beverages

MDPI

Article

Volatile Profiles of Sparkling Wines Produced by the Traditional Method from a Semi-Arid Region

Antonio Mendes de Souza Nascimento [1], Joyce Fagundes de Souza [1], Marcos dos Santos Lima [2] and Giuliano Elias Pereira [1,3,*]

1 Department of Technology and Social Sciences (DTCS III), Campus Juazeiro, Bahia State University, Edgard Chastinet Avenue, Juazeiro, BA 48905-680, Brazil; antonioenologia@gmail.com (A.M.d.S.N.); joyce.fagundes08@gmail.com (J.F.d.S.)

2 Department of Food Technology, Campus Petrolina, Federal Institute of Sertão Pernambucano, Rodovia BR 407, Km 08, S/N, Jardim São Paulo, Petrolina, PE 56314-520, Brazil; marcos.santos@ifsertao-pe.edu.br

3 Brazilian Agricultural Research Corporation (Embrapa), Grape & Wine/Tropical Semi-arid, Rodovia BR 428, Km 152, PO Box 23, Petrolina, PE 56302-970, Brazil

* Correspondence: giuliano.pereira@embrapa.br; Tel.: +55-054-3455-8000

Received: 17 November 2018; Accepted: 3 December 2018; Published: 7 December 2018

check for updates

Abstract: São Francisco Valley (SFV) is located in Northeastern Brazil, in a tropical semi-arid region where one vine can produce two harvests per year, due to high temperatures, solar radiation rates, and irrigation throughout the year. This is the main characteristic differing this from other winegrowing region in the world. The objective of this study was to characterize volatile profiles of sparkling wines produced by the traditional method, using Chenin Blanc and Syrah grapes, the two main varieties used for white and red wines, respectively, grown in the region. The sparkling wines remained on lees for six months maturing. The sparkling wines were characterized by the parameters density, pH, total titratable and volatile acidities, residual sugars, dry extract, alcohol content, total phenolic compounds, in vitro antioxidant activity and volatile fraction. The volatile fraction extraction was performed by the HS-SPME technique and tentative identification of the volatile compounds was carried out with GC-MS using the scan mode. A total of 33 volatile compounds were identified, among them 11 alcohols, 13 esters, five carboxylic acids, and four different chemical classes. The volatile profile of Chenin Blanc sparkling wine was associated mainly to 2,3-butanediol, 3-ethoxypropan-1-ol, diethyl succinate, and ethyl decanoate, while Syrah sparkling wine was characterized by benzaldehyde, butyric acid, and some acetates. This study reported for the first time volatile profiles of traditional sparkling wines from SFV, as new products, contributing to better understand the quality potential of these beverages for a tropical semi-arid region.

Keywords: São Francisco Valley; Syrah and Chenin Blanc grape varieties; GC-MS; sparkling wine; volatile compounds

---

1. Introduction

Wine sector is an important socioeconomic activity for the Southern and Northeastern regions of Brazil. The São Francisco Valley (SFV) is located in the Northeast, between the 8–9° parallels in the South Hemisphere, in a tropical semiarid climate. Climate conditions allow the grape production to be scheduled throughout the year, due to high temperatures, high solar radiation and water availability for irrigation, and one vine is capable of producing two crops annually [1–3]. Products from this region are classified as tropical wines [4].

Sparkling wines comprise the greatest part of the current commercial production in the SFV and it is produced only by Asti and Charmat methods. These wines represent approximately 70% of the total production of fine wines (from *Vitis vinifera* L.) in this region, while red wines represent 29%, and white wines 1% of the total [3]. The main varieties being used for white sparklings are Chenin Blanc, Verdejo, Sauvignon Blanc and Viognier, while rosé sparklings are produced using Syrah, Tempranillo and Grenache, in both cases using the Charmat method [3,5].

In general, the typicality and the chemical and sensory characteristics of wines are depending on factors such as climate, soil type, grape variety, and winemaking process. These elements comprise the set of effects described as the terroir [6]. In the SFV, wineries use several grape varieties, of which Syrah and Chenin Blanc are the most adapted to the local conditions [3,5]. Even wines in the region have been produced for more than three decades, commercial sparkling wines are not produced by traditional method ("Champenoise"). By this method, sparkling wines are produced with two consecutive fermentations, resulting more complex products with higher added value [6,7].

The aroma is one of the most important compound linked to wine quality, influencing its typicality and acceptability. The aromatic profile of sparkling wines from traditional method is associated to volatile compounds belonging to esters, alcohols, acids, and some terpenes, in a very complex matrix [8–10].

The study of the volatile composition of sparkling wines can lead to a better understanding of their quality and typicality, highlighting the possibilities for adjustments in the production process and final composition for commercial products. It can reveal the distinct and unique characteristics of regional wines, associating them to their geographic origin [9]. In Brazil, studies have been carried out to characterize volatile composition of wines produced in the Southern region [8,11–14], however, no study reported about volatiles in traditional sparkling wines from the SFV.

In this context, the objective of the study was to characterize the volatile profiles of sparkling wines produced by the traditional method, using the Chenin Blanc and Syrah grapes grown in the SFV, a tropical semi-arid climate in Brazil.

2. Materials and Methods

2.1. Standards and Chemical Reagents

Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), DPPH (2,2-diphenyl-1-picrylhydrazyl), (ABTS) 2,2-azino-bis (3-ethylbenzthiazoline-6-sulfonic acid), gallic acid, linear alkanes (from C_{11} to C_{24}), the internal standards isocineol, 2-octanone, methyl nonanoate, phenyl acetate, 2-methyl valeric acid, and α-methylbenzyl alcohol were purchased from Sigma Aldrich (St. Louis, MO, USA). Potassium persulfate, sodium carbonate, Folin-Ciocalteu, and ethanol were obtained from Merck (Darmstadt, Germany).

2.2. Grape Samples and Obtention of the Musts and Base Wines

Chenin Blanc and Syrah grapes (*Vitis vinifera* L.) were harvested in September 2015 from a partner winery in the SFV, Brazil (latitude 9°16′ S; longitude 40°52′ W; and altitude 413.5 m) and were used to obtain the musts. The musts were obtained after the crushing and pressing of 31 kg of grapes for each treatment. They were later sulphited by adding 50 mg L^{-1} of sulphite (Ever, Garibaldi, RS, Brazil) and clarified with 400 mg L^{-1} of BentoFlash (Ever, Garibaldi, RS, Brazil). Musts were obtained from the Chenin Blanc (blanc de blanc) and Syrah (blanc de noir) varietals, along with two blends: 50% Chenin Blanc + 50% Syrah-white (CB+SY-W) and 50% Chenin Blanc + 50% Syrah-rosé (CB+SY-R). In the latter case, a light pre-fermentative maceration was carried out for two hours to extract a pinkish color. Activated carbon, in the form of 500 mg L^{-1} Ewerdec W98 (Ever, Garibaldi, RS, Brazil), was added to the musts obtained from the Syrah varietal, as well as the blend 50% Chenin Blanc+50% Syrah-white (CB+SY-W), for the decolorization of the white blend.

For the base wines production, the musts were fermented with *Saccharomyces cerevisiae* var. *bayanus* yeast (200 mg L^{-1} Mycoferm CRIO.SP, supplied by Ever, Garibaldi, RS, Brazil) in glass bottles of 20 L containing 19 L of must. Each treatment had three bottles and the base wines did not undergo malolactic fermentation. The classical analyses performed on the base wines can be visualized in the supplementary table.

