http://dx.doi.org/10.5935/0103-5053.20150110

J. Braz. Chem. Soc., Vol. 26, No. 7, 1411-1430, 2015.
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0103 - 5053 $6.00+0.00

Article

Characterization of the Volatile Profile of Brazilian Moscatel Sparkling Wines Through Solid Phase Microextraction and Gas Chromatography

Karine P. Nicolli,[a] Juliane E. Welke,[b] Mayara Closs,[a] Elina B. Caramão,[a] Gustavo Costa,[b] Vitor Manfroi[b] and Claudia A. Zini[,a]*

[a]Instituto de Química, Programa de Pós-Graduação em Química and [b]Instituto de Ciência e Tecnologia de Alimentos, Universidade Federal do Rio Grande do Sul (UFRGS), Avenida Bento Gonçalves, 9500, 91501-970 Porto Alegre-RS, Brazil

Solid phase microextraction, one-dimensional gas chromatography (1D-GC) and comprehensive two-dimensional gas chromatography (GC×GC) with mass spectrometric detector have been used to characterize the volatile profile of Moscatel sparkling wines. Predominant classes were esters, acids, alcohols and terpenes. The efficiency of GC×GC was apparent due to the higher number of compounds positively and/or tentatively identified through this technique (two and a half times higher than with 1D-GC), as well as by the separation of co-eluted compounds in 1D-GC. Principal components analysis showed that the volatile profile of the majority of sparkling wines is similar. Only two samples differed from others and the compounds responsible for this behavior were nerol, menthol, linalool acetate, limonene and geraniol. Furthermore, a clear separation among sparkling wines done with two Moscato grape varieties (Bianco and Giallo) was observed in cluster analysis due to the higher chromatographic area of terpenes and norisoprenoids verified in Giallo samples.

Keywords: Moscatel sparkling wine, volatiles, comprehensive two-dimensional gas chromatography, GC×GC/TOFMS, aroma

Introduction

Moscatel sparkling wine presents an intense fruity and floral aroma that is produced from a single alcoholic fermentation of the must of grapes of Moscato variety. Moscato, Moscatel, Muscatel and Muscat are synonyms. Moscato has been used to refer to grapes of this family and the word Muscat is frequently used to designate wines produced in Italy, United States of America and Australia. The word Moscatel has been assigned to wines produced in Portugal, Spain and Brazil. Moscatel sparkling wine is similar to Asti, the Italian sparkling wine that is produced in southeastern Piedmont region.[1-3] Whenever research studies are quoted in this manuscript, the word used for the wine designation in the original publication was maintained. The state of Rio Grande do Sul, located in the South part of Brazil, is responsible for more than 90% of the Brazilian wine production.[4] Among sparkling wines, Moscatel is the favorite drink of Brazilian consumers and this preference may be attributed to its unique and characteristic aromatic intensity.[5]

Moscatel sparkling wine production has been presenting a growing trend in the Brazilian market during the last years and its participation in the commercialization of sparkling wines in the national market has doubled from 2004 to 2013.[6] In the international realm, Brazilian Moscatel sparkling wines have been recognized with several gold medals in renowned competitions in various countries, such as France, Spain, Greece, United States, and Argentina.[7]

Aroma is one of the most important factors related to wine quality and volatile compounds play a significant role regarding aroma. The wine volatile profile is influenced by many factors such as grape variety, soil, climatic conditions and the winemaking process.[8] Information on wine aroma and the determination of the relative amount of each volatile component may be employed for varietal differentiation and for the establishment of quality and authenticity criteria, aiming at the improvement of wine quality.[8,9]

Several analytical techniques have been developed and improved for the study of wine volatile compounds, such as, for example liquid-liquid extraction (LLE), dispersive liquid-liquid microextraction (DLLME), solid phase extraction (SPE), stir bar sorptive extraction (SBSE) and solid phase microextraction (SPME).[10-12] DLLME presents the advantage of avoiding the use of large volumes of

*e-mail: cazini@iq.ufrgs.br

organic solvents when compared to LLE, but it is difficult to automate.[12] SPE is frequently used for volatile and semi-volatile compounds extraction or for wine clean up. The large variety of sorbents commercially available makes this technique suitable for the determination of analytes with distinct chemical structures and polarities. Some of its drawbacks are large volumes of sample and solvents compared to microextration techniques.[10] In SBSE a coated stir bar is added to the sample for stirring and extraction (direct SBSE) or be exposed to the headspace (HS-SBSE). Due to the high volume of the extracting phase in SBSE stirrer, which results in low detection limits, it is a good tool for the analysis of wine off-flavors. However, poly(dimethylsiloxane) (PDMS) is the only commercially available coating, while there are several SPME coatings available for compounds of different physicochemical natures, such as carbowax (CW), polyacrylate (PA), etc.[11] Headspace (HS) SPME is considered the most employed technique for the extraction of wine volatiles, as it is simple, fast, sensitive, easy-to-automate and a solvent-free technique. Furthermore, this technique supports multi-phase coatings, which is ideal for complex samples such as wine, which presents several hundreds of compounds from distinct chemical families in different concentrations.[13]

One-dimensional gas chromatography with mass-spectrometric detector (1D-GC/MS) is usually the technique of choice for the determination of volatile compounds of wines and other beverages.[14,15] However, co-elutions usually arise in 1D-GC analyses of complex samples, which eventually may result in misleading identification and quantification of compounds. Furthermore, sensitivity of 1D-GC/MS may be insufficient to detect trace components, which might be important to wine aroma.[16-18] In recent years, comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detector (GC×GC/TOFMS) has also been employed, achieving superior results due to its higher peak capacity, sensitivity, selectivity and resolution.[3,17,19] GC×GC analysis of complex matrices generates a large amount of data and data treatment ends up being a time consuming and tedious task, especially because it is difficult to distinguish which are the most important information among all acquired information. Chemometric tools, such as principal component analysis (PCA), cluster analysis (CLA), discriminant analysis (DA) and Fisher ratio[17,20,21] have been employed in studies related to volatile beverages, such as differentiation of Madeira wines according to grape varieties,[22] observation of the evolution of wine aroma during ageing,[3] characterization of the volatile profile of Brazilian Merlot wine,[17] effect of aging and lees contact on sulfur compounds in Italian sparkling wines,[23] and differentiation among base and sparkling wines according to their volatile compounds.[24]

Sparkling wines of the Moscato grape variety have been widely produced in many places and their volatile compounds have attracted the interest of several researchers due to the importance of this type of sparkling wines.[25-28] However, the volatile composition of Moscatel Brazilian sparkling wines has never been investigated. Despite the economic and social importance of the sparkling wines in the Southern region of Brazil and the need to characterize these products, few studies were performed to elucidate the components present in the volatile fraction of these wines.

This study investigates, for the first time, the volatile components of Brazilian Moscatel sparkling wines in order to characterize them and aims to open perspectives for the discovery of a potential chemical signature of these wines, as well as potential markers of their quality. Therefore, HS-SPME, 1D-GC/MS and GC×GC/TOFMS along with Fisher ratio and PCA were employed to characterize volatiles of Moscatel Brazilian sparkling wines. The potential of GC×GC/TOFMS was verified for the separation of volatile compounds of a representative number of Brazilian Moscatel sparkling wines.

Experimental

Samples, analytical reagents, and supplies

Twenty-one Brazilian Moscatel sparkling wines of 2011, produced in the state of Rio Grande do Sul (RS), Santa Catarina (SC) and Paraná (PR) have been investigated (Table 1). The ethanol content of wines ranged from 7.8 to 8.5%, which is according to the Standards of Identity and Quality established by Brazilian law.[29] These samples were provided by the Brazilian Association of Enology (ABE, Associação Brasileira de Enologia) and Brazilian Agricultural Research Corporation of Grape and Wine (EMBRAPA, Empresa Brasileira de Pesquisa Agropecuária Uva e Vinho). According to the Brazilian Institute of Wine (IBRAVIN, Instituto Brasileiro do Vinho), 83 wineries commercialized Moscatel sparkling wine in 2011 and among them, 21 were studied in the present work. Most companies outsourced their production of Moscatel sparkling wines, which means that 52% of the wineries that have their own production of wine were analyzed (11 of 21 wineries), rendering a study that is representative of the Brazilian scenario. Overall, considering companies with their own production (21), the ones that outsourced their production (44) from other wineries and the ones that did not provide any information (18), 25% of the Brazilian sparkling wines of Moscato variety were investigated in

relation to their volatile components (21 of 83 wineries). Two other sparkling wines from the Piedmont region (Asti Spumante), Italy (2011) were included in this investigation (Table 1).

Standard compounds ethyl isobutanoate, ethyl butanoate, ethyl lactate, ethyl isovalerate, 1-hexanol, isoamyl acetate, hexanoic acid, ethyl hexanoate, hexyl acetate, limonene, eucalyptol, terpinolene, sorbic acid, ethyl sorbate, linalool, 2-phenyl ethyl alcohol, octanoic acid, menthol, diethyl succinate, α-terpineol, ethyl octanoate, nerol, ethyl benzeneacetate, nonanoic acid, β-damascenone, ethyl decanoate, 1-dodecanol, ethyl dodecanoate were purchased from Aldrich (Steinheim, Germany). Pentadecane was utilized as internal standard (IS) and was also purchased from Aldrich. The purity of all these compounds were higher than 90%.

Model wine was prepared with (+)-tartaric acid (6 g L^{-1}) supplied by Synth (São Paulo, Brazil) and 10% of ethanol double-distilled (95%, Vetec, Rio de Janeiro, Brazil) in MilliQ deionised water. The pH was adjusted to 3.5 with sodium hydroxide (Nuclear, São Paulo, SP, Brazil). Ultrapure water was prepared using a Milli-Q water purification system (Millipore, Bedford, MA, USA). The standard solutions were prepared in ethanol and diluted in wine model solution in order to obtain a matrix similar to wine in regards to percentage of ethanol and acidity. This approach minimizes matrix effects and has been extensively used in scientific literature.[31-33]

The SPME fiber (divinylbenzene polydimethylsiloxane (DVB/PDMS) StableFlex) was purchased from Supelco (Bellefonte, PA, USA) and was conditioned according to the manufacturer's recommendation prior to its first use. Sodium chloride (NaCl) of analytical grade was purchased from Nuclear (São Paulo, SP, Brazil) and was oven dried at 110 °C overnight before use. Ten milliliters headspace vials with Teflon septa were purchased from Supelco. A thermostatic chamber, manufactured at the Institute of Physics of Universidade Federal do Rio Grande do Sul (UFRGS) was utilized to keep a constant temperature during HS-SPME (± 0.4 °C).

