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Characterization of the volatile profile of Brazilian Merlot wines through comprehensive two dimensional gas chromatography time-of-flight mass spectrometric detection

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ABSTRACT

Wine aroma is an important characteristic and may be related to certain specific parameters, such as raw material and production process. The complexity of Merlot wine aroma was considered suitable for comprehensive two-dimensional gas chromatography (GC × GC), as this technique offers superior performance when compared to one-dimensional gas chromatography (1D-GC). The profile of volatile compounds of Merlot wine was, for the first time, qualitatively analyzed by HS-SPME-GC × GC with a time-of-flight mass spectrometric detector (TOFMS), resulting in 179 compounds tentatively identified by comparison of experimental GC × GC retention indices and mass spectra with literature 1D-GC data and 155 compounds tentatively identified only by mass spectra comparison. A set of GC × GC experimental retention indices was also, for the first time, presented for a specific inverse set of columns. Esters were present in higher number (94), followed by alcohols (80), ketones (29), acids (29), aldehydes (23), terpenes (23), lactones (16), furans (14), sulfur compounds (9), phenols (7), pyrroles (5), C13-norisoprenoids (3), and pyrans (2). GC × GC/TOFMS parameters were improved and optimal conditions were: a polar (polyethylene glycol)/medium polar (50% phenyl 50% dimethyl arylene siloxane) column set, oven temperature offset of 10 °C, 7 s as modulation period and 1.4 s of hot pulse duration. Co-elutions came up to 138 compounds in ^{1}D and some of them were resolved in ^{2}D. Among the co-eluted compounds, thirty-three volatiles co-eluted in both ^{1}D and ^{2}D and their tentative identification was possible only due to spectral deconvolution. Some compounds that might have important contribution to aroma notes were included in these superimposed peaks. Structurally organized distribution of compounds in the 2D space was observed for esters, aldehydes and ketones, alcohols, thiols, lactones, acids and also inside subgroups, as occurred with esters and alcohols. The Fischer Ratio was useful for establishing the analytes responsible for the main differences between Merlot and non-Merlot wines. Differentiation among Merlot wines and wines of other grape varieties were mainly perceived through the following components: ethyl dodecanoate, 1-hexanol, ethyl nonanoate, ethyl hexanoate, ethyl decanoate, dehydro-2-methyl-3(2H)thiophenone, 3-methyl butanoic acid, ethyl tetradecanoate, methyl octanoate, 1,4 butanediol, and 6-methyloctan-1-ol.

1. Introduction

Brazil is part of a new group of winegrowing countries. Wines produced in the Serra Gaúcha region, located in the state of Rio Grande do Sul in the south part of Brazil represent 90% of the Brazilian wine production. The cultivation of grapevines and wine production have considerable social and economic impact in this region. Aroma is one of the most important factors in determining wine character and quality. The compounds that define wine aroma are related to acceptance or rejection of wines by the consumers. The aroma characteristics are the result of complex interactions among four factors: vineyard geographical site [1], which it is related with the soil and climate characteristics [2], grape variety [3], yeast strain [4], and technical conditions of wine-making [5]. The definition of the *terroir* of a wine product (Indication of Geographical Origin Certification) is an important achievement for the wine industry, as it guarantees product consistency, defining a product that is characteristic of a certain region [6]. Characterization and differentiation of wines of different regions may be possible on the basis of the volatile fraction. There is wide evidence

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that it is possible to establish clear relationships among the volatile fraction of foods or beverages and the following aspects: the raw material employed, the place where material was originated and the process of production followed [7–10].

Wine volatiles are generally found at levels ranging from ng/L to mg/L and their analyses usually require a previous step of isolation and/or concentration. Solid phase microextraction (SPME) is a solventless technique in which sampling, extraction and concentration are integrated in one step, followed by sample introduction in an analytical instrument [11]. The determination of aroma compounds in several matrices is commonly performed by one dimensional gas chromatography (1D-GC). This approach does not mean that full information about volatile components of the sample can be obtained. Chromatograms with many unresolved peaks can be produced by 1D-GC especially when intensive odorants samples were analyzed. The deep analysis of the chromatograms frequently indicates that some peaks are the result of two or more co-eluting compounds. This fact means that too much information is missing and it leads to possible errors in identification and quantification of target components [12]. Furthermore, the complex nature of these samples, including compounds of different kinds of chemical classes requires long GC run times to obtain the maximum separating power. Other observed problem is that some aroma-active compounds are present in trace amounts and their detection can be difficult [10,13].

The comprehensive two-dimensional gas chromatography (GC × GC) emerged as a powerful analytical technique which is an excellent choice to unravel the composition of complex samples. This technique is based on the application of two GC columns coated with different stationary phases connected in series through a special interface called modulator. The modulator is the heart of the instrument because it ensures that separation is both comprehensive (the entire sample is subjected to both separation dimensions) and multidimensional (separation accomplished in one dimension is not lost in the other dimension) [14]. The modulator (i) accumulates and traps (ii) refocus and (iii) rapidly release the adjacent fractions of the first-dimension column [15]. GC × GC is an established technique, offering superior separation capabilities afforded by high peak capacity, selectivity, structural chromatographic peak organization, and sensitivity enhancement compared to 1D-GC. Considerably more information about sample constituents is provided, while the time of the analysis remains the same as in 1D-GC [16].

GC × GC has recently been used for determination of methoxypyrazines in Sauvignon Blanc wines [8], methoxypyrazines in Cabernet Franc berries and the resulting wines [17], furans, lactones, volatile phenols, and acetals in Madeira Wines [18], volatiles in Cabernet Sauvignon wine [19,20], Pinotage wines [21] and Fernão-Pires grapes [10]. Investigations about volatiles of Merlot wines using 1D-GC have been reported [22–28]. Chin et al. [29] used the GC–O (gas chromatography–olfactometry) analysis to select significant odor regions of chromatograms of Merlot wines. Only compounds detected in these regions were tentatively identified by GC × GC/TOFMS. However there is no detailed characterization of volatiles of Merlot wines using GC × GC that could be used in future studies to differentiate wines based in their volatile profile.

The red wine grape (*Vitis vinifera* L.) cultivar Merlot is one of the world's most widely planted red grape cultivars. Merlot is used as both a blending grape and for varietal wines. The wines made from this grape cultivar have fruity and smooth characteristics and have medium body [30]. The aim of this study is to use the HS-SPME coupled to GC × GC/TOFMS to obtain a qualitative characterization of volatiles of Merlot wines of Serra Gaúcha located in the South part of Brazil, using a simple comparison among literature 1D-GC linear temperature programmed retention indices (LTPRI) and experimental GC × GC LTPRI.

2. Materials and methods

2.1. Samples, analytical reagents, and supplies

All wines investigated (Merlot and non Merlot) (~13% ethanol, v/v) were of 2009 vintage and were produced in Serra Gaúcha region (latitude 29°S, longitude 51°W, altitude 600–800 m). These samples were provided by Empresa Brasileira de Pesquisa Agropecuária Uva e Vinho (EMBRAPA). The vinification process for each wine variety has not followed a specific protocol. Twelve wines of Merlot grapes and other twelve samples from non-Merlot varieties were analyzed to determine the volatiles that characterize both groups: Merlot and wine produced from other grape varieties (Chardonnay, 50% Chardonnay/50% Pinot Noir, Sauvignon Blanc, Cabernet Sauvignon). Three samples of each wine variety were analyzed. These varieties were chosen as they are the most commonly employed for wine production in Serra Gaúcha. Standard compounds ethyl acetate, ethyl butanoate, ethyl propanoate, ethyl 2-methylbutanoate (=ethyl isovalerate), ethyl 2-methylpropanoate, ethyl hexanoate, ethyl 2-hydroxypropanoate (=ethyl lactate), ethyl octanoate, ethyl decanoate, diethyl butanedioate (=ethyl succinate), ethyl 3-hydroxybutanoate (=diethyl hidroxybutanoate), propanol, hexanol, 2-phenylethanol, isoamyl acetate, phenylethyl acetate, hexanoic acid, octanoic acid, decanoic acid, dodecanoic acid, terpineol and eugenol were purchased from Aldrich (Steinheim, Germany). Individual stock solutions of each compound were prepared in ethanol purchased from Nuclear (São Paulo, Brazil). Model wine was prepared with (+)-tartaric acid (6 g/L) supplied by Synth (São Paulo, Brazil) and 10% of ethanol in MilliQ deionised water. The pH was adjusted to 3.5 with sodium hydroxide (Nuclear, São Paulo, Brazil). In order to obtain a sample as close to the real wine matrix as possible, the stock standard solutions were diluted in model wine to perform the extraction of each standard compound by SPME to proceed with their identification. Ultra-pure water was prepared using a Milli-Q water purification system (Millipore, Bedford, MA, USA). The SPME fiber (50/30 divinylbenzenecarboxen-polydimethylsiloxane (DVB/CAR/PDMS) StableFlex) was purchased from Supelco (Bellefonte, PA, USA). The fiber was conditioned according to the manufacture's recommendation prior to its first use. Sodium chloride (NaCl) of analytical grade was purchased from Nuclear (São Paulo, Brazil) and was oven dried at 110 °C overnight before use. Twenty microliter headspace vials with magnetic screw caps sealed with silicone septa were purchased from Supelco (Bellefonte, PA, USA).

2.2. Instrumentation

A CTC CombiPAL autosampler (CTC Analytics, Zwingen, Switzerland) with an agitator and SPME fiber conditioning station was used to extract the volatiles from sample vial headspace. The GC × GC system consisted of an Agilent 6890N (Agilent Technologies, Palo Alto, CA, USA) equipped with a Pegasus time-of-flight mass spectrometer (Leco Corporation, St. Joseph, MI, USA). The same GC system (Agilent 6890 N) was equipped with a secondary column oven and non-moving quadjet dual stage thermal modulator. During modulation, cold pulses were generated using dry nitrogen gas cooled by liquid nitrogen, whereas heated dry air was used for hot pulses. The injector, transfer line and ion source temperature were at 250 °C. The oven temperature began at 35 °C for 5 min and was raised to 120 °C at 3 °C/min; reaching 200 °C at 5 °C/min and 250 °C at 10 °C/min, were it was maintained for 5 min. The secondary oven was kept 10 °C above the primary oven throughout the chromatographic run. The modulator was offset by +25 °C in relation to primary oven. Ultra high purity helium was used as carrier gas at a constant flow of 1 mL/min. The MS parameters included electron ionization at 70 eV with ion source

temperature at 250 °C, detector voltage of −1750 V, mass range of 45–450 *m/z*, and acquisition rate of 100 spectra/s. Automated peak find and spectral deconvolution with a baseline offset of 0.5 and signal to noise of 3 were used during data treatment. Tentative identification of wine aroma compounds was achieved comparing experimental linear temperature programmed retention index (LTPRI) with retention indices reported in the literature. The description of this procedure has already been reported in a former publication of this research group, using a non-polar x polar column set [31]. Retention data of a series of n-alkanes (C9–C24), under the same experimental conditions employed for the chromatographic analysis of wine volatiles were used for experimental LTPRI calculation. Mass spectrometric information of each chromatographic peak was compared to NIST mass spectra library, considering a minimum similarity value of 75%. Twenty two compounds (listed in Section 2.1) were identified through comparison of retention time and mass spectra data of unknown compounds with those of authentic standards.