2.3. Sparkling Wine Elaboration

To elaborate sparkling wines through the traditional method, 26 g L^{-1} of inverted sugar was added to the base wines in order to obtain a pressure of 6 atm. In addition, the following enological products were added: *S. cerevisiae* var. *bayanus* yeast (300 mg L^{-1}, Mycoferm CRIO.SP), fermentation activator (350 mg L^{-1}, Zimovit), polyvinylpolypyrrolidone (50 mg L^{-1}, Clarivin) to precipitate the phenolic oxidized compounds, and bentonite (50 mg L^{-1}, BentoFlash) to facilitate the precipitation of yeast cells, forming the tirage liqueur, all supplied by Ever, Garibaldi, RS, Brazil. The wines were stored at 16 ± 2 °C until the second fermentation was achieved. After six months of storage in contact with the lees, at 16 ± 2 °C, the sparkling wines were then disgorged and capped. The sparkling wines were maintained under controlled temperature (18 ± 2 °C) in the absence of light until analysis, performed after 45 days.

2.4. Classical Enological Parameters and Antioxidant Activity in Vitro

Density, pH, titratable acidity (g L^{-1} of tartaric acid), residual sugar (g L^{-1}), dry extract (g L^{-1}), volatile acidity (g L^{-1} of acetic acid) and alcoholic graduation (% v/v) of the sparkling wines were determined according to the International Organization of Vine and Wine [15]. The concentration of total phenolic compounds was determined by the Folin-Ciocalteu method [16] and the results were expressed in milligrams equivalent to gallic acid per liter of sparkling wine (mg GAE L^{-1}). The color was determined by absorbance measurement at 420 nm [17] using a Biospectro spectrophotometer UV-Vis model SP-220 (Curitiba-PR, Brazil).

The antioxidant activity in vitro was determined using the free radical scavenging methods ABTS [18] and DPPH [19]. In both methods, trolox was the analytical standard used to construct the calibration curves and the results were expressed in millimols of trolox equivalent per liter of sparkling wine (mmol TEAC L^{-1}).

2.5. 1D-GC/qMS Instrumentation

A CombiPAL automatic sampler (CTC Analytics, Zwingen, Switzerland) was used to extract the volatile compounds in the headspace of the vials containing the sparkling wine samples. The 1D-GC/qMS system consists of a Shimadzu 17A (Shimadzu, Kyoto, Japan), with a quadrupole mass spectrometry detector, model QP 5050A, equipped with a DB-Wax polar column (30 m × 0.25 mm × 0.25 µm, J & W Scientific, Folsom-CA, USA). Desorption of the volatile compounds was performed directly on the chromatograph injection portico for 5 min, with the injector in the splitless mode. The temperature of the injector was 220 °C and that of the detector of 250 °C, while the programming of the oven temperature started at 35 °C for 5 min. It reached 120 °C at 3 °C min^{-1} and, after 200 °C at 5 °C min^{-1}, reaching the final temperature of 250 °C at 10 °C min^{-1}, remaining for 5 min, according to method Welke et al. [20]. The flow of helium gas (analytical purity 99.9%, Linde, Canoas, RS, Brazil) was 1.0 mL min^{-1}. The quadrupolar mass spectrometry detector was operated in the electronic impact mode at 70 eV, the mass range being monitored from 40–450 m/z and the electron multiplier at 1250 V.

2.6. "Mix of Internal Standards" and Conditions for the Extraction of Volatile Compounds

After analyzing the headspace of the sparkling samples, in order to verify the chemical nature of the volatile compounds, a "mix of internal standards" (ethanolic solution) was prepared for internal normalization of the chromatographic peak areas for each volatile compound tentatively identified [21]. Isocineol (2000 ng mL^{-1}), 2-octanone (2000 ng mL^{-1}), methyl nonanoate (1000 ng mL^{-1}), phenyl acetate (1000 ng mL^{-1}), 2-methyl valeric acid (2000 ng mL^{-1}), and α-methyl benzyl alcohol (2000 ng mL^{-1}) were used in the preparation of the "internal standard mix". It was used to standardize the volatile compounds found in the sparkling samples belonging to the chemical classes of terpenes, alcohols, esters, acetates, acids, and compounds of other chemical classes, respectively. The α-methyl benzyl alcohol was used to the other chemical classes because similarity of its structural formula with the structural formulas of volatile compounds found in the sparkling wine samples.

The extraction of the volatile compounds was performed by solid-phase microextraction technique in the headspace mode (HS-SPME), according to Welke et al. [20]. The extraction was done in 20 mL flasks suitable for headspace analysis, which contained 1 mL of the sparkling sample, 30% NaCl (*m*/*v*) and 50 µL of the internal standards mix. All samples were kept at 55 °C for 45 min prior to extraction. The headspace was sampled using a DVB/CAR/PDMS 50/30 µm fiber, 2 cm length.

2.7. Tentative Identification of Volatile Compounds

The tentative identification of the volatile compounds was performed comparing linear temperature programming retention indices (LTPRI), experimentally obtained (LTPRI-EXP) and the LTPRI reported in the literature (LTPRI-LIT) [22], listed in the online database of NIST (National Institute of Standards and Technology). Retention data of *n*-alkanes series (C9–C24), under the same experimental conditions, were used for experimental LTPRI calculation. The maximum difference between LTPRI-EXP and LTPRI-LIT was not more than 15 units. Another criterion adopted in the process of tentative identification was a minimum of 70% spectral similarity. The mean values of the volatile compounds are expressed as the normalized chromatographic area.

2.8. Statistical Analysis

All results were expressed as mean ± standard deviation of three sparkling wine bottles. The software SPSS Inc. version 17.0 (Chicago, IL, USA) was used for the analysis of variance (ANOVA), Tukey test ($p < 0.05$) and principal component analysis (PCA).

3. Results

3.1. Classical Enological Parameters and Antioxidant Activity

The results for the classic enological parameters and the antioxidant capacity of sparkling wines are shown in Table 1. It can be observed that significant variations did not occur among the sparkling wines in terms of residual sugar and volatile acidity, and the values are within the limits allowed by Brazilian and OIV legislations [15]. However, the results for relative density and dry extract of the four sparkling wines tested showed significant differences and were separated into two groups: the varietals (Chenin Blanc and Syrah), which showed the lowest values, and the blends CB+SY-W and CB+SY-R, which showed the highest values. This may be related to the lower alcohol content values presented by CB+SY-W and CB+SY-R sparkling wines. Sparkling wines generally have higher total acidity as compared to still wines (especially in the case of red wines). Chenin Blanc sparkling wine had the highest total acidity (9.68 g L^{-1}) and the lowest pH (3.42) (Table 1). These results may be justified by the lower degree of maturity of the Chenin Blanc grapes at harvest. Chenin Blanc grapes presented total titratable acidity of 10.15 g L^{-1} (equivalent to tartaric acid), two grams per liter more than titratable acidity of the Syrah must (8.15 g L^{-1}) (data not shown).