Table 1. Brazilian and Italian sparkling wines investigated in this study

Sparkling wine[a]	Grapes varieties[b]	Grape growing site[c]	Letters in Figure S1	Winemaking[c]
A_1	MB	Hills of Monferrato (Piedmont)	–	OW
A_2	MB	Piedmont region	–	OW
M_1	MB, MG	Hills of Garibaldi	g	OS
M_2	MB	NI	–	NI
M_3	MB, MG, MA	Caxias do Sul and Monte Belo	c,i	OW
M_4	MG	NI	–	NI
M_5	MB, MG, MA	Serra Gaúcha	–	OW
M_6	MB	Lages	h	OW
M_7	MB, MG	Garibaldi, Farroupilha and S. Jorge	e,g,m	OW
M_8	MB	Veranópolis and Bento Gonçalves	a,n	OW
M_9	MB, MA, R2	Serra Gaúcha	–	OS
M_{10}	R2, MB	Farroupilha region	e	OW
M_{11}	MB, MG	Colombo	d	OS
M_{12}	MG, MA	NI	–	NI
M_{13}	MG	Canela	b	OW
M_{14}	MB, MG	Garibaldi, Farroupilha, S. Jorge	e,g,m	OS
M_{15}	MB	Flores da Cunha and Farroupilha	e,f	NI
M_{16}	MB	Farroupilha region	e	OW
M_{17}	MB	NI	–	OS
M_{18}	MB, MG, R2	Paraí and Farroupilha	e,j	OS
M_{19}	MB	Pinheiro Machado	k	NI
M_{20}	NI	Serra Gaúcha	–	NI
M_{21}	MG	Bento Gonçalves and Pinto Bandeira	a,l	OS

[a]A: Asti spumante, M: Moscatel sparkling wine; [b]MB: Moscato Bianco, MG: Moscato Giallo, MA: Malvasia, R2: clone of the Moscato variety;[30] [c]OW: wines of its own manufacture, OS: manufacture was outsourced with different partners. NI: non-informed. Wineries of all Moscatel sparkling wines are from Rio Grande do Sul, except M_6 and M_{11} that are from Santa Catarina and Paraná, respectively.

Sample preparation and extraction

The samples were degassed at low temperature (< 10 °C) by ultrasonic waves (ultrasound Ultra Cleaner 1400 from Quimis, Diadema, SP, Brazil) for 30 min in an erlenmeyer flask containing 200 mL of sparkling wine and maintained at approximately 5 °C. HS-SPME was performed with a DVB/PDMS 65 μm film, at 40 °C, without sample agitation, during 30 min, according to previous work.[34] Two mililiters of wine, 2 μL of internal standard (10 mg L^{-1}), and 30% of NaCl (m/v) were placed in 10 mL headspace glass vials. Desorption of volatile compounds occurred in the GC inlet at 250 °C and the fiber was kept in the injection port for 5 min. All samples were analyzed in triplicate and a blank sample (model wine) was verified before the analysis of each sample.

Chromatographic analyses

A Shimadzu gas chromatograph coupled to a quadrupole mass spectrometric detector (GC/MS), model QP2010 (Kyoto, Japan) was employed to perform headspace analyses of volatiles compounds with the following columns: DB-5 (5% diphenyl-95% dimethyl polysiloxane, 60 m × 0.25 mm × 0.25 μm) and DB-WAX (polyethylene glycol, 30 m × 0.25 mm × 0.25 μm). Oven temperature was kept at 45 °C for 5 min and it was heated up to 180 °C at a rate of 3 °C min^{-1}, reaching a final temperature of 240 °C at 20 °C min^{-1}. Injector and detector temperature were kept at 250 °C, while helium (analytical purity 99.999%, Linde Gases, Canoas, RS, Brazil) flow rate was 1.0 mL min^{-1} and desorptions were made in the splitless mode. The MS parameters included electron ionization at 70 eV and the mass range (*m*/*z*) of 45 to 450.

The GC×GC system consisted of an Agilent 6890N (Agilent Technologies, Palo Alto, CA, USA) equipped with a Pegasus IV time-of-flight mass spectrometric detector (Leco Corporation, St. Joseph, MI, USA). The GC system was equipped with a secondary column oven and a non-moving quadjet dual stage thermal modulator. During modulation, cold pulses were generated using dry nitrogen gas cooled by liquid nitrogen, whereas heated nitrogen gas was used for hot pulses. The system was also equipped with a CTC CombiPAL autosampler (CTC Analytics, Zwingen, Switzerland) with an agitator and SPME fiber conditioning station. The injector, transfer line and ion source temperature were at 250 °C. Oven temperature was kept at 45 °C for 0.5 min and was raised to 240 °C at 3 °C min^{-1}. The secondary oven was kept 10 °C above the primary oven throughout the chromatographic run. The first column was a DB-5 (60 m × 0.25 mm × 0.25 μm) and the second column was a DB-17ms (50% phenyl 50% methyl-polysiloxane, 1.70 m × 0.18 mm × 0.18 μm). MS parameters and carrier gas employed, as well as its flow rate were the same reported for 1D-GC/MS. The period of modulation was 7 s, detector voltage −1750 V, and acquisition rate was 100 spectra s^{-1}. Tentative identification of wine aroma compounds in 1D-GC as well as with GC×GC analyses was achieved comparing experimental linear temperature programmed retention index (LTPRI) with retention indices reported in the scientific literature. Retention data of a series of *n*-alkanes (C9-C24), obtained under the same experimental conditions employed for the chromatographic analysis of wine volatiles were used for experimental LTPRI [$LTPRI_{(exp)}$] calculation. Whenever a compound was tentatively identified, differences between experimental and reported LTPRI were not higher than 20. Mass spectrometric information of each chromatographic peak was compared to NIST mass spectra library, considering a minimum similarity value of 80%. This spectral similarity was the same employed for mass spectra obtained by 1D-GC/MS. The minimum value for signal to noise (S/N) ratio that was necessary to consider a chromatographic peak as detected in 1D-GC was three (area% less than 0.01%). In the case of GC×GC, only chromatographic peaks with S/N higher than 150 (area% less than 0.001%) were considered for data treatment, as spectral similarity of peaks below this S/N value were lower than the criteria adopted in the present work. The organized 2D chromatographic distribution of compounds with similar physicochemical characteristics was also an aid for the compound identification process. Semi-quantitative analyses of volatile compounds were performed and the percentages of chromatographic peak areas are reported in Table 2 (also in Table S1, in the Supplementary Information (SI) section). Chromatographic peaks derived from fiber/column coating bleeding and also spurious peaks were excluded from data treatment and, consequently from total area percentage.

Statistical analysis

The chromatographic areas of the analytes were normalized by the chromatographic area of the internal standard. Calculation of Fisher ratios was employed to determine the features that would better describe the data in terms of discriminative power between predefined classes and also to reduce the dimension of the original variables before multivariate analysis. A Fisher ratio is the class-to-class variation of the detector signal divided by the sum of the within-class variations of the detector signal.[35] This approach aims to simplify data treatment, avoiding a previous manual analysis of the data before statistical

treatment. Compounds with Fisher ratios higher than 3009 and 13228 for one-dimensional and two-dimensional data, respectively, were used in the second stage of the statistical analysis (PCA) as these components showed signal-to-noise ratio (S/N) value at least two times higher among the classes of samples. S/N ratio was calculated using ChromaTOF software. Sorbate derivatives (sorbic acid, ethyl and butyl sorbate) were not included in multivariate analysis, since they do not originate from Moscato grapes or fermentation. A more comprehensive discussion about this subject is addressed in Results and Discussion session.

The statistical analyses were conducted using Statistica for Windows program package (version 7.1, Statsoft, Tulsa, Oklahoma, USA, 2005). Principal component analysis (PCA) was the multivariate analysis used to determine which variables (volatile compounds) contribute the most to the differences observed among wines. Excel (2010 version) software was employed for Fisher ratio calculation in 1D-GC. LECO ChromaTOF version 4.22 software was used for GC×GC acquisition control, data processing and Fisher Ratio calculation. Chromatographic areas of the volatile compounds that presented the higher Fisher ratio values were processed using PCA.

Results and Discussion

Sparkling wine volatile profile

1D-GC/MS allowed the identification of 70 compounds in the 21 Brazilian Moscatel sparkling wines: 21 positively identified and 49 tentatively identified using LTPRI and mass spectra comparison. The predominant classes of compounds were esters (27), followed by terpenes (18), alcohols (11), acids (7), norisoprenoids (2), aldehydes (2), phenol (2) and pyran (1). The numbers between parentheses refer to all volatile components tentatively or positively identified in the headspace of 21 wine samples. Wine composition is expressed as chromatographic area percentage of the following classes of components: esters (57.96%), acids (20.13%), alcohols (10.69%), terpenes (11.56%), and others [lower amount of other compounds of different classes, such as norisoprenoids (0.20%), aldehydes (0.05%), phenols (0.14%) and pyran (0.07%)], as shown in Figure 1. The numbers given inside parentheses refer to the average of area percentage found in the 23 samples of Moscatel sparkling wines evaluated in this study (including Italian wines).

1D-GC/MS chromatographic profiles of the 21 Brazilian sparkling wines have shown similarity among them and volatile compounds of the two Italian wines resemble the profile of Brazilian sparkling wines, as well. Even chromatographic area percentages were found to be similar for several compounds, especially for the major ones. All these facts may be verified in Figure 1 and Table S1. This rough homogeneity of the volatile composition of these Moscatel sparkling wines might point to a volatile signature that may be employed for the quality control of Moscatel wines.

Some alcohols, esters, acids and terpenes were found in all sparkling wine samples as major compounds (average chromatographic area percentage: 3.2% alcohols, 1.9% for esters, 2.2% acids and 0.9% for terpenes: 3-methyl-1-butanol (No. 11), ethyl hexanoate (No. 42), hexanoic acid (No. 3), linalool (No. 96), hotrienol (No. 97), 2-phenyl

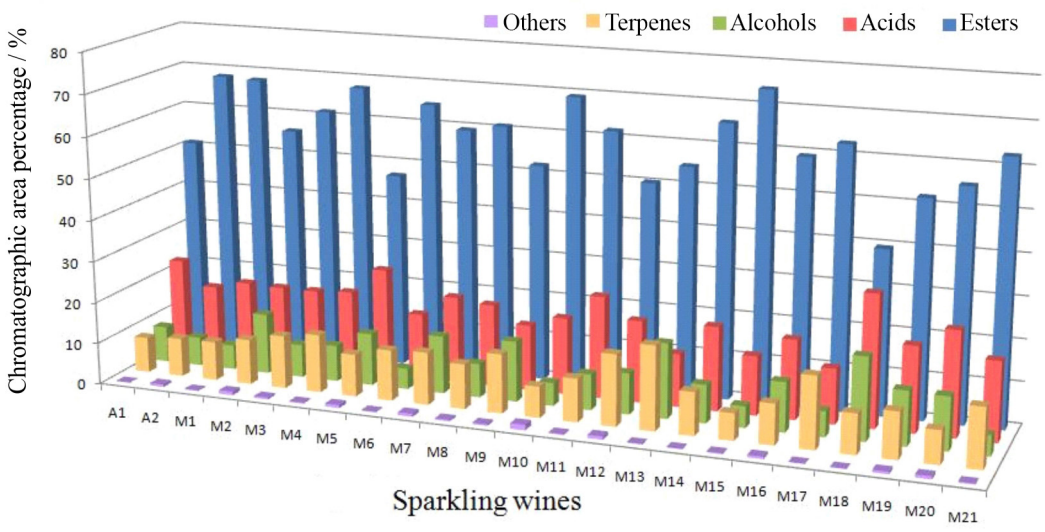

Figure 1. Semi-quantitative analysis of volatile Moscatel sparkling wines according to compound groups (esters, acids, alcohols, terpenes and others), using GC/MS. A_1 and A_2 are Italian (Asti) sparkling wines and sparkling wines designated by M_x are Brazilian wines, where x varies from 1 to 21. Experimental conditions of chromatographic analyses are reported in Chromatographic analyses section.

ethyl alcohol (No. 26), nerol oxide (No. 108), diethyl succinate (No. 58), α-terpineol (No. 120), ethyl octanoate (No. 61), octanoic acid (No. 7), decanoic acid (No. 9), ethyl decanoate (No. 74). Their chromatographic peaks may be seen in Figure 2. The numbers between brackets correspond to those used in the Table S1. Discussion about the possible contribution of these compounds to wine quality is presented later, along with GC×GC results.

