## Odor Potency of Aroma Compounds in Riesling and Vidal blanc Table Wines and Icewines by Gas Chromatography–Olfactometry– Mass Spectrometry

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**ABSTRACT:** This study aimed to elucidate the odor potency of aroma compounds in Riesling and Vidal blanc (syn. Vidal) table wines and icewines from the Niagara Peninsula using stir bar sorptive extraction—gas chromatography—olfactometry—mass spectrometry. Dilution analysis determined the most odor-potent compounds in Vidal and Riesling icewines (n = 2) and table wines (n = 2) from a commercial producer. The top 15 odor-potent compounds in each wine were identified and quantified, resulting in 23 and 24 compounds for Riesling and Vidal, respectively. The most odor-potent compounds were  $\beta$ -damascenone, decanal, 1-hexanol, 1-octen-3-ol, 4-vinylguaiacol, ethyl hexanoate, and ethyl 3-methylbutyrate. In general, icewines had higher concentrations of most aroma compounds compared to table wines. Through computation of odor activity values, the compounds with the highest odor activity for the icewines were  $\beta$ -damascenone, 1-octen-3-ol, ethyl octanoate, *cis*-rose oxide, and ethyl hexanoate. In table wines the highest odor activity values were found for ethyl octanoate,  $\beta$ -damascenone, ethyl hexanoate, *cis*-rose oxide, ethyl 3-methylbutyrate, and 4-vinylguaiacol. These findings provide a foundation to determine impact odorants in icewines and the effects of viticultural and enological practices on wine aroma volatile composition.

**KEYWORDS:** wine aroma, volatile analysis, odor activity values,  $\beta$ -damascenone, esters

## INTRODUCTION

Wine aroma is the result of the complex interaction of hundreds of volatile compounds that together form a matrix to produce a sensory response. The major criterion of a compound to be aromatic, or odor-active, is its volatility, enabling it to reach the olfactory epithelium and elicit a sensory perception. Understanding what contributes to a wine aroma has been the goal of many research initiatives since the 1940s and continues today. The source of wine aroma compounds can be explained by their source of origin<sup>1,2</sup> and can be categorized on the basis of their contribution to the overall aroma of the matrix.<sup>3</sup>

Gas chromatography-mass spectrometry (GC-MS) is the most used analytical instrumentation to determine the concentration of volatile compounds and is widely used in wine aroma analysis. However, this method gives no indication of which compounds in the sample contribute to its aroma, only the amount present in the sample. A common measure to assess the contribution of an aroma compound to a product is through the use of odor activity values (OAVs), which are calculated by dividing the concentration of the analyte by its sensory threshold. An OAV > 1 indicates the compound is found above its sensory threshold and contributes to the product's aroma. The larger the OAV, the more potent the compound is thought to be. OAVs are a good indication of the potential potency of an aroma compound, but are most useful when the sensory threshold is determined in a similar matrix, as it is well established that aroma compounds have different threshold concentrations in air, water, and wine.<sup>2</sup> Furthermore, OAVs provide no information on matrix effects and interactions with other compounds, which can result in aroma enhancement or depression. Finally, an OAV > 1 does not mean the aroma compound will be perceived in the wine.

Gas chromatography–olfactometry (GC-O) is an analytical method used to determine which odor-active compounds in a chromatographic run contribute to the wine aroma. This technique combines a traditional GC fitted with a nondestructive olfactory port enabling a person to smell the effluent. The odor description, when an odor-active compound elutes above its sensory threshold, is recorded along with its retention time to identify the odorant areas of the chromatogram.

GC-O methodologies have diverged into three main categories: dilution analysis, intensity ratings, and frequency detection. Both intensity rating and frequency detection methods provide useful information by identifying and rating the odor-active compounds; however, only dilution analysis provides a quantitative measure of the sensory threshold of a compound. CharmAnalysis<sup>4</sup> is a quantitative dilution analysis technique. In dilution analysis, the sample is serially diluted and sniffed by a small panel of judges until no odor is detected. The compounds that are present in the highest dilutions are those which contribute most to the wine aroma and, therefore, are the most odor-potent compounds.

In CharmAnalysis the sniff judge uses a computer program to indicate the beginning and end of the odor by depressing the mouse button and describes the odor eluting on the basis of a developed lexicon. The charm value produced is based on the peak height (number of dilution detected) and length (duration of odor event).<sup>4</sup> The CharmAnalysis software for dilution analysis was used in this study to determine the most

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odor-potent compounds in Vidal blanc (syn. Vidal) and Riesling icewine and table wine. CharmAnalysis has been previously used to characterize aroma compounds in lychee fruit,<sup>5</sup> Gewurztraminer wines,<sup>6</sup> and Vidal and Riesling wines from Ohio.<sup>7</sup>

For the GC-O results to make sense, the extract sniffed by the judges must be a good representation of the original product. Liquid-liquid extraction of a wine sample using a solvent of similar chemical properties is the traditional method for volatile analysis of the sample by GC and GC-O-MS. Disadvantages of this method include time-consuming extraction procedures, costs associated with solvents and their safe disposal, and the production of artifacts during extraction. In 1990, Pawliszyn developed a solventless extraction technique known as solid phase microextraction (SPME).<sup>8</sup> Advantages of this technique are that it combines sampling, extraction, and concentration and sampling to the GC all into one step using a polymer-coated fiber contained in a modified syringe holder. The major disadvantage of this technique is the small sampling capacity of the fiber, only about 0.6  $\mu$ L for a 100  $\mu$ m PDMS fiber, which affects the sensitivity of recovery.

