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Aroma impact components of rabbiteye blueberry (*Vaccinium ashei*) vinegars

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ABSTRACT

The aroma impact components of the rabbiteye blueberry vinegars made from wine fermented without skin-contact (JV), wine fermented with skin-contact (WV), or blueberries (BV) were evaluated. Headspace volatiles were isolated by solid-phase microextraction (SPME). Headspace volatiles were analysed by gas chromatography–mass spectrometry (GC–MS) and gas chromatography–olfactometry (GCO). The potent odourants were evaluated by the 'Osme' method. Acetic acid, 2/3-methyl-butanoic acid, phenethyl acetate, 2-phenylethanol, octanoic acid, eugenol, and phenylacetic acid were the most important aroma-active compounds identified in all three treatments. The contributions of these compounds to each sample were different. There were more aroma-active compounds identified from the BV than from the other two treatments. The type of fermentation impacts the aroma components of rabbiteye blueberry vinegars.

1. Introduction

There are a variety of different methods for vinegar production. The process can be slow (traditional method) or quick (submerged method) (Wood, 1985). The traditional method is so called surface culture fermentation (Wood, 1985). This is a simple method and requires no advanced engineered equipment. The processing time can be shortened by modifying this method. The modifications include increasing surface area, increasing oxygen concentration of the fermentation room, and decreasing the depth of wine base (Anderson, Tidwell, & Silva, 2000). This study was conducted by using this modified method. The flavour of fruit vinegar is influenced by the raw materials used, the compounds formed during the fermentation, chemical compounds remaining from the raw materials, and the type of fermentation used (Morales, Tesfaye, Garcia-Parrilla, Casas, & Troncoso, 2002). In order to produce good fruit vinegar, choice of raw materials and acetification process are two factors which need to be considered carefully.

By late June, rabbiteye blueberries (*Vaccinium ashei*) are harvested. By this time, the "fresh" market is beginning to be saturated with highbush blueberries from the Northern States. Thus, most Mississippi rabbiteye blueberries are processed for the frozen market. In this process, immature and other "cull" blueberries are discarded. They have the potential to be used in value-added products. The potential use of "processed" blueberries to produce vinegar and antioxidant products is an interesting research idea that could develop new products with no agricultural residues. It is further speculated that rabbiteye blueberry will have more antioxidant capacity than highbush and lowbush. This is due to their thicker skin and higher phenolics. Blueberries are also a good raw material for wine and vinegar production because of their fresh green odour. A blueberry flavouring is composed of linalool, trans-2-hexenol, trans-2-hexenal, cis-3-hexenol, and cis-3-hexenal (Horvat & Senter, 1985). Terpenes, C6 unsaturated aldehydes, and unsaturated alcohols have been reported to be the predominant compounds identified in the volatile extracts of rabbiteye blueberries (Horvat & Senter, 1985). Other aroma compounds such as ethyl acetate, phenethyl acetate, benzaldehyde, myrcenol, α-terpineol, citronellol, benzyl alcohol, 2-phenylethanol, eugenol, isoeugenol, acetic acid, butanoic acid, 2-methylbutanoic acid, and hexanoic acid are also found in blueberries (Hirvi & Honkanen, 1983; Parliment & Kolor, 1975). However, there is no information about the aroma impact components of rabbiteye blueberry (*V. ashei*) vinegars.

Acetic acid is the main aroma compound of vinegar. Other volatile compounds also have a great impact on an overall aroma of the vinegar. To develop new excellent vinegar, the determination of volatile compounds having an impact on an overall aroma of the vinegar is an important preliminary step (Charles et al., 2000). The sensory evaluation is one of the techniques used for the determination of volatile compounds. However, sensory

Abbreviations: JV, vinegar was produced by using blueberry wine fermented without skin-contact; WV, vinegar was produced by using blueberry wine fermented with skin-contact; BV, vinegar was produced directly from blueberries; AUC, the peak area of time–odour intensity plot; I_{Max}, maximum aroma intensity.

