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Volatile Compounds from Must and Wines from Five White Grape Varieties

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Abstract

Viticulture and wine production in challenging environments such as cold and humid areas has substantially expanded in recent years, mostly due to the development of grapevine varieties that show high resistance to fungal diseases and cold temperatures. These interspecific hybrid *Vitis* (IHV) varieties result from multiple crosses between *Vitis vinifera* varieties and North American native species such as *V. riparia and V. labrusca*. Limited scientific information is available on the aroma and winemaking of IHV, and about the relationships between grape and wine composition in regard to compounds of enological interest. In this work, the profile of volatile compounds of grapes and wines from five white IHV varieties largely grown in cold-climate viticulture (Frontenac blanc, Frontenac gris, Seyval, St. Pepin and Vidal) was determined by GC-MS-SPME. Compound classes detected in juice and wine included fatty acid degradation products that represented the largest part of volatile compounds, fatty acid ethyl esters, terpenes, C_{13}-norisoprenoids, and volatile phenols and other phenyl derivatives. The flavor profile of Vidal showed the largest diversity of compounds in both juice and wine, and the overall highest amount of volatile compounds of all varieties. Principal component analysis showed relationships between the presence of certain C_6 compounds, terpene and volatile phenols in musts and in the finished wines.

Keywords

Vitis, GC-MS-SPME, Volatile compounds, Northern viticulture, Cold tolerance, Interspecific hybrid, Quebec, Canada, Seyval, St. Pepin, Vidal, Frontenac gris, Frontenac blanc

Introduction

Predictions are that the global wine market will have reached a value of more than $ 304 billion in 2016 [1]. The economic contribution of the wine industry is significant in several sectors such as agriculture, bio-food processing, trade, manufacturing and tourism, making it a powerful tool for regional development. Wine production, which was previously restricted to areas showing suitable environmental conditions for *Vitis vinifera* varieties such as Pinot noir and Riesling, has become a universal economic activity. Indeed, quality wines are now produced in many areas showing challenging growing conditions such as Eastern Canada, Northern Europe, and Northern Asia [2]. Wine production in challenging cold and humid climate conditions experienced a major boom in recent years with the arrival on the market of interspecific hybrid *Vitis* (IHV) varieties [3]. These varieties are obtained from interspecific crosses between American native *Vitis* species (*Vitis riparia, V. labrusca, V. rupestris, V. lincecumii*) and European *V. vinifera* varieties. IHV varieties are productive, early-maturing, well adapted to cold temperature, and highly resistant to fungal diseases, making them suitable for cultivation in environments that are unsuited for the implementation of traditional *V. vinifera* varieties [4]. The province of Quebec is the third largest wine region in Canada, and has over 800 hectares devoted to grape production [5]. The Quebec wine industry is nearly 100% based on IHV varieties, and local growers grow about 50 different IHV varieties. White wines account for 52% of wine produced in Quebec from more than 20 different white grape varieties, but the main ones are the American varieties Frontenac blanc, Frontenac gris, and St. Pepin, and the French-American varieties Seyval blanc and Vidal.

In recent years, the Quebec wine industry has developed substantially and the quality of local wines became increasingly higher. However, despite these improvements, the lack of detailed knowledge about the oenological characteristics of IHV varieties continues to hinder the development of the industry. Indeed, unlike the traditional *V. vinifera* varieties, whose chemical composition has been widely studied [6-8], knowledge about the chemical composition and oenological potential of IHV varieties remains very limited. In addition, unique genetics confer biochemical characteristics to these varieties that largely differ from those of traditional European varieties, which highly complicates the adaptation of traditional wine production methods [2].

A limited number of studies have focused on the volatile compounds from grapes and wines of IHV varieties. Vidal, the main variety used for ice-wine production in Canada, is one of the few IHV varieties that have been studied [9]. Analysis of Vidal wine aroma by gas chromatography coupled to olfactometry (GC-O) and mass spectrometry (MS) showed that ethyl hexanoate, ethyl octanoate, *cis*-rose oxide, linalool, geraniol, *β*-damascenone and 2-phenylethanol have a significant olfactory impact on wine aroma [9, 10]. In a comparative study, Chisholm et al. [11] found that wines from the white IHV varieties Cayuga, Vidal and Seyval blanc had higher concentrations of undesirable volatile aroma compounds than the *V. vinifera* variety Riesling. On the other hand, studies conducted on the IHV variety Traminette showed that the concentrations of monoterpenes in berries was twice higher than in Riesling and Gewürztraminer berries grown under similar environmental conditions [12].

Data on white IHV varieties grown in northern conditions are scarce. In Quebec, a few studies focused on the impact of different agricultural practices on parameters such as cold tolerance [13], disease susceptibility [14], maturity and fruit quality [15], but most studies focused on agronomic aspects rather than wine production. Yet knowledge of the volatile compounds of *Vitis* varieties is crucial for optimizing the quality of wines. In this context, the aim of the present study was to determine the profiles of volatile compounds in berries and wines from five white IHV varieties (Frontenac blanc, Frontenac gris, Seyval blanc, St. Pepin and Vidal) grown in Quebec, using solid phase microextraction (SPME) coupled with GC-MS, and to establish correlations between the volatile compounds of berry juice and wine.

Materials and Methods

Samples

Samples (four to five biological replicates per grape variety) of the white IHV varieties Frontenac blanc and Frontenac gris [colorless mutants from red Frontenac (*Vitis riparia* x Landot 4511)], Seyval blanc (Seibel 5656 x Seibel 4986), St. Pepin [(Minnesota 78 x Seibel 1000) x Seyval blanc)], and Vidal (St. Emilion x Seibel 4986) were harvested at commercial maturity, in vineyards located in the Montérégie (45°7' N, 72°48' W) and Estrie (45°26' N, 72°53' W) areas (Quebec, Canada), during the 2012 season. Samples (50 kg) were preserved at 4 °C during transportation from the vineyard to the experimental winery.

Reagents and standards

Absolute ethanol was purchased from Commercial Alcohols (Brampton, ON), and L-tartaric acid and sodium chloride (NaCl) from Fisher Scientific (Fair Lawn, NJ). Deuterated standards (d_8-ethyl acetate, ethyl 4,4,4-d_3-butanoate, d_5-2,3,4,5,6-benzyl alcohol, 2-phenyl-d_5-ethanol, d_{11}-hexanoic acid, d_{15}-ethyl octanoate and d_{13}-hexanol) were purchased from C/D/N Isotopes Inc. (Pointe-Claire, QC). β-myrcene was purchased from MP Biomedicals (Santa Ana, CA). Ethyl hexanoate and ethyl propanoate were purchased from Nu-Chek-Prep (Elysian, MN). Ethyl vanillate and nonanal were purchased from Alfa Aesar (Heysam, England). Other reagents and standards were purchased from Sigma-Aldrich (St. Louis, MO) [3].