In a second step of this work, the potential of GC×GC was evaluated in order to elucidate the volatile profile of Moscatel sparkling wines in a broader perspective. Even though this work does not intend to compare both techniques (1D-GC/MS and GC×GC/TOFMS), it is worthy to present some of the differences and similarities found with these two analytical tools, as qMS is one of the most spread GC/MS equipments in laboratories all over the world, while TOFMS is well known as the preferred mass spectrometric detector for GC×GC.[36] Differences related to hardware of 1D-GC and GC×GC refer to different mass spectrometric detectors, slightly different chromatographic conditions, etc.

The use of GC×GC resulted in 173 tentatively identified compounds (among them, 21 positively identified), a number that is two and half times higher than the one obtained by 1D-GC/MS (70). Major classes of compounds verified by GC×GC were the same found in 1D-GC and their mean chromatographic area percentage for Moscatel sparkling wines were: esters (25.03%), acids (23.32%), alcohols (19.31%), terpenes (10.13%). The percentage of chromatographic area of compounds of these classes represents almost 80% of total chromatographic area (peaks with S/N > 150). Sparkling wines also showed other minor classes of volatile compounds with mean chromatographic area percentage as follow: aldehydes (0.06%), lactones (0.02%), ketones (0.07%), norisoprenoids (0.06%), phenols (0.02%), pyrans (0.12%) and sulfurs compounds (0.02%). Table 2 lists the compounds that were tentatively identified using GC×GC/TOFMS. All components detected

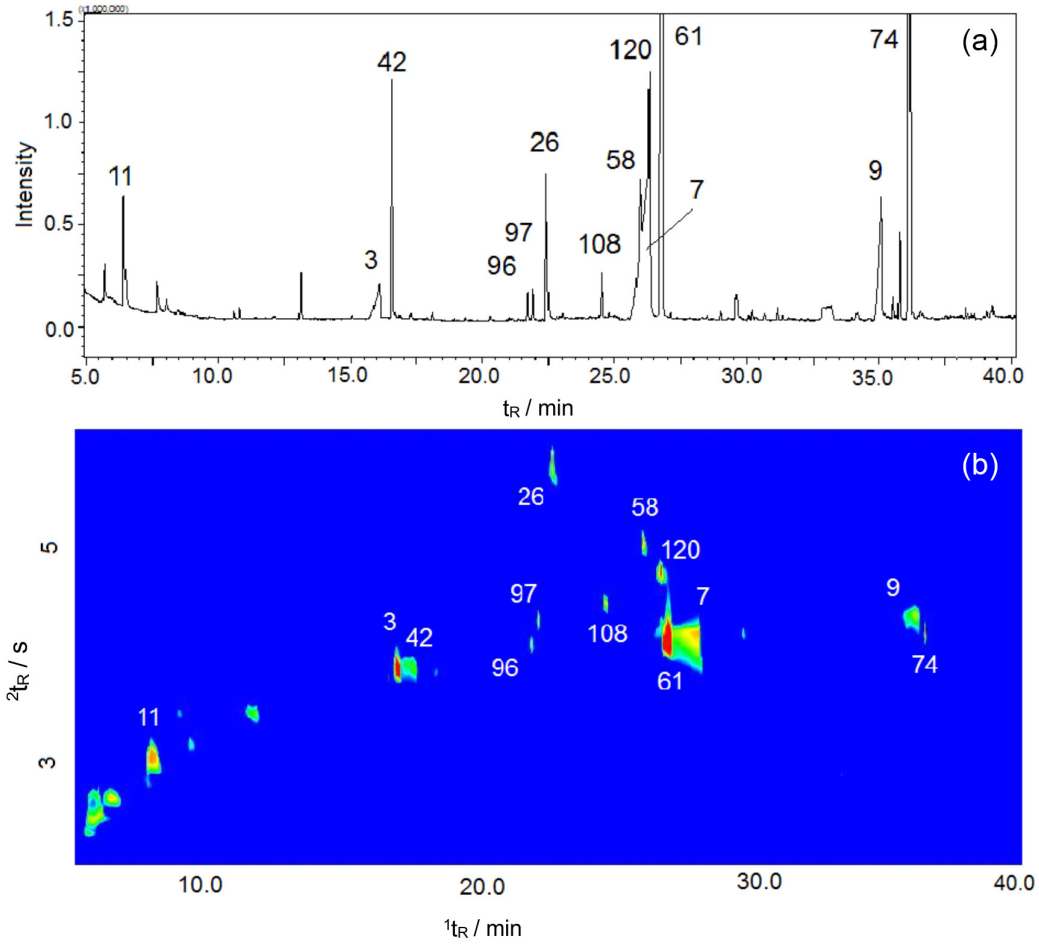

Figure 2. Major compounds of sparkling wines extracted by HS-SPME from 23 Moscatel sparkling wines: 3-methyl-1-butanol (No. 11), hexanoic acid (No. 3), ethyl hexanoate (No. 42), linalool (No. 96), hotrienol (No. 97), 2-phenyl ethyl alcohol (No. 26), nerol oxide (No. 108), diethyl succinate (No. 58), α-terpineol (No. 120), ethyl octanoate (No. 61), octanoic acid (No. 7), decanoic acid (No. 9), ethyl decanoate (No. 74) in a (a) chromatogram obtained by GC/MS; and in (b) color plot obtained by GC×GC/TOFMS. The numbers between brackets correspond to those used in the Table 2.

Table 2. Volatile compounds tentatively identified in the headspace of 23 Moscatel sparkling wines using HS-SPME-1D-GC/MS and HS-SPME-GC×GC/TOFMS (chromatographic conditions are described in the chromatographic analyses session)

No.	Compound[a]	CAS number	^1t_R / min	^2t_R / s	Similarity	Area[b] / %		LTPRI DB-5		LTPRI DB-WAX	
						1D-GC	GC×GC	LTPRI (exp.)	LTPRI (lit.)	LTPRI (exp.)	LTPRI (lit.)
	Acid										
1	butanoic acid	107-92-6	8.517	2.86	916	[c]	0.48	795	789[32]	–	–
2	3-methylbutanoic acid [isovaleric acid]	503-74-2	10.033	2.99	901	[c]	0.15	845	848[32]	–	–
3	hexanoic acid[a]	142-62-1	16.100	3.86	912	2.01	5.20	1007	1013[37]	1860	1861[38]
4	heptanoic acid	616-62-6	18.200	3.11	882	[c]	0.14	1055	1058[39]	–	–
5	2-ethyl-hexanoic acid	149-57-5	21.700	3.84	920	0.05	0.25	1132	1122[31]	1962	1950[40]
6	2,4-hexadienoic acid [sorbic acid]	**110-44-1**	**23.283**	**4.76**	**954**	3.77	**5.10**	**1046**	**1045**[41]	–	–
7	octanoic acid[a]	**124-07-2**	**25.550**	**4.21**	**890**	**10.46**	**9.08**	**1199**	**1192**[42]	**2076**	**2076**[33]
8	nonanoic acid[a]	112-05-0	28.467	4.10	894	0.10	0.03	1281	1270[31]	–	–
9	decanoic acid	**334-48-5**	**33.250**	**4.42**	**930**	**6.60**	**7.96**	**1391**	**1386**[43]	**2286**	**2282**[44]
10	dodecanoic acid	112-37-8	40.367	4.41	840	0.10	0.03	1569	1566[31]	–	–
	Alcohol										
11	3-methyl-1-butanol	123-51-3	7.467	2.72	902	1.62	**8.76**	750	740[31]	1212	1213[45]
12	2-methyl-1-butanol	137-32-6	7.583	2.78	830	0.17	0.61	764	748[46]	–	–
13	1-pentanol	2919-23-5	8.283	2.69	789	[c]	0.01	787	771[31]	–	–
14	2,3-butanediol	513-85-9	8.517	3.26	938	0.45	3.91	795	786[32]	1548	1542[47]
15	1-pentanol, 4-methyl-	626-89-1	9.917	2.99	708	[c]	0.01	840	833[43]	–	–
16	*Z*-3-hexenol	928-96-1	10.500	3.33	947	0.28	0.13	859	849[31]	–	–
17	1-hexanol[a]	111-27-3	10.850	3.28	884	0.14	0.68	872	870[31]	1358	1358[48]
18	2-heptanol	6033-23-4	11.900	3.22	842	0.05	0.04	905	901[31]	–	–
19	1-heptanol	111-70-6	14.700	3.62	855	0.04	0.02	973	966[31]	–	–
20	1-octen-3-ol	3391-86-4	14.933	3.64	905	[c]	0.05	979	979[31]	–	–
21	2-(2-ethoxyethoxy) etanol [carbitol]	111-90-0	16.333	4.72	753	[c]	0.01	1012	1007[49]	–	–
22	2-ethyl-1-hexanol	104-76-7	17.150	3.75	944	0.13	1.07	1031	1028[50]	1496	1492[51]
23	benzyl alcohol	100-51-6	17.500	5.69	891	[c]	0.02	1039	1031[31]	–	–
24	1-octanol	111-87-5	19.017	3.91	924	0.10	0.09	1073	1068[31]	1564	1564[52]
25	2-nonanol	628-99-9	20.417	3.79	895	[c]	0.17	1104	1098[31]	–	–
26	2-phenylethyl alcohol[a]	60-12-8	21.117	6.06	954	3.33	3.63	1117	1107[31]	1919	1922[52]
27	1-nonanol	143-08-8	23.683	4.05	925	[c]	0.01	1174	1169[31]	–	–
28	1-decanol	112-30-1	28.233	4.14	911	[c]	0.02	1276	1269[31]	–	–
29	2-undecanol	1653-30-1	29.400	4.01	862	[c]	0.02	1302	1301[31]	–	–
30	1-dodecanol[a]	112-53-8	36.750	4.30	914	0.09	0.03	1476	1473[53]	1974	1969[51]
31	1-tridecanol	112-70-9	40.717	4.35	912	[c]	0.02	1578	1569[54]	–	–
	Ester										
32	ethyl 2-methylpropanoate [ethyl isobutanoate] [a]	97-62-1	8.050	2.58	868	[c]	0.34	780	765[55]	–	–
33	2-methylpropyl acetate [isobutyl acetate]	110-19-0	8.283	2.67	885	[c]	0.05	787	788[56]	–	–
34	ethyl butanoate[a]	105-54-4	8.867	2.88	950	0.12	1.70	807	804[31]	1055	1047[57]
35	ethyl-2-hydroxypropanoate [ethyl lactate][a]	97-64-3	9.217	3.16	944	0.05	3.52	818	813[58]	1350	1353[33]
36	ethyl 2-butenoate	10544-63-5	10.033	3.36	907	[c]	0.01	845	834[59]	–	–
37	ethyl 3-methylbutanoate [ethyl isovalerate][a]	108-64-5	10.267	3.02	874	[c]	0.18	853	858[31]	–	–
38	3-methylbutyl acetate [isoamyl acetate][a]	123-92-2	11.317	3.14	788	0.11	0.03	887	880[60]	1124	1125[33]
39	propyl butanoate	105-66-8	11.783	3.29	815	[c]	< 0.01	902	899[31]	–	–
40	ethyl pentanoate	539-82-2	11.900	3.32	880	[c]	0.01	905	901[31]	–	–
41	methyl hexanoate	106-70-7	12.717	3.51	910	[c]	0.04	925	927[31]	–	–
42	ethyl hexanoate[a]	123-66-0	15.750	3.84	751	2.58	4.37	999	998[31]	1236	1236[61]

Table 2. Volatile compounds tentatively identified in the headspace of 23 Moscatel sparkling wines using HS-SPME-1D-GC/MS and HS-SPME-GC×GC/TOFMS (chromatographic conditions are described in the chromatographic analyses session) (cont.)