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evaluation technique is limited due to the pungency of acetic acid. Thus, the use of gas chromatography–olfactometry (GCO) technique is a better way to discover aroma difference of vinegars. There are several GCO techniques including the 'CHARM' analysis (Acree, Barnard, & Gunningham, 1984), aroma extract dilution analysis (Ullrich & Grosch, 1987), 'Osme' analysis (McDaniel, Miranda-Lopez, Watson, Micheals, & Libbey, 1990), and odour detection frequency analysis (Linssen, Janssens, Roozen, & Posthumus, 1993). The 'Osme' method is a time–intensity method for GCO (McDaniel et al., 1990). The data collected by the 'Osme' method provides odour description, time, odour intensity, and peak area of time–odour intensity plot.

Several extraction techniques have already been applied to obtain vinegar aroma extracts such as solvent extraction (Gerbi, Zeppa, & Carnacini, 1992; Kahn, Nickol, & Conner, 1972), simultaneous steam distillation–solvent extraction (Blanch, Tabera, Sanz, Herraiz, & Reglero, 1992), and headspace sampling (Castro, Natera, de Valme Garca Moreno, & Garca, 2002).

The objective of this work was to evaluate the aroma impact components of the three different rabbiteye blueberry vinegars by using GCO ('Osme' analysis).

2. Materials and methods

2.1. Materials

Frozen rabbiteye blueberries (*V. ashei*) were obtained from a commercial processor in southern Mississippi. Yeast and red wine vinegar mother were obtained from a winemaking supplier (Beer and Winemaking Supplies, Inc., Northampton, MA). All authentic standards were purchased from Aldrich Chemical Co. (Milwaukee, WI). Carboxen–polydimethylsiloxane (CAR–PDMS) SPME fibres (75 μm) were purchased from Supelco (Bellefonte, PA).

2.2. Blueberry juice processing

Blueberries were crushed and then divided into three portions (Fig. 1). One portion was processed into juice and other portions were used to make wine (BW2) and vinegar (BV). The juice was prepared following crushing and pressing at 4 °C in a small basket press. The juice was filtered through four layers of fine cheesecloth (Fisher Scientific, Fair Lawn, NJ).

2.3. Blueberry wine (BW1) processing

The juice was fermented at 15 °C until the alcohol content reached 6% by using *Saccharomyces cerevisiae* yeast. First racking was performed by siphon to separate the wine from sediment that develops during fermentation. Second racking was completed when no bubbles are observed in the fermentation lock. Finished wine (BW1) was filtered through four layers of fine cheesecloth.

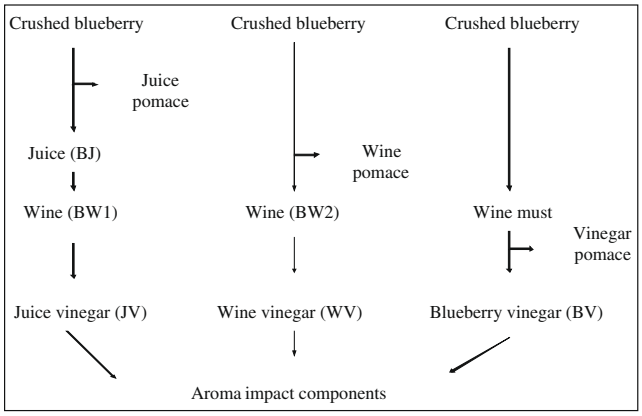

Fig. 1. Illustration of the blueberry vinegars production.

2.4. Blueberry wine (BW2) processing

Blueberry must was inoculated with *S. cerevisiae* yeast and fermented at 15 °C until the alcohol content reached 6%. After fermentation, a portion of the must was pressed and another portion of the must was blended (to be used as wine base of BV production; Fig. 1). The wine and blended must were then transferred to two separate fermenters and fermented again at 15 °C until the alcohol content reached 6%. Finished wine (BW2) was filtered through four layers of fine cheesecloth.

2.5. Vinegar mother preparation

Red wine vinegar mother was inoculated into blueberry wine and placed into a 2-l flask equipped with a cheesecloth plug. To increase the surface area, the flask was filled with inoculated wine to 5 cm high. The flask was then placed in a 30 °C incubator until a bacteria film was formed. The bacteria film was used as inoculums of vinegar making.

