processes

Article

Changes in Volatile Compounds during Grape Brandy Production from '*Cabernet Sauvignon*' and '*Syrah*' Grape Varieties

Ante Lončarić [1,*], Mićo Patljak [1], Ante Blažević [1], Antun Jozinović [1], Jurislav Babić [1], Drago Šubarić [1], Anita Pichler [1], Ivana Flanjak [1], Toni Kujundžić [2] and Borislav Miličević [1]

[1] Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, Franje Kuhača 18, HR 31000 Osijek, Croatia; mpatljak@ptfos.hr (M.P.); ablazevic@ptfos.hr (A.B.); antun.jozinovic@ptfos.hr (A.J.); jurislav.babic@ptfos.hr (J.B.); drago.subaric@ptfos.hr (D.Š.); anita.pichler@ptfos.hr (A.P.); ivana.flanjak@ptfos.hr (I.F.); borislav.milicevic@ptfos.hr (B.M.)

[2] Faculty of Agrobiotechnical Sciences Osijek, Josip Juraj Strossmayer University of Osijek, Vladimira Preloga 1, HR 31000 Osijek, Croatia; toni.kujundzic@fazos.hr

* Correspondence: ante.loncaric@ptfos.hr; Tel.: +385-31-244-350

Abstract: Grape-based brandies are one of the most popular alcoholic beverages in the world. The most popular one, Cognac, comes from the Charentes region of Southwest France, and it is mostly produced from the grape variety '*Ugni Blanc*'. However, wines destined for the elaboration of wine spirits also come from different white grape varieties; '*Colombard*', '*Folle Blanche*', '*Montils*', and '*Semillon*'. In this study, the possibility of using the red grape varieties '*Cabernet Sauvignon*' and '*Syrah*' was investigated with an emphasis on the change of volatile compounds during the production process. During production, some specific volatile compounds such as 2-hexenal, 3-octanone, isopropyl myristate, ethyl palmitate, ethyl oleate, phenethyl acetate, 1-hexanol, and β-damascenone could be attributed to the primary aroma generated from the grape varieties. During the vinification and fermentation process, the development of ethyl hexanoate, ethyl octanoate, 3-methylbutanol, acetic acid, and octanoic acid occurred. Finally, 3-methylbutanol and predominant esters, ethyl hexanoate, ethyl octanoate, ethyl decanoate, and ethyl laurate, were generated during the distillation and maturation process. The composition and concentration of determined predominant esters in produced brandies suggest that both brandies have volatile profiles comparable to some of the world's most popular brandies.

Keywords: grape brandy; '*Cabernet Sauvignon*'; '*Syrah*'; volatile profile; GC-MS

check for updates

Citation: Lončarić, A.; Patljak, M.; Blažević, A.; Jozinović, A.; Babić, J.; Šubarić, D.; Pichler, A.; Flanjak, I.; Kujundžić, T.; Miličević, B. Changes in Volatile Compounds during Grape Brandy Production from '*Cabernet Sauvignon*' and '*Syrah*' Grape Varieties. *Processes* **2022**, *10*, 988. https://doi.org/10.3390/pr10050988

Academic Editor: Jasna Čanadanović-Brunet

Received: 28 April 2022
Accepted: 13 May 2022
Published: 16 May 2022

1. Introduction

According to the European Union legislation, brandy is a spirit drink (alcoholic beverage) produced from wine spirit, whether or not wine distillate is added, distilled at less than 94.8% (*v*/*v*), provided that the distillate does not exceed a maximum of 50% of the alcoholic content of the finished product [1]. Grape brandies should age for at least 6 months in oak casks smaller than 1000 litres in capacity or 12 months with oak receptacles [2]. The most famous wine spirits (French: *eau-de-vie de vin*) are Cognac and Armagnac. Cognac is produced in the Charentes region of Southwest France, and it is produced mostly from the '*Ugni Blanc*' grape variety. However, wines destined for the elaboration of wine spirits also come from different white grape varieties: '*Colombard*', '*Folle Blanche*', '*Montils*', and '*Semillon*'. Cognac is a double-distilled spirit produced in a pot still, while Armagnac distillation takes place in alembic Armagnacais, a continuous column still with 5–15 plates [2]. Besides having those two brandies regulated by more strict regulations, grape brandy is produced all over the world: Spanish brandies from the region of Jeres, South American brandy Pisco from Peru and Chile, and German brandy, which is called weinbrand, etc. [3–5]. All these brandies are produced from different grape varieties. '*Cabernet Sauvignon*' and '*Syrah*' are the main wine grape varieties.

'*Cabernet Sauvignon*' is the most widely planted grape variety around the world [6]. It produces wines with blackcurrant and green bell pepper notes and mint and cedar notes in cooler climates. Wine from moderate climates sees blackcurrant, black cherry, and black olive notes, while the current flavours can become 'jammy' in very hot climates [7]. '*Syrah*' is a dark-skinned grape variety grown throughout the world, primarily to produce red wine. Moderate climates (such as the northern Rhone Valley and parts of Washington State) tend to make medium to full-bodied wines with medium-plus to high levels of tannins and notes of blackberry, mint, and black pepper. '*Syrah*' from hot climates such as Crete and the Barossa Valley and McLaren Vale regions of Australia are more consistently full-bodied with softer tannins, jammier fruit, and spicy notes of liquorice, anise, and earthy leather [8].