2.3. Conditions for the extraction of volatiles and GC × GC optimization

The SPME extraction conditions were 1 mL of sample in a 20 mL glass headspace vials, 30% of NaCl (m/v), without sample agitation, extraction time of 45 min and extraction temperature of 45 °C, according to previous work [32]. All samples were kept at 45 °C for 10 min prior to extraction. The headspace was sampled using a 2 cm DVB/CAR/PDMS 50/30 μm fiber. The volatile and semi-volatile compounds were desorbed in the GC inlet at 250 °C for 5 min. In order to avoid carryover, the fiber was reconditioned for 5 min at 260 °C prior to each analysis. All sample were analyzed in triplicate.

Preliminary experiments were dedicated to find the most appropriate column set. The following sets were tested: (i) DB-5 (5%-phenyl)-methylpolysiloxane; 30 m × 0.25 mm × 0.25 μm) × DB-WAX (100% polyethylene glycol; 1.00 m × 0.10 mm × 0.10 μm), (ii) DB-WAX (30 m × 0.25 mm × 0.25 μm) × DB1ms (100% dimethylpolysiloxane; 1.70 m × 0.10 mm × 0.10 μm) and (iii) DB-WAX (30 m × 0.25 mm 1 × 0.25 μm) × DB17ms (50% phenyl 50% dimethyl arylene siloxane; 1.70 m × 0.18 mm × 0.18 μm). The following step was the optimization of different variables, keeping other parameters constant. The variables tested were: difference of temperature between primary and secondary oven, gas flow rate, modulation period and hot pulse duration. Values chosen for testing the temperature difference between primary and secondary ovens were 10, 20, 40 and 50 °C. Three different modulation periods were tested: 4, 6 and 7 s. After this step, six hot pulse durations were tested: 0.35, 0.7, 1.4 and 2.1 s. The asymmetry factor of a chromatographic peak, which is a measure of peak tailing, was calculated to help choosing the best hot pulse duration. Asymmetry factor is defined as the distance from the center line of the peak to the back slope divided by the distance from the center line of the peak to the front slope, with all measurements made at 10% of the maximum peak height. Asymmetry factor values between 0.8 and 1.2 are considered satisfactory [33].

2.4. Statistical analysis

LECO ChromaTOF version 4.22 software was used for all acquisition control, data processing and Fischer Ratio calculations. Fischer Ratio is calculated by the square of the difference of the average areas of analyte from different classes divided by the sum of the analyte variance between different classes. Repeatability of chromatographic peak areas ranged from 6 to 15%. Esters represented 28% of the tentatively identified volatile compounds in wine headspace and the relative standard deviation (RSD) for them was higher (10–32%) due to chromatographic tail.

Principal component analysis (PCA) was used for visualization of the differences between Merlot and not-Merlot samples in the two dimensional space. The statistical analyses were conducted using STATISTICA for Windows program package (version 7.1, Statsoft, Tulsa, Oklahoma, USA, 2005). PCA was applied with mean-centering data.

3. Results and discussion

3.1. Optimization of comprehensive two-dimensional gas chromatography parameters

Although many compounds were identified in the headspace of Merlot wines, a representative selection of 22 target compounds, which belong to different classes, (esters, alcohols, terpenes and acids) and are regarded as important contributors to wine aroma [34] were used for GC × GC optimization. These compounds were listed in Section 2. Three column configurations were evaluated in order to obtain the best separation among the various target analytes and the interfering matrix compounds. During trial-and-error method optimization, the conventional orthogonal set (nonpolar and polar combination) is commonly the first tested in many works, as it is the most frequently used and usually a successful approach [35,36]. An nonpolar column separation is governed mainly by boiling point differences between analytes, and therefore, the analytes with similar volatilities will be eluted in narrow fractions in the first dimension before being separated via specific interactions with polar phase in second dimension [37]. Most of the standard volatile compounds were eluted in the early stage of the chromatogram at low elution temperatures, and this may result in poor separation for these wine volatiles. The use of the orthogonal system (nonpolar × polar) for wine volatiles also resulted in a poor occupation of the separation space. The same was observed when the inverse orthogonal set (polar × nonpolar) was employed. However, the non-orthogonal polar × medium polar column set resulted in a better distribution of chromatographic peaks in the separation space. Chromatographic separations in the three column sets are shown in Fig. 1. Zhu et al. [38] have already observed that the use of a polar column in ^{1}D and a medium-polar column in ^{2}D can be preferred for the analyses of flavor compounds, including organic acids, alcohols, esters, ketones, aldehydes, acetals, lactones, nitrogen-containing and sulfur-containing compounds in liquor, which is the case of the present work. Robinson et al. [19] used a non polar (5% phenyl 95% dimethyl polysiloxane)-medium polar (50% phenyl) column combination for the analysis of 350 different tentatively identified volatile and semi-volatile compounds found in Australian Cabernet Sauvignon wine headspace, as these authors chose low bleed characteristics for both dimensions. However, some polar volatile compounds presented tailing in the second dimension and were strongly retained by the medium polar stationary phase.

Considering that modulation period plays a vital role, as it affects sensitivity, separation and peak shape, three modulation periods were tested: 4, 6 and 7 s. The use of 7 s as the modulation period avoided wrap around of more retained compounds, which occurred with smaller modulation periods. Isobutyl acetate and ethyl 2-methylpropanoate (ethyl isobutyrate) wrapped around when a modulation period of 4 s was employed. This last compound mentioned co-eluted with two other unknown compounds. Results obtained with 6 s as modulation period showed wrap around for hexyl acetate and ethyl decanoate, which co-eluted with ethyl 4-methyl succinate and 2-propenoic acid.

The standard solution and also a base wine sample were analyzed using the following temperature differences between the primary and the secondary oven: 10, 20, 40 and 50 °C. With increasing temperature difference between the primary and the secondary

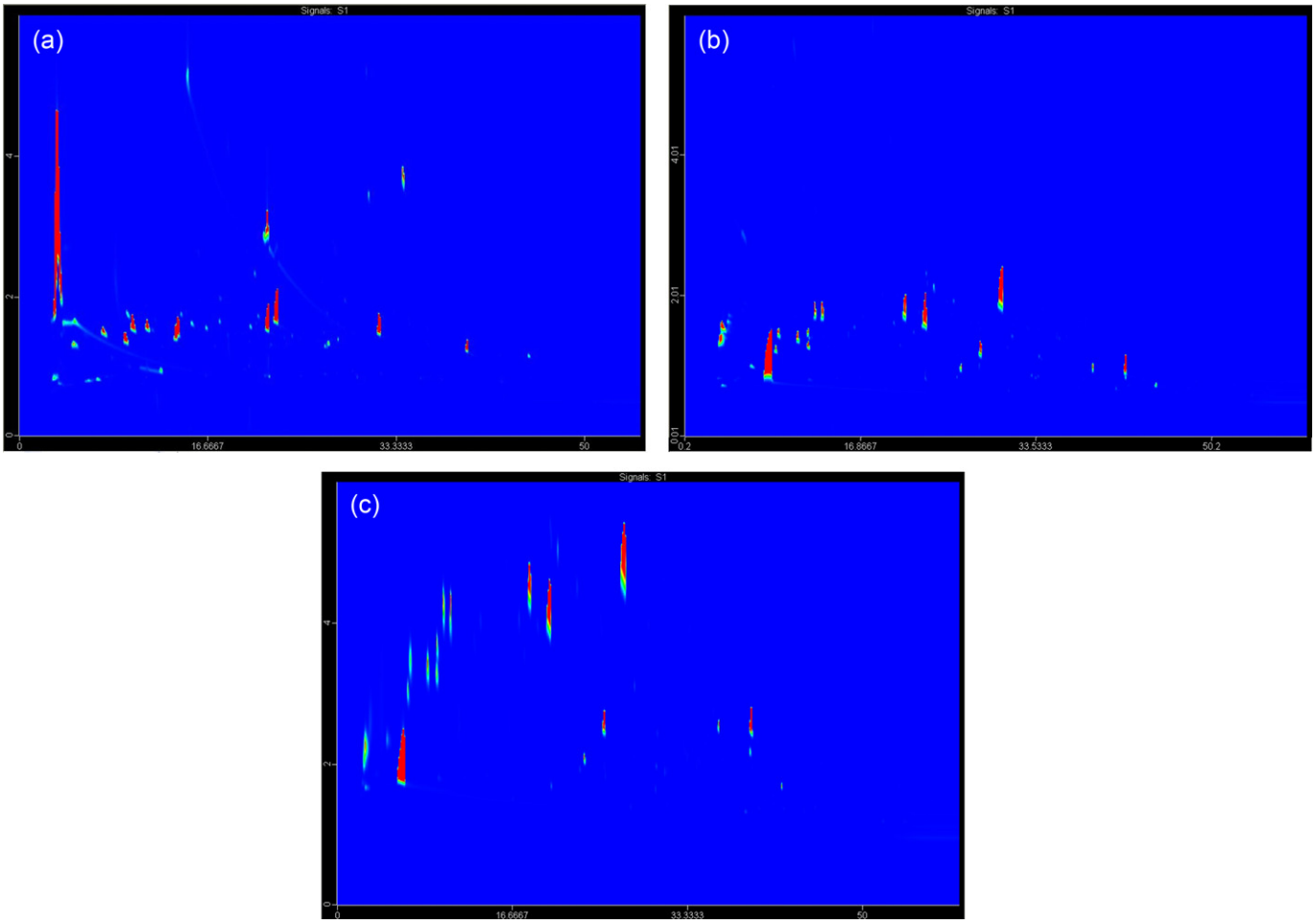

Fig. 1. Separation of 22 volatile compounds in different GC × GC capillary column sets: (a) DB-5 × DB-WAX, (b) DB-WAX × DB1ms and (c) DB-WAX × DB17ms.

oven, distribution of analytes in the separation space was reduced. Thus, the chosen oven temperature offset was 10 °C.

Four hot pulse durations were tested: 0.35, 0.7, 1.4 and 2.1 s. The use of a hot pulse duration of 1.4 s provided better peak shapes, than the other values, especially for compounds such as phenyl acetate, ethyl decanoate and hexyl acetate, among others. The asymmetry factor was calculated for each compound and for all the hot pulse durations (Table S1). Asymmetry factors lower than 0.8 or higher than 1.2 are presented in bold in Table S1.

The final optimized conditions were: DB-WAX × DB17ms column set, oven temperature offset of 10 °C, 7 s as modulation period and 1.4 s of hot pulse duration.