In 1999, a technique based on the same principle as SPME but with several advantages was introduced, known as stir bar sorptive extraction (SBSE), commercially sold as Twister.<sup>10</sup> SBSE uses a 10 mm long glass encased magnetic stir bar coated with a 0.5 mm thick layer of polydimethylsiloxane (PDMS). Analytes are extracted by placing a stir bar either directly in an aqueous mixture or suspended in its headspace. The volatiles partition onto the PDMS coating and are then thermally desorbed into the GC inlet, which is cryocooled with liquid nitrogen. The main advantage of SBSE over SPME is the increased sampling capacity, enabling improved signal-to-noise ratios, increased sensitivity, and low detection and quantitation limits.9 It is for these reasons that SBSE was used for the extraction of volatiles in this study. It is the first time to the authors' knowledge that SBSE has been used in conjunction with CharmAnalysis to determine the odor potency of aroma compounds. However, SBSE has been used extensively for the volatile analysis of grapes,<sup>11</sup> wines,<sup>12–14</sup> and other alcoholic beverages such as beer<sup>15</sup> and malt whiskey.<sup>16</sup>

Ontario is Canada's largest wine region and the Niagara Peninsula its largest appellation, which produces sparkling wines, table wines, and dessert wine from mainly *Vitis vinifera* cultivars. Icewine is the wine style synonymous with the Canadian wine industry made predominantly from Vidal and Riesling with the bulk of its production from the Niagara Peninsula. In 2009, almost 900 000 L of icewine was produced in Ontario and of that 75 and 6% were made from Vidal and Riesling, respectively.<sup>17</sup>

Icewine is a sweet late-harvest dessert wine made from grapes naturally frozen on the vine at -8 °C or colder and pressed while frozen. The resultant wine is concentrated in sugar, acids, and aroma/flavor compounds. In Ontario, Canada, the production of icewine is strictly regulated by the Vintner's Quality Alliance (VQA) of Ontario. For a wine to be labeled icewine under VQA regulations, it must be made from grapes harvested after November 15, with a harvest temperature  $\leq -8$  °C and a must concentration of at least 35 °Brix, with 125 g/L residual sugar and 6.5 g/L titratable acidity in the finished wine. Icewines are characterized by intense aromas of honey, peach, apricot, and caramel with the palate displaying a balance of sweetness and acidity. Although icewine is internationally renowned and produced in many countries, very little is known about this unique wine style and its volatile composition. A survey of icewine research in the literature shows studies that have investigated the sensory and chemical composition of icewine;<sup>18,19</sup> the impact of vintage and viticultural area on some chemical parameters,<sup>20</sup> the polyphenol content;<sup>21,22</sup> and the impact of yeast strain,<sup>23,24</sup> yeast inoculation method<sup>25</sup> and yeast hyperosmotic stress response in icewine fermentations.<sup>26,27</sup> However, there is limited research on the aroma volatile composition of icewine besides a preliminary study by Cliff et al.,<sup>18</sup> and qualitative profiling of icewine volatile fractions using solid-phase microextraction–gas chromatographic–timeof-flight mass spectrometric methods.<sup>28–30</sup>

Other regions have characterized their wines on the basis of aroma composition and the identification of impact odorants that impart to the wines a specific, unique, and identifying aroma that is distinct to that wine style.<sup>31-34</sup> The general aim of this study was to elucidate such compounds in Vidal and Riesling icewines using GC-O-MS. The main objective of this study was to determine and quantify the most odor-potent compounds in Riesling and Vidal table wine and icewine from the Niagara Peninsula, Ontario, Canada. Much is already known about the chemical composition of Vidal and Riesling table wines. Comparison of table wine and icewine should provide information as to how the odor potency changes and what compounds may be affected. The grapes for the commercial table wines and icewines in this study came from the same vineyard block for both the Vidal and Riesling wines. Some of the grapes in the block were harvested at regular commercial harvest for table wines, whereas the rest of the grapes in the block remained on the vine until temperatures permitted icewine harvest. Therefore, differences in odor potency and odor-potent compounds could be attributed only to wine style and harvest date because all other parameters were the same. Because very little is known regarding icewine, the results of this study will aid in the understanding and characterization of Canadian icewine and the aroma compounds important to this wine style.

### MATERIALS AND METHODS

**Wines.** Four commercial wines from the 2004 vintage were donated by Coyotes Run Winery in Niagara-on-the-Lake, ON, Canada, for analysis. They consisted of 2004 Riesling icewine, 2004 dry Riesling table wine, 2004 Vidal icewine, and 2004 off-dry Vidal table wine. All wines of the same cultivar originated from the same vineyard but were harvested at different times to reflect the two different wine styles: table wine and icewine. Three bottles of each wine were analyzed in duplicate.

**Chemicals.** Analytical standards (Table 1) were purchased from Aldrich (Oakville, ON, Canada), Sigma-Aldrich (Oakville, ON, Canada), Fluka (Oakville, ON, Canada), Bedoukian (Danbury, CT, USA), and Acros Organic (NJ, USA).  $\beta$ -Damascenone was a gift from Dr. T. Acree, Cornell University. Chemical standards were diluted in dichloromethane (Caledon, Georgetown, ON, Canada) and stored at -25 °C.

**Volatile Extraction.** Wine volatiles were extracted from the liquid phase by stir bar sorptive extraction (SBSE), commercially known as Twister, using 10 mm stir bar (Gerstel, Baltimore, MD, USA) coated with polydimethylsiloxane (PDMS, 0.5 mm film thickness) in 10 mL extraction vials for 60 min at 1000 rpm. Stir bars were removed from the extraction vial, dried with a lint-free tissue, rinsed with Milli-Q water (Millipore), and stored in a 4 mL amber vial at 4 °C until analysis. Wines were used full strength for GC-MS quantification. For GC-O analysis, wines were diluted 10-fold with a model wine solution made to match the composition of the icewine and table wine. The icewine model wine solution contained 11.57 g/L tartaric acid (EMD Chemical Inc., Darmstadt, Germany), 153 g/L fructose

# Table 1. Chemical Standards, Quantitative and Qualitative Ions, and Calibrated Intervals for Vidal and Riesling Icewines and Table Wines