2.6. Vinegar making

Wines used to make juice vinegar (JV), wine vinegar (WV), and BV were BW1, BW2, and the wine must (previously reserved from BW2 production), respectively (Fig. 1). During the BV production, skin-contact fermentation was involved in the winemaking and acetification process. However, it was only involved in the winemaking process during the WV production. The procedures and equipment used were the same as vinegar mother preparation except the inoculation method. The bacteria film previously made for inoculums of vinegar making was cut into several pieces (30 mm × 30 mm). Each piece of bacteria film was placed on the top of a piece of wine bottle cork (30 mm × 30 mm × 5 mm). The wine bottle corks were boiled in water for several hours to remove undesired materials. Six pieces of wine bottle cork with bacteria film were placed on the surface of wine in a flask. The titratable acidity (AOAC, 2002) was monitored daily until the acidity did not change. After fermentation, BV was pressed to separate BV and vinegar pomace (Fig. 1). All vinegars (JV, WV, and BV) were filtered through four layers of fine cheesecloth and 0.22 μm filters. Vinegars were placed in a −25 °C freezer for subsequent analysis.

2.7. Headspace sampling

Each blueberry vinegar sample (15 ml) and 6.14 g NaCl (Castro et al., 2002) was placed into a 40 ml amber glass vial with a screw cap and a Teflon silica septum. A 25 μl internal standard (0.054 g/ml 4-methyl-2-pentanol in odour-free water containing 80 g/l of acetic acid) was added and then mixed (Castro et al., 2002). The sample was equilibrated in the glass vial at 70 °C for 15 min to allow the aroma volatiles to partition into the headspace of the vial and to reach gas phase equilibrium concentration. Aroma compounds were extracted using a 75 μm carboxen–polydimethylsiloxane (CAR–PDMS) SPME fibre (Supelco, Bellefonte, PA) at 70 °C for 60 min (Castro et al., 2002). The SPME fibre was conditioned prior to sampling according to instructions of supplier (Supelco, Bellefonte, PA) by inserting it into GC injector (250 °C).

2.8. Gas chromatography–mass spectrometry (GC–MS)

A GC–MS system, consisting of a Hewlett–Packard 5890 Series II GC and a HP 5972 mass selective detector (MSD) (Hewlett–Packard Co., Palo Alto, CA), was used to analyse volatile extracts. After headspace sampling, the SPME fibre was injected into a SPME injector of the GC system immediately. For the desorption of the analytes inside the GC injection port, the injection was made in the splitless mode for 2 min at 250 °C injection port temperature. The columns used were a fused silica capillary column (DB-5MS or DB-WAX; J&W Scientific, Folsom, CA). Helium was used as the carrier gas at a constant flow rate of 1.0 ml/min. Oven temperature was programmed from 35 to 250 °C at a ramp rate of 5 °C/min with initial hold time of 5 min and final hold time of 20 min. Injections were performed in triplicate.

2.9. Gas chromatography–flame ionisation detector (GC–FID)

The GC–FID system consisted of a Varian 3400 GC (Varian Instrument Group, Walnut Creek, CA) equipped with a flame ionisation detector. After headspace sampling, the SPME fibre was immediately injected into a SPME injector of the GC system. For the desorption of the analytes inside the GC injection port, the injection was made in the splitless mode for 2 min at 250 °C injection port temperature. The column used was a DB-WAX column. Carrier gas was helium at a constant flow of 1 ml/min; oven temperature was programmed from 35 to 240 °C at a ramp rate of 8 °C/min with initial and final hold times of 5 and 10 min, respectively. The FID and injection port were held at 250 °C. Injections were performed in triplicate.

