pineapple apricot strawberry fruit banana bacon	0±0	0±0	3±5.2	1.04±0.84	5.14±3.68	0±0
4-methylpentyl 4-methylpentanoate	931	Fruity	fruity waxy soapy herbal	0.48±0.08	5.46±3.86	1.76±2.54	0.92±0.92	5.3±1.74	3.94±1.12
Ethyl Butyrate	940	Fruity	fruity juicy pineapple cognac	0.46±0.28	1.5±1.46	7.28±11.68	0.46±0.8	0.72±0.32	1.3±0.16
2-Methylbutyl propionate	950	Fruity	sweet fruity ethereal rummy	4.3±2.92	1.94±3.36	0.76±0.86	0±0	2.56±1.5	0±0
Isobutyl 2-methylbutyrate	976	Fruity	sweety fruity melon	2.42±2.68	3.82±4.74	9.76±8.66	13±12.8	3.4±4.22	11.4±0.88
Heptanoic acid, methyl ester	986	Fruity	sweet fruity green orris waxy floral berry	9.86±12.82	9.84±13.68	6.54±6.16	37.5±26.76	10.72±5.88	4.8±0.82
2-Methylbutanoic acid	993	Acidic	pungent acidic cheesy roquefort cheese cheesy	18.38±19.86	23.9±23.06	32.84±28.44	13.46±23.3	19.24±19.8	47.1±6.2
Ethyl hexanoate	996	Fruity	sweet fruity pineapple waxy green banana	14.12±18.66	13.72±20.34	0±0	8.64±7.56	7.94±0.96	0±0
Hexyl acetate	1005	Fruity	fruity green apple banana sweet	8.98±5.14	20.16±11.44	75.8±71.9	24.36±5.2	56.44±24.74	0±0
Geranyl isovalerate	1008	Fruity	green fruity apple blueberry pineapple	0±0	0±0	0±0	0±0	0.14±0.26	0.26±0
Butanoic acid, 3-methylbutyl ester	1013	Fruity	fruity green apricot pear banana	7.16±5.02	11.58±8.44	5.38±9.34	18.5±20.24	6.04±4.5	17.14±14.84
Methyl heptanoate	1027	Fruity	sweet fruity green orris waxy floral berry	10.22±8.2	21.54±24.48	5.66±6.68	10.08±3.24	6.92±2.32	0.98±1.7
Heptanoic acid	1031	Cheesy	rancid sour cheesy sweaty	0±0	0±0	0±0	0±0	12.46±11.48	9.62±0.4
3-Methylbutyl 2-methylbutanoate	1087	Fruity	sweet fruity citrus cherry blueberry apple	1.56±0.54	2.72±0.24	7.42±9.94	2.74±3.62	330.2±29.48	18.52±0.64
4-Octenoic acid, methyl ester	1114	-	-	7.32±2.1	7.38±2.64	3.86±5.38	4.24±1.94	8.52±5.24	12.64±0.74
Valeric acid	1149	Cheesy	acidic sweaty rancid	4.16±2.7	8.38±1.24	7.9±8.32	7.06±2.42	1.98±0.82	19.32±2.42
Octanoic acid	1163	Fatty	fatty waxy rancid oily vegetable cheesy	11.12±1.64	25.54±5.54	7.14±6.52	33.34±15.74	23.12±12.6	41.14±4.02
Nonanoic acid	1181	Waxy	waxy dirty cheesy dairy	1.36±0.68	1.4±0.22	3.9±6.52	1.64±0.94	0.9±0.62	2.06±0.06
Methyl nonanoate	1209	Fruity	sweet fruity pear waxy tropical winey	1.72±1.52	0.38±0.3	0.82±0.72	1.54±1.68	1.42±0.22	0.56±0.56
Methyl dec-5-enoate	1296	-	-	1.76±0.44	2.7±0.38	1.54±1.34	1.18±0.98	1.3±0.44	1.8±0.24
4-Decenoic acid	1299	Fruity	-	6.42±1.78	5.12±0.6	3.14±2.92	5.28±4.44	5.2±1.9	5.14±0.5
Decenoic acid	1309	Waxy	waxy buttery oily creamy dairy green lactonic plum skin	10.54±2.78	13.16±2.64	8.64±9.78	11.36±5.5	13.8±4.78	11.66±1.98
Methyl 5-bromo-5-hexenoate	1314	-	-	5.84±1.38	5.1±0.18	3.56±3.16	0.14±0.26	0±0	0±0
trans-Geranic acid methyl ester	1323	Waxy	waxy green fruity floral	6.84±2.5	2.2±0.14	1.18±2.06	7.38±4.82	0±0	0±0
Methyl decanoate	1327	Fermented	oily winey fruity floral	4.1±1.36	3.38±0.96	4.38±3.98	0±0	1.72±0.74	4.92±0.6
Methyl 3-undecenoate	1355	-	-	3.24±1.22	6.22±1.3	3.88±3.38	45.42±73.76	3.98±2.14	254.54±31.58
Decanoic acid	1360	Fatty	rancid sour farty citrus	0.04±0.08	4.58±4.92	2.74±3.04	0.8±1	0±0	0.8±0.84
Geranyl acetate	1383	Floral	floral rose lavender green waxy	29.7±19.02	14.92±2.16	8.4±8.78	13.8±12.82	13.1±4.26	9.1±4.84
Geranyl isobutyrate	1514	Floral	Sweet/fruity, waxy	0.66±0.18	1.74±0.88	1.22±1.14	1.04±0.48	2.36±1.38	1.02±0.8
Methyl dodecanoate	1526	Waxy	waxy soapy creamy coconut mushroom	1.34±0.16	2.38±0.52	1.4±1.26	1.1±0.5	0.8±0.06	1.1±0.12
Dodecanoic acid	1556	Fatty	fatty coconut bay	0.2±0.04	0.66±0.14	1.14±0.98	0.86±0.8	0.32±0.1	0.38±0.16
Hexyl octanoate	1589	Green	fruity green waxy berry apple estery	0.58±0.66	0.98±0.48	0.22±0.2	0.38±0.08	0.2±0.22	0.36±0.12
Ethyl dodecanoate	1595	Waxy	sweet waxy floral soapy clean	0.46±0.4	0.84±0.74	0.62±0.66	0.76±0.04	0.46±0.18	0.14±0.26
Totals	**47**			**524.92±579.32**	**373.96±241.24**	**497.3±490.76**	**506.14±355.94**	**813.9±409.18**	**754.16±199.92**
Ketones									
3-Buten-2-one, 3-methyl-	677	-	-	18.32±16.06	3.46±1.2	4.04±4.86	13.3±11.74	2.14±1.88	3.06±2.14
1-Penten-3-one	687	Spicy	pungent peppery mustard garlic onion	0±0	0±0	13.3±23.04	27.58±25.08	13.06±10.32	46.42±36.78
2-Hexanone	793	Fruity	fruity fungal meaty buttery	87.98±109.48	18.94±20.56	6.7±5.92	60±94.46	9.3±15.04	3.26±2.68
2-Heptanone	883	Cheesy	fruity spicy sweet herbal coconut woody	1.36±1.18	2.56±0.4	0.36±0.32	2.46±0.06	0.94±0.62	2.8±3.06