The phenolic compounds are important to the sensorial because they contribute to the astringency, bitterness, and color; in addition, they present bioactive activity, are responsible for several beneficial effects for health [1]. The direct relation between phenolic composition and antioxidant capacity of the sparkling wines can be observed in the CB+SY-R sparkling wine (Table 1), which had higher total polyphenols concentration (190.2 mg L^{-1}) and antioxidant capacity (DPPH = 0.90 mM TEAC L^{-1}). Studying commercial wines from SFV, Padilha et al. [1] evidenced that the antioxidant capacity, determined also by DPPH and ABTS, influenced each individual wine phenolic compounds, which explains the variation of the antioxidant capacity observed in the present study. These total polyphenols values are higher than those found by Caliari et al. [14], studying Moscato Giallo sparkling wines (variation between 88.0 mg L^{-1} and 95.7 mg L^{-1}) in the South of Brazil. The highest concentration of total phenolic compounds in the CB+SY-R sparkling wine can be justified by the pre-fermentative maceration occurred. In a study with Spanish sparkling wines with Pedro Ximenez variety, Ruiz-Moreno et al. [23] also observed higher concentration of total polyphenols in the sparkling wine whose must has been pre-fermentative macerated. In the same way, the absorption at 420 nm (yellow) was higher for the CB+SY-R sparkling wine.

Table 1. Classical analyses, spectrophotometric and antioxidant activity of the sparkling wines elaborated by the traditional method in the SFV.

Assessments *	Traditional Sparkling Wines			
	CB	SY	CB+SY-W	CB+SY-R
Density	0.993 ± 0.01 ^{b}	0.992 ± 0.01 ^{b}	0.995 ± 0.01 ^{a}	0.994 ± 0.01 ^{a}
Residual sugar (g L^{-1})	2.60 ± 0.08 ^{a}	2.67 ± 0.15 ^{a}	2.63 ± 0.06 ^{a}	2.66 ± 0.03 ^{a}
Alcohol content (%*v*/*v*)	12.35 ± 0.37 ^{b}	13.20 ± 0.30 ^{a}	12.09 ± 0.20 ^{b}	12.03 ± 0.17 ^{b}
Dry extract (g L^{-1})	21.79 ± 0.40 ^{b}	22.05 ± 0.35 ^{b}	24.55 ± 0.35 ^{a}	24.95 ± 0.45 ^{a}
pH	3.42 ± 0.02 ^{c}	3.58 ± 0.02 ^{b}	3.53 ± 0.03 ^{b}	3.66 ± 0.01 ^{a}
Total acidity (g L^{-1})	9.68 ± 0.17 ^{a}	8.18 ± 0.07 ^{b}	8.33 ± 0.14 ^{b}	8.25 ± 0.15 ^{b}
Volatile acidity (g L^{-1})	0.46 ± 0.03 ^{a}	0.48 ± 0.04 ^{a}	0.49 ± 0.04 ^{a}	0.48 ± 0.02 ^{a}
A_{420}	0.046 ± 0.01 ^{b}	0.057 ± 0.01 ^{b}	0.045 ± 0.00 ^{b}	0.117 ± 0.01 ^{a}
TP (mg L^{-1})	123.32 ± 2.55 ^{b,c}	134.79 ± 1.93 ^{b}	110.94 ± 1.42 ^{c}	190.22 ± 4.03 ^{a}
DPPH (mMTrolox L^{-1})	0.462 ± 0.22 ^{c}	0.547 ± 0.12 ^{b}	0.454 ± 0.20 ^{c}	0.703 ± 0.19 ^{a}
ABTS (mMTrolox L^{-1})	0.533 ± 0.31 ^{b}	0.942 ± 0.11 ^{a}	0.619 ± 0.19 ^{b}	0.899 ± 0.41 ^{a}

* The results are expressed as mean ± standard deviation of three sparkling wine bottles (triplicate). Different letters on the same line indicate significant differences between samples ($p < 0.05$). A_{420}: index color (absorbance at 420 nm); TP: total phenolics; CB: sparkling wine 100% Chenin Blanc; SY: sparkling wine 100% Syrah; CB+SY-W: sparkling wine 50% Chenin Blanc + 50% Syrah, elaborated as white; and CB+SY-R: sparkling wine 50% Chenin Blanc + 50% Syrah, elaborated as rosé.

3.2. Volatile Composition

A total of 33 volatile compounds were tentatively identified and first time reported in the sparkling wines produced by the traditional method in SFV (Table 2). The values of the calculated LTPRI and the LTPRI from literature, as well as the aromatic descriptors of each compound are also shown in Table 2.

Differences lower than or equal to 15 units between the calculated LTPRI and LTPRI values of the literature were accepted for the tentative identification process of the compounds. It can be noted that from 33 compounds identified in the headspace, 11 are higher alcohols, 13 volatile esters, five carboxylic acids, and four belong to distinct chemical classes: one terpene, one sulfurated, one aldehyde and one phenol (Table 2). The quantity of volatile compounds identified in the sparkling wines from SFV is similar to findings in previous studies carried out in other countries, where monodimensional gas chromatography was also used. Wang et al. [24] identified 26 aromatic compounds in the headspace of Chenin Blanc wines from China, with esters representing the highest number of compounds, while Chin et al. [25] found 35 volatile compounds in Australian Shiraz wines.

The volatile compounds identified in the four traditional sparkling wines from SFV are shown in Table 3. It can be observed that 8 compounds had a normalized chromatographic area of $\geq$ 1:3 alcohols (3-methyl-1-butanol, 2,3-butanediol, 2-phenylethanol), three esters (ethyl octanoate, diethyl butanedioate, 2-phenyl ethyl acetate), and two carboxylic acids (hexanoic and octanoic).

According to von Muhlen et al. [22], these data contribute to the tentative identification of volatile compounds in wines.

Table 2. Volatile compounds tentatively identified in four sparkling wines elaborated by traditional method in the SFV and its aromatic descriptors.