2.10. Gas chromatography–olfactometry (GCO)

The GCO system consisted of a Varian 3400 GC equipped with a sniffing port. After headspace sampling, the SPME fibre was immediately injected into a SPME injector of the GC system. For the desorption of the analytes inside the GC injection port, the injection was made in the splitless mode for two minutes at 250 °C injection port temperature. The same column and conditions as for GC–FID were used. The sniffing port transfer line was held at 250 °C. A humidified air was introduced into the sniff port upstream near the point where the capillary column first entered (the sniffing port). The air carried the capillary column effluent into a glass funnel where 'Osme' analysis was conducted.

2.11. 'Osme' analysis

Two males and one female, aged 28–39, served as the panellists. The panellists were experienced in 'Osme' analysis. Compounds were separated in the capillary column of the GCO system (previously described) and passed through the sniffing port to the panellist who rated the odour intensity of a volatile compound on a 16-point (0–15) sliding scale using a variable resistor. The odour intensity scale ranged from no odour perceived (0) to extreme (15). The sliding scale was interfaced with a personal computer equipped with 'Osme' software (Starkville, MS). At the time of an odour perception, the panellists verbally described the odour property to the DMP-100 mp3 recorder (D-Link Systems, Inc., Irvine, CA). The retention time and verbal description were recorded to permit an odour descriptor to be coupled with a computerised time–odour intensity plot. The 'area under curve' (AUC) is the peak area of time–odour intensity plot. The odour perceived by two out of three panellists and by each panellist two out of three replications would be included in the 'Osme' data.

2.12. Identification of aroma compounds

Positive compound identifications were achieved by comparison of Kovats retention indices, mass spectra, and odour properties with those of standard reference compounds analysed under identical experimental conditions. Tentative identifications were based on matching Kovats retention index values and odour properties of unknowns against those of authentic standards or based on comparing mass spectral data to those in the Wiley138 library and published literature.

3. Results and discussion

3.1. Aroma components isolated from blueberry vinegars

Aroma components detected in the blueberry vinegar samples are listed in Table 1. A total of 47 aroma components were detected. Headspace solid-phase microextraction (HS-SPME), using a carboxen–polydimethylsiloxane fibre, is considered an appropriate analysis of aroma compounds in vinegars (Natera, Castro, de Valme Garca Moreno, Garcia, & Garca, 2002).

Results of 'mean peak area ratio' (compound peak area/internal standard peak area) conducted by GC–MS are shown in Table 1. Six, four, and seven compounds were found to have values greater than 1.00 and were detected in the JV, WV, and BV, respectively. These were abundant compounds found in the blueberry vinegar samples. In addition to acetic acid, 2/3-methylbutanoic acid, octanoic acid, and phenylacetic acid were abundant in the all three vinegar samples. These compounds give the blueberry vinegar sample unique 'floral-sweaty' odour. 2-Methylbutanoic acid, 3-methylbutanoic acid, 2-methylpropanoic acid and phenylacetic acid could be formed from oxidation of Strecker aldehydes. 3-Methylbutanoic acid and 2-phenylethanol were also found in red wine vinegars at high abundance (Charles et al., 2000). Although some compounds, such as 2,3-butanedione, (*E,Z*)-2,6-nonadienal, ethyl butanoate, and linalool, either had low 'mean peak area ratio' or were not detected by GC–MS, the overall odour impacted by these compounds might be important because of their low odour thresholds.

3.2. 'Osme' analysis

The potent odourants in the blueberry vinegar samples were determined using 'Osme' analysis. Results are presented in Table 2. Of the 47 aroma components detected in the blueberry vinegar samples (GC–MS, GCO, and GC–FID), there were 25, 28, and 35 aroma components perceived by panellists in the JV, WV, and BV, respectively. Results indicate that several aroma-impact compounds, such as linalool, phenethyl acetate, 2-phenylethanol, and phenylacetic acid made a major contribution to the 'floral' odour of blueberry vinegar sample. Among these compounds, 2-phenylethanol was the most intense compound in all samples. The maximum aroma intensity (I_{Max}) of 2-phenylethanol in the JV, WV, and BV was 11.9, 9.0, and 10.1, respectively. The AUC of 2-phenylethanol in the JV, WV, and BV was 525.2, 230.1, and 351.6, respectively. 2-Phenylethanol has been found in sherry vinegar (Castro et al., 2002) and red wine vinegars (Charles et al., 2000). It has also been found and quantified (0.03 mg/kg) in highbush blueberry previously (Hirvi & Honkanen, 1983). Phenylacetic acid is also an important aroma-impact compound having a 'floral' odour. It had a medium intensity (JV: 7.7, WV: 6.5, BV: 6.7). The AUC of phenylacetic acid in the JV, WV, and BV were 1862.8, 1758.7, and 1520.1, respectively. Phenylacetaldehyde and phenylacetic acid are formed from L-phenylalanine and glucose (Hofmann & Schieberle, 2000). Although these two compounds have same 'floral-like' odour, phe-