4-Methyl-2-heptanone	945	-	-	1.38±2.04	2.04±3.36	0.16±0.3	4.08±3.18	0.72±0.24	0.26±0.04
Acetophenone	1083	Floral	sweet pungent hawthorn mimosa almond acacia chemical	1.42±1.04	3.88±3.6	54.82±89.86	8.92±5.52	25.3±21.92	12.24±1.06
2-Decanone	1159	Floral	orange floral fatty peach	7.68±8	29.08±4.38	3.64±3.2	13.6±11.64	11.64±0.5	22.52±8.8
7-Decen-2-one	1164	-	-	1.26±2.2	15.04±4.68	18.74±20.66	2±3.46	3.2±5.56	4.62±4.08
Decanone	1193	-	-	122.46±75.36	146.26±37.5	10.06±8.8	15±17.3	3.98±2.86	9.68±8.66
Undec-2-en-6-one	1262	-	-	135.24±50.48	168.82±42.8	15.8±13.68	24.26±18.7	8.42±0.94	29.18±8.58
2-Dodecanone	1342	Citrus	fruity citrus floral orange	25.34±12.86	49.32±12.86	15.34±13.36	26.08±23.56	5.34±1.24	1.42±0.22
2-Nonadecanone	1359	-	-	0.74±0.52	1.74±0.48	0.46±0.4	0.52±0.46	0.62±0.2	0±0
Damascenone	1391	Floral	natural sweet fruity rose plum grape raspberry sugar	44.98±23.14	79.26±28.4	4.34±7.54	22.54±12.24	23.58±4.3	38.12±11.98
Ethyl decanoate	1397	Waxy	sweet waxy fruity apple grape oily brandy	1.32±0.94	8.66±0.86	6.94±6.14	2.14±0.4	6.9±1.52	3.4±0.14
(Z)-6-Pentadecen-2-one	1660	-	-	0.7±0.34	0.4±0.38	0.34±0.36	0.56±0.3	0.3±0.02	0.28±0.06
Totals	**15**			**450.18±303.64**	**529.46±161.46**	**155.04±198.44**	**223.04±228.1**	**115.44±67.16**	**180.36±89.66**
Lactones									
Gamma-hexalactone	1055	Tonka	herbal coconut sweet coumarinic tobacco	65.08±11.8	88.5±15.82	50.64±44.04	78.06±21.3	43.8±6.94	21.66±9.5
Alpha-ionone	1454	Floral	sweet woody floral violet orris tropical fruity	0±0	0±0	0±0	0.72±1.26	1.5±0.46	0±0
Geranylacetone	1454	Floral	fresh green fruity waxy rose woody magnolia tropical	1.44±0.4	2.12±1.84	2.58±2.36	2.7±0.78	0.38±0.16	1.66±0.16
Gamma-decalactone	1488	Fruity	fresh oily waxy peach coconut buttery sweet	0.86±0.9	0.84±0.08	0.56±0.62	1±1.08	0.42±0.14	0±0
Totals	4			**67.38±13.1**	**91.46±17.74**	**53.78±47.02**	**82.48±24.42**	**46.1±7.7**	**23.32±9.66**
Monoterpenes									
Alpha-thujene	933	Woody	woody green herbal	1.34±2.32	5.04±8.76	29.38±36.6	4.2±1.06	18.34±21.62	0±0
Myrcene	971	Spicy	peppery terpenic spicy balsamic plastic	4.52±5.9	9.68±16.76	0±0	37.98±30.74	33.82±13.46	32.46±28.46
Beta-pinene	980	Herbal	dry woody resionous pine hay green eucalyptus camporeous	27.66±41	7.32±2.28	2.14±3.72	4.1±7.12	13.4±3.52	11.16±0.78
Beta-myrcene	991	Spicy	pepper terpenic spicy balsamic plastic	34.54±37.96	63.2±33.96	27.26±24.08	121.9±161.46	49.96±30.52	285.72±29.12
alpha-Phellandrene	1011	Terpenic	citrus herbal terpenic green woody pepper black pepper	0±0	0±0	0±0	0±0	5.44±9.42	10.84±18.78
alpha-Terpinene	1017	Woody	woody terpenic lemon herbal medicinal citrus	2.48±3.04	8.78±9.3	1.56±1.36	1.28±1.14	0±0	4.9±8.48
Beta-phellandrene	1019	Minty	minty terpenic	4.96±1.76	22.32±18.44	15.86±25.16	12.86±4.58	5.48±5.02	9.5±8.3
Terpinolene	1024	Herbal	herbal spicy chamomile green basil	12.42±8.94	14.48±17.44	10.32±14.06	12.48±12.2	10.76±1.14	18.2±4.62
Alpha-phellandrene	1037	Terpenic	citrus herbal terpenic green woody pepper black pepper	8.58±1.88	7.48±7.58	6.24±10.52	11.68±5.76	5.52±0.8	33.14±3.24
D-Limonene	1045	Citrus	citrus orange fresh sweet	4.9±3.64	12.16±14.36	0.98±1.12	22.14±4.26	1.52±2.64	11.18±0.34
cis-beta-ocimene	1048	Floral	warm floral herbal sweet	1.74±2.08	14.5±12.84	1.3±1.36	5.62±9.76	6.12±3.02	30.98±4.28
trans-beta-Ocimene	1053	Floral	citrus tropical green terpenic woody green	0.34±0.32	0.44±0.78	1.36±1.42	0.8±1.12	2.96±2.04	9.14±3.6
Cymene	1063	Terpenic	fresh citrus terpenic woody spicy	27.38±5.88	24.6±8.68	8.62±7.48	2.86±2.66	2.64±0.32	0.2±0.34
gamma-Terpinene	1069	Terpenic	oily woody terpenic lemon lime tropical herbal	1.56±1.82	1.42±0.24	16.9±27.04	8.24±8.12	3.66±6.34	20.36±1.72
beta-Terpineol	1097	Woody	pungent earthy woody	24.52±27.78	33.2±28.18	7.24±10.06	62.92±42.8	22.24±8.72	11.36±0.04
Linalool	1100	Floral	citrus floral sweet bois de rose green blueberry	22.24±13.3	43.3±21.46	21.48±19.48	57.82±51.82	34.08±8.14	231.64±21.28
Dehydro-p-cymene	1105	Phenolic	phenolic spicy styreen clove guaiacol	0.34±0.42	1.24±0.14	0.06±0.1	1.42±0.52	2.12±1.5	0±0
Cosmene	1118	-	-	53.84±35.02	173.82±55.96	7.92±6.9	97.48±52.8	38.96±15.98	85.26±22.98
Allo-ocimene	1146	Floral	sweet floral nut skin pepper herbal tropical	0.24±0.44	3.64±6.32	4.3±5.2	5.42±4.84	0±0	10.38±0.2
Neo-allo-ocimene	1151	-	-	3.74±0.6	16.92±0.86	7.38±6.7	8.24±7.24	16.16±3	13.54±1.32
6-Camphenol	1185	-	-	13.96±3.24	15.36±3.86	12.24±10.6	21.94±9.84	23.14±8.36	24.14±3.1
Terpinen-4-ol	1190	Spicy	peppery woody earthy musty sweet	12.62±10.94	0±0	11.28±10.62	21.58±11.6	8.48±4.28	42±12.14
Myrcenol	1196	Floral	fresh floral lavender citrus	46.42±21.62	57.64±16.4	17.72±28.62	10.54±18.26	1.28±1.18	7.3±6.66
alpha-Terpineol	1198	Terpenic	pine terpenic lilac citrus woody floral	14.56±25.22	75.38±24.94	58.42±50.9	95.74±40.86	27.56±13.78	270.98±23.56
alpha-Terpineol acetate	1201	Herbal	herbal bergamot lavender lime citrus	40.38±12.54	162.68±41.32	93.46±81.94	112.54±68.14	60.26±15.22	43.28±4.9
Myrtenol	1218	Herbal	woody pine balsamic sweet minty medicinal	3.8±3.74	2.14±0.98	12.16±18.56	8.1±9.2	9.7±2.22	4±1.14
Myrtenal	1220	Spicy	sweet spicy cinnamon tonka terpenic camporeous jammy	0±0	0±0	0.52±0.9	0±0	0±0	5.92±0.26
trans-Geraniol	1224	Floral	sweet floral fruity rose waxy citrus	128.5±43.14	134±57.36	79.84±76.26	136.78±76.66	50.38±11.6	339.2±31.76
Verbenone	1230	Camphoreous	camphor menthol celery	8.24±1.54	13.84±2.08	2.74±2.38	17.28±13.64	1.24±0.2	10.44±1.6
Citronellol	1236	Floral	floral leathery waxy rose citrus	11.76±3.4	9.14±3.1	5.26±4.72	11.54±6.14	8.32±1.56	14.64±3.7
Carveol	1244	Minty	minty spearmint cooling green herbal caraway spicy	29.68±5.76	37.2±5.78	3.84±4.02	50.54±33.06	12.1±3.26	58.68±9
beta-Cyclocitral	1248	Tropical	tropical saffron herbal clean rose sweet tobacco green fruity	2.64±4.56	12.96±4.42	104.94±181.76	4.08±7.06	4.7±0.86	0±0
2-Carene	1253	-	-	147.14±254.84	131.12±227.12	35.7±61.86	0±0	120.38±58.66	0±0
Geraniol	1256	Floral	sweet floral fruity rose waxy citrus	728.46±365.86	531.6±244.28	73.54±65.32	589.2±370.7	5.42±9.4	1276.34±147.24
d-Carvone	1267	Minty	spicy bready caraway	3.56±1.9	35.4±8.28	13.08±11.34	16.74±7.46	7.26±2.32	16.62±4.14
Geranial	1273	Citrus	citrus lemon	164.94±50.48	205.14±28.82	17.18±14.9	353.38±155.06	65.54±18.68	444.96±32.74
Methyl geranate	1326	Waxy	waxy green fruity floral	0±0	4.98±0.96	0±0	0±0	4.44±1.66	0±0
Totals	**37**			**1594±1002.88**	**1892.12±934.04**	**712.22±827.06**	**1929.42±1237.68**	**683.38±290.44**	**3388.46±439.82**
Sesquiterpenes									

gamma-Elemene	1308	-	-	2.22±0.96	3.68±0.48	2.18±1.88	1.84±1.28	1.48±0.36	1.8±0.18
Cedrene	1368	Woody	woody cedar sweet fresh	15.46±10	5.88±4.42	5.82±5.9	9.18±8.76	6.4±2.82	5.3±5.34
alpha-Cubebene	1378	Herbal	herbal waxy	0±0	5.1±2.02	4.12±4.32	3.56±3.62	0.34±0.6	15.56±8.16
Longifolene	1401	Woody	sweet woody rose medicinal fir needle	0.66±0.2	1.16±0.1	3.48±5.02	0.66±0.42	1.74±1.38	1.22±0.18
Ylangene	1405	-	-	0.44±0.46	1.38±0.18	0.92±0.86	0.66±0.22	0.5±0.14	0.5±0.1
Copaene	1408	Woody	woody spicy honey	0.56±0.26	1.16±0.46	0.46±0.44	0.4±0.28	0.56±0.1	0.98±0.48
gamma-Muurolene	1430	Woody	herbal woody spicy	0.3±0.14	0.82±0.78	0.8±0.74	0.36±0.04	0.38±0.02	1.12±0.34
beta-Panasinsene	1439	-	-	0.68±0.22	0.66±0.56	0.22±0.38	0.44±0.32	0.3±0.02	0.16±0.28
beta-Copaene	1440	-	-	0.32±0.14	0.42±0.14	0.1±0.2	0.56±0.24	0.54±0.08	1.02±0.94
Caryophyllene	1451	Spicy	sweet woody spicy clove dry	0.64±0.28	8.42±9.18	1.14±1.08	0.7±0.7	2.3±0.38	1.38±0.3
alpha-Elemene	1458	-	-	0.2±0.2	0.18±0.2	0.18±0.32	0.06±0.12	0±0	0.36±0.24
trans-.beta.-Famesene	1462	Woody	woody citrus herbal sweet	0.26±0.14	0.58±0.44	0.38±0.34	0.18±0.16	0.28±0.12	0.34±0.16
beta-Farnesene	1469	Woody	woody citrus herbal sweet	2.22±1.54	1.46±0.4	1.08±1.1	1.3±1.4	0.9±0.18	0.68±0.54
gamma-Muurolene	1483	Woody	herbal woody spicy	2.22±0.66	5.56±1.98	3.82±3.88	3.04±1.72	3.72±1.26	3.28±0.78
beta-Selinene	1501	Herbal	-	0.76±0.3	1.98±0.54	0.6±0.56	0.8±0.44	1.02±0.2	0.84±0.12
alpha-Selinene	1505	-	amber	0.44±0.2	2.4±1.4	0.44±0.4	3.72±1.5	0.94±0.08	3.06±2.04
gamma-Cadinene	1520	-	-	0.38±0.16	1.2±0.54	0.6±0.52	0.5±0.22	0.14±0.14	0.8±0.56
Guaiol	1534	-	-	0.88±0.12	0.78±0.08	0.54±0.52	0.78±0.4	0.48±0.12	0.4±0.12
Cubenene	1541	Spicy	spicy fruity mango	0.76±0.14	1.08±0.14	0.9±0.98	0.9±0.34	0.66±0.18	0.76±0.14
beta-Cadinene	1547	Woody	green woody	1.12±0.38	2.08±0.78	1.12±1.02	1.24±0.72	1.58±0.86	1.96±0.46
Cadina-1,4-diene	1572	Spicy	spicy fruity mango	0.64±0.32	0.94±0.2	0.36±0.34	0.52±0.36	0.36±0.04	0.4±0.14
alpha-Calacorene	1573	-	woody	0.36±0.14	1.1±0.26	0.36±0.3	0.22±0.06	0.2±0.2	0.1±0.08
Caryophyllene oxide	1606	Woody	sweet fresh dry woody spicy	4.2±2.06	1.9±0.02	1.44±1.48	0.9±1.58	1.2±0.34	1.68±1.46
Humulenol-II	1651	-	-	1.46±0.42	5.88±2.26	2.56±2.28	2±0.72	2.12±0.82	3.16±1.2
T-Muurolol	1669	Herbal	herbal spicy honey	1.04±0.8	1.82±0.38	1±0.94	0.3±0.1	0.9±0.4	0.1±0.08
Cadalene	1690	-	-	1.58±0.52	4.98±0.22	2.16±2.04	1.46±0.52	1.36±0.5	2.8±0
Totals	**26**			**39.8±20.76**	**62.6±28.16**	**36.78±37.84**	**36.28±26.24**	**30.4±11.38**	**49.66±25.42**

[z] Relative peak area percent compounds were identified by comparison of mass spectra with NIST14 (National Institute of Standards and Technology, Gaithersburg, MD, USA), Flavors and Fragrances of Natural and Synthetic Compounds (FFNSC3, John Wiley & Sons, Inc., Hoboken, NJ, USA), and Adams Essential Oils (Adams 2007) mass spectral libraries and comparison of calculated Kovats retention indices (Kováts 1958) with previously reported values.