Aromatic Compounds	[a] CAS	[b] LTPRI-EXP	[c] LTPRI-LIT	Aromatic Descriptors
Alcohols				
3-Methyl-1-butanol	123-51-3	1216	1217 [26]	Solvent [13]
3-Methyl-1-pentanol	589-35-5	1328	1331 [26]	Vinous, herbaceous, cocoa [13]
Hexanol-1	111-27-3	1354	1356 [27]	Vegetative, grass cut [14]
3-Ethoxypropan-1-ol	111-35-3	1372	1371 [20]	Fruity [13]
(Z)-3-Hexen-1-ol	928-96-1	1383	1383 [28]	Green, bitter, greasy [13]
Octan-2-ol	5978-70-1	1422	1416 [29]	-
2,3-Butanediol	513-85-9	1539	1545 [26]	Fruity [13]
Butane-1,3-diol	107-88-0	1577	1576 [30]	-
Decan-1-ol	112-30-1	1763	1778 [20]	Sweet, fatty [13]
2-Phenylethanol	60-12-8	1903	1900 [20]	Flower, honey [14]
Dodecan-1-ol	112-53-8	1968	1977 [20]	Unpleasant, floral [9]
Esters				
Ethyl butanoate	105-54-4	1057	1044 [28]	Strawberry, apple [13]
Ethyl hexanoate	123-66-0	1232	1236 [20]	Fruity, green apple, floral [9]
Ethyl octanoate	106-32-1	1436	1429 [20]	Fruity, pineapple [9]
Ethyl decanoate	110-38-3	1638	1638 [20]	Oily / fruity (grape) [9]
Diethyl succinate	123-25-1	1678	1686 [20]	Fruity [13]
Ethyl 9-decenoate	67233-91-4	1690	1689 [29]	Roses [13]
Diethyl pentanedioate	1119-40-0	1780	1780 [20]	-
2-Phenethyl acetate	103-45-7	1808	1821 [20]	Flowery [13]
Diethyl malate	626-11-9	2040	2041 [27]	Peach, cut grass [13]
Monoethyl succinate	3878-55-5	2383	2395 [31]	-
Isoamyl acetate	123-92-2	1123	1125 [26]	Fruity (banana) [14]
Hexyl acetate	142-92-7	1271	1279 [26]	Apple, cherry, pear, floral [13]
Cis-3-Hexen-1-ol acetate	3681-71-8	1316	1319 [26]	-
Acids				
Butanoic acid	107-92-6	1633	1637 [28]	Cheese [9]
Hexanoic acid	142-62-1	1849	1855 [20]	Fatty [9]
Octanoic Acid	124-07-2	2066	2060 [27]	Cheese [14]
n-Decanoic acid	334-48-5	2276	2269 [20]	Fatty, rancid [13]
Dodecanoic acid	143-07-7	2488	2485 [30]	Rancid [14]
Others				
3-(Methylthio)-1-propanol (sulfurated)	505-10-2	1711	1715 [32]	Cooked vegetable [13]
Benzaldehyde (Aldehyde)	96-48-0	1526	1513 [29]	Sweet, buttery [9]
Phenol (Phenol)	108-95-2	2004	2002 [20]	Medicinal [9]
Carvone (Terpene)	2244-16-8	1717	1718 [28]	Herbaceous, bread, spicy, floral [33]

[a] CAS: Chemical Abstracts Service. [b] LTPRI-EXP: Linear temperature-programmed retention indexes experimentally obtained calculated using n-alkanes (C11-C24) in the DB-Wax column. [c] LTPRI-LIT: Linear temperature-programmed retention indexes related in the literature obtained in DB-WAX column or equivalent stationary phase: Torrens et al. [9]; Welke et al. [13]; Caliari et al. [14]; Welke et al. [20]; Gurbuz et al. [26]; Selli et al. [27]; Osorio et al. [28]; Ledauphin et al. [29]; Shimoda et al. [30]; Wada e Shibamoto [31]; Botelho et al. [32]; Gauvin et al. [33].

Higher alcohols are secondary aromatic compounds originating from the fermentation process. They are produced from sugars and amino acids during alcohol fermentation and include aliphatic and aromatic compounds, which can positively or negatively influence the wine aroma [14]. The compound 3-methyl-1-butanol (aroma of solvent, chemical) was the alcohol with greatest normalized chromatographic area, regardless the grape variety used in the sparkling wine production. High values of this compound were also found by Santos et al. [34], and Wang et al. [24] in Chenin Blanc wines. Ubeda et al. [35] reported also high values of 3-methyl-1-butanol in Chilean sparkling wines. However, Condurso et al. [36] noted that this compound has a high perception threshold. Other alcohols, such as 2-phenylethanol (aroma related to honey and flowers) and 2,3-butanediol (fruity aroma) were also found in the sparkling wines from SFV, but without significant differences among the four sparkling wines analyzed (Table 3). According to Ferreira et al. [37], 2-phenylethanol is considered one of the most important aromatic alcohols in terms of wine sensory quality. It was the second highest volatile compound identified in the traditional sparkling wines from SFV, regardless the variety used.

The hexan-1-ol (herbaceous flavour), a compound formed by linoleic and linolenic acids degradation in the pre-fermentative stage [14], was also found in the sparkling wines from SFV. Its presence ranged from 0.166 (Syrah sparkling wine) to 0.550 (CB+SY-R sparkling wine) (Table 3). Significant quantities of this alcohol were also observed by Wang et al. [38] in rosé sparkling wines produced through the traditional method in Australian. Among the other alcohols identified in the sparkling wines from SFV, presence of 3-ethoxypropan-1-ol (particularly in the Chenin Blanc sparkling wine) can be highlighted, despite the normalized chromatographic area low (0.047). This compound can contribute to the volatile composition of sparkling wines with fruity aroma.

Table 3. Normalized chromatographic area of the volatile compounds tentatively identified (using 1D-GC/qMS) in four sparkling wines elaborated by the traditional method in the SFV.