Ordered distribution of volatile compounds of Merlot wines was observed for different classes of compounds when the polar × medium polar column set was employed. This organized distribution of compounds was not observed in the other column sets tested in this work. However, the use of modulation periods below 7 s would negatively affect the structured compound distribution due to the wrap around effect. Fig. 2 shows seven different classes of compounds: esters, aldehydes, ketones, tiols, alcohols, lactones and acids. More polar acid compounds were more retained in the ^{1}D, and eluted at higher temperatures. On the other hand, aromatic compounds (phenol, ethyl benzoate derivatives), lactones and less polar ethyl esters were more retained in the ^{2}D and are displayed at the top of the color plot. The presence of some components of two homologous series was observed for some esters and alcohols. Structurally organized distribution of these compounds is shown in Fig. 3, and the lines drawn in the figure present a trend of organized distribution of these components in the 2D space. A series of structurally similar esters are: (1) ethyl propanoate, (2) ethyl butanoate, (3) 2-methyl-ethyl butanoate, (4) 3-methyl butanoate, (5) ethyl hexanoate, (6) propyl hexanoate, and (7) ethyl octanoate. With respect to alcohols, a similar organized distribution of compounds in the chromatogram is observed, as follows: (1) 1-propanol, (2) 1-butanol, (3) 3-methyl-1-butanol, (4) 4-methyl-1-pentanol, (5) 1-hexanol, (6) 3-ethoxy-1-propanol, (7) 3-hexen-1-ol. Zhu et al. [38] used GC × GC/TOFMS with a polar × medium-polar

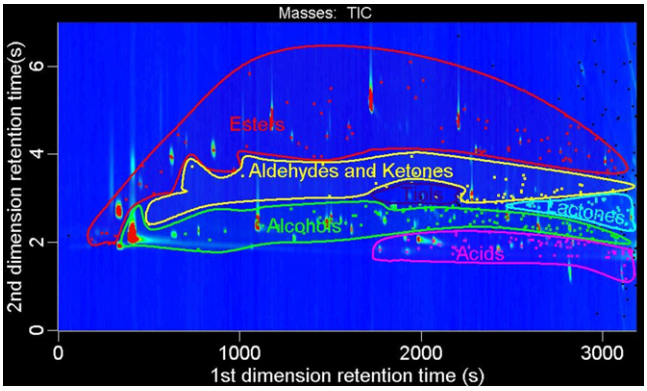

Fig. 2. Structurally ordered color plot of compound classes of flavor volatiles of Merlot wines obtained using DB-WAX (polar) × DB17ms (medium-polar) column combination.

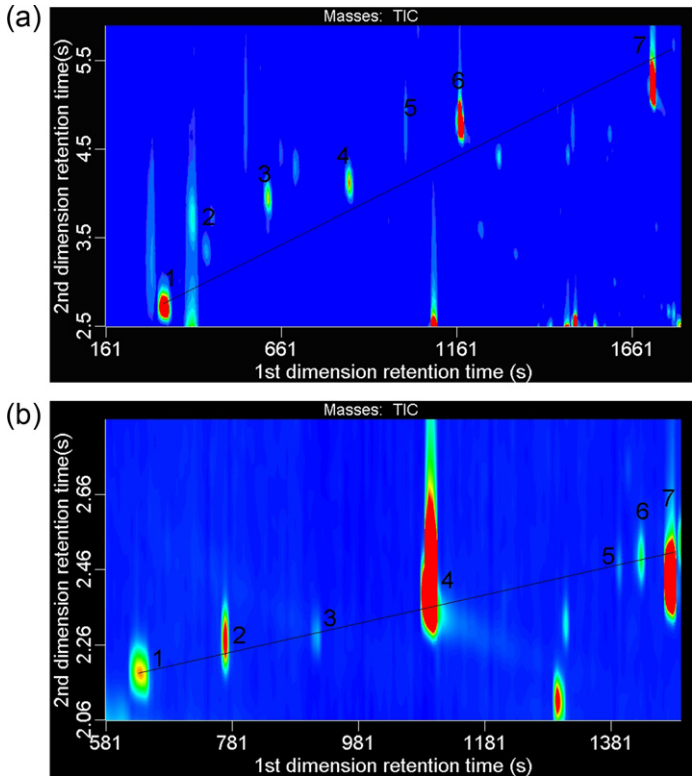

Fig. 3. GC × GC distribution of structurally (a) esters: (1) ethyl propanoate, (2) ethyl butanoate, (3) 2-methyl-ethyl butanoate, (4) 3-methyl butanoate, (5) ethyl hexanoate, (6) propyl hexanoate, (7) ethyl octanoate and (b) alcohols: (1) 1-propanol, (2) 1-butanol, (3) 3-methyl-1-butanol, (4) 4-methyl-1-pentanol, (5) 1-hexanol, (6) 3-ethoxy-1-propanol, (7) 3-hexen-1-ol.

column set to characterize Chinese liquor and obtained different homologous series of volatile compounds, orderly distributed in the 2D space, according to their polarity. Souza et al. [39] showed similar findings for volatiles of cachaça (sugar cane brandy). However, a more detailed presentation of organized distribution of structurally related individual compounds, inside a chemical class, has not yet been presented for volatile compounds of Merlot wines.

3.2. Wine volatile profile

The average number of tentatively identified volatile compounds in a wine headspace single analysis for different wines (Merlot, Cabernet Sauvignon, white wines, etc.) stays around 30–70 when the GC/MS methodologies are employed [22,40–42]. Rocha et al. [10] used GC × GC/TOFMS to analyze monoterpenes in grapes and identified 56 monoterpenes in the Fernão-Pires variety, 20 of which were reported for the first time in grapes. Robinson et al. [19] analyzed five commercial Cabernet Sauvignon wines from Australia using GC × GC and 368 compounds were tentatively identified. In our work a total of 334 compounds were tentatively identified by GC × GC/TOFMS in the headspace of Merlot wine. This suggests that former GC/MS methods were able to identify only part of the volatile compounds identified when employing GC × GC/TOFMS in Merlot and/or red wines, using the extraction techniques considered in the articles quoted (SPME and stir bar sorptive extraction – SBSE). Table 1 lists the compounds that were tentatively identified through comparison of experimental LTPRI and mass spectra with corresponding data reported in the scientific literature. Compounds are listed according to different chemical classes. Zhu et al. [38] reported the tentative identification of volatile compounds of liquor using a polar column in 1D (HP-Innowax) and a medium-polar column in 2D (DB-1701, 14% cyano propyl phenyl methyl siloxane), using the "isovolatility curves" approach for retention indices calculation, but only a limited set of retention indices were presented. According to our knowledge this is the first work that uses the LTPRI obtained in a polar (polyethylene glycol)/ × medium polar column (50% phenyl 50% dimethyl arylene siloxane) set of columns for tentative identification of volatile compounds. It is well known that polar column LTPRI are more prone to variations [31] and in case of this work, a greater variability could be expected, as two polar columns were coupled. However, it was interesting to verify that for some compounds the LTPRI values were very close to literature data (for example experimental/literature LTPRI: for butan-2-ol 1013/1012, for propan-1-ol 1038/1036, for propanoic acid 1536/1535, for nonanal 1388/1390, and for ethyl hexanoate: 1238/1236). However, experimental LTPRI of other compounds showed larger differences when compared to literature LTPRI, as for example experimental/literature LTPRI: for 2-methylpentan-3-ol 1340/1321, for 3-methylbutanoic acid 1684/1667, for hexanal 1107/1092, and for methyl-2- hydroxybenzoate 1775/1756. These and other examples can be clearly seen in Table 1. A maximum deviation of 33 units was observed between the experimental and literature LTPRI values. LTPRI data obtained in polar columns are also more difficult to find in the literature than those obtained in non-polar column. The site www.odour.org.uk was employed as a preliminary source for polar column LTPRI, however all the reference data shown in Table 1 was confirmed through comparison with data found in scientific journals (data partially shown). This set of LTPRI data will certainly be a valuable tool for the tentative identification of volatile and semi-volatile compounds analyzed by 1D-GC and GC × GC. Moreover, the fact that 1D-GC LTPRI may also be employed in a direct comparison with GC × GC LTPRI, even when a polar set of columns is used, represents a simple and handy approach for tentative identification of compounds. Among all the chemical groups found in the volatile content of Merlot wines of Serra Gaúcha, esters were present in higher number (94), followed by alcohols (80), ketones (29), acids (29), aldehydes (23), terpenes (23), lactones (16), furans (14), sulfur compounds (9), phenols (7), pyrroles (5), C13-norisoprenoids (3), and pyrans (2). Even though, quantitative analysis would be necessary for a precise definition of the influence of volatile compounds to wine aroma, a general discussion regarding the possible contribution of several important volatiles compounds is presented, as follows. Predominant presence of esters in Merlot wine is in agreement with previous studies [22,23]. Gürbüz et al. [22] identified 66 compounds in Merlot wines produced in California and Australia. The most abundant esters were ethyl octanoate, ethyl decanoate, ethyl acetate, isopentyl hexanoate and diethyl succinate [22]. Ester compounds are well known for their contribution to the fruity aroma of wines and in this work, they were responsible for the higher chromatographic peak areas. The six major ones were: ethyl 2-hydroxypropanoate, diethyl succinate, diethyl malate, ethyl decanoate, ethyl octanoate and isopentyl 2-hydroxypropanoate. *Saccharomyces cerevisiae* and the associated enzyme, acyl-SCoA, are responsible for the formation of many ethyl esters and alcohols, during the fermentation process [43]. Among the alcohols, excluding the ethanol, the most abundant were: 2,3 butanediol, hexanol, 2-methyl-4-butanol and 1-propanol. These compounds might have both positive and negative impacts on aroma. Hexanol, for example, is usually a minor constituent, but its herbaceous and greasy odors have been related to deleterious effects in wines, although consumers can appreciate a small herbaceous perception in some wines. Phenylethanol contributes to a positive rose (floral) aroma and its presence was also observed in the aroma of Merlot wines produced in Nampa, Idaho, USA analyzed by Qian et al. [23]. It can also be present in grapes,

Table 1
Tentatively identified compounds of Merlot wine volatile compounds.