Technological parameters of musts

For each sample, 200 berries were randomly picked from 15 different randomly selected clusters. Grape juice was manually extracted by pressing berries in food grade polyethylene bags. Total soluble solids (TSS, °Brix), pH and titratable acidity (TA; g tartaric acid eq./L) were measured on fresh must according to Amerine and Ough [16]. Yeast assimilable nitrogen (YAN) concentration was determined by measuring ammoniacal nitrogen (NH_3 and NH_4^+) and primary amino nitrogen, as described by Slegers and coworkers [3].

Winemaking

Samples were stemmed, pressed, treated with potassium metabisulphite (SO_2; 30 mg/L), and placed at 10 °C for 8 to 12 hours to allow the sedimentation of the solid residue. Must was then racked, tempered at 18 °C and inoculated with *Saccharomyces cerevisiae* var. *bayanus* Lalvin QA23 (250 mg/L; Lallemand, Montreal, QC). Fermentations were carried out at 18 °C, with daily monitoring of must density and temperature, until dryness (specific gravity of 0.998 kg/L). Wines were racked, treated with 50 mg/L SO_2, stored at 10 °C in stainless steel kegs and aged for 5 months. After aging, wines were sulfited, filtered (45 µm filters, Buon Vino Super Jet Wine, Cambridge, ON), bottled, and kept in the dark at 10 °C until analyzes that were performed a few days later. Each grape sample (four to five biological replicates per variety) was individually processed and fermented.

Basic wine composition

TA, pH, and ethanol levels were measured according to Amerine and Ough [16]. Volatile acidity (VA) and glycerol concentrations were determined by UV-visible spectroscopy, using commercial test kits, as described by Slegers and coworkers [3].

Analysis of volatile compounds in juice and wine

Juice and wine volatile compounds were extracted by headspace solid-phase microextraction (SPME) and analyzed by gas chromatography coupled to a time-of-flight mass spectrometer (GC-TOF-MS), as detailed by Slegers et al. [3]. Juice samples were prepared as follows: juice (5 mL) was poured in a SPME vial containing NaCl (3 g) and deuterated standards (50 μL of a mixture of ethyl acetate-d_8, ethyl butanoate-4,4,4-d_3, benzyl-2,3,4,5,6-d_5 alcohol, 2-phenyl-d_5-ethanol, hexanoic-d_{11} acid, ethyl octanoate-d_{15} and hexanol-d_{13}) were added. Wine samples were prepared as follows: wine (3 mL) was added to a SPME vial containing NaCl (3 g), distilled water (3 mL) and a mixture of deuterated standards (50 μL; same composition as above) was added. Volatile compounds were extracted by SPME (25 min; 60 °C) using a polydime thylsiloxane:divinylbenzene:carboxen fiber assembly (2 cm grey fiber, Sigma-Aldrich, St. Louis, MO), and desorbed for 5 min, in splitless mode, in the inlet of a GC (Agilent 6890 Series, Santa Clara, CA) attached to a time-of-flight mass spectrometer (Pegasus HT TOF-MS; Leco, St. Joseph, MI) and a computer with the Leco ChromaTOF software (Leco, St. Joseph, MI). Volatile compounds were separated on a DB wax GC column (polyethylene glycol, 60 m × 0.25 mm i.d. × 0.25 μm film thickness; SGE, Austin, TX), and quantified using deuterated standards and 11-point calibration curves (one for juice and one for wine) based on authentic standards, as detailed by Slegers et al [3].

Statistical Analyses

Analyses of variance (ANOVA) based on a mixed model were performed on all data using the Mixed procedure of the SAS software (Statistical Analysis System Institute, Cary, NC). Means were compared using a Tukey's test ($P \leq 0.05$). A principal component analysis (PCA) comparing juice and wine respective volatile compound profiles was performed using the Princomp procedure of SAS software. Variables were selected based both on their frequency among samples and on the results of the ANOVA (significant variables). The analysis of frequency was performed using the Freq procedure of the SAS software. Variables showing a frequency lower than 50% were not included in the PCA, unless they provided significant information on a group of data.

Results and Discussion

Technological parameters of musts and wines

The chemical balance of musts has a significant impact on the style and quality of wines. The most common markers for grape juice quality are TSS and TA. Their values largely depend of the grape variety, the growing conditions and berry ripening [17]. In general, the TSS concentration of grape varieties used for the production of dry white wines ranges from 15 to 25 °Brix [17]. In this study, Frontenac gris showed the highest TSS concentration at 23.2 °Brix (Table 1) whereas Seyval blanc had the lowest concentration, at 19.7 °Brix. These differences partly relate to the intrinsic characteristics of each grape variety, but low TSS concentration is also frequent in northern climate, sometimes because berry ripening cannot be much extended in Fall due to the risk of frost and/or the risk of *Botrytis* infections on berries, which typically occurs when berries tear following heavy rains [18].

Musts from Frontenac gris and Frontenac blanc showed the highest TA with respective values of 15.0 and 16.0 g tartaric ac. eq./L, whereas the lowest TA value was found in Seyval blanc, at 9.5 g tartaric ac. eq./L. The TA of white grapes varieties generally ranges between 4 and 9 g tartaric ac. eq./L [17]. The pH values of musts from all varieties ranged from 2.96 in Seyval blanc juice to 3.18 in Frontenac blanc, which are typical values for white grape varieties. IHV varieties are known to have higher TA and lower pH when compared to *V. vinifera*, especially when they are grown in cold climates [2,18]. In addition, *V. riparia*-based hybrid varieties such as Frontenac

Table 1: Composition of juice (total soluble solids (TSS, °Brix), titratable acidity (TA, g tartaric ac. eq./L), pH, yeast assimilable nitrogen concentration (YAN, mg/L), and wine (alcohol concentration (% v/v), titratable acidity (TA, g tartaric ac. eq./L), pH, glycerol concentration (g/L), volatile acidity (VA, mg acetic ac. eq./L) in the white interspecific hybrid *Vitis* varieties Frontenac white, Frontenac gris, Seyval, Vidal St. Pepin harvested in Quebec during the 2012 season.