					calibrated interval (µg/L)			
analyte	supplier	CAS Registry No.	quantitative ion $(m/z)$	qualitative ions $(m/z)$	Vidal	r <sup>2</sup> value	Riesling	r <sup>2</sup> value
ethyl isobutyrate	Aldrich	97-62-1	43	71, 88, 116	50-150	0.977	150-600	0.923
ethyl butyrate	Aldrich	105-54-4	71	43, 88, 116	20-180	0.962	125-500	0.915
ethyl 2-methylbutyrate	Aldrich	7452-79-1	57	102, 74, 130	5-125	0.997		
ethyl 3-methylbutyrate	Aldrich	108-64-5	88	41, 70, 130	15-135	0.993	15-135	0.973
1-hexanol	Sigma-Aldrich	111-27-3	56	43, 69, 84	1000-6250	0.964	300-4800	0.979
isoamyl acetate	Aldrich	123-92-2	43	70, 55, 87	150-600	0.935		
ethyl valerate	Sigma-Aldrich	539-82-2	88	57, 101, 130	1.0-36	0.995		
1-heptanol	Acros Organics	111-70-6	70	56, 83, 98	2-200	0.996		
1-octen-3-ol	Aldrich	3391-86-4	57	72, 85, 99	1-400	0.999	1.0-400	0.904
ethyl hexanoate	Aldrich	123-66-0	88	99, 60, 144	300-1200	0.999	300-1200	0.993
acetophenone	Aldrich	98-86-2	105	77, 120, 51	1.0-25	0.985	1.0-25	0.979
1-octanol	Sigma-Aldrich	111-87-5	56	41, 69, 84	10.0-20	0.918	2.0-32	0.979
linalool	Sigma-Aldrich	78-70-6	71	93, 121, 154	5-125	0.972	20-500	0.989
cis rose oxide	Fluka	16409-43-1	139	69, 83, 154	3-108	0.998	0.5-24.5	0.998
phenethyl alcohol	Acros Organic	60-12-8	91	122, 65, 51	15000-135000	0.977	15000-60000	0.942
nerol oxide	Bedoukian	1786-08-9	68	83, 41, 152	5.0-80	0.997	20-80	0.993
ethyl benzoate	Aldrich	93-89-0	105	122, 77, 150	1.0-9	0.993	1.0-9	0.995
ethyl octanoate	Aldrich	106-32-1	88	101, 127, 172	400-1600	0.992	300-12000	0.975
decanal	Sigma-Aldrich	112-31-2	57	70, 82, 112	0.25-16	1.000	0.5-4.5	0.984
ethyl phenylacetate	Aldrich	101-97-3	91	164, 65, 136	2.0-50	0.984	2.0-50	0.987
2-phenethyl acetate	Aldrich	103-45-7	104	43, 91, 78			3.0-75	0.991
4-vinylguaiacol	Alfa Aesar	7786-61-0	150	135, 107, 77	20-320	0.944	25-1225	0.987
$\gamma$ -nonalactone	Aldrich	104-61-0	85	41, 114, 156	0.5-200	0.981	10-160	0.976
$\beta$ -damascenone	Gift	23726-93-4	69	105, 121, 190	2.0-8	0.994	2.0-32	0.996
geranyl acetone	Alfa Aesar	3796-70-1	43	69, 151, 194	0.15-0.60	0.991	0.15-0.60	0.990
ethyl cinnamate	Aldrich	103-36-6	131	103, 176, 77			3.0-27	0.975
eta-ionone	Aldrich	79-77-6	177	43, 135, 192			0.01-0.25	0.992

(Caledon), and 11% (v/v) ethanol (Commercial Alcohols Inc., Brampton, ON, Canada), with a pH of 3.61. The table wine model wine solution contained 7.4 g/L tartaric acid, 5 g/L fructose, and 12% (v/v) ethanol, with a pH of 3.33. All wines were spiked with an internal standard, 100  $\mu$ g/L *n*-dodecanol (Sigma) in GC-grade dichloromethane.

Gas Chromatography-Mass Spectrometry (GC-MS). The instrument used was an Agilent 6890N/5975B gas chromatographmass spectrometer equipped with a Gerstel thermal desorption unit (TDS2), a Gerstel cooled injection system (CIS4) programmable temperature vaporization (PTV) inlet, and an olfactometry port (DATU, Geneva, NY, USA). The analytical column was an Agilent HP-5MS, 5% phenyl methyl siloxane, 30 m length, 0.25 mm internal diameter, and 0.25  $\mu$ m film thickness. The carrier gas was 1.4 mL/min 5.0 purity helium (Praxair, Mississauga, ON, Canada). The oven temperature program was as follows: initial temperature, 35 °C; held for 3 min; increased by 6 °C/min to 155 °C; increased by 30 °C/min to a final temperature 240 °C. Thermal desorption was carried out as follows: initial temperature, 30 °C; increased by 60 °C/s to 250 °C, and held for 3 min. The TDS transfer line, temperature 275 °C, was connected to a CIS4 inlet cryocooled to -70 °C with liquid nitrogen in solvent vent mode. After desorption, the CIS4 inlet temperature was increased at 12 °C/s to 280 °C and held for 5 min while analytes were released on the column. The column was attached to a splitter (Gerstel), with a 1:1 split ratio between the MS and the back inlet (olfactory port). The MS detector (electron impact (EI) at 70 eV) was run in scan mode, 30-400 Da for compound identification, and in select ion monitoring (SIM) mode, selecting for one quantitative ion and three qualitative ions for each compound for quantification (Table 1).

GC-Olfactometry (GC-O). All instrumental parameters were the same as listed for the GC-MS. The back detector of the GC was installed as the olfactory port. The effluent from the column was split to the olfactory port and supplemented with 45 mL/min nitrogen gas flow. The sniff tube was heated to 25  $^{\circ}$ C with humidified air to prevent drying and irritation of the judges' nasal passage while sniffing. All GC-O analyses were conducted by a panel of two judges.

Judge Reproducibility. Judges were given four blind repetitions of the same wine over four days to ensure they were detecting similar odor events and identifying the same perception and were reproducible. An odor event was characterized by its odor perception, retention time, and if it was detected in at least three of the four repetitions. Thirty and 26 odor events were detected by judges 1 and 2, respectively, and of those, 21 odor events were the same (same retention index and perception). Judges were therefore deemed reproducible.

*Lexicon Generation.* The judges sniffed all wine at the initial concentration and generated a list of descriptors to describe the aroma perceptions eluting from the GC-O. The judges met to discuss the lexicon terms and through consensus generate the final lexicon. This lexicon was used for subsequent analysis (Table 2).

*CharmAnalysis.* GC-O data were collected by the dilution analysis method CharmAnalysis (DATU), a computer software program that records the retention time, linear retention index (based a series of *n*-alkanes  $C_6-C_{19}$ ; Sigma-Aldrich), and odor perception. Wine was diluted, in model wine, 10-fold for the initial concentration; all subsequent dilutions were 3-fold until no odor events were detected. Each wine at each dilution was extracted using SBSE, sniffed by two judges experienced in aroma recognition until no aroma was detected.

