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# Flavor of Cold-Hardy Grapes: Impact of Berry Maturity and Environmental Conditions

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**ABSTRACT:** Since the arrival on the market of high-quality cold-hardy grape varieties, northern winemaking has been developing tremendously in countries traditionally unsuited for grape and wine production. Cold-hardy grapes are mainly interspecific hybrids of *Vitis vinifera* with *Vitis labrusca* and *Vitis riparia*, making their chemical composition distinct from that of *V. vinifera* varieties traditionally used for winemaking and therefore limiting the use of current knowledge about *V. vinifera* varieties in the assessment of grape maturity. Consequently, to evaluate the flavor development of cold-hardy grapes in the province of Quebec, Canada, the ripening of Frontenac and Marquette berries in two vineyards located in the southwest (SW) and northeast (NE) areas of the province, starting at the beginning of veraison, was studied. Quality attributes, phenolic compounds, and aroma profiles showed significant changes during maturation. Although full maturity was reached for both Frontenac and Marquette in the SW vineyard (1380 accumulated growing degree days, based on 10 °C), the accumulation of 1035 growing degree days was not sufficient to fully ripen Frontenac and Marquette in the NE vineyard. Principal component analysis showed different ripening patterns for the two studied locations. The longer veraison in the SW vineyard resulted in higher quality attributes and higher flavor development for both Frontenac and Marquette. Under the colder conditions in the NE vineyard, metabolite accumulation was driven primarily by berry growth, and flavor development was limited. Besides growing degree days and technological parameters (total soluble solids, pH, titratable acidity), which provide significant guidelines for maturity assessment in cold climate, phenolic maturity may be followed by the accumulation of hydroxycinnamic esters and flavonoids, although the impact of these compound classes on quality remains to be determined in cold-climate wines. In both Frontenac and Marquette, aromatic maturity was best assessed using the ratio of *cis*-3-hexenol to *trans*-2-hexenal, which showed a constant decrease until maturity. Interestingly, a shift in $C_6$ compound profile, illustrated by the progression of the sum of $C_6$ compounds respectively produced from linoleic (C18:2; hexanal and 1-hexanol) and $\alpha$-linolenic (C18:3; *trans*-2-hexenol and *cis*-3-hexenol) acids occurred during ripening, with $\alpha$-linolenic acid (C18:3) degradation products decreasing in both varieties as maturation approached. At harvest, aroma profiles of both Frontenac and Marquette were dominated by $C_6$ compounds (hexanal, *trans*-2-hexenal, 1-hexanol, *cis*-3-hexenol, and hexanoic acid), acetic acid, $\beta$-damascenone, and 2-phenylethanol, with Marquette additionally showing significant levels of monoterpenes (linalool, geraniol, and $\alpha$-citral) and 1-octen-3-ol.

**KEYWORDS:** *grape maturity, Frontenac, Marquette, cold-hardy grapes, aroma profile, phenolic compounds, northern winemaking*

## INTRODUCTION

Northern winemaking has been developing tremendously during the past few years in countries traditionally considered to have an unreceptive environment for grape and wine production. Cold-climate wines, including reds, are now commercialized in regions such as the Northeast and Upper Midwest parts of the United States, central Poland, Inner Mongolia, and Norway.[1−4] In Canada, with about 800 ha in culture, the province of Quebec is the country's third largest wine producer, after the provinces of Ontario and British Columbia, where 5800 and 2700 ha are grown, respectively.[5,6]

The relatively recent development of northern viticulture is directly related to the arrival on the market of cold-hardy grape varieties. Most of these varieties, developed by extensive breeding programs conducted at the University of Minnesota (St. Paul, MN, USA) and the Horticultural Research Institute of Ontario (Vineland Station, ON, Canada), among other institutions, are generally interspecific hybrids of *Vitis vinifera* with *Vitis labrusca* and *Vitis riparia*, two *Vitis* species native to North America.[7,8] The particular genetics of cold-hardy grapes makes them tolerant to very harsh winter conditions, including temperatures as low as −30 °C, and gives them very good disease tolerance, therefore making them suitable for northern wine production, including organic wine production.[2,7−9]

Because of the importance of grape quality in winemaking, grape maturity has been extensively studied in *V. vinifera* varieties and remains a key topic in viticulture. To determine the optimum harvest time for the highest wine quality, researchers have examined many parameters, including technological, phenolic, aromatic, and textural maturity, as well as berry sensory.[10−15] In hybrid grapes, although the effect of harvest date on grape quality on Marechal Foch grape quality was recently published by Sun et al.,[16] variations in overall parameters and their significance for harvest date determination have been studied very little. Moreover, the fact that, in comparison with *V. vinifera* grapes, most hybrid varieties present distinctive chemical characteristics, such as a higher anthocyanin content,[17] higher titratable acidity (TA)[18] and relatively different varietal aroma[19]

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limit the use of current knowledge about *V. vinifera* varieties in the assessment of the maturity of cold-hardy grapes.

Frontenac is an interspecific hybrid of Landot 4511 and *V. riparia* #89 that was developed at the University of Minnesota and introduced into Canada in 1998.[7] Known for the fruitiness of its wines, Frontenac is currently the main red cultivar planted in Quebec and in the U.S. Upper Midwest.[1,6,7] Also developed at the University of Minnesota, Marquette, a newer variety, is an interspecific hybrid of MN 1094, a complex hybrid of *V. riparia*, *V. vinifera*, and other *Vitis* species, with Ravat 262.[7,20] Marquette was released in 2006 and, although present earlier in commercial wineries, was officially introduced into Canada in 2008.[7] Its short growing season, which allows fruit ripening within 1100 growing degree days (GDD; based on 10 °C), and its lower acidity compared with Frontenac make Marquette a promising variety for northern winemaking.[7,20] With Frontenac, Marquette is among the most planted varieties in the U.S. Upper Midwest.[21]

To evaluate the chemical characteristics of Frontenac and Marquette and identify efficient maturity markers for these cold-hardy grape varieties, this study focused on characterizing changes in quality attributes, phenolic compounds, and free aroma profiles during the ripening of Frontenac and Marquette berries grown in two commercial vineyards located in the southwest (SW) and northeast (NE) areas of the province of Quebec, Canada, from veraison to maturity.

## MATERIALS AND METHODS

**Grape Sampling.** Because of the increasing superficies allocated to Frontenac and Marquette (cold-hardy grape varieties of *Vitis* spp.) in Quebec's vineyards, these varieties were selected from among the wide range of cultivars grown in Quebec for wine production.[6] Grape samples were harvested weekly from veraison to commercial harvest (August−October 2011) in two commercial vineyards, one in SW Quebec (Saint-Paul-d'Abbotsford, 45° 26′ N, 72° 53′ W) and one in NE Quebec (Saint-Charles-de-Bellechasse, 46° 46′ N, 70° 57′ W). In the sampling plots (between 150 and 500 plants), the plants had been trained using vertical shoot positioning, and the soil was sandy loam (SW vineyard) or sandy schist (NE vineyard). The Frontenac sampling plots yielded between 3.0 and 4.2 kg per plant, and the Marquette sampling plots yielded 1.8−2.2 kg per plant. Meteorological data were obtained from the nearest automated meteorological stations (45° 43′ N, 72° 88′ W and 46° 47′ N, 67° 43′ W).[22] The SW vineyard accumulated 1380 GDD and a total of 950,100 kJ/m$^2$ (sum of light), and the NE vineyard accumulated 1035 GDD and a total of 599,800 kJ/m$^2$ (sum of light).

Fruit samples consisting of 10−12 clusters representing different sun exposures and positions on the vine were harvested from randomly selected vines throughout the sampled blocks. Samples were kept at 10 °C during transportation to the laboratory, where they were analyzed immediately.

**Chemicals.** 3,4,5-$d_3$-Furfural and 1,1,2-$d_3$-linalool were bought from C/D/N Isotopes (Pointe-Claire, QC, Canada). Ethyl propanoate, ethyl hexanoate, ethyl heptanoate, ethyl octanoate, and hexanoic acid were bought from Nu-Chek-Prep (Elysian, MN, USA). Acetic acid, anhydrous sodium carbonate, *o*-aminoacetophenone, caffeic acid, citral, *β*-citronellol, *β*-damascenone, decanal, ethyl 2-butenoate, ethyl 2-methylbutanoate, ethyl 2-methylpropanoate, ethyl 3-methylbutanoate, ethyl acetate, ethyl butanoate, eugenol, Folin−Ciocalteu reagent, Furaneol (2,5-dimethyl-4-hydroxy-3(2*H*)-furanone), gallic acid, geraniol, D-gluconic acid lactone, hexanal, 1-hexanol, *trans*-2-hexenal, *cis*-3-hexenol, *α*-ionol, *β*-ionone, isoamyl acetate, isoamyl alcohol, isobutylmethoxypyrazine, isopropylmethoxypyrazine, limonene, linalool, nerol, *trans*,*cis*-2,6-nonadienal, 1-octen-3-ol, 2-octanol, quercetin, phenethyl acetate, 2-phenylethanol, rose oxides, and 4-vinylguaiacol were purchased from Sigma-Aldrich (St. Louis, MO, USA).

**Basic Metrics for Grapes and Juice.** For each sample, 10 clusters were manually stemmed and pooled, and 200 berries were randomly selected and weighed. Damaged and unhealthy berries were rejected. The sample was mixed in a glass blender for 30 s. Part of the grape mixture was immediately centrifuged at 10000 rpm for 10 min to recover grape juice, and the remaining (10 g) was placed in an aluminum plate and dried at 65 °C for 8 h, until the final dry weight was stable. To avoid experimental error in the phenolic compound analysis, care was taken to avoid different contact time between the skin, the seeds, and the juice, so contact time was minimized. Grape juice was analyzed for total soluble solids (TSS; °Brix), TA (g/L tartaric acid equiv), and pH, using official methodologies OIV-MA-AS2-02: R2009, OIV-MA-AS313-01: R2009, and OIV-MA-AS313-15: R2009, respectively, from the Organisation Internationale de la Vigne et du Vin.[23−25]

**Juice Phenolics.** Total phenolic compounds were analyzed using the Folin−Ciocalteu method as described by Singleton and Rossi Jr.,[26] adapted for a microplate reader as follows: In each well, 20 *μ*L of the sample (water was used for the blank), 100 *μ*L of a 1/10 water dilution of a commercial Folin−Ciocalteu reagent solution, and 80 *μ*L of 7.5% w/v sodium carbonate solution in water were added. Absorbance was read at 765 nm using a FLUOstar Omega microplate reader (BMG Labtech, Ortenberg, Germany). A standard curve was made using gallic acid.

Total and monomeric anthocyanins were analyzed using the $SO_2$ bleaching method[27] microscaled as follows: A control and an assay were prepared for each sample. Depending on the dilution factor (DF = 20−200), a volume of sample from 40 to 200 *μ*L and a volume of HCl 2% v/v from 2.6 to 2.76 mL were added to a 4.5 mL cuvette, for a final volume of 4 mL. In the control, water (1.2 mL) was added to the cuvette ($l$ = 1 cm), and $NaHSO_3$ 15% w/v was added for the assay, for a final volume of 4 mL. For each sample, both the control and assay were measured at 520 nm using an Agilent model 8452 UV−visible spectrophotometer (Santa Clara, CA, USA). Total anthocyanin content was determined according to method of Amerine and Ough,[28] using the following calculation, with the sample's absorbance ($A$), the path length ($l$) of 1 cm, the extinction coefficient ($\varepsilon$), and the molecular weight (MW) of malvidin-3-glucoside (28000 cm$^3$/mol·cm and 493.3 g/mol, respectively):

$$\text{concentration} = (A \times \text{MW} \times \text{DF})/(\varepsilon \times l)$$

Monomeric color was determined using the difference in absorbance between the control and the assay by means of the same calculation as above.

Total hydroxycinnamic esters and total flavonoids were measured at 320 and 360 nm, respectively, using an Agilent model 8452 UV−visible spectrophotometer and diluted juice samples according to the procedure of Girard et al.[29] Total hydroxycinnamic ester and total flavonoid concentrations were calculated in caffeic acid and quercetin equivalents, respectively, against calibration curves made from authentic standards.[29]

**Volatile Compounds in Juice.** Juice samples (8 mL) were put in amber solid-phase microextraction (SMPE) vials, containing NaCl (3 g) and D-gluconic acid lactone (0.5 g) as inhibitor of grape *β*-glucosidase activity during sample preparation and analysis.[11] Internal standard mixture (50 *μ*L), including 2-octanol, ethyl heptanoate, 1,1,2-$d_3$-linalool, and 3,4,5-$d_3$-furfural, was added. Samples were then vortexed and analyzed immediately.

The efficiency of SPME was optimized for the following parameters: fiber type (pink, 1 cm DVB/PDMS; gray, 2 cm DVB/CAR/PDMS), grape sample type (homogenate; juice), extraction temperature (40, 60, 70 °C), extraction time (25, 40, 60 min), extraction pH (unchanged, basic pH), and addition of D-gluconic acid lactone (with, without). On the basis of the results of the extraction optimization trials, juice samples were extracted using a 2 cm DVB/CAR/PDMS SPME fiber assembly (Supelco, Bellefonte, PA, USA) at a temperature of 60 °C for 25 min under agitation at 500 rpm. D-Gluconic acid lactone was added to the samples, and juice pH was not modified. Samples were desorbed for 10 min on a gas chromatography−mass spectrometry (GC-MS) system (Agilent 6890 series) that was attached to a time-of-flight

**Table 1. Calibration Parameters (Retention Times (RT), Retention Indices (RI), Internal Standards, Quantitation Masses ($m/z$), Ion Ratio Masses, Expected Ion Ratios ($m/z$), Concentration Ranges ($\mu$g/L, unless Otherwise Noted), and Linear Regression Coefficients ($r$)) for the Analysis of Volatile Compounds in Grape Juice Using GC-MS-SPME**