Table 1
Results of 'mean peak area ratio' of aroma compounds in blueberry vinegars.

No.	Compound	Odour descriptor	RI[a]	RI[b]	Identification[c]	Peak area ratio[d]		
						JV	WV	BV
1	Methyl acetate	Fruity	889		MS, RI	0.03 ± 0.01	0.04 ± 0.01	0.11 ± 0.01
2	Ethyl acetate	Fruity	920	604	MS, RI	0.02 ± 0.00	0.02 ± 0.00	0.10 ± 0.01
3	Unknown	Fruity	944		O	–	–	–
4	2,3-Butanedione	Buttery	980		O, RI	–	–	–
5	Ethyl butanoate	Apple, fruity	1033	797	MS, O, RI	–	0.04 ± 0.01	0.03 ± 0.01
6	Isopropyl butanoate	Pungent	1039	847	MS, O, RI	–	0.08 ± 0.01	0.19 ± 0.02
7	3-Hydroxy-2-butanone	Buttery	1260	718	MS, RI	0.05 ± 0.02	0.18 ± 0.03	0.11 ± 0.02
8	Unknown	Woody	1272		O	–	–	–
9	Unknown	Green	1336		O	–	–	–
10	Rose oxide	Fresh, green	1345	1112	MS, O, RI	–	0.02 ± 0.01	0.10 ± 0.02
11	Unknown	Plastic	1364		O	–	–	–
12	Acetic acid	Vinegar	1435	628	P	21.20 ± 2.08	16.40 ± 1.06	15.10 ± 1.32
13	2-Furfural	Nutty	1445		MS, RI	–	0.22 ± 0.04	–
14	Nerol oxide	Fresh floral	1452		MS, O, RI	0.16 ± 0.03	0.02 ± 0.00	0.15 ± 0.02
15	Trans-linalool oxide	Woody	1462	1092	MS, O, RI	0.09 ± 0.03	0.08 ± 0.02	0.17 ± 0.03
16	Benzaldehyde	Nutty	1489	968	P	0.65 ± 0.22	0.5 ± 0.06	0.31 ± 0.04
17	2,3-Butanediol	Fruity	1535	1235	MS, RI	0.04 ± 0.01	0.02 ± 0.00	–
18	Linalool	Floral, cut grass	1548	1098	P	0.06 ± 0.02	0.06 ± 0.02	0.05 ± 0.01
19	2-Methylpropanoic acid	Rancid butter	1558	775	P	0.13 ± 0.05	0.37 ± 0.03	0.36 ± 0.07
20	Hotrienol	Hyacinth, melon	1593	1101	MS, O, RI	0.09 ± 0.02	0.15 ± 0.03	0.06 ± 0.01
21	(*E,Z*)-2,6-Nonadienal	Cucumber	1601		O, RI	–	–	–
22	Myrcenol	Fresh floral	1618		MS, O, RI	0.13 ± 0.04	–	0.17 ± 0.03
23	Ethyl benzoate	Fruity	1642	1300	MS, O, RI	–	0.18 ± 0.04	0.27 ± 0.03
24	2/3-Methylbutanoic acid	Sweaty	1658	868	P	2.52 ± 0.92	3.82 ± 1.23	3.31 ± 0.65
25	Diethyl succinate	Sweet, wine	1672		MS, O, RI	0.08 ± 0.03	0.12 ± 0.03	0.34 ± 0.09
26	α-Terpineol	Pine oil	1686	1206	P	0.63 ± 0.21	0.47 ± 0.12	0.86 ± 0.19
27	Benzyl acetate	Fresh	1706	1164	MS, O, RI	–	–	0.18 ± 0.04
28	Methyl phenylacetate	Sweet, honey	1736	1243	P	–	0.02 ± 0.01	0.17 ± 0.03
29	Methyl salicylate	Mint	1739	1234	MS, O, RI	–	–	0.08 ± 0.02
30	Citronellol	Rose	1761	1237	MS, O, RI	0.07 ± 0.03	0.06 ± 0.01	0.04 ± 0.01
31	Ethyl phenyl acetate	Sweet, honey	1768		MS, O, RI	–	–	0.32 ± 0.05
32	Phenethyl acetate	Sweet, honey	1790	1260	P	3.43 ± 0.97	0.27 ± 0.06	1.52 ± 0.24
33	Hexanoic acid	Sweaty	1832	1019	P	0.5 ± 0.19	0.71 ± 0.15	0.71 ± 0.12
34	Benzyl alcohol	Sweet	1855	1041	MS, RI	0.06 ± 0.02	0.07 ± 0.01	0.11 ± 0.01
35	2-Phenylethanol	Rosy, sweet	1889	1121	P	5.82 ± 1.94	0.53 ± 0.04	1.81 ± 0.31
36	Heptanoic acid	Rancid	1940		MS, O, RI	0.07 ± 0.01	0.11 ± 0.01	0.11 ± 0.04
37	γ-Nonalactone	Coconut	1995	1366	MS, RI	0.04 ± 0.01	0.06 ± 0.01	0.08 ± 0.02
38	4-Ethylguaiacol	Spicy	2001	1287	MS, RI	–	–	0.05 ± 0.01
39	Unknown	Fresh floral	2020		O	–	–	–
40	Octanoic acid	Sweaty	2047	1279	P	4.89 ± 1.44	2.09 ± 0.36	4.66 ± 0.76
41	Eugenol	Clove	2136	1364	P	0.30 ± 0.06	0.19 ± 0.03	0.23 ± 0.04
42	Nonanoic acid	Cheese	2153	1762	MS, RI	0.20 ± 0.05	–	0.18 ± 0.04
43	Decanoic acid	Rancid butter	2260	2013	MS, RI	0.83 ± 0.21	0.13 ± 0.04	1.03 ± 0.24
44	Isoeugenol	Floral	2315	1438	MS, O, RI	–	–	0.20 ± 0.05
45	Benzoic acid	Urine	2403	1276	MS, RI	0.31 ± 0.07	0.40 ± 0.03	0.38 ± 0.10
46	Dodecanoic acid	Waxy	2479	2156	MS, RI	0.14 ± 0.03	–	0.05 ± 0.02
47	Phenylacetic acid	Floral	2553	1262	P	2.46 ± 0.69	2.56 ± 0.21	2.25 ± 0.59