Table 4. Volatile aroma compounds[z] identified in muscadine genotypes grown at, North Carolina (Kings Mountain, NC) and evaluated at the University of Arkansas System Division of Agriculture Clarksville, AR (2021)

Compound Name	Retention Index	Aroma Category	Aroma Descriptor	Paulk	Oh My!®	Lane	RazzMatazz®	Hall	Supreme	JB 08-38-1-10	JB-06-30-2-20	JB-09-15-3-09	Summit
Totals	**198**			**5090.50±526.46**	**3803.86±1997.28**	**5285.38±1420.16**	**3385.84±421**	**5107±81.02**	**4182.38±1710**	**2541.36±636.46**	**2367.12±366.9**	**3741.16±783.14**	**4060.58±820.22**
Alcohols													
2-Butanol	610	Fruity	sweet apricot	0±0	10.66±11.86	13.92±23.22	8.64±12.48	0±0	12.8±21.08	1.06±1.84	2.14±3.72	9.74±8.5	0±0
1-Butanol	644	Fermented	fusel oily sweet balsamic whiskey	3.68±1.2	0±0	2.8±2.48	3.16±5.48	0±0	142.36±242.52	10.48±12.52	2.36±2.12	8.72±1.84	0±0
1-Penten-3-ol	683	Green	ethereal horseradish green radish chrysanthemum vegetable tropical fruity	0±0	7.76±7.16	25.76±22.08	39.68±25.44	18.16±10.56	0±0	50.96±11.88	22.12±38.32	76.28±66.12	0±0
2-Methyl-1-butanol	735	Ethereal	fusel ethereal alcoholic fatty greasy winey whiskey leathery cocoa	3.64±1.88	10±17.36	5.04±6.72	0±0	0±0	0±0	8.4±8.12	25.12±20.36	25.96±20.84	21.76±20.36
3-Methyl-3-buten-1-ol	739	Fruity	sweet fruity	0±0	25.84±44.76	19.76±30.68	34.76±46.76	10.92±12.68	9.76±14	15.08±23.08	38.52±61.48	13.04±4.96	318.32±485.12
1-Pentanol	763	Fermented	pungent fermented bready yeasty fusel winey solvent	0.88±1.56	6.72±8.24	6.48±11.24	8.4±10.76	11.72±2.6	34.6±32.8	2.96±2.76	10.8±9.36	3.96±3.52	0±0
3-Methyl-1-butanol	767	Fermented	fusel alcoholic pungent ethereal cognac fruity banana molasses	66.8±25.28	52.28±49.84	10±10.56	0±0	53.4±29.92	0±0	57.48±8.88	397.04±478.64	39.6±1.68	0±0
3-Hexen-1-ol	781	Green	leafy	0±0	0±0	2.24±3.88	16.6±22.08	8.6±8.6	6.2±10.76	21.52±19.48	50.32±27.52	73.96±14.28	0±0
2-Hexen-1-ol	836	Fruity	fruity green leafy	530.36±907.44	157.52±214.84	415.92±403.32	587.52±996.44	8.96±3.12	10.24±9.24	10.32±9.8	269.64±463.4	26.72±26.8	471.88±810.2
2 Heptanol	861	Citrus	fresh lemongrass herbal sweet floral fruity green	138.72±132.68	81.76±96.08	55.64±95.4	181.44±199.76	387.4±11.44	319.96±292.64	293.12±86.96	210.88±363.24	829.2±125.36	0.16±0.28
1-Hexanol	871	Herbal	ethereal fusel oily fruity alcoholic sweet green	6.32±5.6	8.8±11.36	0±0	0±0	1.84±1.04	0±0	0.32±0.6	0±0	0±0	564.2±969.72
5-Methyl-1-heptanol	894	-	-	8.92±3.36	41.84±70.64	6.64±1.96	7.04±1.68	7.6±2.48	7.76±1.12	6.64±6.6	1.84±3.24	9.68±6.64	3.64±3.88
2-Methyl-1-heptanol	900	-	-	13.76±9.16	24.96±42.32	3.84±3.6	11.88±3.2	10.08±2.4	6.52±6.36	14.36±11.68	9.84±11.56	47.44±3.32	1.72±2.4
2-Methyl-6-hepten-3-ol	919	-	-	0.84±0.44	1.08±0.84	4.6±6.24	0.52±0.28	4.32±2.4	0.28±0.04	0±0	0±0	0.84±0.8	0.4±0.4
2-methyl-2-heptanol	933	-	-	2.28±3.92	3.08±5.4	1.16±1	0±0	0±0	0±0	0.56±0.96	1.12±0.2	2.04±2.4	0.36±0.64
1-Octen-3-ol	960	Earthy	mushroom earthy green oily fungal raw chicken	0±0	0±0	0±0	11.8±20.48	0±0	2.04±3.52	26.72±26.6	9.6±9.2	0±0	17.68±26.12
1- Heptanol	973	Green	musty leafy violet herbal green sweet woody peony	190.36±42.56	139.36±206.88	30.56±15.92	99.6±152.96	33.68±58.36	0±0	4.8±8.32	0±0	21.28±19.44	6.76±11.72
2-Ethylhexanol	1034	Citrus	citrus fresh floral oily sweet	7.52±0.64	0±0	13.08±5.16	0±0	0±0	3.64±1.84	2.4±0.68	1.8±1.64	4.44±3.16	0.36±0.64
1-Octanol	1074	Waxy	waxy green orange aldehydic rose mushroom	21±1.6	10.04±8.2	9.72±3.08	15.92±1.72	9.64±2.76	7.88±6.52	1.4±0.48	1.6±0.28	2.72±1.12	0.24±0.4
1-Phenylethanol	1127	Floral	fresh sweet almond gardenia hyacinth	125.48±163.56	149.48±205.8	42.52±73.64	770.84±216.8	895.8±334.32	436.08±424	70.96±95.04	103.92±103.08	100.88±54.8	0±0
2-Phenylethanol	1129	Floral	floral rose dried rose	0±0	0±0	664.92±225.2	0±0	0±0	0±0	100.88±174.72	0±0	237.32±82.56	259.6±214.56
1-Nonanol	1176	Floral	fresh clean fatty floral rose orange dusty wet oily	8.76±1.72	5.24±6.48	4.6±3.64	6.08±5.56	5.76±3.16	5.64±5.92	1.2±0.32	1.16±0.88	9.92±11.16	2.24±0.84
2,4-Octadien-1-ol	1231	Fatty	fatty chicken creamy waxy	0±0	6.24±6.88	0±0	0±0	0±0	0±0	26.32±5.44	0±0	0±0	16±3.72
1-Decanol	1277	Fatty	fatty waxy floral orange sweet clean watery	3.44±0.32	8.48±13.88	0±0	1.2±1.32	0±0	6.36±10.72	5.12±2.92	2.08±1.24	8.12±0.68	5.4±3.88
4,8-Dimethylnonan-1-ol	1289	-	-	44.32±7.76	0±0	162.28±74.4	8.84±15.32	93.04±12.16	273.72±238.52	0±0	19.92±10.76	55.24±5.72	49.28±1.76
Eugenol	1371	Spicy	sweet spicy clove woody	5.24±0.76	5.2±3.68	6.32±1.56	4.88±1.08	2±0.16	3.88±1.6	0±0	0±0	0±0	0±0
1-Dodecanol	1480	Waxy	earthy soapy waxy fatty honey coconut	1.92±0.2	3.08±3.28	1.76±0.28	1.24±0.28	0.88±0.12	1.16±0.52	3.04±0.96	2.28±0.6	2.76±0.48	1.04±0.12
1-Hexadecanol	1887	Waxy	waxy clean greasy floral oily	0±0	3.68±2.6	2.28±0.68	1.28±0.28	1.12±0.88	0±0	0±0	0±0	0±0	3.64±1.72
Totals	**28**			**1184.24±1311.64**	**773.76±1050.24**	**1525.76±1049.16**	**1829.96±1752.64**	**1564.92±499.16**	**1303.68±1344.8**	**737.16±522.48**	**1186.24±1614.56**	**1619.6±474.68**	**1744.68±2558.48**
Aldehydes													
3-Methylbutanal	643	Aldehydic	ethereal aldehydic chocolate peach fatty	0±0	6.84±6.02	3.48±3.56	0±0	0±0	3.68±4.06	3.28±5.7	3.58±4.4	0±0	0±0
2-Butenal	654	-	-	5.06±1.8	4±3.7	2.5±1.5	0.48±0.42	6.08±5.2	18.14±16.72	11.52±6.84	7.3±8.54	16.54±6.02	13.38±19.46
2-Methylbutanal	669	Cocoa	musty cocoa phenolic coffee nutty malty fermented fatty alcoholic	2.22±3	0.84±1.04	0.64±0.48	1.86±2.96	8.58±7.18	0±0	2.14±3.7	0.5±0.14	1.14±0.72	0±0
Pentanal	701	Fermented	fermented bready fruity nutty berry	1.14±1.96	14.56±21.24	0±0	20.76±18.1	7.18±6.66	0±0	4.82±5.98	14.2±21.5	0±0	0±0
Tiglic aldehyde	728	Green	pungent green ethereal nutty anisic fruity	0±0	23.06±24.14	9.3±16.12	49.66±68.64	25.14±12	9.34±16.2	2.32±2.92	1.14±1.98	5.5±0.86	0±0
3-Methylpentanal	746	-	-	1.78±1.5	0.2±0.36	1.32±2.3	0.76±0.96	0.16±0.3	0±0	0.76±0.84	4.98±4.12	0.26±0.24	0±0
2-Pentenal	754	Green	pungent green apple orange tomato	6.46±0.4	20.76±25.76	1.8±1.7	2.56±1.66	2.7±0.72	45.4±68.1	1.26±1.08	48.92±69.98	12.62±2.72	74.84±56.44
2-Butenal, 3-methyl	787	Fruity	sweet fruity pungent brown nutty almond cherry	0.08±0.12	0±0	8.28±14.1	3.58±4.08	0.5±0.2	0±0	1.42±2.46	4.04±3.94	31.38±30.96	0±0
Hexanal	804	Green	fresh green fatty aldehydic grassy leafy sweaty	0±0	0±0	1.68±2.92	0.34±0.6	0±0	171.76±118.46	22.64±35.52	2.5±3.44	0±0	7.14±6.92
Furfural	841	Bready	sweet woody almond bread baked caramellike phenolic	1098.26±319.24	223.34±211	0±0	47.92±48.46	11.62±4.12	2.5±4.36	14.62±13.32	392.04±414	70.48±42.76	147.24±255.04
2-Hexenal	845	Green	sweet almond bitter fruity green leafy apple plum vegetable	0±0	0±0	136.38±48.36	58.3±84.88	132.86±65.5	341.96±298.98	108.66±180.56	103.82±108.34	3.92±1.06	122.6±155.08
Heptanal	892	Green	fresh aldehydic fatty green herbal cognac ozone	0.3±0.14	0.96±1.26	0.28±0.14	0.22±0.2	0±0	0±0	0.12±0.12	0.2±0.08	0.14±0.14	0.48±0.08
2-Heptenal	957	Green	green fatty	1.06±0.28	6.22±3.72	0.86±0.14	4.58±4.56	1.66±0.04	0.86±0.26	0.9±0.22	3.54±0.36	2.44±1.12	4.98±2.12
Benzaldehyde	966	Fruity	sharp sweet bitter almond cherry	153±19.22	139.86±52.58	113.08±13.24	186.9±110.72	125.74±60.18	136.5±116.9	25.62±22.84	31.32±14.96	87.54±24.4	34.2±6.1
Octanal	1002	Aldehydic	aldehydic waxy citrus orange peel green herbal fresh fatty	19.1±1.52	5.58±9.68	14.4±3.86	8.56±7.72	16.78±2.24	10.9±2.4	26.42±20.46	4.62±6.92	31.12±17.76	22.72±6.4
Phenylacetaldehyde	1059	Green	green sweet floral hyacinth clover honey cocoa	29.42±25.48	170.2±131.28	29.06±25.18	97.78±81.92	64.46±6.76	0±0	21.76±19.58	19.74±34.22	0±0	17.44±30.22
2-Octenal	1066	Fatty	fatty green herbal	22.7±19.7	33.24±47.52	0±0	3.72±6.46	60.64±28.9	57.58±74.24	385.8±304.06	46.68±80.86	164.82±46.72	0±0
3-Methylbenzaldehyde	1090	Fruity	sweety fruity cherry almond bitter phenolic	32.74±3.56	21±15.78	33.2±2.62	31.8±4.46	20.7±5.74	21.8±16.88	0.34±0.14	0.34±0.06	0.34±0.12	0.36±0.22
Nonanal	1103	Aldehydic	waxy aldehydic rose fresh orris orange peel fatty	34.9±6.24	13.56±7.52	9.5±1.5	14.32±5.6	17.76±4.68	10.26±8.88	18.9±3.56	9.96±17.26	30.56±11	8.26±14.3
Alpha-campholenal	1144	Herbal	herbal green woody amber leafy	2.94±3.46	4.54±3.5	3.34±1.92	2.44±4.22	5.44±4.44	6.28±4.68	0±0	2.46±1.78	2.58±1	2.38±0.34
2-Nonenal	1170	Fatty	fatty green waxy cucumber melon	4.02±2.08	73.92±125.42	2.16±0.9	4.06±0.96	3.38±0.28	37.5±58.82	0±0	0±0	0±0	0±0
Decanal	1212	Aldehydic	sweety aldehydic waxy orange peel citrus floral	1.86±1.62	2.24±2.52	3.06±0.8	3.02±0.82	2±0.16	2.02±2.12	2.06±3.08	0.64±1.12	1.04±1.82	3±1.52
2-Decenal	1270	Fatty	fatty orange rose aldehydic floral green	14.06±1.9	0±0	9.76±8.56	5.18±4.48	0±0	3.34±5.78	0±0	0±0	0±0	0±0
Citral	1282	Citrus	sharp lemon sweet	60.94±10.26	114.18±110.22	76.96±25.32	60.48±54.8	34.24±8.3	205.04±286.34	36.66±11.58	24.72±19	63.22±23.5	27.42±4.72
Dodecanal	1419	Aldehydic	soapy waxy aldehydic citrus green floral	0.32±0.08	0.82±1.06	0±0	0±0	0±0	1.42±2.1	0.4±0.22	0±0	0±0	0±0
Pentadecanal	1721	Waxy	fresh waxy	1.14±0.16	9.86±15.02	1.82±0.58	1.1±0.28	0.58±0.06	0±0	5.82±2.5	2.56±1.16	1.5±0.44	1.6±0.42
Totals	**26**			**1493.5±423.72**	**889.78±820.34**	**462.86±175.8**	**610.38±517.96**	**548.2±223.66**	**1086.28±1106.28**	**698.24±647.34**	**729.8±818.28**	**527.14±213.36**	**488.04±559.38**
Aromatic Hydrocarbons													
Toluene	777	Sweet	benzene	2.94±0.46	0.62±0.7	0±0	0.26±0.26	1.2±1.16	7.52±13.02	0.64±1.12	0±0	2.9±5.02	14.64±17.44
1,3-Cyclododecadiene, (E,Z)-	1653	-	-	2.2±1.18	2.6±1.28	2.26±2.1	2.24±1.48	1.56±1.04	3.64±3.24	1.8±0.48	1.8±1.18	0±0	0±0
Totals	**2**			**5.14±1.64**	**3.22±1.98**	**2.26±2.1**	**2.5±1.74**	**2.76±2.2**	**11.16±16.26**	**2.44±1.6**	**1.8±1.18**	**2.9±5.02**	**14.64±17.44**
Epoxides													
Humulene epoxide I	1620	Herbal	-	0.16±0.02	0.38±0.54	0.14±0	0.16±0	0±0	0.4±0.56	0.58±0.02	0.3±0.1	0.36±0.16	0.22±0.02
Humulene epoxide II	1630	-	-	0±0	1.28±1.24	0.64±0.1	0±0	0.22±0.06	0.66±0.56	0.14±0.12	0±0	0±0	0±0
Totals	**2**			**0.16±0.02**	**1.66±1.78**	**0.78±0.1**	**0.16±0**	**0.22±0.06**	**1.06±1.12**	**0.72±0.14**	**0.3±0.1**	**0.36±0.16**	**0.22±0.02**
Esters													
Butanoic acid, methyl ester	709	Fruity	fruity apple sweet banana pineapple	3.06±0.62	7.04±11.54	0.82±1.42	0.4±0.06	0±0	0±0	1.96±3.06	3.18±5.18	11.32±9	6.48±8.64
Ethyl propionate	713	Fruity	sweet fruity rummy juice fruity grape pineapple	0.2±0.34	1.9±3.3	3.06±3.2	1.2±1.16	0±0	0±0	4.06±1.98	0.96±1.66	1.48±1.34	0±0
Propanoic acid, ethyl ester	721	Fruity	sweet fruity rummy juice fruity grape pineapple	0±0	0.12±0.22	0.52±0.9	2.16±0.88	0±0	1.88±3.26	0.36±0.3	2.72±2.7	2.7±4.68	0±0
Methyl butanoate	731	Fruity	pungent ethereal fruity fusel fermented creamy	4±3.14	6.92±11.98	0.22±0.38	0.76±0.8	1.62±1.6	1.74±1.72	0.64±0.74	0.54±0.96	0±0	1.86±2.12
Butanoic Acid	771	Cheesy	sharp acetic cheesy buttery fruity	1.08±1.36	1.66±2.88	1.7±1.02	96.9±148.66	5.84±6.18	24.74±39.6	5.84±5.24	0±0	0±0	0±0
Methyl 2-methylbutanoate	783	Fruity	ethereal estery fruity tutti frutti apple green apple lily of the valley powdery fatty	0.56±0.5	1.44±2.1	16.76±12.58	0±0	0±0	0.94±1.14	32.9±45.1	0±0	0±0	7.26±8.14
Ethyl butanoate	799	Fruity	fruity juicy fruit pineapple cognac	17.2±29.82	26.12±30.42	10.68±10.38	153.24±137.48	73.26±37.36	87.88±64.56	78.42±66.72	46.98±79.72	103.7±3.46	52.26±88.34
Butyl acetate	809	Ethereal	ethereal solvent fruity banana	30.84±25.2	38.46±32.28	1.28±2.22	23.32±23.02	23.04±24.4	0±0	9.24±6.5	5.2±3.78	192.58±151.92	54.76±92.76
Methyl 3-methylbutanoate	814	Fruity	apple fruity pineapple	5.18±2.1	14.78±8.72	14.48±18.18	2.2±2.1	30.08±33.12	5.8±5.04	3.42±4.54	3.48±1.54	0±0	48.64±68.7
Ethyl 2-methylbutanoate	850	Fruity	sharp sweet green apple fruity	100.24±41.52	49.9±57.2	0±0	302.94±211.18	179.34±65.56	128.48±117.96	185.58±154.98	162.96±155.7	77.38±15.88	1.42±2.48
Ethyl 2-methylbutyrate	857	Fruity	sharp sweet green apple fruity	98.44±38.54	22.12±38.32	65.34±3.3	24.92±43.18	0±0	0±0	0±0	0±0	0±0	40.84±70.74
Isobutyl isobutyrate	886	Fruity	ethereal fruity tropical pineapple grape banana	1.76±0.94	0.24±0.44	1.76±2.36	0.84±1.46	0±0	0±0	0.1±0.18	1.4±1.1	0±0	0±0
Hexanoic acid, methyl ester	904	Fruity	ethereal pineapple fruity apricot strawberry banana bacon	3.04±0.58	4.62±6.74	1.8±0.72	5.84±6.98	11.84±12.8	0.88±0.8	2.36±1.2	0.98±1.42	12.14±12.42	1.54±2.38
Propanoic acid	911	Acidic	acidic dairy fruity	3.94±0.94	4.66±3.94	2.28±1	8.48±6.76	3.5±1.54	2.82±0.22	4.82±2.48	2.3±2.94	6.04±1.36	1.34±1.3
Methyl hexanoate	923	Fruity	ethereal fruity pineapple apricot strawberry fruit banana bacon	3.06±2.4	2.7±3.42	0±0	4.62±2.24	2.02±2.4	0±0	0±0	0.6±0.56	1.04±0.72	0±0
4-methylpentyl 4-methylpentanoate	931	Fruity	fruity waxy soapy herbal	2.06±2.68	0±0	1.98±0.74	0±0	0.36±0.34	1.06±0.26	0.26±0.48	0.64±0.12	0.72±0.08	0.6±0.18
Ethyl Butyrate	940	Fruity	fruity juicy pineapple cognac	0.92±0.82	1.02±1.02	0.68±1	0.82±0.72	1.1±0.04	1.86±1.62	0.46±0.44	0.14±0.24	0.8±0.38	0.18±0.32