	Name	CAS number	^1t_R (s)	^2t_R (s)	Similarity	Area	LTPRI (exp)	LTPRI (lit)
Alcohols								
1	Propan-2-ol	67-63-0	609	2.89	794	16,723	925	912[a] 938 [51]
2	Butan-2-ol	78-92-2	637	2.19	873	4563	1013	1012 [52]
3	Propan-1-ol	71-23-8	780	3.67	937	3,030,592	1038	1036 [53]
4	2-Methylpropanol	75-65-0	924	2.28	756	6754	1098	1090 [54]
5	Pentan-3-ol	584-02-1	1085	2.38	845	15,489	1116	1118 [55]
6	Prop-2-en-1-ol	107-18-6	1088	1.98	806	26,367	1138	Nf
7	Butan-1-ol	71-36-3	1099	2.47	926	515,731	1148	1149[a] 1159 [56]
8	2-Methylbutan-1-ol	137-32-6	1211	2.32	902	11,039,734	1191	1204[a] 1196 [57]
9	3-Methylbutan-1-ol (2)	123-51-3	1218	2.39	815	20,300	1200	1206[a] 1208 [55]
10	Pentan-1-ol	71-41-0	1270	4.32	892	43,095	1256	1256[a] 1249 [55]
11	Pent-4-en-2-ol	625-31-0	1330	3.12	809	27,083	1282	Nf
12	Heptan-2-ol	543-49-7	1393	2.47	837	87,761	1326	1318[a] 1318 [58]
13	(*Z*)-2-penten-1-ol	1576-95-0	1396	3.44	786	12,956	1335	1317[a] 1326 [59]
14	2-Methylpentan-3-ol	565-67-3	1400	2.22	910	7328.6	1340	1321 [60]
15	Heptan-4-ol	589-55-9	1407	2.73	806	12,016	1344	Nf
16	3-Methyl-2-buten-1-ol	556-82-1	1414	2.30	802	19,983	1346	1334 [61]
17	3-Methylpentan-1-ol	589-35-5	1428	4.49	922	422,166	1353	1343 [53]
18	4-Methylpentan-1-ol (4)	626-89-1	1477	2.56	938	155,440	1366	1365 [61]
19	3-Ethoxypropan-1-ol (5)	111-35-3	1498	2.49	895	782,661	1371	1364 [62]
20	Hexan-1-ol	111-27-3	1526	2.46	908	11,191,067	1375	1371[a] 1392 [53]
21	(*Z*)-3-hexen-1-ol	928-96-1	1554	2.51	954	248,306	1393	1389[a] 1387 [62]
22	(*Z*)-2-hexen-1-ol	928-94-9	1582	3.01	852	53,013	1397	1407 [56]
23	2-(2-Methylpropoxy)ethanol	4439-24-1	1610	2.64	856	14,590	1400	Nf
24	Octan-3-ol	589-98-0	1624	2.42	874	50,817	1406	1411[a] 1399 [63]
25	(*E*)-4-hexen-1-ol	928-92-7	1666	2.50	834	76,520	1410	1413 [64]
26	3,4-Dimethylhexan-3-ol	19550-08-4	1673	2.90	837	8230	1411	Nf
27	Heptan-1-ol (6)	111-70-6	1694	2.45	930	221,732	1470	1467 [60]
28	4-Methyl-3-penten-1-ol (7)	51174-44-8	1757	4.60	825	2729.8	1478	Nf
29	2-Ethylhexano-1-ol (7)	104-76-7	1757	2.70	934	1,275,504	1483	1491 [54]
30	3-Ethyl-4-methylpentan-1-ol	38514-13-5	1783	2.77	827	39865	1509	Nf
31	Propane-1,2-diol	504-63-2	1790	1.90	806	23087	1599	1603 [62]
32	1-(2-Methoxypropoxy)propan-2-ol	13429-07-7	1796	4.56	864	8144	1541	Nf
33	Octan-1-ol (8)	111-87-5	1799	2.67	934	321,372	1557	1558 [55]
34	Butane-2,3-diol	513-89-3	1802	3.76	936	41,802,099	1563	1583 [53]
35	Butane-1,4-diol	110-63-4	1804	1.96	836	29,934	1578	Nf
36	4-Methylhexan-3-ol (9)	818-81-5	1806	2.70	823	24,067	1583	Nf
37	1-Hepten-4-ol (9)	3521-91-3	1806	2.99	845	14,377	1585	Nf
38	Butane-1,2,4-triol	3068-00-6	1907	6.08	940	28,915	1603	Nf
39	2-(2-Ethoxyethoxy)ethanol	111-90-0	1940	2.72	934	367,119	1622	Nf
40	(*E*)-2-octen-1-ol	18409-17-1	1981	2.09	812	9379	1649	1620[a] 1639 [53]
41	Nonan-1-ol	143-08-8	1990	2.07	891	45560	1676	1661 [65]
42	2,2-Dimethylpropan-1-ol	75-84-3	1995	2.04	799	7048	1684	Nf
43	1-Nonen-3-ol	21964-44-3	1999	2.83	808	42902	1694	Nf
44	4-Propan-2-yloxybutan-2-ol	40091-57-4	2156	2.5	857	12,509	1717	Nf
45	2-Methyloctan-1-ol	615-29-2	2296	2.40	823	211,351	1727	Nf
46	3-Methyl-1-penten-3-ol (18)	918-85-4	2303	2.62	793	3981	1767	Nf
47	Decan-1-ol	112-30-1	2326	2.90	901	100,420	1778	1781 [53]
48	4-Butoxybutan-1-ol	4161-24-4	2345	2.98	782	31,549	1806	Nf
49	Dec-2-en-1-ol	22104-80-9	2357	2.64	814	9076.6	1812	Nf
50	2,4-Dimethylpentan-3-ol	600-36-2	2350	2.74	776	14,536	1818	Nf
51	2,6-Dimethyl-7-octen-2-ol	18479-58-8	2389	3.12	843	7111	1594	Nf
52	2-Phenylpropen-1,2-diol	4217-66-7	2415	2.46	797	18,682	1815	Nf
53	3-Phenylpentane-1,3-diol	84682-28-0	2422	1.87	810	2,506,078	1824	Nf
54	Dec-2-yn-1-ol (23)	4117-14-0	2478	2.8	767	19,161	1829	Nf
55	Undecan-2-ol	1653-30-1	2489	2.73	775	45,637	1831	Nf
56	2-Methyl-5-hexen-3-ol	32815-70-6	2497	2.56	757	4568	1836	Nf
57	3,3-Dimethylbutane-1,2-diol (25)	59562-82-2	2548	3.16	843	3223	1843	Nf
58	2-Butyloctan-1-ol	3913-02-8	2550	6.49	752	12,191	1853	Nf
59	3,7-Dimethyl-2,6-octadien-1-ol	624-15-7	2558	2.56	782	15,779	1856	Nf
60	6-Methyloctan-1-ol (58)	38514-05-5	2561	2.47	793	29,891	1862	Nf
61	4-Methylhept-6-en-3-ol	53907-71-4	2520	2.13	760	8545	1870	Nf

Table 1 (*Continued*)

	Name	CAS number	^1t_R (s)	^2t_R (s)	Similarity	Area	LTPRI $_{(exp)}$	LTPRI $_{(lit)}$
62	Phenylmethanol (benzyl alcohol)	100-51-6	2535	2.19	834	49,090	1895	1869 [62]
63	*trans*-2-Undecen-1-ol	75039-84-8	2549	3.08	791	12,451	1899	Nf
64	2-Phenylethanol	60-12-8	2555	2.34	925	5,691,672	1900	1898 [66]
65	3-Methoxybutan-2-ol (26)	53778-72-6	2569	2.83	750	36,185	1910	1903 [67]
66	Dodecan-1-ol	112-53-8	2572	2.78	781	7158	1984	1977[a] 1983 [65]
67	Undecan-1-ol	112-42-5	2586	2.89	800	14,086	1999	Nf
68	1-Tridecanol	112-70-9	2592	2.79	785	10,720	2078	2063 [68]
69	2-Ethyldodecan-1-ol	19780-33-7	2594	6.01	864	5921	2090	Nf
70	Hexadecan-1-ol	14852-31-4	2610	2.15	815	6590	2172	2152 [60]
71	2-Hexyloctan-1-ol (31)	19780-79-1	2688	6.23	845	6786	2162	Nf
72	2-(2-Hydroxypropoxy)propan-1-ol	106-62-7	2762	3.67	785	6224	2191	Nf
73	4-Hexoxybutan-1-ol	4541-13-3	2807	3.3	807	6558	2229	Nf
74	But-3-ene-1,2-diol (40)	497-06-3	2877	2.21	760	35,846	2253	Nf
75	2-Methylpent-4-en-2-ol (41)	624-97-5	2884	2.11	806	6862	2320	Nf
76	Pentadecan-1-ol (42)	629-76-5	2919	3.96	838	12,714	2353	Nf
77	(Z) 2-Methyl-4-hexen-3-ol (42)	96346-76-8	2919	2.16	776	6877	2395	Nf
78	2-Ethyl hexanediol (51)	94-96-2	3080	1.91	809	49,721	2667[b]	Nf
79	2-Hexyl-1-decanol (54)	2425-77-6	3171	5.13	856	30,568	2760[b]	Nf
80	3,3,6-Trimethylhepta-1,5-dien-4-ol (artemisia alcohol)	27644-04-8	3196	3.45	834	4623	2769[b]	Nf
Acids								
81	Acetic acid	64-19-7	1771	1.86	991	5,950,931	1457	1451 [59]
82	Oxalic acid (10)	144-62-7	1925	1.82	959	187,821	1509	Nf
83	Propanoic acid (13)	79-09-4	1988	1.89	867	80,996	1536	1535 [54]
84	2-Methylpropanoic acid (isobutyric acid)	79-31-2	2107	2.27	753	62,747	1568	1566 [56]
85	2-Methyldecanoic acid	24323-23-7	2114	4.60	822	5334	1584	Nf
86	4-Methyl-2-oxovaleric acid	816-66-0	2133	2.72	766	77,685	1599	Nf
87	Butanoic acid	107-92-6	2184	1.90	929	733,666	1651	1630[a] 1642 [69]
88	3-Methylbutanoic acid	503-74-2	2261	1.92	794	344,709	1684	1667 [56]
89	2-Propylpropanedioic acid	616-62-6	2380	1.91	881	75,809	1711	Nf
90	Pentanoic acid	109-52-4	2428	2.41	820	97,250	1750	1768 [70]
91	2-Propenoic acid	79-10-7	2498	1.85	781	13,736	1818	Nf
92	Hexanoic acid (25)	142-62-1	2548	1.96	919	5,169,620	1871	1855[a] 1863 [53]
93	2-Ethylhexanoic acid (31)	149-57-5	2688	2.01	904	158,131	1974	1969[a]
94	Heptanoic acid	111-14-8	2695	1.96	894	76,274	1976	1950[a] 1955 [58]
95	2-Hexenoic acid	1191-04-4	2716	1.92	821	13,024	1980	Nf
96	Octanoic acid (37)	124-07-2	2828	2.03	931	7,951,238	2096	2092 [70]
97	Nonanoic acid (57)	112-05-0	2933	2.03	900	109,543	2170	2168 [58]
98	3-Phenoxypropanoic acid (43)	7170-38-9	2954	2.25	805	7213	2199	Nf
99	Decanoic acid (46)	334-48-5	3024	2.03	932	2,540,115	2266	2269 [54]
100	Undecanoic acid (49)	112-37-8	3066	3.48	836	101,088	2413[b]	2400[a] 2407 [71]
101	α-Lactic acid (51)	598-82-3	3080	2.38	803	30,251	2678[b]	Nf
102	Tetradecanoic acid	544-63-8	3129	2.39	796	21,627	2695[b]	2692 [62]
103	3-Phenyllactic acid (53)	156-05-8	3164	1.70	779	41,946	2749[b]	Nf
104	Pentadecanoic acid (54)	1002-84-2	3171	2.81	839	23,712	2765[b]	Nf
105	2-Methoxyacetic acid (55)	625-45-6	3178	1.70	806	73,671	2776[b]	Nf
106	2-Decenoic acid (56)	3913-85-7	3185	3.38	802	312,656	2793[b]	Nf
107	2-Methylheptanoic acid (56)	1188-02-9	3185	3.35	819	38,033	2795[b]	Nf
108	Hexadecanoic acid	57-10-3	3200	5.90	851	176,123	2876[b]	2886 [62]
109	Octadecanoic acid	57-11-4	3284	3.45	868	254,557	2890[b]	Nf
Aldehydes								
110	Acetaldehyde	75-07-0	371	3.00	784	6778	715[b]	700[a] 735 [54]
111	2-Propenal	107-02-8	380	2.33	781	8797	725[b]	Nf
112	3-Methylbutan-1-al	590-86-3	385	2.91	779	141,764	905	914[a] 915 [58]
113	Buten-2-al	4170-30-3	630	2.90	807	34,550	1050	Nf
114	Hexanal	66-25-1	735	3.69	871	41,084	1107	1089[a] 1092 [60]
115	Octanal	124-13-0	1316	4.32	882	25,903	1272	1284[a] 1270 [69]
116	Nonanal	124-19-6	1603	4.49	888	149,237	1388	1388[a] 1390 [72]
117	Decanal	112-31-2	1876	4.63	903	154,063	1500	1494[a] 1499 [80]
118	Benzaldehyde	100-52-7	1939	3.05	946	278,107	1506	1503 [67]
119	4-Ethylbenzaldehyde	53951-50-1	2024	3.13	799	9877	1519	1521 [67]

