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Sensory, olfactometry and comprehensive two-dimensional gas chromatography analyses as appropriate tools to characterize the effects of vine management on wine aroma

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ABSTRACT

For the first time, the influence of different vine management was evaluated in relation to volatile profile and sensory perception through GC × GC/TOFMS, QDA, GC-FID, GC/MS, and GC-O. GC × GC/TOFMS analyses and QDA have shown that a larger spacing between vine rows (2 rather than 1 m), attachment of shoots upwards, and irrigation did not result in wine improvement. Conversely, wines elaborated with grapes from a vine with a lower bud load (20 per plant; sample M1) stood out among the other procedures, rendering the most promising wine aroma. GC × GC/TOFMS allowed identification of 220 compounds including 26 aroma active compounds also distinguished by GC-O. Among them, eight volatiles were important to differentiate M1 from other wines, and five out of those eight compounds could only be correctly identified and quantified after separation in second dimension. Higher levels of three volatiles may explain the relation of M1 wine with red and dry fruits.

1. Introduction

Vine management encompasses viticulture practices aimed at improving the enological quality of grapes. The canopy of the vine, namely the aboveground portion of the vine, consisting of leaves, flowers, fruits, branches, buds, shoots, arms, and trunks, is well known to play a key role in both the light energy capture *via* photosynthesis, and in the microclimate around grapes (Keller, 2010). Indeed, vine vigor has been related to the characteristics of its canopy, and in particular to the balance between vegetative (number of leaves) and reproductive (number of grape bunches) growth, which may be achieved through adequate bud load. In the beginning of each growth cycle, buds generate new shoots, onto which leaves and grapes will later develop. Increase in bud load results in a higher number of shoots and bunches per plant. Accordingly, it can also increase the canopy density and shading of the vine. Under such conditions, the proportion of infertile buds increases, favoring shoots without bunches, and leading to greater vegetative and lower reproductive growth in the next cycle. Contrariwise, lower vegetative growth or lower canopy density allows for greater air circulation, which aids in controlling air humidity, and promoting the exposure of grapes to greater light incidence. Therefore, a reduction in fungal growth and improvement in the uniformity of grape maturation may occur (Smart, 1985).

Canopy management, as part of vine management, is categorized as a set of viticulture practices widely used to avoid excessive foliage density that would shade the fruit zone and turn it more humid. Leaf removal (defoliation) in the fruiting zone is the most applied canopy management strategy, to enhance air circulation and light penetration into the canopy. This practice may occur from the flowering stage until *véraison*, and has been shown to affect various parameters that influence wine quality. For instance, this practice has been shown to increase the phenolic content of Istrian Malvasia (Rescic, Mikulic-Petkovsek, & Rusjan, 2016), Pinot Noir (Feng, Skinkis, & Qian, 2017), Nero di Troia (Baiano et al., 2015) and Tempranillo (Vilanova, Diago, Genisheva, Oliveira, & Tardaguila, 2012) wines. Furthermore, defoliation has also been associated with increased sugar concentration and decreased volatile acidity in Nero di Troia (Baiano et al., 2015) and Tempranillo (Moreno et al., 2017; Vilanova et al., 2012) wines. Despite

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the advantages of defoliation, it is important to note that leaf removal in the fruit zone or the apical shoot trimming is not excessive. In general, the grapevine needs 1.2 square meters of leaf surface to maintain the ripening of 1 kg of grapes (Keller, 2010). However, this ratio can vary between cultivars and cultivation conditions.

Aroma, an important parameter in wine quality, may be evaluated through sensorial and chromatographic techniques. Quantitative descriptive analysis (QDA) is one of the most informative tools used in the sensory evaluation of a product. In QDA a comprehensive description of the characteristics of aroma, appearance and flavor of a given wine is performed by a panel of selected and trained judges using an intensity scale (Stone, Sidel, Oliver, Woolsey, & Singleton, 1974). Data obtained by sensory evaluation may be linked to findings gathered using the olfactometric technique, in order to find the aroma-active compounds of a wine. Gas chromatography–olfactometry (GC-O) has been used to study odoriferous compounds that were previously identified mainly with one-dimensional GC (1D-GC) (Gürbüz, Rouseff, & Rouseff, 2006). However, previous studies have shown that wine is a complex matrix, and that co-elutions of volatile compounds may occur in 1D-GC, leading to problematic identification/quantification of co-eluted peaks, which might be resolved with the use of comprehensive two-dimensional chromatography with a time-of-flight mass spectrometric detector (GC × GC/TOFMS) (Nicolli et al., 2015; Welke, Manfroi, Zanus, Lazarotto, & Alcaraz Zini, 2012a; Welke, Zanus, Lazzarotto, & Alcaraz Zini, 2014a).

Association of GC-O and GC × GC/TOFMS data may help to resolve co-elutions and consequently, may also help the identification of compounds in regions indicated by sensory judges, as odor-active, in GC-O analyses (Chin, Eyres, & Marriott, 2011; Villiere et al., 2012). In a former study, 334 volatile compounds were found in commercial Merlot wines from the Serra Gaúcha region (Brazil) through analysis with GC × GC/TOFMS (Welke et al., 2012a). Among these compounds, 17 aroma-active compounds, previously appointed by GC-O analysis as important to Merlot aroma, were only correctly identified and quantified by means of GC × GC/TOFMS, due to co-elutions with other sample compounds (Welke, Nicolli, Barbará, Marques, & Zini, 2017).

The combined use of GC × GC/TOFMS and GC-O was also adopted by Chin et al. (2011) to analyze Shiraz wine from Australia. In that work, eleven aroma-active compounds were identified after the heart-cutting of some regions of the chromatogram (acetic acid, 1-octen-3-ol, ethyl octanoate, methyl-2-oxo-nonanoate, butanoic acid, 2-methylbutanoic acid, 3-methylbutanoic acid, 3-(methylthio)-1-propanol, hexanoic acid, β-damascenone, and ethyl-3-phenylpropanoate). The combined use of QDA and 1D-GC with detection by mass spectrometry and olfactometry towards the study of wine aroma has also already been reported in the literature (Escudero, Campo, Fariña, Cacho, & Ferreira, 2007; Raposo et al., 2016). Escudero et al. (2007) used QDA to understand the role of some groups of odorants on aroma perception of Spanish assemblage aged red wines. The authors identified volatile compounds by gas chromatography with mass spectrometric detector (GC/MS) and GC-O; furthermore, the fruity character of these wines was found to result from the interactions among esters, norisoprenoids, dimethyl sulfide, and ethanol. Raposo et al. (2016) combined QDA, GC/MS, and GC-O to evaluate the influence of replacing SO_2 by a natural extract, named Vineatrol®, on wine aroma. Wines treated with Vineatrol® showed in QDA higher savory intensity, bitterness, astringency and persistence compared to wines treated with SO_2.

To date, only a few studies have evaluated the influence of canopy management on volatile profile, using GC/MS and odor-activity value calculations. Indeed, previous studies have been focused only on leaf removal and volatile profiling (Feng et al., 2017; Moreno et al., 2017; Vilanova et al., 2012). For instance, Feng et al. (2017) highlighted greater concentrations of linalool (floral odor), α-terpineol (floral odor) and β-damascenone (sweet/fruity) in Pinot Noir wine in addition to the highest levels of fruity esters (ethyl octanoate, isoamyl acetate and 2-phenethyl acetate) as compared to Tempranillo wines reported by Vilanova et al. (2012). Moreno et al. (2017) reported an increased concentration of two fruity esters (ethyl butanoate and ethyl hexanoate) in Tempranillo wines. The authors also reported enhancements in 3-methyl-1-butanol (odor described as alcohol/solvent), 2-methylbutanoic acid, and hexanoic acid (both acids, with cheesy odor), as negatively influencing the aroma of wines.

The main objective of the present study was the combined evaluation of three different parameters related to vine canopy management (bud load in single and double space between vines in the planting row; leaf area reduction by apical trimming in different number of leaves per shoot; and trained canopy with and without vertical attached shoots) on the volatile composition and aroma of Merlot wines through sensory, olfactometry, GC, and GC × GC analyses. This is the first report relating information gathered from various platforms (QDA, GC/MS, gas chromatography with flame ionization detector (GC-FID), GC-O and GC × GC/TOFMS) to comprehensively elucidate the volatile profiles of Merlot wines and their associated sensory perception as a result of the influence of different canopy management practices.

2. Materials and methods

2.1. Reagents and chemical standards

Standard compounds purchased from Aldrich (Steinheim, Germany) included isobutanoic acid (2-methylpropanoic acid), isovaleric acid (3-methylbutanoic acid), valeric acid (pentanoic acid), hexanoic acid, octanoic acid, nonanoic acid, dodecanoic acid, 1-hexanol, (*Z*)-2-hexen-1-ol, 1-nonanol, benzyl alcohol, 1-dodecanol, ethyl 3-methylbutanoate, hexyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, diethyl succinate (diethyl butanedioate), 2-phenylethyl acetate, ethyl dodecanoate, furfural, 2-furanmethanol, 2-heptanone, 2(5*H*)-furanone, 4-ethylphenol, eucalyptol, α-terpineol, citronellol, β-damascenone, geraniol, guaiacol, 3-mercaptohexanol. The purity of all listed compounds was higher than 98%.

Model wine was prepared as previously reported (Welke et al., 2012a). Standard solutions were prepared in ethanol and diluted in a wine model solution, in order to obtain a matrix similar to wine with regards to percentage of ethanol and acidity. Wine samples possessed a density of 1.1 g mL^{-1}, pH ranging from 3.4 to 3.5, and ethanol content ranging from 11.5 to 13.2% (*v/v*) (Table S1).

The solid-phase microextraction (SPME) fiber, 2-cm 50/30 μm divinylbenzene/Carboxen/polydimethylsiloxane (DVB/CAR/PDMS) StableFlex, was purchased from Supelco (Bellefonte, PA) and conditioned according to the manufacturer's recommendations prior to its first use. Sodium chloride of analytical grade was purchased from Nuclear (São Paulo, Brazil) and oven dried at 150 °C for two hours before use. Twenty-milliliter headspace vials with Teflon septa were purchased from Supelco.

2.2. Vineyard experimental design

Ten different vine treatments involving distinct parameters of vine management (M) were conducted in a vineyard (30° 44′ 52,591″ S and 55° 23′ 49,637″ W) located in Santana do Livramento, Campanha Gaúcha region, Brazil. According to Table 1, treatments were named as M1 to M10, and they were conducted in the same vertical trellis system vineyard of 'Merlot' (*Vitis vinifera* L.) grafted onto SO4 rootstock, during the 2013/14 growth cycle. The experiments were conducted without irrigation and with attachment of shoots upward. Furthermore, two different spaces between vines (1 m and 2 m) were evaluated and two additional treatments were performed, without shoot attaching in a support wire (M6) and using drip irrigation (M10).

Management experiments (M1-M10) were conducted in the vineyard following a randomized block design formed by three areas (in a direction of less slope and almost without influence of the relief, Areas 1, 2 and 3 of Fig. S1) and five blocks (in the direction of greater slope

Table 1
Management treatments (M) of Merlot vine named as M1 to M10 evaluated in relation to the volatile profile of wines from Campanha Gaúcha region, RS, Brazil. Treatments were conducted without irrigation and attaching shoots upwards, except for treatments M6 (shoots were not attached upwards) and M10 (with mechanical irrigation).

managements	soil[a]	spacing (m)[b]	bud load/plant	number of leaves/branch
M1	A B	1 m	20 ± 1	15 ± 1
M2	A B	1 m	30 ± 3	6 ± 1
M3	A B	1 m	30 ± 3	10 ± 1
M4	A B	1 m	30 ± 3	15 ± 1
M5	A B	1 m	30 ± 3	20 ± 1
M6	A B	1 m	30 ± 3	20 ± 1 without tying[c]
M7	A B	1 m	40 ± 3	15 ± 1
M8	A B	2 m	40 ± 2	15 ± 1
M9	A B	2 m	60 ± 5	15 ± 1
M10	A B	1 m	30 ± 3	15 ± 1 irrigation

[a] (A): arenosol soil (sandy) at 170 m above sea level and (B): acrisol soil (clayey) at 180 m above sea level (B).
[b] Spacing between rows of vines.
[c] This treatment was performed without attaching shoots upwards.

and with contrast of relief and soil type, Blocks A-E of Fig. S1). This provided 15 parcels and area of 89.6 m^2 for each parcel. Each parcel contained 32 or 16 plants when the space between vines was 1 or 2 m, respectively. Grapes were harvested from blocks A and B, which represent the highest relief/soil contrast. The vineyard presents a 10 m slope difference between blocks A and B, which results in differences in soil characteristics. According to the International Soil Classification System of Food and Agriculture Organization of the United Nations (IUSS Working Group WRB., 2015), at 170 m the soil was characterized as arenosol, "block A" (sandy), whereas at 180 m altitude, the vineyard soil was predominantly acrisol, "block B" (clayey). Around 14 kg of grapes were harvested from each of the three areas of blocks A and B. Grapes from the three areas of each block were combined and 40 kg of each one of the management experiments (M1–M10) were vinified separately, resulting in 20 microvinifications simultaneously performed.

Grape harvesting period was defined through weekly evaluations of the ripeness level of the grapes, including °Brix, pH and total titratable acidity (TTA). These analyses were done from 15 days after the beginning of color change (*veraison*), for which 50 berries from each parcel of the vineyard (Fig. S1) were obtained from 32 or 16 plants (spacing 1 or 2 m, respectively). The grapes were harvested and directed to vinification when they reached 20 °Brix; pH 3.55; 40 mEq L^{-1} TTA.

Information regarding precipitation, sunshine duration, temperature and humidity during 2013/14 in the region of Santana do Livramento (RS, Brazil), where the vineyard was located is presented in Table S2.

2.3. Wine production

Wines were prepared in Embrapa Grape and Wine, Bento Gonçalves, Brazil, using a traditional winemaking method for red wines (Blouin & Peynaud, 2012). After harvest, grapes were stored for less than 24 h in a cold chamber. Microvinifications were performed in a vertical container of stainless steel similar to those used in industrially produced wines. Grapes obtained from each treatment, as listed in Table 1, were weighed, destemmed and crushed. Individual musts were treated with 80 mg L^{-1} of $K_2S_2O_5$ (Veneto Mercantil Importadora, Bento Gonçalves, Brazil) for one hour. Subsequently, 150 mg·L^{-1} of active dry yeast *Saccharomyces cerevisiae* (Maurivim PDM®, Amazon Group, Monte Belo do Sul, Brazil) was added to 20-L glass bottles fitted with Muller valves.

Each must was fermented and macerated for 14 days at 25.0 ± 2 °C and its evolution was monitored daily by the measurement of density using an electronic hydrostatic balance (Super Alcomat, Gibertini Elettronica SRL, Milano, Italy). The fermentation was considered complete when the density became constant and lower than 0.997, which according to Ribéreau-Gayon, Glories, Maujean, and Dubourdieu (2006) corresponds to a residual sugar content lower than the maximum concentration of 5 g L^{-1} that is allowed for dry wine according to Brazilian legislation (Brazil, 2004). After the wine was drawn off, the 20-L bottles were subsequently placed in a cold chamber at 0 °C for six months to allow for stabilization. Each vinification (M1 to M10 obtained from two points of the vineyard, A and B) resulted in 20 L of wine. All microvinification steps were similar to those used in large-scale vinification processes.

Table S1 shows the °Brix of the grapes and the respective physicochemical parameters of resulting wines (pH, total acidity, alcohol content), in accordance with the different management treatments employed during grape cultivation (M1–M10, Table 1).

2.3.1. Determination of wine volatile profile

Volatile compounds were extracted by headspace SPME (HS-SPME) with a 2-cm DVB/CAR/PDMS fiber, according to conditions optimized in previous work (Welke, Zanus, Lazarotto, Schmitt, & Zini, 2012b). In short, one milliliter of wine and 0.3 g of NaCl were placed in a 20-mL headspace glass vial. HS-SPME was carried out at 55 °C for 45 min without agitation throughout the equilibration and extraction. Desorption of volatile compounds occurred in the GC injection port at 250 °C for 5 min. GC × GC/TOFMS, GC-FID, GC/MS, and GC-O were used to determine the volatile profile of Merlot wines and the odoriferous importance of volatile compounds. HS-SPME-GC-O analyses were performed in four replications, using four headspace vials with aliquots of 1 mL of wine from every bottle of wine. One bottle coming from each different wine management was employed for these analyses. Similarly, for GC × GC/TOFMS, GC-FID and GC/MS analyses, three replications of SPME/analysis were made.

2.3.2. Determination of wine volatile compounds by GC × GC/TOFMS

The GC × GC system consisted of an Agilent 6890N (Agilent Technologies, Santa Clara, CA) equipped with a Pegasus IV time-of-flight mass spectrometric detector (Leco Corporation, St. Joseph, MI). Chromatographic conditions were the same as used in a previous study (Welke et al., 2012a) with a polar (DB-WAX, polyethylene glycol, 30 m × 0.25 mm × 0.25 mm) and medium-polar (DB-17ms, 50% phenyl 50% methylpolysiloxane, 1.70 m × 0.18 mm × 0.18 μm) as first and second columns, respectively, of GC × GC. Individual solutions of standard compounds were accurately weighed and dissolved in absolute ethanol, then mixed and diluted with the model wine solution (preparation described in Section 2.1), to achieve the required range of concentration to quantify individual volatile compounds present in wines. Method validation was carried out in accordance with the International Conference on Harmonization (ICH) guidelines (ICH, 2005). Quantification of positively identified compounds was obtained by interpolation of the calibration graphs constructed with the respective pure reference compounds. The concentration ranges of the standard compounds used to obtain the calibration curves are shown in Table S3. A similar procedure was employed for tentatively identified compounds; in this case, the calibration curve of the most structurally similar reference compound was employed for calculation of concentrations of the different compounds.

2.3.3. Determination of aroma compounds by GC-O, GC/MS and GC-FID

The odoriferous importance of the volatiles present in the wine was determined using the OSME (named after the Greek word that means odor, *οσμη*) technique to obtain the GC-O data, as previously described (Welke et al., 2017). A consensus aromagram was built for each wine under study, averaging all peaks detected at least twice by at least two panelists. A QP2010 GC/MS (Shimadzu, Kyoto, Japan) with 6890 GC-FID (Agilent Technologies) was employed to identify the odor-active compounds described by the olfactometry judges, using the same experimental parameters utilized for GC-O.