The quality of the wine spirit from which brandy is produced depends on many factors during the production process; however, we can distinguish the following: primary aroma substances which are generated from the grape varieties; secondary aroma substances generated during the vinification and fermentation process following the aroma substances generated during the distillation and maturation process [9]. The main aroma compounds of grapes belong to the chemical classes of terpenols, linalool, geraniol, nerol, etc.; norisoprenoids, β-damascone, β-damascenone, etc., and benzenoids, β-phenylethanol, methyl salicylate, etc. [10]. Volatiles originating from the fermentation process are mainly constituted by alcohols, 2-methyl-1-propanol, β-phenylethanol, isoamyl alcohols formed by the Ehrlich pathway and fruity esters, such as ethyl esters and acetates, ethyl hexanoate, octanoate, and decanoate, isoamyl acetates [10]. Moreover, other volatiles such as acetals, ethoxy derivatives, and other terpenols such as α-terpineol, terpinen-4-ol are formed by the hydrolytic reactions which occur during distillation and that are promoted by the high ethanol content and temperature [11]. Regarding the first factor, the preferred grape varieties for wine spirit production are the ones that are rich in fruit acids, fruit-associated neutral aroma compounds and with higher yields. Grape acids, predominantly tartaric acid, act as a natural preservative, which is necessary since sulphur dioxide should not be added to musts and wines during wine spirit production. Musts and wines are not treated with sulphur dioxide since, later, it could be transferred into the distillate and thus decrease its quality by neutralising the aromatic perception [12,13]. Grape with a fruit-associated neutral aroma is favoured for the production of wine spirits since the utilisation of such grapes ensures cost-effectiveness in the production of wine spirits. All these parameters are largely controlled by the growing season and other atmosphere-driven conditions, such as growing season length, radiation levels, winter minimum temperatures, and spring and fall frosts [14]. A study conducted by Costa et al. [14] used a long-time series of biochemical data in field conditions for many berry quality aspects (berry weight, titratable acidity, pH, potential alcohol, anthocyanins, and total phenols index) over a long period of time (6–19 years). They concluded that at berry maturity, high temperatures tend to decrease berry weight, titratable acidity, anthocyanins, and total phenols index and increase pH and potential alcohol. These outcomes are in line with previous findings. For example, in cooler years, the titratable acidity levels are frequently higher; thus, the grapes become undesirable for the production of high-quality wines [15]. This can be explained by the increased respiration of tartaric and malic acids at increased temperatures, thus leading to a drop in titratable acidity and increased pH [16]. Sugar and total soluble solids accumulation are also lower in cooler and rainier years, which may result in lower potential alcohol levels in the final product [6,14,17–20]. It is obvious that unfavourable climatic conditions can lead to the unfavourable quality of grapes intended for wine production, in which case the production of wine spirit may be an option.

The aim of this study was to investigate the possibility of the production of grape brandy from atypical grape varieties for grape brandy production. Hence, the present study aims to determine the changes in volatile compounds during grape brandy production from '*Cabernet Sauvignon*' and '*Syrah*' grape varieties.

2. Materials and Methods

2.1. Grape Varieties

'*Cabernet Sauvignon*' and '*Syrah*' grapes (*Vitis vinifera* L.) were sourced at cultivation area Nature Park Papuk, Kutjevo vineyard, Croatia. Grapes were hand-harvested at commercial maturity. Sampling of the must, base wine, wine spirit, and brandy for each variety was conducted.

2.2. Base Wine Production

The base wines were produced in the Polytechnic Požega winery. After hand harvesting the grapes, the musts were obtained by pressing without the addition of sulphur dioxide and pectolytic enzymes. The musts were immediately transferred into vats for fermentation (34 L) and fermented for 27 days with commercial *Saccharomyces bayanus* wine yeasts, SIHA Active Yeast 10 (EATON, France) in glass containers at temperatures between 17 and 19 °C. Commercial yeast nutrient Bio Yeast cell walls (EATON, France) in the amount of 30 g/hL were utilised. The physicochemical parameters of musts and wines are presented in Tables 1 and 2. The produced base wine was used for distillation.

Table 1. Physicochemical parameters of musts.

	'*Cabernet Sauvignon*'	**'*Syrah*'**
Soluble solids content (°Oe)	94.00	90.00
pH	3.32	3.52
Total acidity (g/L)	9.00	7.50

Table 2. Standard physicochemical parameters of base wines.

	'*Cabernet Sauvignon*'	**'*Syrah*'**
φ (alcohol)/%	13.18	12.63
γ (total dry extract) (g/L)	30.70	26.90
γ(reducing sugars) (g/L)	2.64	2.78
Total acidity/(g/L)	7.35	6.60
Volatile acidity (g/L)	0.72	0.62
Non-volatile acidity (g/L)	6.13	5.98
pH	3.41	3.54
γ (free SO_2) (mg/L)	-	-
γ(total SO_2) (mg/L)	-	-

2.3. Distillation

For both base wines ('*Cabernet Sauvignon*' and '*Syrah*'), double distillation, also known as '*à repasse*', was implemented. The distillation process is described in Table 3. The distillation was carried out in a stainless steel distillation device controlled with a microprocessor PID controller with universal input. The capacity of the device is 20 L/h, and it is heated by electric heaters with a total power of 15 kW.

2.4. Aging

The obtained wine spirits were aged in small barrique oak barrels (3 L), seasoned with '*Cabernet Sauvignon*' or '*Syrah*' wines. The wine spirit (55% vol. of alcohol) was aged for six months, during which samples for the determination of volatile compounds were taken every month.

Table 3. Distillation process.

	1st Distillation	
	'Cabernet Sauvignon'	*'Syrah'*
Volume (mL)	28,720.00	27,000.00
'heads' (mL)	143.50	133.00
φ (alcohol)/%	68.00	64.00
'heart' (mL)	7525.00	7800.00
φ (alcohol)/%	39.02	39.00
'tails' (mL)	1105.00	1065.00
	2nd distillation	
Volume (mL)	7525.00	7800.0
'heads' (mL)	73.00	78.00
φ (alcohol)/%	85.00	85.00
'heart' (mL)	3300.00	3200.00
φ (alcohol)/%	74.00	72.00
'tails' (mL)	965.00	1000.00
φ (alcohol)/%	26.00	24.00
Recovery (%) of Ethanol	64.55	67.57

2.5. Chemical Composition Analysis of Musts and Base Wine

Reducing sugars in wine and retentates were determined according to the Luff-Schoorl method. Free and total SO_2 were measured by titration with iodine and starch as indicators. Titration with 0.25 mol/L NaOH was applied for total acids measurement and 0.1 mol/L NaOH for volatile acids determination with phenolphthalein indicator. Total acids were expressed as the g/L of tartaric acid and volatile acids as the g/L of acetic acid [21]. Alcohol content and total extract were measured on an Electronic hydrostatic balance Super Alcomat (Gibertini Elettronic, Milano, Italy) and digital distilling unit Super Dee (Gibertini Elettronic, Milano, Italy).

