

Article

Influence of Oak Chips and Oak Barrel Ageing on Volatile Profile in Chardonnay Wine of Romania

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Abstract: The influence of the addition of oak chips and barrel ageing on basic wine parameters and volatile compounds of Chardonnay wines has been studied. Chardonnay wines were obtained by the traditional wine-making process. Oak chips (4 g/L—non-toasted and light toasted) were added at the final stage of the winemaking process for ageing 1, 2 and 3 months, respectively. Also, the control wine was aged in non-toasted barrels for the same period of time. Following Liquid-liquid extraction-gas chromatography-mass spectrometry analysis, alcohols, esters, fatty acids, lactones, and phenolic compounds were identified and quantified. The light toasted wine was clearly separated by phenolic compounds (vanillin, *p*-vinyl guaiacol and acetovanillone). The floral aroma supplied by 2-phenylethanol was slowly increased by ageing with odor activity values (OAV) higher in aged samples than control wine (1.07). The vanilla scent could be easily perceived in all aged samples, mainly for light toasted chip-treated samples with OAV values between 2.30 and 2.37. After 3 months, the volatile compounds of wine from non-toasted medium (chips and barrels) were almost similar from the volatile profile point of view. This could have economic and vinification management implications since oak barrels are expensive and the wine oak barrel aging is a long process. All wines studied in this research can provide a viable alternative to young varietal wines.

Keywords: Chardonnay wine; chips; barrels; *Quercus robur*; volatile compounds; light toast

1. Introduction

The quality of a wine depends mainly on its chemical composition and also on the expectation of the consumer. Each type of consumer will define wine quality differently depending on their expectations and needs [1]. Expectations of the consumer vary depending on the type of wine: white, red, rose, sweet, dry; young or aged wine [2]. Chardonnay

is one of the flexible varieties which could adapt to different growth regions with varied weather and soil characteristics [3]. Among white wines, Chardonnay lends itself to a wide variety of production styles, which can be tailored to the target market and that make this grape variety unique. Presently, two tendencies exist for Chardonnay aroma profiles: fruity and light styles and flavored and complex styles [3]. These styles are targeted by current market trends and popularity of wines. Chardonnay allows winemakers different stylistic choices compared to other white wine varieties. Wines can be aged in oak (barrel or chips) and stored after bottling for different periods of time, depending on the desired style [4]. Oak (*Quercus* sp.) wood is used in the manufacture of barrels due to its chemical and physical properties. Among the other tree species used in winemaking, the oak is unique due to the size and shape of the annual circles that give it durability when transformed into barrel staves [5]. The technological processes used in carpentry, such as seasoning and toasting the wood staves, give the final characteristics of the barrels [6]. Maturing wines in oak barrels is a traditional practice used to improve sensory and quality characteristics. Although fermentation and maturation in oak barrels is desirable for many wine centers, this is not always possible due to high costs [7,8]. However, an alternative of obtaining wines with significant aromas is the use of oak, non-toasted or toasted (different levels) chips that can be added during the fermentation process of the wine or at the end of alcoholic fermentation [7,9,10]. Some studies examine the addition of wood chips in wine during or after alcoholic fermentation [7,10]. Also, the presence of lees during ageing can improve the organoleptic characteristics of some wines [11]. Recently, the use of alternative vessels to oak barrels during winemaking has become increasingly popular, but little is known about their impact on the chemical composition of the resulting wines [12].

The volatile compounds extracted from the wood depend on a number of factors such as the degree of toasting, the contact duration with wine [13,14], but also on their geographical origin [5,15]. The addition of oak chips to finished wines and their effect on the chemical composition of the wine and its sensory characteristics has been widely studied [3,7,9]. The effects of the chips addition in the alcoholic fermentation of wine led to contradictory results regarding the stabilization of the wine color, but all studies reported changes in the content of volatile and phenolic compounds [5,10,13,15]. Red wine maturation in barrels has been a common practice for centuries. In recent years, the maturation of white wines encountered an increased interest in obtaining wines with improved sensory and quality properties. In Europe, the use of oak wood pieces in winemaking was approved in 2006 (Council Regulation EC No.2165/2005) [16] and since then the addition of oak chips has been generalized. The new EU Delegated Regulation 2019/934 currently regulates the use of oak wood chips in wine practices, which are used for several technological purposes. The main objective is the release of desirable compounds, such as aromas and polyphenolics, from the wood fragments into the wine during aging [16]. The volatile compositions of Chardonnay wines aged in barrels or with chips is studied extensively in Spain [17,18], Greece [19], Italy [20], Australia [21]. Our research is the first attempt to study the volatile composition of Romanian Chardonnay wines, aged through different methods. Chardonnay is one of the grapevine varieties most distributed across the world [17], but in Romania, Chardonnay variety is planted on 2511 hectares representing about 3% of total vineyards [22].

The purpose of the present study was to examine the effects of two types of French oak chips (non-toasted and light toasted) and non-toasted Romanian oak barrel, during short ageing periods on Chardonnay white wine composition by using gas chromatography coupled to mass spectrometry (GC–MS). Unlike most other white wine varieties which are not aged, Chardonnay wines commonly spend between several weeks to a year for ageing in oak barrels. We focused on identifying the chemical compounds according to contact time and wood type. This study provides important scientific content to winemakers.