2.3.4. Data processing

Positive identification of the compounds was carried through comparisons of retention data and mass spectra of standard compounds listed in Section 2.1 and those found in samples. For unavailable standards, tentative identification of wine aroma compounds in 1D-GC as well as with GC × GC analyses was achieved by comparing their experimental retention indices (RI_{exp}) with RI reported in scientific (RI_{lit}) literature (Ledauphin et al., 2004; Selli, Canbas, Cabaroglu, Erten, & Günata, 2006; Welke et al., 2012a). Retention data of a series of *n*-alkanes (C_9–C_{24}, Supelco, Bellefonte, PA), obtained under the same chromatographic conditions employed for the chromatographic analyses of wine volatiles were used for experimental RI_{exp} calculation. A compound was said to be tentatively identified if experimental and reported RI did not differ by more than 15 units. In addition, similarity between mass spectrometric information of each chromatographic peak and NIST (National Institute of Standards and Technology, Gaithersburg, USA) mass spectra library was at least 80%. Ethyl acetate was the only one exception regarding RI differences ($\Delta RI = 18$) in comparison with the NIST mass spectra library, due to column overload, although its mass spectral similarity was higher than 85%. Table S4 presents RI_{exp} and RI_{lit} of volatile compounds of wines. The minimum value for the signal to noise (S/N) ratio necessary to consider a chromatographic peak as detected was set as 3 in 1D-GC, and 30 in GC × GC. As a second criterion for peak detection, only peaks with chromatographic area percentage higher than 0.01% for 1D-GC, and higher than 0.001% for GC × GC were considered as detected. The area percentage of each peak was calculated considering the total area of the chromatographic peaks as 100%.

2.4. Characterization of the wines sensory profile using quantitative descriptive analysis (QDA)

Sensory profiles of Merlot wines prepared using grapes from the above-mentioned different experiments related to canopy management (M1 to M10), were characterized using QDA (Stone et al., 1974). Fifteen well-experienced judges in wine sensory evaluation from the Brazilian Agricultural Research Corporation (Embrapa) were invited to take part in the study. The volunteers were initially screened as described by Biasoto, Netto, Marques, and da Silva (2014). The judges generated a consensual list with 20 sensory descriptors, including their definitions and references for the panel training, using Kelly's Repertory Grid Method (Moskowitz, 1983). In the descriptive ballot for wine evaluation, descriptors were associated with a 9-cm unstructured scale, anchored at the left and right extremes with the terms “none/weak” and “strong”, respectively. The descriptive terms were selected by the panel to characterize the sensory profile of Merlot wines, including appearance (color intensity, red–purple tonality, brightness), aroma (aromatic intensity, undesirable aroma, aroma of red fruits, dry fruits, spice and alcoholic, herbaceous, vegetal, caramel aroma), and taste/mouth sensations (persistence, sourness, bitterness, sweetness, defect in mouth, astringency, body and smell-taste harmony). After the training, a final selection of the panel was carried out, where each panelist evaluated three of the wine samples, in three replications, using the descriptive ballot. Judges that showed adequate discriminative power ($pF_{wine} \leq 0.30$), reproducibility ($pF_{replication} \geq 0.05$) and consensus with the panel for at least 80% of the descriptors were selected to take part in the final panel. Ten judges composed the final panel. Overall, each panelist evaluated each wine sample in six replications, using an incomplete balanced block design for ten treatments (design plan 11.6), as proposed by Cochran and Cox (1957). Wine samples (30 mL) were tested at 18 °C, in wine tasting cups (ISO, 1977), coded with three-digit numbers and covered with watch glasses. The sensorial analyses procedures (QDA and GC-O) were approved by the Research Ethics Committee (CEP/UNIVASF protocol No. 1.346.299/2015 and CAAE 49561715.1.0000.5196), in compliance with Resolution 466/12, of the National Health Council, Brazil.

2.5. Statistical analysis

LECO ChromaTOF version 4.22 software was used for GC × GC/TOFMS acquisition control, data processing and Fisher Ratio calculation. Fisher ratios were calculated as previously described by Welke, Zanus, Lazzarotto, Pulgati, and Zini (2014b). The chromatographic areas of volatile compounds presenting higher Fisher ratio values were employed in principal component analysis (PCA). These compounds were concluded as responsible for the main observed differences among the wines produced using grapes grown under different conditions of canopy management (M1 to M10 as described in Table 1). PCA were run using Statistica for Windows program package (version 7.1; Statsoft, Tulsa, OK, 2005). Data resulting from sensory analyses were also investigated with PCA. These statistical analyses were conducted after mean centering of data, and were used to visualize the similarities and differences of the volatile profiles of wines according to the different treatments of canopy management.

Student's *t*-test tool from Microsoft Excel (version 15.13.3, 2015) was employed to determine if significant differences occurred among the concentrations of volatile compounds that were used in PCA of wines. The same approach was used for the notes attributed to the wines in QDA.

3. Results and discussion

In the first part of this study, all wines (M1 to M10 as presented in Table 1) elaborated with grapes of both soil classes (arenosol (A) and acrisol (B)) were evaluated by QDA, in order to find the wine that would present the best sensory attributes. Samples were also analyzed by GC × GC/TOFMS, in order to verify if the various conditions of canopy management resulted in differences in volatile profile. Subsequently, the wine chosen in QDA as exhibiting highest quality underwent GC-O, GC-FID and GC/MS analyses. Data obtained were used to find out the aroma-active compounds responsible for the sensory quality of this wine and what were the conditions of canopy management that has led to such higher quality.

3.1. Influence of vine management on the volatile profile and sensory profile

Tables 2 and S2 show 220 compounds that were either positively or tentatively identified out of more than 1000 compounds detected in Merlot wines by GC × GC/TOFMS (criteria of data processing and identification of compounds is described in Section 2.3.4). Compounds are listed in Tables 2 and S2 according to their chemical class and in increasing order of RI.

These 220 compounds found in the headspace of 20 Merlot wines from Campanha Gaúcha belong to ten chemical classes, namely esters (50) and alcohols (50) present in higher number, followed by terpenes (44), acids (19), aldehydes (15), ketones (13), lactones (8), phenols (7), furans (7) and sulfur compounds (7). The predominant presence of esters and alcohols has already been observed in a previous study of Merlot volatile profile (94 esters and 80 alcohols) from Serra Gaúcha, Brazil, also analyzed by HS-SPME-GC × GC/TOFMS (Welke et al., 2012a). These two chemical classes of compounds were the two major

Table 2
Positively and/or tentatively identified volatile compounds of Merlot wines of Campanha Gaúcha region, Brazil, using HS-SPME-GC × GC/TOFMS with their respective Chemical Abstract Service (CAS) numbers, retention times in the first (^1t_R) and in the second (^2t_R) chromatographic dimensions, experimental retention index (**RI_{exp}**) and Fisher ratio values. Chromatographic conditions are described in Section 2.4. and literature retention indices are defined in Table S4.

#	Compound[a,b]	CAS[c]	^1t_R	^2t_R	RI_{exp}[d]	Fisher ratio	Fisher ratio (%)[e]
acids							
1	acetic acid	64-19-7	26.95	1.76	1461	328	4
2	formic acid **(15)**	64-18-6	29.75	1.69	1529	254	3
3	propanoic acid **(16)**	97-85-8	30.57	1.77	1550	251	3
4	2-methylpropanoic acid [isobutanoic acid] **(18) a**	2445-69-4	31.73	1.82	1579	949	13
5	butanoic acid	107-92-6	34.07	1.82	1639	248	3
6	3-methylbutanoic acid [isovaleric acid] **(22) a**	503-74-2	35.58	1.87	1679	607	8
7	2-methylbutanoic acid **(22)**	116-53-0	35.70	1.87	1682	412	6
8	pentanoic acid [valeric acid] **a**	109-52-4	38.15	1.85	1748	500	7
9	hexanoic acid **(27) a**	142-62-1	42.00	1.95	1856	3908	53
10	2-ethylhexanoic acid	149-57-5	45.50	1.98	1958	510	7
11	heptanoic acid	111-14-8	45.62	1.94	1962	246	3
12	2-hexenoic acid	13419-69-7	46.08	1.88	1976	247	3
13	octanoic acid **(33) a**	124-07-2	49.00	2.09	2067	2168	30
14	nonanoic acid **(35) a**	112-05-0	52.27	2.04	2173	360	5
15	decanoic acid **(36)**	334-48-5	55.42	2.15	2280	244	3
16	9-decenoic acid **(37)**	1443632-9	57.28	2.06	2344	470	6
17	geranic acid	459-80-3	57.40	2.10	2348	628	9
18	benzenecarboxylic acid	6585-0	59.62	1.77	2424	615	8
19	dodecanoic acid **a**	143-07-7	60.32	1.90	2448	1675	23
alcohols							
20	ethyl alcohol	64-17-5	5.60	1.98	921	243	3
21	1-propanol **(1) a**	71-23-8	8.63	2.08	1027	7342	100
22	3-methyl-2-butanol	598-75-4	10.50	3.31	1059	440	6
23	2-methyl-1-propanol	78-83-1	10.85	2.21	1089	379	5
24	2-propen-1-ol	107-18-6	11.78	1.94	1119	447	6
25	2-pentanol	6032-29-7	12.02	2.28	1124	434	6
26	1-butanol	71-36-3	12.95	2.17	1145	964	13
27	1-penten-3-ol **(3)**	616-25-1	13.77	2.15	1163	482	7
28	2-methyl-2-hexanol **(4)**	625-23-0	15.28	2.70	1198	468	6
29	2-methyl-1-butanol **(5)**	137-32-6	15.87	2.47	1210	340	5
30	3-methyl-1-butanol **(5)**	123-51-3	15.98	2.34	1213	445	6
31	2-hexanol	626-93-7	16.57	2.46	1226	441	6
32	3-methyl-3-buten-1-ol **(6)**	763-32-6	17.73	2.19	1251	674	9
33	1-pentanol **(6)**	71-41-0	17.73	2.28	1251	466	6
34	4-heptanol	589-55-9	19.25	2.73	1285	594	8
35	3-heptanol	589-82-2	19.83	2.70	1298	771	11
36	4-methyl-1-pentanol	626-89-1	20.65	2.37	1316	670	9
37	2-heptanol	543-49-7	20.88	2.63	1321	453	6
38	2-penten-1-ol **(8)**	20273-24-9	21.00	2.17	1324	566	8
39	2-methyl-2-buten-1-ol **(8)**	4675-87-0	21.00	2.19	1324	242	3
40	3-methyl-1-pentanol	589-35-5	21.23	2.40	1329	747	10
41	1-hexanol **a**	111-27-3	22.40	2.47	1355	3530	48
42	3-hexen-1-ol **(9)**	544-12-7	22.87	2.38	1366	674	9
43	3-ethoxy-1-propanol	111-35-3	23.33	2.38	1376	238	3
44	2-hexen-1-ol **a**	2305-21-7	25.20	2.29	1419	490	7
45	2-octanol	123-96-6	25.32	2.80	1422	625	9
46	1-octen-3-ol	3391-86-4	26.60	2.60	1453	237	3
47	1-heptanol **(12)**	111-70-6	26.83	2.56	1458	239	3
48	2-ethyl-1-hexanol	104-76-7	28.23	2.71	1492	916	12
49	4-hepten-1-ol	20851-55-2	28.82	2.47	1506	648	9
50	2-nonanol	628-99-9	29.28	2.98	1518	529	7
51	2,3-butanediol **a**	513-85-9	30.33	1.99	1544	3108	42
52	1-octanol **(17)**	111-87-5	31.03	2.70	1562	866	12
53	1,3-butanediol	107-88-0	31.85	1.95	1582	736	10
54	2-(2-ethoxyethoxy)ethanol	111-90-0	33.37	2.50	1621	636	9
55	1-nonanol **a**	143-08-8	35.00	2.84	1664	761	10
56	(*Z*)-6-nonen-1-ol **(23)**	35854-86-5	37.22	2.71	1723	319	4
57	2-undecanol **(23)**	1653-30-1	37.22	3.29	1723	235	3
58	1-decanol	112-30-1	38.85	2.97	1768	233	3
59	(*Z*) -4-decen-1-ol	57074-37-0	40.02	2.88	1800	572	8
60	2-dodecanol	10203-28-8	40.83	3.44	1824	464	6
61	2-butyl-1-octanol **(28)**	08-02-13	42.23	3.26	1864	476	6
62	1-undecanol **(29)**	112-42-5	42.47	3.10	1870	459	6
63	2-methyl-1-undecanol **(29)**	10522-26-6	42.47	3.28	1870	231	3
64	benzyl alcohol **(30) a**	100-51-6	42.93	2.22	1883	1169	16
65	phenylethyl alcohol **(31)**	60-12-8	44.10	2.49	1917	803	11
66	1-dodecanol **a**	112-53-8	45.85	3.26	1969	671	9
67	1-tridecanol **(33)**	112-70-9	49.12	3.41	2071	542	7
68	1-tetradecanol	112-72-1	52.38	3.51	2178	400	5
69	1-hexadecanol	36653-82-4	58.33	3.66	2381	229	3

(*continued on next page*)

Table 2 (*continued*)

#	Compound[a,b]	CAS[c]	^1t_R	^2t_R	RI_{exp}[d]	Fisher ratio	Fisher ratio (%)[e]
aldehydes							
70	2-propenal	107-02-8	4.08	2.02	894	251	3
71	3-methylbutanal	590-86-3	4.90	2.73	913	617	8
72	2-butenal **(1)**	4170-30-3	8.63	2.62	1027	490	7
73	2-methyl-2-butenal	1115-11-3	10.62	3.06	1068	253	3
74	3-methyl-2-butenal	107-86-8	15.40	2.97	1200	537	7
75	nonanal	124-19-6	24.15	4.41	1396	467	6
76	decanal	112-31-2	28.58	4.57	1501	449	6
77	benzaldehyde	100-52-7	29.63	2.94	1527	914	12
78	2,6,6-trimethyl-1-cyclohexene-1-carboxaldehyde	432-25-7	33.25	4.49	1619	803	11
79	benzeneacetaldehyde	122-78-1	34.42	2.96	1649	1577	21
80	dodecanal	112-54-9	36.87	4.83	1714	577	8
81	4-(1-methylethyl)benzaldehyde	122-03-2	39.32	3.57	1781	585	8
82	3-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-propenal	4951-40-0	44.92	3.57	1942	2407	33
83	hexadecanal **(34)**	629-80-1	51.10	5.29	2136	1307	18
84	octadecanal **(37)**	638-66-4	57.28	5.49	2346	254	3
esters							
85	ethyl acetate **a**	141-78-6	4.32	2.47	905	2154	29
86	ethyl propanoate	105-37-3	6.30	3.44	955	519	7
87	ethyl 2-propenoate	140-88-5	7.00	2.88	989	557	8
88	2-methylpropyl acetate	110-19-0	7.58	3.40	1007	585	8
89	ethyl butanoate	105-54-4	8.40	3.72	1021	668	9
90	ethyl 2-methylbutanoate **(2)**	7452-79-1	8.98	4.22	1037	1017	14
91	ethyl 3-methylbutanoate **a**	108-64-5	9.57	4.11	1052	721	10
92	isoamyl acetate	123-92-2	11.90	4.02	1122	886	12
93	ethyl 2-butenoate **(3)**	10544-63-5	13.77	3.53	1164	494	7
94	methyl hexanoate	106-70-7	14.82	4.11	1188	351	5
95	ethyl hexanoate **a**	123-66-0	16.92	4.76	1234	1690	23
96	hexyl acetate **a**	142-92-7	18.78	4.36	1275	514	7
97	ethyl 2-oxopropanoate **(7)**	617-35-6	18.90	2.69	1277	485	7
98	ethyl 2-hexenoate	1552-67-6	21.93	4.40	1346	415	6
99	ethyl 2-hydroxypropanoate	97-64-3	22.05	2.35	1347	858	12
100	methyl octanoate **(10)**	111-11-5	23.92	4.64	1390	261	4
101	ethyl 2-hydroxy-3-methyl-butanoate	07-06-41	25.55	2.74	1428	462	6
102	ethyl octanoate **(11) a**	106-32-1	25.90	5.17	1437	2077	28
103	isoamyl hexanoate **(12)**	2198-61-0	26.83	5.74	1460	265	4
104	ethyl 3-hydroxybutanoate	5405-41-4	29.52	2.41	1524	871	12
105	ethyl nonanoate	123-29-5	30.10	5.28	1539	444	6
106	ethyl 2-hydroxy-4-methylpentanoate **(16)**	10348-47-7	30.57	2.77	1550	855	12
107	isoamyl lactate	19329-89-6	31.50	2.73	1574	1747	24
108	diethyl propanedioate	105-53-3	31.97	3.05	1586	736	10
109	ethyl decanoate **a**	110-38-3	34.07	5.44	1641	266	4
110	ethyl methyl butanedioate **(20)**	627-73-6	34.18	3.06	1643	980	13
111	3-methylbutyl octanoate	2035-99-6	34.88	5.95	1662	645	9
112	ethyl benzoate **(21)**	93-89-0	35.23	3.58	1670	1051	14
113	diethyl butanedioate [diethyl succinate] **(22) a**	123-25-1	35.70	3.38	1682	660	9
114	ethyl 3-hydroxyhexanoate	2305-25-1	35.82	2.77	1685	267	4
115	ethyl 9-decenoate	67233-91-4	36.17	4.82	1695	724	10
116	methyl 2-hydroxybenzoate	119-36-8	39.20	3.25	1778	547	7
117	diethyl pentanedioate	818-38-2	39.55	3.49	1788	467	6
118	ethyl benzeneacetate **(25)**	101-97-3	39.67	3.54	1791	985	13
119	2-phenylethyl formate **(25)**	104-62-1	39.67	3.06	1791	1050	14
120	methyl dodecanoate	111-82-0	40.13	5.20	1804	463	6
121	ethyl 2-hydroxybenzoate	118-61-6	40.48	3.51	1814	434	6
122	2-phenylethyl acetate **(26) a**	103-45-7	40.72	3.45	1821	3033	41
123	ethyl dodecanoate **a**	106-33-2	41.65	5.61	1848	975	13
124	isoamyl pentadecanoate **(28)**	2306-91-4	42.23	6.13	1865	633	9
125	2-phenylethyl 2-methylpropanoate **(30)**	103-48-0	42.93	4.06	1884	611	8
126	diethyl hexanedioate	141-28-6	43.75	3.85	1908	2301	31
127	methyl tetradecanoate	124-10-7	47.13	5.43	2009	779	11
128	diethyl hydroxybutanedioate **(32)**	626-11-9	48.42	2.48	2048	559	8
129	ethyl tetradecanoate **(32)**	124-06-1	48.42	5.83	2050	669	9
130	ethyl 3-phenyl-2-propenoate **(34)**	103-36-6	51.10	3.42	2135	524	7
131	2-phenylethyl hexanoate **(35)**	6290-37-5	52.27	4.29	2174	599	8
132	methyl hexadecanoate	112-39-0	53.55	5.64	2218	271	4
133	ethyl hexadecanoate	628-97-7	54.72	5.99	2258	266	4
134	ethyl hydrogen succinate	1070-34-4	58.68	1.84	2392	275	4
furans							
135	2,3,5-trimethylfuran	10504-04-8	9.10	3.65	1042	1110	15
136	2-pentylfuran	3777-69-3	16.80	4.47	1232	497	7
137	furfural **(13) a**	98-01-1	27.42	2.38	1472	627	9
138	1-(2-furanyl)ethanone **(14)**	1192-62-7	28.93	2.61	1509	792	11
139	5-methyl-2-furancarboxaldehyde **(18)**	620-02-0	31.73	2.70	1580	692	9
140	ethyl 2-furancarboxylate	614-99-3	33.72	2.92	1631	231	3