[a] Retention index on DB-Wax column.
[b] Retention index on DB-5 ms column.
[c] *Abbreviations:* MS, mass spectra; O, odour properties; RI, comparison of Kovats retention index values and odour properties with published literature; P, comparison of Kovats retention index values, mass spectra, and odour properties with those of standard reference compounds analysed under identical experimental conditions.
[d] Mean peak area ratio ± standard deviation.

nylacetaldehyde has a much higher FD factor (Hofmann & Schieberle, 2000). Phenylacetaldehyde was not found in this study or any other vinegar studies (Castro et al., 2002; Charles et al., 2000; Morales et al., 2002) while phenylacetic acid was present in high abundance.

In addition to the 'floral' odour, the 'sweaty' odour is another major contributor to the aroma of the blueberry vinegar sample. These aroma-impact compounds include acetic acid, 2-methylpropanoic acid, 2/3-methylbutanoic acid, hexanoic acid, heptanoic acid, and octanoic acid (Table 2). Among these volatile acids, 2/3-methylbutanoic acid was the most intense compound in all samples. The I_{Max} of 2/3-methylbutanoic acid in the JV, WV, and BV were 12.1, 11.2, and 11.3, respectively. It has been found that 3-methylbutanoic acid is converted from leucine (Tressl & Drawert, 1973). This compound was reported to be a major volatile compound found in red wine vinegars (Charles et al., 2000). In this study, 2/3-methylbutanoic acid also had the highest intensity (JV: 12.1; WV: 11.2; BV: 11.3) and AUC (JV: 430.6; WV: 362.5; BV: 420.4) among volatile acids in all samples. Therefore, it is the most important volatile acid and one of the most predominant aroma-impact compounds of the blueberry vinegar.

Some compounds found in this study, such as compounds 2, 12, 13, 15, 16, 18, 24, 26, 30, 32, 33, 34, 35, 41, and 44 (Table 2), have also been found in blueberries previously studied (Hirvi & Honkanen, 1983; Horvat & Senter, 1985; Overton & Manura, 1999; Parliment & Kolor, 1975) However, according to Horvat and Senter (1985), a blueberry flavouring is composed of linalool, trans-2-hexenol, trans-2-hexenal, cis-3-hexenol, and cis-3-hexenal. The last four compounds were not detected in this study. This is considered the main difference between blueberry and the blueberry vinegar.