2-Methylbutyl propionate	950	Fruity	sweet fruity ethereal rummy	1.26±0.52	0.14±0.24	0.4±0.08	2.96±2.86	0.42±0.14	1.56±1.1	0.12±0.22	8.44±7.4	0.68±0.3	0±0
Isobutyl 2-methylbutyrate	976	Fruity	sweety fruity melon	16±3.72	1.38±1.24	6.14±6.98	5.3±4.6	14.44±0.76	11.98±2.62	2.38±1.64	8.3±2.28	8.64±7.54	8.08±10.28
Heptanoic acid, methyl ester	986	Fruity	sweet fruity green orris waxy floral berry	0±0	6.3±5.2	0±0	7.36±3.3	7.24±0.42	3.68±3.2	2.82±2.52	6.56±5.44	10±2.88	11.88±10.98
2-Methylbutanoic acid	993	Acidic	pungent acidic cheesy roquefort cheese cheesy	20.46±5.24	3.82±4.42	17.82±1.08	5.8±3.22	14.62±11.24	29.86±26.7	10.72±6.38	10.12±9.3	2.06±0.52	33.96±13.52
Ethyl hexanoate	996	Fruity	sweet fruity pineapple waxy green banana	1.22±1.16	9.02±6.44	0±0	5.08±3.54	2.4±1.92	2.24±1.96	1.72±0.26	3.34±3.08	1.08±0.14	0±0
Hexyl acetate	1005	Fruity	fruity green apple banana sweet	32.96±28.64	0±0	65.9±57.06	46.5±61.86	0±0	0±0	7.74±1.1	12.54±10.46	0±0	0±0
Geranyl isovalerate	1008	Fruity	green fruity apple blueberry pineapple	1.04±0.26	0.02±0.04	0.66±0.78	1.14±1.16	1.7±0.96	1.7±1	0.08±0	0.04±0.04	4.56±1.92	0±0
Butanoic acid, 3-methylbutyl ester	1013	Fruity	fruity green apricot pear banana	0±0	0±0	0±0	1.16±2.02	5.6±9.68	0±0	0±0	0±0	0±0	6.52±8.12
Methyl heptanoate	1027	Fruity	sweet fruity green orris waxy floral berry	0.74±0.06	4.3±3.1	0.16±0.28	4.88±1.44	2.56±0.8	4.04±6.3	5.26±5.28	0±0	0±0	15.52±7.4
Heptanoic acid	1031	Cheesy	rancid sour cheesy sweaty	6.24±0.78	7.08±1.26	4.44±1.54	9.32±2.24	10.16±2.48	4.26±3.7	9.42±3.86	5.1±3.72	5.2±1	0±0
3-Methylbutyl 2-methylbutanoate	1087	Fruity	sweet fruity citrus cherry blueberry apple	24.02±7.38	228.84±354.24	12.18±3.72	8.4±4.56	9.3±5.8	2.48±1.66	0±0	0.82±0.88	3.2±4.86	2.92±4.44
4-Octenoic acid, methyl ester	1114	-	-	21.12±7.16	50±51.88	18.04±11.24	16.94±7.4	18.1±5.62	25.38±7.96	4.84±1.7	4.5±1.42	20.64±19.58	154.66±140.04
Methyl octanoate	1121	Waxy	waxy green sweet orange aldehydic vegetable herbal	294.3±290.66	752.38±659.56	0±0	0±0	656±433.84	457.86±553	0±0	0±0	1058.4±580.32	0±0
Allyl isovalerate	1123	Fruity	sweet fruity banana apple pineapple cherry	64.04±11.82	0±0	98.7±49.44	0±0	78.8±72.98	0±0	0±0	0±0	0±0	474.54±585.86
Ethyl 3-hydroxyhexanoate	1130	Fruity	fruity grape woody burnt wood hay spicy pineapple cranberry dusty woody	5.48±1	0±0	0±0	0±0	0±0	0±0	1.96±1.7	2.24±3.88	0±0	0±0
Valeric acid	1149	Cheesy	acidic sweaty rancid	15.42±8.88	0±0	25.7±9.04	2.88±1.02	6.86±1.08	2.34±1.44	0.5±0.1	0.5±0.38	0±0	4.82±4.18
Octanoic acid	1163	Fatty	fatty waxy rancid oily vegetable cheesy	122.88±46.02	0.92±1.6	107.76±4.72	51.28±44.62	0±0	37.14±37.76	1.92±2.72	2.44±2.22	0±0	6.3±1.8
Nonanoic acid	1181	Waxy	waxy dirty cheesy dairy	0.94±0.98	2.5±3.86	0.96±0.58	0.98±0.46	2.34±0.64	4.48±2.98	1.68±0.64	1.46±0.82	3.4±0.5	1.8±0.64
Methyl nonanoate	1209	Fruity	sweet fruity pear waxy tropical winey	0.88±0.32	0.16±0.14	0.38±0.1	1.08±0.22	0.78±0.18	0.5±0.5	1.68±0.74	0.54±0.1	1.34±0.08	0.8±0.26
methyl carvacrol	1250	Herbal	herbal spicy leafy citrus	5.68±4.94	0±0	0±0	0.94±1.64	0±0	24.82±38.7	0±0	0±0	0±0	0±0
Methyl dec-5-enoate	1296	-	-	3.8±0.44	4.56±2.3	2.86±1.08	2.8±1.42	1.68±0.2	2.1±1.94	2.12±0.3	1.06±0.56	3.14±1.1	1.76±0.64
4-Decenoic acid	1299	Fruity	-	4.18±0.34	1.74±1.16	3.32±1.28	9.08±1.9	2.36±0.28	3.76±2.74	12.4±4.02	1.5±1.02	6.42±1.96	8.78±2.62
Decenoic acid	1309	Waxy	waxy buttery oily creamy dairy green lactonic plum skin	7.68±3.38	9±6.72	5.8±1.84	10.54±2.5	9.58±3.02	8.66±4.58	0±0	8.84±4.36	8.08±1.22	11.22±5.14
Methyl 5-bromo-5-hexenoate	1314	-	-	1.88±0.16	1.62±0.64	3.1±1.38	1.96±1.14	0.88±0.78	1.58±1.66	10.88±2.88	0±0	5.62±7.16	3.34±1.68
trans-Geranic acid methyl ester	1323	Waxy	waxy green fruity floral	0.6±0.52	1.06±1.22	0±0	0.44±0.44	2.08±0.78	1.62±0.5	2.66±1.26	1.6±0.1	1.74±0.32	4.06±1.52
Methyl decanoate	1327	Fermented	oily winey fruity floral	2.22±0.22	3.36±1.72	1.88±0.88	2.96±0.74	1.1±0.64	2±2.34	6.88±1.42	4.02±1.44	7.76±3.9	3.92±0.3
Methyl 3-undecenoate	1355	-	-	12.66±1.04	22.48±19.98	0±0	10.7±5.68	6.4±0.46	6.62±5.38	21.78±10.3	2.84±0.92	4.04±0.44	2.9±0.28
Decanoic acid	1360	Fatty	rancid sour farty citrus	0.56±0.98	0±0	0±0	2.04±0.68	0.8±0.32	1.7±0.76	0.56±0.12	0±0	0±0	0±0
Geranyl acetate	1383	Floral	floral rose lavender green waxy	16.02±7.76	15.98±17.54	5.46±1.04	4.5±0.9	4.14±2.3	4.58±3.44	36.7±8.66	28.26±7.24	54.26±24.86	18.38±4.46
4-tert-Butylphenyl acetate	1412	-	-	3±0.08	3.62±3.62	2.82±1.2	2.52±1.24	1.18±0.18	1.98±0.86	2.8±0.76	0.98±0.36	0±0	0.08±0.14
Geranyl isobutyrate	1514	Floral	Sweet/fruity, waxy	1.98±0.32	3.02±1.68	2.28±0.72	3.38±1.98	1.36±0.6	1.28±0.8	2.86±0.52	1.38±0.66	1.76±1.26	0.74±0.16
Methyl dodecanoate	1526	Waxy	waxy soapy creamy coconut mushroom	1.72±0.18	1.36±1.34	0.9±0.44	1.24±0.38	0.42±0.46	3.48±4.86	1.28±0.3	1.1±0.38	2.32±0.26	1.44±0.42
Dodecanoic acid	1556	Fatty	fatty coconut bay	0.34±0.28	0±0	0.4±0.36	0.6±0.18	0.26±0.1	1.24±0.76	0±0	0±0	0±0	0±0
Hexyl octanoate	1589	Green	fruity green waxy berry apple estery	0.18±0.04	1.56±1.96	0.22±0.06	0.32±0.16	0.28±0.14	0.16±0.14	0.42±0.26	0.42±0.02	1.7±1.86	0.26±0.1
Ethyl dodecanoate	1595	Waxy	sweet waxy floral soapy clean	0.46±0.14	0.98±1.16	0.46±0.2	0.46±0.22	0.44±0.04	0.76±0.42	6.76±2.98	0.98±0.2	0±0	0.66±0.14
Totals	**52**			**967.54±586.92**	**1320.9±1368.78**	**512.1±216.52**	**854.18±752.4**	**1196.28±744.18**	**913.92±957.94**	**491.36±356.58**	**352±326.3**	**1625.94±865.22**	**996.52±1151.22**
Ketones													
3-Buten-2-one, 3-methyl-	677	-	-	5.32±1.04	0±0	0±0	4.26±7.4	10.96±12.5	5.22±5.88	4.34±4.96	0±0	18.58±21.26	0±0
1-Penten-3-one	687	Spicy	pungent peppery mustard garlic onion	53.46±45.72	15.26±12.44	8.58±7.5	0±0	23.58±10.44	0±0	6.52±11.32	3.34±3.84	2.02±0.02	0±0
Methyl Isobutyl Ketone	716	Green	sharp solvent green herbal fruity dairy spicy	1.82±3.16	0±0	0.14±0.24	0±0	0±0	0±0	0±0	0.38±0.66	0±0	3.92±3.52
2-Hexanone	793	Fruity	fruity fungal meaty buttery	86.66±92.76	0±0	18.02±30.16	1.54±2.36	0±0	0.94±1.64	3.02±3.36	2.7±3.24	10.1±8.56	7.22±7.02
2-Heptanone	883	Cheesy	fruity spicy sweet herbal coconut woody	1.84±0.96	2.08±2.94	0.8±0.32	1.24±0.96	3.54±0.96	2.62±2.36	1.3±1.26	1.66±1.44	1.3±1.58	1.64±1.94
4-Methyl-2-heptanone	945	-	-	0.08±0.14	0.2±0.36	0±0	0.12±0.2	0.06±0.1	1.02±1.78	0.04±0.08	0.12±0.1	0±0	4.48±3.7
Acetophenone	1083	Floral	sweet pungent hawthorn mimosa almond acacia chemical	0±0	3.82±4.44	4.52±1.3	8.64±4.44	6.32±9.88	2.04±1.44	1.22±1.18	3.12±2.84	3.88±1.64	2.12±0.64
2-Decanone	1159	Floral	orange floral fatty peach	0±0	49.24±45.46	0±0	0±0	37.2±1.64	0.1±0.18	4.66±1.5	6.22±3.86	5.18±1.64	6.6±1.8
7-Decen-2-one	1164	-	-	13.78±17.92	2.96±2.92	38.6±43.86	61.24±91.86	63.04±10.34	0±0	0±0	5.08±0.74	0±0	8.7±1.24
Decanone	1193	-	-	10.04±8.7	6.74±4.24	3.96±5.06	5.78±5.2	30.78±4.98	18.36±24.22	41.66±40.42	10.46±8.98	24.8±8.88	48.54±11.44
Undec-2-en-6-one	1262	-	-	119.24±22.66	77.16±38.4	103.06±32.78	158.56±44.72	6.94±6.02	166.72±234.1	52.94±36.22	0±0	32.08±6.46	59.3±20.54
2-Dodecanone	1342	Citrus	fruity citrus floral orange	10.36±3.3	3.88±3.64	0±0	8.26±8.58	47.68±8.66	1.4±0.26	0.9±0.16	1.74±1.72	5.28±1.7	24.34±9.82
2-Nonadecanone	1359	-	-	1.14±0.12	0.4±0.34	324±97.6	1.24±0.4	0.82±0.66	1.4±0.64	3.94±0.4	0.2±0.24	2.54±3.36	0.66±0.14