Table 1 (*Continued*)

	Name	CAS number	^1t_R (s)	^2t_R (s)	Similarity	Area	LTPRI $_{(exp)}$	LTPRI $_{(lit)}$
120	2-Phenylacetaldehyde (benzeneacetaldehyde)	122-78-1	2128	2.85	929	186,447	1630	1623[a]
121	4-Methylbenzaldehyde (14)	104-87-0	2163	4.36	791	6167	1638	1639[a]
122	Undecanal (16)	112-44-7	2212	3.10	838	14,281	1645	1659[a] 1622 [65]
123	2-Hydroxybenzaldehyde (17)	90-02-8	2275	2.70	770	4114	1670	Nf
124	Dodecanal	112-54-9	2331	4.06	892	17,334	1733	1710[a] 1720 [80]
125	Tridecanal	10486-19-8	2499	3.97	819	5092	1800	1824 [71]
126	3-Phenylpropen-2-al (cinnamaldehyde) (27)	104-55-2	2576	2.77	791	4682	1933	Nf
127	Tetradecanal (24)	124-25-4	2527	2.77	769	8230	2051	2034 [51]
128	Pentadecanal (29)	2765-11-9	2653	3.93	816	7625	2054	Nf
129	2,4-Dimethylpentanal	27944-79-2	2681	3.49	856	4012	2060	Nf
130	4-Methoxybenzaldehyde (p-anisaldehyde) (34)	123-11-5	2793	2.64	804	3904	2114	Nf
131	Hexadecanal (34)	629-80-1	2793	3.92	820	5866	2141	Nf
132	3-Hydroxybutanal	107-89-1	3017	1.67	835	9756	2580[b]	Nf
Esters								
133	Ethyl acetate	141-78-6	329	2.72	770	133,916	870[b]	885 [53]
134	Ethyl 2-methylpropanoate (ethyl isobutyrate)	97-62-1	359	2.39	887	92,497	955	960 [22]
135	Ethyl 3-methylbutanoate	108-64-5	695	2.22	834	26,676	1088	1072 [65]
136	Butyl acetate	123-86-4	732	2.89	884	7854	1063	1075 [73]
137	Butyl butanoate	109-21-7	1009	4.54	889	9980	1208	1221 [73]
138	Ethyl hexanoate	123-66-0	1162	4.81	908	362,956	1238	1238[a] 1236 [73]
139	Ethyl orthoformate	122-51-0	1225	3.64	825	147,607	1274	Nf
140	Ethyl heptanoate	106-30-9	1376	4.43	796	9974	1349	1336 [73]
141	2-Methylpropyl 3-methylbutanoate (isobutyl isovalerate)	589-59-3	1399	2.86	873	3076	1355	Nf
142	Ethyl 2-hydroxypropanoate (ethyl lactate) (4)	97-64-3	1477	3.45	938	38,358,131	1339	1334 [58]
143	Ethyl 2-hexenoate (4)	27829-72-7	1477	4.45	819	15,523	1357	1360 [53]
144	Methyl octanoate	111-11-5	1526	4.67	865	34,287	1381	1378 [52]
145	Ethyl 2-hydroxybutanoate	52089-54-0	1638	2.63	798	20,528	1401	1400 [58]
146	Ethyl 2-hydroxy-3-methylbutanoate (6)	2441-06-7	1694	2.84	897	79,027	1403	1399 [58]
147	Ethyl 2-oxopropanoate	617-35-6	1707	2.79	803	18,372	1405	Nf
148	2-Dimethylaminoethanol acetate	1421-89-2	1709	4.19	825	7955	1409	Nf
149	Methyl 6-heptenoate	1745-17-1	1722	4.01	809	5337	1421	Nf
150	Ethyl octanoate	106-32-1	1725	5.16	919	2,565,310	1429	1424 [52]
151	Ethylethoxy-3-propanonate	763-69-9	1736	3.86	800	30,524	1432	Nf
152	(*Z*)-methyl 3-octenoate	69668-85-5	1749	4.16	876	43,188	1437	Nf
153	Methyl dimethoxyacetate	39026-94-3	1797	2.88	832	112,626	1442	Nf
154	2-Methylpropyl 2-hydroxypropanoate (isobutyl lactate)	585-24-0	1770	3.97	787	108,270	1455	Nf
155	Ethyl diethoxyacetate	6065-82-3	1778	2.69	804	8039	1475	1487 [65]
156	Methyl nonanoate	1731-84-6	1791	4.1	813	11,842	1491	Nf
157	Heptan-2-yl butanoate (1-methylhexyl butyrate) (9)	89-91-8	1806	3.28	801	45,737	1496	Nf
158	Ethyl 3-hydroxybutanoate (10)	5405-41-4	1925	2.53	929	97,773	1514	1513 [54]
159	Ethyl nonanoate (11)	123-29-5	1946	5.30	806	12,997	1520	1526 [52]
160	Ethyl methoxyacetate (12)	3938-96-3	1967	2.36	803	4055	1522	Nf
161	Ethyl 2-hydroxy-4-methylpentanoate (13)	10348-47-7	1988	2.89	876	378,822	1538	1547 [56]
162	Ethyl 3-hydroxypentanoate	54074-85-0	2022	2.65	800	8754	1552	1552 [54]
163	Diethyl propanedioate	105-53-3	2037	3.04	869	17,546	1571	1572 [52]
164	3-Methylbutyl propanoate (isoamyl propionate)	105-68-0	2051	2.00	830	19,774	1581	Nf
165	Butyl 2-hydroxypropanoate	138-22-7	2075	2.69	843	12,024	1589	Nf
166	Methyl decanoate	110-42-9	2079	3.49	834	10,987	1600	1593 [68]
167	Ethyl 4-oxopentanoate	539-88-8	2100	2.93	801	2878	1614	1607 [65]
168	Methyl 9-oxononanoate (15)	1931-63-1	2198	3.97	827	80,163	1618	Nf
169	Isoamyl lactate (16)	19329-89-6	2212	2.78	835	1,013,593	1619	1614 [63]
170	Ethyl decanoate	110-38-3	2219	4.7	923	2,924,593	1643	1638 [65]
171	Ethyl benzoate	2035-99-6	2233	3.30	809	26,358	1665	1664 [65]
172	Isoamyl octanoate	2035-99-6	2254	5.03	826	28,354	1668	1655 [68]
173	Ethyl 3-hydroxyhexanoate (17)	2305-25-1	2275	2.69	781	14,750	1674	1675 [54]
174	Diethyl butanedioate (diethyl succinate)	123-25-1	2296	3.07	961	10,873,346	1686	1690 [62]

Table 1 (*Continued*)

	Name	CAS number	^1t_R (s)	^2t_R (s)	Similarity	Area	LTPRI $_{(exp)}$	LTPRI $_{(lit)}$
175	Ethyl (*Z*)-dec-4-enoate (20)	7367-84-2	2317	4.12	781	7486	1695	1687 [68]
176	Ethyl 2-hydroxy-2-methylpropanoate	80-55-7	2366	1.77	786	11,352	1705	Nf
177	Ethyl dec-9-enoate	67233-91-4	2443	4.10	802	35,914	1708	1711 [53]
178	Diethyl 2-methylbutanedioate	4676-51-1	2457	3.35	835	9487	1728	Nf
179	Ethyl undecanoate (22)	627-90-7	2464	4.27	755	9987	1739	1732 [52]
180	Diethyl (*Z*)-but-2-enedioate (diethyl malate) (22)	141-05-9	2464	3.11	886	18,525	1744	Nf
181	Ethyl 2-hydroxy-2-methylbutanoate	77-70-3	2506	2.29	823	6344	1761	Nf
182	Methyl 2-hydroxybenzoate (24)	9041-28-5	2527	2.93	778	9585	1775	1756 [66]
183	Diethyl pentanedioate	818-38-2	2541	3.04	915	33,843	1780	1768 [52]
184	Ethyl 2-phenylacetate (58)	101-97-3	2561	3.12	933	574,408	1783	Nf
185	Methyl dodecanoate (26)	111-82-0	2569	4.09	862	10,239	1809	1793 [52]
186	Ethenyl decanoate (27)	4704-31-8	2576	3.57	804	7373	1812	Nf
187	2-Phenylethyl acetate	103-45-7	2604	3.02	939	513,216	1821	1829 [53]
188	Propan-2-yl dodecanoate (osopropyl laurate) (28)	10233-13-3	2611	4.56	799	11,235	1833	Nf
190	Ethyl dodecanoate (30)	106-33-2	2667	4.30	894	478,413	1856	1835 [52]
191	3-Hydroxy-2,4,4-trimethylpentyl 2-methylpropanoate (31)	74367-34-3	2688	3.00	845	172,128	1859	Nf
192	2-Methylpropyl benzoate (isobutyl benzoate) (31)	120-50-3	2688	3.45	799	9652	1862	Nf
193	3-Methylbutyl decanoate (isopentyl decanoate)	2306-91-4	2765	4.57	784	42,948	1868	1871 [53]
194	Ethyl 3-phenylpropanoate	2021-28-5	2772	3.19	751	9877	1892	1872 [58]
195	Methyl tridecanoate (34)	1731-88-0	2793	3.85	882	697,588	1921	Nf
189	Propan-2-yl tetradecanoate (isopropyl myristate) (35)	110-27-0	2800	2.43	807	9987	1845	1823 [60]
196	Methyl tetradecanoate	124-10-7	2806	4.06	862	58,882	2021	2034 [71]
197	Diethyl-2-hydroxybutanedioate (36)	626-11-9	2814	2.33	892	3,163,111	2038	2041 [62]
198	Ethyl tetradecanoate (36)	124-06-1	2814	4.27	802	48,108	2057	2065 [53]
199	Ethyl 3-phenylprop-2-enoate (37)	103-36-6	2828	2.94	823	10,842	2118	Nf
200	2-Hydroxy-3-methylsuccinate	23394-53-8	2835	2.64	780	8102	2200	Nf
201	Methyl (*Z*)-hexadec-9-enoate (methyl palmitoleate) (38)	1120-25-8	2856	3.65	761	21,981	2219	Nf
202	Ethyl hexadecanoate (38)	628-97-7	2856	3.87	828	92,551	2243	2246 [52]
203	Diethyl (*E*)-but-2-enedioate (39)	623-91-6	2870	2.38	829	6548	2234	Nf
204	Methyl 9-oxononanoate (39)	1931-63-1	2870	2.86	871	42,503	2258	Nf
205	Methylbenzyl acetate (40)	93-92-5	2877	4.88	774	15,799	2287	Nf
206	Prop-2-ynyl propanoate (41)	1932-92-9	2884	3.32	780	9876	2313	Nf
207	Methyl 5-methoxy-3-oxopentanoate	62462-05-9	2912	2.34	761	21,795	2318	Nf
208	Dibutyl (*Z*)-but-2-enedioate (butyl maleate) (42)	105-76-0	2919	3.11	891	110,203	2329	Nf
209	Methyl 8-oxooctanoate (42)	4316-48-7	2919	2.82	807	5953	2335	Nf
210	2-Hydroxy-3-methyl-diethyl succinate (57)	3878-55-5	2933	2.03	890	255,964	2577	Nf
211	Dimethyl 2-propoxybutanedioate	325984-06-3	2940	2.25	758	9825	2362	Nf
213	Dibutyl (*E*)-but-2-enedioate (butyl fumarate) (43)	105-75-9	2954	3.27	759	9764	2367	Nf
214	2-Phenylethyl octanoate (44)	5457-70-5	2961	3.00	812	4217	2373	Nf
215	Methyl 3-hydroxy-2-methylpropanoate	80657-57-4	2989	2.08	806	8863	2378	Nf
216	Prop-2-enyl propanoate (allyl propionate)	2408-20-0	3003	2.03	800	12,715	2400	Nf
217	Ethyl 3-hydroxytridecanoate	107141-15-1	3010	2.79	772	34,583	2433[b]	Nf
218	Ethyl 3-(1-ethoxyethoxy)-2-methylbutanoate (47)	86845-49-0	3038	2.29	834	34,347	2564[b]	Nf
219	Decyl decanoate (45)	1654-86-0	2968	5.62	833	75,457	2588[b]	2565 [75]
220	Ethyl 4-ethoxybenzoate (48)	23676-09-7	3052	3.01	767	5965	2593[b]	Nf
221	2-Ethylhexyl benzoate (50)	5444-75-7	3073	3.58	776	10923	2598[b]	Nf
222	Methyl 8-hydroxyoctanoate	20257-95-8	3087	2.35	818	25,607	2602[b]	Nf
223	2-Phenylethyl 2-phenylacetate	102-20-5	3108	0.23	812	109,658	2618[b]	Nf
224	Ethyl 3-hydroxy-4-methylpentanoate (52)	40309-42-0	3122	2.41	845	8908	2624[b]	Nf
225	Methyl 2-methylundecanoate (53)	55955-69-6	3164	3.78	838	4579	2629[b]	Nf