*Top 15.* Each wine was sorted by Charm value<sup>35</sup> for each judge. The top 15 odor events for each judge in each wine were retained and subsequently identified and quantified. Charm values for each judge were normalized to the highest Charm value for that judge into odor

## Table 2. Lexicon of Terms Used for GC-O To Describe Perception of Odor Events<sup>a</sup>

banana	honey
black pepper	mushroom
bread/yeast	musty
caramel/butterscotch/burnt sugar	peach
citrus (grapefruit, lime, orange)	pear
clove	petrol
coconut	tropical fruit
coffee	vinegar
cotton candy	vinyl/plastic
dried fruit/raisin	walnut
earthy/green	wood
floral	other
fruity	0005

<sup>*a*</sup>All terms were self-generated by the GC-O judges as descriptors of the aromas eluting from the undiluted wine samples and were agreed upon through consensus.

spectrum values (OSV) for comparison between judges and wines<sup>35</sup> (Table 3).

Identification and Quantification. Compounds were identified by comparison of retention time, odor perception, and mass spectra (Wiley7Nist05 library) to pure standards. Three-point calibration curves were run for each analyte in model wine solution to ensure linearity ( $r^2 > 0.9$ ; Table 1). Standard curve concentrations and compounds were quantified on the basis of the ratio of the peak area of the compound relative to the peak area of the internal standard to determine the concentration of the analytes. Three bottles of each wine were analyzed in duplicate with relative standard deviation between replicates ranging from 0.5 and 12%.

**Statistical Analysis.** Two-tailed *t* tests (Microsoft Excel) were used to determine differences between table wines and icewines from each cultivar at p < 0.05.

## RESULTS

**GC-O.** Icewines and table wines had similar odor-active compounds but differences in their odor potency (Table 3). For each of the judges, the top 15 odor-active compounds were retained, determined by descending Charm values. The Charm values were then converted to odor spectrum values (OSV), which are the odor potency normalized to the most potent odorant detected<sup>35</sup> to enable comparison between judges, wines, and cultivars. This is the same principle as in MS, where the ion fragments are normalized and expressed as a percentage relative to the most abundant ion fragment produced in a spectrometer.

Table 3. Combined List of the Top 15 Aroma Compounds Determined through CharmAnalysis for Vidal and Riesling Icewine (IW) and Table Wine (TW) Sorted by Linear Retention Index (LRI) Converted to Odor Spectrum Values (OSV) for Comparison Indicating Odor Perception and Identification<sup>a</sup>

			V	idal			Ries	ling			
no.	LRI	IW 1	IW 2	TW 1	TW 2	IW 1	IW 2	TW 1	TW 2	odor perception	compound
1	745			7	3			22		fruity	ethyl isobutyrate
2	782			9	3			6	15	fruity	ethyl butyrate
3	832			100	8					fruity	ethyl 2-methylbutryrate
4	843	21	8		2	15	7	52	22	fruity, tropical	ethyl 3-methylbutyrate
5	852	99	39		6	71	15	68	32	bread/yeast	1-hexanol
6	859			5						banana	isoamyl acetate
7	905	3								coffee	ethyl valerate
8	957	78								vinyl/plastic	1-heptanol
9	963	67	30	11	5	4	6	35		mushroom	1-octen-3-ol
10	981	44		29	6	1	6	49	16	tropical fruity	ethyl hexanoate
11	1018			12						plastic, musty	unknown 1018
12	1027			22						wood	unknown 1027
13	1050	9	11				10			caramel	acetophenone
14	1063	2	100	23	31	1		21	89	mushroom, musty	1-octanol
15	1090	39	6				5			fruity, floral	linalool
16	1096	24	9		10	18	9		17	citrus, floral	cis-rose oxide
17	1104		6		3	2	6	4		floral	phenethyl alcohol
18	1127			43	13	2		47	12	wood	nerol oxide
19	1165		60				5		6	floral, yeast	ethyl benzoate
20	1176			22				16		green, citrus	ethyl octanoate
21	1184	100	87	78	100	100	51	98	100	petrol	decanal
22	1228	3	15			7		4	18	caramel	ethyl phenylacetate
23	1240					2				floral	2-phenethyl acetate
24	1300	21	14	33	7			37	6	clove	4-vinylguaiacol
25	1350		8				4		7	coconut	γ-nonalactone
26	1372	85	84	58	63	59	100	100	59	pear	$\beta$ -damascenone
27	1444		37	57				29	9	floral	geranyl acetone
28	1455						5			fruity	ethyl cinnamate
29	1481					1				floral	$\beta$ -ionone
30	1658						2			floral	unknown 1658
31	1722	44			1				6	black pepper	unknown 1722
32	1761						4			floral	unknown 1761

"No value indicates the compound was not detected in the top 15 by that judge for that wine.

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In total, 32 odor events were identified by combining all compounds in each of the top 15 lists in Vidal and Riesling icewine and table wine (Table 3). Of these 32 compounds, 24 and 23 odor events were found in Vidal and Riesling wines, respectively. Four compounds identified in the top 15 of Vidal wines were not found in Riesling: ethyl 2-methylbutyrate, isoamyl acetate, ethyl valerate, and 1-heptanol. Similarly, three odor-active volatiles, 2-phenylethyl acetate, ethyl cinnamate, and  $\beta$ -ionone, were identified in the Riesling top 15 but were not found in Vidal. The results do not imply that the above-mentioned compounds are not present in Vidal and Riesling wines, because in most cases they are, only that they were not the most odor-potent and therefore were not listed in the top 15 odor events in any wine by either judge for the other cultivar.

Five odor events could not be identified because no chromatographic peak was recorded by MS to associate with the odor peak. It is well-known that the human nose is a more sensitive detector than a GC-MS for certain compounds;<sup>35</sup> therefore, it is not surprising or uncommon to have unidentified odor events. These five unknowns, on the basis of their linear retention indices, were named by those numbers: unknowns 1018, 1027, 1658, 1722, and 1761 (Table 3). Unknown 1722, detected in both Vidal and Riesling wines, was described as smelling of black pepper. However, no compound could be detected by the SCAN mode of the GC-MS that matched the mass spectrum, odor perception, and retention time. No further study was conducted to determine the identities of the five unknowns.

Only two odor events were found in all wines by both judges through CharmAnalysis, decanal and  $\beta$ -damascenone. Both had high odor potency, listed in the top three odor-potent events in all cases. Decanal had the highest odor potency value (OSV = 100) in Vidal and Riesling icewine by judge 1 and Vidal and Riesling table wine by judge 2. Decanal was described as having a petroleum, vinyl/plastic, citrus, green aroma.  $\beta$ -Damascenone had the highest odor potency in Riesling icewine by judge 1, and in table wine by judge 2, it was described as a distinct pear aroma.