Variety	Juice				Wine				
	TSS (° Brix)	TA (g tartaric acid eq./L)	pH	YAN (mg/L)	Alcohol (% v/v)	TA (g tartaric acid eq./L)	pH	Glycerol (g/L)	VA (mg acetic ac. eq./L)
Frontenac blanc	22.3 ab [a]	16.0 b	3.18 b	304 ab	12.9 b	10.5 a	3.08 a	1.36 a	0.23 ab
Frontenac gris	23.2 b	15.0 b	3.14 b	376 b	12.6 ab	12.4 a	3.05 a	1.38 a	0.16 a
Seyval blanc	19.7 a	9.50 a	2.96 a	183 ab	10.4 a	9.05 a	2.98 a	1.29 a	0.26 ab
St. Pepin	20.3 ab	11.3 a	3.05 ab	275 ab	11.8 ab	9.15 a	3.03 a	1.45 a	0.21 ab
Vidal	20.1 ab	10.6 a	3.15 b	112 a	11.6 ab	8.53 a	3.12 a	1.30 a	0.47 b

[a] Values represent the mean of 3 to 5 biological replicates per variety. Values on the same column followed by different letters are significantly different according to Tukey's test (P≤ 0.05).

Table 2: Concentration of free volatiles (μg/L) in juice of the white interspecific hybrid *Vitis* varieties Frontenac white, Frontenac gris, Seyval, Vidal St. Pepin harvested in Quebec during the 2012 season.

Volatile Compound	Concentration (μg/L) [a]				
	Frontenac blanc	**Frontenac gris**	**Seyval**	**St. Pepin**	**Vidal**
Fatty acids degradation products					
hexanal	220 ± 26.1	47.2 ± 44.3	33.5 ± 21.6	22.6 ± 22	59.1 ± 63.2
hexanol	196 ± 57 a	153 ± 46 a	309 ± 94 a	653 ± 240 b	383 ± 130 a
cis-3-hexenal	16.5 ± 12.2 a	53.8 ± 25.1 b	20.3 ± 15.5 a	13.7 ± 7.1 a	14.8 ± 11 a
cis-3-hexenol	41 ± 13.1 a	37.9 ± 16.3 a	50.3 ± 35.8 a	48.1 ± 23.7 a	170 ± 113 b
trans-2-hexenal	690 ± 456 ab	965 ± 372 b	450 ± 232 ab	308 ± 350 a	394 ± 209 ab
trans-2-hexenol	994 ± 179 c	830 ± 198 bc	504 ± 131 ab	986 ± 249 c	435 ± 158 a
trans, cis-2,6-nonadienal	0.29 ± 0.11 ab	0.36 ± 0.14 b	0.13 ± 0.1 ab	0.08 ± 0.17 a	0.04 ± 0.09 a
trans, trans-2,4-hexadienal	32.5 ± 26.1	38 ± 17.5	11.1 ± 11.2	12.1 ± 13.7	19.3 ± 10
heptanol	*tr*	0.02 ± 0.01	0.42 ± 0.9	0.36 ± 0.68	*tr*
trans-2-heptenal	1.58 ± 1.32	1.44 ± 0.73	1.91 ± 1.32	1.39 ± 1.77	1.04 ± 1.11
trans, cis-2,4-heptadienal	0.48 ± 0.13	0.5 ± 0.14	0.37 ± 0.21	0.34 ± 0.06	0.34 ± 0.09
trans, trans-2,4-heptadienal	2.43 ± 0.61	2.43 ± 0.69	1.9 ± 1.08	1.98 ± 0.46	1.74 ± 0.23
1-octen-3-ol	1.05 ± 0.63	0.83 ± 0.35	1.22 ± 1.56	3.38 ± 5.74	1.55 ± 1.13
1-octen-3-one	0.1 ± 0.17	0.01 ± 0.01	0.51 ± 0.53	0.32 ± 0.62	0 ± 0.01
2-octanone	0.1 ± 0.1	0.06 ± 0.05	0.27 ± 0.41	0.6 ± 0.84	0.07 ± 0.01
decanal	0.47 ± 0.55	0.94 ± 0.01	0.75 ± 0.42	0.72 ± 0.48	0.55 ± 0.5
2-undecanone	0.4 ± 0.34	0.28 ± 0.19	0.76 ± 0.8	0.89 ± 0.56	*tr*
Sum	*2000 ± 634 a*	*2131 ± 475 a*	*1498 ± 216 a*	*2052 ± 83 a*	*1480 ± 466 a*
C_{13}-norisoprenoids					
β-damascenone	5.45 ± 2.62 a	2.94 ± 1.07 a	3.24 ± 1.78 a	17.6 ± 7.1 b	6.86 ± 4.43 b
α-ionone	0.47 ± 0.18 a	0.32 ± 0.08 a	0.7 ± 0.63 ab	1.39 ± 0.5 ab	2.19 ± 1.44 b
α-ionol	1.73 ± 0.7 a	1.39 ± 0.28 a	2.72 ± 1.86 ab	4.85 ± 1.61 b	1.33 ± 0.79 a
β-ionone	0.11 ± 0.01	0.1 ± 0.01	0.08 ± 0.01	0.1 ± 0.03	0.1 ± 0.02
Terpenes [b]					
β-myrcene	1.4 ± 0.93	1.39 ± 0.93	1.87 ± 0.09	1.46 ± 0.97	2.57 ± 4.31
(R)-(+)-limonene	0.12 ± 0.03 a	0.13 ± 0.01 a	0.14 ± 0.07 a	0.28 ± 0.18 a	2.29 ± 1.22 b
linalool	0.99 ± 0.06 a	1.02 ± 0.14 a	2.37 ± 1.27 a	3.11 ± 0.68 ab	10.3 ± 8.1 b
α-terpineol	0.02 ± 0.01 a	0.02 ± 0.01 a	4.93 ± 5.51 a	22.3 ± 17.6 ab	38.2 ± 14.5 b
nerol	*nd*	0.01 ± 0.02	0.07 ± 0.13	0.04 ± 0.04	0.26 ± 0.38
Sum	*2.53 ± 0.99 a*	*2.57 ± 1 a*	*9.38 ± 6.54 a*	*27.2 ± 17.1 ab*	*53.6 ± 27.4* b
Fatty acid ethyl esters [b]					
ethyl propanoate	*tr*	0.06 ± 0.11	*nd*	1.01 ± 0.44	0.89 ± 1.99
ethyl 2-methylpropanoate	*nd*	0.21 ± 0.42	*nd*	*nd*	*nd*
ethyl butanoate	*tr*	*nd*	*nd*	20.3 ± 11.7	*nd*
ethyl 3-methylbutanoate	*nd*	*nd*	*nd*	0.17 ± 0.2	*nd*
ethyl 2-butenoate	*tr*	*tr*	0.1 ± 0.11 a	11.5 ± 10 b	*nd*
ethyl hexanoate	*tr*	*tr*	0.05 ± 0.08	0.42 ± 0.82	*tr*
Sum	*tr*	*0.27 ± 0.39 a*	*0.15 ± 0.14 a*	*33.5 ± 22 b*	*0.89 ± 1.99* a
Volatile phenols and benzene derivatives					
2-phenylacetaldehyde	0.89 ± 1.62 a	0.8 ± 1.3 a	2.55 ± 4.58 a	2.88 ± 3.97 a	54.4 ± 46.1 b
phenethyl acetate	*tr*	*tr*	0.06 ± 0.09	0.07 ± 0.02	0.14 ± 0.29
2-phenylethanol	3.88 ± 7.52	2.79 ± 5.39	3.79 ± 8.25	0.8 ± 0.78	39 ± 60.1
eugenol	0.52 ± 0.36	0.43 ± 0.29	*nd*	0.12 ± 0.25	*nd*
p-vinylguaiacol	3.98 ± 1.71 c	1.45 ± 0.56 ab	0.74 ± 0.48 ab	0.41 ± 0.29 a	3.96 ± 3.64 bc
Sum	*9.28 ± 10.2 a*	*5.48 ± 5.56 a*	*7.13 ± 12.9 a*	*4.28 ± 4.7 a*	*97.5 ± 51.6 b*