| peak | compound | absolute RT (s) | RI[a] (DB-WAX) | internal standard | quant mass ($m/z$) | ion ratio masses ($m/z$) | expected ion ratio | concn range ($\mu$g/L)[b] | $r$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | ethyl acetate | 404 | 907 | ethyl heptanoate | 70 | 70/61 | 0.86 | 0.4−242 | 0.971 |
| 2 | ethyl propanoate | 492 | 951 | ethyl heptanoate | 102 | 74/102 | 1.8 | 1.0−608 | 0.999 |
| 3 | ethyl 2-methylpropanoate | 506 | 955 | ethyl heptanoate | 71 | 71/116 | 5.3 | 0.04−20 | 0.998 |
| 4 | ethyl butanoate | 613 | 1028 | ethyl heptanoate | 88 | 88/101 | 6.2 | 0.3−197 | 0.997 |
| 5 | ethyl 2-methylbutanoate | 641 | 1050 | ethyl heptanoate | 102 | 102/115 | 7.6 | 0.05−29 | 0.997 |
| 6 | ethyl 3-methylbutanoate | 668 | 1060 | ethyl heptanoate | 85 | 85/115 | 5.7 | 0.9−509 | 0.998 |
| 7 | hexanal | 693 | 1084 | 2-octanol | 72 | 72/82 | 1.5 | 12−7171 | 0.994 |
| 8 | isoamyl acetate | 766 | 1117 | ethyl heptanoate | 70 | 70/87 | 3.2 | 7−2094 | 0.988 |
| 9 | ethyl 2-butenoate | 850 | 1151 | ethyl heptanoate | 99 | 99/86 | 6.9 | 11−6567 | 0.959 |
| 10 | limonene | 922 | 1201 | 1,1,2-$d_3$-linalool | 93 | 93/121 | 5.1 | 0.1−69 | 0.948 |
| 11 | isoamyl alcohol | 954 | 1205 | ethyl heptanoate | 70 | 70/55 | 0.59 | 58−33600 | 0.992 |
| 12 | *trans*-2-hexenal | 968 | 1220 | 2-octanol | 83 | 83/98 | 3.7 | 1−615 | 0.994 |
| 13 | ethyl hexanoate | 996 | 1220 | ethyl heptanoate | 88 | 88/101 | 4.1 | 0.2−92 | 0.991 |
| 14 | ethyl heptanoate[c] | 1196 | | | 88 | 88/113 | 4.8 | | |
| 15 | 1-hexanol | 1242 | 1360 | 2-octanol | 56 | 56/84 | 16 | 6−3625 | 0.994 |
| 16 | *cis*-rose oxide[b] | 1246 | | 1,1,2-$d_3$-linalool | 139 | 139/154 | 8.6 | 11−6238 | 0.981 |
| 17 | *trans*-rose oxide[b] | 1273 | 1373 | 1,1,2-$d_3$-linalool | 139 | 139/154 | 9.4 | 2.4−688 | 0.989 |
| 18 | *cis*-3-hexenol | 1303 | 1391 | 2-octanol | 67 | 67/82 | 3.5 | 0.3−196 | 0.991 |
| 19 | 2-octanol[c] | 1372 | 1332 | | 45 | 45/84 | 27 | | |
| 20 | ethyl octanoate | 1402 | 1436 | ethyl heptanoate | 88 | 88/127 | 6.3 | 0.1−70 | 0.997 |
| 21 | 1-octen-3-ol | 1428 | 1394 | 2-octanol | 57 | 57/85 | 17 | 0.05−26 | 0.983 |
| 22 | acetic acid[b] | 1427 | 1450 | ethyl heptanoate | 60 | 60/45 | 0.44 | 0.05−14.9 | 0.970 |
| 23 | 3,4,5-$d_3$-furfural[c] | 1450 | 1455 | | 99 | 99/98 | 1.2 | | |
| 24 | isopropylmethoxypyrazine[b] | 1489 | 1427 | 3,4,5-$d_3$-furfural | 152 | 152/137 | 1.8 | 0.32−186 | 0.909 |
| 25 | decanal | 1522 | 1484 | 2-octanol | 82 | 57/82 | 2.4 | 0.06−34 | 0.982 |
| 26 | isobutylmethoxypyrazine[b] | 1578 | 1510 | 3,4,5-$d_3$-furfural | 151 | 151/124 | 0.60 | 0.4−214 | 0.955 |
| 27 | 1,1,2-$d_3$-linalool[c] | 1604 | 1537 | | 74 | 74/124 | 6.2 | | |
| 28 | linalool | 1608 | 1537 | 1,1,2-$d_3$-linalool | 71 | 71/121 | 8.4 | 0.1−61 | 0.993 |
| 29 | *trans*,*cis*-2,6-nonadienal | 1686 | 1575 | 1,1,2-$d_3$-linalool | 70 | 70/81 | 5.0 | 0.03−20 | 0.979 |
| 30 | $\beta$-citral | 1857 | 1667 | 1,1,2-$d_3$-linalool | 69 | 94/109 | 1.1 | 0.08−45 | 0.975 |
| 31 | $\alpha$-citral | 1942 | 1715 | 1,1,2-$d_3$-linalool | 69 | 94/109 | 1.2 | 0.2−106 | 0.985 |
| 32 | citronellol | 1993 | 1762 | 1,1,2-$d_3$-linalool | 69 | 69/95 | 2.7 | 0.2−138 | 0.992 |
| 33 | nerol | 2054 | 1770 | 1,1,2-$d_3$-linalool | 69 | 69/93 | 5.5 | 0.7−383 | 0.993 |
| 34 | phenethyl acetate | 2080 | 1829 | 1,1,2-$d_3$-linalool | 104 | 104/91 | 3.5 | 0.05−29 | 0.981 |
| 35 | $\beta$-damascenone | 2100 | 1813 | 1,1,2-$d_3$-linalool | 69 | 69/121 | 6.3 | 0.032−0.38 | 0.983 |
| 36 | hexanoic acid | 2125 | 1829 | ethyl heptanoate | 60 | 60/87 | 7.0 | 0.06−36 | 0.970 |
| 37 | geraniol | 2127 | 1847 | 1,1,2-$d_3$-linalool | 69 | 69/93 | 7.5 | 0.3−38 | 0.993 |
| 38 | 2-phenylethanol | 2231 | 1925 | 1,1,2-$d_3$-linalool | 92 | 92/122 | 2.3 | 4.3−2524 | 0.998 |
| 39 | $\beta$-ionone[b] | 2284 | 1912 | 1,1,2-$d_3$-linalool | 177 | 177/192 | 3.5 | 0.002−1.17 | 0.973 |
| 40 | 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone | 2411 | 2043 | 3,4,5-$d_3$-furfural | 128 | 128/85 | 0.21 | 63−13955 | 0.982 |
| 41 | eugenol | 2604 | 2141 | 1,1,2-$d_3$-linalool | 164 | 164/104 | 1.8 | 0.09−55 | 0.984 |
| 42 | 4-vinylguaiacol | 2641 | 2198 | 1,1,2-$d_3$-linalool | 150 | 150/135 | 0.56 | 0.18−103 | 0.983 |
| 43 | *o*-aminoacetophenone | 2679 | 2223 | 1,1,2-$d_3$-linalool | 135 | 135/92 | 0.80 | 0.18−53 | 0.959 |

[a]Retention indices were obtained from ref 66. [b]All concentrations are expressed in micrograms per liter ($\mu$g/L), except for *cis*- and *trans*-rose oxides, isopropylmethoxypyrazine, isobutylmethoxypyrazine, and $\beta$-ionone concentrations, which are expressed in nanograms per liter (ng/L), and acetic acid concentration, which is expressed in milligrams per liter (mg/L). [c]Internal standard.

detector (Pegasus HT TOFMS; Leco, St. Joseph, MI, USA) connected to a computer with Leco ChromaTOF software. An open tubular DB-WAX column (polyethylene glycol, 60 m × 0.25 mm i.d. × 0.25 $\mu$m film thickness; SGE, Austin, TX, USA) in splitless mode was used. The injector, transfer line, and ion source (70 eV) were maintained at 270, 170, and 200 °C, respectively. The oven temperature was programmed as follows: hold at 30 °C for 1 min; increase to 40 °C at a rate of 10 °C/min; increase to 240 °C at a rate of 4 °C/min and hold for 2 min; and increase to 250 °C at a rate of 20 °C/min and hold for 5 min. Helium was used as the carrier gas under constant flow (1 mL/min). Mass spectra were acquired at a rate of 20 spectra per second. A 10-point calibration curve was built using authentic reference standards (Table 1) and the following matrix, based on hybrid grape must composition:[30] water-based solution containing glucose (85 g/L), fructose (100 g/L), and tartaric acid (8.5 g/L), with a pH of 3.3 adjusted with 10 N KOH. The lowest signal-to-noise ratio used for quantitation was 2.

**Berry Relative Growth Rate (RGR).** Berry RGR was calculated according to the method of Hofmann and Poorter,[31] using the formula

$$\mathrm{RGR} = (\ln(\overline{W_2}) - \ln(\overline{W_1}))/(t_2 - t_1)$$

where $\bar{W}_1$ and $\bar{W}_2$ are berry average weight at sampling times ($t$) 1 and 2, in days, respectively. The average weight of three samples of 200 berries was used for each sampling time.

**Statistical Analysis.** Analysis of variance and tests for normality and data homogeneity were carried out using the Mixed procedure of the SAS software (SAS Institute, Cary, NC, USA) and the "mmaov.sas" macro, developed by Saxton and Auge.[32] Mean comparison and letters were generated using the "mmaov.sas" macro, at $\alpha = 0.01$. Principal component analysis (PCA) was carried out using the Princomp procedure of SAS, without rotation, for both Frontenac and Marquette. For a given grape variety, variables showing a frequency lower than 60% within data were removed from the PCA, unless they were significant to a group of data.

## RESULTS

**Primary Quality Attributes.** In the SW vineyard, Frontenac reached an average of 21.5 °Brix and had a maturity index of 1.6, TA of 13.6 g/L tartaric acid equiv, and pH of 3.3 (Table 2). In the same vineyard, Marquette had a higher TSS content (24.5 °Brix), a lower acidity (8.7 g/L tartaric acid equiv), a higher maturity index (2.8), and a higher pH (3.5) in comparison with Frontenac. In the NE vineyard, Frontenac had a lower TSS content (16.9 °Brix), a higher TA (19.2 g/L tartaric acid equiv), a lower maturity index (0.89), and a lower pH (3.14) than in the SW vineyard (Table 3). Similarly, Marquette had a lower TSS content (19.2 °Brix), a higher TA (14.5 g/L tartaric acid equiv), a lower maturity index (1.3), and a lower pH (3.3) in the NW vineyard than in the SW vineyard.

**Phenolic Maturity.** Although it showed significant differences during maturation, the accumulation of total phenolic compounds followed an irregular progression in Frontenac and Marquette and was poorly correlated with GDD for both studied vineyards ($r^2 \leq 0.492$, Tables 2 and 3). In the SW vineyard, for both varieties, total and monomeric anthocyanin concentrations were significantly higher when 1130 GDD had accumulated, whereas the highest anthocyanin levels were reached at 1035 and 1018 GDD in the NE vineyard, for Frontenac and Marquette, respectively. In the NE vineyard, accumulation of total and monomeric anthocyanin was significantly correlated with GDD for both varieties ($r^2 \geq 0.632$, Table 3).

Other phenolic compounds measured in grape juice during the ripening of Frontenac and Marquette included hydroxycinnamic esters (as caffeic acid equiv) and flavonoids (as quercetin equiv). Both hydroxycinnamic esters and flavonoids increased during ripening, reaching 303−492 mg/L caffeic acid equiv and 243−323 mg/L quercetin equiv, respectively, by harvest, with the exception of Frontenac in the SW vineyard, in which hydroxycinnamic esters and flavonoids reached their maximum levels at 1333 GDD (523 mg/L caffeic acid equiv and 401 mg/L quercetin equiv, respectively) and declined until harvest. In both vineyards, the accumulation of hydroxycinnamic esters and flavonoids was significantly correlated with GDD in Frontenac ($r^2 \geq 0.687$, Tables 2 and 3), whereas only flavonoids showed significant correlation with GDD in Marquette ($r^2 \geq 0.735$, Tables 2 and 3).

**Volatile Compounds.** During maturation, volatile aroma profiles of Frontenac and Marquette were principally composed of the $C_6$ compounds hexanal (7), *trans*-2-hexenal (12), 1-hexanol (15), *cis*-3-hexenol (18), and hexanoic acid (36), the $C_{13}$-norisoprenoid $\beta$-damascenone (35), the volatile phenol 2-phenylethanol (38), and acetic acid (22) (Tables 4−7) (numbers in parentheses refer to the peak numbers in Table 1). Additionally, Marquette was found to have significant amounts of the terpenoids linalool (28), geraniol (37), and, to a lesser extent, *cis*-rose oxide (16), $\alpha$-citral (31), and nerol (33) (Tables 5 and 7). With the exception of ethyl hexanoate (13), both Frontenac and Marquette showed trace levels for most short-chain ethyl esters included in the GC-MS-SPME analyses.

Differences in volatile compounds profiles were observed between Frontenac and Marquette during ripening. For example, hexanal (7) showed variable concentrations in Frontenac as berries ripened, whereas this compound significantly increased in Marquette from the SW vineyard, reaching about 4133 $\mu$g/L at the last sampling ($r^2 = 0.650$, Table 5). *cis*-3-Hexenol (18), another $C_6$ compound, showed a similar pattern in Frontenac and Marquette from the SW vineyard, decreasing significantly from 1156 $\mu$g/L (931 GDD) to 43 $\mu$g/L (1380 GDD; $r^2 = 0.824$, Table 4) in Frontenac and from 2115 $\mu$g/L (931 GDD) to 93 $\mu$g/L (1333 GDD; $r^2 = 0.958$, Table 5) in Marquette. At the last sampling, the level of *cis*-3-hexenol remained higher in Frontenac (644 $\mu$g/L) and Marquette (259 $\mu$g/L) grown in the NE vineyard (Tables 6 and 7).

The occurrence of monoterpenes such as linalool (28), $\beta$-citral (30), $\alpha$-citral (31), and geraniol (37) differed between Frontenac and Marquette. During the veraison of Frontenac, monoterpene level remained lower than 2 $\mu$g/L in berries from both studied vineyards. In contrast, Marquette showed significant levels of different monoterpenes. In particular, linalool and geraniol reached 5 and 22 $\mu$g/L, respectively, at the last sampling in the SW vineyard. From veraison to maturity, both geraniol and $\alpha$-citral accumulated consistently in Marquette from the SW vineyard ($r^2 = 0.934$ and 0.853, respectively, Table 5). Although no significant correlation was found with GDD in the NE vineyard, geraniol increased significantly in Marquette berries during veraison, to reach 9.5 $\mu$g/L at the last sampling (Table 7).

The major volatile phenol found in Frontenac and Marquette was 2-phenyethanol (38), which increased significantly during the maturation of Frontenac in the SW vineyard, until the last sampling (9 $\mu$g/L; $r^2 = 0.540$, Table 4). For Marquette, a similar pattern was observed in the NE vineyard for 2-phenylethanol (38), which increased from 33 to 60 $\mu$g/L between 848 and 1035 GDD ($r^2 = 0.560$, Table 7), whereas an irregular accumulation was found for this compound in the SW vineyard ($r^2 = 0.066$, Table 5).

**Principal Component Analysis.** PCA of berry chemical composition, including quality attributes, phenolic compounds, and volatile compounds, showed different ripening patterns for the studied vineyards (Figures 1 and 2). For Frontenac, veraison, characterized by berry softening and beginning of color change, started around August 11 (931 GDD) for the SW vineyard and around September 6 (903 GDD) for the NE vineyard. At this time, Frontenac grapes showed comparable chemical composition between the two vineyards, with high TA and high levels of *cis*-3-hexenol (18), $\beta$-ionone (39), and eugenol (41), as shown in the first quadrant of Figure 1. Subsequently, berries from the SW vineyard progressed toward principal component 1 (PC 1; 31.3% of variability) to the second quadrant, representing the decrease in TA and the increase of TSS, pH, hydroxycinnamic esters, and flavonoids. From 1076 to 1333 GDD, the aroma profile of Frontenac berries from the SW vineyard evolved in the second quadrant, corresponding to the accumulation of different aroma compounds such as hexanal (7), *trans*-2-hexenal (12), acetic acid (22), $\beta$-citral (30), and hexanoic acid (36). By the end of veraison (1333−1380 GDD), these berries progressed toward principal component 2 (PC 2; 12.9% of variability) to the third quadrant, representing the accumulation of 2-phenylethanol