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Table 2 (*continued*)

#	Compound[a,b]	CAS[c]	^1t_R	^2t_R	RI_{exp}[d]	Fisher ratio	Fisher ratio (%)[e]
141	2-furanmethanol **(21) a**	98-00-0	35.23	2.00	1670	531	7
ketones							
142	2-pentanone	107-87-9	6.53	2.90	965	535	7
143	2,3-butanedione	431-03-8	6.65	2.27	980	505	7
144	3-hexanone **(2)**	589-38-8	8.98	3.54	1037	193	3
145	2,3-pentanedione	600-14-6	9.45	2.63	1048	644	9
146	3-penten-2-one	625-33-2	12.13	2.89	1127	537	7
147	2-heptanone **a**	110-43-0	14.47	3.85	1179	600	8
148	cyclopentanone	120-92-3	14.58	3.36	1182	456	6
149	3-hydroxy-2-butanone	513-86-0	19.37	2.18	1287	508	7
150	6-methyl-5-hepten-2-one	110-93-0	21.70	3.71	1340	539	7
151	2-methyl-2-cyclopenten-1-one **(9)**	1120-73-6	22.87	3.34	1366	489	7
152	2-nonanone **(10)**	821-55-6	23.92	4.30	1390	313	4
153	2,3-dimethyl-2-cyclopenten-1-one	1121-05-7	29.98	3.50	1536	404	6
154	acetophenone	98-86-2	34.53	3.11	1652	233	3
lactones							
155	5-methyl-2(3 H)-furanone [α-angelica lactone] **(11)**	591-12-8	25.90	2.67	1436	234	3
156	butyrolactone	96-48-0	33.83	2.60	1633	936	13
157	5-ethoxydihydro-2(3 H)-furanone **(24)**	932-85-4	37.45	2.83	1729	634	9
158	2(5 H)-furanone [γ-crotolactone] **a**	497-23-4	38.50	2.30	1758	374	5
159	5-butyldihydro-2(3 H)-furanone [γ-octalactone] **(31)**	104-50-7	44.10	3.27	1918	237	3
160	5-pentyldihydro-2(3 H)-furanone [γ-nonalactone]	104-61-0	47.83	3.28	2030	760	10
161	pantolactone	599-04-2	48.07	2.07	2037	452	6
162	5-hexyldihydro-2(3 H)-furanone	706-14-9	51.45	3.38	2147	549	7
phenols							
163	phenol	108-95-2	47.37	1.90	2015	916	12
164	4-ethyl-2-methoxyphenol	2785-89-9	47.95	2.66	2034	271	4
165	4-methylphenol	106-44-5	49.82	2.00	2092	275	4
166	4-ethylphenol **a**	123-07-9	52.62	2.06	2184	481	7
167	2-(1,1-dimethylethyl)-4-methylphenol	2409-55-4	54.37	2.33	2244	455	6
168	2-(1,1-dimethylethyl)-5-methylphenol	88-60-8	55.07	2.33	2268	272	4
169	2,4-bis(1,1-dimethylethyl)-phenol	96-76-4	56.70	2.58	2324	277	4
terpenes							
170	α-thujene	02-05-67	7.82	5.49	1012	577	8
171	α-pinene	7785-70-8	13.53	5.17	1159	490	7
172	limonene	138-86-3	14.93	5.85	1191	512	7
173	eucalyptol **(4) a**	470-82-6	15.28	6.40	1199	1239	17
174	γ-terpinolene	99-85-4	17.15	5.92	1240	570	8
175	β-ocimene **(6)**	13877-91-3	17.73	5.05	1252	491	7
176	*p*-cymene	527-84-4	18.43	5.00	1268	1392	19
177	α-terpinolene **(7)**	586-62-9	18.90	5.95	1278	723	10
178	*p*-cymenene **(11)**	1195-32-0	25.90	4.22	1437	760	10
179	myrcenol **(13)**	18479-58-8	27.42	3.05	1472	414	6
180	camphor **(14)**	464-48-2	28.93	4.74	1510	538	7
181	linalool **a**	78-70-6	30.68	2.95	1553	1283	17
182	dihydro-α-terpineol **(17)**	498-81-7	31.03	3.46	1562	393	5
183	terpinen-4-ol **(19)**	562-74-3	32.67	3.67	1604	230	3
184	aromadendrene **(19)**	25246-27-9	32.67	0.71	1602	235	3
185	hotrienol	29957-43-5	33.13	2.82	1615	795	11
186	menthol **(20)**	15356-70-4	34.18	3.20	1643	231	3
187	β-farnesene	18794-84-8	35.12	6.02	1668	868	12
188	carvotanacetone	499-71-8	35.47	4.33	1677	488	7
189	α-terpineol **a**	98-55-5	36.40	3.21	1700	1391	19
190	isopiperitone **(23)**	89-81-6	37.22	4.08	1723	830	11
191	β-bisabolene	495-61-4	37.33	6.37	1728	715	10
192	(*Z,E*)-α-farnesene **(24)**	26560-14-5	37.45	5.94	1731	680	9
193	carvone	99-49-0	37.57	3.89	1733	633	9
194	(*E,E*)-α-farnesene	502-61-4	38.27	5.79	1753	228	3
195	δ-cadinene	483-76-1	38.38	6.75	1757	226	3
196	citronellol **a**	106-22-9	38.97	2.83	1771	963	13
197	α-curcumene	644-30-4	39.08	5.63	1776	766	10
198	sabinol	471-16-9	40.37	2.91	1810	1398	19
199	β-damascenone **(26) a**	23696-85-7	40.72	4.45	1821	1615	22
200	anethole	104-46-1	41.07	3.63	1831	446	6
201	geraniol **a**	106-24-1	41.88	2.77	1854	535	7
202	geranyl acetone **(27)**	3796-70-1	42.00	4.38	1858	745	10
203	*o*-guaiacol **a**	90-05-1	42.35	2.41	1867	221	3
204	nerolidol	7212-44-4	48.30	3.70	2045	533	7
205	cubenol	21284-22-0	48.65	4.71	2057	227	3
206	elemol	639-99-6	49.47	3.72	2082	222	3
207	spathulenol	77171-55-2	50.75	4.02	2124	281	4
208	τ-cadinol	01-11-37	52.15	4.14	2170	792	11
209	α-bisabolol	515-69-5	53.67	3.98	2221	220	3

(*continued on next page*)

Table 2 (*continued*)

#	Compound[a,b]	CAS[c]	^1t_R	^2t_R	RI_{exp}[d]	Fisher ratio	Fisher ratio (%)[e]
210	carvacrol	499-75-2	53.78	2.27	2224	283	4
211	β-eudesmol	473-15-4	53.90	4.07	2229	619	8
212	α-cadinol	481-34-5	54.02	3.95	2233	755	10
213	aromadendrene oxide **(36)**	85710-39-0	55.53	3.63	2285	287	4
sulfur compounds							
214	*S*-methyl thioacetate	1534-08-3	8.87	2.88	1034	461	6
215	dihydro-2-methyl-3(2 H)-thiophenone **(15)**	13679-85-1	29.75	3.24	1530	285	4
216	2-(methylthio)ethanol	5271-38-5	29.87	2.21	1532	221	3
217	ethyl 3-(methylthio)propanoate	13327-56-5	31.38	3.50	1571	758	10
218	2-thiophenecarboxaldehyde	98-03-3	36.28	2.69	1697	752	10
219	3-(methylthio)-1-propanol **(23) a**	505-10-2	37.22	2.30	1723	4033	55
220	benzothiazole	95-16-9	45.38	3.18	1956	842	11

[a] Positively identified compounds.

[b] Co-elutions were numbered from 1 to 37 and these numbers are written between parentheses after the compound's name. Whenever compounds are followed by the same number, they co-eluted in ^{1}D.

[c] CAS: Chemical Abstract Service.

[d] RI_{exp}: experimental retention index (RI) calculated using *n*-alkanes (C_9–C_{24}) with a DB-Wax (100% polyethyleneglycol) column, as part of a DB-Wax × DB-17 ms ([50%-phenyl]-methylpolysiloxane) column set.

[e] The highest Fisher ratio value is defined as 100% and the others correspond to x%.

classes identified in Merlot wines from Australia through analysis by 1D-GC/MS (28 esters and 19 alcohols among 66 tentatively identified compounds) (Gürbüz et al., 2006).

Fisher ratio values indicated 24 volatile compounds as mainly responsible for the differences among Merlot wines produced using grapes grown under different conditions of canopy management. These compounds that presented Fisher ratio corresponding to at least 15% of the Fisher ratio value of the most discriminant compound (1-propanol, Fisher ratio: 7342) were used in PCA. This approach has been successfully applied to differentiate other types of wines in previous studies (Nicolli et al., 2015; Welke et al., 2014b), and was used to ensure that all volatiles responsible for the differentiation of wines according to the applied canopy management practices were considered in the PCA.

The 24 compounds that presented higher Fisher ratio values were (# refers to the numbers of compounds shown in all tables of this study and are listed in decreasing Fisher ratio order): 1-propanol (#21), 3-methylthio-1-propanol (#219), hexanoic acid (#9), 1-hexanol (#41), 2,3-butanediol (#51), 2-phenylethyl acetate (#122), 3-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-propenal (#82), diethyl hexanedioate (#126), octanoic acid (#13), ethyl acetate (#85), ethyl octanoate (#102), isoamyl lactate (#107), ethyl hexanoate (#95), dodecanoic acid (#19), β-damascenone (#199), benzene acetaldehyde (#79), sabinol (#198), *p*-cymene (#176), α-terpineol (#189), hexadecanal (#83), linalool (#181), eucalyptol (#173), benzyl alcohol (#64) and 2,3,5-trimethylfuran (#135). Among them, 16 (67%) were positively identified and they are presented in Table 2 with an "a" after their names. In the case of *p*-cymene, its isomer *o*-cymene possesses a similar mass spectrum and retention index; however *p*-cymene is much more abundant in nature (Joglekar, Panaskar, & Arvindekar, 2014).

This approach enabled the selection of three principal components (PC1, PC2 and PC3) with eigenvalues greater than 1, which explained 85.8% of the total variance observed in the data (Table S5). Eigenvalues corresponding to the variance of each PC and the number of significant eigenvalues were determined by the Kaiser rule, which considers only the components with eigenvalues greater than 1. Variables related to PC1 and PC2, which explain 78.2% of the total variance in the volatile composition of wines from different treatments of vine management (M1–M10), are positioned according to factor loadings and the distribution of the samples in the plan is defined by the first two components as shown in Fig. 1. Variables with higher loading values correspond to those that significantly contributed to explain each factor (PC1, PC2, and PC3), and are marked in bold letters in Table S5.

Table S6 provides the mean score of descriptive attributes (± standard deviation) evaluated by the sensory trained panel during QDA. Fig. 2 shows the PCA of data generated by QDA and enables visualization of similarities and differences among produced wines (M1 to M10) and their sensory profiles. The first two PC with eigenvalues greater than 1 explain 86.8% of the sensory variation among wine samples. Table S7 provides eigenvalues, cumulative variances, and loadings for each sensory attribute in each PC.

The results of the two PCA, shown in Figs. 1 and 2, are firstly discussed with focus on factors related to soil class, irrigation, and spacing between vines in planting row. Next, the effects of distinct canopy management conditions (buds load per plant, number of leaves per shoot and attach of shoots upwards) are evaluated.

According to PCA (Fig. 1), the differences in soil class (arenosol (A) and acrisol (B)) among the vineyard areas where treatments were conducted seemed to have little or no influence on the volatile composition of the wines. Samples from the same type of vine management, but from different soils are located close to each other in the PCA plot. The *t*-test showed that soil factor did not significantly contribute to the observed differences in concentrations of volatile compounds at a 95% confidence level ($p > 0.05$), as shown by *p*-values for each type of management (pM1 = 0.99, pM2 = 0.94, pM3 = 0.82, pM4 = 0.96, pM5 = 0.89, pM6 = 0.71, pM7 = 0.97, pM8 = 0.88, pM9 = 0.91, and pM10 = 0.94). Similarly, differences in soil classes (arenosol (A) and acrisol (B)) have not resulted in significant distinctions in the aroma notes attributed to each sensory descriptor (Fig. 2) at a 95% confidence level ($p > 0.05$). P-values related to each type of management are as follows: pM1 = 0.50, pM2 = 0.95, pM3 = 0.74, pM4 = 0.84, pM5 = 0.85, pM6 = 0.75, pM7 = 0.71, pM8 = 0.89, pM9 = 0.71, and pM10 = 0.76).

The lack of difference between wines produced from grapes growing in both soil classes can be explained by the similarity of some physicochemical characteristics of both classes, such as low-activity clays, low base saturation in the root zone (up to 100 cm) and high drainage capacity. These characteristics mainly refer to the availability of soil nutrients for vine development. The low-activity clay in both soils probably results in low retention of water and nutrients, the low base saturation causes low capacity of adsorption of minerals (Ca^{2+}, Mg^{2+} and K^+) in the soil, and high drainage capacity reduces the supply of nutrients to the vine. It is also important to point out that the soil may be related to the restrictive vegetative vigor of vines, which is an intrinsic feature of vineyards of Campanha Gaúcha. Average values for some soil parameters are as follows: 10% clay, 87 mg dm^{-3} of K^+, 30.5 mmol dm^{-3} of Ca^{+2}, 10.7 mmol dm^{-3} of Mg^{+2}, capacity of water retention at the vine root level of 57 mm (IUSS Working Group WRB, 2015). Therefore, vinifications using grapes harvested at these two

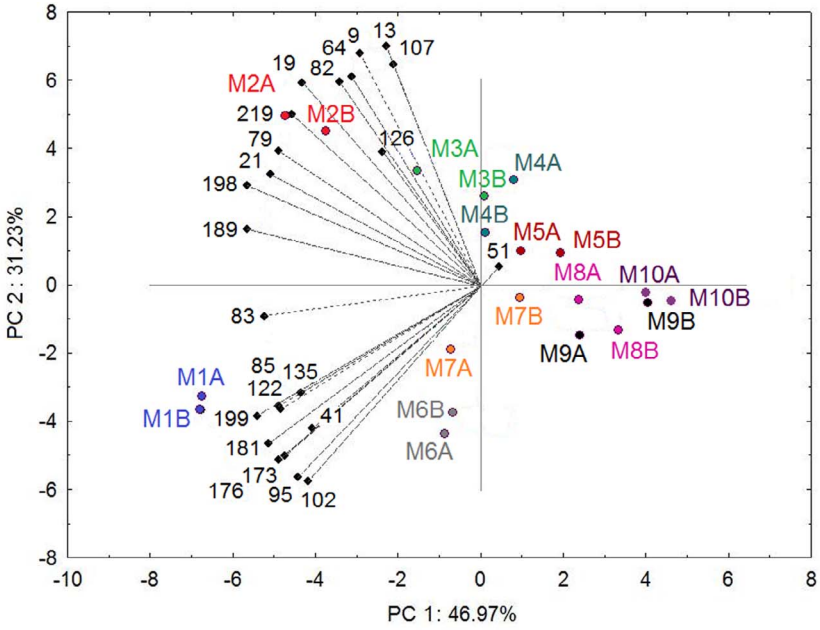

Fig. 1. Plot of the two first principal components obtained in principal component analysis based on the 24 most discriminating volatile compounds of Merlot wines produced with grapes coming from different vine management practices (M1 to M10, Table 1). Compounds are numbered according to Tables 2 and S4. (A): arenosol soil; (B): acrisol soil.

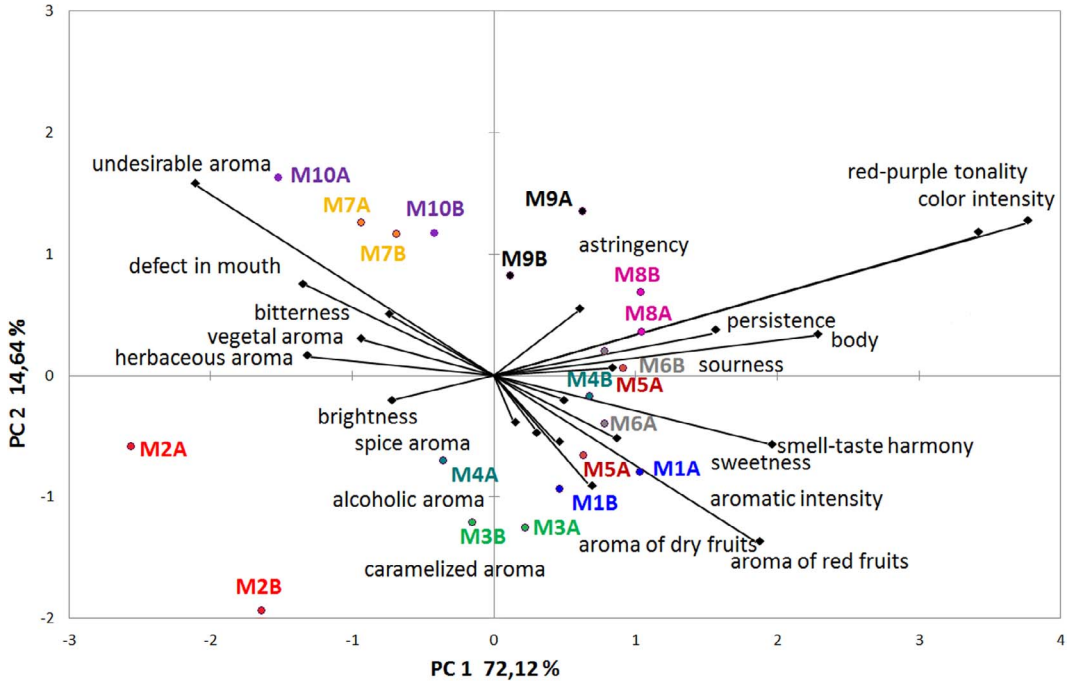

Fig. 2. Plot of the two first principal components obtained with principal component analysis based on quantitative descriptive analysis results for Merlot wines produced with grapes coming from different vine management practices (M1 to M10, Table 1). Table S7 shows eigenvalues, cumulative variances, and loadings for each sensory attribute for each PC. (A): arenosol soil; (B): acrisol soil.

points of the vineyard may be considered as replicates of management experiments.