Damascenone	1391	Floral	natural sweet fruity rose plum grape raspberry sugar	60.02±5.2	66.24±56.2	111.22±61.74	53.08±16.88	50.88±21.9	156.5±120.82	52.5±17.84	39.6±27.8	39.7±12.1	22.16±17.36
Ethyl decanoate	1397	Waxy	sweet waxy fruity apple grape oily brandy	5.08±1.02	4.92±4.1	4.24±1.06	7.58±2.36	1.28±0.18	1±0.88	1.86±0.22	4.42±1.84	6±1.28	3.14±0.96
(Z)-6-Pentadecen-2-one	1660	-	-	0.52±0.08	1.08±1.26	0.26±0.06	0.58±0.36	0.16±0.14	0.12±0.1	0.74±0.4	0.38±0.16	0±0	0.52±0.16
Totals	**16**			**369.36±202.78**	**233.98±176.74**	**617.4±281.68**	**312.12±185.72**	**283.24±88.4**	**357.44±394.3**	**175.64±119.32**	**79.42±57.46**	**151.46±68.48**	**193.34±80.28**
Lactones													
Gamma-hexalactone	1055	Tonka	herbal coconut sweet coumarinic tobacco	37.22±16.1	40.82±35.34	11.72±9.44	44.64±6.74	25±8.6	85.24±76.82	17.22±15.3	18.42±16.26	82±32.46	0±0
Geranylacetone	1454	Floral	fresh green fruity waxy rose woody magnolia tropical	2.4±0.34	3.88±2.52	2.92±0.9	3.9±1.12	2.38±0.48	1.54±1.44	1.58±0.36	3.52±2	3.96±1.52	3.14±0.36
Gamma-decalactone	1488	Fruity	fresh oily waxy peach coconut buttery sweet	1.08±0.2	0.66±0.12	0.92±0.12	0±0	0.42±0.06	1.32±2.3	1.28±0.26	0.58±0.22	2.06±0.88	0.5±0.08
Totals	**3**			**40.7±16.64**	**45.36±37.98**	**15.56±10.46**	**48.54±7.86**	**27.8±9.14**	**88.1±80.56**	**20.08±15.92**	**22.52±18.48**	**88.02±34.86**	**3.64±0.44**
Monoterpenes													
Alpha-thujene	933	Woody	woody green herbal	30.32±30.04	0±0	0±0	51.7±66.84	37.72±17.38	48.34±41.86	1.34±2.34	0±0	8.64±0.92	10.58±14.7
Myrcene	971	Spicy	peppery terpenic spicy balsamic plastic	0±0	0±0	30.76±28.36	35.58±47.22	71.16±10.14	80.24±31.14	0±0	3.32±2.38	12.8±22.18	2.14±3.7
Beta-pinene	980	Herbal	dry woody resionous pine hay green eucalyptus camporeous	18.1±1.68	11.28±0.52	9.54±0.86	12.96±8.68	5.5±5.92	17.12±13.08	4.64±7.1	2.24±1.96	2.38±2.14	15.4±23.02
Beta-myrcene	991	Spicy	pepper terpenic spicy balsamic plastic	80.34±8.56	29.06±6.94	159.86±70.02	15.86±7.68	274.74±200.46	59.9±10.34	23.46±14.64	8.02±4.58	12.52±3.02	36.04±50
alpha-Phellandrene	1011	Terpenic	citrus herbal terpenic green woody pepper black pepper	0±0	51.26±52.32	18.6±32.22	0±0	0±0	0±0	0±0	5.1±8	0±0	0±0
alpha-Terpinene	1017	Woody	woody terpenic lemon herbal medicinal citrus	15.82±2.1	5.28±4.72	6.94±6.58	13.02±5.56	13.6±3.82	22.28±14.16	0.96±0.96	1.68±1.52	0±0	4.8±2.64
Beta-phellandrene	1019	Minty	minty terpenic	6.38±1.06	10.06±9.34	10.56±2.38	10.44±2.44	0±0	8.54±6.44	1.88±3.24	12.78±10.3	1.06±1.84	3.06±2.78
Terpinolene	1024	Herbal	herbal spicy chamomile green basil	9.18±2.6	8.38±6.3	6.52±5.76	6.28±5.48	7.92±4.48	18.82±7.36	6.76±5.04	24.3±25.7	29.28±7.44	21.74±1.9
Alpha-phellandrene	1037	Terpenic	citrus herbal terpenic green woody pepper black pepper	8.94±2.98	2.14±2.1	8.58±2.04	6.02±4.68	23.16±12.64	14.2±12.34	0±0	0±0	0±0	4.22±7.3
cis-beta-Ocimene	1040	Floral	warm floral herbal sweet	0±0	7.94±8.62	0±0	0.64±1.1	9.24±1.14	0±0	3.4±1.36	0.84±1.38	2.24±0.52	5.56±2.52
D-Limonene	1045	Citrus	citrus orange fresh sweet	7.14±0.58	0.2±0.34	0±0	2.98±3.92	0±0	1.12±1.52	0±0	0.7±0.48	0.5±0.5	0±0
cis-beta-ocimene	1048	Floral	warm floral herbal sweet	0±0	1.18±0.9	17.2±6.86	9.12±11.14	19.8±9.08	2.14±2.26	0.9±0.66	0.08±0.08	1.44±0.46	3.54±3.7
trans-beta-Ocimene	1053	Floral	citrus tropical green terpenic woody green	0.66±0.58	1.68±1.48	0.12±0.22	0.42±0.74	0.28±0.48	0.92±1.6	2.1±1.24	3.26±1.72	3±0.36	4.96±2.68
Cymene	1063	Terpenic	fresh citrus terpenic woody spicy	5.04±2.24	0±0	1.74±1.68	3.96±3.82	3.04±0.26	1.12±1.96	0.06±0.12	3.72±3.22	0.12±0.2	31.52±6.2
gamma-Terpinene	1069	Terpenic	oily woody terpenic lemon lime tropical herbal	0±0	4.54±7.86	148.62±89.16	2.36±2.44	1.88±3.28	0±0	0±0	1.14±1.02	0±0	0.88±1.52
beta-Terpineol	1097	Woody	pungent earthy woody	0.6±1.04	21.54±11	1.4±1.26	5.3±6.66	9.02±7.66	29.82±20.1	3.16±0.8	1.32±1	1.44±0.24	29.24±23.02
Linalool	1100	Floral	citrus floral sweet bois de rose green blueberry	262.9±71.3	0±0	194.18±74.1	23.68±9.42	170.8±34.4	0±0	2.26±0.56	13.72±10.26	2.04±0.68	58.94±50.38
Dehydro-p-cymene	1105	Phenolic	phenolic spicy styreen clove guaiacol	4.94±4.28	5.82±8.34	5.66±1.56	7.58±5.36	7.56±0.82	5.86±5.54	0±0	0.18±0.3	0±0	0.72±0.62
Cosmene	1118	-	-	6.02±4.44	0±0	9.92±2.38	28.7±26.98	1.64±0.72	3.16±1.62	2.24±1.32	2.62±1.28	5.04±6.54	0±0
Allo-ocimene	1146	Floral	sweet floral nut skin pepper herbal tropical	2.4±1.14	2.84±1.58	0.8±1.38	3.28±1.28	1.1±1.92	3.08±2.02	1.92±0.58	0±0	0±0	4.02±1.56
Neo-allo-ocimene	1151	-	-	0±0	2.64±2.28	5.42±1	0.6±1.04	24.12±1.4	4.1±6.28	8.66±2.88	8.78±4.22	11.3±1.74	6.18±3.44
6-Camphenol	1185	-	-	9.54±11.98	15.18±3.22	19.56±5.6	2.9±0.54	45.84±7.58	56.14±48.76	41.18±28.08	18.42±17.08	35.12±11.12	4.64±1.18
Terpinen-4-ol	1190	Spicy	peppery woody earthy musty sweet	22.38±8.56	14.2±20.56	37.3±13.78	6.48±2	0±0	20.18±15.72	7.74±5.48	5.36±4.1	3.76±4.1	2.14±3.72
Myrcenol	1196	Floral	fresh floral lavender citrus	1.04±1.8	6.82±3.7	0±0	2.18±2.3	12.44±10.78	5.38±5.52	5.74±9.94	0±0	1.44±2.5	6.72±2.96
alpha-Terpineol	1198	Terpenic	pine terpenic lilac citrus woody floral	352.64±190.18	48.4±29.94	340.36±175.06	104.94±24.7	138.2±9.8	20.84±20.74	100.06±42.8	25.62±14.72	30.6±3.74	88.34±33.96
alpha-Terpineol acetate	1201	Herbal	herbal bergamot lavender lime citrus	125.64±21.34	40.16±46.56	22.42±19.46	42.7±6.42	50.66±5.94	48.18±7.12	66.24±24.2	63.54±35.94	94.7±22.92	68.48±8.54
Myrtenol	1218	Herbal	woody pine balsamic sweet minty medicinal	1.68±1.46	2.8±1.52	4.22±1.04	3.24±1.24	0±0	1.74±1.7	2.8±1.42	1.42±0.76	3.84±0.28	2.5±0.84
Myrtenal	1220	Spicy	sweet spicy cinnamon tonka terpenic camporeous jammy	4.88±1.44	3.24±5.6	0±0	2.34±0.76	7.02±1.3	3.8±3.08	1.02±0.34	1.7±0.44	4.44±3.82	9.48±5.8
trans-Geraniol	1224	Floral	sweet floral fruity rose waxy citrus	106.64±11.86	19.76±1.98	308.7±119.12	41±12.96	133.44±26.96	49.14±32.98	39.28±8.62	11.4±10.08	17.24±4.24	149.08±4.8
Verbenone	1230	Camphoreous	camphor menthol celery	4.02±0.4	0.56±0.44	9.6±5.28	0.5±0.16	7.68±1.02	2.32±1.8	3.9±0.4	3.24±0.82	3.22±0.12	1.2±2.1
Citronellol	1236	Floral	floral leathery waxy rose citrus	14.86±8.08	5.54±4.88	11±3.56	22.72±11.82	5.2±1.9	24.54±15.62	2.44±0.98	7.18±3.96	19.02±8.52	1.06±1.16
Carveol	1244	Minty	minty spearmint cooling green herbal caraway spicy	18.44±7.74	14.54±8.9	24.92±5.76	20.12±10.38	23.62±2.44	27.08±14.66	1.8±1.58	4.82±4.22	10.82±2.96	17.56±3.02
beta-Cyclocitral	1248	Tropical	tropical saffron herbal clean rose sweet tobacco green fruity	2.84±4.92	0±0	0±0	0±0	0±0	0±0	5.66±2.92	0.82±1.44	0±0	0±0
2-Carene	1253	-	-	0±0	0±0	0±0	0±0	0±0	91.08±157.76	0±0	255.94±200.34	0±0	114.36±198.08
Geraniol	1256	Floral	sweet floral fruity rose waxy citrus	341.9±51.56	54.38±26.62	1129.54±423.8	14.74±25.56	923±43.56	138.52±91.7	345.22±255.74	23.62±13.56	125.8±38.24	624.16±292.36
d-Carvone	1267	Minty	spicy bready caraway	4.42±3.82	407.34±684.96	75.28±102.32	71.88±119.1	7.18±0.76	175.08±298	30.2±15.86	9.28±5.38	23.48±7.64	23.84±5.34
Geranial	1273	Citrus	citrus lemon	79.6±9.64	35.1±24.44	219.76±100.72	24.2±36.24	177.3±87.7	27.34±15.68	3.5±3.14	5.06±2.8	0±0	70.56±12.68
Methyl geranate	1326	Waxy	waxy green fruity floral	2.5±0.58	3.16±4.4	2.38±0.96	2.92±1.08	0.48±0.44	1.04±1.06	0.54±0.94	0±0	0±0	0±0