Others					
isoamyl acetate	0.03 ± 0.06	0.03 ± 0.07	0.19 ± 0.24	0.36 ± 0.54	0.04 ± 0.06
isoamyl alcohol	*tr*	*nd*	*tr*	0.04 ± 0.08	*tr*

[a]Values represent the mean ± standard deviation of 3 to 5 biological replicates per variety. Values on the same line followed by different letters are significantly different according to Tukey's test (P≤ 0.05). Values on the same line without letters are not significantly different according to Tukey's test (P≤ 0.05).
[b]Ethyl 2-methybutanoate and *β*-citronellol were not detected in any sample; ethyl octanoate was found in trace in all varieties but not all samples.
nd: not detected
tr: compound found below the limit of quantification in most samples.

gris and Frontenac blanc typically show high TA due to their high concentration of tartaric acid [3, 18]. High TA may be adjusted by deacidification, which is common practice in the production of cold-climate wine [2, 3]. Indeed, pH and TA corrections are typical of wine production, regardless of the climate [6, 17].

A sufficient concentration of YAN (≥150 mg/L) in musts is essential to prevent stuck fermentations in winemaking. The YAN concentration of IHV varieties can be highly variable (between 8 mg/L and 928 mg/L) and higher cold tolerance in grape varieties generally results in higher nitrogen concentration [19]. The must from Frontenac gris, one of the most cold-hardy varieties among those analyzed, contained the highest YAN concentration (376 mg/L, Table 1) whereas Vidal, which typically needs winter protection in Quebec, had the lowest YAN concentration (112 mg/L). Such low YAN values in Vidal musts resulted in slower fermentations and may explain the slightly higher VA concentration found in Vidal wine samples (0.47 mg acetic acid eq./L). The production of VA by yeast is inversely proportional to the amount of YAN present in the must [20].

Volatile compounds from musts and wine

Volatile compounds (40) from five chemical and metabolic classes were quantified in musts: 1) C_6 compounds and other fatty acid degradation products (FADP); 2) C_{13}-norisoprenoids; 3) terpenes; 4) fatty acid ethyl esters (FAEE); 5) Volatile phenols and other phenyl derivatives (Table 2). Analysis of the volatile compounds of wine resulted in identification and quantification of 36 volatile compounds including berry-related (C_6 compounds, terpenes, C_{13}-norisoprenoids, volatile phenols) and fermentation-related (higher alcohols, aromatic and aliphatic esters and acetates, free fatty acids) compounds (Table 3).

C_6 compounds and other FADP

Fatty acid degradation products (FADP) are the main volatile compounds found in the must of many grape varieties and mostly include six-carbons saturated and unsaturated alcohols and aldehydes such as hexanal and *cis*-3-hexenol [3]. FADP accounted for 99% of the volatile fraction of Frontenac gris, Frontenac blanc and Seyval blanc, whereas the proportion of FADP accounted for 96% and 90% of total quantified volatile compounds in the musts of St. Pepin and Vidal, respectively. In *V. vinifera*, C_6 compounds constitute the largest proportion of free volatile compounds in the so-called "neutral" varieties and are significant contributors to the herbaceous character found in grape musts [21]. In agreement with the present work, previous studies have shown that C_6 compounds are the main constituents of the flavor profile in several IHV varieties representing, in most cases, over 94% of total volatile compounds [3, 22]. The C_6 aldehyde *trans*-2-hexenal and the C_6 alcohols *trans*-2-hexenol and hexanol constituted the major share of the total volatile composition in the musts of the studied IHV varieties, which is typical in grape juice [3, 18].

Hexanol was the major C_6 compound found in the wines, and its concentration ranged from 391 μg/L in Frontenac blanc to 558 μg/L in Seyval blanc (Table 3), suggesting that its sensory impact is very limited since the odor perception threshold of hexanol is estimated at 8000 μg/L in wine [23] (Table 4). These values compare to those found in wines from *V. vinifera* varieties for which reported values ranged from 117 to 1101 μg/L in six grape varieties grown in Portugal, including Riesling (195 μg/L), and Sauvignon Blanc (390 μg/L) [24, 25]. Both the concentration and the sensory impact of C_6 compounds are known to decrease in wine when compared to grape juice. Indeed, the highly odor-active C_6 aldehydes found in grape juice are reduced to alcohol during winemaking, whereas specific C_6 compounds are transformed into desirable esters and acetates [26]. C_6 compounds from grapes may therefore contribute to fruity notes in wine [26].

However, C_6 compounds and other FADP may also negatively impact wine aroma when their concentrations exceed their olfactory detection threshold [27]. In this study, C_9 aldehydes nonanal and *trans,cis*-2,6-nonadienal showed odor activity values much higher than 1 (27 and 73, in average, respectively), suggesting that they may have significantly impacted wine aroma (Table 4). Nonanal aroma is described as waxy with citrus and cucumber hints, whereas *trans, cis*-2,6-nonadienal has a herbaceous scent with notes of cucumber and melon. The concentrations of nonanal determined in the wines ranged from 22.4 μg/L in Seyval blanc to 34.1 μg/L in St. Pepin (Table 3). In contrast, nonanal concentration has been reported to range from 1 μg/L [28] to 19 μg/L [29] in *V. vinifera* Chardonnay. Similarly, *trans,cis*-2,6-nonadienal is rarely reported in the volatile compound profile of wines from *V. vinifera* varieties; a recent study indicated that *trans*-2,*cis*-6-nonadienal was not detected in any of 18 Spanish wines [28].