2.6. GC-FID Analysis of Primary Volatile Compounds

The ethanol content in the analysed samples was determined according to the method of Wang et al. [22], while other identified volatile compounds (methanol, acetaldehyde, ethyl acetate, 2-methylpropanol, 2-butanol, and isoamyl alcohol) were determined as described in Annex 1 (method III.2. The determination of other volatile compounds by gas chromatography: aldehydes, higher alcohols, ethyl acetate, and methanol) of Ordinance on analytical methods for spirits and alcoholic beverages [23]. Analysis of primary volatile compounds was performed on a Shimadzu GC-2010 Plus gas chromatograph equipped with a flame ionisation detector (FID). Qualitative and quantitative analysis was conducted using LabSoultion GCsolution (Release 2.41SU1) software. Separation of volatile compounds was achieved on the InertCap Pure-Wax GC column (30 m, 0.53 mm i.d. and 1.0 µm thick stationary phase) using nitrogen as the carrier gas with a flow rate of 2.42 mL/min. Injector and FID detector temperatures were set at 250 °C and 260 °C, respectively. The injection volume was 1 µL with a split ratio of 1:10. An initial column temperature of 45 °C was held for 8 min and then gradually increased by 15 °C min^{-1} until the final temperature of 200 °C was reached. The final temperature was held for 5 min. Identification of separated compounds was based on the retention times and comparison with retention times of pure components. For quantitative analysis, an internal standard method was applied, using acetonitrile (purity $\geq$ 99.9%, J.T. Baker, Deventer, The Netherlands) as an internal standard for ethanol determination and 1-pentanol (purity $\geq$ 99.8%, Dr. Ehrenstorfer, Augsburg, Germany) as an internal standard for determination of other identified volatile compounds. All analyses were carried out in duplicate. Ethanol content was expressed as alcoholic strength (% vol), and the content of other volatile compounds was expressed as milligrams per litre of pure alcohol at 100% vol (mg/L a.a.).

2.7. Gas Chromatography–Mass Spectrometry (GC/MS) Analysis

Volatile compounds in samples were analysed using an Agilent 7890B gas chromatograph with an Agilent 5977A mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). Sample preparation was conducted with solid-phase microextraction (SPME), where 1 g of sodium chloride was mixed with 5 mL of sample in a 10 mL glass vial. Before extraction, 5 µL of myrtenol (Merck KGaA, Darmstadt, Germany) (1 mg/L) as an internal standard were added to each sample. Such pre-pared vials were closed and set on a magnetic stirrer (300 rpm) and heated at 40 °C. In vial headspace, SPME fibre (polydimethylsiloxane/divinylbenzene sorbent, 65 µm, Supelco, Bellefonte, PA, USA) was inserted. After 45 min of adsorption, the SPME fibre was transferred in the GC injection port for 7 min at 250 °C. The volatiles were desorbed at splitless mode into the HP-5MS column (30 m × 0.25 mm × 0.25 µm). The temperature gradient was as follows: from 40 °C (held 10 min) to 120 °C at 3 °C/min; to 250 °C at 10 °C/min. For each compound, the linear retention index was calculated [24] using C7–C30 saturated alkanes standards analysed under the same GC/MS conditions. Samples were analysed in triplicate, and the results were expressed as an average value.

3. Results and Discussion

3.1. Musts

For the production of base wines, typically, non-aromatic grape varieties with higher acidity and lower sugar content are preferred. The soluble solids content of '*Cabernet Sauvignon*' (CS) and '*Syrah*' (SY) musts were 245.69 g/L and 235.13 g/L, while total acidity was 9.0 and 7.5 g/L, respectively (Table 1). The soluble solids content of the examined musts was relatively higher than recommended for the production of base wines, which was around 80 °Oe (208.77 g/L of sugars), meaning that this must will produce base wine with a higher percentage of alcohol. The total acidity of musts was in the range that is recommended (6–10 g/L) [25]. The volatile profile of CS and SY musts is presented in Table 4. A total of 45 volatile compounds were detected in '*Cabernet Sauvignon*' or '*Syrah*' musts which could be classified as: aldehydes and ketones, esters, alcohols, terpenes, acids, furans, volatile phenols, and aromatic compounds. Many of these volatile compounds are commonly found in musts and are derived from grapes [11,26]. Alcohols are the main volatile compounds found in musts, with 1-hexanol as the predominant alcohol found in both CS (431.39 µg/L) and SY (355.9 µg/L). The alcohol profiles of the SY must with seven types of alcohols were more diverse than that of CS must, which only contained two types of alcohols. All identified alcohols are specific and can be found in musts from these grape varieties [8,26]. The ester profile is also different in the type and amount of esters present in musts. In general, the SY must contained higher content and a higher number of esters when compared with CS. The most common ester in CS was isopropyl myristate, followed by phenthyl acetate and 1-hexyl acetate (24.69, 22.56, and 19.28 µg/L, respectively). In SY must, ethyl palmitate (49.93 µg/L) was the dominant ester, followed by ethyl 2-hexenoate (27.15 µg/L) and ethyl oleate (23.92 µg/L). The composition of aldehyde and ketones varied between the examined musts; however, the total concentration was similar, 51.43 µg/L for CS and 51.01 µg/L for SY must. The concentration of acids in the musts was low and ranged within 31.77–11.91 µg/L. Terpenes and norisoprenoides ranged within 128.29–70.91 µg/L in CS and SY musts, respectively. The β-damascenone was the main compound found in this group. Considering aromatic compounds, the SY must contain a considerably higher concentration of total aromatic compounds compared with CS must. The main aromatic compound in SY must was 2-phenylethanol, whose odour is described as flowery, pollen, and perfume [26]. Furthermore, unripe grapes and continuous presses may induce herbaceous character by liberating compounds, such as hexanols (1-hexanol and 2-hexanol) and hexenols (cis-3- hexene-1-ol, trans-2-hexen-1-ol, cis-2-hexen-1-ol). 1-octen-3-ol is characterised by a mushroom odour, and it is found in grapes infected by *Botrytis cinerea*. The β-damascenone is a norisoprenoide that is naturally present in grapes, and it is a highly odoriferous compound with a powerful and pleasant fragrance providing a fruity–flowery and honey-like character [13].

Table 4. Volatile compounds (μg/L) identified in '*Cabernet Sauvignon*' and '*Syrah*' musts.