No.	Compound[a]	CAS number	^1t_R / min	^2t_R / s	Similarity	Area[b] / %		LTPRI DB-5		LTPRI DB-WAX	
						1D-GC	GC×GC	LTPRI (exp.)	LTPRI (lit.)	LTPRI (exp.)	LTPRI (lit.)
43	*Z*-3-hexenyl acetate	3681-71-8	16.100	3.97	808	0.03	< 0.01	1007	1002[31]	–	–
44	hexyl acetate[a]	142-92-7	16.333	3.78	863	0.07	0.22	1012	1009[31]	1276	1275[33]
45	ethyl 2-hexenoate	1552-67-6	17.733	4.24	933	[c]	0.02	1044	1046[62]	–	–
46	ethyl 2-furoate	614-99-3	18.200	5.54	960	0.04	0.46	1055	1047[37]	–	–
47	ethyl 2-hydroxy-4-methyl-pentanoate	10348-47-7	18.433	4.08	863	[c]	0.03	1060	1054[63]	–	–
48	diethyl propanedioate	105-53-3	19.017	5.12	885	[c]	< 0.01	1073	1068[64]	–	–
49	methyl benzoate	93-58-3	20.067	5.69	808	[c]	< 0.01	1097	1090[31]	–	–
50	propyl hexanoate	626-77-7	20.067	3.91	926	[c]	0.01	1097	1091[59]	–	–
51	ethyl 2,4-hexadienoate [ethyl sorbate][a]	**2396-84-1**	**20.300**	**4.76**	**931**	**10.20**	**0.62**	**1102**	**1089**[59]	–	–
52	ethyl heptanoate	106-30-9	20.183	3.92	906	[c]	0.03	1099	1098[31]	–	–
53	ethylmethyl butanedioate [ethylmethyl succinate]	627-73-6	20.767	5.32	829	[c]	< 0.01	1112	1116[65]	–	–
54	heptyl acetate	112-06-1	20.883	3.93	805	[c]	< 0.01	1114	1114[31]	–	–
55	methyl octanoate	111-11-5	21.467	4.00	939	0.05	0.18	1127	1127[31]	1391	1391[66]
56	2-methylpropyl hexanoate	16397-75-4	22.633	3.86	784	[c]	< 0.01	1152	1149[67]	–	–
57	ethyl benzoate	93-89-0	23.567	5.64	933	[c]	0.02	1172	1173[31]	–	–
58	diethyl butanedioate [diethyl succinate][a]	**123-25-1**	**24.033**	**5.31**	**901**	**5.06**	**2.35**	**1182**	**1176**[31]	**1685**	**1687**[38]
59	*Z*-diethyl-2-butenedioate	623-91-6	24.267	4.76	721	[c]	< 0.01	1187	1177[68]	–	–
60	methyl 2-hydroxy-benzoate	119-36-8	24.733	5.91	923	[c]	0.02	1197	1195[69]	–	–
61	ethyl octanoate[a]	**106-32-1**	**24.733**	**4.10**	**912**	**31.36**	**7.30**	**1197**	**1197**[31]	**1439**	**1436**[33]
62	octyl acetate	103-09-3	25.316	3.01	850	0.14	0.05	1210	1211[70]	–	–
63	ethyl bezeneacetate[a]	101-97-3	26.950	6.05	952	0.16	0.85	1247	1246[31]	1791	1796[2]
64	3-methylbutyl hexanoate [isoamyl hexanoate]	2198-61-0	27.183	4.00	926	0.05	0.05	1252	1254[71]	–	–
65	2-phenylethyl acetate	103-45-7	27.417	6.05	934	0.57	1.32	1257	1254[31]	1822	1815[33]
66	diethyl hydroxybutanedioate	626-11-9	28.000	5.77	881	0.13	0.33	1270	1260[63]	–	–
67	diethyl pentadioate	818-38-2	28.583	5.29	918	[c]	0.02	1283	1281[37]	–	–
68	propyl octanoate	624-13-5	29.050	4.09	786	0.09	< 0.01	1292	1282[72]	–	–
69	ethyl nonanoate	123-29-5	29.167	4.11	909	0.10	0.02	1297	1294[73]	1539	1535[74]
70	methyl decanoate	110-42-9	30.450	4.18	874	0.10	0.02	1326	1325[31]	–	–
71	ethyl benzenepropanoate	2021-28-5	31.500	5.99	926	[c]	0.01	1351	1355[75]	–	–
72	ethyl-4-decenoate	76649-16-6	32.083	4.86	772	[c]	0.11	1382	1388[76]	1685	1687[77]
73	ethyl 9-decenoate	67233-91-4	33.133	4.40	833	0.96	0.14	1388	1389[73]	1695	1689[78]
74	ethyl decanoate[a]	110-38-3	33.483	4.23	**890**	**25.50**	**0.40**	**1397**	**1395**[31]	**1643**	**1645**[66]
75	ester	–	34.883	5.17	776	[c]	0.06	1431	nf	–	–
76	2-pheny ethyl butanoate	103-52-6	35.350	5.96	915	0.05	0.02	1442	1439[31]	–	–
77	3-methylbutyl octanoate [isoamyl octanoate]	2035-99-6	35.583	4.13	932	0.31	0.04	1448	1450[71]	1661	1655[77]
78	ethyl 3-phenylprop-2-enoate [ethyl cinnamate]	103-36-6	36.400	6.58	900	[c]	0.01	1468	1460[79]	–	–
79	propyl decanoate	30673-60-0	37.530	3.01	740	0.05	< 0.01	1493	1494[80]	–	–
80	methyl dodecanoate	111-82-0	38.617	4.31	765	[c]	< 0.01	1523	1524[31]	–	–
81	ethyl dodecanoate[a]	106-33-2	41.300	4.28	896	0.43	0.03	1593	1594[31]	1849	1850[52]
82	3-methylbutyl decanoate [isoamyl decanoate]	2306-91-4	43.167	4.26	827	0.01	< 0.01	1644	1644[73]	–	–
83	methyl tetradecanoate	124-10-7	46.083	4.43	879	[c]	0.01	1726	1722[31]	–	–
84	ethyl tetradecanoate	124-06-1	48.417	4.40	874	[c]	0.01	1792	1795[31]	–	–

Table 2. Volatile compounds tentatively identified in the headspace of 23 Moscatel sparkling wines using HS-SPME-1D-GC/MS and HS-SPME-GC×GC/TOFMS (chromatographic conditions are described in the chromatographic analyses session) (cont.)

No.	Compound[a]	CAS number	^1t_R / min	^2t_R / s	Similarity	Area[b] / %		LTPRI DB-5		LTPRI DB-WAX	
						1D-GC	GC×GC	LTPRI (exp.)	LTPRI (lit.)	LTPRI (exp.)	LTPRI (lit.)
85	ethyl hexadecanoate	628-97-7	54.950	4.54	856	[c]	0.02	1995	1992[31]	–	–
	Terpene										
86	2-methyl-6-methylene-1,7-octadiene [α-myrcene]	123-35-3	15.400	3.36	891	[c]	0.01	991	990[31]	–	–
87	1-isopropyl-4-methyl-1,3-cyclohexadiene [α-terpinene]	99-86-5	16.567	3.61	766	[c]	0.01	1018	1018[31]	–	–
88	1-methyl-4-(1-methylethenyl)-cyclohexene [limonene][a]	5989-54-8	17.033	3.70	947	[c]	0.25	1028	1029[31]	–	–
89	1,3,3-trimethyl-2-oxabicyclo[2.2.2] octane [eucalyptol][a]	470-82-6	17.267	3.91	917	[c]	0.03	1033	1030[81]	–	–
90	*Z*-3,7-dimethyl-1,3,6-octatriene [*Z*-β-ocimene]	926-98-7	17.383	3.65	756	[c]	0.01	1036	1037[31]	–	–
91	*E*-3,7-dimethyl-1,3,6-octatriene [*E*-β-ocimene]	3338-55-4	17.967	3.65	909	[c]	0.02	1049	1050[31]	–	–
92	1-isopropyl-4-methyl-1,4-cyclohexadiene [γ-terpinene]	99-85-4	18.433	3.88	820	[c]	0.01	1060	1059[31]	–	–
93	Z-5-ethenyl-5-methyloxolan-2-yl] propan-2-ol [*Z*-linalool oxide] (furanoid)	34995-77-2	19.133	4.11	900	0.13	0.46	1076	1072[31]	1446	1453[82]
94	1-methyl-4-(1-methylethylidene)-1-cyclohexene [terpinolene][a]	586-62-9	19.717	4.04	882	0.10	0.03	1089	1088[31]	–	–
95	2-(5-ethenyl-5-methyloxolan-2-yl) propan-2-ol [*E*-linalool oxide] (furanoid)	5989-33-3	19.833	4.25	911	0.10	0.22	1091	1086[31]	–	–
96	2,6-dimethyl-2,7-octadiene-6-ol [linalool][a]	78-70-6	20.300	4.08	917	0.47	0.66	1102	1098[31]	1556	1555[83]
97	(*5E*)-3,7-dimethyl-1,5,7-octatrien-3-ol [hotrienol]	29957-43-5	20.533	4.38	893	0.58	1.27	1107	1104[84]	1619	1620[33]
98	tetrahydro-4-methyl-2-(2-methylpropenyl)-2H-pyran [*Z*-rose oxide]	876-18-6	20.767	4.16	864	[c]	0.11	1112	1108[31]	–	–
99	1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol [fenchol]	2-9-2217	21.000	4.48	859	[c]	0.01	1117	1116[31]	–	–
100	2-methyl-6-methylideneoct-7-en-2-ol[myrcenol]	543-39-5	21.233	4.31	926	0.10	0.06	1122	1122[31]	–	–
101	4-methyl-2-(2-methylprop-1-enyl) oxane [*E*-rose oxide]	16409-43-1	21.700	4.31	801	[c]	0.01	1132	1125[31]	–	–
102	4-isopropyl-1-methyl-3-cyclohexen-1-ol [1-terpinenol]	586-82-3	21.933	4.48	817	[c]	0.01	1137	1147[85]	–	–
103	*Z*-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-ol [*Z*-verbenol]	18881-04-4	21.150	3.01	750	0.04	< 0.01	1141	1131[31]	–	–
104	3,7-dimethyloct-6-en-1-al [citronellal]	106-23-0	22.283	4.76	795	[c]	0.01	1144	1153[31]	–	–
105	1-methyl-4-prop-1-en-2-ylcyclohexan-1-ol [*Z*-βterpineol]	138-87-4	22.400	4.63	833	[c]	< 0.01	1147	1144[31]	–	–
106	1,7,7-trimethylbicyclo[2.2.1]heptan-2-one [camphor]	464-48-2	22.400	5.42	916	[c]	0.01	1147	1146[31]	–	–
107	(*5Z*)-2,6-dimethylocta-5,7-dien-2-ol [*Z*-ocimenol]	5986-38-9	22.750	4.43	871	0.05	0.08	1154	1155[86]	–	–
108	4-methyl-2-(2-methylprop-1-enyl)-3,6-dihydro-2H-pyran [nerol oxide]	1786-08-9	22.867	4.55	912	0.64	1.38	1157	1158[31]	1472	1464[87]
109	exo-1,7,7-trimethylbicyclo(2.2.1) heptan-2-ol [isoborneol]	124-76-5	22.983	4.88	823	[c]	< 0.01	1159	1160[31]	–	–
110	(*Z*)-2-methyl-5-(prop-1-en-2-yl) cyclohexanone [Z-dihydrocarvone]	5948-04-9	23.100	5.20	765	[c]	< 0.01	1167	1186[88]	–	–