Terpenes

β-myrcene, linalool and *α*-terpineol were the main terpenes quantified in the musts of the IHV varieties. Musts from Vidal grapes showed a significantly higher concentration in terpenes (57.6 μg/L), mainly linalool and *α*-terpineol, compared to the other varieties (Table 2). The concentration of

Table 3: Concentration of free volatiles (μg/L, except where otherwise indicated) of wines from the white interspecific hybrid *Vitis* varieties Frontenac white, Frontenac gris, Seyval, Vidal St. Pepin harvested in Quebec during the 2012 season.

Volatile compound	Concentration [a,b]				
	Frontenac blanc	Frontenac gris	Seyval	St. Pepin	Vidal
Fatty acids degradation products					
hexanal	2.98 ± 0.93	2.36 ± 0.59	2.62 ± 2.4	3.95 ± 2.51	1.21 ± 1.06
hexanol	391 ± 201	491 ± 52	558 ± 136	476 ± 59	394 ± 51
trans-3-hexenol	18.2 ± 3.7 ab	13.7 ± 2.9 ab	11.1 ± 5 ab	22.3 ± 8.4 b	7.5 ± 2.23 a
cis-3-hexenol	27 ± 8.6 a	35 ± 8.7 a	57.7 ± 25 a	31 ± 12 a	144.9 ± 26.3 b
nonanal	27.4 ± 10.1	29.4 ± 5.1	22.4 ± 5.6	34.1 ± 10.5	25.5 ± 3.5
trans,cis-2,6-nonadienal	0.26 ± 0.45	1.53 ± 2.66	0.55 ± 0.84	0.71 ± 0.91	0.62 ± 1.07
Sum	*467 ± 197*	*573 ± 49*	*652 ± 118*	*567 ± 51*	*573 ± 38*
C_{13}-norisoprenoids					
β-damascenone	2.67 ± 0.24	2.99 ± 0.82	0.82 ± 0.77	2.66 ± 1.68	2.23 ± 0.3
Terpenes					
β-myrcene	*tr*	*tr*	*tr*	*tr*	*tr*
p-cymenene	0.57 ± 0.61 ab	0.5 ± 0.71 ab	0.51 ± 0.72 a	0.44 ± 0.29 a	2.05 ± 0.68 b
linalool	7.28 ± 3.65 a	6.99 ± 0.69 a	8.36 ± 7.08 a	10.2 ± 9.3 ab	23.4 ± 1.16 b
α-terpineol	2.24 ± 0.44	3.95 ± 0.92	4.61 ± 2.44	10.6 ± 11.01	12.3 ± 1.64
β-citronellol	6.67 ± 2.94 a	6.99 ± 0.34 a	4.26 ± 2.46 a	5.91 ± 2.2 a	14.4 ± 4.7 b
nerol	*nd*	*nd*	*nd*	*nd*	1.09 ± 0.05
geraniol	0.13 ± 0.17	*nd*	*tr*	1.88 ± 3.76	1.74 ± 0.68
Sum	*16.9 ± 6.5 a*	*18.4 ± 1 a*	*17.7 ± 5.9 a*	*29 ± 25.4 ab*	*55 ± 4.5 b*
Fatty acid ethyl esters					
ethyl 2-methylpropanoate	213 ± 21	193 ± 57	223 ± 41	274 ± 40	188 ± 9
ethyl butanoate	164 ± 48	157 ± 55	79 ± 122	115 ± 95	112 ± 29
ethyl 2-methylbutanoate	15.2 ± 2.6 ab	23.3 ± 9 ab	27.4 ± 4.3 b	24.7 ± 8.2 b	8.7 ± 3.4 a
ethyl 3-methylbutanoate	20.1 ± 2.8 ab	25.1 ± 4 b	21.2 ± 3.2 b	21.7 ± 5.2 b	10.9 ± 2.3 a
ethyl hexanoate	2274 ± 1192	1628 ± 586	1449 ± 828	1911 ± 262	2598 ± 568
ethyl octanoate	6544 ± 4243	5170 ± 3666	5107 ± 3526	6030 ± 1101	12089 ± 3553
ethyl decanoate	1752 ± 1560 a	3991 ± 2450 a	4833 ± 3238 a	4215 ± 2030 a	12264 ± 3779 b
ethyl 3-hydroxyhexanoate	6.7 ± 2.1	9.6 ± 4.6	7 ± 4.6	11.3 ± 3.4	8.5 ± 6.8
Sum (mg/L)	*11.0 ± 4.3 a*	*11.2 ± 6.6 a*	*11.7 ± 7.7 a*	*12.6 ± 2.3 ab*	*27.3 ± 7.8 b*
Aromatic esters					
phenethyl acetate	20.1 ± 19.1 a	27.3 ± 34.8 a	62.7 ± 45.3 ab	105 ± 17 bc	150 ± 13.8 c
ethyl dihydrocinnamate	*tr*	*tr*	*tr*	0.06 ± 0.1	*tr*
ethyl cinnamate	*nd*	*nd*	*nd*	0.05 ± 0.09	*nd*
ethyl vanillate	4.95 ± 1.47 b	5.21 ± 2.58 b	2.7 ± 2.07 ab	1.29 ± 1.37 a	1.07 ± 0.85 a
Sum	*25.1 ± 19.4 a*	*32.6 ± 33.9 a*	*65.5 ± 45 ab*	*107 ± 18 bc*	*151 ± 13 c*
Fatty acids					
hexanoic acid (mg/L)	6.35 ± 1.96 a	5.16 ± 2.29 a	5.96 ± 2.77 a	6.86 ± 1.56 a	12.2 ± 1.2 b
octanoic acid (mg/L)	14.4 ± 2.35 a	15.5 ± 4.9 a	20 ± 9.9 a	20.5 ± 2.5 a	38.1 ± 1.7 b
Sum (mg/L)	*20.8 ± 0.5 a*	*20.6 ± 0.7 a*	*26 ± 1.2 a*	*27.4 ± 4 a*	*50.3 ± 1.7 b*
Volatile phenols					
eugenol	1.16 ± 0.47 ab	2.17 ± 0.74 b	0.7 ± 0.31 a	0.5 ± 0.38 a	0.17 ± 0.17 a
p-vinylguaiacol	14.9 ± 12.2 ab	25 ± 11 ab	10.1 ± 8.4 a	19.6 ± 16.3 ab	42.8 ± 6.2 b
Sum	*16.1 ± 12.3 ab*	*27.1 ± 11.7 ab*	*10.8 ± 8.4 a*	*20.1 ± 16.5 ab*	*43 ± 6.2 b*
Other fermentation compounds					
isobutyl acetate	0.47 ± 0.41	*nd*	0.35 ± 0.44	*nd*	*nd*
isobutanol	162 ± 26 ab	168 ± 42 b	125 ± 18 ab	161 ± 18 b	95 ± 29 a