Ethyl 3-methylbutyrate, 1-hexanol, 1-octen-3-ol, ethyl hexanoate, and 1-octanol were five compounds that were odorpotent in almost all cases; they were missing from only one wine. 1-Hexanol was found to be the second most odor-potent aroma in Vidal and Riesling icewine by judge 1. 1-Octanol was the most odor-potent compound in Vidal table wine by judge 1. Other odor-potent compounds found in most wines were *cis*-rose oxide, phenethyl alcohol, nerol oxide, ethyl phenylacetate, and 4-vinylguaiacol (Table 3).

The fruity, sweet-smelling esters, ethyl isobutyrate, ethyl butyrate, and ethyl 2-methylbutyrate, were found to have more odor potency in table wines than in icewines for both Vidal and Riesling. Ethyl 2-methylbutyrate was found to be the most odor-potent compound in Vidal table wine by judge 1. Similarly, the clove-smelling 4-vinylguaiacol and floral-smelling geranyl acetone were more odor-potent in Riesling table wine than in icewine. The reverse was found with acetophenone, which had higher odor potency in the icewines than in table wines.

**GC-MS.** The odor-potent compounds determined through GC-O analysis were quantified and their odor activity values (OAVs) determined on the basis of published sensory thresholds (Table 4).

Statistical analysis (t test) found that Vidal icewines and table wines were different for 22 of 24 compounds; only ethyl isobutyrate and 1-hexanol were not different. Vidal icewine had a higher concentration of most compounds, 15 of the 22 different compounds, than the table wine. Ethyl butyrate, isoamyl acetate, ethyl hexanoate, acetophenone, ethyl octanoate, decanal, and 4-vinylguaiacol had a higher concentration in the table wine than in the icewine. No compounds were unique to either wine style for Vidal.

Riesling icewines and table wines were different for 18 of 23 compounds quantified. Five compounds, ethyl isobutyrate, ethyl butyrate, ethyl 3-methylbutryate, 1-hexanol, and acetophenone, were not different. Similar to Vidal, 14 of the 18 compounds had higher concentrations in icewine than in table wine. Only ethyl hexanoate, ethyl octanoate, decanal, and geranyl acetone had higher concentrations in table wine. Riesling icewine had one unique compound, 1-octanol, which was not detected in the table wine.

Both Vidal and Riesling table wine had higher concentrations of ethyl hexanoate, ethyl octanoate, and decanal than in icewine. The table wine concentrations were 82 and 21% higher for ethyl hexanoate, 260 and 132% higher for ethyl octanoate, and 1300 and 368% higher for decanal in Vidal and Riesling, respectively. The reverse was found for 1-octen-3-ol; its concentrations were over 2500 and 300% higher in Vidal and Riesling icewines, respectively, than in table wines.

 $\beta$ -Damascenone, linalool, and *cis*-rose oxide have all been previously identified as odor-potent compounds in Vidal and Riesling wines.<sup>7</sup>  $\gamma$ -Nonalactone, ethyl phenylacetate, and isoamyl acetate are important impact odorants identified in other wine styles and were found to be odor-potent in these commercial wines. With the exception of isoamyl acetate, which had 20% higher concentration in Vidal table wine, all of these compounds had higher concentrations in the Vidal and Riesling icewines.

Large concentration differences were found between Vidal and Riesling icewines and table wines. Vidal showed larger concentration differences between table wine and icewine than Riesling (Table 4).

**Odor Activity Values.** The concentration of each compound was divided by its sensory threshold (Table 5) to determine its odor activity value (Table 4). Any OAV > 1 is considered to be above its sensory threshold and is said to contribute to the aroma of the product. The higher the value >1, the more potent or dominant a compound will be. Vidal icewines and table wines had 15 and 14 compounds, respectively, above their sensory threshold (OAV > 1). Linalool and ethyl 2-methylbutyrate were above their sensory thresholds for icewine but not table wine, and decanal was found above its sensory threshold only in Vidal table wine. Riesling ice wine and table wine were found above their sensory thresholds for the same 12 compounds.

The highest OAVs in Vidal and Riesling icewines were determined for  $\beta$ -damascenone (902 and 186, respectively), and ethyl octanoate had the highest OAVs (533 and 205, respectively) in table wines.  $\beta$ -Damascenone had the second highest OAV in both table wines (224 for Vidal; 78 for Riesling). Ethyl octanoate had the second highest OAV in Riesling icewine (88) and the third highest OAV in Vidal icewine (147). Other compounds with high OAVs for Vidal icewine were 1-octen-3-ol and *cis*-rose oxide, both with OAVs > 100. Vidal was found to have higher OAVs than Riesling for the most odor potent compounds (Table 4).