Irrigation applied to vines of M10 treatment (Fig. 1) has not contributed to the differentiation among vines based on volatile compounds of the corresponding wines (pM10 = 0.81 according to t-test at a 95% confidence level). Talaverano et al. (2017), and Ou, Du, Shellie, Ross, and Qian (2010) have found lower concentrations of volatile compounds in Tempranillo and Merlot wines, when irrigation was employed in their vines. This occurred especially for those volatiles that impart a positive note to aroma. The region where Tempranillo vines were grown was characterized by a growing season rainfall (from 1 April to 30 September) of 123 mm in 2010 and 150 mm in 2011 (Talaverano et al., 2017). Regarding the growing season of the Merlot vines region, the precipitation provided about 25% of the grape's vapor transpiration needs, making irrigation a production necessity (Ou et al., 2010). Therefore, deficit irrigation has been a management practice proposed to restrict the vegetative growth and enhance grape quality (Ou et al., 2010; Talaverano et al., 2017). In accordance with this information, QDA showed that the use of vine irrigation resulted in a wine (M10) with negative sensory attributes of taste/mouth sensations (bitterness and defect in mouth) and aroma (undesirable, vegetal, and herbaceous) (Fig. 2). These negative descriptions may occur since the vegetative growth of vines may be favored by the use of irrigation, which impairs the perception of fruity/floral notes, and favors

vegetative/herbaceous aroma (Ou et al., 2010; Talaverano et al., 2017). In addition, during these experiments rainfall was 19% above the average for this region.

Fig. 1 shows that wines produced with grapes from the treatments using 2 m of space between vines with 40 buds (M8) or 60 buds per plant (M9) were not discriminated from other wine samples, especially M3, M4, M5, M7, M10, in which the 1 m space was used. Therefore, the use of 2 m of space between vines did not contribute significantly to the differentiation in the concentration of the wine volatile compounds (pM8 = 0.78 and pM9 = 0.71) in relation to the median concentration of the other wines (M3, M4, M5, M7, M10) according to t-test at a 95% confidence level ($p > 0.05$).

Fig. 2 shows that M8 and M9 are located near to one another in the PCA plot, and were associated with astringency, color intensity and red–purple tonality (Fig. 2), as these wines received the highest notes for these sensory attributes in QDA. Astringency was 4.0 for both M8 and M9 wines and the median of notes for other wines was 3.7; color intensity: 6.9 and 6.2 for M8 and M9, respectively, median of notes for other wines was 5.2; red purple tonality: 7.0 and 6.5 for M8 and M9, respectively, median of notes for other wines was 5.7. Astringency perception is related to tannins in wine and may indicate that the higher exposure of grape clusters to sunlight provided by the 2 m spacing between rows of vines (in comparison to 1 m) accelerated technological maturation, although phenolic maturation had not been reached at the time when grapes were harvested. Technological maturation was measured by soluble solid content around 20° Brix (Table S1), according to the recommendation of Ribéreau-Gayon et al. (2006). Unripe grapes, in terms of phenol content, contain high amounts of extractable and strongly astringent tannins in their seeds, which are transferred to wine during the maceration step. As grape ripeness progresses, tannins become polymerized and consequently less aggressive to taste. Furthermore, polymerized tannins present in wine may help in the stabilization and intensification of color (Springer, Chen, Stahlecker, Cousins, & Sacks, 2016). However, in addition to a different spacing between vines in the planting rows, other variables (bud load and number of leaves) were distinct in the treatments M1 and M2.

PCA shown in Figs. 1 and 2 indicate that wine samples from treatments M1 and M2 were clearly separated from other samples. Among all the treatments related to canopy management M1, presented the lowest bud load (20 per plant) and M2 the lowest number of leaves (6 per shoots). These characteristics seemed to result in wines with different volatile composition. Higher exposure to solar incidence and air circulation through the canopy of treatment M1 may justify the differences in the volatile profile of wines shown in the PCA in relation to other samples. On the other hand, the six leaves per shoot of M2 may represent a lower limit of vegetative growth for the vine, which might be the explanation for the lowest quality of the wine produced from these grapes.

According to PCA (Fig. 1), the volatile compounds that were mainly responsible for distinguishing M1 and M2 wines from the other canopy management experiments and that consequently presented the highest loadings in PC1 (Table S5) were α-terpineol (#189), sabinol (#198), β-damascenone (#199), hexadecanal (#83), linalool (#181), 1-propanol (#21), 2-phenylethyl acetate (#122), eucalyptol (#173), benzeneacetaldehyde (#79), ethyl acetate (#85), p-cymene (#176), 3-methylthio-1-propanol (#219), ethyl hexanoate (#95), 2,3,5-trimethylfuran (#135) and 1-hexanol (#41). In contrast, attachment of shoots upwards (M6), which is supposed to decrease solar incidence and air circulation through grape clusters, did not result in differentiation from other wine samples (pM6 = 0.84 according to t-test at 95% confidence level) and, therefore, did not significantly affect the wine quality.

The second principal component (PC2) was responsible for differentiating M1 from M2. Compounds with the highest loadings in PC2 (Fig. 1, Table S5) were octanoic acid (#13), hexanoic acid (#9), isoamyl lactate (#107), benzyl alcohol (#64), 3-(2,6,6-trimethyl-1-cyclohexen-1-il)-2-propenal (#82), dodecanoic acid (#19) and ethyl octanoate (#102). In addition, the two compounds (2,3-butanediol, #51 and diethyl hexanedioate, #126) with the highest loadings in PC3 (Table S5) also contributed to differentiate M1 from M2.

Table S8 shows the concentrations of the volatile compounds higher in M1 (β-damascenone, 2-phenylethyl acetate, eucalyptol, p-cymene, ethyl hexanoate, 2,3,5-trimethylfuran, 1-hexanol, ethyl octanoate) and M2 (α-terpineol, 1-propanol, benzeneacetaldehyde, 3-methylthio-1-propanol, isoamyl lactate, benzyl alcohol, 3-(2,6,6-trimethyl-1-cyclohexen-1-il)-2-propenal, dodecanoic acid, diethyl hexanedioate), in comparison with other wines. Concentrations presented in this table were calculated as follows: first, the average was made for wines of each vine management treatment for blocks A and B and then the wine corresponding to the lower average was placed in the same line of the table. In some cases, more than one wine presented the same mean value for concentration and, in these cases, more than one wine treatment, corresponding to a specific vine management was placed in the same line. For example, the concentration of eucalyptol was 94% higher in M1 than in other wine samples and M10 presented the lowest concentration for this analyte. Concentrations of the other compounds shown in Table S8 were 18–84% higher in M1 wine than in the other wines. The p-value is lower than 0.05 (5.0×10^{-5}), which means that the differences between concentrations are significant. Regarding M2, the level of diethyl hexanedioate was 90% higher than those found in M5, M6, and M8 wines. Other compounds were found in concentrations 8 to 80% higher in M2 than in other wines. The levels of linalool and sabinol were the only ones that were not statistically different according to t-test (p = 0.0502 and 0.2582, respectively). Therefore, the significant difference observed for the other compounds of Table S8 may have contributed to the differentiation of the samples according to the sensorial profile shown in Fig. 2.

Odors reported in the scientific literature for the most contributing compounds (highest loading for PC1, PC2, and PC3) in the PCA (Fig. 1) are shown in Table S5. Among them, 63% contributed positively to wine aroma (especially fruity and floral notes), 17% contributed negatively to the quality of wine, and another 20% had an unknown odor contribution. Quantitative results obtained by GC × GC/TOFMS for volatile compounds of all wine samples under study are shown in Table 3. Table S3 presents figures of merit of the quantitative analytical method, including concentration range, limits of quantification and detection, recovery, repeatability, and intermediate precision.

A closer look at the compounds that characterize M1 and M2 according to the PCA (Fig. 1 and Table S5) disclosed that compounds that imparted negative notes to aroma are associated with M2, and were found in higher levels in this wine than in any other wine (M1 and M3-M10). Selected examples include: 3-methylthio-1-propanol (#219 of Table 3, boiled cabbage odor, 266 μg L^{-1}; median concentration found in other wines: 180 μg L^{-1}), dodecanoic acid (#19, metallic/oil odor, 18.4 μg L^{-1}; median concentration in other wines: 9.1 μg L^{-1}), hexanoic acid (#9, cheese/fatty odor, > 2160 μg L^{-1}; median concentration in other wines: 1530 μg L^{-1}), and octanoic acid (#13, fatty odor). The concentration of hexanoic acid in M2 was above the upper limit of the linear dynamic range. Octanoic acid was present in all samples and could not be quantified due to its concentration also being above the upper limit of the linear dynamic range (> 540 μg L^{-1}). However, its peak area was higher in M2 wine than in any other sample.

The high concentrations of 3-methylthio-1-propanol and some acids (hexanoic, octanoid and dodecanoic) in M2 wine reveals that primary metabolism (e.g., glucose production *via* photosynthesis and formation of amino acids necessary for vine survival) appears to have been favored over secondary metabolism (e.g. formation of carotenoids, terpenes and others) (Jackson, 2014). The mechanism of formation of 3-methylthio-1-propanol has been proposed to happen from the deamination of methionine (sulfur amino acid), followed by decarboxylation and reduction reactions during fermentation (Etschmann et al., 2008).

Table 3
Concentration of the 24 volatile compounds indicated by Fisher ratio as the most discriminating among the samples of Merlot wines produced using grapes grown according to ten different vine managements (M1 to M10 as described in Table 1). Chromatographic conditions are described in section 2.4.

#	Compound	Concentration (μg L^{-1}) ± SD																			
	Managements	M1		M2		M3		M4		M5		M6		M7		M8		M9		M10	
	Altitude (m)	170	180	170	180	170	180	170	180	170	180	170	180	170	180	170	180	170	180	170	180
189	α-terpineol[a]	7.2 ± 0.8	7.2 ± 0.7	7.4 ± 0.7	7.2 ± 0.9	6.8 ± 0.5	6.8 ± 0.4	6.4 ± 0.5	6.8 ± 0.3	6.6 ± 0.4	6.6 ± 0.6	6.6 ± 0.5	6.7 ± 0.5	6.5 ± 0.4	6.8 ± 0.4	6.6 ± 0.5	6.5 ± 0.4	6.6 ± 0.5	6.5 ± 0.3	6.2 ± 0.4	6.2 ± 0.4
198	sabinol[a]	6.4 ± 0.7	6.4 ± 0.7	6.5 ± 0.7	6.5 ± 0.7	6.2 ± 0.7	6.3 ± 0.7	6.2 ± 0.8	6.3 ± 0.7	6.2 ± 0.7	6.2 ± 0.5	6.1 ± 0.7	6.2 ± 0.7	6.2 ± 0.6	6.2 ± 0.7	6.1 ± 0.7	6.0 ± 0.7	6.1 ± 0.8	6.0 ± 0.7	6.0 ± 0.7	6.0 ± 0.8
199	β-damascenone[h]	121 ± 17.2	129 ± 22.2	88.2 ± 8.2	52.7 ± 6.5	45.0 ± 4.6	24.7 ± 3.2	18.1 ± 3.6	44.5 ± 4.9	44.2 ± 3.8	31.1 ± 3.9	77.8 ± 6.2	81.9 ± 7.5	69.7 ± 4.6	58.2 ± 4.7	43.6 ± 4.3	40.3 ± 4.1	40.2 ± 5.2	25.1 ± 3.9	19.5 ± 4.7	19.4 ± 3.2
83	hexadecanal[b]	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5
181	linalool [a]	7.0 ± 0.5	7.1 ± 0.7	6.1 ± 0.4	6.2 ± 0.4	6.2 ± 0.5	5.9 ± 0.3	5.8 ± 0.5	6.0 ± 0.4	6.0 ± 0.4	5.8 ± 0.5	6.4 ± 0.6	6.4 ± 0.4	6.5 ± 0.4	6.2 ± 0.4	6.0 ± 0.3	6.0 ± 0.4	6.1 ± 0.6	5.8 ± 0.3	5.8 ± 0.4	5.8 ± 0.5
21	1-propanol [b]	215 ± 17.3	217 ± 18.6	236 ± 28.2	223 ± 33.5	238 ± 31.6	197 ± 13.2	195 ± 16.6	181 ± 14.3	202 ± 16.8	196 ± 23.6	189 ± 16.1	176 ± 15.5	159 ± 12.6	152 ± 9.7	159 ± 11.3	151 ± 14.0	162 ± 9.8	123 ± 13.7	134 ± 19.0	126 ± 14.7
122	2-phenylethyl acetate[i]	19.4 ± 1.8	19.2 ± 1.1	11.1 ± 0.7	16.2 ± 0.9	13.6 ± 0.4	11.3 ± 0.4	13.1 ± 0.3	14.2 ± 0.4	12.6 ± 0.2	10.8 ± 0.5	17.3 ± 0.7	18.2 ± 0.9	15.1 ± 0.3	13.6 ± 0.7	11.9 ± 0.5	12.6 ± 0.2	11.7 ± 0.6	8.8 ± 0.6	8.1 ± 0.1	7.3 ± 0.3
173	eucalyptol[j]	95.1 ± 9.7	103.5 ± 7.7	36.4 ± 1.3	12.4 ± 0.9	8.0 ± 0.6	< 6.25	< 6.25	< 6.25	< 6.25	< 6.25	58.5 ± 0.9	53.5 ± 1.5	47.0 ± 0.4	20.0 ± 1.1	8.2 ± 0.8	7.6 ± 0.2	10.0 ± 0.7	< 6.25	< 6.25	< 6.25
79	benzeneacetaldehyde[c]	189 ± 19.8	177 ± 12.5	178 ± 20.1	185 ± 14.8	178 ± 17.1	170 ± 12.5	162 ± 10.8	166 ± 10.5	156 ± 9.4	148 ± 9.9	114 ± 11.5	113 ± 9.5	104 ± 8.7	108 ± 9.4	99.5 ± 9.5	91.9 ± 8.7	91.5 ± 8.5	102 ± 9.8	86.6 ± 8.4	85.3 ± 6.4
85	ethyl acetate[d]	> 110	> 110	> 110	> 110	> 110	> 110	> 110	> 110	> 110	> 110	> 110	> 110	> 110	> 110	> 110	> 110	> 110	> 110	> 110	> 110
176	*p*-cymene[a]	39.9 ± 3.8	34.7 ± 2.8	19.3 ± 1.7	8.3 ± 0.9	7.2 ± 0.3	7.7 ± 0.6	7.4 ± 0.5	7.7 ± 0.4	7.7 ± 0.4	7.0 ± 0.5	33.0 ± 1.6	21.3 ± 1.8	17.6 ± 0.8	9.4 ± 0.7	7.1 ± 0.5	7.0 ± 0.4	8.0 ± 0.5	6.8 ± 0.6	6.5 ± 0.5	6.5 ± 0.4
219	3-methylthio-1-propanol [e]	236 ± 20.6	226 ± 18.7	258 ± 13.2	274 ± 18.9	250 ± 12.2	222 ± 10.4	234 ± 15.5	218 ± 17.3	189 ± 15.4	219 ± 14.6	161 ± 16.5	173 ± 11.9	178 ± 10.4	182 ± 9.4	163 ± 13.5	125 ± 12.7	132 ± 14.5	163 ± 14.9	162 ± 9.4	138 ± 11.4
95	ethyl hexanoate[d]	26.2 ± 0.9	36.3 ± 0.8	7.9 ± 0.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	25.1 ± 1.5	18.7 ± 1.2	14.7 ± 0.4	6.6 ± 0.9	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5
135	2,3,5-trimethyl furan [f]	102 ± 13.2	93.6 ± 11.8	15.4 ± 1.7	15.6 ± 0.9	6.0 ± 0.3	6.0 ± 0.2	16.0 ± 0.5	6.0 ± 0.8	21.1 ± 1.4	6.0 ± 0.5	6.0 ± 1.0	6.0 ± 0.8	6.0 ± 0.7	6.0 ± 0.7	6.0 ± 0.5	6.0 ± 0.4	33.2 ± 1.5	6.0 ± 0.09	6.0 ± 0.5	6.0 ± 0.8
41	1-hexanol[b]	435 ± 30.9	436 ± 48.7	316 ± 19.2	406 ± 25.9	331 ± 22.8	301 ± 20.4	228 ± 15.8	274 ± 19.6	295 ± 12.4	234 ± 17.6	393 ± 16.2	414 ± 21.3	411 ± 25.4	379 ± 19.7	329 ± 15.5	333 ± 18.5	352 ± 17.9	252 ± 13.8	304 ± 19.4	238 ± 17.4
13	octanoic acid[k]	> 540	> 540	> 540	> 540	> 540	> 540	> 540	> 540	> 540	> 540	> 540	> 540	> 540	> 540	> 540	> 540	> 540	> 540	> 540	> 540
9	hexanoic acid[l]	1690 ± 99.9	1700 ± 88.5	> 2160	> 2160	2160 ± 103	1850 ± 90.9	> 2160	2040 ± 114	1640 ± 97.4	1410 ± 77.6	1280 ± 71.2	661 ± 39.3	1530 ± 95.4	1760 ± 99.7	1570 ± 85.5	1300 ± 84.5	1280 ± 72.9	1300 ± 75.8	1500 ± 89.4	1340 ± 78.4
107	isoamyl lactate[d]	8.2 ± 0.2	11.1 ± 0.8	28.4 ± 0.7	27.4 ± 0.9	29.1 ± 1.3	25.9 ± 1.2	23.0 ± 1.5	5.9 ± 0.8	22.1 ± 1.4	6.0 ± 0.5	< 5.5	< 5.5	14.4 ± 0.7	5.7 ± 0.2	8.7 ± 0.5	< 5.5	8.4 ± 0.5	< 5.5	14.8 ± 0.5	8.5 ± 0.4
64	benzyl alcohol[c]	48.5 ± 3.2	48.6 ± 2.7	122 ± 37.9	70.9 ± 11.9	62.2 ± 8.3	72.9 ± 6.8	83.2 ± 10.7	70.4 ± 6.6	61.2 ± 5.2	62.2 ± 7.1	27.0 ± 1.8	40.7 ± 3.8	35.4 ± 2.4	41.3 ± 2.6	20.1 ± 1.5	22.4 ± 0.9	21.2 ± 1.0	24.3 ± 0.9	44.5 ± 1.5	35.2 ± 1.1
82	3-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-propenal [b]	< 4.5	< 4.5	8.6	8.7	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5	< 4.5
19	dodecanoic acid[m]	12.7 ± 0.7	12.6 ± 0.8	19.9 ± 0.5	16.9 ± 0.9	14.8 ± 0.3	12.6 ± 0.6	12.9 ± 0.5	12.2 ± 0.8	10.4 ± 0.9	9.6 ± 0.5	6.3 ± 0.4	6.9 ± 0.5	8.9 ± 0.7	9.4 ± 0.8	8.2 ± 0.5	7.9 ± 0.4	7.1 ± 0.5	6.6 ± 0.7	6.8 ± 0.5	7.4 ± 0.8
102	ethyl octanoate[n]	19.7 ± 0.8	22.7 ± 0.9	12.9 ± 0.6	12.2 ± 0.6	11.5 ± 0.4	11.3 ± 0.4	11.1 ± 0.5	11.5 ± 0.7	11.1 ± 0.4	10.9 ± 0.6	23.2 ± 0.9	17.8 ± 0.8	16.5 ± 0.9	12.8 ± 0.7	11.2 ± 0.7	10.9 ± 0.6	11.4 ± 0.5	10.9 ± 0.9	10.8 ± 0.7	10.6 ± 0.8
51	2,3-butanediol [b]	> 450	> 450	> 450	> 450	> 450	> 450	> 450	> 450	> 450	> 450	> 450	> 450	> 450	> 450	> 450	> 450	> 450	> 450	> 450	> 450
126	diethyl hexanedioate[g]	76.6 ± 7.2	< 50.0	365 ± 24.7	613 ± 58.7	553 ± 40.6	338 ± 27.2	71.3 ± 6.5	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	568 ± 45.7	326 ± 28.9	< 50.0	< 50.0	158 ± 17.0	< 50.0	< 50.0	174 ± 13.8