Another group of components, having a 'fruity' odour, made some contributions to the overall aroma of the blueberry vinegar.

Table 2
Results of 'Osme' analysis.

No.	Compound	JV			WV			BV		
		I_{Max}[a]	AUC[b]	FID[c]	I_{Max}	AUC	FID	I_{Max}	AUC	FID
3	Unknown	1.7	11.4	31.0	1.5	5.5	40.0	1.7	7.6	73.0
4	2,3-Butanedione	–	–	–	2.8	19.1	–	2.6	15.5	–
5	Ethyl butanoate	–	–	–	3.5	27.3	67.0	3.1	22.1	45.0
6	Isopropyl butanoate	–	–	–	–	–	–	2.0	11.5	176.0
8	Unknown	2.4	15.1	98.0	2.5	17.1	72.0	1.6	4.7	60.0
9	Unknown	3.9	36.7	91.0	4.9	54.9	51.0	4.5	54.4	85.0
10	Rose oxide	1.8	7.2	–	1.5	4.9	36.0	2.5	15.1	221.0
11	Unknown	–	–	–	3.1	18.9	51.0	3.4	23.6	74.0
12	Acetic acid	6.2	125.1	35201.0	6.3	149.6	25379.0	5.9	158.8	26961.0
14	Nerol oxide	–	–	–	–	–	–	1.5	5.2	203.0
15	Trans-linalool oxide	–	–	–	–	–	–	2.4	16.9	82.0
16	Benzaldehyde	2.2	10.4	1205	2.6	13.1	762	3.4	19.4	556.0
18	Linalool	5.1	40.0	84.0	5.3	52.3	98.0	3.8	25.1	69.0
19	2-Methylpropanoic acid	5.4	72.5	203.0	4.6	37.4	632.0	3.3	28.2	451.0
20	Hotrienol	3.4	16.6	112.0	3.7	26.3	121.0	2.8	13.2	78.0
21	(*E*,*Z*)-2,6-Nonadienal	–	–	–	4.5	40.1	268.0	2.3	10.6	58.0
22	Myrcenol	4.1	39.7	230.0	–	–	–	3.0	21.8	272.0
23	Ethyl benzoate	3.1	19.0	–	3.7	35.2	283.0	3.5	31.8	432.0
24	2/3-Methylbutanoic acid	12.1	430.6	3722.0	11.2	362.5	5676.0	11.3	420.4	5739.0
25	Diethyl succinate	2.4	20.5	95.0	3.8	37.7	184.0	2.9	26.7	649.0
26	α-Terpineol	2.4	14.8	785.0	3.5	27.0	864.0	1.7	10.5	1110.0
27	Benzyl acetate	2.4	20.2	–	1.0	3.2	–	2.2	14.8	278.0
28	Methyl phenylacetate	–	–	–	4.7	50.7	31.0	4.1	67.8	190.0
29	Methyl salicylate	–	–	–	–	–	–	1.8	13.5	98.0
30	Citronellol	3.0	19.8	58.0	3.3	22.0	89	3.1	21.0	76.0
31	Ethyl phenyl acetate	–	–	–	–	–	–	3.7	52.8	375.0
32	Phenethyl acetate	6.7	148.9	5443.0	4.7	93.4	390.0	7.8	170.8	2194.0
33	Hexanoic acid	4.6	52.2	688.0	4.4	46.1	1118.0	5.4	73.4	1412.0
35	2-Phenylethanol	11.9	525.2	8757.0	9.0	230.1	811.0	10.8	351.6	2603.0
36	Heptanoic acid	2.5	28.3	120.0	6.3	145.4	193.0	5.2	100.0	265.0
39	Unknown	2.6	23.9	150.0	–	–	–	3.2	35.7	157.0
40	Octanoic acid	7.6	410.3	6789.0	7.7	315.1	3948.0	9.3	389.7	6897.0
41	Eugenol	5.1	96.4	520.0	7.0	165.2	289.0	6.7	190.6	430.0
44	Isoeugenol	–	–	–	–	–	–	2.2	11.5	321.0
47	Phenylacetic acid	7.7	1863.0	3856.0	6.5	1759.0	3903.0	6.7	1520.0	3760.0