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compound			Vidal				1	Riesling		
compound	concn (	(μg/L)	OA	V		concn	(µg/L)	OA	V	
•	TW	IW	TW	IW	significance	TW	IW	ΜŢ	IW	significance
ethyl isobutyrate	$72.3 \pm 0.7$	$71.3 \pm 0.2$	4.82	4.75	su	$189 \pm 0.2$	$189 \pm 0.5$	12.6	12.6	su
ethyl butyrate	$162 \pm 3$	$78.6 \pm 0.1$	8.09	3.93	* *	$137 \pm 0.4$	$137 \pm 0.2$	6.87	6.86	su
ethyl 2-methylbutyrate	$14.2 \pm 0.8$	$27.4 \pm 0.5$	0.79	1.52	*					
ethyl 3-methylbutyrate	$25.3 \pm 0.3$	$29.9 \pm 0.5$	8.43	9.97	*	$24.1 \pm 0.3$	$23.8 \pm 0.5$	8.03	7.92	su
1-hexanol	$1707 \pm 74$	$1513 \pm 1.8$	0.21	0.19	su	$727 \pm 16$	$773 \pm 30$	0.09	0.10	su
isoamyl acetate	$205 \pm 9.2$	$173 \pm 1.5$	6.83	5.77	*					
ethyl valerate	$2.06 \pm 0.3$	$9.70 \pm 0.6$	1.38	6.47	*					
1-heptanol	$7.94 \pm 0.1$	$28.6 \pm 1.3$	2.65	9.55	*					
1-octen-3-ol	$6.97 \pm 0.1$	$188 \pm 4.9$	6.97	188	***	$4.58 \pm 0.1$	$18.5 \pm 1.3$	4.59	18.5	*
ethyl hexanoate	$878 \pm 28$	$480 \pm 30$	62.7	34.3	*	$461 \pm 4.9$	$381 \pm 14$	32.9	27.2	*
acetophenone	$1.84 \pm 0.1$	$1.50 \pm 0.5$	0.03	0.02	*	$1.94 \pm 0.1$	$1.93 \pm 0.02$	0.03	0.03	su
1-octanol	$9.34 \pm 0.2$	$10.6 \pm 0.1$	0.09	0.10	*	pu	$4.78 \pm 0.1$		0.04	* *
linalool	$12.8 \pm 0.1$	$46.9 \pm 2.1$	0.51	1.88	*	$34.3 \pm 0.1$	$50.3 \pm 0.2$	1.37	2.01	* *
cis-rose oxide	$5.03 \pm 0.1$	$22.2 \pm 1.2$	25.2	111	*	$0.63 \pm 0.01$	$2.24 \pm 0.2$	3.16	11.2	**
phenethyl alcohol	$15274 \pm 256$	$20140 \pm 6.7$	1.09	1.44	*	$16102 \pm 97$	$16853 \pm 182$	1.15	1.20	*
nerol oxide	$6.98 \pm 0.1$	$25.8 \pm 1.5$	0.002	0.01	*	$18.3 \pm 0.4$	$30.9 \pm 0.6$	0.01	0.01	**
ethyl benzoate	$0.65 \pm 0.03$	$3.36 \pm 0.22$	0.001	0.01	*	$0.95 \pm 0.01$	$1.19 \pm 0.1$	0.002	0.002	*
ethyl octanoate	$2665 \pm 13$	$739 \pm 65$	533	148	**	$1025 \pm 23$	$441 \pm 28$	205	88.3	*
decanal	$13.7 \pm 0.5$	$0.95 \pm 0.2$	6.84	0.48	**	$1.59 \pm 0.1$	$0.34 \pm 0.2$	0.80	0.17	* *
ethyl phenylacetate	$4.29 \pm 0.1$	10.00.4	0.06	0.14	*	$7.14 \pm 0.2$	$8.69 \pm 0.1$	0.10	0.12	*
2-phenethyl acetate						$4.79 \pm 0.01$	$9.21 \pm 0.1$	0.02	0.04	***
<i>p</i> -vinylguaicol	$111 \pm 1.6$	$81.2 \pm 1.5$	1.11	8.12	*	$79.1 \pm 0.1$	$82.4 \pm 0.1$	7.91	8.24	* *
$\gamma$ -nonalactone	$2.78 \pm 0.01$	$8.02 \pm 0.1$	0.09	0.27	**	$15.4 \pm 0.1$	$17.9 \pm 0.1$	0.51	0.60	***
eta-damascenone	$11.3 \pm 0.6$	$45.1 \pm 1.0$	225	902	**	$3.89 \pm 0.1$	$9.30 \pm 0.2$	77.8	186	* *
geranyl acetone	$0.26 \pm 0.01$	$0.30 \pm 0.01$	0.004	0.01	*	$0.33 \pm 0.01$	$0.23 \pm 0.1$	0.01	0.004	*
ethyl cinnamate						$4.71 \pm 0.01$	$5.99 \pm 0.2$	4.28	5.45	*
eta-ionone						$0.03 \pm 0.00$	$0.06 \pm 0.01$	0.33	0.71	*

Table 5. Odor Perception and Sensory Threshold of Aroma Compounds Used for Compound Identification and Calculation of Odor Activity Values

compound	odor perception	odor threshold ( $\mu$ g/L)	ref
ethyl isobutyrate	sweet	15	53
ethyl butyrate	apple	20	34
ethyl 2-methylbutryrate	apple	18	53
ethyl 3-methylbutyrate	fruit	3	53
1-hexanol	green, resin	8000	34
isoamyl acetate	banana	30	34
ethyl valerate	fruity	1.5	56
1-heptanol	nutty, green	3	52
1-octen-3-ol	mushroom	1	51
ethyl hexanoate	apple, fruit	14	53
acetophenone	flower, almond	65	51
1-octanol	chemical, burnt	110	51
Linalool	floral	25	53
cis-rose oxide	lychee, rose	0.2	34
phenethyl alcohol	honey, spice	14000	53
nerol oxide	oil, flower	3000	55
ethyl benzoate	floral, fruit	575	53
ethyl octanoate	fruity	5	53
decanal	soap, tallow	2	52
ethyl phenylacetate	fruit, sweet	73	57
2-phenethyl acetate	rose, honey	250	34
4-vinylguaiacol	clove, curry	10	53
$\gamma$ -nonalactone	coconut, peach	30	54
$\beta$ -damascenone	apple, rose	0.05	34
geranyl acetone	magnolia, green	60	51
ethyl cinnamate	honey, spice	1.1	53
$\beta$ -ionone	floral (violet)	0.09	53

Some compounds with high Charm or OSV value (and therefore deemed odor-potent through CharmAnalysis analysis) were not found to have OAVs > 1, and therefore are considered to be below their sensory thresholds. However, all compounds were detected as odor-active by the judges through GC-O analysis because they were identified by their aromas as they eluted from the column. Decanal, 1-hexanol, and 1-octanol are three such compounds that were among the most odor-potent compounds found through GC-O but having low OAVs. Decanal was found above its sensory threshold (OAV = 6.8) only in Vidal table wine. 1-Hexanol and 1-octanol were not found above their sensory thresholds (OAV > 1) in any wine.