SD: Standard Deviation; # Compounds numbered as in Table 1. Quantification was performed with external calibration curves for the following compounds: [a]α-terpineol; [b] 1-hexanol; [c] benzyl alcohol; [d] ethyl hexanoate; [e] 3-mercaptohexanol; [f] 2-furanmethanol; [g] diethyl butanedioate;[h] β-damascenone;[i] 2-phenylethyl acetate; [j] eucalyptol; [k]octanoic acid; [l]hexanoic acid; [m] dodecanoic acid; [n] octanoic acid. The concentration ranges used in the calibration curves are shown in Table S3. When the amount of a compound was lower or higher than the concentration range used in the calibration curve, the concentration of that compound was expressed as " < " the lowest level of the curve and " > " than the highest level of the curve.

Acids are formed from acetyl coenzyme A (acetyl-CoA), which is derived from the oxidation of pyruvate (formed from glucose) or amino acid deamination during fermentation. Moreover, the high concentrations of acids in M2 wines may reduce yeast activity, and consequently result in lower concentrations of esters (2-phenylethyl acetate, ethyl hexanoate and ethyl octanoate), which would accordingly decrease fruity aroma notes, as previously reported by Saerens et al. (2008). Although the available scientific literature does not report the threshold concentration of acids likely to affect yeast activity, it is relevant to mention that the sum of concentrations of all acids present in M2 wine was 20% higher than those of other wine samples.

In contrast, compounds related to M1 contributed positively to wine aroma (Fig. 1 and Table S5), and were found in higher concentrations in this wine than in other samples (M2-M10). The following compounds were identified as corresponding to this phenomenon: 2-phenylethyl acetate (#122 of Table 3, roses odor, 19.3 $\mu g\,L^{-1}$; median concentration in the other wines: 12.6 $\mu g\,L^{-1}$), β-damascenone (#199, roses/candy odor, 125 $\mu g\,L^{-1}$; median concentration in other wines: 43.9 $\mu g\,L^{-1}$), linalool (#181, rose odor, 7.1 $\mu g\,L^{-1}$; median concentration in other wines: 6 $\mu g\,L^{-1}$), eucalyptol (#173, mint odor, 99.3 $\mu g\,L^{-1}$; median concentration in other wines: 16.2 $\mu g\,L^{-1}$), *p*-cymene (# 176, solvent, gasoline, citrus, 37.3 $\mu g\,L^{-1}$; median concentration in other wines: 7.9 $\mu g\,L^{-1}$), ethyl hexanoate (# 95, fruity odor, 31.2 $\mu g\,L^{-1}$; median concentration in other wines: 14.7 $\mu g\,L^{-1}$), 1-hexanol (#41, fruity odor, 436 $\mu g\,L^{-1}$; median concentration in other wines: 361 $\mu g\,L^{-1}$), ethyl octanoate (#102, fruity odor, 21.2 $\mu g\,L^{-1}$; median concentration in other wines: 11.3 $\mu g\,L^{-1}$) and ethyl acetate (#85, fruity odor). The concentration of the latter ester could not be quantified, since it was found in a higher concentration than the upper limit of the linear dynamic range for all samples, > 110 $\mu g\,L^{-1}$). The peak area of ethyl acetate in M1 wine was higher than in all the other wine samples; however its contribution would only be negative to aroma in the range of $mg\,L^{-1}$.

The lower number of leaves per plant in treatment M2 was expected to facilitate the incidence of sunlight on the grape clusters, as this type of procedure has already been reported to result in positive characteristics of aroma in Pinot Noir wines from the Valley of Oregon (Northwest region of USA, 44°54′N, 123°06′W) (Feng et al., 2017), in Tempranillo wines from La Rioja (42°15′N, 2°30′W) (Vilanova et al., 2012) and Extramadura (38°51′N, 6°40′W) (Moreno et al., 2017) from Northern and Western Spain, respectively. Defoliation, including 100% removal of leaves has resulted in higher concentrations of esters, terpenes and C_{13}-norisoprenoids, known to contribute fruity and floral notes to the aroma of these wines (Feng et al., 2017; Moreno et al., 2017; Vilanova et al., 2012). However, Merlot wines from Campanha Gaúcha have not followed this same pattern, even when the most severe leaves removal procedure was applied (M2). In contrast, positive aroma characteristics were observed for vines kept at the lowest bud load (M1), which seems to have favored the balance between restricted vegetative growth and gain in grape quality, as displayed through the volatile profile of M1.

The same two wine samples M1 and M2 have also been separated from each other according to the sensory profile assessed through QDA, as shown in Fig. 2. PC1 was responsible for the differentiation between M1 and M2, as can be seen from the attributes in the left and right sides of the PCA. M2 wine is located at the left side of the PCA, and therefore associated with sensory descriptors that negatively qualify wine, especially those of taste/mouth sensations (defect in the mouth and bitterness) and aroma (undesirable, herbaceous, vegetal). These negative aroma notes may be attributed to the higher levels of selected acids [hexanoic (# 9), octanoic (# 13) and dodecanoic (# 19)] and 3-methylthio-1-propanol (# 219) found in M2 wine in comparison to other samples, as has been already reported in Fig. 1. M7 and M10 wines also stood out in relation to other samples in PCA due to these negative sensorial characteristics, which in the case of M7 may be attributed to the higher levels of eucalyptol (# 173, mint) and diethyl hexanedioate (# 126) than those found in other samples, although the contribution of diethyl hexanedioate to aroma has not been found in the literature. M10 was the sample that presented the lowest levels of some positive aroma compounds, such as β-damascenone (# 199), linalool (# 181), 2-phenylethyl acetate (#122) and *p*-cymene (# 176), which may have intensified the negative perception of the aroma of the acids [hexanoic (# 9), octanoic (# 13) and dodecanoic (# 19)], benzeneacetaldehyde (# 79), eucalyptol (# 173) and 3-methylthio-1-propanol (# 219).

In contrast, only positive sensory attributes were related to sample M1, including those related to mouth sensations (sweetness and smell-taste harmony), and aroma (red fruits, dry fruits and aromatic intensity). The high concentrations of some esters [2-phenylethyl acetate (# 122) and ethyl hexanoate (# 95)], terpenes [linalool (# 181), eucalyptol (# 173) and *p*-cymene (# 176)] and of a C_{13}-norisoprenoid (β-damascenone (# 199) (Table 3) found in M1 wine are likely responsible for the observed distinctions between M1 and M2, as well as its distinction from other wines, (Figs. 1 and 2) possibly also contributing to the characteristic aromas perceived in sensory analysis.

M6 was the only treatment in which vine shoots grew freely, with no fixation to the vineyard structure and without upward organization of the shoots. This practice did not result in any differentiating sensory characteristic attributed to the corresponding wine. PCA obtained from the data of QDA (Fig. 2) shows that wine M6 is located close to other wines (M1, M4, M5 and M8) in which the practice of shoots attachment was used (M5 represents the same treatment, except for the shoots that were attached upwards). It would be expected that the free shoots would provide many shaded environments in the fruit zone that would impart restrictive conditions to maturation of bunches. However, as it did not happen, it means that the microclimate was not contrasting enough to overcome a more important intrinsic characteristic of the vineyard, which is low vigor.

3.2. Aroma-active compounds

Keeping in mind that M1 wine was chosen as representative of the best sensory evaluation in QDA, and considering such wine also had both high levels of volatiles that may positively influence aroma, and lower concentrations of compounds related to aromatic defects verified by GC × GC, wine produced from M1 was chosen for evaluation by GC-O. M1 wine sample produced from grapes harvested from arenosol soil (A) was used for GC-O analyses, since no significant differences were observed in relation to grapes cultivated at acrisol soil (B) (see Sections 3.1 and 3.2), considering their concentrations of volatile compounds, as well as with regards to sensory analysis.

Twenty-six odorous volatile compounds were found in M1 wine, of which 77% contributed positively to aroma, imparting mainly notes described as fruity, floral, and sweet, among others. Table 4 shows the identification of odorous volatile compounds of M1 wine in ascending order of RI. Eight of the 26 odoriferous compounds detected by GC-O were considered important to differentiate the wines from different vine management experiments (M1–M10), in accordance with GC × GC data, as shown in Section 3.1: hexanoic acid (#9 of Table 4), 1-propanol (#21), 2,3-butanediol (#51), ethyl hexanoate (#95), ethyl octanoate (#102), 2-phenylethyl acetate (#122), diethyl hexanedioate (#126) and 3-methylthio-1-propanol (#219). Table 4 also shows the intensity of odor perceived in the chromatographic effluent, the percentage of odoriferous peak area relative to the total area of peaks of the aromagram, and the aroma described by the judges during GC-O.

Among these compounds only hexanoic acid (#9, odor described as pungent, rancid and wax) and 3-methylthio-1-propanol (#219, cooked green beans, wet bush, gas, green odor) contributed negatively to aroma. The other six compounds represent a positive influence (fruity, floral, and sweet notes) to wine aroma, with the concentrations of four out of six compounds found to be higher in M1 in comparison with the other wines under study (M2–M10). The concentrations of these four compounds in M1 and their average concentrations in other wine

Table 4
Twenty-six odoriferous compounds found in a Merlot wine elaborated using grapes grown according to a canopy management treatment named M1 (20 buds per plant, 15 leaves per branch and 1 m of spacing between each row of the vine), using gas chromatography with different detectors: olfactometry, mass spectrometric and flame ionization.

#	Compounds	RI_{OSME}[a]	RI_{FID}[a]	Imax(cm)[b]	% OSME área ± SD[c]	Aroma described by the sensory panel
	acids					
1	acetic acid	1457	1459	7.64	7.06 ± 1.2	vinegar
5	butanoic acid	1654	1664	5.01	3.03 ± 0.6	cheese, pungent
9	hexanoic acid	1856	1851	5.76	3.30 ± 0.7	pungent, rancid, wax, bittersweet
14	nonanoic acid	2156	2171	5.58	4.84 ± 0.8	fruit, floral, ripe fruit, sweet
	alcohols				18.24	
21	1-propanol	1054	1043	5.80	4.23 ± 0.2	fruit, sweet
23	isobutanol	1080	1099	5.14	3.03 ± 0.9	fruit, citric, ripe fruit, fresh
30	3-methyl-1-butanol	1209	1217	6.50	5.52 ± 0.9	pungent, solvent
51	2,3-butanediol	1546	1544	3.57	1.43 ± 0.3	fruit, floral
52	1-octanol	1569	1562	4.20	2.20 ± 0.4	fruit, sweet
58	1-decanol	1750	1759	4.62	2.63 ± 0.5	fruit, floral, sweet
65	phenylethyl alcohol	1910	1918	7.09	5.95 ± 1.0	roses, floral
	esters				25.00	
86	ethyl propanoate	969	967	4.59	2.61 ± 0.5	fruit, floral, red fruits, sweet
89	ethyl butanoate	1039	1020	4.97	2.73 ± 0.4	fruit, sweet
92	isoamyl acetate	1124	1126	5.38	3.31 ± 0.6	banana, fruit, fresh, solvent
95	ethyl hexanoate	1236	1239	5.05	3.06 ± 0.6	fruit, sweet
102	ethyl octanoate	1413	1440	4.09	1.43 ± 0.3	fruit, sweet
109	ethyl decanoate	1628	1643	4.22	2.16 ± 0.4	fruit, floral, burnt, sweet
113	diethyl butanedioate	1677	1684	8.16	7.19 ± 1.3	stinky, cheese
118	ethyl benzeneacetate	1795	1791	4.92	3.03 ± 0.6	floral
122	2- phehylethyl acetate	1828	1820	6.11	4.40 ± 0.8	roses, floral, jasmin
126	diethyl hexanodioate	1890	1910	5.81	3.47 ± 0.7	floral, fruit, jelly, sweet
129	ethyl tetradecanoate	2049	2048	7.02	6.39 ± 1.3	sweet, caramel, sweetsauce
132	methyl hexadecanoate	2227	2220	4.39	4.89 ± 0.9	fruit
	ketone				44.67	
143	2,3-butanedione	984	973	5.10	3.47 ± 0.7	fruit, sweet, red fruits, fresh
	terpene					
193	carvone	1738	1734	5.59	2.91 ± 0.5	fruit, fresh, green
	Sulfur compound					
219	3-methylthio-1-propanol	1726	1720	7.24	5.71 ± 0.9	cooked green beans, wet bush, gas, green

Compounds numbered as in Table 1.
a Experimental retention index (RI) calculated using *n*-alkanes (C_9-C_{24}) on DB-Wax (100% polyethyleneglycol) for both GC-O (RI_{OSME}) and GC-FID (RI_{FID}) analyses. In GC-O, the retention time of the maximum intensity of the odor peak was used in RI calculation.
b Maximum intensity (Imax, evaluated on a 10-cm scale anchored at the left and right extremities by the intensity terms "none" and "highly", respectively) was obtained as an average intensity of the consensual aromagram constructed after the analyses of the sample by 4 judges in four replicates.
c % OSME area ± standard deviation: corresponds to the percentage of area of an odoriferous compound in relation to the sum of the area of all compounds detected when the OSME technique was used to obtain information on the volatiles determined by GC-O, through a sensory panel.

samples are as follows: 1-propanol (#21 in Table 3; 217 and 178 μg L^{-1}, respectively), ethyl hexanoate (#95, 36.3 and 14.7 μg L^{-1}, respectively), ethyl octanoate (#102, 22.7 and 11.3 μg L^{-1}, respectively) and 2-phenylethyl acetate (#122, 19.2 and 12.6 μg L^{-1}, respectively).

A careful inspection of the GC × GC/TOFMS data related to the eight compounds appointed both as aroma-active and as important to differentiate wines of the ten types of vine management treatments (M1–M10) has shown that GC × GC/TOFMS was necessary to resolve five co-elutions involving 13 compounds. These volatile compounds were correctly identified and quantified only after their separation in the second chromatographic dimension. The observed co-elutions (Table 2) are: (1st) hexanoic acid (# 9, odor described as pungent, rancid and wax) co-eluted with geranyl acetone (# 202, green odor); (2nd) 1-propanol (# 21, fruity and sweet odor) co-eluted with 2-butenal (# 72, pungent odor); (3rd) ethyl octanoate (# 102, fruity and sweet odor) co-eluted with 5-methyl-2(3*H*)-furanone (# 155, sweet and vanilla odor) and *p*-cymenene (# 178, citrus and pine odor; (4th) 2-phenylethyl acetate (# 122, roses, floral and jasmine odor) co-eluted with β-damascenone (# 199, rose, candy and citrus odor); (5th) 3-methylthio-1-propanol (# 219, cooked green beans, wet bush, gas and green odor) co-eluted with isopiperitone (# 190, minty odor), (*Z*)-6-nonen-1-ol (# 56, melon odor) and 2-undecanol (# 57, minty odor). Most of the co-eluted compounds that were resolved by GC × GC/TOFMS lend positive notes to wine aroma, and therefore, knowledge regarding their presence is important for further studies that involve wine quality improvement through modifications related to vine management, maceration, vinification, etc. Several strategies may be employed for wine quality improvement with the use of data related to volatile compounds, such as the promotion of higher efficiency of extraction of precursors of these compounds from grapes during maceration, the use of different microorganisms in the wine process (yeasts and lactic bacteria), distinct winemaking conditions that favor the formation of these compounds, etc.