Aromatic Compounds	Traditional Sparkling Wines *			
	Chenin Blanc	Syrah	CB+SY-W	CB+SY-R
Alcohols				
3-Methyl-1-butanol	12.87 ± 2.57 [a]	8.590 ± 1.94 [a]	7.146 ± 4.01 [a]	7.524 ± 2.99 [a]
3-Methyl-1-pentanol	0.084 ± 0.02 [a,b]	0.072 ± 0.01 [b]	0.081 ± 0.01 [a,b]	0.114 ± 0.01 [a]
Hexan-1-ol	0.256 ± 0.18 [a,b]	0.166 ± 0.08 [b]	0.246 ± 0.11 [a,b]	0.550 ± 0.11 [a]
3-Ethoxypropan-1-ol	0.047 ± 0.01 [a]	0.018 ± 0.01 [b]	0.032 ± 0.02 [a,b]	0.027 ± 0.01 [b]
(Z)-3-Hexen-1-ol	0.046 ± 0.01 [a]	0.135 ± 0.09 [a]	0.105 ± 0.02 [a]	0.076 ± 0.01 [a]
Octan-2-ol	0.187 ± 0.05 [a]	0.183 ± 0.02 [a]	0.228 ± 0.01 [a]	0.187 ± 0.02 [a]
Butane-2,3-diol	1.380 ± 0.90 [a]	0.738 ± 0.18 [a]	0.762 ± 0.53 [a]	0.809 ± 0.41 [a]
Butane-1,3-diol	0.442 ± 0.25 [a]	0.406 ± 0.03 [a]	0.472 ± 0.11 [a]	0.396 ± 0.17 [a]
Decan-1-ol	0.022 ± 0.01 [b]	0.035 ± 0.01 [a,b]	0.048 ± 0.01 [a]	0.024 ± 0.01 [b]
2-Phenylethanol	8.354 ± 2.56 [a]	6.094 ± 1.13 [a]	4.289 ± 3.10 [a]	4.567 ± 1.64 [a]
Dodecan-1-ol	0.073 ± 0.05 [a]	0.055 ± 0.03 [a]	0.014 ± 0.01 [a]	0.021 ± 0.01 [a]
Esters				
Ethyl butanoate	0.139 ± 0.02 [a]	0.094 ± 0.03 [a]	0.121 ± 0.04 [a]	0.106 ± 0.03 [a]
Ethyl hexanoate	0.406 ± 0.05 [a]	0.789 ± 0.15 [a]	0.660 ± 0.22 [a]	0.669 ± 0.29 [a]
Ethyl octanoate	1.501 ± 0.15 [a,b]	1.966 ± 0.08 [a]	1.338 ± 0.21 [b]	1.346 ± 0.31 [b]
Ethyl decanoate	0.315 ± 0.05 [a]	0.059 ± 0.01 [c]	0.102 ± 0.02 [b,c]	0.156 ± 0.02 [b]
Diethyl succinate	2.906 ± 0.90 [a]	0.582 ± 0.24 [b]	1.754 ± 0.72 [a,b]	1.219 ± 0.16 [b]
Ethyl 9-decenoate	0.051 ± 0.01 [a]	0.042 ± 0.01 [a,b]	0.025 ± 0.01 [b]	0.049 ± 0.01 [a]
Diethyl pentanedioate	0.062 ± 0.02 [a]	0.011 ± 0.00 [b]	0.032 ± 0.01 [b]	0.024 ± 0.01 [b]
2-Phenethyl acetate	1.935 ± 0.57 [a]	0.308 ± 0.11 [b]	1.0736 ± 0.44 [a,b]	1.036 ± 0.16 [a,b]
Diethyl malate	0.584 ± 0.17 [a]	0.043 ± 0.02 [b]	0.189 ± 0.09 [b]	0.112 ± 0.03 [b]
Monoethyl succinate	0.052 ± 0.02 [b]	0.391 ± 0.23 [a,b]	0.781 ± 0.50 [a]	0.024 ± 0.01 [b]
Isoamyl acetate	0.089 ± 0.06 [b]	0.684 ± 0.15 [a]	0.339 ± 0.23 [a,b]	0.259 ± 0.11 [b]
Hexyl acetate	0.015 ± 0.01 [b]	0.119 ± 0.04 [a]	0.036 ± 0.02 [b]	0.052 ± 0.03 [a,b]
Cis-3-Hexen-1-ol acetate	0.015 ± 0.01 [b]	0.034 ± 0.01 [a]	0.018 ± 0.01 [b]	0.016 ± 0.01 [b]
Acids				
Butanoic acid	0.075 ± 0.07 [c]	0.107 ± 0.02 [a]	0.092 ± 0.10 [b]	0.085±0.04 [b,c]
Hexanoic acid	3.394 ± 0.25 [a]	3.300 ± 0.11 [a]	3.067 ± 0.70 [a]	2.890 ± 0.45 [a]
Octanoic Acid	6.231 ± 3.22 [b]	7.450 ± 2.23 [a]	6.854 ± 0.40 [a,b]	6.934 ± 0.51 [a,b]
n-Decanoic acid	0.826 ± 0.59 [a,b]	0.386 ± 0.06 [b]	0.496 ± 0.06 [b]	1.314 ± 0.14 [a]
Dodecanoic acid	0.086 ± 0.11 [a]	0.025 ± 0.01 [a]	0.021 ± 0.01 [a]	0.025 ± 0.01 [a]
Others				
3-(Methylthio)-1-propanol (sulphur)	0.014 ± 0.01 [a]	0.009 ± 0.01 [a]	0.008 ± 0.01 [a]	0.031 ± 0.01 [a]
Benzaldehyde (Aldehyde)	0.066 ± 0.02 [b]	0.070 ± 0.01 [a]	0.063 ± 0.02 [a,b]	0.063 ± 0.05 [a,b]
Phenol (Phenol)	0.051 ±0.01 [b]	0.067 ± 0.01 [a]	0.051 ± 0.01 [a b]	0.056 ± 0.02 [a,b]
Carvone (Terpene)	0.082 ± 0.02 [a]	0.015 ± 0.01 [b]	0.092 ± 0.03 [a]	0.029 ± 0.01 [b]

* The results are expressed as mean ± standard deviation of three sparkling wine bottles. Different letters on the same line indicate significant differences between samples ($p < 0.05$). CB+SY-W: sparkling wine 50% Chenin Blanc + 50% Syrah, winemaked in white. CB+SY-R: sparkling wine 50% Chenin Blanc + 50% Syrah, winemaked in rosé.

Esters contribute to sensory attributes of wines, mainly in relation to floral and fruity aromas [12,14]. The concentrations of these esters are influenced by multiple factors, including yeasts, temperature of fermentation, aeration degree during alcoholic fermentation, and sugar concentration [6]. A notable ester was diethyl succinate (fruity aroma), which presented higher chromatographic area in the Chenin Blanc sparkling wine (Table 3), which suggests that this compound is one of the most relevant esters for the volatile profile in SFV. This compound was the third most important in rosés sparkling wines from

Australia [38], and concentrations ranged from 3.9 μg L^{-1} to 10,000 μg L^{-1}. However, Wang et al. [24] noted that diethyl succinate was one of the lowest ester compounds in Chenin Blanc wines in China.

The compounds 2-phenylethyl acetate and ethyl octanoate contribute to the floral and fruity aroma, respectively, and they were also found in the sparkling wines produced in the SFV. 2-phenylethyl acetate was found with the highest area in the Chenin Blanc sparkling wine (Table 3). Isoamyl, hexyl and *cis*-3-hexen-1-ol acetates were present in high chromatographic areas in Syrah sparkling wine, while Chenin Blanc showed higher chromatographic areas of ethyl decanoate, diethyl pentanedioate and diethyl malate (Table 3). In relation to the esters ethyl butanoate and ethyl hexanoate, no difference was found between the four sparkling wines analyzed.

Carboxylic acids are produced during alcohol fermentation and may have different origins. The hexanoic, octanoic, and decanoic acids can also be formed during the catabolism of the long chain fatty acids [6]. Depending on the concentration, these acids are related to a decrease in the sensory quality of wines [9,14]. Shinohara [39] showed that in concentrations of 4 to 10 mg L^{-1} the C6 to C10 acids contribute to an agreeable wine aroma, while in concentrations above 20 mg L^{-1} they have a negative impact on the organoleptic quality of wines.

The sparkling wines produced by traditional method in the SFV presented higher normalized chromatographic areas for octonoic, hexanoic and n-decanoic acids (the last on was higher in CB+SY-R sparkling wines, as shown in Table 3). The high chromatographic areas of these acids may be related to two alcoholic fermentations that sparkling wines elaborated by traditional methods have undergone. Welke et al. [8] observed an increase of the chromatographic area for almost all the acids identified in the volatile profile of base wines and their resulting sparklings.

Sulphur compounds are originated from fermentative process contributing to the aromatic complexity of the wines, when present in low concentrations. However, in high concentrations, they may be responsible for unpleasant aromas [40]. As reported in Table 3, the 3-(methylthio)-1-propanol was identified in low normalized chromatographic areas in the sparkling wines produced in the SFV (ranging from 0.027 to 0.031).

Aldehydes are formed from decarboxylation of unsaturated fatty acids and they can also be considered as products of lipoxygenase catalysis [41]. The presence of benzaldehyde was statistically higher in the Syrah sparkling wine, as compared to the others. But in general, the chromatographic areas was lower than 0.4 in the headspace for all the sparkling wines of the SFV (Table 3).

The volatile phenols can have a negative effect on the global aroma of wines, providing aromas described as “animal”, “horse sweat”, “leather”, or “medicinal”. However, in low concentrations they contribute to increasing the aroma complexity [9]. The presence of this type of volatile compound in the sparkling wines of the SFV was discrete, ranging from 0.051 (Chenin Blanc and CB+SY-W) to 0.067 (Syrah) in the chromatographic area (Table 3).