Table 2. Volatile compounds tentatively identified in the headspace of 23 Moscatel sparkling wines using HS-SPME-1D-GC/MS and HS-SPME-GC×GC/TOFMS (chromatographic conditions are described in the chromatographic analyses session) (cont.)

No.	Compound[a]	CAS number	^1t_R / min	^2t_R / s	Similarity	Area[b] / %		LTPRI DB-5		LTPRI DB-WAX	
						1D-GC	GC×GC	LTPRI (exp.)	LTPRI (lit.)	LTPRI (exp.)	LTPRI (lit.)
111	1-methyl-4-prop-1-en-2-ylcyclohexan-1-ol [β-terpineol]	138-87-4	23.333	4.45	888	[c]	0.12	1167	1163[31]	–	–
112	*p*-mentha-1,5-dien-8-ol	1686-20-0	23.450	5.07	735	0.05	0.003	1169	1165[70]	–	–
113	endo-1,7,7-trimethylbicyclo[2.2.1] heptan-2-ol [borneol]	124-76-5	23.450	4.91	783	[c]	0.01	1169	1169[31]	–	–
114	2,2,6-trimethyl-6-vinyltetrahydro-2H-pyran-3-ol [epoxylinalool]	14049-11-7	23.567	4.94	888	0.03	0.20	1172	1165[31]	–	–
115	5-Methyl-2-(1-methylethyl) cyclohexanol [menthol][a]	89-78-1	23.567	3.61	793	[c]	0.08	1172	1171[31]	–	–
116	1-methyl-4-(1-methylethyl)-cyclohexanol	21129-27-1	23.800	4.44	863	[c]	0.01	1177	1188[89]	–	–
117	2-isopropyl-5-methylcyclohexanol [isomenthol]	23283-97-8	23.800	4.89	840	[c]	0.03	1177	1182[31]	–	–
118	1-methyl-4-isopropyl-1-cyclohexen-4-ol [4-terpineol]	562-74-3	23.917	4.75	776	[c]	0.10	1179	1177[31]	–	–
119	2-(4-methylphenyl)-2-propanol [*p*-cymen-8-ol]	1197-01-9	24.383	5.51	895	[c]	< 0.01	1189	1182[31]	–	–
120	2-(4-methyl-3-cyclohexen-1-yl)-2-propanol [α-terpineol][a]	**10482-56-1**	**24.617**	**4.97**	**836**	**7.16**	**4.45**	**1191**	**1188**[31]	**1700**	**1700**[90]
121	2,6,6-Trimethyl-1-cyclohexen-1-carboxaldehyde [β-cyclocitral]	432-25-7	25.900	5.45	840	[c]	0.01	1223	1217[31]	–	–
122	(2*Z*)-3,7-dimethyl-2,6-octadien-1-ol [nerol][a]	106-25-2	26.250	4.63	901	0.06	0.01	1231	1229[31]	1773	1771[91]
123	3,7-dimethyl-6-octen-1-ol [citronellol]	1117-61-9	26.250	4.37	931	0.06	0.01	1231	1225[31]	1807	1804[82]
124	5-isopropenyl-2-methyl-2-cyclohexen-1-one [carvone]	6485-40-1	26.950	5.80	846	[c]	< 0.01	1247	1243[31]	–	–
125	2,6-dimethyl-trans-2,6-octadien-8-ol [geraniol]	106-25-2	27.417	4.71	905	[c]	0.15	1257	1252[31]	–	–
126	3,7-dimethyl-1,6-octadien-3-yl acetate [linalool acetate]	115-95-7	27.883	4.02	789	0.06	0.05	1268	1257[31]	–	–
127	3,7-dimethyl-1,2,6-octadienal [citral]	5392-40-5	28.117	5.18	759	[c]	< 0.01	1273	1267[31]	–	–
128	2,6-dimethyl-1,7-octadiene-3,6-diol	51276-33-6	28.350	5.34	760	[c]	< 0.01	1278	1274[37]	–	–
129	1-ethoxy-3,7-dimethyl-2,6-octadiene [geranyl ethyl ether]	40267-72-9	28.817	4.13	808	0.14	0.20	1289	1297[92]	–	–
130	3,7-dimethyl-2,6-octadienoic acid [geranic acid]	459-80-3	32.200	4.79	746	[c]	0.02	1367	1355[74]	–	–
131	6,10-dimethyl-5,9-undecadien-2-one [geranyl acetone]	3796-70-1	35.817	4.96	881	0.08	0.01	1453	1453[31]	–	–
132	*Z*-3,7,11-Trimethy-1,6,10-dodecatrien-3-o[*Z*-nerolidol]	7212-44-4	39.083	4.59	863	[c]	< 0.01	1535	1531[31]	–	–
133	*E*-3,7,11-trimethyldodeca-1,6,10-trien-3-ol [*E*-nerolidol]	142-50-7	40.250	4.67	907	[c]	0.01	1566	1561[31]	–	–
134	2-[*E*-4,8-dimethyl-2,3,4,5,6,7-hexahydro-1H-naphthalen-2-yl] propan-2-ol [eudesmol]	1209-71-8	42.933	5.63	825	[c]	< 0.01	1638	1632[31]	–	–
135	methyl 2-(3-oxo-2-pentylcyclopentyl) acetate [methyl dihydrojasmonate]	24851-98-7	43.633	6.23	736	0.05	< 0.01	1660	1656[93]	–	–
	Aldehyde										
136	furfural	98-01-1	9.917	4.24	962	0.10	0.22	841	836[31]	–	–
137	benzaldehyde	100-52-7	14.233	5.38	921	[c]	0.01	962	960[31]	–	–
138	benzeneacetaldeyde	122-78-1	17.850	6.00	917	[c]	0.02	1047	1045[94]	–	–

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No.	Compound[a]	CAS number	^1t_R / min	^2t_R / s	Similarity	Area[b] / %		LTPRI DB-5		LTPRI DB-WAX	
						1D-GC	GC×GC	LTPRI (exp.)	LTPRI (lit.)	LTPRI (exp.)	LTPRI (lit.)
139	(*Z*,*Z*)-3,6-nonadienal	21944-83-2	20.183	4.41	768	[c]	0.08	1099	1100[31]	–	–
140	decanal	112-31-2	25.200	4.24	844	0.01	0.01	1207	1201[31]	–	–
141	*p*-menth-1-en-9-al	29548-14-9	25.783	5.31	887	[c]	0.04	1220	1217[94]	–	–
142	undecanal	112-44-7	29.633	4.33	927	[c]	< 0.01	1307	1306[31]	–	–
143	dodecanal	112-54-9	33.950	4.39	898	[c]	< 0.01	1408	1398[46]	–	–
	Lactone										
144	γ-butyrolactone	96-48-0	12.717	6.57	926	[c]	0.02	925	918[32]	–	–
145	γ-caprolactone	695-06-7	18.433	6.74	797	[c]	< 0.01	1060	1064[46]	–	–
146	γ-octalactone	104-50-7	27.650	6.75	908	[c]	0.02	1262	1262[95]	–	–
147	γ-nonalactone	104-61-0	32.200	6.65	894	[c]	0.04	1367	1361[31]	–	–
148	γ-decalactone	706-14-9	36.517	6.59	889	[c]	0.02	1471	1476[50]	–	–
149	δ-decalactone	705-86-2	37.800	0.08	760	[c]	< 0.01	1502	1493[50]	–	–
	Ketone										
150	2-heptanone	110-43-0	11.550	3.48	906	[c]	0.05	895	892[31]	–	–
151	6-methyl-5-hepten-2-one	110-93-0	15.283	4.16	878	[c]	0.01	988	985[31]	–	–
152	2,2,6-trimethyl-cyclohexanone	2408-37-9	17.383	4.41	800	[c]	< 0.01	1036	1036[50]	–	–
153	Acetophenone	98-86-2	18.783	6.08	904	[c]	0.01	1068	1065[31]	–	–
154	2-nonanone	821-55-6	19.950	4.12	916	[c]	0.14	1094	1090[31]	–	–
155	2-undecanone	112-12-9	29.050	4.33	816	[c]	0.01	1294	1294[31]	–	–
156	dihydro-5-pentyl-2(3H)-furanone	104-61-0	32.200	6.65	888	[c]	0.13	1367	1365[31]	–	–
157	5-hexyldihydro-2(3H)-furanone	706-14-9	36.517	6.58	918	[c]	0.02	1471	1476[50]	–	–
	Norisoprenoid										
158	2,10,10-trimethyl-6-methylidene-1-oxaspiro[4.5]dec-7-ene [vitispirane]	65416-59-3	28.200	3.01	750	0.12	< 0.01	1280	1279[31]	–	–
159	*E*-1-(2,6,6-Trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one [β-damascenone][a]	23726-93-4	33.017	5.58	885	0.09	0.15	1386	1384[31]	–	–
	Phenol										
160	Phenol	108-95-2	15.283	4.78	879	[c]	0.01	988	998[53]	–	–
161	4-ethyl-phenol	123-07-9	23.683	5.46	910	[c]	0.02	1174	1168[53]	–	–
162	4-ethyl-2-methoxy-phenol	2785-89-9	28.467	5.94	880	[c]	0.01	1281	1283[96]	–	–
163	2,3,5,6-tetramethyl phenol	527-35-5	29.700	3.10	740	0.06	< 0.01	1307	1319[97]	–	–
164	2-methoxy-4-vinylphenol	7786-61-0	29.983	6.53	856	[c]	0.02	1315	1312[98]	–	–
165	2,4-bis(1,1-dimethylethyl) phenol	96-76-4	38.267	5.22	862	0.20	0.02	1514	1519[43]	2322	Nf
	Pyran										
166	2-ethoxytetrahydro-2H-pyran	4819-83-4	12.367	3.59	753	[c]	< 0.01	916	920[99]	–	–
167	2-ethenyltetrahydro-2,6,6-trimethyl-2H-pyran	7392-19-0	14.583	3.37	871	0.05	0.31	971	972[73]	1106	Nf
168	tetrahydro-4-methyl-2-(2-methyl-1-propenyl)-2H-pyran	16409-43-1	20.883	4.13	893	[c]	0.02	1114	1112[74]	–	–
	Sulfur compound										
169	3-methylthio-1-propanol	505-10-2	15.167	5.11	866	[c]	0.01	985	982[79]	–	–
170	dihydro-2-methyl-3(2H)-thiophenone	13679-85-1	15.283	5.97	896	[c]	0.03	988	998[100]	–	–
171	5-ethenyl-4-methyl-thiazole	1759-28-0	17.150	5.34	767	[c]	< 0.01	1031	1022[101]	–	–
172	ethyl 3-(methylthio)propanoate	13327-56-5	20.300	5.32	887	[c]	0.01	1102	1098[71]	–	–
173	Benzothiazole	95-16-9	26.250	0.79	866	[c]	< 0.01	1231	1226[53]	–	–
174	Ni	–	7.233	2.47	802	[c]	0.94	753	–	–	–
175	Ni	–	15.517	3.66	805	[c]	0.33	993	–	–	–
176	Ni	–	21.000	6.31	733	[c]	1.58	1117	–	–	–
177	Ni	–	24.150	4.19	872	[c]	0.72	1184	–	–	–