Totals	**38**			**1551.8±469.98**	**837.02±992.36**	**2841.46±1304.28**	**603.34±477.74**	**2214.34±516.18**	**1013.16±911.52**	**721.06±445.28**	**531.22±395.04**	**467.28±158.98**	**1427.66±778.22**
Sesquiterpenes													
gamma-Elemene	1308	-	-	2.6±0.46	1.94±2.36	1.16±0.38	1.66±0.68	0.88±0.28	2.26±2.16	2.52±0.96	2.06±1.48	2.16±0.44	1.84±0.38
Cedrene	1368	Woody	woody cedar sweet fresh	10.84±6	10.76±13	4.84±1.12	3.18±0.7	3.12±0.9	2.86±0.78	20.34±4.86	16.94±3.84	25.7±9.78	11.5±3.52
alpha-Cubebene	1378	Herbal	herbal waxy	2.32±0.88	0.1±0.2	23.02±13.24	1.32±0.64	11.62±3.14	9.2±5.74	0.24±0.42	0.16±0.14	0±0	0±0
Longifolene	1401	Woody	sweet woody rose medicinal fir needle	3.18±0.32	3.56±1.9	0.68±1.18	2.64±1.44	1.92±0.62	1.38±0.48	1.74±0.5	1.32±0.56	2.44±0.32	1.36±0.18
Ylangene	1405	-	-	0±0	0±0	2.9±0.1	0.34±0.6	0±0	1.4±2.06	0±0	0±0	0.42±0.2	0.4±0.06
Copaene	1408	Woody	woody spicy honey	0.86±0.12	0.78±0.42	0.18±0.3	0.24±0.2	0.28±0.24	0±0	1.34±0.7	1.1±0.74	1.02±1.08	0.4±0.12
gamma-Caryophyllene	1414	Spicy	sweet woody spicy clove dry	0±0	0.12±0.2	0±0	0.36±0.12	0±0	0±0	0±0	0.12±0.12	0.68±0.64	0.18±0.04
epsilon-Muurolene	1423	-	-	0.26±0.02	0.56±0.56	0.44±0.12	0.5±0.08	0±0	0.14±0.14	0±0	0.08±0.06	0±0	0.06±0.06
gamma-Muurolene	1430	Woody	herbal woody spicy	0.6±0.12	0.44±0.48	0.64±0.24	0.38±0.12	0.16±0.22	1.48±1	1.46±0.78	0.7±0.16	1.64±0.1	0.64±1.14
beta-Panasinsene	1439	-	-	0.6±0.18	0.68±0.88	0.24±0.06	0.16±0	0.26±0.24	0.3±0.1	0.1±0.08	0.36±0.32	0±0	0±0
beta-Copaene	1440	-	-	0.58±0.1	0.96±0.94	0.14±0.04	0.46±0.14	0.34±0.08	0.44±0.26	0.6±0.12	0.46±0.36	0.4±0.06	0.2±0
Caryophyllene	1451	Spicy	sweet woody spicy clove dry	1.14±0.06	2.42±1.38	1.7±0.42	1.54±1.12	0.96±0.38	1.06±0.46	1.06±0.1	0.94±0.48	1.88±0.62	1.08±0.46
alpha-Elemene	1458	-	-	0±0	0.24±0.2	0±0	0.46±0.16	0±0	0±0	0.38±0.34	0±0	0±0	0±0
trans-.beta.-Famesene	1462	Woody	woody citrus herbal sweet	0.72±0.04	0.04±0.08	0.62±0.1	0.24±0.02	0.18±0.04	0.4±0.42	0±0	0±0	1.56±1.76	0.3±0.02
beta-Farnesene	1469	Woody	woody citrus herbal sweet	1.36±0.14	3.28±3.5	1.26±0.2	1.3±0.28	0.74±0.14	0.56±0.54	6.24±3.08	3.38±1.12	1.9±0.44	1.04±0.26
gamma-Muurolene	1483	Woody	herbal woody spicy	3.78±1.8	3.64±3.26	3.32±2.2	2.98±1.04	2.84±1.06	2.38±0.6	5.6±0.82	3.4±1.44	3.68±1	2.42±0.76
beta-Selinene	1501	Herbal	-	0.66±0.12	1.48±1	0.84±0.14	1.82±1.7	0.9±0.22	2.9±3.54	0.42±0.06	0.6±0.68	1.34±0.54	0.9±0.16
alpha-Selinene	1505	-	amber	0.48±0.22	0.52±0.3	0.56±0.2	1.62±0.56	0.04±0.08	0.18±0.18	1.14±0.1	0.88±0.56	0±0	0±0
gamma-Cadinene	1520	-	-	1.14±0.3	1±0.86	0.72±0.14	0.52±0.18	0.38±0.2	1.34±1.56	1.14±0.22	0.56±0.42	0.86±0.44	0.94±0.74
Guaiol	1534	-	-	0.98±0.12	1.66±2.08	1.12±0.24	0.78±0.16	0.68±0.18	1.36±0.48	1.5±0.14	2.12±0.32	1.18±0.36	1.28±0.32
.alpha.-Muurolene	1539	-	-	1.14±0.06	0±0	0±0	1.3±0.28	0±0	0±0	0.84±0.26	1.78±0.84	1.4±0.08	1.06±0.06
Cubenene	1541	Spicy	spicy fruity mango	0±0	1.94±1.28	1.46±0.38	0±0	0.88±0.12	1.72±1.3	0.28±0.24	0±0	0±0	0±0
beta-Cadinene	1547	Woody	green woody	2.1±0.42	8.78±7.96	2.56±0.4	1.64±0.36	0.64±0.12	0.92±0.38	2.42±0.06	1.68±0.3	1.26±0.38	1.1±0.3
alpha-Cadinene	1563	Woody	woody dry	0.4±0.1	0.16±0.16	0.42±0.02	0±0	0.22±0.02	1.02±0.94	0.24±0.06	0±0	0.48±0.24	0.26±0.02
trans-Calamenene	1569	-	-	0.3±0.04	1.64±2.84	0.52±0.3	0±0	0.22±0.24	0±0	0±0	0±0	0.5±0.1	0.3±0.06
Cadina-1,4-diene	1572	Spicy	spicy fruity mango	0.44±0.08	1.14±0.9	0.6±0.14	0.5±0.24	0.34±0.08	1.02±0.74	1.46±0.62	0.96±0.3	0±0	0±0
alpha-Calacorene	1573	-	woody	0.54±0.04	1.7±2.04	0.88±0.34	0.64±0.36	0.66±0.48	0.58±0.22	0.8±0.74	0.36±0.22	0.34±0.14	0.38±0.22
Caryophyllene oxide	1606	Woody	sweet fresh dry woody spicy	1.64±0.62	1.58±2.14	1.52±1.24	0.36±0.12	0.96±0.28	1.04±0.5	0±0	4.6±1.24	6.1±2.18	1.64±0.4
Humulenol-II	1651	-	-	0.38±0.04	0.98±0.72	0±0	0.56±0.26	0±0	0±0	0±0	0±0	2.64±1.36	1.16±0.2
T-Muurolol	1669	Herbal	herbal spicy honey	1.24±0.18	2.94±4.98	0.5±0	1.3±0.9	0.62±0.16	1.62±0.86	0.82±0.28	0.54±0.1	0.98±0.5	0.58±0.16
Cadalene	1690	-	-	2.24±0.2	2.36±1.86	2.5±0.48	1.86±0.78	1.56±0.56	2.6±1.14	2.46±0.28	1.46±0.46	2±0.42	1.86±0.56
Totals	**31**			**42.52±12.78**	**57.4±58.48**	**55.34±23.72**	**30.66±13.24**	**31.4±10.08**	**40.16±26.58**	**55.14±15.82**	**46.56±16.26**	**62.56±23.18**	**32.88±10.2**