Compound	'*Cabernet Sauvignon*'	'*Syrah*'
Alcohols		
3-methylbutanol	n.d. *	99.13 ± 2.5
1-hexanol	431.39 ± 29.27	355.90 ± 19.16
1-octen-3-ol	n.d.	40.87 ± 3.9
3-octanol	n.d.	21.95 ± 0.42
1-octanol	n.d.	16.17 ± 0.85
Hotrienol	n.d.	49.40 ± 6.59
Dodecanol	6.73 ± 0.13	5.58 ± 0.23
Total	**438.12**	**589.00**
Aldehydes and ketones		
2-hexenal	35.96 ± 5.36	n.d.
Benzeneacetaldehyde	8.39 ± 0.42	13.09 ± 0.21
3-octanone	n.d.	24.41 ± 1.25
Decanal	n.d.	9.04 ± 0.3
Dodecanal	4.61 ± 0.23	4.47 ± 0.28
Alpha-hexylcinnamic aldehyde	2.47 ± 0.18	n.d.
Total	**51.43**	**51.01**
Esters		
Ethyl hexanoate	n.d.	23.60 ± 2.72
1-hexyl acetate	19.28 ± 0.83	13.67 ± 2.04
Ethyl 2-hexenoate	n.d.	27.15 ± 2.6
Ethyl palmitate	n.d.	49.93 ± 1.15
Ethyl linoleate	n.d.	23.05 ± 1.34
Ethyl oleate	n.d.	23.92 ± 0.59
Ethyl myristate	n.d.	4.22 ± 0.44
Isopropyl myristate	24.69 ± 0.35	14.22 ± 1.46
Ethyl laurate	n.d.	19.80 ± 0
Phenethyl acetate	22.56 ± 1.95	n.d.
Ethyl decanoate	n.d.	4.20 ± 0.01
Total	**66.53**	**203.76**
Terpenes and norisoprenoides		
Linalool	9.40 ± 0.49	10.71 ± 0.38
Gamma-terpinene	n.d.	11.42 ± 0.34
β-damascenone	97.93 ± 1.73	23.04 ± 1.27
Geranyl acetone	9.94 ± 0.71	8.30 ± 0.23
Trans-Caryophyllene	n.d.	8.60 ± 0.16
α-ionone	1.74 ± 0.21	n.d.
β-ionone	2.66 ± 0.35	3.71 ± 0.32
Perilla alcohol	6.65 ± 0.08	5.13 ± 0.39
Total	**128.29**	**70.91**
Acids		
Hexanoic acid	8.64 ± 0.72	n.d.
Nonanoic acid	11.61 ± 0.62	5.48 ± 0.24
Decanoic acid	7.96 ± 0.74	6.43 ± 0.13
Dodecanoic acid	1.60 ± 0.11	n.d.
Tetradecanoic acid	1.97 ± 0.02	n.d.

Table 4. *Cont.*

Compound	*'Cabernet Sauvignon'*	*'Syrah'*
Total	**31.77**	**11.91**
Furans		
Phellandral	5.84 ± 0.35	n.d.
Total	5.84	0
Volatile phenols		
4-ethyl phenol	n.d.	183.58 ± 12.54
4-vinylphenol	n.d.	14.40 ± 0.09
Total	**0.00**	**197.98**
Aromatic compounds		
Benzaldehyde	n.d.	9.34 ± 0.98
2-phenylethanol	n.d.	180.50 ± 6
Nonanone	6.55 ± 0.09	4.11 ± 0.47
p-cymene	7.56 ± 0.47	22.76 ± 2.43
Dihydro-methyl-jasmonate	6.82 ± 0.11	4.80 ± 0.22
Total	**20.93**	**221.51**

* n.d.—not detected.

3.2. Base Wines

After the fermentation, the base wines were obtained. The standard physicochemical parameters of base wines are provided in Table 2. The overall results are in agreement with measurements carried out by other authors for CS and SY wines [27–30]; however, the results do not include the detection of free and total sulphur dioxide since it was not added during the production of base wines. In the '*Cabernet Sauvignon*' and '*Syrah*' base wines, 23 volatile compounds were detected (Table 5). Alcohols represented the largest group in terms of concentration of aroma compounds identified in both base wines. 3-methylbutanol was the most predominant alcohol in both CS (10,498.70 µg/L) and SY (8442.74 µg/L) base wines. Esters were the second largest group found in base wines, and total concentrations were in the 6593.37–4562.83 µg/L range. The most predominant esters were ethyl octanoate (1648.75–1408.73 µg/L) and ethyl hexanoate (2041.08–1977.14 µg/L); both esters are commonly found in CS and SY wines and contribute to the aroma of fruity, anis, pineapple, pear, and floral odour [8,26]. Acids ranged within 5487.88–3791.03 µg/L, and octanoic acid had the highest concentration in both base wines CS (3963.74 µg/L) and SY (1865.10 µg/L). The octanoic acid has a rancid, harsh, and cheesy odour, and it is commonly found in CS and SY wines [8,26]. The high content of organic acids in base wines for brandy production contributes not only to protection from microbial spoilage and the negative effect of oxidative processes but also to the intensification of ester formation during distillation, which is important for creating a brandy bouquet [31]. 2-phenylethanol was the main aromatic compound found in CS (1101.44 µg/L) and SY (1154.43 µg/L) base wines. 2-phenylethanol together with phenethyl acetate were considered to be responsible for the "rose" in brandies [32].

3.3. Wine Spirit

The changes in volatile compounds during the first and second distillation are provided in Table 6. The predominant esters in the first CS distillate were ethyl octanoate (6630.85 µg/L), phenethyl acetate (7145.27 µg/L), and ethyl decanoate (5792.73 µg/L), while in the SY distillate, the predominant esters were isoamyl acetate (3127.2 µg/L), ethyl octanoate (5997.03 µg/L), and ethyl decanoate (2499.78 µg/L). The main alcohol in both distillates was 3-methylbutanol, with a concentration of 31,173.29 and 85,481.35 µg/L for CS and SY, respectively. Considering acids in CS distillate, decanoic acid and myristic acid were found, while in SY distillate, only acetic acid was found. The second distillation caused a decrease in total ester concentration by 57.82% and 64.11% and in total alcohol concentration by 19.79% and 9.43% in the CS and SY distillate, respectively.

Table 5. Volatile compounds (μg/L) identified in '*Cabernet Sauvignon*' and '*Syrah*' base wines.