In this study, thirty-seven co-elutions (including the above mentioned compounds) were resolved by GC × GC/TOFMS. These co-elutions were numbered from 1 to 37 in Table 2. A more detailed discussion related to the co-eluted compounds resolved by GC × GC/TOFMS as they relate to the aroma of wine of different grape cultivars has been reported in a previous study, in which co-elutions involving unpleasant aroma compounds such as 2-propen-1-ol, butanoic acid, isovaleric acid, and 2-methylbutanoic acid were shown (Welke et al., 2017).

4. Conclusions

Merlot wines produced with grapes of vines that presented 20 buds per plant and 15 leaves per shoot (M1) presented higher levels of fruity (1-propanol, ethyl hexanoate and ethyl octanoate) and floral (2-

phenylethyl acetate) aroma compounds. The presence of these components may explain the differentiation of M1 wines from other wines, particularly in relation to QDA positive attributes described as red/dry fruits and high aromatic intensity. Twenty buds per plant was the lowest bud load among the treatments investigated (30, 40 60 buds/plant for other treatments) and resulted in an appropriate balance between vegetative and reproductive development of vines for this region of Campanha Gaúcha. In addition, 15 leaves per shoot (other treatments used 6, 10, and 20 leaves) provided adequate photosynthetic surface, keeping air circulation and light incidence in the bunch microclimate. These results may provide guidance for vine management in this region of Campanha Gaúcha, although even neighboring vineyards may present distinct characteristics and might demand further studies. In contrast, the larger spacing between vines in the rows (2 m in relation to 1 m), as well as the effects of freely growing shoots (not attached), and the presence of irrigation did not result in improvement of wine quality under the experimental conditions of this study.

Combination of several analytical techniques (GC × GC/TOFMS, QDA, GC-FID, GC/MS and GC-O) was for the first time successfully employed to verify the influence of vine management on aroma/volatile profile of Merlot wines and was an essential strategy to separate, identify and quantify the major compounds responsible for wine aroma. This strategy was able to provide a linkage between specific compounds and their aroma in the complex wine matrix, disclosing the effect of coeluting compounds that could mask, enhance or change the sensory perception of aroma compounds. With the prospect of achieving a higher wine quality, this approach may be employed to assess the influence of other parameters involved in wine production (from vine management, passing through vinification, ageing and storage) on wine quality. In addition, this same approach may also be used with other complex matrices (food and beverage, for example) having this same objective in mind.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2017.09.078.

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Supplementary Material

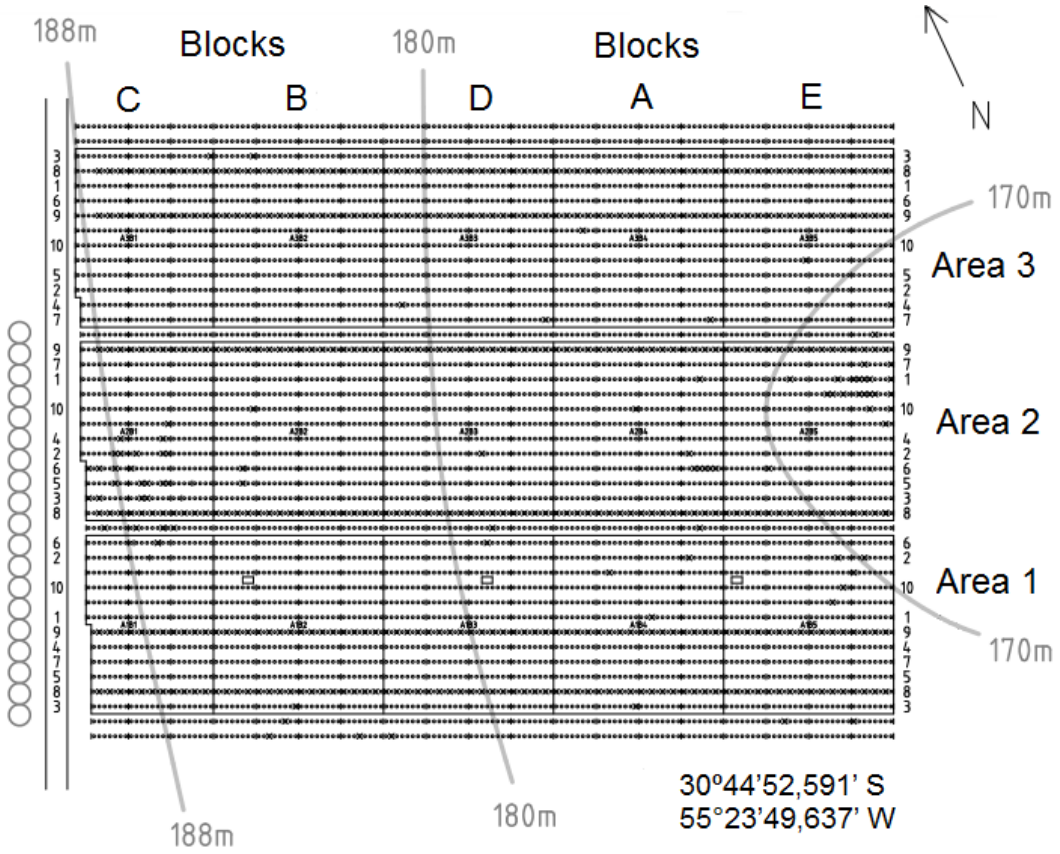

Figure S1. Area of the vineyard located in Santana do Livramento, RS, Brazil (30º44'52,591' S e 55°23'49,637' W), in which the management experiments were carried out (M1-10 as described in Table 1). The randomized design was formed by three areas (in a direction of less slope and almost without influence of the relief, Areas 1, 2 and 3) and five blocks (in the direction of greater slope and with contrast of relief and soil type, Blocks A-E), which resulted in 15 parcels (89.6 m^2 per parcel).

Table S1. °Brix of the grapes and the respective physical-chemical parameters (pH, total acidity, alcohol content) of wines elaborated according to canopy managements showed in **Table 1**.

Management treatment (M)*	°Brix	pH	Total acidity (mEq/L)	Alcohol content at 20°C (% v/v)
M1A	20.4	3.5	49.9	12.3
M1B	20.6	3.5	51.0	13.2
M2A	18.9	3.5	51.4	11.9
M2B	18.9	3.5	50.3	11.4
M3A	20.9	3.5	52.2	12.6
M3B	20.4	3.5	48.6	12.8
M4A	20.4	3.5	50.5	12.4
M4B	21.2	3.5	47.8	13.2
M5A	21.1	3.5	51.4	12.8
M5B	21.0	3.5	50.3	12.9
M6A	21.3	3.4	56.6	12.7
M6B	21.8	3.5	51.4	13.1
M7A	20.4	3.5	51.6	12.4
M7B	20.9	3.4	52.6	12.9
M8A	20.6	3.5	54.1	12.3
M8B	20.9	3.5	54.3	12.2
M9A	20.0	3.5	50.5	12.3
M9B	21.0	3.5	51.6	12.9
M10A	21.1	3.5	49.1	12.3
M10B	20.7	3.5	54.1	12.9

* (A) refers to wine samples that were made from grapes harvested at 170 m (arenosol, sandy) and (B) designates wine samples that were made from grapes harvested at 180 m (acrisol, clayey).

Table S2. Monthly average of temperature (T), relative humidity (H), solar radiation (R), and precipitation during the cycle of 2013/14 in Santana do Livramento, RS, Brazil.

				Precipitation (mm)	
Month	**T (°C)**	**H (%)**	**R (MJ m^2 day^{-1})**	**2013/14**	**Normal** (average of 30 years)
August	10.6	74.5	11.5	64.6	109.0
September	14.7	75.7	14.3	129.7	134.0
October	17.0	75.0	20.0	139.1	132.0
November	21.9	73.0	24.2	291.2	96.0
December	24.2	63.8	26.2	14.5	99.0
January	24.2	73.0	22.5	146.2	108.0
February	22.9	78.0	21.1	171.1	114.0
Accumulated				956.4	791.4

Table S3. Figures of merit of the headspace solid phase microextraction and comprehensive two-dimensional gas chromatography with time of flight mass spectrometry (HS-SPME-GC×GC/TOFMS) method used for the determination of the concentration of volatile compounds in Merlot wines.

							Repeatibility		Intermediate precision			
#	Compound[a]	Regression equation	R^2	Concentration range (µg/L)	LOD (µg/L)	LOQ (µg/L)	RSD (%)[b]	RSD (%)[c]	RSD (%)[b]	RSD (%)[c]	Recovery (%)[b]	Recovery (%)[c]
9	hexanoic acid	y = 4984.9x + 659836.6	0.978	36.0-2160.0	6.9	20.8	14.6	3.4	14.6	16.4	111.1	115.1
13	octanoic acid	y = 19504.4x - 166974.9	0.914	10.8-540.0	3.6	10.8	14.0	1.0	21.3	28.8	92.6	118.7
19	dodecanoic acid	y = 15675.4x - 23182.7	0.991	5.7-114.0	1.8	5.5	15.6	6.3	30.6	22.8	118.8	87.7
41	1-hexanol	y = 15800.6x + 30943.3	1.000	4.5-450.0	0.7	2.0	1.7	0.7	10.9	4.9	82.2	94.4
64	benzyl alcohol	y = 9352.8x - 8850.9	0.998	14.2-710.0	2.6	8.0	30.1	6.8	29.9	8.3	78.9	80.3
95	ethyl hexanoate	y = 114960.0x - 214252.6	0.995	5.5-110.0	1.8	5.4	5.5	4.0	25.0	27.6	113.4	90.9
102	ethyl octanoate	y = 423926.5x - 4190824.0	0.974	5.7-114.0	1.4	4.2	14.3	10.4	28.5	28.7	122.8	87.7
113	diethyl butanedioate	y = 17921.3x + 3035611.2	0.966	50.0-3000.0	10.9	33.0	10.5	22.4	26.0	16.2	118.0	86.3
122	2-phenylethyl acetate	y = 224949.7x -224199.6	1.000	1.1-106.0	0.3	1.0	25.9	4.2	30.1	7.1	94.3	84.9
141	2-furanmethanol	y = 533.2x - 2225.7	0.926	4.4-89.0	1.5	4.4	7.0	6.2	14.0	10.7	112.4	112.4
173	eucalyptol	y = 5616.7x - 15412.6	0.980	6.2-625.0	0.8	2.4	8.2	21.8	19.6	27.2	80.0	85.9
189	α-terpineol	y = 169457.5x - 961222.2	0.910	4.4-86.0	0.4	1.1	11.0	1.2	17.1	12.7	116.3	93.0
199	β-damascenone	y = 3346.1x - 41847.0	0.996	4.0-395.0	0.5	1.7	19.2	3.3	16.5	20.8	79.8	80.1
221	3-mercaptohexanol	y= 6879.4x - 40552.9	0.975	0.7-350.0	0.2	0.7	2.9	2.0	18.0	26.3	118.6	81.2

a Compounds numbered as in Table 1;b Lowest concentration of the regression equation; c Highest concentration of the regression equation

Table S4. Positively and/or tentatively identified volatile compounds of Merlot wines of Campanha Gaúcha region, Brazil, using HS-SPME-GC×GC/TOFMS with their respective, experimental retention indices (RI_{exp}) and RI reported in scientific literature (RI_{lit}).

#	Compound	RI_{exp} [a]	RI_{lit} [b]	Ref[c]
	acids			
1	acetic acid	1461	1451	(Welke, Manfroi, Zanus, Lazarotto, & Alcaraz Zini, 2012)
2	formic acid	1529	1528	(Vichi et al., 2003)
3	propanoic acid	1550	1535	(Welke et al., 2012)
4	2-methyl-propanoic acid [isobutanoic acid]	1579	1566	(Welke et al., 2012)
5	butanoic acid	1639	1630	(Welke et al., 2012)
6	3-methyl-butanoic acid [isovaleric acid]	1679	1675	(Ledauphin et al., 2004)
7	2-methyl-butanoic acid	1682	1686	(Selli, Canbas, Cabaroglu, Erten, & Günata, 2006)
8	pentanoic acid [valeric acid]	1748	1746	(Ledauphin et al., 2004)
9	hexanoic acid	1856	1855	(Welke et al., 2012)
10	2-ethyl-hexanoic acid	1958	1969	(Welke et al., 2012)
11	heptanoic acid	1962	1950	(Welke et al., 2012)
12	2-hexenoic acid	1976	1971	(Wada & Shibamoto, 1997)
13	octanoic acid	2067	2069	(Ledauphin et al., 2004)
14	nonanoic acid	2173	2168	(Welke et al., 2012)
15	decanoic acid	2280	2269	(Welke et al., 2012)
16	9-decenoic acid	2344	2348	(Mahajan, Goddik, & Qian, 2004)
17	geranic acid	2348	2353	(Selli et al., 2006)
18	benzenecarboxylic acid	2424	2423	(Moio & Addeo, 1998)
19	dodecanoic acid	2448	2449	(Selli et al., 2006)
	alcohols			
20	ethyl alcohol	921	932	(Shimoda, Peralta, & Osajima, 1996)
21	1-propanol	1027	1030	(Ledauphin et al., 2004)
22	3-methyl-2-butanol	1059	1079	(Korhonen, 1984)
23	2-methyl-1-propanol	1089	1090	(Welke et al., 2012)
24	2-propen-1-ol	1119	1124	(Sanz, Ansorena, Bello, & Cid, 2001)
25	2-pentanol	1124	1119	(Ledauphin et al., 2004)
26	1-butanol	1145	1149	(Welke et al., 2012)
27	1-penten-3-ol	1163	1165	(Tatsuka, Suekane, Sakai, & Sumitani, 1990)
28	2-methyl-2-hexanol	1198	1196	(Bonastre & Grenier, 1968)
29	2-methyl-1-butanol	1210	1213	(Welke et al., 2012)
30	3-methyl-1-butanol	1213	1216	(Welke et al., 2012)

31	2-hexanol	1226	1216	(Ledauphin et al., 2004)
32	3-methyl-3-buten-1-ol	1251	1240	(Selli et al., 2006)
33	1-pentanol	1251	1256	(Welke et al., 2012)
34	4-heptanol	1285	1285	(Hayata, Sakamoto, Kozuka, Sakamoto, & Osajima, 2002)
35	3-heptanol	1298	1306	(Shimoda & Shibamoto, 1990)
36	4-methyl-1-pentanol	1316	1312	(Ledauphin et al., 2004)
37	2-heptanol	1321	1318	(Welke et al., 2012)
38	2-penten-1-ol	1324	1325	(Tatsuka et al., 1990)
39	2-methyl-2-buten-1-ol	1324	1328	(Soria, Gonzalez, Lorenzo, Martinez-Castro, & Sanza, 2004)
40	3-methyl-1-pentanol	1329	1343	(Welke et al., 2012)
41	1-hexanol	1355	1371	(Welke et al., 2012)
42	3-hexen-1-ol	1366	1381	(Ledauphin et al., 2004)
43	3-ethoxy-1-propanol	1376	1370	(Ledauphin et al., 2004)
44	2-hexen-1-ol	1419	1409	(Tatsuka et al., 1990)
45	2-octanol	1422	1418	(Fan & Qian, 2006)
46	1-octen-3-ol	1453	1456	(Tatsuka et al., 1990)
47	1-heptanol	1458	1467	(Welke et al., 2012)
48	2-ethyl-1-hexanol	1492	1491	(Welke et al., 2012)
49	4-hepten-1-ol	1506	1502	(Ledauphin et al., 2004)
50	2-nonanol	1518	1521	(Ledauphin et al., 2004)
51	2,3-butanediol	1544	1545	(Gürbüz, Rouseff, & Rouseff, 2006)
52	1-octanol	1562	1559	(Ledauphin et al., 2004)
53	1,3-butanediol	1582	1578	(Kim, Shin, Baek, & Lee, 2001)
54	2-(2-ethoxyethoxy)-ethanol	1621	1619	(Shimoda, Shigematsu, Shiratsuchi, & Osajima, 1995)
55	1-nonanol	1664	1676	(Welke et al., 2012)
56	*Z*-6-nonen-1-ol	1723	1714	(Hayata et al., 2003)
57	2-undecanol	1723	1723	(Ledauphin et al., 2004)
58	1-decanol	1768	1781	(Welke et al., 2012)
59	*Z*-4-decen-1-ol	1800	1797	(Tamura, Kihara, & Sugisawa, 1990)
60	2-dodecanol	1824	1820	(Soria, Sanz, & Martinez-Castro, 2008)
61	2-butyl-1-octanol	1864	1848	(Moreira, Trugo, Pietroluongo, & de Maria, 2002)
62	1-undecanol	1870	1883	(Soria et al., 2008)
63	2-methyl-1-undecanol	1870	1875	(Vinogradov, 2004)
64	benzyl alcohol	1883	1869	(Welke et al., 2012)
65	phenylethyl alcohol	1917	1914	(Ledauphin et al., 2004)
66	1-dodecanol	1969	1970	(Ledauphin et al., 2004)
67	1-tridecanol	2071	2063	(Welke et al., 2012)