## DISCUSSION

Comparison of GC-O to OAV Results. The most potent odorants determined by CharmAnalysis were decanal,  $\beta$ -damascenone, and 1-hexanol in Vidal and Riesling icewines and table wines. Calculation of OAVs gave a different pattern of odor potency. Whereas  $\beta$ -damascenone had a high OAV and was the most odor-potent compound in Vidal and Riesling icewines and the second-most potent compound in table wines, decanal, 1-hexanol, and octanol all had OAVs < 1 with the exception of Vidal table wine, which had an OAV of 6 for decanal. Therefore, on the basis of OAV, those compounds found to be highly odor-potent by Charm are not considered to contribute to the aroma of the wine on the basis of their calculated odor activity. Other potent odorants determined by CharmAnalysis were 1-octen-3-ol, cis-rose oxide, ethyl 2- and 3-methylbutyrate, ethyl hexanoate, nerol oxide, ethyl phenylacetate, and 4-vinylguaicol. High OAVs in icewines were found

for 1-octen-3-ol, ethyl octanoate, *cis*-rose oxide, and ethyl hexanoate and in table wines for ethyl octanoate followed by  $\beta$ -damascenone, ethyl hexanoate, *cis*-rose oxide, and 4-vinyl-guaiacol.

Discrepancies between GC-O and OAV are not uncommon due to a variety of factors. The Charm response will differ from the sensory response of a wine because the volatility of compounds in the GC effluent is 100%, whereas the volatility of compounds in the wine matrix may differ due to the extraction method, especially if the volatiles are not extracted from the headspace of the wine.<sup>4</sup> Dilution analysis methods such as CharmAnalysis are based on a linear correlation between odor intensity and concentration. It has been shown that this relationship is logarithmic and better explained by Stevens' power law<sup>36</sup> than dilution analysis.<sup>37</sup> It is therefore considered necessary to compare quantitative results through conversion to OAV to determine the real contribution of various compounds to the aroma.<sup>38</sup> OAVs are thought to be more representative of a food (wine) matrix because they consider concentration and sensory threshold, but this too has its shortcoming.<sup>2,39</sup>

Whenever possible, the sensory thresholds were taken from the literature in a model wine solution. However, in some case this was not possible, which may explain some of the discrepancies between differences in the odor potency determination by Charm and OAV. Because OAVs were determined from published sensory thresholds and not conducted in this study, there could be matrix effects that affect the sensory detection threshold of a compound, either inflating or suppressing its importance. The high sugar concentration of the icewine may be one of these matrix effects that affect how aromas are perceived. This is a potential area of future research. 1-Hexanol was found to be odor-potent through Charm, but due to the published sensory threshold of 8000  $\mu$ g/L in a 10% ethanol solution<sup>40</sup> was not found to have an OAV > 1. The concentration of 1-hexanol in the experimental wines ranged from 700 to 1700  $\mu$ g/L, well below the published sensory threshold. Because the concentration of 1-hexanol was not found to differ between table wines and icewines, it was not a compound that could be used to characterize either wine style.

Escudero et al.<sup>39</sup> aimed to characterize the aroma of Maccabeo wine and found, similar to this study, that not all compounds with high flavor dilution (FD) were found to have OAV > 1. In fact, they found that having a high OAV is not necessary and does not mean that a compound will affect the aroma of a wine. The results of this study found the most potent odorants by GC-O aroma extract dilution analysis and OAV were not able to elicit the same sensory perception in reconstitution studies, nor were they found to be impact odorants by omission and addition studies. Two compounds with low FD and OAV values, 4-mercapto-4-methylpent-2-one and 2-methyl-3-furanthiol, contributed most to the aroma of the wine. They proposed the concept of an aroma buffer in wine. This buffer is a mix of ethanol, esters, acids, volatile phenols,  $\beta$ -damascenone, and fusel alcohols, which can only be broken by a compound with very different aroma properties adding a new aroma perception to the wine. The same could be true for Vidal and Riesling wines, however; reconstitution, omission, and additional studies were not conducted on these wines. Therefore, this could be an area of future research to validate this hypothesis.

Decanal results from fatty acid degradation during fermentation and has not previously been identified as a potent

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odorant in either Vidal or Riesling wines. Decanal could have a low OAV due to bad extraction or quantification because it elutes very close to ethyl octanoate and, therefore, its odor potency is underestimated. Another explanation for the low OAV of decanal, even though it was found to be highly odor potent in experimental wine, may be due to its interaction with ethanol. Ethanol has the power to enhance the odor of some volatiles such as decanal.<sup>3</sup> The aroma buffer previously mentioned could also account for these discrepancies.

Odor-Potent Compounds. The Charm values and OAVs of the icewines and table wines differed for many attributes. In general, the icewines were found to have higher ratings than table wines for most compounds; this is not surprising considering icewines are characterized by their intense aroma profiles. In addition, pressing icewine grapes frozen would concentrate the volatile fraction of the must and wine, leaving most of the water behind as ice. Genovese et al.41 found that sweet Fiano wines, made from later harvested (26 °Brix), semidried to 32 °Brix, 20% Botrytis-infected grapes, had higher concentrations of terpenes,  $\beta$ -damascenone, lactones, aldehydes, and ketones than wine made from base Fiano wine (22 °Brix). They attributed the higher concentrations in the sweet, passito-style, wines to the over-ripeness and drying process of the grapes, resulting in the concentration of the aromatic compounds in the skins and facilitating an easier transfer to the must during winemaking. These conditions would be analogous to icewine grapes hanging throughout the fall before freeze events occur.

 $\beta$ -Damascenone was a highly potent odorant in Vidal and Riesling icewine and table wine as determined by both Charm and OAV in this study. This is consistent with previous GC-O analysis of Vidal and Riesling table wines;<sup>7,42,43</sup> however,  $\beta$ -damascenone was not previously identified in icewine.<sup>18</sup> The result of carotenoid breakdown, the C13 norisoprenoid,  $\beta$ -damascenone, is released through enzymatic or acid hydrolysis during fermentation and wine aging from its grape glycoconjugate precursors. It has an extremely low sensory threshold (0.05  $\mu$ g/L) and has been widely reported in natural products. Generally,  $\beta$ damascenone is not an impact odorant; it is found to have a high OAV but does not contribute a distinct character to the wine in sensory studies.<sup>6,39,40</sup> Whereas  $\beta$ -damascenone does possess a distinct aroma, it requires a large change in concentration to perceive a significant change in its intensity.<sup>39</sup> In red wine,  $\beta$ -damascenone has been shown to enhance the fruity character while suppressing the green, vegetal notes of methoxypyrazines.<sup>44</sup> The concentration of  $\beta$ -damascenone in Vidal icewine was 300% higher than in table wine' perhaps this concentration is great enough to break the aroma buffer proposed by other researchers.<sup>39</sup> Only future research will be able to address these questions.