Compound	'*Cabernet Sauvignon*'	'*Syrah*'
Alcohols		
3-methylbutanol	10,498.70 ± 93.32	8442.74 ± 360.6
1-hexanol	226.47 ± 61.74	153.43 ± 0.69
2,3-butanediol	692.05 ± 105.59	319.85 ± 87.05
Total	**11,417.22**	**8916.02**
Esters		
Ethyl acetate	646.82 ± 12.76	344.03 ± 0.99
Ethyl hexanoate	2041.08 ± 107.86	1977.14 ± 20.37
Ethyl octanoate	1648.75 ± 1.45	1408.73 ± 0.30
Ethyl palmitate	489.90 ± 32.02	205.57 ± 6.70
Isoamyl acetate	374.94 ± 42.51	n.d. *
Ethyl myristate	121.34 ± 13.86	82.14 ± 0.74
Isopropyl myristate	188.23 ± 7.77	216.46 ± 10.43
Ethyl laurate	880.41 ± 45.65	247.63 ± 0.16
Phenethyl acetate	201.90 ± 10.07	81.13 ± 2.45
Total	**6593.37**	**4562.83**
Terpenes		
Linalool	276.59 ± 8.67	n.d.
β-damascenone	17.93 ± 1.41	18.56 ± 0.43
Total	**294.52**	**18.56**
Acids		
Acetic acid	514.15 ± 41.44	175.38 ± 1.85
Hexanoic acid	357.36 ± 9.92	n.d.
Octanoic acid	3963.74 ± 89.26	1865.10 ± 3.84
Capric acid	45.50 ± 59.55	933.24 ± 4.64
Caproic acid	n.d.	196.84 ± 1.89
Myristic acid	70.64 ± 1.88	99.82 ± 0.29
Decanoic acid	244.96 ± 6.29	340.47 ± 5.76
Dodecanoic acid	291.53 ± 5.90	180.18 ± 3.54
Total	**5487.88**	**3791.03**
Aromatic compounds		
2-phenylethanol	1101.44 ± 51.94	1154.43 ± 64.29
Total	**1101.44**	**1154.43**

* n.d.—not detected.

Table 6. Volatile compounds (μg/L) identified in '*Cabernet Sauvignon*' and '*Syrah*' wine spirit.

Compounds	1st Distillation	
	'*Cabernet Sauvignon*'	'*Syrah*'
Esters		
Isoamylacetate	1699.26 ± 56.88	3127.20 ± 783.19
Ethyl hexanoate	4493.33 ± 309.36	n.d. *
Ethyl octanoate	6630.85 ± 9.96	5997.03 ± 69.93
Phenethyl acetate	7145.27 ± 295.87	n.d.
Ethyl decanoate	5792.73 ± 17.29	2499.78 ± 94.52
Ethyl laurate	2320.88 ± 16.66	877.65 ± 42.86
Ethyl myristate	61.59 ± 2.16	n.d.
Total	**28,143.91**	**12,501.66**
Alcohols		
3-methylbutanol	31,173.29 ± 2.73	85,481.35 ± 2194.48
1-hexanol	1196.89 ± 42.45	5286.73 ± 12.69
2-phenylethanol	271.72 ± 12.32	n.d.
Total	**32,641.90**	**90,768.08**
Acids		
Acetic acid	n.d.	1473.06 ± 64.84
Decanoic acid	279.77 ± 2.67	n.d.
Myristic acid	101.13 ± 0.12	n.d.
Total	**380.90**	**1473.06**

Table 6. *Cont.*

	2nd distillation	
	'Cabernet Sauvignon'	*'Syrah'*
Esters		
Ethyl hexanoate	1524.36 ± 69.18	n.d.
Ethyl octanoate	7148.06 ± 99.8	3566.46 ± 88.04
Phenethyl acetate	n.d.	313.23 ± 2.27
Ethyl decanoate	1815.29 ± 75.47	607.09 ± 0.23
Ethyl laurate	762.20 ± 10.44	n.d.
Ethyl palmitate	622.22 ± 5.62	n.d.
Total	**11,872.13**	**4486.78**
Alcohols		
3-methylbutanol	24,464.58 ± 723.11	80,593.73 ± 341.83
1-hexanol	1716.89 ± 2.41	741.65 ± 9.01
2-phenylethanol	n.d.	871.01 ± 23.17
Total	**26,181.47**	**82,206.39**
Acids		
Acetic acid	n.d.	1988.67 ± 77.52
Hexanoic acid	1270.72 ± 7.59	n.d.
Total	**1270.72**	**1988.67**
	Final distillate	
	'Cabernet Sauvignon'	*'Syrah'*
Esters		
Isoamyl acetate	799.76 ± 47.5	1131.90 ± 17.06
Ethyl hexanoate	1038.98 ± 22.58	n.d.
N-Hexyl acetate	111.50 ± 5.91	n.d.
Ethyl octanoate	739.28 ± 42.26	2879.02 ± 4.63
Ethyl decanoate	169.31 ± 0.83	1159.59 ± 28.27
Ethyl laurate	106.17 ± 2.6	172.26 ± 1.97
Ethyl myristate	79.76 ± 3.25	n.d.
Ethyl palmitate	99.90 ± 3.01	n.d.
Total	**3144.66**	**6342.77**
Alcohols		
3-methylbutanol	2317.22 ± 4.71	8084.11 ± 250.25
1-hexanol	205.39 ± 7.06	584.88 ± 27.49
2-phenylethanol	n.d.	542.57 ± 11.82
Total	**205.39**	**14,697.92**
Acids		
Acetic acid	n.d.	1771.4 ± 73.24
Total	**0**	**1771.4**

* n.d.—not detected.

The final distillate was obtained by diluting the second distillate to an alcohol content of 55% with demineralised water (<10 µS) and resting the distillate for one week before filling it into 3 L barrique oak barrels. After resting, the predominant esters in final CS distillate were isoamyl acetate (799.76 µg/L), ethyl hexanoate (1038.98 µg/L), and ethyl octanoate (739.28 µg/L), while in the final SY distillate, isoamyl acetate (1131.9 µg/L), ethyl octanoate (2879.02 µg/L), and ethyl decanoate (1159.59 µg/L) were the most represented. The alcohol profile of the final CS and SY distillate was also different in the type and amount of alcohol present in musts. The final CS distillate contained 3-methylbutanol (2317.22 µg/L) and 1-hexanol (205.39 µg/L), while the final SY distillate contained 3-methylbutanol (2879.02 µg/L), 1-hexanol (1159.59 µg/L), and phenethyl alcohol (172.26 µg/L). All of the above-mentioned esters and alcohols represent characteristic chemical markers for the heart, as reported by Tsakiris et al. [2]. In the case of isoamyl acetate, below 0.02 mg/L, this compound is just one of the many sweet–fruity compounds with a very weak sensory effect. Between 0.2 and 1.4 mg/L, the importance of isoamyl acetate grows to the point that it becomes an important contributor to the fruity note [33].