**Table 2. Impact of Maturity, Expressed in Growing Degree Days, on Berry Dry Weight, Relative Growth Rate, and Chemical Composition of Frontenac and Marquette Grapes Grown in the Southwest Vineyard (Saint-Paul-d'Abbotsford, QC, Canada) during the 2011 Season**

| metric | growing degree days (based on 10 °C)[a] | | | | | | | | | | $r^2$[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 931 | 1005 | 1076 | 1130 | 1197 | 1242 | 1271 | 1333 | 1343 | 1380 | |
| **Frontenac** | | | | | | | | | | | |
| berry dry wt (g/berry) | 0.15 ± 0.03 a | 0.28 ± 0.01 b | 0.33 ± 0.01 bc | 0.34 ± 0.02 cd | 0.39 ± 0.03 de | 0.42 ± 0.03 e | 0.44 ± 0.04 e | 0.40 ± 0.02 de | 0.41 ± 0.02 e | 0.41 ± 0.02 e | 0.911*[c] |
| rel growth rate (g/g·day) | | 0.0083 | 0.0244 | 0.0050 | 0.0193 | 0.0115 | 0.0043 | −0.0136 | 0.0049 | −0.0009 | 0.470 |
| TSS (°Brix) | 7.9 ± 1.3 a | 10.6 ± 0.9 b | 14.0 ± 0.8 c | 14.3 ± 0.5 c | 17.1 ± 1.5 d | 18.0 ± 0.4 de | 19.5 ± 0.3 efg | 18.9 ± 0.9 def | 20.5 ± 0.6 fg | 21.5 ± 1.3 g | 0.950* |
| TA (g/L tartaric acid equiv) | 37.8 ± 0.1 f | 26.0 ± 0.5 e | 21.0 ± 0.6 d | 19.8 ± 1.0 d | 16.6 ± 0.9 c | 15.7 ± 0.2 bc | 14.5 ± 0.7 ab | 14.6 ± 0.7 ab | 13.7 ± 0.4 a | 13.6 ± 1.1 a | 0.673* |
| maturity index[d] | 0.23 ± 0.01 a | 0.41 ± 0.04 a | 0.67 ± 0.03 b | 0.72 ± 0.05 b | 1.04 ± 0.15 c | 1.15 ± 0.02 cd | 1.35 ± 0.07 de | 1.30 ± 0.10 de | 1.49 ± 0.05 ef | 1.59 ± 0.20 f | 0.939* |
| pH | 2.93 ± 0.03 a | 3.02 ± 0.03 ab | 3.12 ± 0.04 bc | 3.05 ± 0.03 ab | 3.23 ± 0.05 cd | 3.15 ± 0.07 bc | 3.37 ± 0.06 e | 3.36 ± 0.05 e | 3.31 ± 0.04 de | 3.31 ± 0.12 de | 0.682* |
| total polyphenols (mg/L gallic acid equiv) | 1640 ± 146 e | 1209 ± 139 ab | 1315 ± 103 abc | 1373 ± 40 bcd | 1129 ± 32 a | 1135 ± 88 a | 1464 ± 84 cde | 1433 ± 36 cd | 1533 ± 65 de | 1422 ± 70 cd | 0.400 |
| monomeric anthocyanins (mg/L malvidin-3-glucoside equiv) | 6.03 ± 5.0 a | 15.0 ± 6.7 a | 37.4 ± 7.9 ab | 451 ± 98 f | 121 ± 38 bc | 157 ± 15 cd | 194 ± 18 cde | 216 ± 36 de | 276 ± 14 e | 240 ± 24 de | 0.362 |
| total anthocyanins (mg/L malvidin-3-glucoside equiv) | 56.9 ± 18 a | 69.6 ± 22 a | 112 ± 6.8 ab | 554 ± 110 e | 196 ± 67 bc | 214 ± 16 bc | 255 ± 22 cd | 286 ± 45 cd | 336 ± 10 d | 295 ± 48 cd | 0.332 |
| total hydroxycinnamic esters (mg/L caffeic acid equiv) | 205 ± 53 a | 209 ± 52 a | 315 ± 8 ab | 328 ± 39 abc | 374 ± 117 bcd | 360 ± 26 bcd | 400 ± 52 bcde | 523 ± 28 e | 475 ± 35 de | 445 ± 60 cde | 0.749* |
| total flavonoids (mg/L quercetin equiv) | 150 ± 46 a | 160 ± 40 a | 246 ± 10 ab | 270 ± 35 bc | 293 ± 98 bcd | 274 ± 16 bc | 304 ± 39 bcd | 401 ± 33 d | 361 ± 29 cd | 323 ± 59 bcd | 0.687* |
| **Marquette** | | | | | | | | | | | |
| berry dry wt (g/berry) | 0.21 ± 0.07 a | 0.32 ± 0.03 b | 0.38 ± 0.02 bc | 0.41 ± 0.01 cd | 0.46 ± 0.02 de | 0.50 ± 0.02 e | 0.51 ± 0.02 e | 0.49 ± 0.01 e | n/a[e] | n/a | 0.930* |
| rel growth rate (g/g·day) | | 0.0057 | 0.0256 | 0.0117 | 0.0164 | 0.0131 | 0.0015 | −0.0061 | n/a | n/a | 0.749* |
| TSS (°Brix) | 8.83 ± 0.87 a | 14.3 ± 0.6 b | 17.5 ± 1.3 c | 18.5 ± 1.3 c | 22.5 ± 0.3 de | 22.1 ± 0.7 d | 24.4 ± 0.9 e | 24.5 ± 0.8 e | n/a | n/a | 0.964* |
| TA (g/L tartaric acid equiv) | 19.5 ± 0.7 e | 18.9 ± 0.3 e | 14.7 ± 0.5 d | 12.1 ± 0.7 c | 10.4 ± 0.5 b | 9.3 ± 0.1 ab | 9.4 ± 0.4 ab | 8.7 ± 0.5 a | n/a | n/a | 0.944* |
| maturity index[d] | 0.46 ± 0.08 a | 0.76 ± 0.03 a | 1.19 ± 0.13 b | 1.54 ± 0.20 c | 2.16 ± 0.12 d | 2.37 ± 0.09 de | 2.60 ± 0.12 ef | 2.82 ± 0.09 f | n/a | n/a | 0.978* |
| pH | 2.96 ± 0.03 a | 3.07 ± 0.02 ab | 3.25 ± 0.05 c | 3.25 ± 0.03 c | 3.24 ± 0.04 bc | 3.40 ± 0.01 cd | 3.49 ± 0.06 d | 3.50 ± 0.14 d | n/a | n/a | 0.869* |
| total polyphenols (m/L gallic acid equiv) | 1927 ± 7 c | 1520 ± 144 ab | 1421 ± 132 ab | 1514 ± 101 ab | 1520 ± 101 ab | 1346 ± 78 a | 1639 ± 138 b | 1544 ± 122 ab | n/a | n/a | 0.492 |
| monomeric anthocyanins (mg/L malvidin-3-glucoside equiv) | 15.3 ± 4.8 a | 82.6 ± 4.5 ab | 94.7 ± 11 ab | 623 ± 138 d | 210 ± 27 bc | 200 ± 17 bc | 247 ± 12 c | 234 ± 21 c | n/a | n/a | 0.331 |
| total anthocyanins (mg/L malvidin-3-glucoside equiv) | 146 ± 14 a | 166 ± 7 abc | 162 ± 6 ab | 700 ± 136 d | 264 ± 25 abc | 245 ± 14 abc | 294 ± 13 c | 279 ± 21 bc | n/a | n/a | 0.220 |
| total hydroxycinnamic esters (mg/L caffeic acid equiv) | 557 ± 21 e | 400 ± 24 bc | 371 ± 22 ab | 334 ± 12 a | 415 ± 30 bc | 422 ± 14 bc | 449 ± 47 cd | 492 ± 6 d | n/a | n/a | 0.781* |
| total flavonoids (mg/L quercetin equiv) | 402 ± 37 c | 278 ± 30 ab | 261 ± 14 a | 253 ± 9 a | 277 ± 26 ab | 280 ± 8 ab | 287 ± 26 ab | 317 ± 8 b | n/a | n/a | 0.735* |

[a]Mean ± standard deviation of three samples. Samples in the same row followed by a different letter are significantly different at $P \leq 0.01$. [b]Quadratic regression coefficient of variable against growing degree days. [c]An asterisk indicates significance at $P \leq 0.0001$. [d]Ratio of total soluble solids to titratable acidity (g/L tartaric acid eq.). [e]n/a, not available; last Marquette sampling in this vineyard was done at 1333 growing degree days (at full maturity).



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**Table 3. Impact of Maturity, Expressed in Growing Degree Days, on Berry Composition of Frontenac and Marquette Grapes Grown in the Northeast Vineyard (Saint-Charles-de-Bellechasse, QC, Canada) during the 2011 Season**

| metric | growing degree days (based on 10 °C)[a] | | | | | | | $r^2$[b] |
|---|---|---|---|---|---|---|---|---|
| | 848 | 903 | 943 | 951 | 1003 | 1018 | 1035 | |
| **Frontenac** | | | | | | | | |
| berry dry wt (g/berry) | 0.21 ± 0.02 a | 0.25 ± 0.03 a | 0.33 ± 0.05 b | 0.35 ± 0.02 b | 0.38 ± 0.01 b | 0.38 ± 0.02 b | 0.37 ± 0.03 b | 0.849*[c] |
| rel growth rate (g/g·day) | | 0.0286 | 0.0401 | 0.0076 | 0.0110 | 0.0001 | −0.0044 | 0.667 |
| TSS (°Brix) | 6.30 ± 1.0 a | 9.42 ± 0.69 b | 12.4 ± 2.1 bc | 14.3 ± 0.98 cd | 15.5 ± 0.29 d | 14.8 ± 0.15 cd | 16.9 ± 1.9 d | 0.883* |
| TA (g/L tartaric acid equiv) | 30.3 ± 3.3 e | 29.4 ± 0.8 de | 26.2 ± 1.1 cd | 23.4 ± 0.8 bc | 20.2 ± 0.5 ab | 20.4 ± 0.5 ab | 19.2 ± 1.1 a | 0.876* |
| maturity index[d] | 0.21 ± 0.01 a | 0.32 ± 0.02 ab | 0.48 ± 0.10 bc | 0.61 ± 0.06 cd | 0.77 ± 0.02 de | 0.73 ± 0.02 de | 0.89 ± 0.15 e | 0.901* |
| pH | 2.79 ± 0.03 a | 2.95 ± 0.01 abc | 2.88 ± 0.07 ab | 3.07 ± 0.02 bc | 3.02 ± 0.03 bc | 3.03 ± 0.21 bc | 3.14 ± 0.05 c | 0.504 |
| total polyphenols (mg/L gallic acid equiv) | 1614 ± 161 c | 1401 ± 93 abc | 1226 ± 169 ab | 1546 ± 190 bd | 1300 ± 85 abc | 1143 ± 118 a | 1427 ± 218 abc | 0.257 |
| monomeric anthocyanins (mg/L malvidin-3-glucoside equiv) | 0.53 ± 0.57 a | 10.7 ± 5.5 a | 83.3 ± 68 ab | 261 ± 83 bc | 625 ± 83 de | 465 ± 27 cd | 767 ± 233 e | 0.846* |
| total anthocyanins (mg/L malvidin-3-glucoside equiv) | 15.4 ± 2.2 a | 31.7 ± 12 a | 131 ± 74 ab | 333 ± 68 bc | 701 ± 49 de | 541 ± 49 cd | 834 ± 233 e | 0.858* |
| total hydroxycinnamic esters (mg/L caffeic acid equiv) | 10.1 ± 1.4 a | 6.57 ± 2.7 a | 159 ± 15 b | 239 ± 12 c | 264 ± 35 c | 251 ± 60 c | 303 ± 22 c | 0.837* |
| total flavonoids (mg/L quercetin equiv) | 58.6 ± 7.9 a | 64.5 ± 9.2 a | 125 ± 12 b | 194 ± 12 c | 221 ± 26 cd | 208 ± 50 c | 281 ± 26 d | 0.837* |
| **Marquette** | | | | | | | | |
| berry dry wt (g/berry) | 0.20 ± 0.01 a | 0.27 ± 0.03 ab | 0.31 ± 0.04 abc | 0.37 ± 0.07 bc | 0.38 ± 0.08 bc | 0.42 ± 0.05 c | 0.38 ± 0.01 bc | 0.704* |
| rel growth rate (g/g·day) | | 0.0425 | 0.0202 | 0.0274 | 0.0006 | 0.0150 | −0.0139 | 0.817* |
| TSS (°Brix) | 7.56 ± 0.6 a | 11.2 ± 1.0 b | 13.3 ± 0.6 bc | 15.7 ± 1.6 cd | 16.6 ± 1.0 de | 17.5 ± 1.0 de | 19.2 ± 1.8 e | 0.912* |
| TA (g/L tartaric acid equiv) | 29.3 ± 0.8 d | 25.0 ± 0.3 c | 20.0 ± 0.8 b | 18.9 ± 0.9 b | 15.8 ± 0.5 a | 14.5 ± 1.2 a | 14.5 ± 0.4 a | 0.973* |
| maturity index[d] | 0.26 ± 0.01 a | 0.45 ± 0.04 ab | 0.67 ± 0.04 bc | 0.83 ± 0.12 cd | 1.05 ± 0.09 de | 1.22 ± 0.18 ef | 1.33 ± 0.16 f | 0.933* |
| pH | 2.74 ± 0.10 a | 3.02 ± 0.10 b | 2.96 ± 0.03 b | 3.08 ± 0.05 bc | 3.08 ± 0.05 bc | 3.23 ± 0.02 cd | 3.32 ± 0.06 d | 0.794* |
| total polyphenols (mg/L gallic acid equiv) | 1785 ± 318 a | 1951 ± 25 a | 1834 ± 54 a | 1488 ± 405 a | 1454 ± 87 a | 1432 ± 147 a | 1673 ± 263 a | 0.210 |
| monomeric anthocyanins (mg/L malvidin-3-glucoside equiv) | 2.78 ± 0.6 a | 39.7 ± 5.0 a | 79.0 ± 51 ab | 221 ± 69 bc | 368 ± 79 cd | 387 ± 87 d | 287 ± 83 cd | 0.632* |
| total anthocyanins (mg/L malvidin-3-glucoside equiv) | 23.3 ± 4.0 a | 73.7 ± 8.0 a | 133 ± 62 ab | 285 ± 62 bc | 430 ± 79 cd | 457 ± 87 d | 359 ± 81 cd | 0.663* |
| total hydroxycinnamic esters (mg/L caffeic acid equiv) | 29.0 ± 11 a | 15.7 ± 1.7 a | 325 ± 10 b | 318 ± 55 b | 320 ± 21 b | 341 ± 10 b | 360 ± 58 b | 0.361 |
| total flavonoids (mg/L quercetin equiv) | 162 ± 11 a | 165 ± 18 a | 182 ± 13 ab | 194 ± 27 ab | 209 ± 8 abc | 228 ± 5 bc | 243 ± 36 c | 0.741* |

[a]Mean ± standard deviation of three samples. Samples in the same row followed by a different letter are significantly different at $P \leq 0.01$. [b]Quadratic regression coefficient of variable against growing degree days. [c]An asterisk indicates significance at $P \leq 0.0001$. [d]Ratio of total soluble solids to titratable acidity (g/L tartaric acid equiv).



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**Table 4. Impact of Maturity, Expressed in Growing Degree Days, on Volatile Compounds in the Juice of Frontenac Berries Grown in the Southwest Vineyard (Saint-Paul-d'Abbotsford, QC, Canada) during the 2011 Season, Using GC-MS-SPME Analysis**