Table 1 (*Continued*)

	Name	CAS number	^1t_R (s)	^2t_R (s)	Similarity	Area	LTPRI $_{(exp)}$	LTPRI $_{(lit)}$
226	Dodecyl 2-propylpentanoate	22632-60-6	3179	2.14	822	25,583	2651[b]	Nf
227	Diethyl 2,3-dihydroxybutanedioate (ethyl tartrate)	87-91-2	3208	2.07	783	8008	2733[b]	Nf
Ketones								
228	Propan-2-one (acetone) (1)	67-64-1	301	5.18	831	17,424	800[b]	818 [54]
229	Butan-2-one	78-93-3	315	2.66	795	43,157	889[b]	903 [75]
230	Butane-2,3-dione	431-03-8	497	2.44	764	42,622	1000	975 [75]
231	Pent-3-en-2-one	625-33-2	1015	2.42	809	9567	1132	Nf
232	Cyclopentanone (2)	120-92-3	1218	3.53	797	77,625	1186	1154 [67]
233	4-Methylheptan-2-one (3)	6137-06-0	1309	4.49	789	9639	1295	Nf
234	1-Hydroxypropan-2-one (3)	116-09-6	1309	2.24	768	13,966	1300	1295 [72]
235	3-Hydroxybutan-2-one	513-86-0	1351	2.32	970	747,559	1309	1304 [58]
236	Cyclohexanone	108-94-1	1456	3.93	773	13,804	1311	1314[a] 1285 [74]
237	6-Methylhept-5-en-2-one (5)	110-93-0	1498	3.81	828	47,785	1332	1339[a] 1338 [75]
238	4-Hydroxy-4-methylpentan-2-one (5)	123-42-2	1498	4.01	806	9875	1372	1339 [69]
239	3,3,5-Trimethyl-2-cyclohexen-1-one	22319-25-1	1526	2.13	821	13,283	1410	1406[a]
240	(E)-4-Methylhept-4-en-3-one	78-59-1	1617	3.63	830	23,345	1424	Nf
241	3,4-Dimethylcyclopent-2-en-1-one	30434-64-1	1701	3.71	843	9899	1439	Nf
242	Decan-2-one (12)	693-54-9	1967	3.88	807	8327	1489	1493[a]
243	2,3-Dimethylcyclopent-2-en-1-one	1121-05-7	2093	3.59	751	9917	1530	1535[a]
244	3-Methylcyclohex-2-en-1-one	1193-18-6	2219	2.53	753	9898	1592	1579 [74]
245	1-Phenylethanone (acetophenone) (20)	98-86-2	2317	2.97	931	84,301	1665	1649 [75]
246	2-Hydroxycyclopent-2-en-1-one	10493-98-8	2373	2.12	851	23,436	1702	Nf
247	3-Butylcyclohexan-1-one	39178-69-3	2429	1.99	796	9759	1711	Nf
248	Dodecan-2-one	6175-49-1	2455	4.06	779	8765	1806	1809 [60]
249	4-Methylhexan-2-one	105-42-0	2492	3.88	801	9987	1886	Nf
250	3-Methylcyclopentane-1,2-dione	765-70-8	2520	2.23	811	9874	1883	Nf
251	4-Hydroxy-8-methyl-3,5,7-nonatrien-2-one (27)	593288-46-1	2576	4.25	771	9679	2128	Nf
252	4-Phenylbut-3-en-2-one (32)	122-57-6	2702	2.79	770	9987	2103	Nf
253	1,5-Dimethoxypentan-3-one (32)	53005-18-8	2702	2.05	804	5734	2248	Nf
254	3,4-Dimethylidenecyclopentan-1-one	27646-73-7	2751	3.31	797	19418	2384	Nf
255	(E)-4-Methylhept-3-en-2-one (33)	22319-25-1	2779	2.13	764	16381	2422[b]	Nf
256	4-Hydroxyhexan-3-one (52)	4984-85-4	3122	1.76	806	12737	2744[b]	Nf
Terpenes								
257	6,6-Dimethyl-5-methylidenebicyclo[2.2.1]heptane (camphene)	79-92-5	1253	5.92	809	10,897	1075	1077 [26]
259	1-(4,7,7-Trimethyl-3-bicyclo[4.1.0]hept-4-enyl)ethanone (2-acetyl-carene)	3608-11-5	1729	4.80	821	46,210	1159	Nf
259	1-Methyl-4-(1-methylethyl)benzene (ρ-cymene)	99-87-6	1897	5.08	790	15,224	1301	1268[a] 1282 [71]
260	2-[5-Ethenyl-5-methyloxolan-2-yl]propan-2-ol ((*E*)-linalool oxide)	34995-77-2	2002	3.61	818	65,405	1426	1458[a] 1438 [54]
261	(5E)-3,7-dimethylocta-1,5,7-trien-3-ol (ho-trienol)	53834-70-1	2121	2.78	792	18,642	1424	1449 [62]
262	3,7-Dimethyl-1,6-octadien-3-ol (linalool)	78-70-6	2142	3.04	911	179,909	1554	1554 [59]
263	1-Ethenyl-1-methyl-2,4-bis(prop-1-en-2-yl)cyclohexane (elemene) (15)	11029-06-4	2198	5.48	831	14,690	1576	1582 [76]
264	4-Methyl-1-propan-2-ylcyclohex-3-en-1-ol (4-terpineol) (18)	562-74-3	2303	2.99	888	157,803	1608	1602 [65]

Table 1 (*Continued*)

	Name	CAS number	^1t_R (s)	^2t_R (s)	Similarity	Area	LTPRI $_{(exp)}$	LTPRI $_{(lit)}$
265	5-Methyl-2-propan-2-ylcyclohexan-1-ol (menthol) (19)	89-78-1	2310	3.06	792	8134	1635	1637 [54]
266	2-(4-Methyl-1-cyclohex-3-enyl)propan-2-ol (α-terpineol) (19)	98-55-5	2310	3.53	776	10,765	1659	1668 [77]
267	Sesquichamene (21)	470-40-6	2359	6.34	807	9799	1675	Nf
268	(Z)-2-methyl-5-(6-methyl-5-methylidene-6-bicyclo[2.2.1]heptanyl)pent-2-en-1-ol ((Z)-β-Santalol) (23)	77-42-9	2478	3.39	759	11,235	1692	Nf
269	2-Methyl-2-prop-1-en-2-ylcyclohexan-1-ol (dihydrocarveol)	38049-26-2	2478	5.08	824	12,503	1709	1720 [78]
270	(7E,9E,11E,13E)-pentadeca-7,9,11,13-tetraen-1-ol ((E)-α-Santalol) (33)	11031-45-1	2779	4.17	807	23,280	1742	Nf
271	α-Citronellol (44)	7540-51-4	2961	2.64	855	40,319	1781	1778 [51]
272	(2Z)-3,7-dimethylocta-2,6-dien-1-ol (nerol) (48)	106-25-2	3052	2.60	801	10,005	1792	1797 [65]
273	(E)-3-(2,6,6-trimethylcyclohexen-1-yl)prop-2-enal (isomethyl ionone)	4951-40-0	3059	4.76	789	27,716	1872	1900 [65]
274	(Z)-α-bisabolene epoxide (49)	111536-37-9	3066	3.23	782	9987	2007	Nf
275	Patchoulane (50)	25491-20-7	3073	1.07	768	11,374	2060	Nf
276	4-Allyl-2-methoxyphenol (51)	97-53-0	3080	2.45	823	10,006	2183	2175 [71]
277	3,7,11-Trimethyldodeca-2,6,10-trien-1-ol (farnesol)	4602-84-0	3115	6.37	809	23,623	2356	2350 [52]
278	(2Z) 2-methyl-6-[(4-methyl-3-cyclohexen-1-yl] 2,6-Heptadien-1-ol ((Z)-lanceol) (55)	10067-28-4	3178	0.32	768	11,632	2449[b]	Nf
279	(3E)-3-[6-hydroxy-5-(hydroxymethyl)-5,8a-dimethyl-2-methylidene-3,4,4a,6,7,8-hexahydro-1H-naphthalen-1-yl]ethylidene]-4-hydroxyoxolan-2-one (andrographolide)	5508-58-7	3192	5.91	755	13,819	2635[b]	Nf
Phenols								
280	2-Methoxyphenol (guaiacol) (58)	90-05-1	2561	2.32	837	9047	1877	1889 [22]
281	2-Methoxy-4-methylphenol (ρ-methylguaiacol)	93-51-6	2653	2.39	799	10,098	1965	1956 [79]
282	Phenol (32)	108-95-2	2702	1.95	929	135,649	2002	1973 [57] 1978 [85]
283	4-Ethyl-2-methoxyphenol (4-ethylguaiacol) (35)	2785-89-9	2800	2.48	874	27,972	2030	2033 [65]
284	4-Ethylphenol	123-07-9	2808	2.04	909	59,749	2204	2185 [58]
285	4-Ethenyl-2-methoxyphenol (4-vinylguaiacol)	7786-61-0	2840	2.30	832	9908	2214	2200 [80]
286	5-Methyl-2,4-di(propan-2-yl)phenol (45)	40625,-96,-5	2968	3.13	790	24,633	2282	Nf
	C13-norisoprenoids							
287	(E)-1-(2,6,6-Trimethyl-1-cyclohexa-1,3-dienyl)but-2-en-1-one (β-damascenone)	23726-93-4	2506	3.69	859	9239	1839	1831 [22]
288	(5E)-6,10-dimethylundeca-5,9-dien-2-one ((E)-geranylacetone)	3796-70-1	2512	3.55	888	75,681	1849	1856 [65]
289	Methyl 3-oxo-2-pentylcyclopentaneacetate (methyl dihydrojasmonate)	24851-98-7	2700	2.81	803	20,478	2262	2276 [81]
Pyrans								
290	Tetrahydro-2H-pyran-2-one (δ- valerolactone)	542-28-9	2304	2.63	845	20,493	1589	1609 [82]
291	2H-Pyran-2,6(3H)-dione	108-55-4	2821	2.04	846	64,174	2427[b]	Nf
Furans								
292	2-Methylfuran	534-22-5	245	2.54	812	16,306	798[b]	815 [75]
293	2-Ethylfuran	3208-16-0	280	2.14	920	352,760	805[b]	Nf
294	2,5-Dihydrofuran (1)	1708-29-8	301	2.51	824	124,700	820[b]	Nf