Table 2. Volatile compounds tentatively identified in the headspace of 23 Moscatel sparkling wines using HS-SPME-1D-GC/MS and HS-SPME-GC×GC/TOFMS. (Chromatographic conditions are described in the Chromatographic analyses session) (cont.)

No.	Compound[a]	CAS number	^1t_R / min	^2t_R / s	Similarity	Area[b] / %		LTPRI DB-5		LTPRI DB-WAX	
						1D-GC	GC×GC	LTPRI (exp.)	LTPRI (lit.)	LTPRI (exp.)	LTPRI (lit.)
178	Ni	–	27.417	4.20	742	[c]	1.09	1257	–	–	–
179	Ni	–	36.602	–	–	0.17	–	1409	–	–	–
180	Ni	–	39.291	–	–	0.29	–	1475	–	–	–
181	Ni	–	41.475	–	–	0.12	–	1536	–	–	–
Σ	Tentatively identified compounds	–	–	–	–	69	173	–	–	–	–

[a]Mass spectrum and LTPRI consistent with those of an authentic standard. Compounds positively identified; [b]normalized area percentage; bold letters designate normalized area percentage above 5%; [c]compounds found only in GC×GC. LTPRI: linear-temperature-programmed retention index; $LTPRI_{(lit.)}$: values of LTPRI found in scientific literature; $LTPRI_{(exp.)}$: LTPRI experimentally obtained; Nf: LTPRI not found in the scientific literature. Mass spectrum consistent with spectra found in scientific literature and LTPRI according with literature data for a DB-5 and DB-WAX columns (differences of ± 20 units between experimental and reference values); Ni: non identified.

in both 1D-GC and GC×GC received the same numbering in Table S1 and Table 2. Among all the chemical groups found in the volatile content of Brazilian sparkling wines, esters were present in higher number (54), followed by terpenes (50), alcohols (21), acids (10), aldehydes (8), ketones (8), lactones (6), phenols (6), sulfur compounds (5), norisoprenoids (2) and pyrans (3). The numbers between parentheses refer to all volatile components tentatively or positively identified in the headspace of 23 wine samples.

The number of studies about volatile compounds of Moscatel sparkling wines is not abundant in the scientific literature. Due to this lack of information, some other research articles related to Moscatel still wines are considered in this discussion for the sake of comparison, as the grapes employed for vinification are the same. Furthermore, taking into account that data acquired in this study are semi-quantitative, a general discussion regarding the possible contribution of several important volatile compounds in the investigated wines is performed, even though a precise definition of the influence of each volatile compound to wine aroma would require quantitative and sensorial analyses.[102] Aroma descriptors found in the literature are employed for a general discussion regarding the influence of the presence of a volatile compound to the wine aroma and such an approach has already been adopted in other scientific publications.[3,15]

Esters, known to contribute to the fruity aroma, were responsible for the higher chromatographic area percentage and represented the predominant class of compounds in both GC×GC and 1D-GC. These compounds are enzymatically produced during yeast fermentation and their concentration is dependent on several factors, mainly: yeast strain, fermentation temperature, aeration degree, and sugar content.[103] Esters that showed higher chromatographic areas in the headspace of Brazilian Moscatel sparkling wines were: ethyl octanoate (No. 61 of Table 2, 7.30%), ethyl hexanoate (No. 42 of Table 2, 4.37%), diethyl succinate (No. 58 of Table 2, 2.35%) and 2-phenylethyl acetate (No. 65 of Table 2, 1.32%). Bordiga *et al.*[3] also found ethyl octanoate and ethyl hexanoate as major esters of ''Asti Spumante'' and ''Moscato d'Asti'' sparkling wines from Italy. In addition, isoamyl acetate and β-phenylethylacetate were found in significant concentrations in these Italian wines. Other minor esters were found only when GC×GC was used in the analyses of Brazilian Moscatel sparkling wines, including ethyl isobutanoate (No. 32, 0.34%), isobutyl acetate (No. 33, 0.05%), ethyl 2-butenoate (No. 36, 0.01%) and others indicated in Table 2. These minor esters were not found in Italian ''Asti Spumante'' and ''Moscato d'Asti'' sparkling wines analysed using GC×GC/TOFMS[3] and Spanish Muscat still wines evaluated using 1D-GC/MS.[27] However, these compounds were detected in Pinotage still wines from South Africa analyzed by GC×GC/TOFMS.[16] Ethyl isobutanoate and isobutyl acetate were also found in Australian Cabernet Sauvignon still wines when GC×GC/TOFMS was employed as analytical tool.[104] The same compounds were verified, using GC/MS, in Greek dry still white wines elaborated with Moschofilero, Debina and Moschato Alexandrias grapes.[73] Considering that GC×GC provided a higher number of tentatively and positively identified esters, the following discussion on volatile compounds is mainly focuses on GC×GC results.

Terpenes were the second class in terms of number of volatile compounds identified in Moscatel sparkling wines. The most abundant terpenes were: α-terpineol (No. 120 of Table 2, average normalized area percentage of 4.45%), hotrienol (No. 97 of Table 2, average normalized area percentage of 1.27%) and linalool (No. 96 of Table 2, average normalized area percentage of 0.66%). Terpenes may be found in grape skin and the pressing of the grapes is responsible for the extraction of these compounds from grapes to wine. These compounds generally remain

unchanged after the fermentation process.[105] Terpenes are known for their floral contribution to aroma and this is specially important to Moscatel sparkling wines, as they are appreciated due to their floral notes, besides fruity characteristics.[2,25-27]

Alcohols were the third class in terms of number of volatiles detected in Moscatel sparkling wines. Alcohols are produced from sugars and amino acids during the alcoholic fermentation and include representative aliphatic and aromatic components. Alcohols may impart both positive and negative effects to wine aroma.[103] One of the major alcohols present in the Moscatel sparkling wines was 2-phenylethyl alcohol (No. 26 of Table 2, average normalized area percentage of 3.63%), which usually contributes with a positive rose (floral) aroma.[105] 3-Methyl-1-butanol (No. 11 of Table 2, average normalized area percentage of 8.76%) was also found as a predominant alcohol of Moscatel sparklings and may negatively influence the aroma (notes described as solvent).[105]

Acids were the fourth most abundant chemical class in Moscatel sparkling wines and the compounds with higher chromatographic area percentages were octanoic acid (No. 7 of Table 2, average normalized area percentage of 26.59%) and decanoic acid (No. 9 of Table 2, average normalized area percentage of 7.96%). The volatile acidity of wine originates during fermentation of must and furthermore, its concentration may increase during the preparation and storage of wine because of microbiological contamination. Their contribution to aroma depends on their concentration range in wine and may be negatively characterized by notes of rancidity whenever their concentration is greater than 20 mg L^{-1}.[106]

Minor classes of Moscatel sparkling wines as sulfur compounds and lactones were only detected when GC×GC was used. Sulfur compounds in wines may be formed by degradation of sulfur containing amino acids or they may result of the degradation of sulfur pesticides employed in the protection of the grape cultivars.[103] Dihydro-2-methyl-3(2H)-thiophenone (No. 170 of Table 2, average normalized area percentage of 0.03%) was the major sulfur compound found in Moscatel sparklings and this compound may negatively contribute to aroma (odor described as "burned", "burned rubber", or "roasted coffee").[107] Another sulfur compound tentatively identified in Moscatel sparkling wines was 3-methylthio-1-propanol (No. 169 of Table 2, average normalized area percentage of 0.01%, cooked cabbage odor), which also has negative influence to aroma due to odor described as "cauliflower" or "cooked vegetables".[23]

γ-Nonalactone (No. 147 of Table 2, average normalized area percentage of 0.04%) presents an aroma described as fruity and was the main lactone tentatively identified in Moscatel sparkling wines. These compounds are cyclic esters formed by enzimatic cyclisation between carboxyl and hidroxyl groups of the corresponding γ-hidroxylcarboxylic acid during fermentation.[105] Other lactones were also tentatively identified in Moscatel sparkling wines such as γ-butyrolactone (No. 144 of Table 2, average normalized area percentage of 0.02%), γ-caprolactone (No. 145 of Table 2, average normalized area percentage < 0.01%), γ-octalactone (No. 146 of Table 2, average normalized area percentage of 0.02%), γ-decalactone (No. 148 of Table 2, average normalized area percentage of 0.02%) and δ-decalactone (No. 149 of Table 2, average normalized area percentage < 0.01%). Considering these lactones, only γ-butyrolactone and γ-decalactone may contribute negatively to aroma with odors described as smoky and chemical, respectively.[108,109]

In addition to the fact that several compounds were tentatively identified only through the lens of the superior performance of GC×GC, the 2D technique was also useful to resolve co-elutions of sparkling wine compounds due to the extra selectivity provided by the second chromatographic dimension. Polar columns are well established in the literature as the most appropriate for determining polar compounds in wine.[17] The use of a polar column instead of non-polar, as employed in our study, may be an alternative to avoid co-eluting compounds. However, even with a polar column in the first dimension (^{1}D) of GC×GC, some compounds might co-elute with others. In a previous work of our research group, the co-elution of diethyl succinate (No. 58 of Table 2) with ethyl-4-decenoate (No. 72 of Table 2) of the headspace of a Chardonnay wine was observed when a WAX column was employed in ^{1}D and a medium polar column was placed in the second dimension (^{2}D, DB-17ms).[102] Other aspect that should be taken into consideration is that polar columns are more prone to thermal and oxygen damage, resulting in a less robust performance than the one provided by non-polar columns.[110] These facts provide other reasons for the use of non-polar columns in the first chromatographic dimension.