68	1-tetradecanol	2178	2175	(Hanai & Hong, 1989)
69	1-hexadecanol	2381	2382	(Ledauphin et al., 2004)
	aldehydes			
70	2-propenal	894	876	(Héberger & Görgényi, 1999)
71	3-methyl-butanal	913	900	(Shimoda & Shibamoto, 1990)
72	2-butenal	1027	1038	(Umano, Hagi, Nakahara, Shyoji, & Shibamoto, 1995)
73	2-methyl-2-butenal	1068	1075	(Fröhlich, Duque, & Schreier, 1989)
74	3-methyl-2-butenal	1200	1200	(Chung, 1999)
75	nonanal	1396	1385	(Ledauphin et al., 2004)
76	decanal	1501	1494	(Welke et al., 2012)
77	benzaldehyde	1527	1513	(Ledauphin et al., 2004)
78	2,6,6-trimethyl-1-cyclohexene-1-carboxaldehyde	1619	1606	(Ledauphin et al., 2004)
79	benzeneacetaldehyde	1649	1631	(Ledauphin et al., 2004)
80	dodecanal	1714	1710	(Welke et al., 2012)
81	4-(1-methylethyl)-benzaldehyde	1781	1781	(Shimoda, Shiratsuchi, Minegishi, & Osajima, 1993)
82	3-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-propenal	1942	1952	(Zhao, Xu, Li, Fan, & Jiang, 2009)
83	hexadecanal	2136	2123	(Liu, Yang, & Wu, 2001)
84	octadecanal	2346	2336	(Liu et al., 2001)
	esters			
85	ethyl acetate	905	887	(Tatsuka et al., 1990)
86	ethyl propanoate	955	968	(Mihara, Tateba, Nishimura, Machii, & Kishino, 1987)
87	ethyl 2-propenoate	989	992	(Horna, 1985)
88	2-methylpropyl acetate	1007	1005	(Gürbüz et al., 2006)
89	ethyl butanoate	1021	1023	(Ledauphin et al., 2004)
90	ethyl 2-methyl-butanoate	1037	1036	(Ledauphin et al., 2004)
91	ethyl 3-methyl-butanoate	1052	1053	(Ledauphin et al., 2004)
92	3-methyl-1-butanol acetate	1122	1124	(Tatsuka et al., 1990)
93	ethyl 2-butenoate	1164	1161	(Mihara et al., 1987)
94	methyl hexanoate	1188	1176	(Ledauphin et al., 2004)
95	ethyl hexanoate	1234	1238	(Welke et al., 2012)
96	hexyl acetate	1275	1276	(Tatsuka et al., 1990)
97	ethyl 2-oxo-propanoate	1277	1268	(Umano et al., 1995)
98	ethyl 2-hexenoate	1346	1329	(Zhao et al., 2009)
99	ethyl 2-hydroxy-propanoate	1347	1334	(Welke et al., 2012)
100	methyl octanoate	1390	1386	(Ledauphin et al., 2004)
101	ethyl 2-hydroxy-3-methyl-butanoate	1428	1422	(Ledauphin et al., 2004)
102	ethyl octanoate	1437	1424	(Welke et al., 2012)
103	isopentyl hexanoate	1460	1452	(Ledauphin et al., 2004)
104	ethyl 3-hydroxy-butanoate	1524	1518	(Ledauphin et al., 2004)

105	ethyl nonanoate	1539	1530	(Ledauphin et al., 2004)
106	ethyl 2-hydroxy-4-methyl-pentanoate	1550	1547	(Welke et al., 2012)
107	isoamyl lactate	1574	1570	(Ledauphin et al., 2004)
108	diethyl propanedioate	1586	1580	(Ledauphin et al., 2004)
109	ethyl decanoate	1641	1638	(Welke et al., 2012)
110	ethyl methyl butanedioate	1643	1632	(Ledauphin et al., 2004)
111	3-methylbutyl octanoate	1662	1658	(Ledauphin et al., 2004)
112	ethyl benzoate	1670	1664	(Welke et al., 2012)
113	diethyl butanedioate [diethyl succinate]	1682	1690	(Welke et al., 2012)
114	ethyl 3-hydroxy-hexanoate	1685	1675	(Umano, K.; Hagi, Y.; Nakahara, K.; Shoji, A.; Shibamoto, 1992)
115	ethyl 9-decenoate	1695	1689	(Ledauphin et al., 2004)
116	methyl 2-hydroxy-benzoate	1778	1775	(Welke et al., 2012)
117	diethyl pentanedioate	1788	1780	(Ledauphin et al., 2004)
118	ethyl benzeneacetate	1791	1783	(Ledauphin et al., 2004)
119	2-phenylethyl formate	1791	1784	(Werkhoff & Güntert, 30AD)
120	methyl dodecanoate	1804	1793	(Welke et al., 2012)
121	ethyl 2-hydroxy-benzoate	1814	1798	(Ledauphin et al., 2004)
122	2-phenylethyl acetate	1821	1829	(Welke et al., 2012)
123	ethyl dodecanoate	1848	1835	(Welke et al., 2012)
124	3-methylbutyl pentadecanoate	1865	1859	(Ledauphin et al., 2004)
125	2-phenylethyl 2-methyl-propanoate	1884	1877	(Umano, Hagi, Nakahara, Shoji, & Shibamoto, 2000)
126	diethyl hexanedioate	1908	1897	(Ledauphin et al., 2004)
127	methyl tetradecanoate	2009	2006	(Ledauphin et al., 2004)
128	diethyl hydroxy-butanedioate	2048	2041	(Selli et al., 2006)
129	ethyl tetradecanoate	2050	2065	(Welke et al., 2012)
130	ethyl 3-phenyl-2-propenoate	2135	2125	(Guth, 1997)
131	2-phenylethyl hexanoate	2174	2164	(Ledauphin et al., 2004)
132	methyl hexadecanoate	2218	2223	(Ledauphin et al., 2004)
133	ethyl hexadecanoate	2258	2246	(Welke et al., 2012)
134	ethyl hydrogen succinate	2392	2395	(Wada & Shibamoto, 1997)
	furans			
135	2,3,5-trimethyl-furan	1042	1056	(Shimoda & Shibamoto, 1990)
136	2-pentyl-furan	1232	1235	(Tatsuka et al., 1990)
137	furfural	1472	1462	(Ledauphin et al., 2004)
138	1-(2-furanyl)-ethanone	1509	1500	(Ledauphin et al., 2004)
139	5-methyl-2-furancarboxaldehyde	1580	1570	(Welke et al., 2012)
140	ethyl 2-furancarboxylate	1631	1618	(Welke et al., 2012)
141	2-furanmethanol	1670	1662	(Ledauphin et al., 2004)
	ketones			
142	2-pentanone	965	974	(Tatsuka et al., 1990)
143	2,3-butanedione	980	977	(Tatsuka et al., 1990)
144	3-hexanone	1037	1050	(Umano et al., 1995)

145	2,3-pentanedione	1048	1055	(Umano et al., 1995)
146	3-penten-2-one	1127	1126	(Tatsuka et al., 1990)
147	2-heptanone	1179	1173	(Ledauphin et al., 2004)
148	cyclopentanone	1182	1192	(Soria et al., 2008)
149	3-hydroxy-2-butanone	1287	1304	(Welke et al., 2012)
150	6-methyl-5-hepten-2-one	1340	1339	(Tatsuka et al., 1990)
151	2-methyl-2-cyclopenten-1-one	1366	1366	(Umano et al., 1995)
152	2-nonanone	1390	1382	(Ledauphin et al., 2004)
153	2,3-dimethyl-2-cyclopenten-1-one	1536	1535	(Shiratsuchi, Shimoda, Minegishi, & Osajima, 1993)
154	acetophenone	1652	1649	(Welke et al., 2012)
	lactones			
155	5-methyl-2(3H)-furanone [α-angelicalactona]	1436	1435	(Umano et al., 1995)
156	butyrolactone	1633	1635	(Selli et al., 2006)
157	5-ethoxydihydro-2(3H)-furanone	1729	1728	(Natali, Chinnici, & Riponi, 2006)
158	2(5H)-furanone [γ-crotolactone]	1758	1746	(Umano et al., 1995)
159	5-butyldihydro-2(3H)-furanone [γ-octalactone]	1918	1911	(Chang, Sheng, Yang, & An, 1989)
160	5-pentyldihydro-2(3H)-furanone [γ-nonalactone]	2030	2010	(Umano, K.; Hagi, Y.; Nakahara, K.; Shoji, A.; Shibamoto, 1992)
161	pantolactone	2037	2033	(Mebazaa et al., 2009)
162	5-hexyldihydro-2(3H)-furanone	2147	2138	(Ledauphin et al., 2004)
	phenols			
163	phenol	2015	2015	(Gerbino & Castello, 1995)
164	4-ethyl-2-methoxy-phenol	2034	2033	(Welke et al., 2012)
165	4-methyl-phenol	2092	2091	(Shiratsuchi, Shimoda, Imayoshi, Noda, & Osajima, 1994)
166	4-ethyl-phenol	2184	2190	(Ledauphin et al., 2004)
167	2-(1,1-dimethylethyl)-4-methyl-phenol	2244	2235	(Chung, 1999)
168	2-(1,1-dimethylethyl)-5-methyl-phenol	2268	2260	(Shiratsuchi et al., 1994)
169	2,4-bis(1,1-dimethylethyl)-phenol	2324	2321	(Shiratsuchi et al., 1994)
	terpenes			
170	2-methyl-5-(1-methylethyl)-bicyclo[3.1.0]hex-2-ene [α-thujene]	1012	1020	(Shellie, Mondello, Marriott, & Dugo, 2002)
171	2,6,6-trimethylbicyclo[3.1.1]hept-2-ene [α-pinene]	1159	1165	(Tatsuka et al., 1990)
172	1-methyl-4-(1-methylethenyl)-cyclohexene [limonene]	1191	1198	(Tatsuka et al., 1990)
173	1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane [eucalyptol]	1199	1209	(Tatsuka et al., 1990)
174	1-methyl-4-(1-methylethyl)-1,4-cyclohexadiene [γ-terpinolene]	1240	1243	(Umano, Hagi, Tamura, Shoji, & Shibamoto, 1994)
175	3,7-dimethyl-1,3,6-octatriene [β-ocimene]	1252	1234	(Umano et al., 1994)
176	1-methyl-2-(1-methylethyl)-benzene [*p*-cymene]	1268	1266	(Umano et al., 2000)

177	1-methyl-4-(1-methylethylidene)-cyclohexene [α-terpinolene]	1278	1280	(Umano et al., 1994)
178	1-methyl-4-(1-methylethenyl)-benzene [*p*-cymenene]	1437	1433	(Umano et al., 1994)
179	2,6-dimethyl-7-octen-2-ol [myrcenol]	1472	1470	(Chang et al., 1989)
180	(1S)-1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-one [camphor]	1510	1507	(Kjeldsen, Christensen, & Edelenbos, 2003)
181	3,7-dimethyl-1,6-octadien-3-ol[linalool]	1553	1555	(Welke et al., 2012)
182	α-4-trimethyl-cyclohexanemethanol [α-terpineol dihydro]	1562	1560	(Kollmannsberger, H.; Nitz, S.; Drawert, 1992)
183	4-methyl-1-(1-methylethyl)-3-cyclohexen-1-ol [terpinen-4-ol]	1604	1602	(Welke et al., 2012)
184	1,1,7-trimethyl-4-methylenedecahydro-1H-cyclopropa[e]azulene [aromadendrene]	1602	1610	(Umano et al., 2000)
185	3,7-dimethyl-1,5,7-octatrien-3-ol [hotrienol]	1615	1611	(Takeoka, Flath, Güntert, & Jennings, 1988)
186	(1à,2á,5à)-5-methyl-2-(1-methylethyl)-cyclohexanol [menthol]	1643	1637	(Umano, K.; Hagi, Y.; Nakahara, K.; Shoji, A.; Shibamoto, 1992)
187	*E*-7,11-dimethyl-3-methylene-1,6,10-dodecatriene [β-farnesene]	1668	1664	(Ledauphin et al., 2004)
188	2-methyl-5-(1-methylethyl)-2-cyclohexen-1-one	1677	1697	(Baser, Demirci, Dekebo, & Dagne, 2003)
189	α-4-trimethyl-3-cyclohexene-1-methanol [α-terpineol]	1700	1695	(Tatsuka et al., 1990)
190	3-methyl-6-(1-methylethyl)-2-cyclohexen-1-one [isopiperitone]	1723	1722	(Gonny, Cavaleiro, Salgueiro, & Casanova, 2006)
191	1-methyl-4-(5-methyl-1-methylene-4-hexenyl)-cyclohexene [β-bisabolene]	1728	1722	(Gonny et al., 2006)
192	*Z,E*-3,7,11-trimethyl-1,3,6,10-dodecatetraene [*Z,E*-α-farnesene]	1731	1726	(Umano et al., 2000)
193	2-methyl-5-(1-methylethenyl)-2-cyclohexen-1-one [carvone]	1733	1748	(Mihara et al., 1987)
194	*E,E*- 3,7,11-trimethyl-1,3,6,10-dodecatetraene [*E,E*-α-farnesene]	1753	1754	(Tatsuka et al., 1990)
195	(1S-*cis*)-1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-naphthalene [δ-cadinene]	1757	1753	(Umano et al., 2000)
196	3,7-dimethyl-6-octen-1-ol [citronellol]	1771	1778	(Welke et al., 2012)
197	1-(1,5-dimethyl-4-hexenyl)-4-methyl-benzene [α-curcumene]	1776	1768	(Gonny et al., 2006)
198	(1à,3à,5à)-4-methylene-1-(1-methylethyl)-bicyclo[3.1.0]hexan-3-ol [sabinol]	1810	1800	(Baser et al., 2003)
199	1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one [β-damascenone]	1821	1831	(Welke et al., 2012)
200	1-methoxy-4-(1-propenyl)-benzene [anethol]	1831	1815	(Lee, Umano, Shibamoto, & Lee, 2005)
201	*E*-3,7-dimethyl-2,6-octadien-1-ol [geraniol]	1854	1853	(Tatsuka et al., 1990)
202	*Z*-6,10-dimethyl-5,9-undecadien-2-one	1858	1856	(Welke et al., 2012)

	[geranyl acetone]			
203	2-methoxy-phenol [o-guaiacol]	1867	1855	(Ledauphin et al., 2004)
204	3,7,11-trimethyl-1,6,10-dodecatrien-3-ol [nerolidol]	2045	2039	(Gyawali & Kim, 2012)
205	[1S-(1α,4β,4aβ,8aα)]-1-isopropyl-4,7-dimethyl-1,3,4,5,6,8a-hexahydro-4a(2H)-naphthalenol [cubenol]	2057	2062	(Gonny et al., 2006)
206	[1R-(1à,3à,4á)]-4-ethenyl-à,à,4-trimethyl-3-(1-methylethenyl)-cyclohexanemethanol [elemol]	2082	2079	(Umano et al., 1994)
207	(1aS,4aS,7R,7aS,7bS)-1,1,7-trimethyl-4-methylenedecahydro-1H-cyclopropa[e]azulen-7-ol [spathulenol]	2124	2124	(Gonny et al., 2006)
208	(1S,4S,4aR,8aR)-1,6-dimethyl-4-propan-2-yl-3,4,4a,7,8,8a-hexahydro-2H-naphthalen-1-ol [τ-cadinol]	2170	2170	(Gonny et al., 2006)
209	(R*,R*)-alpha,4-dimethyl-alpha-(4-methyl-3-pentenyl)-3-cyclohexene-1-methanol [α-bisabolol]	2221	2214	(Umano et al., 1994)
210	2-methyl-5-(1-methylethyl)-phenol [carvacrol]	2224	2215	(Gonny et al., 2006)
211	decahydro-à,à,4a-trimethyl-8-methylene-2-naphthalenemethanol [β-eudesmol]	2229	2231	(Gonny et al., 2006)
212	(1R,4S,4aR,8aR)-4-Isopropyl-1,6-dimethyl-1,2,3,4,4a,7,8,8a-octahydronaphthalen-1-ol [α-cadinol]	2233	2231	(Gonny et al., 2006)
213	aromadendrene oxide	2285	2299	(Guo et al., 2008)
	sulfur compounds			
214	methylthiol acetate	1034	1047	(Stashenko, Macku, & Shibamato, 1992)
215	dihydro-2-methyl-3(2H)-thiophenone	1530	1518	(Ledauphin et al., 2004)
216	2-(methylthio)-ethanol	1532	1516	(Umano et al., 2000)
217	ethyl 3-(methylthio)propanoate	1571	1562	(Ledauphin et al., 2004)
218	2-thiophenecarboxaldehyde	1697	1684	(Ledauphin et al., 2004)
219	3-(methylthio)-1-propanol	1723	1720	(Ledauphin et al., 2004)
220	benzothiazole	1956	1956	(Welke et al., 2012)

[a]RI_{exp}: experimental retention index (RI) calculated using *n*-alkanes (C9-C24) in DB-Wax (100% polyethyleneglycol) × DB-17 ms ([50%-phenyl]-methylpolysiloxane) column set.

[b]RI_{lit}: literature RI on a DB-WAX column or equivalent stationary phase in 1D-GC.

[c]Ref: references

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Table S5. Loadings obtained in the principal component analysis of the 24 volatile compounds indicated by Fisher ratio as the most discriminating among the samples of Merlot wines produced using grapes grown under 10 different conditions of canopy management (M1 to M10 as described in **Table 1**). The variables with higher loading values are the ones that contributed most to explain that specific factor (**in bold**).

	Principal Component (PC)	**PC1**	**PC2**	**PC3**	
	Eigenvalue	11.3	7.5	1.8	
#	**Variance (%)**	47.0	31.2	7.6	
	Cumulative variance (%)	47.0	78.2	85.8	**Aroma**
189	α-terpineol	**-0.896**	0.201	-0.054	floral, lily [a]
198	sabinol	**-0.895**	0.351	0.016	nf
199	β-damascenone	**-0.858**	-0.449	-0.075	rose, candy[b]
83	hexadecanal	**-0.829**	-0.103	0.282	nf
181	linalool	**-0.814**	-0.545	-0.110	rose [a]
21	1-propanol	**-0.808**	0.392	0.135	fruity [a]
122	2-phenylethyl acetate	**-0.777**	-0.415	-0.017	jasmine, plum, floral [b]
173	eucalyptol	**-0.776**	-0.603	0.001	mint[c]
79	benzeneacetaldehyde	**-0.774**	0.473	0.337	sweetish roasted, caramel-like [d]
85	ethyl acetate	**-0.767**	-0.427	-0.242	fruity[a]
176	*p*-cymene	**-0.751**	-0.589	0.112	solvent, gasoline[e], citrus[j]
219	3-methylthio-1-propanol	**-0.725**	0.600	0.177	boiledcabbage[a]
95	ethyl hexanoate	**-0.700**	-0.664	0.039	fruity[a]
135	2,3,5-trimethyl furane	**-0.690**	-0.371	0.293	nf
41	1-hexanol	**-0.648**	-0.494	-0.431	fruity[a]
13	octanoic acid	-0.362	**0.838**	-0.268	fatty[a]
9	hexanoic acid	-0.466	**0.812**	-0.016	cheese, fatty[f]
107	isoamyl lactate	-0.335	**0.775**	-0.090	fruity[g]
64	benzyl alcohol	-0.495	**0.732**	0.209	sweet, floral [h]
82	3-(2,6,6-trimethyl-1-cyclohexen-1-il)-2-propenal	-0.541	**0.712**	-0.129	nf
19	dodecanoic acid	-0.687	**0.712**	-0.003	metallic, oil[i]
102	ethyl octanoate	-0.663	**-0.676**	0.025	fruity[f]
51	2,3-butanodiol	0.069	0.071	**0.824**	berry, sweet [b]
126	diethyl hexanodioate	-0.377	0.471	**-0.626**	nf

Compounds numbered as in Table 2.