3.4. Grape Brandy

According to the EU Regulation (EU) 2019/787, brandy is produced from wine spirit to which wine distillate may be added, provided that that wine distillate is distilled at less than 94.8% vol. and does not exceed a maximum of 50% of the alcoholic content of the finished product. According to legislation, it must also contain a number of volatile substances equal to or exceeding 1.25 g/L of pure alcohol (a.a.) and must possess a maximum methanol content of 2.0 g/L of pure alcohol (200 g per hectolitre of 100% vol. alcohol). The results of primary volatile compounds are presented in Table 7. Both produced brandies contained above 1.25 g/L of pure alcohol of volatile substances, CS brandy 2.70 g/L of pure alcohol and SY brandy 2.71 g/L of pure alcohol. The methanol content was below the regulated maximum of 2 g/L of pure alcohol; 0.4 g/L of pure alcohol of methanol was found in both brandies. Methanol (methyl alcohol) is not produced by alcoholic fermentation. It is formed exclusively from the enzymatic hydrolysis of the methoxyl groups of pectins during fermentation. It is always present in very small quantities in wine. However, in wine spirits, it is found in higher concentrations in the range of 0.30–0.70 g/L of pure alcohol (ethanol). Its smell and taste are similar to ethanol, and since it is present in low concentrations, it does not affect the sensory quality of the spirit. However, it affects spirit safety since its toxicity is well known [13].

Table 7. Primary volatile compounds identified in different fractions of 2nd distillation and in final '*Cabernet Sauvignon*' and '*Syrah*' distillate.

	2nd Distillation			**Final Distillate**
	'Heads'	**'Heart'**	**'Tails'**	
'*Cabernet Sauvignon*'				
Ethanol (% vol.)	87.58 ± 0.17	73.18 ± 0.26	27.51 ± 0.43	55.56 ± 0.47
Methanol (mg/L a.a.)	1267.60 ± 120.00	440.0 ± 9.60	0.0 ± 0.00	400.00 ± 1.00
Acetaldehyde (mg/L a.a.)	499.30 ± 51.90	103.30 ± 0.60	0.0 ± 0.00	83.40 ± 14.40
Ethyl acetate (mg/L a.a.)	82,242.10 ± 107.00	512.90 ± 11.00	0.0 ± 0.00	447.30 ± 12.30
2-methylpropanol (mg/L a.a.)	284.90 ± 402.90	42.60 ± 0.10	107.40 ± 1.60	35.80 ± 4.80
2-butanol (mg/L a.a.)	7146.60 ± 439.90	539.80 ± 38.00	25.80 ± 1.20	451.60 ± 94.70
Isoamyl alcohol (mg/L a.a.)	13,417.40 ± 274.60	1928.20 ± 11.80	256.10 ± 9.00	1676.80 ± 45.90
'*Syrah*'				
Ethanol (% vol.)	81.74 ± 0.22	70.61 ± 1.77	30.24 ± 0.32	55.32 ± 0.22
Methanol (mg/L a.a.)	145.30 ± 9.200	403.70 ± 9.40	0.00 ± 0.00	403.70 ± 1.60
Acetaldehyde (mg/L a.a.)	1110.30 ± 10.6	49.40 ± 0.20	94.90 ± 72.40	52.00 ± 0.20
Ethyl acetate (mg/L a.a.)	8399.00 ± 11.70	426.00 ± 10.30	341.10 ± 5.80	367.00 ± 1.00
2-methylpropanol (mg/L a.a.)	0.00 ± 0.00	52.50 ± 74.30	0.00 ± 0.00	0.00 ± 0.00
2-butanol (mg/L a.a.)	1042.10 ± 24.20	846.80 ± 40.30	29.20 ± 20.20	662.90 ± 52.50
Isoamyl alcohol (mg/L a.a.)	1324.60 ± 10.40	1798.00 ± 33.20	483.20 ± 5.90	1590.00 ± 0.40

Hundreds of volatile compounds have been identified in grape brandies; however, esters, as we said before, are one of the most important compounds that contribute to aroma. Brandy, in order to develop the specific aroma, should be matured for at least six months in oak casks with a capacity of fewer than 1000 litres each. For the purpose of this investigation, wine spirit, 55% vol., was placed in 3 L barrique oak barrels and maturated for six months, the predominant esters were determined every month, and the results are presented in Figures 1 and 2. During the maturation of CS brandy, the content of the predominant esters increased by 123% (ethyl hexanoate), 38% (ehyl octanoate), 100% (ethyl decanoate), and 100% (ethyl laurate). In the case of SY brandy, during maturation, the content of ethyl hexanoate, ethyl decanoate, and ethyl laurate increased by 34, 88, and 52%, respectively, while the content of ethyl hexanoate decreased by 27%. Together, the predominant esters represent 59.46% (CS) and 85.71% (SY) of the total esters in the produced brandies. Investigating the profile of volatile compounds in 11 world popular brandies, Zhao et al. [32] reported 50 esters with a total concentration between 113.43–847.60 mg/L.

The predominant esters, as in our experiment, were ethyl hexanoate (0–10.28 mg/L), ehyl octanoate (23.51–301.55 mg/L), ethyl decanoate (37.39–377.58 mg/L), and ethyl laurate (0.06–87.22 mg/L) and together they represent 49–90% of the total esters in investigated brandies [32].

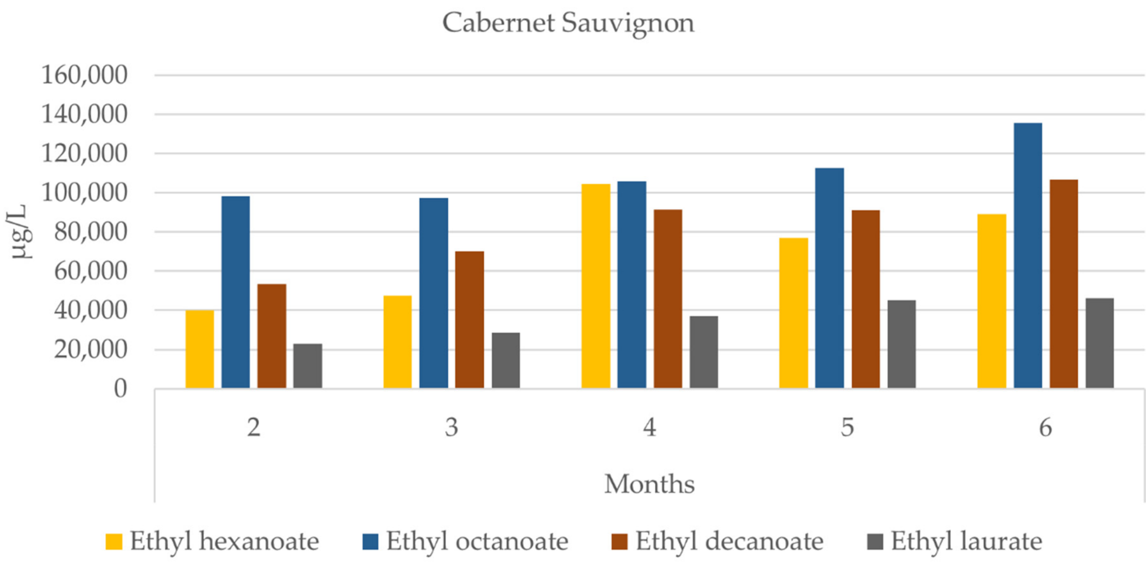

Figure 1. Changes in esters concentration in '*Cabernet Sauvignon*' brandy during six months ageing in barrique oak barrels.