[a] Maximum aroma intensity.
[b] Area under the curve.
[c] Integrated FID peak area.

This group of compounds is mainly esters such as methyl acetate, ethyl acetate, ethyl butanoate, ethyl benzoate, and one unknown (Table 2). Methyl acetate and ethyl acetate were detected by GC–MS or GC–FID but not perceived by panellists. Ethyl butanoate was perceived at intensity 3.1 to 3.5 in the WV and BV, respectively, but not perceived in the JV. Ethyl benzoate was perceived at intensity 3.1–3.7 in all samples. Ester is produced from an alcohol through fermentation or reaction of an alcohol and an acid, especially during ageing. According to Palacios, Valcarcel, Caro, and Perez (2000), the concentration of ethyl acetate depends on the alcohol content and the acidity of the aged vinegar. Palacios et al. (2000) also reported that it is possible to find high levels of ethyl acetate in very old vinegars with significant amounts of residual alcohol (>1% ethanol; v/v). In this study, the quick process with no ageing was used to produce vinegars. The esters might mainly result from raw material.

In addition to acetic acid, compounds eluting after a Kovats retention index (DB-WAX) of 1658, appear to be the most important contributors to the aroma of the blueberry vinegar. The most intense aroma compounds found in the samples (Table 2) were in this region. These included 2/3-methylbutanoic acid, phenethyl acetate, 2-phenylethanol, octanoic acid, eugenol, and phenylacetic acid.

3.3. Effect of fermentation type

The JV and WV were made from blueberry wines fermented without (JV) and with (WV) skin-contact, respectively. The BV was produced directly from blueberries. During the BV production, skin-contact fermentation was involved in the winemaking and acetification process. However, it was only involved in the winemaking process during the WV production. Results indicated that more aroma compounds were found in the BV than WV or JV. The results were reasonable because more enzymes, microorganisms, and more substrate were present during the BV production. Thus, more aroma components were produced and released. However, the quality of the BV is more difficult to control.

4. Conclusion

Forty seven aroma-active components were detected in the blueberry vinegar samples. Among these components, there were 25, 28, and 35 aroma components perceived by panellists in the JV, WV, and BV, respectively. Twenty two aroma-active components were common to the three analysed vinegars. The BV had the largest numbers of components detected, and the JV had the smallest numbers of components detected. On the basis of the results of this study, the aroma of the blueberry vinegars could be due to compounds 18, 32, 35, 47, 12, 19, 24, 33, 36, and 40. Among these, compounds 24, 32, 35, 40, and 47 were the most intense compounds. These compounds were all found in blueberries previously. However, winemaking and acetification process enhanced them and changed the odour dramatically from 'fresh-green' odour to 'floral-sweaty' odour.

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