[z] Relative peak area percent compounds were identified by comparison of mass spectra with NIST14 (National Institute of Standards and Technology, Gaithersburg, MD, USA), Flavors and Fragrances of Natural and Synthetic Compounds (FFNSC3, John Wiley & Sons, Inc., Hoboken, NJ, USA), and Adams Essential Oils (Adams 2007) mass spectral libraries and comparison of calculated Kovats retention indices (Kováts 1958) with previously reported values.

Table 5. Principal components (PC) [zy] analysis of volatile aroma compounds in fresh-market muscadines grown and evaluated at the University of Arkansas System Division of Agriculture (2021).

		Principal Component 1 (52.56%) AM-148 → AM 70	**Principal Component 2 (27.37%)** AM-154 → Lactones
Positive loadings	*Compound classifications*	Lactones	Alcohols
		Alcohols	Ketones
		Monoterpenes	Lactones
		Aldehydes	
		Ketones	
		Sesquiterpenes	
		Epoxides	
	Genotype	AM-135	AM-148
		AM-26	AM-26
		AM-154	AM-77
		AM-70	AM-135
			AM-70
Negative loadings	*Compound classifications*	Esters	Aromatic hydrocarbons
		Aromatic hydrocarbons	Sesquiterpenes
			Epoxides
			Esters
			Monoterpenes
			Aldehydes
	Genotype	AM-77	AM-154
		AM-148	

[z]Percent of variation in data explained by each component, total 79.93%.

[y]Compound class variables represent the sum of the total ion chromatogram (TIC) relative peak areas (%) of positively identified compounds within each compound class (Table 3)

Table 6. Principal components (PC)[zy] analysis of volatile aroma compounds in fresh-market muscadines grown in North Carolina (Kings Mountain, NC) and evaluated at the University of Arkansas System Division of Agriculture (2021).

	Principal Component 1 (28.42%) Alcohols → Oh My!®	**Principal Component 2 (21.24%)** Lane → Esters	**Principal Component 3 (16.73%)** JB-06-30-2-20 → Ketones	
Compound classifications	Aldehydes			
	Epoxides	Alcohols	Aromatic hydrocarbons	Esters
	Esters	Aromatic hydrocarbons	Monoterpenes	Alcohols
	Lactones	Esters	Epoxides	Aldehydes
	Sesquiterpenes	Lactones	Ketones	Lactones
Genotype	Paulk	Summit	Paulk	
	Supreme	Hall	Lane	
	JB 08-38-1-10	Supreme	Hall	
	JB-06-30-2-20	JB-09-15-3-09	Supreme	
	JB-09-15-3-09	RazzMatazz®	JB-09-15-3-09	
	Oh My!®		Oh My!®	
Compound classifications	Alcohols	Aldehydes	Sesquiterpenes	
	Aromatic hydrocarbons	Epoxides		
	Ketones	Ketones		
	Monoterpenes	Monoterpenes		
		Sesquiterpenes		
Genotype	Summit	Paulk	Summit	
	Lane	Lane	JB 08-38-1-10	
	Hall	JB 08-38-1-10	JB-06-30-2-20	
	RazzMatazz®	JB-06-30-2-20	RazzMatazz®	
		Oh My!®		

[z]Percent of variation in data explained by each component, total 66.39%.