| | | growing degree days (based on 10 °C) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| peak | compound[a] | 931 | 1005 | 1076 | 1130 | 1197 | 1242 | 1271 | 1333 | 1343 | 1380 | $r^2$[b] |
| 7 | hexanal | 361 ± 214 a | 695 ± 273 ab | 1161 ± 132 bc | 1110 ± 210 bc | 529 ± 100 ab | 1060 ± 470 bc | 1370 ± 360 c | 973 ± 222 abc | 1422 ± 413 c | 778 ± 161 abc | 0.271 |
| 10 | limonene | 0.24 ± 0.01 a | tr[d] | 0.17 ± 0.15 a | 0.23 ± 0.02 a | 0.38 ± 0.13 a | 0.79 ± 0.47 b | 0.27 ± 0.05 a | 0.21 ± 0.01 a | 0.36 ± 0.001 a | 0.38 ± 0.02 a | 0.117 |
| 12 | *trans*-2-hexenal | 1072 ± 96 a | 2022 ± 347 b | 2956 ± 70 cd | 3177 ± 295 cd | 3271 ± 286 d | 2098 ± 107 b | 3102 ± 129 cd | 2635 ± 377 bc | 3234 ± 353 cd | 2318 ± 315 b | 0.612*[c] |
| 13 | ethyl hexanoate | 0.19 ± 0.01 a | 0.23 ± 0.04 ab | 0.28 ± 0.02 ab | 0.33 ± 0.03 b | 0.29 ± 0.05 ab | 0.30 ± 0.11 ab | 0.24 ± 0.03 ab | 0.23 ± 0.04 ab | 0.18 ± 0.03 a | 0.22 ± 0.09 ab | 0.390 |
| 15 | 1-hexanol | 88.7 ± 20 a | 236 ± 91 ab | 183 ± 103 ab | 178 ± 86 ab | 205 ± 62 ab | 337 ± 37 b | 348 ± 109 b | 276 ± 49 b | 233 ± 78 ab | 291 ± 113 b | 0.320 |
| 18 | *cis*-3-hexenol | 1156 ± 138 d | 1729 ± 103 e | 1195 ± 171 d | 1167 ± 90 d | 390 ± 141 c | 282 ± 49 bc | 268 ± 44 bc | 145 ± 38 ab | 62.7 ± 7.3 ab | 43.0 ± 8.0 a | 0.824* |
| 21 | 1-octen-3-ol | 0.39 ± 0.2 cd | 0.22 ± 0.05 abcd | 0.34 ± 0.17 bcd | 0.26 ± 0.03 abcd | 0.22 ± 0.05 abcd | 0.17 ± 0.01 abc | 0.17 ± 0.03 abc | 0.14 ± 0.04 ab | 0.06 ± 0.01 a | 0.42 ± 0.21 d | 0.184 |
| 22 | acetic acid[e] | 2.49 ± 2.5 a | 4.44 ± 1.3 ab | 14.8 ± 5.2 abc | 17.6 ± 1.3 c | 17.2 ± 10.2 c | 10.1 ± 0.8 abc | 16.3 ± 8.5 bc | 16.7 ± 5.7 bc | 8.17 ± 3.8 abc | 6.3 ± 5.6 abc | 0.415 |
| 25 | decanal | 0.28 ± 0.01 b | 0.28 ± 0.01 bc | 0.29 ± 0.01 c | 0.29 ± 0.01 c | 0.29 ± 0.01 bc | 0.30 ± 0.01 cd | 0.31 ± 0.01 d | 0.29 ± 0.001 bc | 0.07 ± 0.001 a | 0.07 ± 0.001 a | 0.602* |
| 26 | isobutylmethoxypyrazine[e] | 62.6 ± 101 a | 155 ± 213 a | tr | tr | tr | tr | tr | tr | tr | tr | |
| 28 | linalool | 0.27 ± 0.07 cd | 0.27 ± 0.02 cd | 0.22 ± 0.04 bcd | 0.12 ± 0.06 abc | 0.30 ± 0.07 d | 0.33 ± 0.04 d | 0.06 ± 0.04 ab | tr | 0.23 ± 0.04 cd | 0.18 ± 0.16 abcd | 0.113 |
| 29 | *trans,cis*-2,6-nonadienal | tr | 0.15 ± 0.06 a | 0.19 ± 0.07 ab | 0.20 ± 0.06 ab | 0.30 ± 0.02 bc | 0.36 ± 0.04 c | 0.32 ± 0.07 bd | 0.26 ± 0.10 abc | 0.21 ± 0.05 ab | 0.21 ± 0.04 ab | 0.663* |
| 30 | *β*-citral | 0.10 ± 0.01 a | tr | tr | 0.23 ± 0.14 a | 0.51 ± 0.35 a | 3.24 ± 0.86 b | 0.39 ± 0.25 a | 0.11 ± 0.04 a | | | 0.151 |
| 31 | *α*-citral | 0.70 ± 0.02 | | | tr | tr | tr | tr | tr | tr | | |
| 33 | nerol | 0.64 ± 0.01 a | | tr | 0.60 ± 0.01 a | 0.62 ± 0.01 a | 0.62 ± 0.001 a | tr | tr | | | |
| 35 | *β*-damascenone | 0.85 ± 0.24 a | 1.21 ± 0.28 ab | 1.27 ± 0.18 ab | 1.08 ± 0.45 a | 2.14 ± 0.85 bc | 2.36 ± 0.43 c | 0.96 ± 0.14 a | 1.01 ± 0.11 a | 0.92 ± 0.31 a | 1.19 ± 0.75 ab | 0.200 |
| 36 | hexanoic acid | 5.86 ± 2.1 a | 13.5 ± 3.5 abc | 28.4 ± 5.7 d | 25.6 ± 1.2 cd | 19.4 ± 7.0 bcd | 16.6 ± 0.95 abcd | 21.0 ± 12.0 cd | 13.9 ± 5.1 abc | 7.16 ± 3.8 ab | 6.56 ± 2.9 a | 0.593* |
| 37 | geraniol | 0.83 ± 0.07 ab | | 0.90 ± 0.08 ab | 0.76 ± 0.13 ab | 0.98 ± 0.15 b | tr | 0.64 ± 0.08 ab | 0.39 ± 0.34 a | tr | tr | 0.269 |
| 38 | 2-phenylethanol | tr | 0.76 ± 0.22 a | tr | tr | 2.19 ± 1.0 b | tr | tr | tr | 8.18 ± 0.55 c | 8.96 ± 0.40 c | 0.540* |
| 39 | *β*-ionone[e] | 41.9 ± 2.5 f | 29.4 ± 1.1 e | 21 ± 5.5 bcd | 18 ± 1.9 abc | 25.3 ± 5.1 de | 23.5 ± 2.5 cde | 16.2 ± 1.3 ab | 12.5 ± 1.9 a | 17.6 ± 0.6 abc | 17.5 ± 0.8 abc | 0.720* |
| 40 | 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone | tr | | | tr | tr | | tr | tr | tr | 154 ± 83 | |
| 41 | eugenol | 1.31 ± 0.2 d | 0.89 ± 0.23 c | 0.46 ± 0.10 ab | 0.37 ± 0.07 a | 0.72 ± 0.13 bc | 0.51 ± 0.10 ab | 0.54 ± 0.13 ab | 0.48 ± 0.06 ab | 0.32 ± 0.12 a | 0.48 ± 0.07 ab | 0.648* |
| 42 | 4-vinylguaiacol | 0.57 ± 0.05 b | 0.44 ± 0.02 ab | tr | 0.37 ± 0.01 ab | 0.57 ± 0.23 b | 0.39 ± 0.07 ab | 0.40 ± 0.08 ab | 0.32 ± 0.02 a | | | 0.436 |

[a]Mean ± standard deviation of three samples. Samples in the same row followed by a different letter are significantly different at $P \leq 0.01$. Ethyl acetate, ethyl propanoate, ethyl 2-methylpropanoate, isoamyl acetate, ethyl 2-butenoate, isoamyl alcohol, *trans*- and *cis*-rose oxides, ethyl octanoate, and *o*-aminoacetophenone were found in traces in samples, at different sampling times. [b]Quadratic regression coefficient of variable against growing degree days. [c]An asterisk indicates significance at $P \leq 0.0001$. [d]tr, trace compounds: compounds that were found in one or two of the three samples or were present at concentrations lower than the limit of quantitation (see Table 1). [e]All concentrations are expressed in micrograms per liter (μg/L), except for isobutylmethoxypyrazine and *β*-ionone concentrations, which are expressed in nanograms per liter (ng/L), and acetic acid concentration, which is expressed in milligrams per liter (mg/L).



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**Table 5. Impact of Maturity, Expressed in Growing Degree Days, on Volatile Compounds Concentration in the Juice of Marquette Berries Grown in the Southwest Vineyard (Saint-Paul-d'Abbotsford, QC, Canada) during the 2011 Season, Using GC-MS-SPME Analysis**

| | | growing degree days (based on 10 °C) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| peak | compound[a] | 931 | 1005 | 1076 | 1130 | 1197 | 1242 | 1271 | 1333 | $r^2$[b] |
| 1 | ethyl acetate | | | | | 60.8 ± 9.8 a | 20.8 ± 6.9 b | | tr[d] | |
| 7 | hexanal | 171 ± 138 a | 1398 ± 534 ab | 1819 ± 1087 ab | 2698 ± 477 bc | 1640 ± 566 ab | 2696 ± 896 bc | 4120 ± 1375 c | 4133 ± 364 c | 0.650*[c] |
| 10 | limonene | 0.25 ± 0.01 a | 0.30 ± 0.04 a | 0.39 ± 0.16 ab | 0.28 ± 0.03 a | 0.64 ± 0.11 b | 0.94 ± 0.2 c | 0.63 ± 0.08 b | 0.57 ± 0.08 b | 0.483 |
| 12 | *trans*-2-hexenal | 1292 ± 155 ab | 2390 ± 221 b | 1338 ± 506 ab | 2326 ± 318 b | 1195 ± 250 a | 1678 ± 279 ab | 2361 ± 390 b | 1947 ± 992 ab | 0.029 |
| 13 | ethyl hexanoate | 0.05 ± 0.01 a | 0.07 ± 0.01 a | 0.28 ± 0.03 c | 0.24 ± 0.02 bc | 0.30 ± 0.04 c | tr | tr | 0.09 ± 0.03 ab | 0.418 |
| 15 | 1-hexanol | 869 ± 225 a | 835 ± 52 a | 902 ± 118 a | 694 ± 82 a | 768 ± 101 a | 735 ± 242 a | 984 ± 110 a | 903 ± 125 a | 0.100 |
| 16 | *cis*-rose oxide[e] | 25.1 ± 2.6 ab | 27.4 ± 5.7 abc | 36.2 ± 20 abc | 15.1 ± 1.4 a | 33.4 ± 2.8 abc | 49.6 ± 16 bc | 50.6 ± 2.3 c | 51.4 ± 1.9 c | |
| 17 | *trans*-rose oxide[e] | 1.63 ± 0.07 a | 2.48 ± 0.91 ab | tr | | tr | 4.34 ± 1.7 b | 1.73 ± 1.0 ab | tr | |
| 18 | *cis*-3-hexenol | 2115 ± 362 f | 1528 ± 256 f | 938 ± 83 e | 455 ± 47 d | 225 ± 61 c | 127 ± 26 ab | 183 ± 19 bc | 93.3 ± 19 a | 0.958* |
| 21 | 1-octen-3-ol | 4.35 ± 3.1 a | 2.16 ± 0.64 a | 2.64 ± 0.45 a | 2.44 ± 1.3 a | 2.98 ± 1.7 a | 3.70 ± 1.8 a | 1.83 ± 0.44 a | 2.10 ± 0.67 a | 0.084 |
| 22 | acetic acid[e] | 12.9 ± 3.0 a | 5.75 ± 4.2 a | 10.7 ± 6.9 a | 3.60 ± 1.3 a | 8.36 ± 2.5 a | 4.83 ± 2.2 a | tr | 3.16 ± 0.6 a | 0.118 |
| 25 | decanal | 0.18 ± 0.16 a | 0.28 ± 0.01 ab | 0.29 ± 0.01 ab | 0.29 ± 0.001 ab | 0.28 ± 0.01 ab | 0.29 ± 0.001 ab | 0.30 ± 0.001 ab | 0.35 ± 0.09 b | 0.269 |
| 28 | linalool | 0.94 ± 0.07 a | 1.49 ± 0.56 ab | 2.57 ± 1.2 abc | 1.64 ± 0.53 ab | 6.77 ± 2.4 de | 8.30 ± 2.0 e | 4.11 ± 0.94 bcd | 5.03 ± 0.9 cd | 0.479 |
| 29 | *trans,cis*-2,6-nonadienal | 0.10 ± 0.01 a | 0.15 ± 0.01 abc | 0.15 ± 0.02 abc | 0.14 ± 0.02 ab | 0.26 ± 0.02 d | 0.24 ± 0.07 bcd | 0.25 ± 0.08 cd | 0.27 ± 0.05 d | 0.634* |
| 30 | *β*-citral | tr | tr | 0.61 ± 0.37 a | 0.37 ± 0.06 a | 0.79 ± 0.13 a | tr | 0.73 ± 0.26 a | 0.53 ± 0.03 a | 0.132 |
| 31 | *α*-citral | tr | 0.81 ± 0.06 a | 0.98 ± 0.15 ab | 1.19 ± 0.15 ab | 1.25 ± 0.04 b | 1.32 ± 0.05 bc | 1.68 ± 0.20 cd | 1.83 ± 0.07 d | 0.853* |
| 32 | citronellol | 0.32 ± 0.03 a | 0.42 ± 0.04 a | 0.46 ± 0.13 a | 0.39 ± 0.02 a | 0.46 ± 0.05 a | 1.05 ± 0.1 c | 0.68 ± 0.05 b | 0.71 ± 0.1 b | 0.235 |
| 33 | nerol | 0.68 ± 0.02 ab | 0.78 ± 0.03 ab | 0.89 ± 0.11 abc | 0.90 ± 0.09 abc | 1.29 ± 0.10 bc | 1.49 ± 0.16 c | tr | | 0.392 |
| 34 | phenethyl acetate | | | | | | | | 0.03 ± 0.04 | |
| 35 | *β*-damascenone | 0.18 ± 0.02 a | 0.84 ± 0.23 bcd | 1.48 ± 1.1 b | 0.73 ± 0.1 b | 1.38 ± 0.4 cd | 1.55 ± 0.2 d | 0.79 ± 0.1 bc | 0.94 ± 0.2 bcd | 0.346 |
| 36 | hexanoic acid | 47.4 ± 5.2 a | 36.2 ± 6.3 a | 78.5 ± 44 a | 25.2 ± 4.6 a | 46.9 ± 13 a | 35.0 ± 22 a | tr | 33.1 ± 19 a | 0.089 |
| 37 | geraniol | 1.42 ± 0.16 a | 2.56 ± 0.30 a | 4.56 ± 1.5 a | 6.04 ± 2.3 ab | 10.6 ± 1.1 bc | 13.9 ± 0.7 c | 15.2 ± 2.3 c | 22.4 ± 4.6 d | 0.934* |
| 38 | 2-phenylethanol | 35.8 ± 3.4 a | 34.6 ± 6.2 a | 63.4 ± 51 a | 20.0 ± 2.6 a | 54.6 ± 12.4 a | 37.1 ± 14.6 a | 22.4 ± 6.3 a | 30.0 ± 3.6 a | 0.066 |
| 39 | *β*-ionone[e] | 25.9 ± 1.9 a | 26 ± 5.5 a | 30.7 ± 19.9 a | 14.7 ± 1.5 a | 24.9 ± 6.4 a | 16.4 ± 2.4 a | 14 ± 1.1 a | 15.1 ± 3.3 a | 0.259 |
| 41 | eugenol | 0.38 ± 0.10 a | 0.61 ± 0.07 a | 0.91 ± 0.75 a | 0.32 ± 0.07 a | 0.84 ± 0.13 a | 0.62 ± 0.25 a | 0.31 ± 0.11 a | 0.42 ± 0.10 a | 0.116 |
| 42 | 4-vinylguaiacol | 0.64 ± 0.19 a | 0.61 ± 0.15 a | 0.51 ± 0.18 a | 0.33 ± 0.04 a | 0.39 ± 0.10 a | 0.39 ± 0.09 a | | | 0.507 |

[a]Mean ± standard deviation of three samples. Samples in the same row followed by a different letter are significantly different at $P \leq 0.01$. Ethyl 2-methylpropanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, isoamyl acetate, ethyl 2-butenoate, isoamyl alcohol, ethyl octanoate, isopropylmethoxypyrazine, isobutylmethoxypyrazine, 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone, and *o*-aminoacetophenone were found in trace in samples, at different sampling times. [b]Quadratic regression coefficient of variable against growing degree days. [c]An asterisk indicates significance at $P \leq 0.0001$. [d]tr, trace compounds: compounds that were found in one or two of the three samples or were present at concentrations lower than the limit of quantitation (see Table 1). [e]All concentrations are expressed in micrograms per liter (μg/L), except for *cis*- and *trans*-rose oxides and *β*-ionone concentrations, which are expressed in nanograms per liter (ng/L), and acetic acid concentration, which is expressed in milligrams per liter (mg/L).