Terpenes, like norisoprenoids, contribute to wine aroma as free odor-active compounds present in the grapes and as glycosidically bound nonvolatiles released during processing and storage. Terpenes found to be odor-potent in this study were linalool and *cis*-rose oxide with high Charm values and OAV > 1. Nerol oxide was found in the top 15 compounds for Vidal and Riesling wines but had OAV < 0.01 due to its high sensory threshold reported in the literature. All three terpenes were found to have higher concentrations in icewines than in table wines. *cis*-Rose oxide and linalool are both impact odorants in white wine cultivars Gewurztraminer<sup>6,40</sup> and Muscat,<sup>45</sup> respectively. The terpene composition of grape cultivars provides them with a "fingerprint" by which they can be identified regardless of grape maturity, vintage, or origin.<sup>46</sup> Although linalool has been previously reported as odor-potent through GC-O analysis,<sup>7,43</sup> no specific impact compound has been related to either Vidal or Riesling wines.

Esters and alcohols are the main aroma compounds originating from yeast metabolism during fermentation. Esters generally provide fruity and citrus aromas to the wine and are found to contribute to the base aroma of the wine and not as an impact odorant with the exception of isoamyl acetate and ethyl phenylacetate.<sup>47</sup> Ethyl octanoate and ethyl hexanoate were the two most odor-potent esters in the experimental wines, with higher OAV and concentrations in table wines than in icewines for Vidal and Riesling.

Ethyl hexanoate and 2-phenethyl alcohol were found in high levels in Gewurztraminer wines, likely a result of fermentation, and were found to vary among wine samples, suggesting the differences in winemaking can affect their concentration.<sup>6</sup> These compounds were previously found to contribute to the wine bouquet resulting from fermentation and therefore were not suitable for the identification of wine origin or grape cultivar; that is, they were not impact odorants.48 Ethyl hexanoate, ethyl butyrate, ethyl octanoate, and ethyl decanoate form a family of compounds produced from the same metabolic pathway and demonstrate similar aromas; together in a group our noses cannot differentiate one from another.<sup>47</sup> As a result, it is not possible to determine their individual sensory impacts or odor potencies in a wine matrix. Therefore, even though ethyl octanoate was found to have the highest OAV in table wine by GC-O, this does not mean that removing it will alter the sensory perception of the wine because the other esters are still present in the aroma matrix of the product.

1-Octen-3-ol has a mushroom aroma and was found to have much higher concentration and odor activity in icewine than in table wine for Vidal and Riesling. 1-Octen-3-ol has been associated with Botrytis-affected wines as an impact odorant,<sup>1</sup> with wines made from grapes infected with powdery mildew (Uncinula necator)<sup>49</sup> and with fungal infections in grapes and musts.<sup>50</sup> The concentration of 1-octen-3-ol is unaffected by fermentation, unlike 1-octen-3-one; therefore, if present in the must, it will be present in the finished wine.<sup>49</sup> Its concentrations were 27 and 4 times greater in Vidal and Riesling icewines, respectively, with the second highest OAV in Vidal icewine and the fourth highest in Riesling icewine. The higher concentration and odor potency of this compound in icewines is best explained by the presence of Botrytis. A similar result was found by comparing the concentration of sweet Fiano wine to base Fiano wines in the Campania region of southern Italy, where the concentration of 1-octen-3-ol was over 5500% higher in the sweet, passito-style, wine.<sup>41</sup>

4-Vinylguaiacol is a volatile phenol with an influence on wine flavor formed from thermal or enzymatic decarboxylation of cinnamic acid, *p*-coumaric acid, and ferulic acid. This volatile phenol has previously been shown to be odor-potent in Croatian Riesling table wines, contributing a smoky/spicy note.<sup>43</sup>

In general, the most odor-potent compounds found through GC-O in this study,  $\beta$ -damascenone, ethyl octanoate, ethyl hexanoate, ethyl butyrate, ethyl 2-methylbutyrate, ethyl 3-methylbutyrate, phenylethyl alcohol, 4-vinylguaiacol, and linalool, have been previously identified in Vidal and Riesling table wines.<sup>7,42,43</sup> To date, only one study has performed GC-O on icewines, which identified 34 volatiles as odor active in Vidal and Riesling icewines, and it was concluded that no single impact compound was found and that icewine aroma was a

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complex interaction of the many volatiles present in the wine.<sup>18</sup> Although our findings would support that research, the list of volatiles identified in this study as odor-active are quite different; in fact, with the exception of several esters, no compounds are shared. This is most likely due to different extraction methods and GC-O methodologies. By using dilution analysis compared to frequency detection, only the most odorpotent compounds were identified in this study. Many of these compounds had low concentrations; for example,  $\beta$ -damascenone, linalool, *cis*-rose oxide, and 1-octen-3-ol and eluted close to large acid and ester peaks, which at the undiluted concentrations the aroma perceptions could have been combined with the larger peak on the mass spectra and misinterpreted during identification.

In conclusion, Vidal icewine was characterized by 15 odoractive compounds with OAVs > 1; the most odor-active were  $\beta$ -damascenone, 1-octen-3-ol, ethyl hexanoate, *cis*-rose oxide, and ethyl hexanoate. Vidal table wine was characterized by 14 odor-active compounds with OAVs > 1; the most odor-active were ethyl octanoate,  $\beta$ -damascenone, ethyl hexanoate, *cis*-rose oxide, and 4-vinylguaiacol. Riesling icewine was characterized by 12 odor-active compounds with OAV > 1;  $\beta$ -damascenone, ethyl octanoate, ethyl hexanoate, 1-octen-3-ol, and ethyl isobutyrate were the most odor-active. Riesling table wine was characterized by the same 12 compounds as Riesling icewines; however, the highest OAVs were mostly associated with esters: ethyl octanoate,  $\beta$ -damascenone, ethyl hexanoate, ethyl isobutyrate, and ethyl-3-methylbutyrate.

This study provides information regarding the volatile composition of two Vidal and two Riesling table wines and icewines; however, we cannot make any conclusions about impact odorants or odor importance, but only the potential sensory significance of the compounds. Table wines had lower concentrations and OAVs for most aroma compounds with the exception of 4-vinylguaiacol, decanal, ethyl octanoate, and ethyl hexanoate. These results can be used as a foundation to determine impact odorants in icewines through reconstitution and omission studies and could be used as markers to identify changes in the odor-active composition of wines related to viticultural and enological practices.

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