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nf: not found in the literature

Table S6. Mean score of descriptive attributes (± standard deviation) obtained by Quantitative Descriptive Analysis (QDA) for appearance, aroma and taste/mouth sensations evaluated by the sensory trained panel for each Merlot wine produced using grapes grown according to ten different vine managements (M1 to M10 as described in Table 1).

ATRIBUTES	M1A	M1B	M2A	M2B	M3A	M3B	M4A	M4B	M5A	M5B	M6A	M6B	M7A	M7B	M8A	M8B	M9A	M9B	M10A	M10B
appearance																				
color intensity	6.4 ± 0.2 abc	5.7 ± 0.4 cde	1.9 ± 0.3 f	2.2 ± 0.3 g	4.9 ± 0.4 d	4.6 ± 0.5 f	4.6 ± 0.7 de	6.0 ± 0.3 bcd	5.8 ± 0.3c	6.4 ± 0.3 ab	6.1 ± 0.5 bc	6.3 ± 0.6 bc	4.7 ± 0.8 de	4.7 ± 0.4 f	6.8 ± 0.4 a	7.1 ± 0.2 a	6.7 ± 0.3 ab	5.6 ± 0.4 de	4.2 ± 0.8 e	5.2 ± 0.3 ef
red-purple tonality	6.3 ± 0.5 abc	5.9 ± 0.4 bcd	2.4 ± 0.2 g	3.1 ± 0.2 f	5.2 ± 0.5 de	5.0 ± 0.6 e	4.8 ± 0.8 ef	6.3 ± 0.4b	5.9 ± 0.4 cd	6.5 ± 0.4 ab	6.2 ± 0.6 bc	6.5 ± 0.4 ab	4.7 ± 0.8 ef	5.4 ± 0.2 de	7.0 ± 0.6 a	7.0 ± 0.2 a	6.9 ± 0.3 ab	6.2 ± 0.4 bc	4.4 ± 0.8 f	5.5 ± 0.5 cde
brightness	5.3 ± 0.5b	6.1 ± 0.3 ab	6.7 ± 0.4 a	6.7 ± 0.3 a	5.8 ± 0.5 ab	6.4 ± 0.6 ab	5.7 ± 0.5 b	6.0 ± 0.3ab	5.3 ± 0.7 b	5.8 ± 0.6 b	5.8 ± 0.4 ab	6.1 ± 0.3 ab	5.8 ± 0.4 ab	6.6 ± 0.5 ab	5.4 ± 0.4 b	5.9 ± 0.4 b	5.4 ± 0.7 b	6.23 ± 0.4 ab	5.6 ± 0.4 b	6.3 ± 0.5 ab
aroma																				
aromatic intensity	6.1 ± 0.2 a	5.0 ± 0.4 abcd	4.7 ± 0.5 cd	4.6 ± 0.2 cd	5.4 ± 0.6 abc	5.4 ± 0.7 ab	5.2 ± 0.5 bc	5.3 ± 0.7 abc	5.4 ± 0.5 abc	4.9 ± 0.3 abcd	5.7 ± 0.5 ab	4.9 ± 0.5 abcd	4.8 ± 0.5 cd	4.7 ± 0.6 bcd	5.2 ± 0.5 bc	5.5 ± 0.3 a	5.1 ± 0.6 bcd	4.5 ± 0.3 d	4.3 ± 0.4 d	5.0 ± 0.3 abcd
undesirable aroma	0.2 ± 0.1 d	0.2 ± 0.0 e	2.8 ± 0.6 a	1.0 ± 0.2 bc	0.2 ± 0.1 d	0.5 ± 0.2 de	1.0 ± 0.1 bc	0.5 ± 0.2 de	0.5 ± 0.1 bcd	0.3 ± 0.1 de	0.4 ± 0.1 cd	0.5 ± 0.2 de	2.9 ± 0.1 a	1.9 ± 0.4 a	0.7 ± 0.1 bcd	0.8 ± 0.3 bcd	1.3 ± 0.1 b	1.2 ± 0.3 b	3.0 ± 0.1 a	2.0 ± 0.5 a
aroma of red fruits	5.1 ± 0.5 a	4.3 ± 0.5 a	2.4 ± 0.6 e	3.4 ± 0.2 bcd	4.4 ± 0.7 ab	4.3 ± 0.6 a	4.0 ± 0.6 bc	4.0 ± 0.7 abc	4.7 ± 0.3 ab	3.9 ± 0.3 abc	4.6 ± 0.3 ab	4.1 ± 0.6 abc	3.0 ± 0.9 de	2.3 ± 0.7 e	4.3 ± 0.9 abc	3.9 ± 0.6 abc	3.5 ± 0.9 cd	3.4 ± 0.7 cd	2.2 ± 0.9 e	3.0 ± 0.2 de
aroma of dry fruits	2.9 ± 0.3 a	2.6 ± 0.3 a	2.0 ± 0.5 cd	2.4 ± 0.2 ab	2.6 ± 0.2 abc	2.6 ± 0.2 a	2.7 ± 0.5 abc	2.5 ± 0.2 ab	2.8 ± 0.3 ab	2.3 ± 0.4 ab	2.7 ± 0.4 abc	2.2 ± 0.2 abc	1.7 ± 0.4 d	1.5 ± 0.1 d	2.5 ± 0.6 abc	2.6 ± 0.5 a	2.1 ± 0.4 bcd	1.9 ± 0.2 bcd	1.7 ± 0.6 d	1.6 ± 0.1 d
alcoholic aroma	3.9 ± 0.3 a	2.8 ± 0.5 a	2.8 ± 0.4 b	2.7 ± 0.5 a	3.3 ± 0.4 ab	2.2 ± 0.4 ab	3.1 ± 0.5 b	2.4 ± 0.3 ab	3.2 ± 0.3ab	2.2 ± 0.4 ab	3.2 ± 0.5 ab	2.2 ± 0.2 ab	2.7 ± 0.5 b	1.8 ± 0.2 b	3.3 ± 0.6 ab	2.7 ± 0.3 a	3.1 ± 0.5 b	2.1 ± 0.5 ab	2.8 ± 0.5 b	2.4 ± 0.4 ab
herbaceous aroma	1.6 ± 0.5 cd	1.5 ± 0.5 ab	2.9 ± 0.5 b	2.1 ± 0.4 a	2.0 ± 0.5 bc	1.7 ± 0.3 ab	2.1 ± 0.4 bc	1.4 ± 0.4ab	1.5 ± 0.4 cd	1.2 ± 0.5 b	0.9 ± 0.2 d	1.0 ± 0.3 b	2.4 ± 0.2 ab	1.9 ± 0.3 a	1.6 ± 0.5 cd	1.5 ± 0.3 ab	1.8 ± 0.3 bc	1.4 ± 0.3 ab	2.8 ± 0.3 a	1.7 ± 0.3 ab
spices aroma	2.2 ± 0.3 a	1.9 ± 0.5 a	1.6 ± 0.3 a	2.0 ± 0.3 a	2.0 ± 0.3 a	1.8 ± 0.4 a	1.9 ± 0.3 a	1.7 ± 0.3 a	1.8 ± 0.4 a	1.6 ± 0.4 a	1.7 ± 0.2 a	1.5 ± 0.3 a	1.4 ± 0.3 a	1.4 ± 0.2 a	1.9 ± 0.4 a	2.0 ± 0.3 a	1.5 ± 0.5 a	1.7 ± 0.4 a	1.7 ± 0.2 a	1.7 ± 0.3 a
vegetal aroma	1.7 ± 0.6 bcd	1.2 ± 0.4 bcd	2.5 ± 0.2 a	1.8 ± 0.5 ab	1.4 ± 0.2 bcd	1.5 ± 0.3abcd	1.6 ± 0.3 bcd	1.1 ± 0.2 bc	1.3 ± 0.3 dc	1.1 ± 0.2bc	1.2 ± 0.4 d	0.9 ± 0.3 d	1.9 ± 0.3 abc	1.9 ± 0.3 a	1.3 ± 0.2 dc	1.5 ± 0.3 abcd	1.8 ± 0.4 abcd	1.6 ± 0.6 abc	2.1 ± 0.4 ab	1.9 ± 0.5 a
caramelized aroma	1.7 ± 0.4 ab	1.5 ± 0.3 abc	1.1 ± 0.4 bc	1.6 ± 0.2 abc	1.5 ± 0.3 abc	1.7 ± 0.3 ab	1.5 ± 0.2 abc	1.5 ± 0.4 abc	1.7 ± 0.4 ab	1.4 ± 0.2 abc	1.8 ± 0.5 a	1.2 ± 0.5 bcd	1.0 ± 0.4 c	1.1 ± 0.3 cd	1.6 ± 0.4 abc	1.8 ± 0.3 a	1.2 ± 0.3 abc	1.4 ± 0.3 abcd	1.0 ± 0.3 c	0.9 ± 0.1 d
taste/mouth sensations																				
persistence	5.5 ± 0.3 a	4.7 ± 0.5 abc	3.4 ± 0.5 e	3.9 ± 0.3 d	5.3 ± 0.4 abc	4.4 ± 0.5 cd	4.6 ± 0.7cd	5.1 ± 0.4 abc	5.4 ± 0.3 ab	5.3 ± 0.4 ab	5.1 ± 0.4 abcd	5.1 ± 0.6 abc	4.7 ± 0.6 bcd	4.6 ± 0.7 bcd	5.6 ± 0.8 a	5.5 ± 0.5 a	5.4 ± 0.4 ab	4.9 ± 0.4 abc	4.4 ± 0.4 d	4.7 ± 0.4 abc
sourness	4.2 ± 0.4 a	4.3 ± 0.5 ab	3.4 ± 0.5 b	3.6 ± 0.3 b	3.7 ± 0.6 ab	4.0 ± 0.6 ab	3.7 ± 0.5 ab	4.6 ± 0.4 a	3.7 ± 0.3 ab	4.4 ± 0.5 a	4.3 ± 0.4 a	4.6 ± 0.2 a	3.2 ± 0.5 b	4.0 ± 0.4 ab	3.9 ± 0.6 ab	4.4 ± 0.7 a	3.9 ± 0.3 ab	4.6 ± 0.9 a	3.2 ± 0.5 b	4.5 ± 0.4 a
bitterness	2.2 ± 0.3 bc	1.8 ± 0.4 b	2.9 ± 0.4 ab	2.3 ± 0.5 ab	2.3 ± 0.3 bc	2.2 ± 0.5 ab	2.7 ± 0.2 abc	1.9 ± 0.4 b	2.5 ± 0.4 bc	2.0 ± 0.4 ab	2.6 ± 0.5 abc	1.9 ± 0.2 b	2.9 ± 0.6 ab	2.3 ± 0.3 ab	2.0 ± 0.5 c	2.2 ± 0.2ab	2.9 ± 0.4 ab	2.5 ± 0.4 ab	3.3 ± 0.4 a	2.7 ± 0.5 a
swetness	2.7 ± 0.4 a	2.4 ± 0.7 a	2.2 ± 0.4 a	2.0 ± 0.5ab	2.7 ± 0.6 a	2.0 ± 0.4 ab	2.2 ± 0.5 a	2.4 ± 0.4 a	2.6 ± 0.2 a	2.5 ± 0.4 a	2.6 ± 0.5 a	2.5 ± 0.4 a	2.3 ± 0.3 a	1.7 ± 0.6 b	2.7 ± 0.2 a	2.5 ± 0.4 a	2.3 ± 0.5 a	2.0 ± 0.3 ab	2.2 ± 0.6 a	2.1 ± 0.3 ab
defect in mouth	0.9 ± 0.3 b	0.6 ± 0.2 d	2.4 ± 0.2 a	1.1 ± 0.4 abcd	0.7 ± 0.2b	1.0 ± 0.2 bcd	1.2 ± 0.3 b	0.8 ± 0.3 bcd	0.8 ± 0.2 b	0.7 ± 0.3 cd	1.1 ± 0.3 b	0.9 ± 0.4 bcd	2.1 ± 0.3 a	1.4 ± 0.5 ab	0.7 ± 0.3 b	1.1 ± 0.4 abcd	1.0 ± 0.3 b	1.2 ± 0.2 abc	2.6 ± 0.3 a	1.6 ± 0.4 a
astringency	3.9 ± 0.4 a	3.0 ± 0.6 bc	2.9 ± 0.4 a	2.9 ± 0.4 c	3.9 ± 0.5 a	3.5 ± 0.7 abc	3.9 ± 0.4 a	3.8 ± 0.4 ab	3.9 ± 0.7 a	3.4 ± 0.4 abc	4.1 ± 0.5 a	3.7 ± 0.3 abc	3.8 ± 0.7 a	3.6 ± 0.4 abc	4.0 ± 0.5 a	4.0 ± 0.8 a	4.1 ± 0.5 a	4.0 ± 0.7 a	3.9 ± 0.7 a	3.6 ± 0.7 abc
body	5.0 ± 0.7 a	4.5 ± 0.4 abc	2.1 ± 0.2 e	2.9 ± 0.4 d	4.6 ± 0.2 abc	4.1 ± 0.2 c	4.2 ± 0.5bc	5.0 ± 0.4a	4.9 ± 0.5 ab	5.1 ± 0.3 a	5.0 ± 0.3 a	4.9 ± 0.8 ab	4.1 ± 0.6 cd	4.1 ± 0.7 c	5.1 ± 0.5 a	5.2 ± 0.3 a	4.9 ± 0.4 ab	4.5 ± 0.6 abc	3.4 ± 0.4 d	4.2 ± 0.6 bc
smell and taste harmony	5.3 ± 0.4 a	5.1 ± 0.3 ab	3.0 ± 0.7 d	3.5 ± 0.3 d	5.1 ± 0.3 ab	4.8 ± 0.3 ab	4.1 ± 0.4 bc	5.0 ± 0.2 ab	5.0 ± 0.3 ab	5.3 ± 0.5 a	4.8 ± 0.8 abc	5.0 ± 0.5 ab	3.9 ± 0.8 cd	3.9 ± 0.6 cd	5.0 ± 0.5 ab	5.1 ± 0.3 ab	4.5 ± 0.4 abc	4.4 ± 0.4 bc	3.0 ± 0.8 d	3.9± 0.4 cd

* In the same line means showing common letter are not significantly different (p = 5%)

Table S7. Loadings obtained in the principal component analysis of sensory attributes of 20 wine samples described by quantitative descriptive analysis (QDA) as show in **Fig. 2**.

	PC1	**PC2**
% cumulative	72.1	86.8
Eigenvalue	6.1	1.2
color intensity	**1.269**	0.423
red-purple tonality	**1.151**	0.387
body	**0.765**	0.111
undesirable aroma	**-0.713**	0.532
smell-taste harmony	**0.667**	-0.195
aroma of red fruits	**0.624**	-0.462
persistence	**0.520**	0.117
herbaceous aroma	**-0.436**	0.053
defect in mouth	**-0.456**	0.255
vegeral aroma	**-0.319**	0.101
sourness	**0.300**	0.023
aromatic intensity	**0.287**	-0.172
brightness	**-0.243**	-0.069
bitterness	**-0.247**	0.168
astringency	**0.205**	0.184
sweetness	**0.165**	-0.066
aroma of dry fruits	0.224	**-0.299**
caramelized aroma	0.149	**-0.188**
alcoholic aroma	0.106	**-0.161**
spice aroma	0.047	**-0.127**

Table S8. Higher and lower concentrations of volatile compounds that are the main responsible for distinguishing M1 and M2 from wines produced with grapes from different canopy managements, according to PCA of Figure 1.

Compound	**Concentration (μg L^{-1})**			
Managements	**Higher**	**Lower**	**Difference in concentration between M1/M2 and other wines**	p^a
Compounds related to M1 sample according PCA				
Sample	**M1**	**Other samples**		
β-damascenone	124.8	19.5 (M10)	M1 84% > M10	$8.2\ 10^{-4}$
linalool	7.1	5.8 (M10)	M1 18% > M10	$\mathbf{5.0\ 10^{-2}}$
2-phenylethyl acetate	19.3	7.7 (M10)	M1 60% > M10	$1.9\ 10^{-4}$
eucalyptol	99.3	6.3 (M4, M5, M10)	M1 94% > M4, M5, M10	$5.0\ 10^{-5}$
p-cymene	37.3	6.5 (M10)	M1 83% > M10	$9.0\ 10^{-5}$
ethyl hexanoate	31.3	5.5 (M3 - M5, M8 - M10)	M1 82% > M3 - M5, M8 - M10	$9.9\ 10^{-7}$
2,3,5-trimethyl furane	97.9	6.0 (M3, M6 - M8, M10)	M1 94% > M3, M6 - M8, M10	$2.2\ 10^{-4}$
1-hexanol	435.9	250.7 (M4)	M1 42% > M4	$1.8\ 10^{-3}$
ethyl octanoate	21.2	10.7 (M10)	M1 50% > M10	$1.1\ 10^{-4}$
Compounds related to M2 sample according PCA				
	M2	**Other samples**	**Difference**	
α-terpineol	7.3	6.2 (M10)	M2 15% > M10	$1.8\ 10^{-2}$
sabinol	6.5	6.0 (M10)	M2 8% > M10	$\mathbf{2.6\ 10^{-1}}$
1-propanol	229.4	130.4 (M10)	M2 43% > M10	$9.1\ 10^{-4}$
benzeneacetaldehyde	181.3	85.9 (M10)	M2 52% > M10	$9.9\ 10^{-5}$
3-methylthio-1-propanol	266.3	144.0 (M8)	M2 46% > M8	$5.8\ 10^{-5}$
isoamyl lactate	27.9	5.5 (M6)	M2 80% > M6	$1.2\ 10^{-7}$
benzyl alcohol	96.2	21.3 (M8)	M2 79% > M8	$5.7\ 10^{-4}$
3-(2,6,6-trimethyl-1-cyclohexen-1-il)-2-propenal	8.7	4.5 (M1, M3-M10)	M2 48% > M1, M3 - M10	$3.1\ 10^{-3}$
dodecanoic acid	18.4	6.6 (M6)	M2 64% > M6	$2.0\ 10^{-6}$
diethyl hexanodioate	489.1	50.0 (M5, M6, M8)	M2 90% > M5, M6, M8	$5.3\ 10^{-6}$

[a] $p < 0.05$: concentration with significant difference according to Student's t-test.

%= (1- mean of the minimum concentration obtained among wines of different treatments/mean of the maximum concentration obtained in M1 or M2) x 100