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**Table 6. Impact of Maturity, Expressed in Growing Degree Days, on Volatile Compounds Concentration in the Juice of Frontenac Berries Grown in the Northeast Vineyard (Saint-Charles-de-Bellechasse, QC, Canada) during the 2011 Season, Using GC-MS-SPME Analysis**

| | | growing degree days (based on 10 °C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| peak | compound[a] | 848 | 903 | 943 | 951 | 1003 | 1018 | 1035 | $r^2$ [b] |
| 7 | hexanal | 245 ± 76 a | 536 ± 118 a | 390 ± 145 a | 758 ± 191 a | 931 ± 294 a | 619 ± 523 a | 815 ± 413 a | 0.345 |
| 10 | limonene | 0.32 ± 0.01 a | 0.50 ± 0.21 a | 0.22 ± 0.01 a | 0.26 ± 0.05 a | 0.23 ± 0.01 a | 0.38 ± 0.03 a | tr[d] | 0.055 |
| 12 | *trans*-2-hexenal | 683 ± 416 a | 1117 ± 221 ab | 1250 ± 285 abc | 1960 ± 506 bcd | 2076 ± 283 bcd | 2307 ± 111 cd | 2650 ± 640 d | 0.747*[c] |
| 13 | ethyl hexanoate | 0.18 ± 0.01 a | 0.23 ± 0.01 a | 0.24 ± 0.04 a | 0.26 ± 0.04 a | 0.26 ± 0.01 a | 0.29 ± 0.15 a | 0.25 ± 0.05 a | 0.293 |
| 15 | 1-hexanol | 48.9 ± 12 a | 33.0 ± 7.7 a | 108 ± 38 a | 104 ± 23 a | 207 ± 7 a | 837 ± 521 b | 366 ± 114 a | 0.429 |
| 18 | *cis*-3-hexenol | 753 ± 95 a | 508 ± 167 a | 636 ± 181 a | 976 ± 285 a | 755 ± 48 a | 879 ± 72 a | 644 ± 403 a | 0.012 |
| 20 | ethyl octanoate | | | | | 0.30 ± 0.02 | tr | tr | |
| 21 | 1-octen-3-ol | 0.09 ± 0.02 a | 0.18 ± 0.05 a | 0.25 ± 0.04 a | 0.37 ± 0.05 ab | 0.21 ± 0.05 a | 0.12 ± 0.08 a | 0.68 ± 0.32 b | 0.168 |
| 22 | acetic acid[e] | 1.79 ± 0.6 a | 3.56 ± 1.3 a | 3.17 ± 1.7 a | 5.19 ± 2.2 a | 3.72 ± 0.6 a | 5.13 ± 4.3 a | 3.06 ± 2.1 a | 0.182 |
| 25 | decanal | 0.29 ± 0.01 b | 0.28 ± 0.01 b | 0.30 ± 0.01 b | tr | tr | 0.07 ± 0.001 a | 0.07 ± 0.01 a | 0.236 |
| 26 | isobutylmethoxypyrazine[e] | 35.4 ± 15.8 b | 19.3 ± 11.9 ab | 4.73 ± 4.19 a | tr | tr | tr | tr | |
| 28 | linalool | 0.42 ± 0.02 a | 0.53 ± 0.4 a | 0.30 ± 0.13 a | 0.26 ± 0.05 a | 0.25 ± 0.10 a | 0.50 ± 0.01 a | 0.54 ± 0.06 a | 0.208 |
| 29 | *trans,cis*-2,6-nonadienal | | | tr | 0.15 ± 0.05 a | 0.24 ± 0.02 b | 0.39 ± 0.02 c | 0.25 ± 0.03 b | 0.790* |
| 30 | $\beta$-citral | 0.68 ± 0.8 | tr | tr | tr | tr | - | tr | |
| 33 | nerol | 0.93 ± 0.43 a | 0.44 ± 0.38 a | tr | tr | - | - | - | |
| 35 | $\beta$-damascenone | 1.27 ± 0.18 a | 1.39 ± 0.35 a | 1.94 ± 0.59 a | 1.71 ± 0.16 a | 2.28 ± 0.96 a | 1.89 ± 0.47 a | 1.46 ± 0.79 a | 0.174 |
| 36 | hexanoic acid | 5.58 ± 1.6 a | 7.06 ± 3.1 a | 10.7 ± 6.0 a | 14.9 ± 5.0 a | 7.53 ± 3.1 a | 8.17 ± 1.5 a | 9.64 ± 3.9 a | 0.206 |
| 38 | 2-phenylethanol | 3.44 ± 1.5 a | tr | tr | tr | tr | 11.7 ± 2.3 a | 13.5 ± 4.4 a | 0.723* |
| 39 | $\beta$-ionone[e] | 81.9 ± 22 a | 29.2 ± 5.1 a | 23.8 ± 1.1 a | 23.0 ± 5.5 a | 21.9 ± 6.3 a | 28.0 ± 2.5 a | 21.1 ± 1.0 a | 0.819* |
| 41 | eugenol | 0.83 ± 0.27 a | 0.46 ± 0.11 a | 0.36 ± 0.09 a | 0.38 ± 0.18 a | 0.40 ± 0.14 a | 0.56 ± 0.12 a | 0.39 ± 0.36 a | 0.411 |
| 42 | 4-vinylguaiacol | 0.48 ± 0.06 a | 0.47 ± 0.13 a | 0.47 ± 0.13 a | 0.36 ± 0.03 a | 0.61 ± 0.26 a | | | 0.396 |

[a]Mean ± standard deviation of three samples. Samples in the same row followed by a different letter are significantly different at $P \leq 0.01$. Ethyl acetate, ethyl butanoate, ethyl 2-methylbutanoate, isoamyl acetate, ethyl 2-butenoate, isoamyl alcohol, *trans*-rose oxide, $\alpha$-citral, geraniol, and *o*-aminoacetophenone were found in trace in samples, at different sampling times. [b]Quadratic regression coefficient of variable against growing degree days. [c]An asterisk indicates significance at $P \leq 0.0001$. [d]tr, trace compounds: compounds that were found in one or two of the three samples or were present at concentrations lower than the limit of quantitation (see Table 1). [e]All concentrations are expressed in micrograms per liter ($\mu$g/L), except for isobutylmethoxypyrazine and $\beta$-ionone concentrations, which are expressed in nanograms per liter (ng/L), and acetic acid concentration, which is expressed in milligrams per liter (mg/L).



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**Table 7. Impact of Maturity, Expressed in Growing Degree Days, on Volatile Compounds in the Juice of Marquette Berries Grown in the Northeast Vineyard (Saint-Charles-de-Bellechasse, QC, Canada) during the 2011 Season, Using GC-MS-SPME Analysis**

| | | growing degree days (based on 10 °C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| peak | compound[a] | 848 | 903 | 943 | 951 | 1003 | 1018 | 1035 | $r^2$ [b] |
| 7 | hexanal | 106 ± 120 a[b,d] | 733 ± 387 ab | 57 ± 28 a | 1485 ± 424 b | 1653 ± 586 b | 829 ± 272 ab | 1124 ± 580 ab | 0.322 |
| 10 | limonene | 0.55 ± 0.18 a | 1.00 ± 0.69 a | tr[d] | 0.36 ± 0.06 a | 0.32 ± 0.10 a | 0.43 ± 0.01 a | 0.50 ± 0.06 a | 0.145 |
| 11 | isoamyl alcohol | tr | tr | tr | tr | tr | tr | 51.1 ± 54 | |
| 12 | *trans*-2-hexenal | 598 ± 25 a | 1244 ± 231 bc | 942 ± 86 ab | 1501 ± 176 cd | 1792 ± 168 d | 1792 ± 151 d | 1813 ± 347 d | 0.747*[c] |
| 13 | ethyl hexanoate | 0.19 ± 0.01 a | 0.30 ± 0.04 a | 0.26 ± 0.07 a | 0.19 ± 0.01 a | 0.27 ± 0.05 a | 0.30 ± 0.08 a | 0.39 ± 0.2 a | 0.242 |
| 15 | 1-hexanol | 281 ± 54 a | 394 ± 107 a | 416 ± 59 a | 525 ± 71 a | 523 ± 204 a | 1385 ± 12 b | 1418 ± 341 b | 0.618 |
| 18 | *cis*-3-hexenol | 827 ± 133 bc | 1195 ± 235 c | 682 ± 83 b | 792 ± 216 b | 490 ± 110 ab | 278 ± 98 a | 259 ± 111 a | 0.724* |
| 20 | ethyl octanoate | | | | | tr | tr | tr | |
| 21 | 1-octen-3-ol | 0.56 ± 0.12 a | 1.00 ± 0.11 a | 2.31 ± 0.49 a | 2.28 ± 0.53 a | 2.26 ± 1.0 a | 2.36 ± 1.0 ab | 4.77 ± 2.1 b | 0.510 |
| 22 | acetic acid[e] | 3.94 ± 1.3 a | 11.7 ± 4.3 b | 4.68 ± 2.4 a | 2.49 ± 1.1 a | 3.21 ± 0.9 a | 1.61 ± 0.1 a | tr | 0.065 |
| 25 | decanal | tr | tr | tr | 0.28 ± 0.01 b | 0.29 ± 0.01 b | 0.07 ± 0.01 a | 0.06 ± 0.01 a | 0.143 |
| 28 | linalool | 1.99 ± 0.82 a | 1.88 ± 1.4 a | 5.92 ± 3.7 a | 1.69 ± 0.15 a | 2.24 ± 0.99 a | 3.56 ± 1.7 a | 3.74 ± 1.6 a | 0.058 |
| 29 | *trans*,*cis*-2,6-nonadienal | | | tr | 0.13 ± 0.03 a | 0.13 ± 0.04 a | 0.15 ± 0.05 a | 0.19 ± 0.02 a | 0.715* |
| 30 | $\beta$-citral | tr | tr | tr | 1.20 ± 0.28 | tr | | | 0.326 |
| 31 | $\alpha$-citral | tr | tr | tr | 0.79 ± 0.01 a | 0.82 ± 0.05 a | 0.71 ± 0.02 a | 0.77 ± 0.08 a | 0.299 |
| 33 | nerol | 0.75 ± 0.08 a | 0.88 ± 0.33 a | tr | tr | | tr | tr | 0.588 |
| 35 | $\beta$-damascenone | 0.73 ± 0.33 a | 0.46 ± 0.10 a | 0.86 ± 0.29 a | 1.32 ± 0.64 a | 1.46 ± 0.42 a | 0.88 ± 0.17 a | 1.38 ± 0.43 a | 0.257 |
| 36 | hexanoic acid | 16.5 ± 8.1 a | 40.9 ± 10.3 a | 43.8 ± 23 a | 19.6 ± 4.1 a | 17.5 ± 6.0 a | 45.7 ± 32 a | 55.7 ± 40 a | 0.098 |
| 37 | geraniol | 1.69 ± 0.4 a | 2.28 ± 1.4 a | tr | 2.31 ± 0.05 a | 2.98 ± 0.67 ab | 6.48 ± 0.53 bc | 9.51 ± 1.4 c | 0.599 |
| 38 | 2-phenylethanol | 32.5 ± 7.7 a | 21.1 ± 2.0 a | 24.4 ± 6.9 a | 29.4 ± 7.4 a | 28.7 ± 6.7 a | 33.2 ± 8.8 a | 60.2 ± 11.5 b | 0.560 |
| 39 | $\beta$-ionone[e] | 25.8 ± 15 a | 22.8 ± 3.6 a | 23.7 ± 5.1 a | 23.6 ± 6.9 a | 19.0 ± 3.9 a | 19.9 ± 2.2 a | 25.3 ± 3.4 a | 0.050 |
| 41 | eugenol | 0.22 ± 0.02 a | 0.22 ± 0.10 a | 0.29 ± 0.05 a | 0.22 ± 0.05 a | 0.27 ± 0.04 a | 0.26 ± 0.13 a | 0.74 ± 0.26 b | 0.462 |
| 42 | 4-vinylguaiacol | 0.59 ± 0.26 ab | 0.51 ± 0.16 ab | 0.72 ± 0.12 b | 0.40 ± 0.04 a | 0.42 ± 0.07ab | | | 0.668* |

[a]Mean ± standard deviation of three samples. Samples in the same row followed by a different letter are significantly different at $P \leq 0.01$. Ethyl acetate, ethyl butanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, isoamyl acetate, ethyl 2-butenoate, *trans*- and *cis*-rose oxides, isobutylmethoxypyrazine, citronellol, phenethyl acetate, 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone, and *o*-aminoacetophenone were found in trace in samples, at different sampling times. [b]Quadratic regression coefficient of variable against growing degree-days. [c]An asterisk indicates significance at $P \leq 0.0001$. [d]tr, trace compounds: compounds that were found in one or two of the three samples or were present at concentrations lower than the limit of quantitation (see Table 1). [e]All concentrations are expressed in micrograms per liter ($\mu$g/L), except for $\beta$-ionone concentration, which is expressed in nanograms per liter (ng/L), and acetic acid concentration, which is expressed in milligrams per liter (mg/L).



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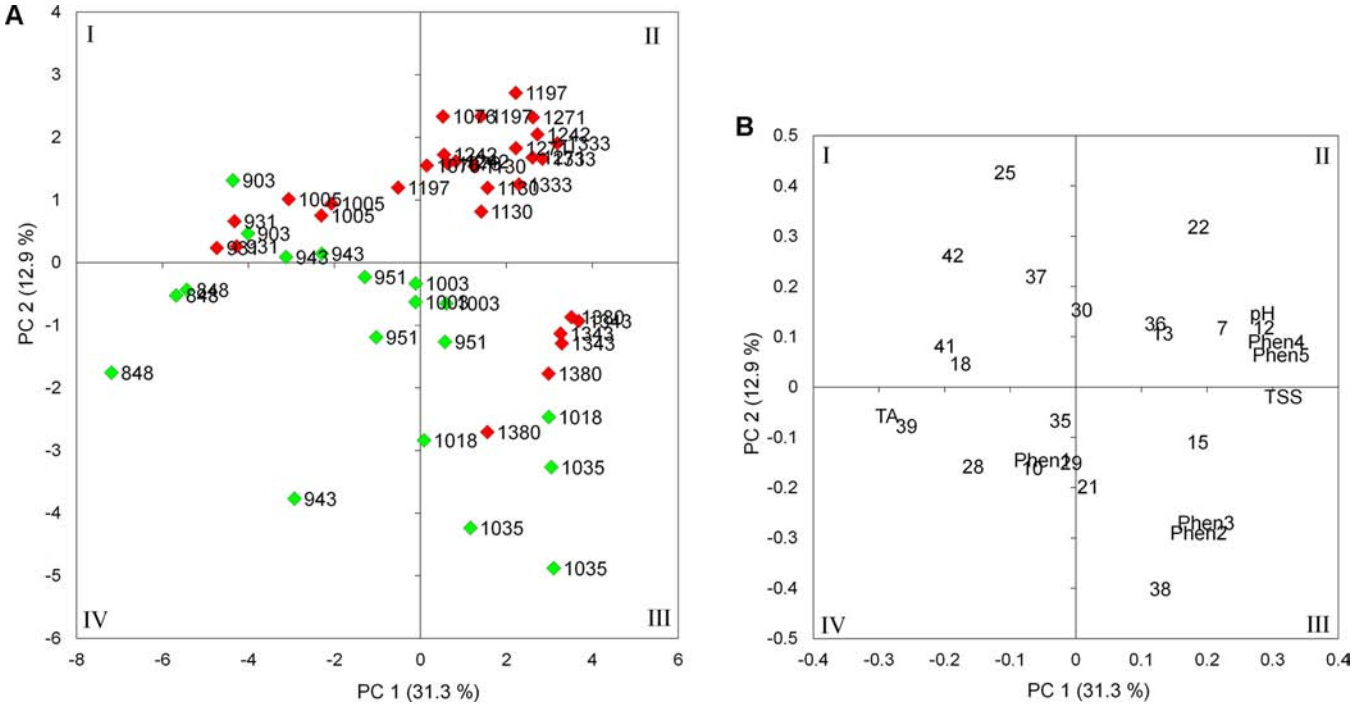


**Figure 1.** Principal component analysis of berry quality attribute, phenolic compounds, and juice free aroma profiles of samples (A, plotted according to GDD, based on 10 °C) and variables (B) during the ripening of Frontenac grapes in two vineyards located in southwest (Saint-Paul-d'Abbotsford, QC, Canada; in red, $n$ = 30) and northeast (Saint-Charles-de-Bellechasse, QC, Canada; in green, $n$ = 21) areas of the province of Quebec during the 2011 season. Quadrants are identified I–IV, clockwise. Variables ID: pH, total soluble solids (TTS), titratable acidity (TA), total phenolics (Phen1), monomeric anthocyanins (Phen2), total anthocyanins (Phen3), hydroxycinnamic esters (Phen4), flavonoids (Phen5), hexanal (7), limonene (10), *trans*-2-hexenal (12), ethyl hexanoate (13), 1-hexanol (15), *cis*-3-hexenol (18), 1-octen-3-ol (21), acetic acid (22), decanal (25), linalool (28), *trans*,*cis*-2,9-nonadienal (29), $\beta$-citral (30), $\beta$-damascenone (35), hexanoic acid (36), geraniol (37), 2-phenylethanol (38), $\beta$-ionone (39), eugenol (41), vinyl guaiacol (42). Numbers in parentheses refer to peak numbers from Table 1.