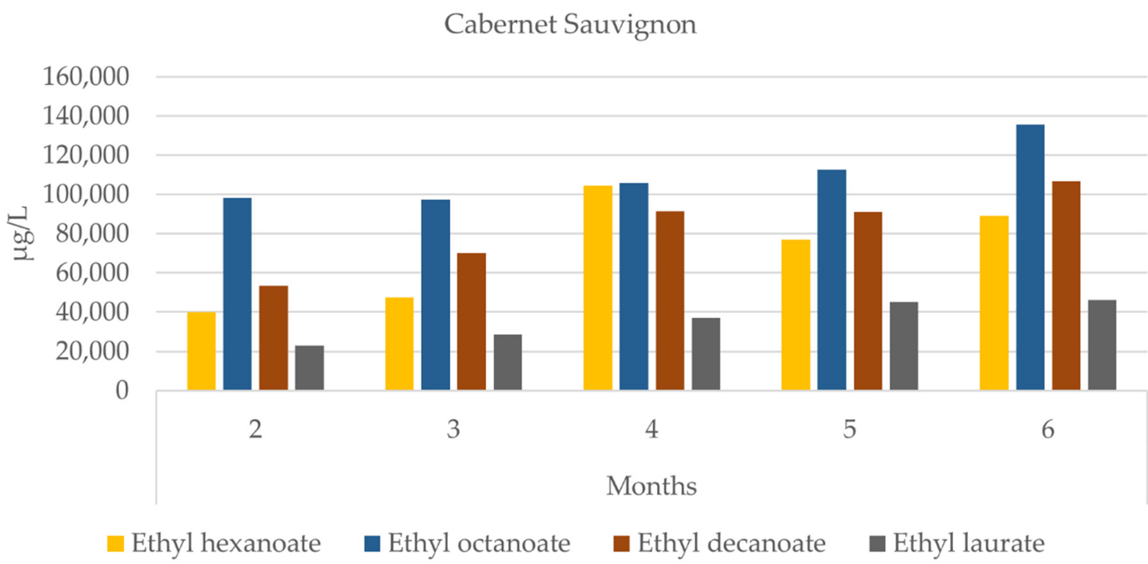

Figure 2. Changes in esters concentration in '*Syrah*' brandy during six month ageing in barrique oak barrels.

4. Conclusions

This study provides insight into changes in volatile compounds during grape brandy production from non-typical grape varieties, '*Cabernet Sauvignon*' and '*Syrah*'. During production, some specific volatile compounds such as 2-hexenal, 3-octanone, isopropyl myristate, ethyl palmitate, ethyl oleate, phenethyl acetate, 1-hexanol, and β-damascenone could be attributed to the primary aroma generated from the grape varieties. During the vinification and fermentation process, the development of ethyl hexanoate, ethyl octanoate, 3-methylbutanol, acetic acid, and octanoic acid occurred. Finally, 3-methylbutanol and predominant esters, ethyl hexanoate, ethyl octanoate, ethyl decanoate, and ethyl laurate, were generated during the distillation and maturation process. During maturation, the content of the predominant esters increased, except in the case of ethyl octanoate in SY brandy. The composition and concentration of the determined predominant esters suggest that both brandies have volatile profiles comparable to some of the world's most popular brandies.