The terpenes are responsible for the younger and floral aromas of wines and they are related to the varietal aromas of certain groups of varieties, mainly muscats [8,14]. In this study, the only terpene that was tentatively identified was carvone, which presented the highest normalized chromatographic area in CB+SY-W and Chenin Blanc sparkling wines (Table 3). Despite being related to varietal aromas, terpenes are not frequently identified in wines from Chenin Blanc and Syrah varieties. Wang et al. [24] found two terpenes in Chenin Blanc wines and Zang et al. [42] identified four in Syrah wines.

In order to link volatile compounds and identify main parameters contributing to discriminate four different sparkling wines from SFV, principal component analysis (PCA) was applied in the average of three replicates of the results obtained with 1D-GC/qMS (Table 3), from each one of the four sparklings evaluated. The PCA (Figure 1) showed that two PCs explained 81.57% of total variability of the data, separating the sparkling wines samples according to the grape varieties and blends used.

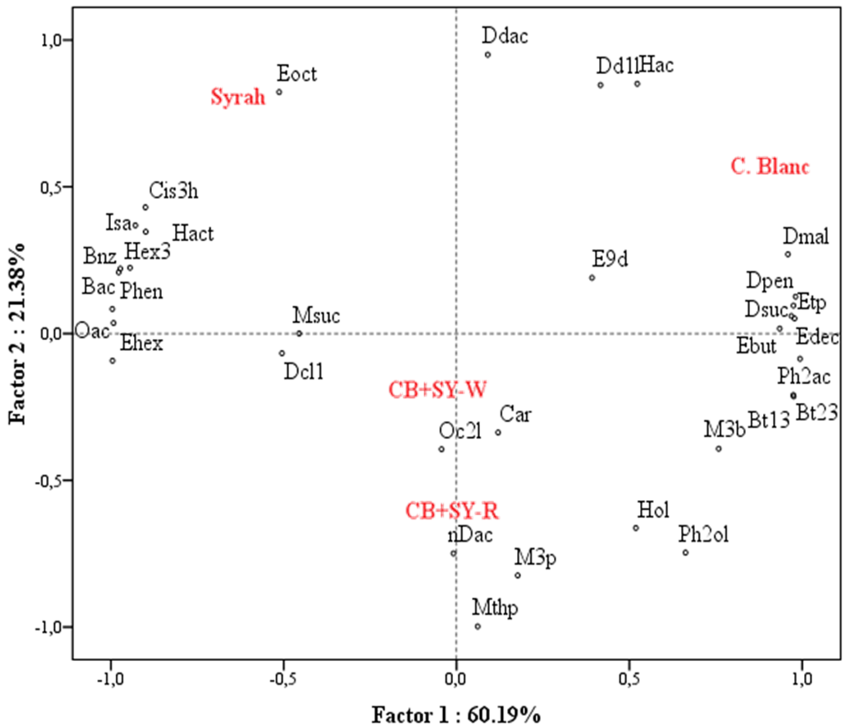

Figure 1. Principal component analysis (PCA) performed with results of volatile compounds identified in the sparkling wines produced by the traditional method in the SFV from Chenin Blanc and Syrah varieties. Legend: Carvone (Car), 3-Methyl-1-butanol (M3b), 3-methyl-1-pentanol (M3p), hexan-1-ol (Hol), 3-ethoxypropan-1-ol (Etp), (*Z*)-3-hexen-1-ol (Hex3), octan-2-ol (Oc2l), 2,3-Butanediol (Bt23), 1,3-butanediol (Bt13), decan-1-ol (Dcl1), 2-phenylethanol (Ph2ol), dodecan-1-ol (Dd1l), ethyl butanoate (Ebut), ethyl hexanoate (Ehex), ethyl octanoate (Eoct), ethyl decanoate (Edec), diethyl succinate (Dsuc), ethyl 9-decenoate (E9d), diethyl pentanedioate (Dpen), 2-phenylethyl acetate (Ph2ac), diethyl malate (Dmal), monoethyl succinate (Msuc), isoamyl acetate (Isa), hexyl acetate (Hact), *cis*-3-hexen-1-ol acetate (Cis3h), butanoic acid (Bac), hexanoic acid (Hac), octanoic acid (Oac), *n*-decanoic acid (nDac), dodecanoic acid (Ddac), 3-(methylthio)-1-propanol (Mthp), benzaldehyde (Bnz), and phenol (Phen). Sparkling wine 50% Chenin Blanc and 50% Syrah, elaborated as white (CB+SY-B), sparkling wine 50% Chenin Blanc and 50% Syrah, elaborated as rosé (CB+SY-R).

The first principal component (PC1) explained 60.19% of the total variability from GC-MS data, separating the sparkling wines produced from Chenin Blanc, located in the positive side of the *X*-axis, from the Syrah sparkling wine located in the negative side of the *X*-axis (Figure 1). It can be observed that Chenin Blanc sparkling wines were characterized principally by the volatile compounds 1,3-butanediol (Bt13), 2,3-butanediol (Bt23), 3-ethoxypropan-1-ol (Etp), 2-phenylethyl acetate (Ph2ac), diethyl succinate (Dsuc), diethyl pentanedioate (Dpen), ethyl decanoate (Edec), ethyl butanoate (Ebut), diethyl malate (Dmal), 3-methyl-1-butanol (M3b), and 2-phenylethanol (Ph2ol), which present, especially, the floral and fruity aromatic descriptors. Syrah sparkling wines were characterized by the compounds benzaldehyde (Bnz), butanoic acid (Bac), phenol (Phen), isoamyl acetate (Isa), octanoic acid (Oac), cis-3-hexen-1-ol acetate (Cis3h), ethyl hexanoate (Ehex), (z)-3-hexen-1-ol (Hex3) and hexyl acetate (Hact), whose aromatic descriptors are sweet, buttery, cheese, fruity, vegetal, oily, cherry, and pear.

The second principal component (PC2) explained 21.38% of the data variability and grouped CB+SY-W and CB+SY-R sparkling wines in the negative side of the *Y*-axis, separated from the other two varietal wines (Syrah and Chenin Blanc), located in the positive side of *Y*-axis. CB+SY-W and CB+SY-R sparkling wines were characterized by the compounds 3-(methylthio)-1-propanol and 3-methyl-1-pentanol. These results showed that blending two varieties, even different wines, one white and other rosé, volatile profile of the blends were similar and could not be distinguished.

In this study, the volatile compounds present in sparkling wines produced in the SFV using the traditional method, with the two most important varieties in the region, were determined and reported for the first time. The wines presented different characteristics whose volatile compounds allowed to discriminate between samples with specific typicality of each wine to be preliminarily described. In the next step of this research, quantitative analysis should be carried out as well as the determination of the odor activity value (OAV). In addition, the correlation of the data obtained from sensory analysis should allow improving the information obtained and better describe the sparkling wines produced by the traditional method in the SFV.

4. Conclusions

The determination of the volatile profile of sparkling wines produced from Chenin Blanc and Syrah varieties has shown that variety used can influence significantly the volatile characteristics of the sparkling wines. However, when grapes were blended, even different wines between white and rosé, they do not present specific aromatic characteristics that distinguish them.