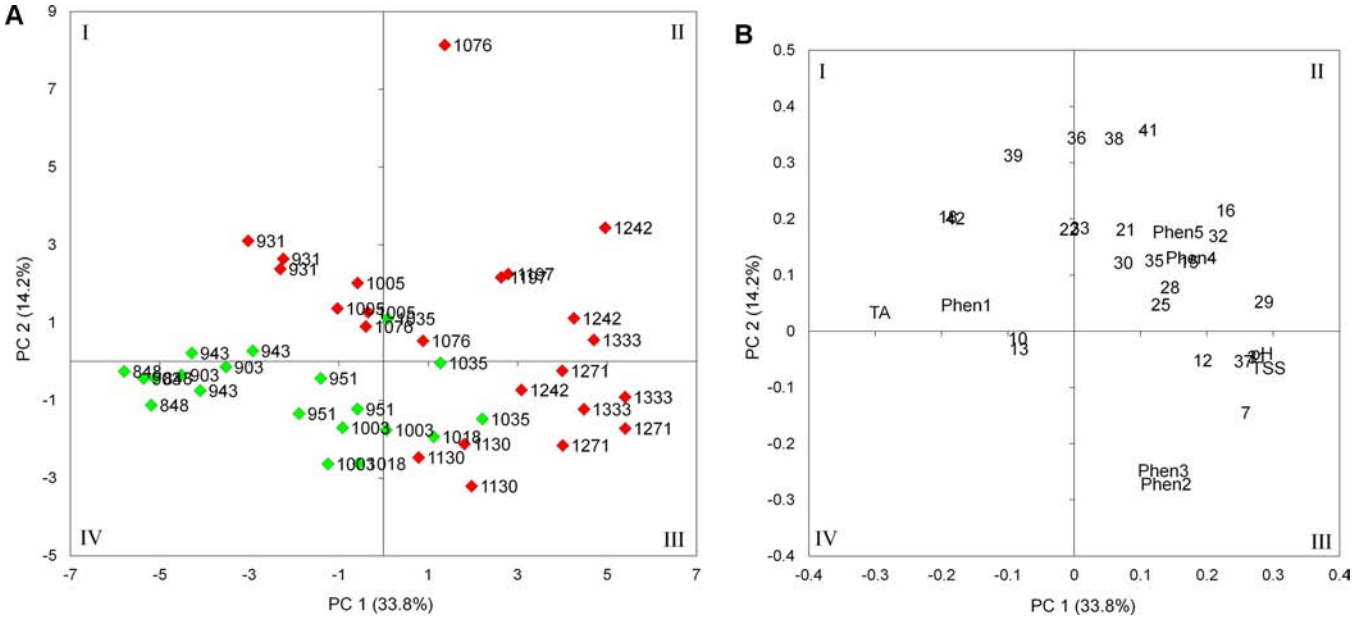


**Figure 2.** Principal component analysis of berry quality attribute, phenolic compounds, and juice aroma profiles of samples (A, plotted according to GDD, based on 10 °C) and variables (B) during the ripening of Marquette grapes in two vineyards located in southwest (Saint-Paul-d'Abbotsford, QC, Canada; in red, $n$ = 30) and northeast (Saint-Charles-de-Bellechasse, QC, Canada; in green, $n$ = 21) areas of the province of Quebec during the 2011 season. Quadrants are identified I–IV (clockwise). Variables: pH, total soluble solids (TTS), titratable acidity (TA), total phenolics (Phen1), monomeric anthocyanins (Phen2), total anthocyanins (Phen3), hydroxycinnamic esters (Phen4), flavonoids (Phen5), hexanal (7), limonene (10), *trans*-2-hexenal (12), ethyl hexanoate (13), 1-hexanol (15), *cis*-rose oxide (16), *cis*-3-hexenol (18), 1-octen-3-ol (21), acetic acid (22), decanal (25), linalool (28), *trans*,*cis*-2,9-nonadienal (29), $\beta$-citral (30), $\alpha$-citral (31), citronellol (32), nerol (33), $\beta$-damascenone (35), hexanoic acid (36), geraniol (37), 2-phenylethanol (38), $\beta$-ionone (39), eugenol (41), 4-vinylguaiacol (42). Numbers in parentheses refer to peak numbers from Table 1.


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(38) and the decrease of decanal (25), β-citral (30), and 4-vinylguaiacol (42).

Although they began veraison with a chemical composition similar to that of berries from the SW vineyard, Frontenac berries from the NE vineyard followed a slightly different pattern. From 903 to 1003 GDD, the berry flavor profile progressed toward PC 1 (31.3% of variability), from the fourth to the third quadrant, representing the decrease in TA and the increase in pH, TSS, hydroxycinnamic esters (Phen4) and flavonoids (Phen5), and *trans*-2-hexenal (12) (Figure 1). From 1003 to 1035 GDD, berry chemical composition evolved within the fourth quadrant, toward PC 2 (12.9% of variability), representing the accumulation of monomeric (Phen2) and total (Phen3) anthocyanins, 1-hexanol (15), 1-octen-3-ol (21), *trans*,*cis*-2,6-nonadienal (29), and 2-phenylethanol (38) and the decrease of decanal (25) and 4-vinylguaiacol (43).

For Marquette, veraison started around August 11 (931 GDD) in the SW vineyard and around August 31 (848 GDD) in the NE vineyard. Marquette grapes showed different maturity patterns in the studied vineyards, starting with a slightly different chemical composition at the beginning of veraison. From 931 to 1130 GDD, Marquette from the SW vineyard evolved downward toward PC 2 (14.2% of variability) and toward PC 1 (33.8% of variability), from the first to the third quadrant, corresponding to the decrease in TA and *cis*-3-hexenol (18) and the increase in TSS, pH, monomeric (Phen2) and total (Phen3) anthocyanins, and hexanal (7). Subsequently, from 1130 to 1333 GDD, berries first evolved upward toward PC 2 and toward PC 1, to reach a midpoint area between the second and third quadrants, corresponding to fully ripened berries. This stage related to the final decrease in *cis*-3-hexenol and to the increase in terpenoids such as *cis*-rose oxide (16), linalool (28), α-citral (31), citronellol (32), and geraniol (37) and herbaceous aroma compounds such as hexanal (7) and *trans*,*cis*-2,9-nonadienal (29).

In contrast, Marquette berries from the NE vineyard started in the fourth quadrant and moved toward PC 1 and PC 2 to the third quadrant, reaching an area adjacent to the 1130 GDD-accumulated berries from the SW vineyard. This progression corresponded to the decrease in TA and to the increase in TSS, anthocyanins (Phen2 and Phen3), hydroxycinnamic esters (Phen4), and flavonoids (Phen5). The aroma profile evolved consequently, showing the decrease in *cis*-3-hexenol (18), decanal (25), and 4-vinylguaiacol (42) and the increase in hexanal (7), *trans*-2-hexenal (12), 1-hexanol (15), 1-octen-3-ol (21), *trans*,*cis*-2,9-nonadienal (29), α-citral (31), geraniol (37), 2-phenylethanol (38), and eugenol (41).

## DISCUSSION

**Chemical Changes during Maturity.** The accumulation rate of TSS and the decline in TA, often referred to as "technological maturity," have been extensively studied in *Vitis* sp. varieties, including hybrid cultivars.[10,11,16,29,33] In general, the accumulation of TSS and the decline of TA are fast at the beginning of veraison and slow as maturity approaches.[33] Similar patterns were observed in Frontenac and Marquette in this study.

With some exceptions,[34,35] studies on the phenolic compounds variations during berry ripening mainly focused on anthocyanin, total phenolics, and tannins.[12,13] Similar to some *V. vinifera* varieties,[34] flavonoids (Phen5) from Frontenac and Marquette showed a consistent progression during berry ripening, with most samples reaching a maximum value by the end of veraison, or 2 weeks before the last sampling. In contrast, hydroxycinnamic esters (Phen4) increased during the ripening of Frontenac and Marquette, whereas they decreased during the ripening of *V. vinifera* varieties Grenache and Carignane.[35]

Changes in volatile compounds profile during maturity vary widely among *Vitis* sp. varieties and growing conditions.[11,15,29,36,37] In this study, the most noticeable changes in volatile compounds during the ripening of Frontenac and Marquette were the shift in $C_6$ compound profiles as maturity approached and the accumulation of geraniol in Marquette.

**Impact of Climate and Grape Development.** Frontenac and Marquette berries followed different ripening patterns in both studied vineyards. Differences in growing conditions and climate significantly affected the way sugars, acidity, pH, phenolic compounds, and aroma profiles changed during ripening. In the context of northern viticulture, fruit development occurs between the last spring frost and the first temperature drop in the fall, along with late spring and early fall frosts in some years. In this study, the time elapsed between the beginning of veraison and the last sampling is one of the major differences between the studied locations. In the SW vineyard, the entire veraison of Marquette and Frontenac occurred within 402 and 449 GDD, respectively, whereas the entire sampling period in the NE vineyard allowed the accumulation of 187 GDD for both varieties until first frost. Both Frontenac and Marquette reached adequate maturity for winemaking in the SW vineyard; however, the shorter season experienced in the NE vineyard was not sufficient to fully ripen both varieties. Nevertheless, Marquette reached a more acceptable sugar to acidity balance for winemaking compared with Frontenac in this vineyard (maturity index of 1.3 compared to 0.9, respectively, Table 3), suggesting that the former could potentially be a suitable choice for wineries located in colder areas such as the northeast areas of Quebec, whereas Frontenac may be better suited to regions that reach a minimum of 1300 GDD (based on 10 °C). Despite the fact that proper vine balance management aiming at enhancing leaf area to fruit weight ratio may provide some tools to optimize Frontenac ripening under slightly colder conditions, such practices are likely to be insufficient to counter a significantly colder climate. Moreover, although significant improvements of fruit basic composition (namely TSS, TA, and pH) have been reported in both *V. vinifera* and hybrid cultivars when the leaf area to fruit weight ratio was increased, using either different training systems, shoot thinning, or cluster thinning, some studies reported variable results among grape varieties and sometimes no significant changes at all.[38−43] Such data suggest that, under northern conditions, year-to-year specific climate may easily overwhelm the expected benefits from an increased leaf area to fruit weight ratio on basic juice chemistry, therefore suggesting that when veraison is limited in time by the upcoming fall frost, maintaining an optimum vine balance during the whole season is even more critical and should be accurately defined to achieve fruit maturity.

To explore the impact of climate and plant physiology on berry ripening, principal components 1 and 2 were correlated with meteorological data (GDD; mean, maximum, and minimum temperatures; and sum of light) and basis physiological data (relative growth rate and berry dry weight) (Table 8). In Frontenac, the correlations showed that PC 1, representing the evolution of quality attributes (TSS, TA, pH), hydroxycinnamic esters (Phen4), flavonoids (Phen5), and $C_6$ compounds (hexanal (7), *trans*-2-hexenal (12), 1-hexanol (15), and *cis*-3-hexenol (18)) during the first part of veraison was largely

**Table 8. Quadratic Correlation Matrix of Principal Components 1 and 2 (PC 1 and PC 2, Dependent Variables) against Meteorological Data (Growing Degree Days (GDD), Average Maximum Temperature, Average Minimum Temperature, Mean Temperature, Change in Temperature ($\Delta T$), and Sum of Light) and Physiological Data (Relative Growth Rate (RGR) and Berry Dry Weight) Measured on a Weekly Basis in the Southwest Vineyard (SW; Saint-Paul-d'Abbotsford, QC, Canada) and Northeast Vineyard (NE; Saint-Charles-de-Bellechasse, QC, Canada) during the 2011 Season (Data Were Analyzed Together (Both Locations) and as Separate Blocks (SW and NE))**

| | PC 1 | | | PC 2 | | |
|---|---|---|---|---|---|---|
| independent variable | both locations | SW | NE | both locations | SW | NE |
| | | | **Frontenac** | | | |
| accumulated GDD (based on 10 °C)[a] | 0.778*[d] | 0.894* | 0.895* | 0.109 | 0.590* | 0.521 |
| av weekly max temp (°C)[b] | 0.254 | 0.838* | 0.526 | 0.323* | 0.271 | 0.349 |
| av weekly min temp (°C)[b] | 0.184 | 0.579* | 0.483 | 0.435* | 0.325 | 0.392 |
| av weekly mean temp (°C)[b] | 0.258 | 0.729* | 0.528 | 0.364* | 0.263 | 0.388 |
| av weekly $\Delta T$ ($T_{max} - T_{min}$) (°C)[b] | 0.087 | 0.116 | 0.374 | 0.479* | 0.708* | 0.518 |
| av weekly sum of light (kJ/m)[b] | 0.344* | 0.778* | 0.276 | 0.078 | 0.252 | 0.044 |
| RGR (g/g·day)[c] | 0.474* | 0.190 | 0.811* | 0.072 | 0.238 | 0.746* |
| berry dry wt (g) | 0.729* | 0.803* | 0.723* | 0.015 | 0.007 | 0.383 |
| | | | **Marquette** | | | |
| accumulated GDD (based on 10 °C)[a] | 0.927* | 0.948* | 0.860* | 0.007 | 0.186 | 0.095 |
| av weekly max temp (°C)[b] | 0.037 | 0.783* | 0.540 | 0.387* | 0.340 | 0.097 |
| av weekly min temp (°C)[b] | 0.012 | 0.595* | 0.483 | 0.307 | 0.267 | 0.317 |
| av weekly mean temp (°C)[b] | 0.042 | 0.750* | 0.542 | 0.347 | 0.301 | 0.003 |
| av weekly $\Delta T$ ($T_{max} - T_{min}$) (°C)[b] | 0.003 | 0.096 | 0.333 | 0.032 | 0.110 | 0.312 |
| av weekly sum of light (kJ/m)[b] | 0.083 | 0.707* | 0.277 | 0.204 | 0.161 | 0.474 |
| RGR (g/g·day)[c] | 0.421* | 0.265 | 0.615 | 0.029 | 0.262 | 0.224 |
| berry dry wt (g) | 0.815* | 0.908* | 0.711* | 0.030 | 0.115 | 0.166 |

[a]Growing degree days accumulated on the sampling day. [b]Data used for the correlation were the average of the last 7 days prior to the sampling day. [c]Calculated from two samplings of three samples each, conducted 1 week apart, and based on berry dry weight. [d]An asterisk indicates significance at $P \leq 0.0001$.

dependent on the accumulation of GDD ($r^2 = 0.778$, $P \leq 0.0001$), sum of light ($r^2 = 0.344$, $P \leq 0.0001$), relative growth rate (RGR, $r^2 = 0.474$, $P \leq 0.0001$), and berry dry weight ($r^2 = 0.729$, $P \leq 0.0001$) in both studied vineyards. However, when the vineyards were considered separately, PC 1 was strongly correlated with average weekly maximum, minimum, and mean temperatures ($r^2 = 0.838$, 0.579, and 0.729, respectively, $P \leq 0.0001$) and with sum of light ($r^2 = 0.778$, $P \leq 0.0001$) in the SW vineyard, suggesting that under favorable growing conditions, the accumulation of metabolites, including aroma and phenolic compounds, was strongly affected by the meteorological conditions. In the NE vineyard, although GDD showed significant correlation with PC 1 ($r^2 = 0.895$, $P \leq 0.0001$), the strong correlations of PC 1 with relative growth rate ($r^2 = 0.811$, $P \leq 0.0001$) and berry dry weight ($r^2 = 0.723$, $P \leq 0.0001$) suggested that under colder conditions, the accumulation of metabolites was driven primarily by berry development itself rather than being enhanced by favorable temperature and light and was therefore limited.

Even though PC 1 represented slightly different variables (increases in TSS, pH, hexanal (7), *trans*-2-hexenal (12), linalool (28), *trans*,*cis*-2,6-nonadienal (29), $\alpha$-citral (31), and geraniol (37) and decrease of TA) in Marquette, patterns similar to Frontenac were observed in both locations. Thus, under the favorable conditions in the SW vineyard, temperatures (maximum, minimum, and mean) and sum of light were strongly correlated with PC 1 ($r^2 \geq 0.595$, $P \leq 0.0001$, Table 9), whereas under the colder conditions in the NE vineyard, metabolite accumulation was driven primarily by berry development, represented by the correlation of PC 1 with berry dry weight ($r^2 = 0.711$, $P \leq 0.0001$). These observations are in agreement with previously reported data stating that lower temperatures may negatively affect grape chemical composition, especially with regard to TSS, TA, and pH.[44]

In Frontenac, PC 2 related to the final ripening stages and correlated significantly with temperature data (maximum, minimum, mean, and daily change in temperature ($\Delta T$)), suggesting that temperature had a noticeable impact on the final accumulation of 2-phenylethanol (38) and the decrease of decanal (25), *cis*-3-hexenol (18), $\beta$-citral (30), hexanoic acid (36), geraniol (37), and 4-vinylguaiacol (42). In contrast, light may have little impact on flavor changes occurring near maturity (1333−1380 GDD), as no correlation was found between this parameter and PC 2. Similarly, in Marquette, poor correlation between environmental data and PC 2 suggests that variations in chemical composition occurring around maturity (1242−1333 GDD) cannot be explained by either temperature or light conditions.