Table 1 (*Continued*)

	Name	CAS number	^1t_R (s)	^2t_R (s)	Similarity	Area	LTPRI $_{(exp)}$	LTPRI $_{(lit)}$
295	Tetrahydrofuran	109-99-9	308	2.99	762	263,530	829[b]	Nf
296	2-Pentylfuran	3777-69-3	1155	4.57	801	12,390	1258	1230 [79]
297	Furan-2-carbaldehyde (furfuraldehyde, furfural)	98-01-1	1323	2.51	961	4,164,340	1465	1465[a] 1460 [65]
298	5-Methylfuran-2-carbaldehyde (5-methyl-2-furaldehyde) (8)	620-02-0	1799	2.75	910	104,143	1600	1570 [65]
299	Ethyl furan-2-carboxylate (ethyl 2-furoate)	614-99-3	2065	2.84	937	413,294	1627	1618 [65]
300	Furan-2-ylmethanol (2-furanmethanol)	98-00-0	2170	2.35	756	12,061	1680	1661 [60]
301	2-(Furan-2-ylmethoxymethyl)furan (30)	4437-22-3	2667	3.33	780	57,108	1996	Nf
302	Furan-2,5-dicarbaldehyde	823-82-5	2744	2.24	807	9866	2006	Nf
303	Ethyl 5-oxotetrahydro-2-furancarboxylate	1126-51-8	2737	2.29	939	577,789	2174	Nf
304	5-(Hydroxymethyl)furan-2-carbaldehyde (47)	67-47-0	3038	2.59	807	9989	2515	2485 [54]
Lactones								
305	2-Methyldihydro-(2H)-furan-3-one	3188-00-9	1135	2.74	766	25,817	1246	1260 [83]
306	Dihydro-(3H)-furan-2-one	96-48-0	2177	2.59	962	331,301	1690	Nf
307	3-Methyl-5H-furan-2-one (17)	22122-36-7	2275	2.37	765	8686	1700	1683 [52]
308	5-Ethyloxolan-2-one (5-ethyldihydro-(3H)-furan-2-one, γ-hexalactone) (20)	695-06-7	2317	2.23	801	9943	1714	1694 [84]
309	3-Methyl-2H-furan-5-one (21)	591-11-7	2359	2.42	769	6545	1726	1694 [57]
310	5-Ethyltetrahydrofuran-2-one	695-06-7	2408	2.77	786	36,909	1772	Nf
311	5-Ethoxy-(3H)dihydrofuran-2-one	932-85-4	2418	2.66	807	3045	1794	Nf
312	5H-furan-2-one	497-23-4	2500	2.27	868	44,276	1703	1716 [84]
313	(E) 5-butyl-4-methyloxolan-2-one (whiskey lactone)	39212-23-2	2542	2.92	907	106,065	1910	1910 [22]
314	3-Butyldihydro-(3H)-furan-2-one	19340-56-8	2551	2.85	793	10,023	1937	1915 [79]
315	5-Pentyloxolan-2-one (5-pentyldihydro-(3H)-furan-2-one)	104-61-0	2596	2.84	887	10,002	2007	2007 [84]
316	5-Acetyloxolan-2-one (5-acetyldihydro-(3H)-furan-2-one) (28)	29393-32-6	2611	2.29	909	60,708	2013	2026 [85]
317	5-Hexyloxolan-2-one (5-hexyldihydro-(3H)-furan-2-one, γ-decalactone) (29)	706-14-9	2653	2.88	839	11,433	2145	2138 [51]
318	3-Hydroxy-4,4-dimethyloxolan-2-one [3-hydroxy-4,4-dimethyldihydro-2(3H)-furanone] (35)	79-50-5	2800	2.05	775	57,722	2158	Nf
319	3-Hydroxy-4,5-dimethyl-5H-furan-2-one (sotolon)	28664-35-9	2883	2.07	879	96,309	2195	2190 [22]
320	3H-2-benzofuran-1-one (isobenzofuranone) (46)	87-41-2	3024	2.31	770	10,147	2365	2356 [86]
Pyrroles								
321	1H-pyrrole (10)	109-97-7	1925	2.08	769	11,751	1498	1507 [72]
322	1-Ethylpyrrole-2-carbaldehyde	2167-14-8	2135	3.09	762	2695	1616	Nf
323	1-Methylpyrrole-2-carbaldehyde (14)	1192-58-1	2163	2.83	764	3179	1632	1626[a]
324	Pyrrolidin-2-one (35)	616-45-5	2800	2.23	802	9007	2017	2002[a]
325	1H-pyrrole-2-carbaldehyde	1003-29-8	2820	2.04	829	5123	2038	2032 [86]
Sulfur compounds								
326	Ethanethiol	75-08-1	310	2.24	807	3121	900[b]	918[a]
327	Ethyl 2-methylsulfanylacetate (ethyl 2-(methylthio) acetate)	4455-13-4	1750	3.36	834	9283	1450	Nf
328	2-Methylthiolan-3-one (dihydro-2-methyl-3(2H)-thiophenone) (11)	13679-85-1	1946	3.35	915	131,644	1528	1506 [52]

Table 1 (*Continued*)

	Name	CAS number	^1t_R (s)	^2t_R (s)	Similarity	Area	LTPRI $_{(exp)}$	LTPRI $_{(lit)}$
329	Ethyl 3-methylsulfanylpropanoate	13327-56-5	2044	3.51	836	17,020	1560	Nf
330	Thiophene-2-carbaldehyde (18)	98-03-3	2303	2.60	859	9041	1689	1702 [86]
331	Methylimino-sulfanylidenemethane (methyl isothiocyanate)	556-61-6	2338	3.49	805	5623	1724	Nf
332	3-(Methylsulfanyl)propan-1-ol (3-(methylthio)-1-propanol)	505-10-2	2450	2.28	855	24,245	1722	1721 [86]
333	1,3-Benzothiazole (32)	95-16-9	2702	2.84	863	13,884	1956	1937 [66]
334	(7,7-Dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonic acid (camphorsulfonic acid)	5872-08-2	2870	2.36	763	4262	2277	Nf

Compounds followed by the same number between parentheses correspond to co-elutions.
nf, no found; LTPRI, linear-temperature-programmed retention index; LTPRI(lit), literature LTPRI on a DB-WAX columns or equivalent stationary phase.
[a] www.odour.org.uk.
[b] Extrapolated LTPRI for compounds with LTPRI <900 and >2400.

but it is largely produced during the fermentation by wine yeast [44].

Terpene alcohols, including linalool, terpineol, nerol and hotrienol are also important to wine aroma. These compounds impart the aroma of flower, rose, geranium and floral with a slight woody note, respectively. They have a very low sensory thresholds and may contribute to aroma even when present in very low amounts: linalool, 100 μg/L; terpineol, 400 μg/L; nerol, 300 μg/L and ho-trienol 110 μg/L [43].

Among the identified lactones, sotolon (3-hydroxy-4,5-dimethyldihydro-2(5H)-furanone) is one of the most important compound associated with botrytized wines and its odor is described as "nutty" at low concentrations and "curry" at higher levels [45]. Another identified lactone, 3-hydroxy-4,4-dimethyloxolan-2-one, was separated from three other components in the second dimension. The contribution to the aroma of this lactone was not found in literature. Fig. 4 shows that four chromatographic peaks are superimposed in ^{1}D. Spectral deconvolution based on mass spectra differences is useful in this case, especially for propan-2-yl tetradecanoate (isopropyl myristate) and 4-ethyl-2-methoxyphenol (4-ethylguaiacol), because they also co-elute in the second dimension column. In Fig. 4B, mass spectra of the four compounds are compared with mass spectra of NIST library. Other 29 compounds also co-eluted in both first and second dimension and were identified only with spectral deconvolution.

Other significant contribution for wine aroma comes from acids. Acetic acid, which is a by-product of fermentation, was found in all samples. The presence of this specific acid is very important as it is responsible for imparting a vinegar-like character to wine. Other acids identified in the samples were octanoic, nonanoic, decanoic and dodecanoic, which also lend a bad effect to the overall wine aroma [46].

Sulfur compounds were represented by thiazoles (odor described as "popcorn" and "peanut") and thiophenes (odor of "burned", "burned rubber", or "roasted coffee") and they are responsible for unpleasant odors in wines [47]. On the other side, some pyrroles may contribute positively to wine aroma and, among them, pyrrole-2-carboxaldehyde may be cited as the most abundant pyrrole of Merlot wines. This volatile compound has a sweet aroma [48] and was also found in the Brazilian Merlot wine under investigation (Table 1).

Among carbonyl compounds, acetaldehyde was found as a minor chromatographic peak. It is usually reported as one of the most important sensory carbonyl compounds formed during vinification [49]. At low levels, it may be responsible for a pleasant fruity aroma, but at high concentrations it possesses a pungent irritating odor [50]. Furthermore, the most important ketone among the ones found in Merlot samples was 3-hydroxy-2-butanone (acetoin), which also has a butter-like character [30].

Co-elutions come up to 138 compounds in ^{1}D and some of them are resolved in ^{2}D. Co-eluting compounds are indicated in Table 1 by the same numbers between parentheses, written just after the name of the compound. The separation of nonanoic acid (peak 98, ^1t_R = 2933s, ^2t_R = 2.03 s) from 2-hydroxy-3-methyl-diethyl succinate (peak 214, ^1t_R = 2933s, ^2t_R = 2.03 s) in the WAX column illustrates very well the importance of the enhanced selectivity achieved with the second dimension, as nonanoic acid lends a bad effect to the overall wine aroma, contributing with an odor of cheese [46]. 2-hydroxy-3-methyl-diethyl succinate was for the first time identified in Merlot wine and there is no information about its aroma in the scientific literature (Fig. S1, Supplementary material).