isoamyl acetate	598 ± 452	331 ± 537	335 ± 300	766 ± 324	918 ± 463
hexyl acetate	4.24 ± 4.05 a	1.67 ± 1.6 a	9.71 ±7.63 ab	13.6 ± 3.7 ab	22.3 ± 6.2 b
acetoin (mg/L)	16.1 ± 18.4	12.2 ± 5.4	4.02 ± 4.37	2.97 ± 1.99	6.05 ± 2.31
ethyl lactate (mg/L)	31.2 ± 42.3	27.2 ± 25.2	13.1 ± 18.8	5.79 ± 1.45	22.2 ± 33.8
butyrolactone	263 ± 12	277 ± 8	287 ± 44	257 ± 12	277 ± 21
2-phenylethanol (mg/L)	34.8 ± 7.3	43.9 ± 17.4	54.9 ± 11.7	54.8 ± 14.2	50.7 ± 11.6

[a] Concentrations are in µg/L, unless otherwise indicated.

[b] Values represent the mean ± standard deviation of 3 to 5 biological replicates per variety. Values on the same line followed by different letters are significantly different according to Tukey's test ($P \leq 0.05$). Values on the same line without letters are not significantly different according to Tukey's test ($P \leq 0.05$).

nd: not detected

tr: compound found below the limit of quantification in most samples.

linalool (10.3 µg/L) measured in Vidal must is comparable to those previously observed in neutral *V. vinifera* white varieties, whereas its *α*-terpineol concentration (38.2 µg/L) better relates to the amounts reported in aromatic *V. vinifera* varieties. Indeed, previous studies showed linalool and *α*-terpineol concentrations ranging from 64.2 to 198 µg/L, and from 9.5 to 37 µg/L, respectively, in grape varieties described as "aromatic" [30, 31]. Similar to most grape varieties analyzed in the present studies, the neutral grape varieties Albillo [30], Bical [31], Fiano [32], and Palomino Fino [33] have been reported to contain low concentrations of linalool (0 to 6.7 µg/L) and *α*-terpineol (0 to 3.2 µg/L).

Consistent with the profile of must volatile compounds, Vidal wines showed the highest terpene concentration (55.0 µg/L, Table 3). Terpene concentration ranged from 17 µg/L in Frontenac blanc to 29 µg/L in St. Pepin. Linalool, *α*-terpineol and *β*-citronellol were the main terpenes found in the wines. The concentration of linalool in Vidal wine (23 µg/L) compared with reported values in Riesling (16 µg/L) [24]. Terpenes are known to bring desirable floral and citrus aroma in wine, and linalool has been identified as an impact odorant in young Vidal wine [10]. In this study, the odor-activity value for linalool in Vidal wine was > 1 (Table 4), suggesting that this compound contributes to Vidal wine aroma.

C_{13}-norisoprenoids

C_{13}-norisoprenoids such as *β*-damascenone and *β*-ionone, contribute to the varietal aroma of many grape varieties due to their extremely low olfactory perception thresholds (0.05 and 0.09 µg/L, respectively, Table 4) [34]. In this study, the concentrations of C_{13}-norisoprenoids in grape musts ranged from 4.7 µg/L in Frontenac gris to 24.0 µg/L in St. Pepin, with the main compounds being *β*-damascenone and *α*-ionol (Table 2). The variety St. Pepin showed the highest concentration of *β*-damascenone at 17.6 µg/L, yet this compound concentration reached beyond its odor threshold in all varieties, suggesting that it significantly impacts the sensory aroma of juice from IHV varieties, as observed in *V. vinifera* and *V. labrusca*. [35, 36].

β-Damascenone has a fruity, floral scent reminiscent of baked apple, and has been reported to significantly contribute to the aroma of Vidal wine [9, 10]. It was the main C_{13}-norisoprenoid quantified in IHV wines where its concentration ranged from 0.8 µg/L in Seyval blanc to 3.0 µg/L in Frontenac gris (Table 3). In contrast with musts, no significant differences between the varieties were found for *β*-damascenone. *β*-damascenone concentration decreases during winemaking due to reactions with sulfites and molecular rearrangements, especially in acidic conditions [37].

Volatile phenols and other phenyl derivatives

Volatile phenols occurring in grapes mostly derive from the shikimate metabolic pathway [34]. In this study, 2-phenylacetaldehyde and 2-phenylethanol were the main volatile phenols identified in IHV varieties, and had the highest concentrations in Vidal musts with values of 54 and 39 µg/L, respectively (Table 2). A high concentration of 2-phenylacetaldehyde seems unusual in grape must since it has either not been detected (*V. labrusca*, *V. amurensis*) or recovered in amounts ranging from traces in Cabernet Gernisht to 14 µg/L in Muscadine [22, 35, 38]. However, recent work from our group showed very high concentrations (298 to 413 µg/L) of 2-phenyacetaldehyde in the IHV Sabrevois and St. Croix, suggesting that certain varieties carry this particularity [3].

The main volatile phenol identified in IHV wines was *p*-vinylguaiacol. Other aromatic derivatives such as phenethyl acetate were also present in significant amounts (Table 3). Vidal wines showed the highest concentration in both *p*-vinylguaiacol (42.8 µg/L) and phenethyl acetate (150 µg/L). *p*-Vinylguaiacol, whose flavor is reminiscent of spices and roasted peanuts, has an odor threshold of 40 µg/L in wines [23] suggesting that it may impact Vidal wine aroma (OAV > 1; Table 4). *p*-Vinylguaiacol had been identified as an impact odorant of Vidal wine, but only at a concentration of 111 µg/L [9].

Fatty acid ethyl esters and free fatty acids

The concentration in fatty acid ethyl ester derivatives in must was insignificant in most IHV varieties analyzed, except in St. Pepin musts, where a significant concentration (34 µg/L, Table 2), and a larger variety of fatty acid ethyl ester structures were found. The main fatty acid esters found in St. Pepin were ethyl butanoate and the unsaturated ethyl 2-butenoate, but their concentration varied among St. Pepin samples, hence explaining the large standard deviations. The presence of ethyl esters is unusual in most grape varieties used in wine production but has been reported in American *Vitis* spp. such

Table 4: Odor perception threshold (OPT; µg/L) and odor activity value (OAV) of wines from the white interspecific hybrid *Vitis* varieties Frontenac white, Frontenac gris, Seyval, Vidal St. Pepin harvested in Quebec during the 2012 season.