[y]Compound class variables represent the sum of the total ion chromatogram (TIC) relative peak areas (%) of positively identified compounds within each compound class (Table 4)

A. Arkansas

B. North Carolina

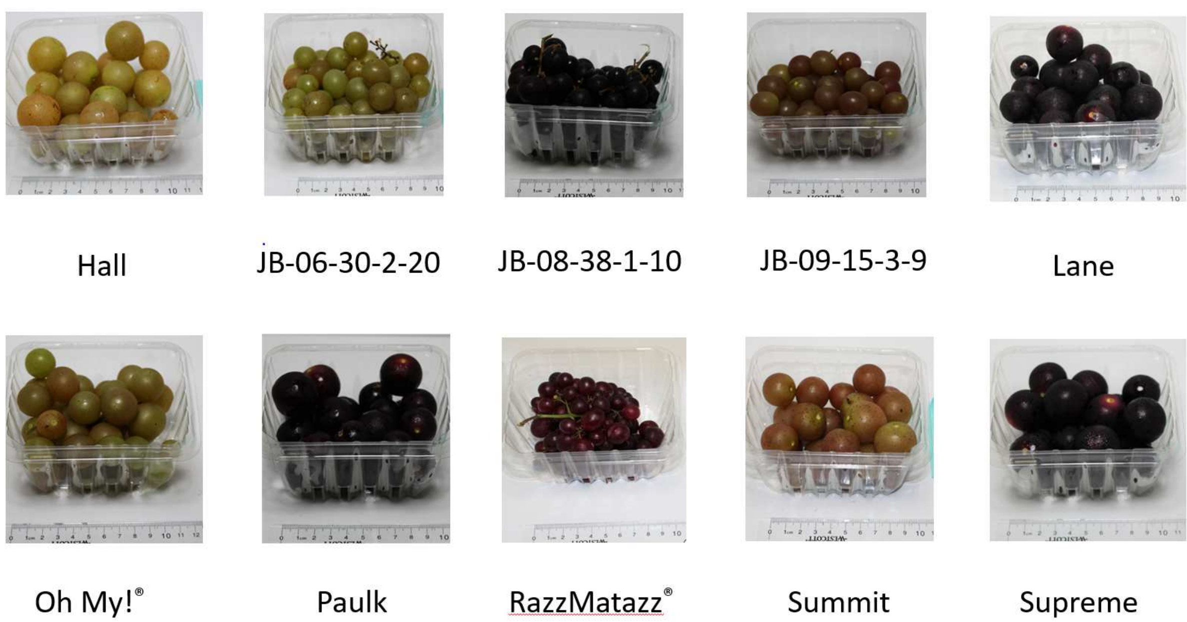

Fig. 1. Photo at harvest (day 0) of clamshells of muscadine grapes grown in Arkansas (A) and North Carolina (B) and evaluated at the University of Arkansas System Division of Agriculture (2021).

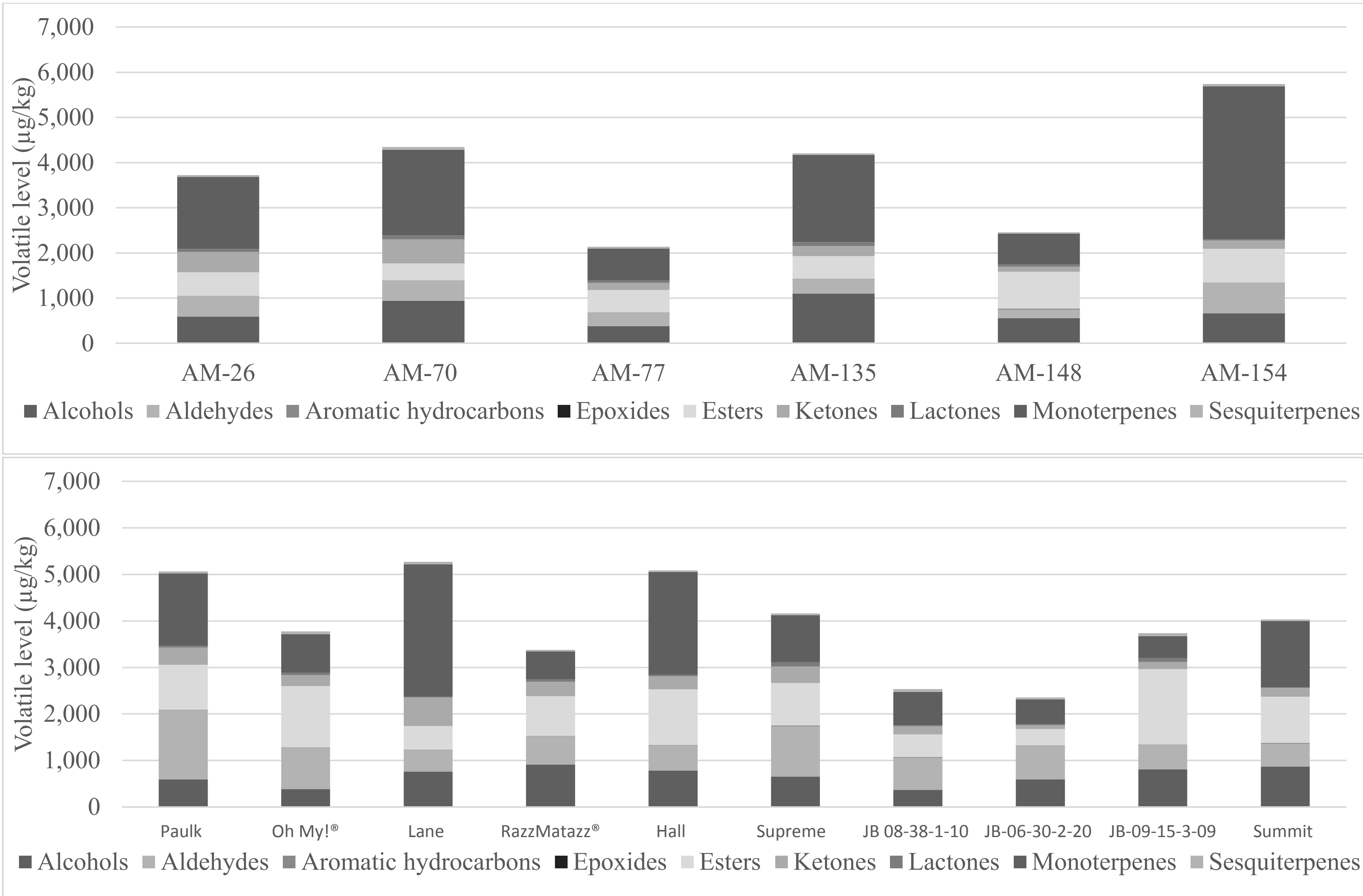

Fig 2. Total concentrations of volatile aroma compounds identified in muscadine grapes grown in Arkansas (top, Clarksville, AR) and North Carolina (bottom, Kings Mountain, NC) and evaluated at the University of Arkansas System Division of Agriculture (2021)

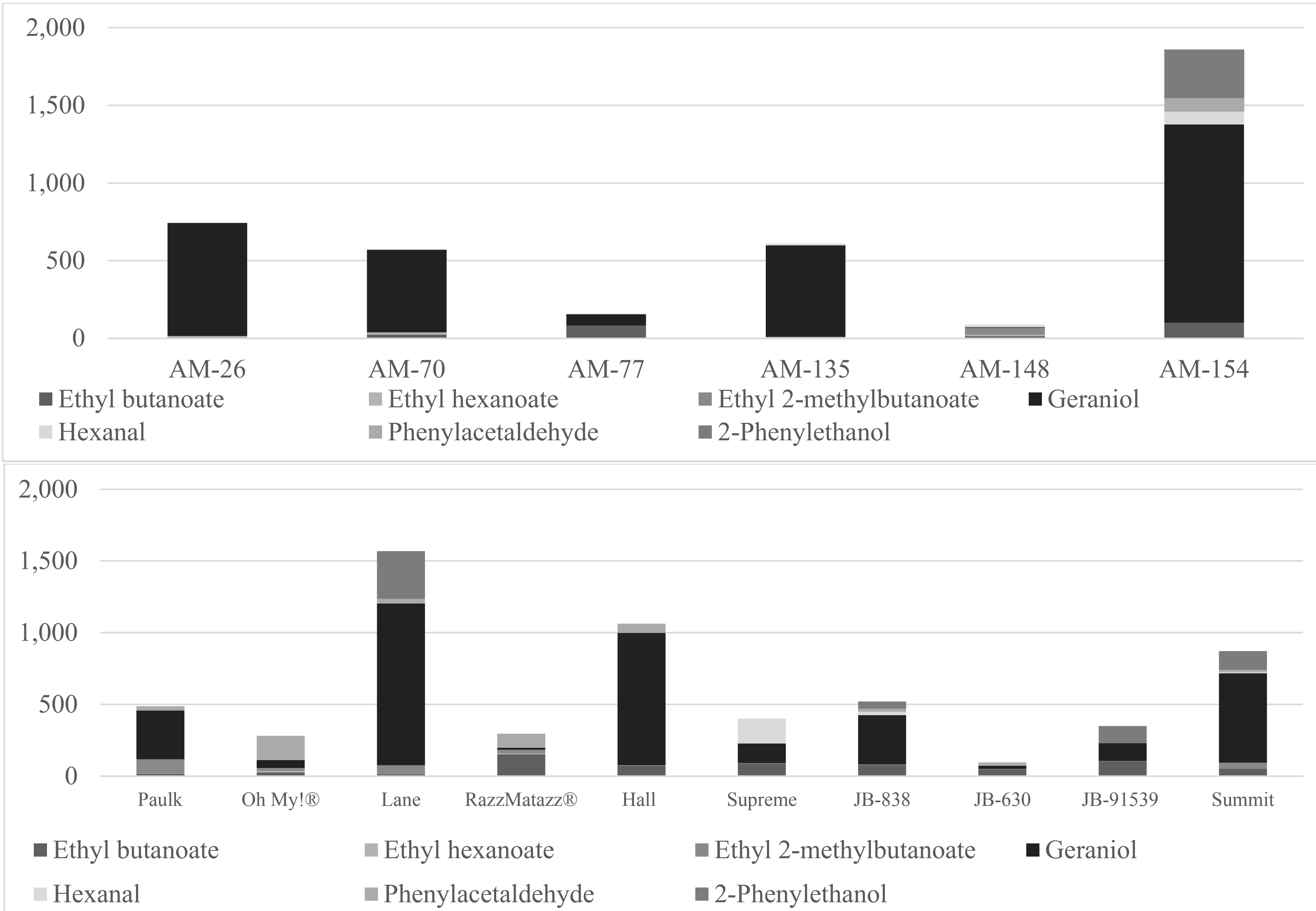

Fig 3. Total concentrations of impactful volatile aroma compounds identified (µg/kg) in muscadine grapes grown in Arkansas (Clarksville, AR, top) and North Carolina (Kings Mountain, NC, bottom) and evaluated at the University of Arkansas System Division of Agriculture (2021).

Overall Conclusions

The evaluation of Arkansas-grown hops, Arkansas-grown fresh-market blackberries, and Arkansas and North Carolina-grown muscadines provided insight into both quality and volatile profiles for these specialty horticultural crops. Regardless of crop, genotype (cultivar and breeding selection) had a strong influence on quality and volatile attributes. In hops, both the volatile and quality attributes were strongly tied to cultivar in both years (2020 and 2021). In blackberries, there was an interaction effect between the cultivar and harvest date in both 2020 and 2021 for the composition attributes. Muscadine grape attributes also varied by genotype, showing potential for some of the genotypes for fresh-market. Examining impactful volatiles (attributes that have high levels of aromatic impact) can provide a more complete aroma profile than the total volatile levels, and different impactful volatiles were identified in each crop. Overall this research showed the potential economic impact of these specialty crops and provided important profiles for crops that can be grown in Arkansas.

Appendix

To:	Renee Terrell Threlfall FDSC B-3
From:	Douglas James Adams, Chair IRB Committee
Date:	06/11/2019
Action:	**Exemption Granted**
Action Date:	06/11/2019
Protocol #:	1905199069
Study Title:	Identifying Marketable Attributes of Hops Cultivars Grown Commercially in Arkansas and Other Regions

The above-referenced protocol has been determined to be exempt.

If you wish to make any modifications in the approved protocol that may affect the level of risk to your participants, you must seek approval prior to implementing those changes. All modifications must provide sufficient detail to assess the impact of the change.

If you have any questions or need any assistance from the IRB, please contact the IRB coordinator at 109 MLKG Building, 5/2208, or irb@uark.edu

cc: Amanda L McWhirt, Key Personnel