The co-elution of ethyl sorbate (No. 51 of Table 2) and linalool (No. 96 of Table 2) in ^{1}D is shown in Figure 3. The ethyl sorbate is produced due to addition of potassium sorbate, which forms sorbic acid during fermentation, which reacts with the ethyl alcohol of the sparkling wine via an esterification reaction. Potassium sorbate is used to inhibit molds and yeasts in many foods, such as cheese, wine, yogurt and fruit drinks. This salt has been used with sweet wines (as Moscato wine and Asti Spumante) in favor of their stability. The use of sorbic acid and its more soluble salt (potassium sorbate)

is authorized in many countries, including Brazil, at a maximum concentration of 200 mg L^{-1}.[111–113] Ethyl sorbate has been found only in some samples (M7, M15 and M17, Table S1) because the addition of potassium sorbate is not performed in all wineries. Linalool was not identified using 1D-GC when ethyl sorbate was detected, as ethyl sorbate chromatographic area was higher than the area of linalool. These compounds co-eluted in ^{1}D and were separated in ^{2}D using GC×GC (Figure 3).

Detection and correct identification of linalool are important goals that have not been achieved with 1D-GC/MS using the stationary phase employed in this work due to co-elution, as it is an oxygenated monoterpene that may contribute with the aroma of roses.[105] On the other side, ethyl sorbate may negatively contribute to wine aroma as its odor has been described as celery.[114] GC×GC/TOMS allowed the identification of this monoterpene, however the use of a polar stationary phase could be also an alternative for the separation of these compounds in 1D-GC/MS, as already mentioned for other co-elutions. Furthermore, the importance of the identification of linalool is related to the typical floral aroma that this terpene attributes to Moscato wines.[2,25-27]

Linalool was found to be the predominant terpene in grapes of Moscatel de Grano Menudo variety cultivated in La Mancha Region, Spain[26] and α-terpineol was a predominant terpene in Muscatel still wines produced in Valencia, Spain.[25] Similar findings were observed in still wines obtained from Muscat grapes collected in the region included in the Denomination of Origin (DO) "Jerez-Xérèz-Sherry" (Spain)[27] and in Sicilia region (Italy).[28] It seems that linalol and α-terpineol are also among the terpenes considered as characteristic of these Spanish and Italian still wines[27] and may also be considered as characteristic of the Brazilian Moscatel sparkling wines, as they are present in all samples investigated in this study.

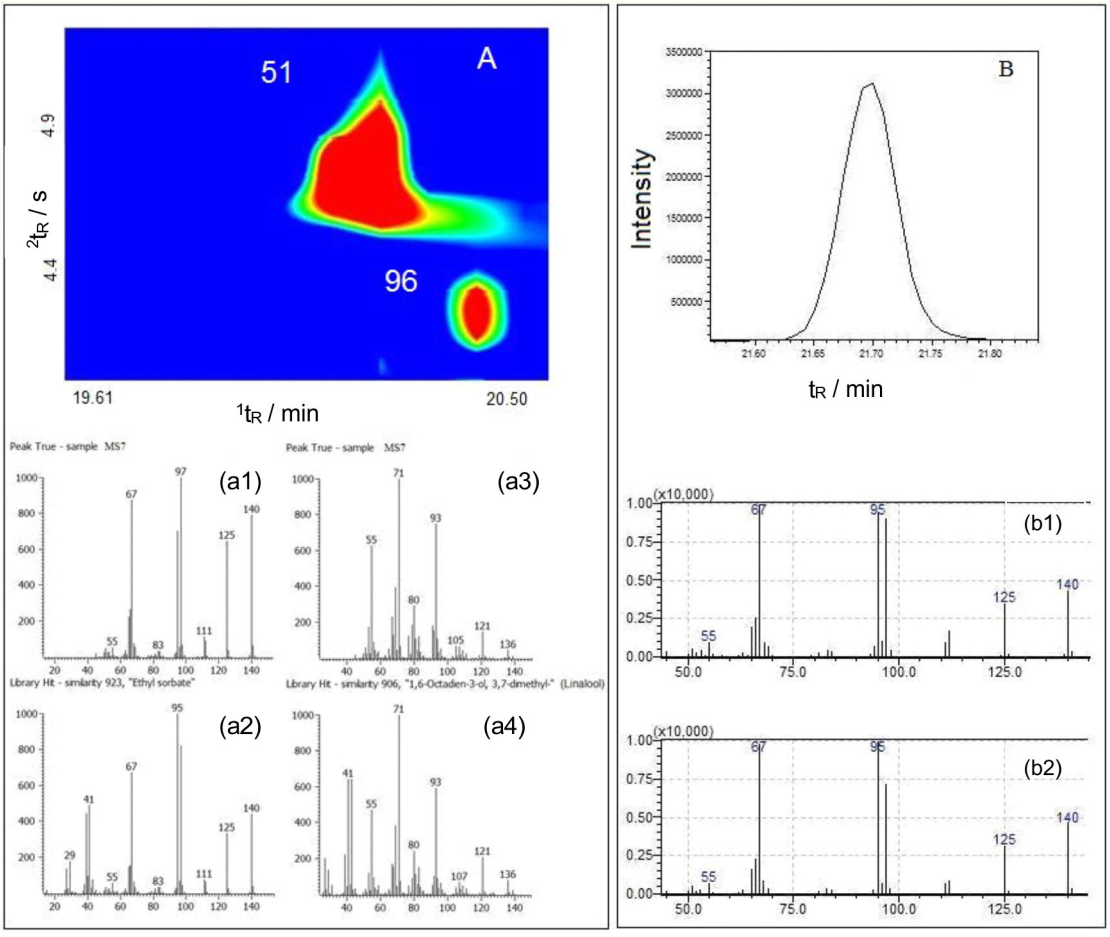

Figure 3. Co-elution of ethyl sorbate (No. 51 in Table 2) ($^{1}t_R$ = 20.30 min and $^{2}t_R$ = 4.76 s) with linalool (No. 96 in Table 2) ($^{1}t_R$ = 20.41 min and $^{2}t_R$ = 4.04 s) in the first dimension and separation of these compounds in the second dimension (A) shown in a zoomed area of a color plot. The spectra (a1) and (a3) were obtained experimentally with GC×GC/TOFMS for ethyl sorbate and linalool, respectively. Below them, mass spectra (a2) and (a4) are the ones reported in the scientific literature for the above mentioned compounds. On the right side of the figure, a one-dimensional chromatogram (B) is presented, as well as the mass spectrum obtained experimentally by 1D-GC/MS for the co-eluted components (b1) and also the mass spectrum reported in the scientific literature for ethyl sorbate (b2).[38]

Multivariate analysis of volatile compounds of Moscatel sparkling wines

Multivariate analysis was done using 1D-GC and GC×GC data in order to compare the potential of these two techniques to elucidate the main differences between Moscatel sparkling wines. Compounds with higher Fisher ratios for 1D-GC and GC×GC were used in the second stage of the statistical analysis (PCA). A PCA using the areas of all tentatively identified chromatographic peaks has not resulted in differentiation of the wine samples under study. In a second step, Fisher ratio was employed to select the most discriminating compounds in order to perform principal component analysis. Compounds used in PCA are presented in decreasing order of Fisher ratio in Table 3. Sorbate derivatives (sorbic acid, ethyl and butyl sorbate) were not included in multivariate analysis, since these compounds are not markers of Moscato grape or fermentation. These compounds are formed due to the addition of an antimicrobian additive called potassium sorbate, as previously mentioned.[111] Furthermore, Table 3 shows the loadings that indicate the relative importance of each volatile compound for each wine that was distinguished from the other sparkling wines. Variables with higher loading values are the ones that significantly contributed to explain the factors and they are marked in bold letters in Table 3. Variables related to components 1 and 2 were positioned according to factor loadings in Figure 4.

Considering 1D-GC/MS data, compounds with higher Fisher ratio included: 2-phenylethyl acetate, propyl decanoate, 2-phenylethyl alcohol, propyl octanoate, α-terpineol and linalool (Table 3). A differentiation between M_{13}, M_{17}, M_{18}, from other Moscatel sparkling wines can be observed in Figure 4a. The two principal components (PC) account for 89.13% of total variance of the data. PC1 was responsible for differentiation of the M_{13}, M_{18} and PC2 was responsible for M_{17}. Figure 4b shows the corresponding

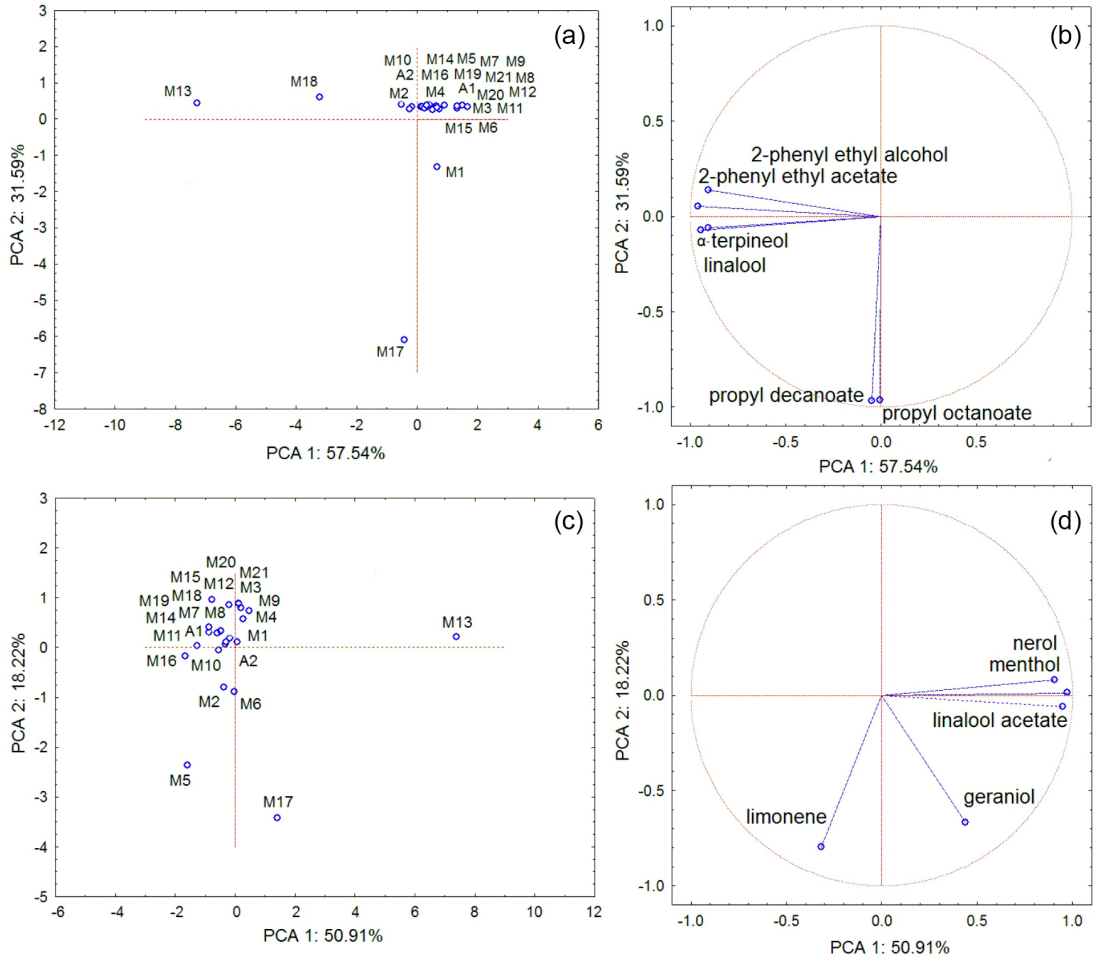

Figure 4. Graphs resulting of the principal component analysis of the normalized chromatographic areas of the volatile compounds of the Moscatel sparkling wines with the highest Fisher ratios. (a) Distinction among the Moscatel sparkling wines and (b) relation between volatile compounds and the wine samples based on 1D-GC/MS data; (c) distinction among the Moscatel sparkling wines and (d) relation between volatile compounds and wine samples based on GC×GC/TOFMS data.