Volatile compound	OPT (ref.)	OAV				
		Frontenac blanc	Frontenac gris	Seyval	St. Pepin	Vidal
Fatty acids degradation products						
hexanal	5 [e]	0,6	<0.5	0.5	1	<0.5
hexanol	8000 [b]	<0.5	<0.5	<0.5	<0.5	<0.5
trans-3-hexenol	1000 [f]	<0.5	<0.5	<0.5	<0.5	<0.5
cis-3-hexenol	400 [b]	<0.5	<0.5	<0.5	<0.5	<0.5
nonanal	1 [g]	27	29	22	34	25
trans,cis-2,6-nona-dienal	0.01 [j]	26	153	55	71	62
C_{13}-norisoprenoids						
β-damascenone	0.05 [b]	53	60	16	53	45
Terpenes						
β-myrcene	14 [c]	-	-	-	-	-
p-cymenene	ND	-	-	-	-	-
linalool	25.2 [a]	<0.5	<0.5	<0.5	<0.5	1
α-terpineol	250 [b]	<0.5	<0.5	<0.5	<0.5	<0.5
β-citronellol	100 [b]	<0.5	<0.5	<0.5	<0.5	<0.5
nerol	400 [k]	-	-	-		<0.5
geraniol	30 [a]	<0.5	-	-	<0.5	<0.5
Fatty acid ethyl esters						
ethyl 2-methylpropanoate	15 [a]	14	13	15	18	13
ethyl butanoate	20 [b]	8	8	4	6	6
ethyl 2-methylbutanoate	18 [a]	1	1	2	1	0
ethyl 3-methylbutanoate	3 [a]	7	8	7	7	4
ethyl hexanoate	14 [a]	162	116	103	137	186
ethyl octanoate	5 [a]	1309	1034	1021	1206	2418
ethyl decanoate	200 [a]	9	20	24	21	61
ethyl 3-hydroxyhexanoate	45 [h]	<0.5	<0.5	<0.5	<0.5	<0.5
Aromatic esters						
phenethyl acetate	250 [a]	<0.5	<0.5	<0.5	<0.5	1
ethyl dihydrocinna-mate	1.6 [a]	-	-	-	<0.5	-
ethyl cinnamate	1.1 [a]	-	-	-	<0.5	-
ethyl vanillate	990 [i]	<0.5	<0.5	<0.5	<0.5	<0.5
Fatty acids						
hexanoic acid (mg/L)	0.42 [a]	15	12	14	16	29
octanoic acid (mg/L)	0.5 [a]	29	31	40	41	76
Volatil phenols						
eugenol	6 [a]	<0.5	<0.5	<0.5	<0.5	<0.5
p-vinylguaiacol	40 [b]	<0.5	0.6	<0.5	0.5	1
Other fermentation compounds						
isobutyl acetate	6140 [h]	<0.5	-	<0.5	-	-
isobutanol	40 000 [b]	<0.5	<0.5	<0.5	<0.5	<0.5
isoamyl acetate	30 [b]	15	8	8	19	23
hexyl acetate	26 [d]	<0.5	<0.5	<0.5	1	1
acetoin (mg/L)	150 [d]	<0.5	<0.5	<0.5	<0.5	<0.5
ethyl lactate (mg/L)	100 [h]	<0.5	<0.5	<0.5	<0.5	<0.5
butyrolactone	100 000 [h]	<0.5	<0.5	<0.5	<0.5	<0.5
2-phenylethanol (mg/L)	14 [a]	2	3	4	4	4

Odor perception threshold references: [a] [45]; [b] [23]; [c] [46]; [d] [47]; [e] [48]; [f] [49]; [g] [50]; [h] [51]; [i] [52]; [j] [53]; [k] [54]

as *V. labrusca* and hybrids derived from this species such as Concord, Niagara and Elvira [22, 39], or IHV that include *V. labrusca* in their genetic background such as Sabrevois [3].

The concentration of fatty acid ethyl esters of varietal origin in wine is negligible compared to that produced by yeast during alcoholic fermentation, which constitute the major class of volatile compounds found in wine. Vidal wine showed the highest concentration in aliphatic ethyl esters at 27.3 mg/L (Table 3), with top values for ethyl hexanoate (2.6 mg/L), ethyl octanoate (12.1 mg/L) and ethyl decanoate (12.3 mg/L). Both ethyl hexanoate and octanoate had been previously reported as major contributors to the flavor of Vidal wine [9]. Ferreira and coworkers showed that fatty acid ethyl esters play a significant role in the delicate aroma of white wines [40].

Free fatty acids such as hexanoic and octanoic acids have typical cheese and rancid aromas and may negatively impact wine aroma when their total concentration exceeds 20 mg/L [41]. The highest concentration of free fatty acids was observed in Vidal wine, where concentrations of hexanoic and octanoic acids reached 12.2 and 38.1 mg/L, respectively (Table 3). These values are relatively high compared to reported values for *V. vinifera* white wine with reported concentration ranging from 0.05 mg/L in Chardonnay to 13.7 mg/L in Sauvignon Blanc, for hexanoic acid, and from non-detectable to 12.2 mg/L in Sauvignon Blanc, for octanoic acid [42, 43].

Relationships between must and wine composition

PCA was used to compare the volatile composition of musts and wines (Figure 1). The first two principal components (PC 1 and PC 2) explained 56.8% of the variance observed between samples. The biplot of grape varieties (Figure 1A) revealed the distinctive volatile composition of Vidal must and wine compared to the other analyzed varieties.

The complex biochemical reactions ongoing during wine fermentation results in significant changes in the volatile compound profile of wine when compared to grape must. The biplot of variables (Figure 1B) shows some of the relationships found between the composition of must and wine of white IHV varieties, especially for grape-related compounds such as C_6 compounds, terpenes and volatile phenols.

The structure and the diversity of C_6 compounds is highly impacted by fermentation, yet the PCA showed a clear correlation between the concentration of *cis*-3-hexenol and *trans*-2-hexenol in the musts and the presence of *cis*-3-hexenol

(PC 1, 40.8% of variance) and *trans*-3-hexenol (PC 2, 15.6% of variance) in wine, respectively. The presence of *trans,cis*-2,6-nonadienal in wine was slightly related to the presence of this compound in the must, and was negatively correlated with the presence of terpenes in both must and wine over PC 1. High concentrations of fatty acid ethyl esters in the must (PC 2), as found in St. Pepin, corresponded to higher concentration in nonanal in the wine.