3.3. Multivariate analysis of Merlot wine volatile compounds

Fischer Ratios were calculated to determine which analytes are responsible for the main differences between Merlot wines and wines of other grape varieties. The higher the Fischer Ratio numerical value, the greater the variance between classes (Merlot and non-Merlot) is for a particular compound. The compounds with higher values of Fischer Ratio in decreasing order were: ethyl dodecanoate, 1-hexanol, ethyl nonanoate, ethyl hexanoate, ethyl decanoate, dehydro-2-methyl-3(2H)thiophenone, 3-methyl butanoic acid, ethyl tetradecanoate, methyl octanoate, 1,4 butanediol, and 6-methyloctan-1-ol. Based on the correlation matrix, multivariate analysis was carried out using principal component analysis (PCA) to determine the mutual relationship among the volatile flavor compounds of Merlot wines. A clear differentiation between Merlot wines and other wines was observed (Fig. 5a). The two principal components (PC) account for 98.57% of total variance of the data. Merlot and non-Merlot wines have similar scores on PC1, which means that PC1 did not contribute for differentiation between these wines. In this case, PC2 was responsible for this differentiation. Fig. 5b shows the corresponding loadings plot that indicates the relative importance of each volatile compound for each wine class. The Merlot wines may be seen in the upper part of the plot, where PC1 is negative and PC2 is positive. The variable with highest contribution to

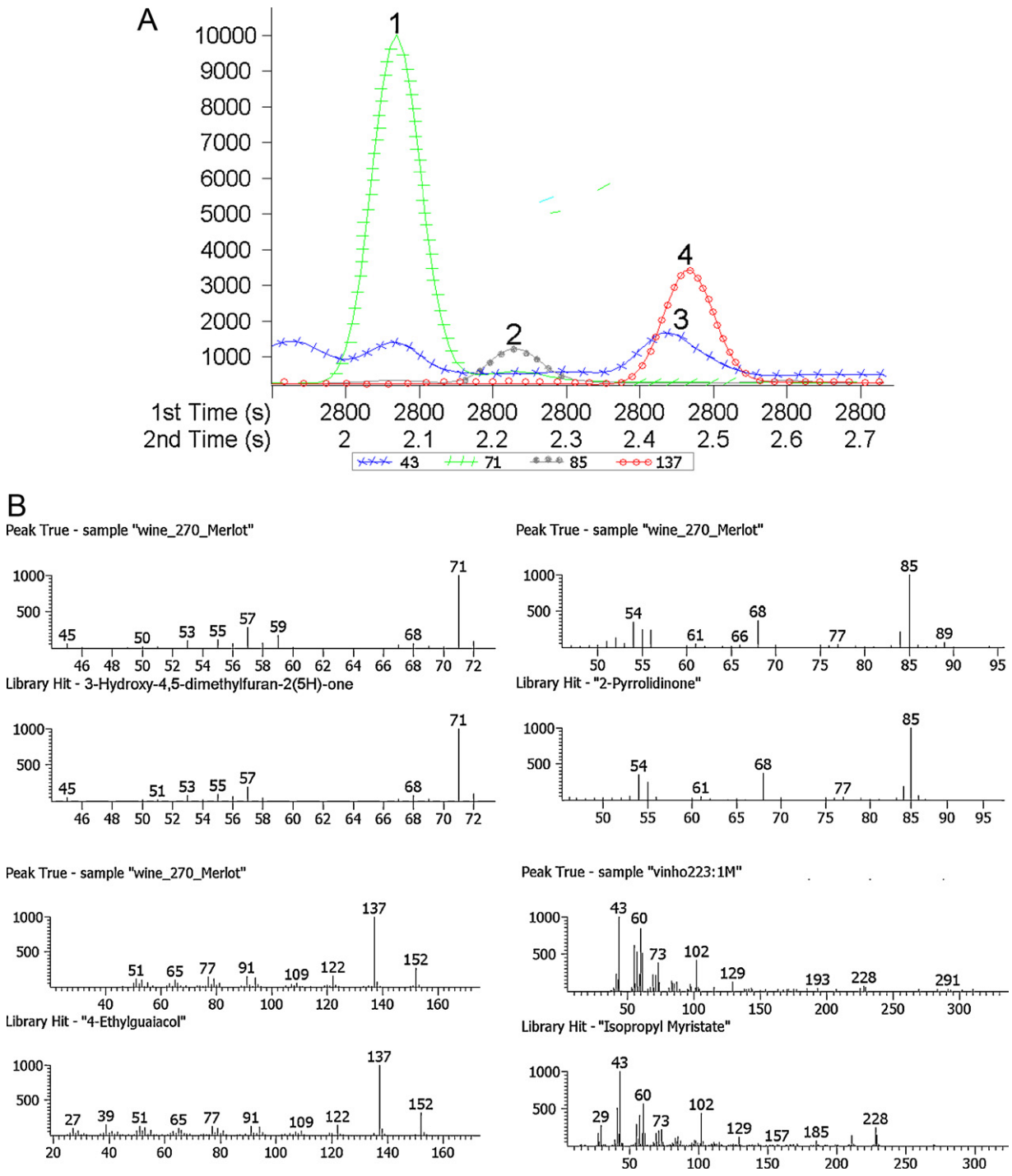

Fig. 4. (A) Modulated peaks of four compounds found in Merlot wine: (1) *green line*, 3-hydroxy-4,4-dimethyloxolan-2-one, *m/z* 71; (2) *gray line*, 2-pyrrolidinone, *m/z* 85; (3) *blue line*, isopropyl myristate, *m/z* 43; (4) *red line*, 4-ethylguaicol, *m/z* 137. (B) Deconvoluted mass spectra of compounds in (A). (For interpretation of references to color in this figure legend, the reader is referred to the web version of this article.)

the first PC was ethyl hexanoate (−13.83, herbaceous aroma). The second PC (16.65% of total variability) is strongly correlated to 6-methyloctan-1-ol (7.11) and ethyl hexanoate (−4.90). 6-Methyloctan-1-ol was for the first time tentatively identified in Merlot wine headspace and there is no information on its aroma in the scientific literature. Furthermore, this compound co-eluted in the first dimension with two other compounds: ethyl 2-phenylacetate (peak 186, $^{1}t_{R}$ = 2561 s, $^{2}t_{R}$ = 3.12 s) and 2-methoxyphenol (peak 284, $^{1}t_{R}$ = 2561 s, $^{2}t_{R}$ = 2.32 s) and was separated from them in the second dimension. Fig. 5b shows the corresponding loadings plot that indicates the relative importance of each volatile compound for each wine class. The Merlot wines may be seen in the upper part of the plot, where PC1 is negative and PC2 is positive.

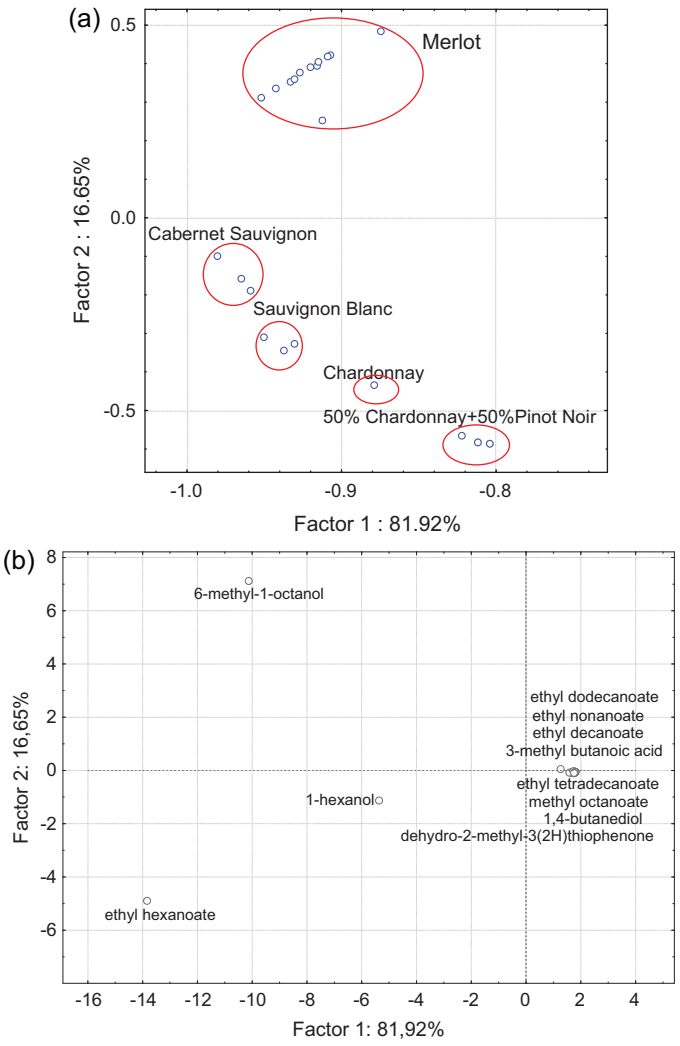

Fig. 5. PC1 vs. PC2 scatter plot of the main sources of variability among Merlot wines (a) distinction between the samples and (b) relation between volatile compounds and the type of wine.

4. Conclusions

Analysis of volatiles of Merlot wines by HS-SPME-GC × GC/TOFMS is reported for the first time. In addition this is the first study on volatile composition of Merlot wines produced in the Serra Gaúcha. A total of 334 compounds were tentatively identified by GC × GC/TOFMS in the headspace of Brazilian Merlot wines and this shows a superior peak capacity and selectivity of the 2D technique when applied to wine headspace, as this number of compounds is higher than what is reported in the literature for HS-SPME-1D-GC/MS analysis. A comparison among experimental GC × GC LTPRI of a polar set of columns was successfully applied to a polar 1D-GC LTPRI, presenting a maximum difference of 33 units among them. This simple approach may be a valuable tool for future works dealing with identification of volatile and semi volatile compounds. Several co-elutions in the first dimension could be resolved in the second dimension column and some of them included compounds that may contribute with important aroma notes, as well as compounds that were tentatively identified for the first time in Merlot wine headspace (e.g. 2-hydroxy-3-methyl-diethyl succinate). Additionally, mass spectra deconvolution was an especially useful tool when chromatographic peaks of totally or partially co-eluted compounds were tentatively identified through deconvoluted mass spectra. Structurally organized distribution of compounds according to their chemical classes was also important for the identification of volatile compounds, such as esters, acids, alcohols, aldehydes, ketones, thiols and lactones. These results indicate that GC × GC/TOFMS is the analytical tool of choice for the analysis of complex wine samples, and it also shows that 1D-GC/MS may provide misleading results for qualitative and, consequently, quantitative analysis. A statistical treatment of the GC × GC/TOFMS data proved to be a remarkable tool for distinguishing Merlot wines from non Merlot wines. GC × GC/TOFMS associated with non target methods will be an important tool for assessing headspace compositional differences among wines and also among other spirits, beverages and food, according to specific raw materials, soil, climate, production process, etc.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2012.01.002.

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