Finally, because Frontenac berries in both studied vineyards had a similar composition at the beginning of veraison, whereas Marquette grapes had considerably different compositions depending on the vineyards at the same growing stage, it is hypothesized that preveraison growing conditions significantly affect chemical composition of Marquette berries but have a lesser impact on Frontenac berries. Additionally, of particular interest, GDD proved to be an efficient tool to approximate berry chemical composition, because it strongly related to PC 1 for both grape varieties and both studied vineyards. However, our results showed that, in northern climate viticulture, vineyard conditions should be carefully analyzed and seriously considered when grape varieties are selected at implantation.

**Maturity Markers.** In winemaking, the global concept of enological maturity is reached when various factors are in balance, giving the potential of producing the most qualitative

wine.[45] Therefore, maturity markers may be defined as the consistent increase of desirable compounds or the consistent decrease of undesirable compounds in berries, following a curve sufficiently predictable to give an accurate guideline on harvest time. Besides basic juice metrics (TSS, TA, and pH), which are extensively used to make harvest decision, many attempts have been made to determine the optimum harvest time, including the assessment of phenolic and volatile compounds.[10−16,29,33,36,37] However, because none of these measurements gives a precise answer and because berry maturity is closely related to the wine style, winemakers may select specific maturity markers to base their harvest decisions on the desired wine style. In this study, because full maturity was reached only in the SW vineyard for both Frontenac and Marquette, this location was primarily considered for the determination of phenolic and aromatic maturity markers.

In *V. vinifera* varieties, phenolic maturity typically refers to the levels of anthocyanin and tannin in the berry and to their extractability, which increase with berry ripening.[45] In hybrid cultivars, color is rarely an issue in winemaking, because of the high levels of anthocyanin at harvest,[46,47] so this parameter may be of little significance to define optimum ripeness. On the other side, in our study, classical measurements such as total phenolic compounds gave poor regressions with other maturity parameters. In contrast, a consistent accumulation of hydroxycinnamic esters and flavonoids was observed during the ripening of both Frontenac and Marquette. As discussed later in this work, it is not clear that these classes of phenolic compounds are desirable in wines made from hybrid varieties. However, their strong correlation with the progression of quality attributes such as TSS, TA, and pH suggests that they may be efficient phenolic maturity indicators for Frontenac and Marquette. Further studies are needed to determine how these compounds affect sensory attributes of wines made from hybrid cultivars and evaluate their suitability as phenolic maturity markers in hybrid grape varieties.

Most attempts to relate berry aroma profile to optimum maturity were made using monoterpenes and/or $C_6$ compound analysis, therefore focusing on the decrease of vegetal notes to the benefit of positive aromas.[11,15,29,36,37] In non-*vinifera* varieties, studies have mostly focused on the development of compounds related to "hybrid character", such as methyl anthranylate, 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (40), and *o*-aminoacetophenone (43) during ripening.[48] In this study, significant quadratic regressions were found between GDD and volatile compounds such as *trans*-2-hexenal (12), *cis*-3-hexenol (18), decanal (25), *cis*,*trans*-2,6-nonadienal (29), hexanoic acid (36), 2-phenylethanol (38), $\beta$-ionone (39), and eugenol (41) in Frontenac (Figure 3) and hexenal (7), *cis*-3-hexenol (18), *cis*,*trans*-2,6-nonadienal (29), $\alpha$-citral (31), and geraniol (37) in Marquette (Figure 4). However, for some of these compounds, their variability among samples or their very low levels in grape must ($\geq$2 $\mu$g/L) decrease their usefulness as maturity markers, which reduced the selection of possible markers to monoterpenes and $C_6$ compounds.

In Marquette, the monoterpene geraniol (37) increased reliably during the ripening (Figure 4). Geraniol (37), as other terpenes, is generally considered as a positive aroma, contributing floral and fruity notes in wines, and may constitute a valued maturity marker for Marquette in this respect. However, because this compound increased with ripening, concentration targets are necessary to make harvest decisions. Although an increase in geraniol (37) has been observed with increased maturity levels in the aromatic variety Muscat,[11,15] the impact of significant levels of geraniol in Marquette and its retention during winemaking need to be documented to recommend the use of this marker.

Both Marquette and Frontenac exhibited a shift in $C_6$ compound profile during maturity. This shift was illustrated by the increase of *trans*-2-hexenal (12) in Frontenac (Figure 3) and hexanal (7) in Marquette (Figure 4) and by the decrease by 25−30 times of *cis*-3-hexenol in both varieties. *cis*-3-Hexenol (18), also called "leaf alcohol", has an herbaceous aroma and may enhance green notes in wine in this respect, as it seems to be stable under fermentation conditions, unlike the $C_6$ aldehydes *trans*-2-hexenal and hexanal, which are rapidly reduced to their alcohol counterpart during winemaking.[49,50] Thus, reduction of *cis*-3-hexenol during grape maturity may be critical to enhance wine quality, making this compound a significant marker for harvest decisions. Indeed, low levels of *cis*-3-hexenol have been associated with higher TSS levels in Muscat,[15] whereas a significant decrease during veraison has been observed in the Chinese *V. vinifera* varieties Jingxiu and Bimeijia and in the hybrid variety Jingya.[51]

One potent irritant about the use of *cis*-3-hexenol as a maturity marker is that it did not show a consistent decrease in Frontenac from the NE vineyard (Figure 3). Although such poor regression may relate to the variability observed between samples in this specific location, the correlations were significantly improved by using the ratio of *cis*-3-hexanol to *trans*-2-hexenal (Figure 5A). Because *cis*-3-hexenol and *trans*-2-hexenal have the same metabolic precursor, the aldehyde *trans*-3-hexenal,[52] the decrease of the ratio of *cis*-3-hexanol to *trans*-2-hexenal suggests that the enal isomerase (EI) pathway leading to *trans*-2-hexenal may become favored over the alcohol dehydrogenase (ADH) pathway leading to *cis*-3-hexenol, as maturity approaches.[52] However, because of the significant 1-hexanol levels found in both Marquette and Frontenac, this shift between the EI and ADH pathways cannot be explained by a decrease in ADH activity but could rather relate to a decrease in the use of $\alpha$-linolenic acid (C18:3), the metabolic precursor of *trans*-3-hexenal, in the latest ripening stages, as illustrated by the progression of the sum of $C_6$ compounds, respectively, produced from linoleic (C18:2; hexanal and 1-hexanol) and $\alpha$-linolenic (C18:3; *trans*-2-hexenol and *cis*-3-hexenol) acids (Figure 6). Interestingly, in Marquette, $\alpha$-linolenic acid (C18:3) degradation products dominated $C_6$ compound profiles at the beginning of veraison, whereas linoleic acid (C18:2) degradation products predominated in mature berries. Such a shift was not observed in Frontenac, in which $\alpha$-linolenic acid (C18:3) degradation products dominated $C_6$ compound profiles during the whole ripening, as previously observed in Cabernet Sauvignon and Riesling,[52] although the gap between both pathways decreased in Frontenac as maturity approached. Because unsaturated fatty acids are closely related to cold tolerance,[53] further analysis of fatty acid profiles in maturing berries may provide some tools to determine how the shift in $C_6$ compound profile observed in this study relates to the fatty acid metabolism of cold-hardy grapes and, perhaps, to their cold tolerance.

**Low-Cost Markers for Wineries.** In Quebec, small- to medium-sized wineries, which constitute the major part of the local industry, usually monitor grape ripening using TSS, pH, and sometimes TA, or a combination of two of these parameters. Although available, phenolic maturity is used very little, partly because the instruments currently available on the

market provide imprecise and sometimes erroneous measurements for hybrid grape varieties. Thus, in this study, the measurement of total phenolic compounds using the Folin–Ciocalteu assay, which is traditionally used to evaluate phenolic maturity in *V. vinifera* varieties, gave nonsignificant correlations for both Marquette and Frontenac in both locations ($r^2 < 0.50$, Tables 2 and 3). Nevertheless, because the wine industry needs fast, effective, and low-cost maturity assessment tests, we evaluated whether the measurement of basic parameters such as TSS, pH, and TA and different phenolic classes could provide a suitable maturity assessment for wineries. To achieve that goal, we correlated ratios of different quality attributes to ratios of different classes of phenolic compounds, totaling four different measurements, and used linear regression to evaluate their potential as a simple maturity tool. The most relevant correlations are presented in Table 9.

**Table 9. Linear Correlation Matrix of Quality Attribute Ratios (Independent Variable) against Phenolic Maturity Ratios (Dependent Variable) for Frontenac and Marquette Grapes Grown in the Southwest Vineyard (SW; Saint-Paul-d'Abbotsford, QC, Canada) and Northeast Vineyard (NE; Saint-Charles-de-Bellechasse, QC, Canada) during the 2011 Season (Data Were Analyzed Together (Both Locations) and as Separate Blocks (SW and NE))**

| | | block | | |
|---|---|---|---|---|
| independent variable[a] | dependent variable | SW | NE | both locations |
| | **Frontenac** | | | |
| maturity index (TSS/TA) | total anthocyanins/total phenolics | 0.179 | 0.897*[b] | 0.086 |
| | total flavonoids/total phenolics | 0.490* | 0.860* | 0.651* |
| | total hydroxycinnamic esters/total phenolics | 0.572* | 0.800* | 0.684* |
| | total anthocyanins/total flavonoids | 0.040 | 0.908* | 0.007 |
| TSS/pH | total anthocyanins/total phenolics | 0.272 | 0.718* | 0.260* |
| | total flavonoids/total phenolics | 0.555* | 0.747* | 0.639* |
| | total hydroxycinnamic esters/total phenolics | 0.621* | 0.770* | 0.649* |
| | total anthocyanins/total flavonoids | 0.095 | 0.802* | 0.124 |
| | **Marquette** | | | |
| maturity index (TSS/TA) | total anthocyanins/total phenolics | 0.081 | 0.768* | 0.117 |
| | total flavonoids/total phenolics | 0.0004 | 0.700* | 0.343* |
| | total hydroxycinnamic esters/total phenolics | 0.136 | 0.418 | 0.337* |
| | total anthocyanins/total flavonoids | 0.055 | 0.676* | 0.031 |
| TSS/pH | total anthocyanins/total phenolics | 0.107 | 0.709* | 0.242 |
| | total flavonoids/total phenolics | 0.038 | 0.676* | 0.246 |
| | total hydroxycinnamic esters/total phenolics | 0.029 | 0.508 | 0.318* |
| | total anthocyanins/total flavonoids | 0.089 | 0.621* | 0.128 |

[a]TSS, total soluble solids; TA, titratable acidity. [b]An asterisk indicates significance at $P \leq 0.0001$.

As expected from the PCA, Frontenac showed significant correlations between the ratio of TSS to TA or TSS to pH and ratios of flavonoids or hydroxycinnamic esters to total phenolics ($r^2 \geq 0.49$, $P \leq 0.0001$) for both vineyards. Those data suggest that these four measurements (TSS, TA, hydroxycinnamic esters, and total phenolic compounds; or TSS, pH, total flavonoids, and total phenolic compounds) could provide a suitable maturity assessment in different locations for Frontenac.

For Marquette, significant correlations ($r^2 \geq 0.65$) were found between quality attributes and the ratios of different phenolic compound classes. Among these factors, the correlations found when both locations were considered, although significant, were still weak ($r^2 \geq 0.31–0.34$, $P \leq 0.0001$), suggesting that phenolic measurements may be less reliable in Marquette than in Frontenac, from one location to another.

**Grape Quality at Harvest.** Frontenac is known among cold-hardy grapes as a particularly acidic variety;[18,47] consequently, it retained higher acidity than did Marquette in both locations in the present study. Slightly different data were observed elsewhere for Frontenac, particularly in Minnesota, where this variety previously reached a higher TSS level (26–27 °Brix), retained higher TA (about 15 g/L tartaric acid equiv), and had a lower pH (3.0) in comparison to what we observed in Quebec.[18] Similarly, Minnesota-grown Marquette showed higher TA in Minnesota, compared to our samples from the SW vineyard.[18] Although higher TA levels are typical in cold-climate viticulture, differences between TA levels may be attributable to environmental parameters, such as temperatures and light intensity, that can significantly affect the decrease in organic acids during ripening.[44,54,55]

At harvest, the total phenolic concentrations found in our samples were higher than previously reported data for other cold-hardy grape varieties grown in Nova Scotia, Canada, such as Lucie Kuhlmann, Baco Noir, and Marechal Foch.[46] In contrast, anthocyanin concentration was similar to previously reported data for hybrid grape cultivars.[46] Total phenolic compounds and total and monomeric anthocyanins showed higher levels in Frontenac and Marquette (up to 10 times higher for anthocyanins) compared with previously reported data for red *V. vinifera* varieties such as Pinot noir and Merlot.[56] Both monomeric and total anthocyanin levels were higher in the NE vineyard than in the SW vineyard, a difference that could be related to higher summer temperature peaks recorded in the latter location. In fact, although high UV exposure from sunny conditions can enhance anthocyanin biosynthesis, hot temperatures negatively affect this process.[57]

Hydroxycinnamic esters were twice as concentrated in our samples (303–492 mg/L caffeic acid equiv) compared with juice from *V. vinifera* varieties, showing 84–194 mg/L caffeic acid equiv hydroxycinnamic esters.[56] High levels of hydroxycinnamic esters could be detrimental to the quality of wine made from low-tannin varieties such as Frontenac because they can either act as precursors of unwanted volatile phenols,[58] thus providing the finished wine with "animal" or "barnyard" off-flavors,[45] or bring astringency or bitterness to wine.[59] By inhibiting the cinnamate decarboxylase, the enzyme responsible for the conversion of hydroxycinnamic esters to volatile phenols,[45] the addition of enological tannins at the beginning of the alcoholic fermentation may provide a partial solution to high levels of hydroxycinnamic esters in cold-hardy grape musts.[45] Flavonoids were also noticeably more concentrated in our samples (243–323 mg/L) compared with *V. vinifera* varieties, which contains between 50 and 100 mg/L quercetin equiv.[56] Similar to hydroxycinnamic esters, and because they can be increased considerably by maceration during red wine production,[56] flavonoids could be significant contributors to the

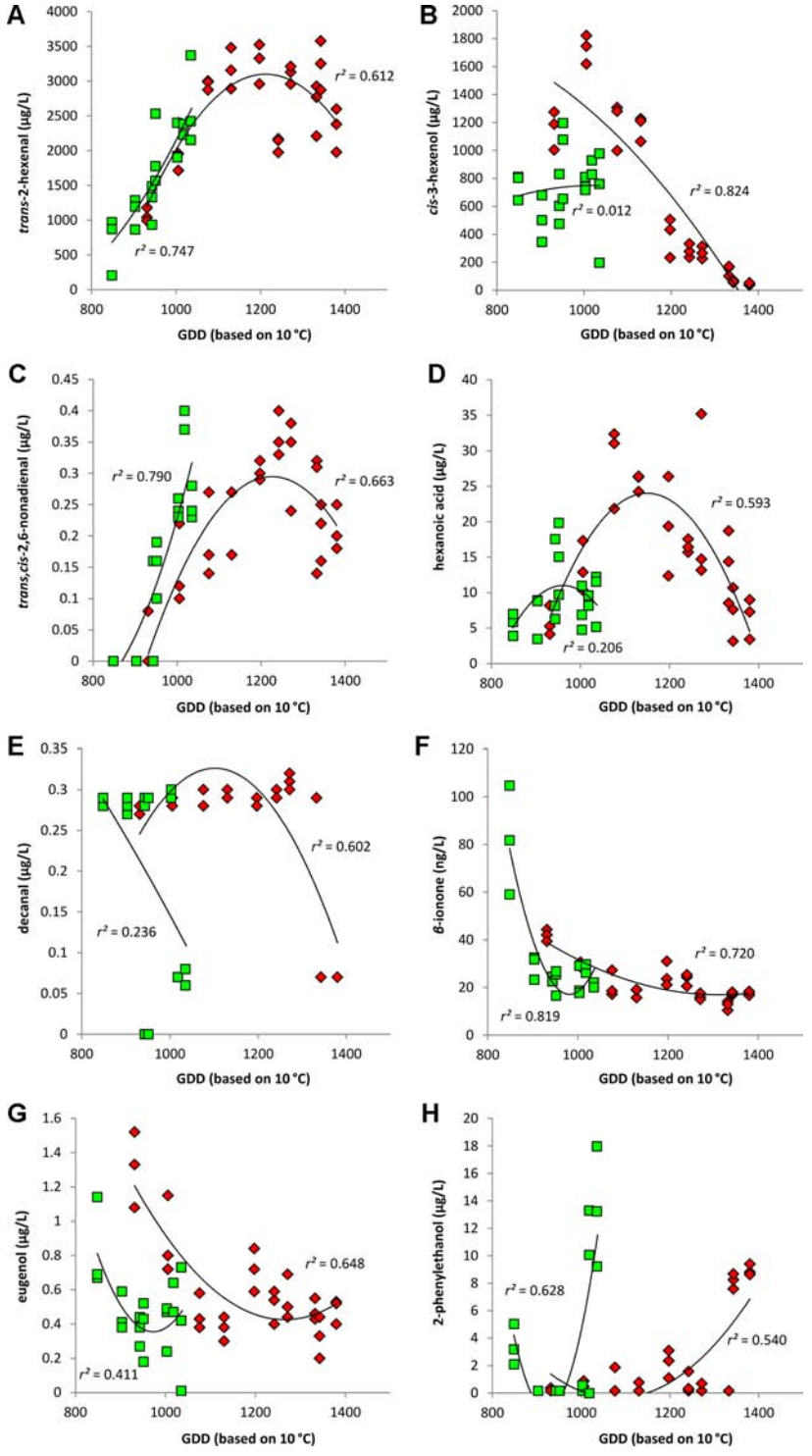


**Figure 3.** Quadratic regression of *trans*-2-hexenal (A), *cis*-3-hexenol (B), *trans*,*cis*-2,6-nonadienal (C), hexanoic acid (D), decanal (E), *β*-ionone (F), eugenol (G), and 2-phenylethanol (H) against GDD (based on 10 °C) during the ripening of Frontenac grapes in two vineyards located in southwest (Saint-Paul-d'Abbotsford, QC, Canada; red diamonds, $n = 30$) and northeast (Saint-Charles-de-Bellechasse, QC, Canada; green squares, $n = 21$) areas of the province of Quebec during the 2011 season.

mouthfeel of Frontenac and Marquette wines, bringing either a velvety astringency or bitterness, depending on their concentration.[59,60] Interestingly, high flavonoid levels (200 mg/L) have been associated with ultrapremium red wines versus standard red wines.[61] Further investigations are needed to determine the implication of hydroxycinnamic esters and flavonoids in hybrid grape winemaking.