Higher linalool concentration in the musts generally correlated with higher terpene concentrations in wine. However, fermentation significantly impacted the profile of terpenes found in wine, when compared to must. Indeed, certain terpene (*β*-myrcene, *α*-terpineol and nerol) decreased in the wine compared to the amount initially found in the must. Similarly, certain terpenes such as (R)-(+)-limonene were detected in musts but not in wines, whereas others such as geraniol, *p*-cymenene and *β*-citronellol were detected in wines but not in musts. Such changes may result from chemical rearrangements occurring during the winemaking process or during maturation in the bottle [25, 44]. For example, geraniol may be the precursor of other monoterpenes such as neral, geranial, nerol and *β*-citronellol, and that process may be affected by yeast in a specific way [44]. These rearrangements significantly impact wine aroma by modifying the odor perception threshold and the sensory descriptors of terpenes. On the other hand, the occurrence of many terpenes in wine results from the enzymatic or chemical hydrolysis of glycosylated precursors present in the must during the winemaking process [6].

Finally, both eugenol and *p*-vinylguaiacol showed a strong correlation between must and wine. Both of them increased in wine when compared to must, suggesting that non-volatile precursors may be present in the musts of IHV varieties. A similar relationship has been found in red IHV varieties [3]. Although glycosylated precursors of volatile phenols are present in grapes, the presence of vinyl phenols in white wine may result from the breakdown of *p*-cinnamic acid and ferulic acid [6].

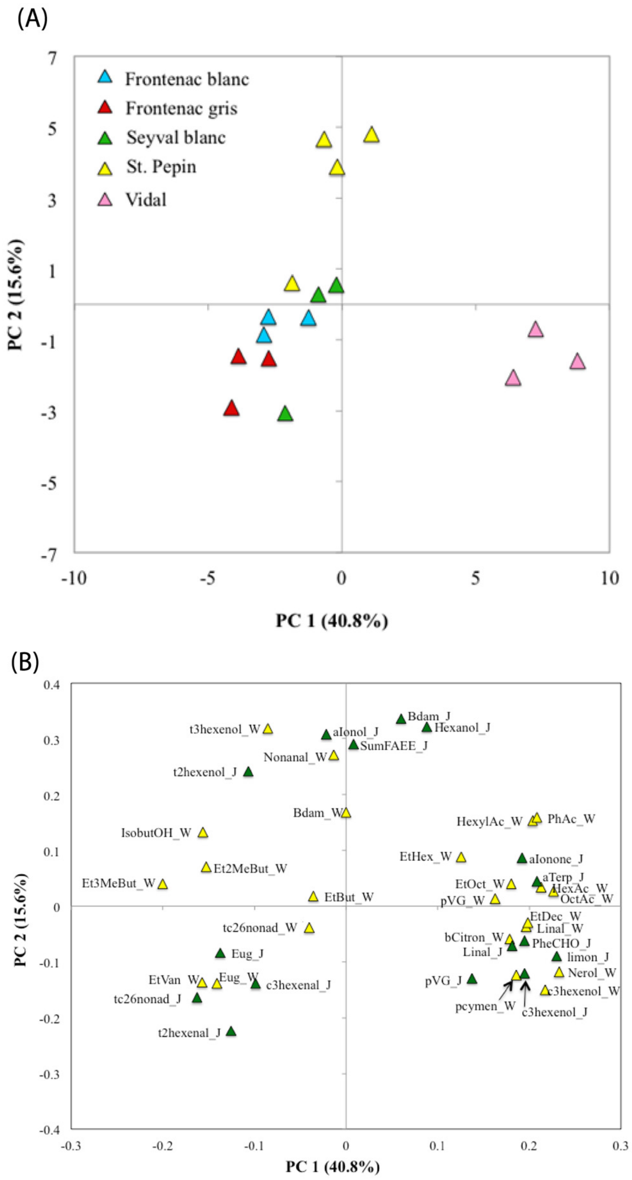

Figure 1: Principal Component Analysis (PCA) of the volatile composition of juice and wine from the interspecific hybrid *Vitis* varieties Frontenac blanc, Frontenac gris, Seyval blanc, St. Pepin and Vidal. **(A)** Biplot of varieties: Frontenac blanc (blue), Frontenac gris (red), Seyval blanc (green), St. Pepin (yellow) and Vidal (pink). **(B)** Biplot of variables, identified as follow: Juice volatile compounds (green triangles; labeled as _J): hexanol (Hexanol_J), *cis*-3-hexenol (c3hexenol_J), *trans*-2-hexenol (t2hexenol_J), *trans*-2-hexenal (t2hexenal_J), *trans,cis*-2,6-nonadienal (tc26nonad_J), *α*-ionol (aIonol_J), *α*-ionone (aIonone_J), *β*-damascenone (Bdam_J), (R)-(+)-limonene (limon_J), *α*-terpineol (aTerp_J), linalool (Linal_J), sum of fatty acid ethyl ester (FAEE_J), eugenol (Eug_J), *p*-vinylguaiacol (pVG_J), 2-phenylacetaldehyde (PheCHO_J). Wine volatile compounds (yellow triangles; labeled as _W): *trans*-3-hexenol (t3hexenol_W), *cis*-3-hexenol (c3hexenol_W), nonanal (Nonanal_W), *trans, cis*-2,6-nonadienal (tc26nonad_W), *β*-damascenone (Bdam_W), *p*-cymenene (pcymen_W), linalool (Linal_W), *β*-citronellol (bCitron_W), nerol (Nerol_W), ethyl butanoate (EtBut_W), ethyl 2-methylbutanoate (Et2MeBut_W), ethyl 3-methylbutanoate (Et3MeBut_W), ethyl hexanoate (EtHex_W), ethyl octanoate (EtOct_W), ethyl decanoate (EtDec_W), phenylethyl acetate (PhAc_W), ethyl vanillate (EtVan_W), hexanoic acid (HexAc_W), octanoic acid (OctAc_W), eugenol (Eug_W), *p*-vinylguaiacol (pVG_W), isobutanol (isobutOH_W), hexyl acetate (HexylAc_W).

Conclusion

The volatile compounds of musts and wines from hybrid grapes Frontenac gris, Frontenac blanc, Seyval, St. Pepin and Vidal grown in Quebec for the production of white wines was analyzed by GC-MS-SPME. Vidal showed the highest concentration in volatile compounds, as well as the widest chemical diversity in both must and wine. Vidal showed higher concentration of terpenes in musts and in wines, and fatty acid ethyl esters in its wines. On the contrary, Frontenac gris, Frontenac blanc, and Seyval blanc exhibited more neutral flavor profiles. The musts from St. Pepin showed the highest concentration of *β*-damascenone. PCA showed many correlations between must and wine: for instance, both C_6 compounds and terpenes from musts were highly correlated with those later found in wine, suggesting that certain of these compounds could be used as markers for grape quality in the future. Knowledge gained on the volatile composition of these interspecific hybrid *Vitis* varieties will contribute to develop viticulture and winemaking practices that will optimize the quality of their wines and maximize their potential on the global wine market.

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