Table 3. Tentatively identified compounds appointed by Fisher ratio and PCA as the most important for differentiation of Moscatel sparkling wines analyzed (Table 1) by GC/MS and GC×GC/TOFMS. The variables with higher loadings values are the ones that contributed most significantly to explain that specific factor and they are marked in bold letters

Compound[a]	$LTPRI_{exp}$[b]	$LTPRI_{lit}$[c]	Fisher ratio	PC1[d]	PC2[d]	Observation
GC/MS						
2-Phenylethyl acetate (No. 65)	1257	1254	6541	**–0.961**	0.054	co-elute with geraniol
Propyl decanoate (No. 79)	1493	1493	5845	–0.048	**–0.967**	–
2-Phenylethyl alcohol (No. 26)	1117	1107	5477	**–0.905**	0.138	co-elute with myrcenol
Propyl octanoate (No. 68)	1292	1282	3552	–0.005	**–0.965**	2-undecanone
α-Terpineol (No. 120)	1191	1188	3440	**–0.904**	–0.062	co-elute with octanoic acid
Linalool (No. 96)	1102	1098	3009	**–0.942**	–0.073	co-elute with 2-nonanol, ethyl heptanoate, (*Z,Z*)-3,6-nonadienal, ethyl sorbate
GC×GC/TOFMS						
Nerol (No. 122)	1231	1229	101779	**0.904**	0.082	co-elute with citronellol
Menthol (No. 115)	1172	1171	72784	**0.970**	0.012	co-elute with epoxylinalol
Linalool acetate (No. 126)	1268	1257	48741	**0.950**	–0.061	–
Limonene (No. 88)	1028	1029	26773	–0.318	**–0.797**	nd in 1D-GC
Geraniol (No. 125)	1257	1252	13228	0.436	**–0.668**	co-elute with 2-phenyl ethyl acetate

[a]Designated number of the compound in Table S1 and Table 2; [b]$LTPRI_{exp}$: linear-temperature-programmed retention index experimentally obtained using DB-5 for GC/MS and GC×GC/TOFMS; [c]$LTPRI_{lit}$: values of LTPRI found in scientific literature for DB-5; [d]principal component.

loading plot that indicates the relative importance of each volatile compound for each Moscatel sparkling wine. The variables with highest contribution to the first PC were 2-phenylethyl acetate, linalool, phenylethyl alcohol and α-terpineol. The second PC is correlated with propyl decanoate and propyl octanoate (Table 3).

Principal component analysis was also performed with GC×GC/TOFMS data and acquired results partially confirmed those obtained by one-dimensional chromatography (Figure 4). The compounds with higher values of Fisher ratio in decreasing order were: nerol, menthol, linalool acetate, limonene and geraniol. A differentiation between M_5, M_{13} and M_{17} Brazilian sparkling wines and other wines is observed in Figure 4c. The two PC account for 69.13% of total variance of the data. In this case, PC1 (represented by menthol, linalool acetate and nerol) was responsible for differentiation between M_{13} and others sparkling wine and PC2 (limonene and geraniol) was responsible for the differentiation of M_5 and M_{17} from the other wines.

Results found through statistical analyses of 1D-GC and GC×GC data may seem as contradictory information, as different compounds were pointed in both cases to account for differences among volatiles of Moscatel sparkling wines. Meanwhile, sparkling wine M_{18} has been distinguished from the other wines only when 1D-GC data was employed in the PCA. However, a more detailed investigation shows that all compounds responsible for the differentiation of M_{18} co-eluted with other compounds, according to Table 3 and were separated in the second chromatographic dimension. These co-elutions were: (*i*) 2-phenyl ethyl acetate and geraniol, (*ii*) 2-phenyl ethyl alcohol and myrcenol, (*iii*) linalool and ethyl sorbate, and (*iv*) α-terpineol and ethyl octanoate and octanoic acid. Some of these same compounds [linalool, 2-phenyl ethyl acetate, 2-phenyl ethyl alcohol, α-terpineol] were important for the distinction of M_{13} in the PCA of 1D-GC data, and this explains why this sparkling wine showed other volatile compounds as relevant for its differentiation in PCA based on GC×GC data. M_{13} has been distinguished from the other samples mainly due to the presence of nerol (odor described as floral/rose), linalool acetate (odor describe as floral/minty) and menthol. This sparkling wine probably showed a more intense floral note due to the presence of a higher relative amount of terpenes.[105] Relative chromatographic area percentages of these terpenes were lower in others sparkling wines, as can be seen in Table S1. Some of them co-eluted with other compounds in 1D-GC, as in the case of nerol (No. 122 of Table 2, $LTPIR_{exp}$ = 1228; also Table 3), which co-eluted with citronellol (No. 123 of Table 2, $LTPRI_{exp}$ = 1228 also Table 3) and menthol (No. 115 of Table 2, $LTPRI_{exp}$ = 1172), which co-eluted with epoxylinalool (No. 114 of Table 2, $LTPIR_{exp}$ = 1172 also Table 3).

Although the number of samples of Moscato Giallo and Moscato Bianco is small, an interesting aspect may

be highlighted with respect to differentiation of Moscatel sparkling wines elaborated with these two grape varieties. Due to varietal contribution of terpenes and C13-norisoprenoids to Moscato wine aroma,[1] these compounds were chosen to investigate possible grouping of Moscatel wines made with Moscato Giallo and Moscato Bianco grapes, using hierarchical cluster analysis (Figure 5). Compounds that allowed distinction between Giallo and Moscato samples due to their higher chromatographic areas were α-terpineol, linalool, vitispirane, β-damascenone, citronellol, nerol oxide, *p*-mentha-1,5-dien-8-ol, linalool oxide, geranyl acetone, hotrienol, *Z*-ocimenol, terpinolene, and methyl dihydrojasmonate. Future work will encompass a higher number of samples in order to reach the designation of variety markers for Moscatel sparkling wines of Serra Gaúcha.

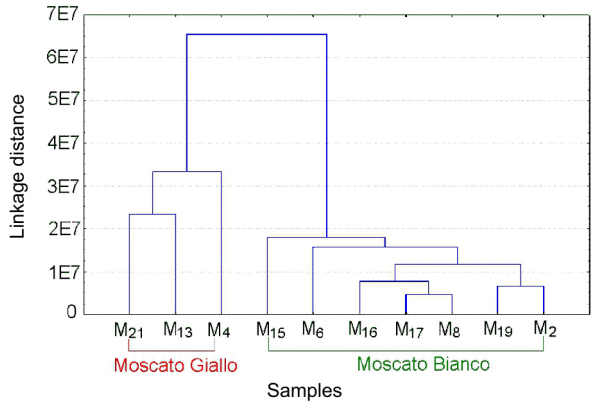

Figure 5. Dendogram for Moscato Giallo and Moscato Bianco sparkling wine samples obtained using the terpenes (α-terpineol, No. 120 of Table 2; linalool, No. 96 of Table 2; citronellol, No. 123 of Table 2; nerol oxide, No. 108 of Table 2; *p*-mentha-1,5-dien-8-ol, No. 112 of Table 2; *Z*-linalool oxide, No. 93 of Table 2; geranyl acetone No. 131 of Table 2, hotrienol, No. 97 of Table 2; *Z*-ocimenol, No. 107 of Table 2 and terpinolene, No. 94 of Table 2) and C13-norisoprenoids (vitispirane, No. 158 of Table 2; methyl dihydrojasmonate, No. 135 of Table 2; and β-damascenone, No. 159 of Table 2) appointed by multivariate analysis (Fisher ratio and PCA).

Conclusions

The chromatographic profile of the volatile fraction of 23 Moscatel sparkling wines, obtained by HS-SPME-1D-GC/MS has proved to be similar in regards to qualitative and semi-quantitative analyses, which has indicated that there is a homogeneous volatile signature for 21 of the Brazilian Moscatel sparkling wines of various trademarks and also for two Italian Asti sparkling wines. Major classes of compounds, in terms of chromatographic area percentage, were esters, acids, alcohols and terpenes.

The higher efficiency of GC×GC/TOFMS for this particular type of sample was verified through the higher number of compounds tentatively identified by GC×GC (two and a half times higher than with 1D-GC), as well as by the separation of partially co-eluted compounds in 1D-GC/MS. The principal component analysis of the volatile components that presented higher Fisher ratio also helped to show that the volatile profile of the majority of Moscatel sparkling wines is similar, considering both chromatographic techniques (1D-GC/MS and GC×GC/TOFMS). Some of the potentially discriminating volatile compounds obtained by 1D-GC were not confirmed by the PCA resulting from GC×GC data, and this was clearly explained by the presence of some co-elutions of these compounds in 1D-GC. A preliminary hierarchical cluster analysis of terpenes and norisoprenoids of sparkling wines of Giallo and Bianco grape varieties showed that the Giallo grape seems to be richer in these compounds.

These results open perspectives for future research of possible varietal indicators and markers of geographical location that may serve the purposes of certification, as well as quality control. It also show that 1D-GC/MS results may be biased and misleading. The choice of a chromatographic technique for the investigation of volatile compounds of sparkling wines is linked to the goal of the investigation, i.e., the GC×GC allows a more detailed study of volatile compounds of wines and would be the technique of choice for a non-target study of volatiles compounds of Moscatel sparkling wines. 1D-GC leads to preliminary results that may satisfy the interest of the wine industry in case co-eluting compounds are not the objective of the study. However, 1D-GC/MS results may be biased and misleading and GC×GC should be employed in first place to verify which are the varietal or geographical markers in order to guarantee the absence of co-elutions in 1D regarding target compounds. Whenever 1D-GC/MS is the only available analytical tool an optimized 1D-GC/MS method should be developed with an appropriate stationary phase and used in a second step, after GC×GC analysis, having the volatiles markers as a focus.

Supplementary Information

Supplementary information is available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgements

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), and the Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS) for financial support and scholarships.

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Submitted: January 17, 2015
Published online: May 5, 2015

FAPERGS has sponsored the publication of this article.