Considering the normalized chromatographic area, the sparkling wine produced with the Chenin Blanc variety had its volatile profile mainly characterized by the presence of butane-1,3-diol, 2,3-butanediol, 2-phenethyl acetate, diethyl succinate, diethyl pentanedioate, and ethyl decanoate, with floral and fruity aromatic descriptors. The presence of 3-ethoxypropan-1-ol can be highlighted, presented in higher concentration on Chenin Blanc varietal, and also diethyl succinate. The Syrah sparkling wine showed a volatile profile related to compounds such as benzaldehyde, butanoic acid, isoamyl acetate, (*Z*)-3-hexen-1-ol, *cis*-3-hexen-1-ol acetate, and hexyl acetate, whose flavors are associated to sweet aromatic notes, butter, cheese, fruity, vegetable, oily, cherry, and pear. The sparkling wines produced from the blend between the Chenin Blanc and Syrah grape varieties (CB+SY-B and CB+SY-R) had their volatile profiles related to compounds 3-(methylthio)-1-propanol and 3-methyl-1-pentanol, which aromatic descriptors are related to vegetal, vinous, herbaceous, and cocoa aromas.

Supplementary Materials: The following are available online at http://www.mdpi.com/2306-5710/4/4/103/s1. Supplementary Table 1. Classical analysis of the base wines used in the elaboration of the sparkling wines produced by the traditional method in the SFV.

Author Contributions: Conceptualization and formal analysis: A.M.d.S.N, J.F.d.S., and G.E.P; writing and methodology: A.M.d.S.N, M.d.S.L., and G.E.P; resources: G.E.P.

Funding: This research was funded by CNPq (National Council for Scientific and Technological Development), project number 403438/2013-6, and CAPES (Coordination for the Improvement of Higher Education Personnel).

Acknowledgments: The authors would like to thank CNPq (National Council for Scientific and Technological Development) and the CAPES (Coordination for the Improvement of Higher Education Personnel). The authors also thank Miolo Wine Group for supplying grapes; UNEB, IF Sertão-PE, and UFRGS for their academic support in the study.

Conflicts of Interest: The author declares that there is no conflict of interests regarding the publication of this case study article.

References

1. Padilha, C.V.S.; Biasoto, A.C.T.; Corrêa, L.C.; Lima, M.S.; Pereira, G.E. Phenolic compounds profile and antioxidant activity of commercial tropical red wines (*Vitis vinifera* L.) from São Francisco Valley, Brazil. *J. Food Biochem.* **2016**, *41*, 1–9. [CrossRef]
2. Lima, M.S.; Silani, I.S.V.; Toaldo, I.M.; Correa, L.C.; Biasoto, A.C.T.; Pereira, G.E.; Bordignon-Luiz, M.T.; Ninow, J.L. Phenolic compounds, organic acids and antioxidant activity of grape juices produced from new Brazilian varieties planted in the Northeast Region of Brazil. *Food Chem.* **2014**, *161*, 94–103. [CrossRef] [PubMed]
3. Pereira, G.E.; Padilha, C.; Marques, A.T.B.; Canuto, K.M.; Mendes, A.; Souza, J.F. Le poids des consommateurs sur l'evolution des vins: L'exemple de la Vallee Du Sao Francisco, Bresil. In *Vin et Civilisation lês étapes*

de l'humanisation; Perard, J., Perrot, M., Eds.; Centre Georges Chevrier: Dijon, France, 2016; pp. 301–310, ISBN 978-2-918173-19-9.
4. Tonietto, J.; Pereira, G.E. A concept for the viticulture of "tropical wines". In Proceedings of the IXTH International Terroir Congress, Dijon and Reims, France, 25–29 June 2012; pp. 34–37.
5. Camargo, U.A.; Pereira, G.E.; Guerra, C.C. Wine grape cultivars adaptation and selection for tropical wines. *Acta Hortic.* **2011**, *919*, 121–129. [CrossRef]
6. Ribéreau-Gayon, P.; Glories, Y.; Maujean, A.; Dubourdieu, D.; Donéche, B.; Lonvaud, A. *Handbook of Enology. The Chemistry of Wine and Stabilization and Treatments*, 2nd ed.; Wiley & Sons: Bordeaux, France, 2006; Volume 2, p. 451, ISBN 978-0-470-01037-2.
7. Herrero, P.; Sáenz-Navajas, P.; Culleré, L.; Ferreira, V.; Chatin, A.; Chaperon, V.; Litoux-Desrues, F.; Escudero, A. Chemosensory characterization of Chardonnay and Pinot Noir base wines of Champagne. Two very different varieties for a common product. *Food Chem.* **2016**, *207*, 239–250. [CrossRef] [PubMed]
8. Welke, J.E.; Zanus, M.; Lazzarotto, M.; Pulgati, F.H.; Zini, C.A. Main differences between volatiles of sparkling and base wines accessed through comprehensive two dimensional gas chromatography with time-of-flight mass spectrometric detection and chemometric tools. *Food Chem.* **2014**, *164*, 427–437. [CrossRef] [PubMed]
9. Torrens, J.; Riu-Aumatell, M.; Vichi, S.; López-Tamames, E.; Buxaderas, S. Assessment of Volatile and Sensory Profiles between Base and Sparkling Wines. *J. Agric. Food Chem.* **2010**, *58*, 2455–2461. [CrossRef] [PubMed]
10. Carlin, S.; Vrhovsek, U.; Franceschi, P.; Lotti, C.; Bontempo, L.; Camin, F.; Toubiana, D.; Zottele, F.; Toller, G.; Fait, A.; et al. Regional features of northern Italian sparkling wines, identified using solid-phase micro-extraction and comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry. *Food Chem.* **2016**, *208*, 68–80. [CrossRef]
11. Welke, J.E.; Manfroi, V.; Zanus, M.; Lazzarotto, M.; Zini, C.A. Differentiation of wines according to grape variety using multivariate analysis of comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection data. *Food Chem.* **2013**, *141*, 3897–3905. [CrossRef]
12. Caliari, V.; Burin, V.M.; Rosier, J.P.; Bordignon-Luiz, M.T. Aromatic profile of Brazilian sparkling wines produced with classical and innovative grape varieties. *Food Res. Int.* **2014**, *62*, 965–973. [CrossRef]
13. Welke, J.E.; Zanus, M.; Lazzarotto, M.; Zini, C.A. Quantitative analysis of headspace volatile compounds using comprehensive two-dimensional gas chromatography and their contribution to the aroma of Chardonnay wine. *Food Res. Int.* **2014**, *59*, 85–99. [CrossRef]
14. Caliari, V.; Panceri, C.P.; Rosier, J.P.; Bourdignon-Luiz, M.T. Effect of the Traditional, Charmat and Asti method production on the volatile composition of Moscato Giallo sparkling wines. *LWT Food Sci. Technol.* **2015**, *61*, 393–400. [CrossRef]
15. OIV. *Compendium of International Methods of Analysis of Vines and Musts*; OIV: Paris, France, 2016; Volume 2, 504p, ISBN 979-10-91799-47-8.
16. Singleton, V.L.; Rossi, J.A. Colorimetry of total phenolics with phosphomolybdic–phosphotungstic acid reagents. *Am. J. Enol. Viticult.* **1965**, *16*, 144–158.
17. Glories, Y. La couleur des vins rouges. 2ème partie mesure, origine et interpretation. *Journal International des Sciences de la vigne et du vin* **1984**, *18*, 253–271.
18. Re, R.; Pellegrini, N.; Proteggente, A.; Pannala, A.; Yang, M.; Rice-Evans, C. Antioxidant activity applying an improved ABTS radical cation decolorization assay. *Free Radic. Biol. Med.* **1999**, *26*, 1231–1237. [CrossRef]
19. Kim, Y.K.; Guo, Q.; Packer, L. Free radical scavenging activity of red ginseng aqueous extracts. *Toxicology* **2002**, *172*, 149–156. [CrossRef]
20. Welke, J.E.; Manfroi, V.; Zanus, M.; Lazarotto, M.; Zini, C.A. Characterization of the volatile profile of Brazilian Merlot wines through comprehensive two dimensional gas chromatography time-of-flight mass spectrometric detection. *J. Chromatogr. A* **2012**, *1226*, 124–139. [CrossRef] [PubMed]
21. Massart, D.L.; Vandeginste, B.G.M.; Buydens, S.J.; Lewi, P.J.; Smeyers-Verbeke, J. *Handbook of Chemometrics and Qualimetrics—Parte B*; Elsevier: Amsterdam, The Netherlands, 1997; p. 713, ISBN 9780080887036.
22. Von Muhlen, C.; Zini, C.A.; Caramão, E.B.; Marriott, P.J. Comparative study of *Eucalyptus dunnii* volatile oil composition using retention indices and comprehensive two-dimensional gas chromatography coupled to time-of-flight and quadrupole mass spectrometry. *J. Chromatogr. A* **2008**, *1200*, 34–42. [CrossRef]
23. Ruiz-Moreno, M.J.; Muñoz-Redondo, J.M.; Cuevas, F.J.; Marrufo-Curtido, A.; León, J.M.; Ramírez, P.; Moreno-Rojas, J.M. The influence of pre-fermentative maceration and ageing factors on ester profile and marker determination of Pedro Ximenez sparkling wines. *Food Chem.* **2017**, *230*, 697–704. [CrossRef]