Author Contributions: Conceptualisation, A.L. and B.M.; methodology, I.F.; formal analysis, M.P., A.B. and A.P.; writing—original draft preparation, A.L. and A.J.; writing—review and editing, J.B. and T.K.; supervision, D.Š. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. EU. *The Regulation (EC) No 787/2019 of the European Parliament and of the Council*; EU: Brussels, Belgium, 2019.
2. Tsakiris, A.; Kallithraka, S.; Kourkoutas, Y. Grape brandy production, composition and sensory evaluation. *J. Sci. Food Agric.* **2014**, *94*, 404–414. [CrossRef] [PubMed]
3. Castillo-Vergara, M.; Alvarez-Marin, A.; Carvajal-Cortes, S.; Salinas-Flores, S. Implementation of a Cleaner Production Agreement and impact analysis in the grape brandy (pisco) industry in Chile. *J. Clean. Prod.* **2015**, *96*, 110–117. [CrossRef]
4. Sánchez-Guillén, M.M.; Schwarz-Rodríguez, M.; Rodríguez-Dodero, M.C.; García-Moreno, M.V.; Guillén-Sánchez, D.A.; García-Barroso, C. Discriminant ability of phenolic compounds and short chain organic acids profiles in the determination of quality parameters of Brandy de Jerez. *Food Chem.* **2019**, *286*, 275–281. [CrossRef] [PubMed]
5. Aylott, R. *Analytical Strategies Supporting Protected Designations of Origin for Alcoholic Beverages*, 1st ed.; Elsevier: Amsterdam, The Netherlands, 2013; Volume 60, ISBN 9780444595621.
6. Ramos, M.C.; Jones, G.V. Relationships between Cabernet Sauvignon phenology and climate in two Spanish viticultural regions: Observations and predicted future changes. *J. Agric. Sci.* **2018**, *156*, 1079–1089. [CrossRef]
7. Nan, L.; Liu, L.; Li, Y.; Huang, J.; Wang, Y.; Wang, C.; Wang, Z.; Xu, C. Comparison of Aroma Compounds in Cabernet Sauvignon Red Wines from Five Growing Regions in Xinjiang in China. *J. Food Qual.* **2021**, *2021*, 5562518. [CrossRef]
8. Geffroy, O.; Morère, M.; Lopez, R.; Pasquier, G.; Condoret, J.S. Investigating the Aroma of Syrah Wines from the Northern Rhone Valley Using Supercritical CO2-Dearomatized Wine as a Matrix for Reconstitution Studies. *J. Agric. Food Chem.* **2020**, *68*, 11512–11523. [CrossRef]
9. Milicevic, B.; Banovic, M.; Kovacevic-Ganic, K.; Gracin, L. Impact of grape varieties on wine distillates flavour. *Food Technol. Biotechnol.* **2002**, *40*, 227–232.
10. Flamini, R. *Mass Spectrometry in Grape and Wine Chemistry Wiley-Interscience Series in Mass Spectrometry*; Wiley-Blackwell: Hoboken, NJ, USA, 2009; ISBN 9780470392478.
11. Mayr Marangon, C.; De Rosso, M.; Carraro, R.; Flamini, R. Changes in volatile compounds of grape pomace distillate (Italian grappa) during one-year ageing in oak and cherry barrels. *Food Chem.* **2021**, *344*, 128658. [CrossRef]
12. Louw, L.; Lambrechts, M.G. *Grape-Based Brandies: Production, Sensory Properties and Sensory Evaluation*; Woodhead Publishing Limited: Sawston, UK, 2012.
13. Tsakiris, A.; Kallithraka, S.; Kourkoutas, Y. *Brandy and Cognac: Manufacture and Chemical Composition*, 3rd ed.; Elsevier Ltd.: Amsterdam, The Netherlands, 2015; ISBN 9780123849533.
14. Costa, C.; Graça, A.; Fontes, N.; Teixeira, M.; Gerós, H.; Santos, J.A. The interplay between atmospheric conditions and grape berry quality parameters in Portugal. *Appl. Sci.* **2020**, *10*, 4943. [CrossRef]
15. Ubalde, J.M.; Sort, X.; Zayas, A.; Poch, R.M. Effects of Soil and Climatic Conditions on Grape Ripening and Wine Quality of Cabernet Sauvignon. *J. Wine Res.* **2010**, *21*, 1–17. [CrossRef]
16. Ruffner, H.P.; Hawker, J.S.; Hale, C.R. Temperature and enzymic control of malate metabolism in berries of Vitis vinifera. *Phytochemistry* **1976**, *15*, 1877–1880. [CrossRef]
17. Keller, M. Managing grapevines to optimise fruit development in a challenging environment: A climate change primer for viticulturists. *Aust. J. Grape Wine Res.* **2010**, *16*, 56–69. [CrossRef]
18. Poudel, P.R.; Mochioka, R.; Beppu, K.; Kataoka, I. Influence of temperature on berry composition of interspecific hybrid wine grape "Kadainou R-1" (*Vitis ficifolia* var. ganebu × *V. vinifera* 'Muscat of Alexandria'). *J. Jpn. Soc. Hortic. Sci.* **2009**, *78*, 169–174. [CrossRef]
19. Mori, K.; Sugaya, S.; Gemma, H. Decreased anthocyanin biosynthesis in grape berries grown under elevated night temperature condition. *Sci. Hortic.* **2005**, *105*, 319–330. [CrossRef]
20. Feliciano, R.P.; Antunes, C.; Ramos, A.; Serra, A.T.; Figueira, M.E.; Duarte, C.M.M.; de Carvalho, A.; Bronze, M.R. Characterization of traditional and exotic apple varieties from Portugal. Part 1—Nutritional, phytochemical and sensory evaluation. *J. Funct. Foods* **2010**, *2*, 35–45. [CrossRef]
21. International Organisation of Vine and Wine. *Compendium of International Methods of Wine and Must Analysis*; International Organisation of Vine and Wine: Paris, France, 2020; ISBN 9782850380037.

22. Wang, M.L.; Choong, Y.M.; Su, N.W.; Lee, M.H. A rapid method for determination of ethanol in alcoholic beverages using capillary gas chromatography. *J. Food Drug Anal.* **2003**, *11*, 133–140. [CrossRef]
23. Ordinance on analytical methods for spirits and alcoholic beverages. *MAFWM* **2005**, *11*, 1–10.
24. Van Den Dool, H.; Kratz, P.D. A generalization of the retention index system including linear temperature programmed gas—Liquid partition chromatography. *J. Chromatogr. A* **1963**, *11*, 463–471. [CrossRef]
25. Jackson, R.S. Specific and Distinctive Wine Styles. In *Wine Science*; Academic Press: Cambridge, MA, USA, 2014; ISBN 9780123814685.
26. Jiang, B.; Zhang, Z. Volatile Compounds of Young Wines from Cabernet Sauvignon, Cabernet Gernischet and Chardonnay Varieties Grown in the Loess Plateau Region of China. *Molecules* **2010**, *15*, 9184–9196. [CrossRef]
27. Rizzon, L.A.; Miele, A. Physicochemical Characteristics of the Brazilian Cabernet Sauvignon Wine as a Function of the Vintage. Available online: https://www.alice.cnptia.embrapa.br/bitstream/doc/542397/1/OIVBudapest2007ArticleRizzonandMiele.pdf (accessed on 27 April 2022).
28. Souza, S.C.; Theodoro, K.H.; Souza, É.R.; Da Motta, S.; Glória, M.B.A. Bioactive amines in Brazilian wines: Types, levels and correlation with physico-chemical parameters. *Braz. Arch. Biol. Technol.* **2005**, *48*, 53–62. [CrossRef]
29. Eliete Iochims dos Santos, C.; Raquel Manfredi da Silva, L.; Appel Boufleur, L.; Debastiani, R.; Alberici Stefenon, C.; Amaral, L.; Lúcia Yoneama, M.; Dias, J.F. Elemental characterisation of Cabernet Sauvignon wines using Particle-Induced X-ray Emission (PIXE). *Food Chem.* **2010**, *121*, 244–250. [CrossRef]
30. De Carvalho, E.S.S.; Biasoto, A.C.T.; Nassur, R.d.C.M.R.; Barros, A.P.A.; Leão, P.C.S.; Lima, E.d.S.; De Camargo, A.C.; Mamede, M.E.d.O. Physicochemical characteristics, phenolic profile, and antioxidant capacity, of Syrah tropical wines: Effects of vineyard management practices. *J. Food Bioact.* **2020**, *9*, 70–78. [CrossRef]
31. Saerens, S.M.G.; Delvaux, F.R.; Verstrepen, K.J.; Thevelein, J.M. Production and biological function of volatile esters in Saccharomyces cerevisiae. *Microb. Biotechnol.* **2010**, *3*, 165–177. [CrossRef] [PubMed]
32. Zhao, Y.; Xu, Y.; Li, J.; Fan, W.; Jiang, W. Profile of volatile compounds in 11 brandies by headspace solid-phase microextraction followed by gas chromatography-mass spectrometry. *J. Food Sci.* **2009**, *74*, C90–C99. [CrossRef] [PubMed]
33. Ferreira, V. Volatile Aroma Compounds and Wine Sensory Attributes. In *Managing Wine Quality*; Elsevier: Amsterdam, The Netherlands, 2010; pp. 3–28.