The volatile aroma profile of ripe Frontenac and Marquette juices from the SW vineyard showed significant levels of $C_6$ compounds (hexanal (7), *trans*-2-hexenal (12), 1-hexanol (15), *cis*-3-hexenol (18), hexanoic acid (36)), acetic acid (22), *β*-damascenone (35), and 2-phenylethanol (38)). Frontenac additionally showed significant levels of 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (40) at 1380 GDD, whereas the monoterpenes


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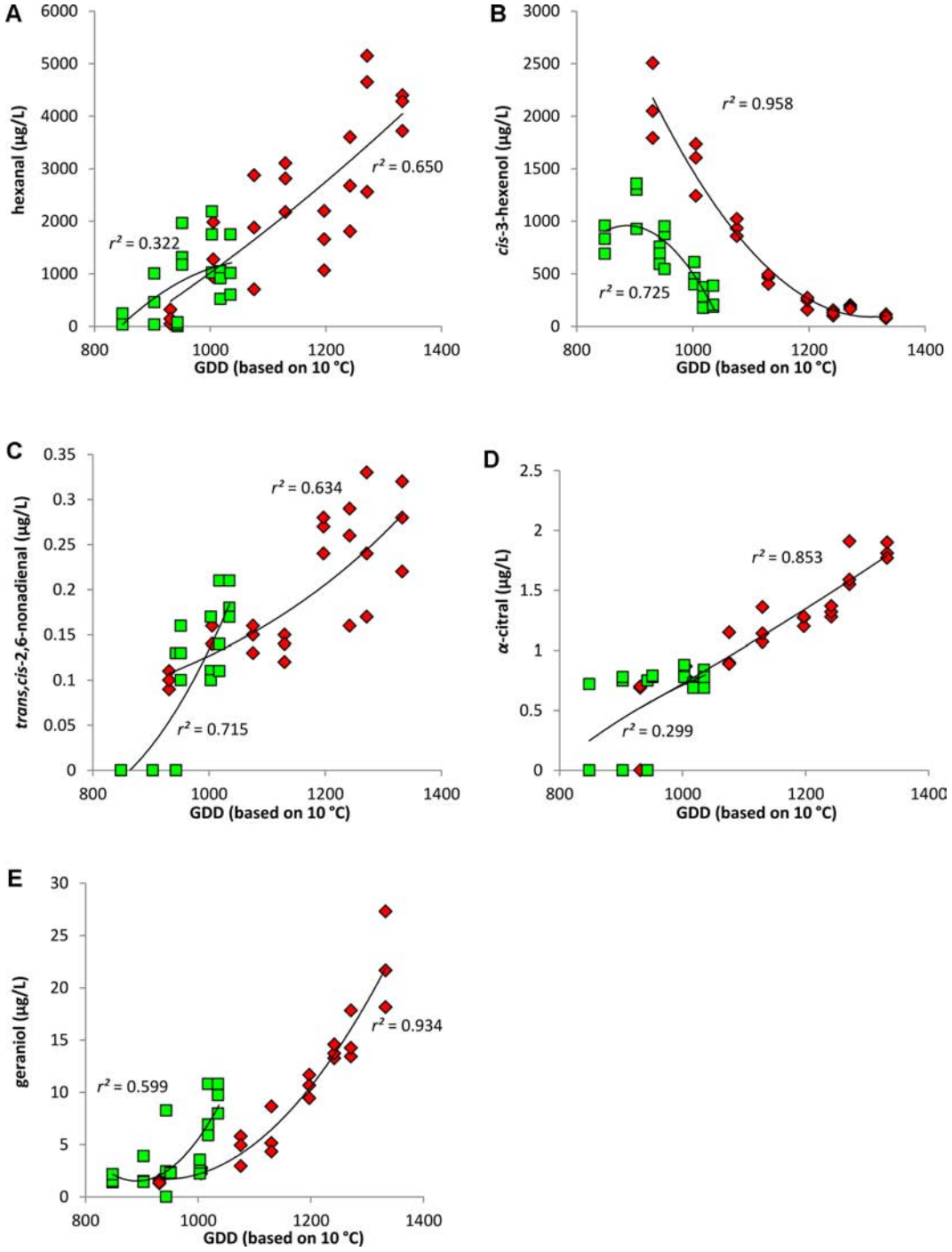


**Figure 4.** Quadratic regression of hexanal (A), *cis*-3-hexenol (B), *trans,cis*-2,6-nonadienal (C), α-citral (D), and geraniol (E) against GDD (based on 10 °C) during the ripening of Marquette grapes in two vineyards located in southwest (Saint-Paul-d'Abbotsford, QC, Canada; red diamonds, $n$ = 24) and northeast (Saint-Charles-de-Bellechasse, QC, Canada; green squares, $n$ = 21) areas of the province of Quebec during the 2011 season.

linalool (28), geraniol (37), and α-citral (31) and the alcohol 1-octen-3-ol (21) showed significant levels in Marquette. With the exception of 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone, geraniol, and α-citral, all of these compounds have previously been reported as impact odorant of Cabernet Sauvignon, Cabernet franc, and Merlot juice,[62] whereas 1-hexanol and 2-phenylethanol were reported as impact odorants of Frontenac wines.[63]

In Frontenac from the NE vineyard, the *cis*-3-hexenol level remained very high at the last sampling, which agrees with the lack of ripeness experienced in this location. In contrast, in the SW vineyard, 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone showed a significant level in berries at the last sampling, at 1380 GDD. Accumulation of 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone has been associated with ripeness and over-ripeness in strawberries.[64] In grapes, the glycosylated form of 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone has been shown to increase during the ripening of *V. vinifera* grapes var. Agliano.[65] High levels of 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone are known to provide "foxiness" to wines made from hybrid grape varieties, due to their American vine species genetic, present at different extents in cold-hardy grapes.[45] Because 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone is a Maillard reaction product, its presence in Frontenac

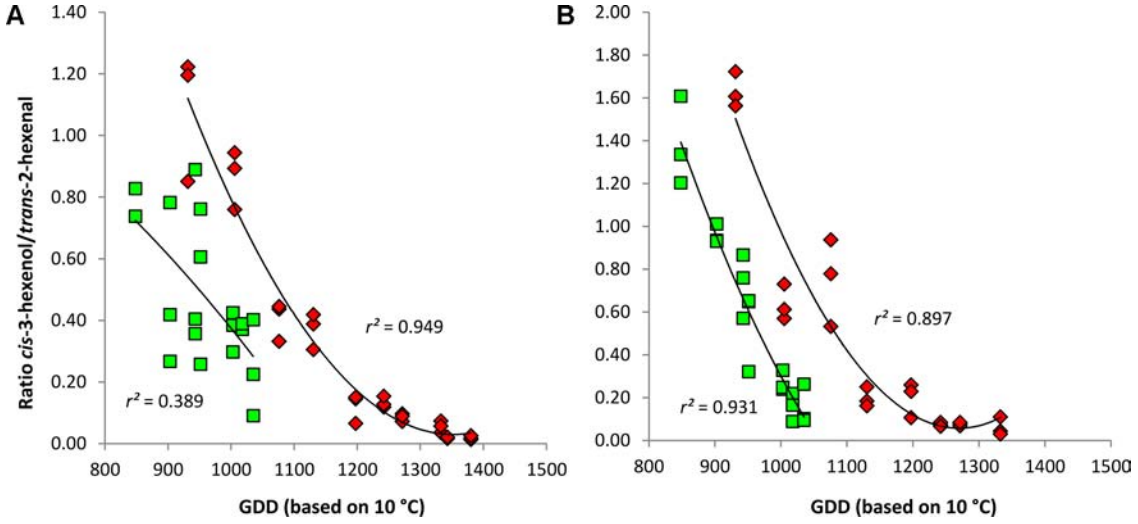


**Figure 5.** Change in the ratio of *cis*-3-hexenol to *trans*-2-hexenal during the ripening (plotted according to GDD, based on 10 °C) of Frontenac (A) and Marquette (B) grapes in two vineyards located in southwest (Saint-Paul-d'Abbotsford, QC, Canada; red diamonds, $n$ = 30 for Frontenac; $n$ = 24 for Marquette) and northeast (Saint-Charles-de-Bellechasse, QC, Canada; green squares, $n$ = 21 for each variety) areas of the province of Quebec during the 2011 season.

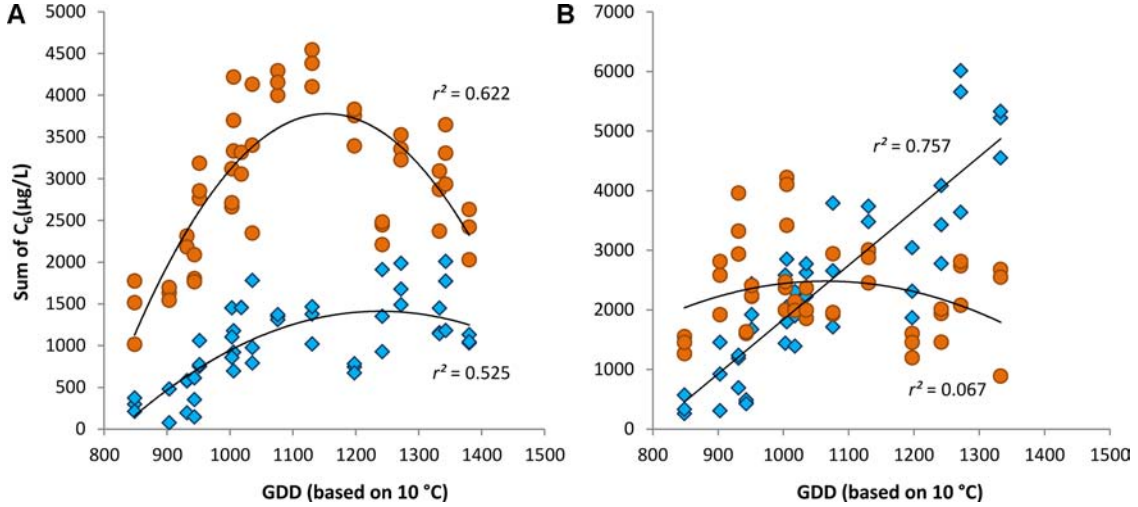


**Figure 6.** Sum of linoleic acid (C18:2) degradation products (hexanal, 1-hexanol; blue diamonds) and linolenic acid (C18:3) degradation products (*trans*-2-hexenal, *cis*-3-hexenol; orange dots), during the ripening (plotted according to GDD, based on 10 °C) of Frontenac (A, $n$ = 51) and Marquette (B, $n$ = 45) grapes in two vineyards located in the province of Quebec during the 2011 season.

may be enhanced by hot temperature, when occurring around maturity, suggesting that, in the SW vineyard, the optimum aromatic maturity was reached at 1343 GDD, the stage preceding the appearance of 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone.

In Marquette, positive aromas (*β*-damascenone (35), linalool (28), geraniol (37), and 2-phenylethanol (38)) reached their highest levels at 1242 GDD in the SW vineyard, suggesting that optimum aromatic maturity was reached for winemaking at this stage. Assuming that deacidification using either chemical, physical, or microbiological processes is part of the northern winemaking process, these results suggest that grapes could have been picked as early as 1242 GDD: the sugar/acidity balance was somewhat acceptable for northern condition (22.1 °Brix and 9.3 g/L tartaric acid equiv) and no significant changes in quality attributes occurred after this stage. Although herbaceous compounds such as hexanal (7) and *trans*-2-hexenal (12) showed significant levels at this stage, they are of limited significance with regard to winemaking, as pointed out earlier, because they are rapidly reduced during fermentation.[50,53] On the other side, because *cis*-3-hexenol level was still higher than 100 ug/L at this stage, and continued to decrease until 1333 GDD, further research is needed to determine how the balance of *cis*-3-hexenol to positive aroma such as linalool, *β*-damascenone, geraniol or 2-phenylethanol impacts wine quality.

In conclusion, the changes in quality attributes and phenolic and volatile compounds was studied for the first time in Quebec, Canada, during the ripening of the cold-hardy grape varieties Frontenac and Marquette, in two vineyards presenting different environmental conditions. Our data showed that full maturity was reached for both Frontenac and Marquette in the SW vineyard, where 1380 GDD were accumulated during the 2011 season, whereas the accumulation of 1035 GDD was not sufficient to fully ripen Frontenac and Marquette in the NE vineyard. Longer veraison, as experienced by grapes picked in the SW vineyard, provided higher quality attributes

(higher TSS, lower TA, etc.) and higher flavor development for both Frontenac and Marquette. In contrast, under the colder conditions in the NE vineyard, metabolite accumulation was driven primarily by berry growth, and flavor development was limited. Besides GDD and technological parameters (TSS, pH, and TA), which provide significant guidelines for maturity assessment in cold climates, phenolic maturity may be followed by the accumulation of hydroxycinnamic esters and flavonoids, although the impact of these compound classes on quality remains to be determined in cold-climate wines. In both Frontenac and Marquette, aromatic maturity was best assessed using the ratio of *cis*-3-hexenol to *trans*-2-hexenal, which showed a constant decrease during maturity. The accumulation of geraniol may also be followed in Marquette, although further studies are needed to relate the optimum geraniol level to the optimum berry maturity. Interestingly, a shift in $C_6$ compound profile, illustrated by the progression of the sum of $C_6$ compounds respectively produced from linoleic (C18:2; hexanal and 1-hexanol) and $\alpha$-linolenic (C18:3; *trans*-2-hexenol and *cis*-3-hexenol) acids occurred during ripening, with $\alpha$-linolenic acid (C18:3) degradation products decreasing in both varieties, as maturity approched. At harvest, aroma profile of both Frontenac and Marquette were dominated by $C_6$ compounds (hexanal (7), *trans*-2-hexenal (12), 1-hexanol (15), *cis*-3-hexenol (18), hexanoic acid (36), acetic acid (22), $\beta$-damascenone (35), and 2-phenylethanol (38)), with Marquette additionally showing significant levels of monoterpenes (linalool (28), geraniol (37), and $\alpha$-citral (31)) and 1-octen-3-ol (21).

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