24. Wang, J.; Huo, S.; Zhang, Y.; Liu, Y.; Fan, W. Impact of various maceration techniques on the phenolic and volatile composition of Chenin Blanc wines. *Int. J. Food Sci. Technol.* **2016**, *51*, 2360–2366. [CrossRef]
25. Chin, S.T.; Eyresb, G.T.; Marriotta, P.J. Cumulative solid phase microextraction sampling for gas chromatography-olfactometry of Shiraz wine. *J. Chromatogr. A* **2012**, *1255*, 221–227. [CrossRef]
26. Gurbuz, O.; Rouseff, J.M.; Rouseff, R.L. Comparison of aroma volatiles in commercial Merlot and Cabernet Sauvignon wines using gas chromatography—Olfactometry and gas chromatography—Mass spectrometry. *J. Agric. Food Chem.* **2006**, *54*, 3990–3996. [CrossRef] [PubMed]
27. Selli, S.; Canbas, A.; Cabaroglu, T.; Erten, H.; Gunata, Z. Aroma components of cv. Muscat of Bornova wines and influence of skin contact treatment. *Food Chem.* **2006**, *94*, 319–326. [CrossRef]
28. Osorio, C.; Alarcon, M.; Moreno, C.; Bonilla, A.; Barrios, J.; Garzon, C.; Duque, C. Characterization of Odor-Active Volatiles in Champa (*Campomanesia lineatifolia* R. P.). *J. Agric. Food Chem.* **2006**, *54*, 509–516. [CrossRef] [PubMed]
29. Ledauphin, J.; Saint-Clair, J.F.; Lablanquie, O.; Guichard, H.; Founier, N.; Guichard, E.; Barillier, D. Identification of trace volatile compounds in freshly distilled calvados and cognac using preparative separations coupled with gas chromatography-mass spectrometry. *J. Agric. Food Chem.* **2004**, *52*, 5124–5134. [CrossRef] [PubMed]
30. Shimoda, M.; Wu, Y.; Osajima, Y. Aroma compounds from aqueous solution of Haze (Rhus succedanea) honey determined by adsorptive column chromatography. *J. Agric. Food Chem.* **1996**, *44*, 3913–3918. [CrossRef]
31. Wada, K.; Shibamoto, T. Isolation and identification of volatile compounds from a wine using solid phase extraction, gas chromatography, and gas chromatography/mass spectrometry. *J. Agric. Food Chem.* **1997**, *45*, 4362–4366. [CrossRef]
32. Botelho, G.; Caldeira, I.; Mendes-Faia, A.; Clímaco, M.C. Evaluation of two quantitative gas chromatography-olfactometry methods for clonal red wines differentiation. *Flavour Fragance J.* **2007**, *22*, 414–420. [CrossRef]
33. Gauvin, A.; Lecomte, H.; Smadja, J. Comparative investigations of the essential oils of two scented geranium (*Pelargonium* spp.) cultivars grown on Reunion Island. *Flavour Fragance J.* **2004**, *19*, 455–460. [CrossRef]
34. Santos, A.P.C.; Vanderlinde, R.; Machado, B.A.S.; Mamede, M.E.O. Improving production of aromatic compounds by indigenous yeasts in Chenin Blanc grape must. *Afr. J. Agric. Res.* **2016**, *11*, 2433–2442. [CrossRef]
35. Ubeda, C.; Callejón, R.M.; Troncoso, A.M.; Peña-Neira, A.; Morales, M.L. Volatile profile characterisation of Chilean sparkling wines produced by traditional and Charmat methods via sequential stir bar sorptive extraction. *Food Chem.* **2016**, *207*, 261–271. [CrossRef]
36. Condurso, C.; Cincotta, F.; Tripodi, G.; Sparacio, A.; Giglio, D.M.L.; Verzera, A. Effects of cluster thinning on wine quality of Syrah cultivar (*Vitis vinifera* L.). *Eur. Food Res. Technol.* **2016**, *242*, 1719–1726. [CrossRef]
37. Ferreira, A.C.S.; Rodrigues, P.; Hogg, T.; De Pinho, P.G. Influence of some technological parameters on the formation of dimethyl sulfide, 2-mercaptoethanol, methionol, and dimethyl sulfone in Port Wines. *J. Agric. Food Chem.* **2003**, *51*, 727–732. [CrossRef] [PubMed]
38. Wang, J.; Capone, D.L.; Wilkinson, K.L.; Jeffery, D.W. Chemical and sensory profiles of rosé wines from Australia. *Food Chem.* **2016**, *196*, 682–693. [CrossRef] [PubMed]
39. Shinohara, T. Gas chromatographic analysis of volatile fatty acids in wines. *Agric. Biol. Chem.* **1985**, *49*, 2211–2212. [CrossRef]
40. Kinzurik, M.I.; Herbst-Johnstone, M.; Gardner, R.C.; Fedrizzi, B. Evolution of Volatile Sulfur Compounds during Wine Fermentation. *J. Agric. Food Chem.* **2015**, *36*, 8017–8024. [CrossRef] [PubMed]
41. Noguerol-Pato, R.; Gonzalez-Barreiro, C.; Cancho-Grande, B.; Simal-Gandara, J. Quantitative determination and characterisation of the main odourants of Mencia monovarietal red wines. *Food Chem.* **2009**, *117*, 473–484. [CrossRef]
42. Zhang, M.; Pan, Q.; Yan, G.; Duan, C. Using headspace solid phase micro-extraction for analysis of aromatic compounds during alcoholic fermentation of red wine. *Food Chem.* **2011**, *125*, 743–749. [CrossRef]