2. Materials and Methods

2.1. Oak Wood Origin

The barrels used were made up of Romanian oak from *Quercus robur*, from the forest located in the Western Romania (Ineu area; 46°26' N 21°50' E). The raw staves (100 cm × 11 cm × 2.2 cm) were naturally seasoned for 24 months at the Transylvania Bois® Tonnellerie (Sighetu Marmației, Romania). Once assembled, the barrels (225 L) were not submitted to toasting procedures. For the purpose of the study, non-toasted barrels were provided to the wine cellar. The oak chips (*Quercus robur*) were provided by Sodinal® (Wine and Beverage Division of AVeX Group, Paris, France), with dimensions of 0.6 cm × 1.2 cm × 0.15 cm (width × length × thickness). The oak chips used were non-toasted and light toasted, respectively.

2.2. White Wine Vinification and Sample Collection

Chardonnay grapes (*Vitis vinifera* L.) were manually harvested at maturity in Teaca winery (Lechinta, Bistrita Nasaud County, Romania) during the 2017 vintage (225 g/L sugar in grape juice, 8.95 g/L must total acidity expressed as tartaric acid and 104 g weight of 100 berries). The Lechinta grapevine growth area is known for the high acidity of wines, due to climatic conditions (oenoclimatic aptitude index of 4221) [23]. Grapes were crushed and destemmed (Enoitalia® WE223S, Cerreto, Italy) on the harvest day. A pneumatic press (Vaslin–Bucher® RPS 50, France) was used, filled at 75–80% of its capacity. Potassium metabisulphite (4.5 ± 0.5 g/hL) was added during the transfer of the must to the stainless steel tank (5000 L capacity). *Saccharomyces cerevisiae* (Zymaflore VL1, Laffort®, Bordeaux, France), a commercial active dry yeast was included at a rate of 20 g/hL to perform alcoholic fermentation at 16 °C. Malolactic fermentation (MLF) could take place spontaneously, no bacterial culture was added to performed MLF, and no supplementary sulfitation was made to inhibit the MLF. Three sets of experiments were performed depending on the container in which maturation took place (Table 1). When alcoholic fermentation ended, the control wine was transferred to new non-toasted oak barrels at full capacity (first experiment). The control wine was transferred to demijohns (glass container of 50 L) with 4 g/L non-toasted oak chips (second experiment) and 4 g/L light-toasted oak chips (third experiment). Wines were kept in oak barrels and glass containers with chips for ageing during 3 months at a controlled temperature of 14–16 °C. Sampling was performed at 1, 2 and 3 months of wood contact. Wine samples were stored at 4 °C until the moment of analysis. Each experiment had three sets of containers, meaning three non-toasted barrels, three glass containers with light toasted chips, and three glass containers with non-toasted chips.

Table 1. Experimental design.

Time of Maturation (Months)	Type of Vessel Maturation	Oak Chips (4 g/L)	Abbreviations
1	Demijohns/Glass	Non-toasted	N1M
		Light-toasted	L1M
	Barrel	Non-toasted	BAR1M
2	Demijohns/Glass	Non-toasted	N2M
		light-toasted	L2M
	Barrel	Non-toasted	BAR2M
3	Demijohns/Glass	Non-toasted	N3M
		Light-toasted	L3M
	Barrel	Non-toasted	BAR3M
Control Wine—unaged wine			CW

2.3. Oenological Parameters in Wines

Basic oenological parameters of wines such as pH, alcoholic strength (% v/v), titratable and volatile acidity (g/L tartaric acid, and g/L acetic acid, respectively), were analyzed

in accordance with official International Organisation of Vine and Wine methods [24] and Bora et al. [25]. All parameters were determined in triplicate.

2.4. Reagents and Standards

The reference standards, 2-phenyl ethanol, ethyl decanoate, butyrolactone, isoamyl alcohol and 1-octanol (used as internal standard) were provided by Fluka® (Buch, Switzerland). Dichloromethane used for the extraction of volatile compounds was purchased from Merck® (Darmstadt, Germany). Standard stock solutions were prepared by dissolving 10 mg of each reference compound in 10 mL of dichloromethane. The calibration curve of 2-phenyl-ethanol was used for the volatile concentration calculation. The range of standard concentration was 64–12,900 µg/L.

2.5. Liquid-Liquid Extraction of Volatile Compounds

The extraction method elaborated by Andujar-Ortiz et al. [26] was adapted and used for the isolation of volatile compounds from wine samples. Into an Erlenmeyer flask were introduced 50 mL of wine spiked with 1-octanol (concentration 614 µg/L) as the internal standard and 20 mL of dichloromethane, and it was equipped with a cork. The extraction was performed under continuous stirring in an ice bath for 30 min. The mixture was then kept for 15 min in an Elmasonic S ultrasonic bath (Elma, Germany) at the same temperature to avoid the formation of an emulsion. After separation, the organic layer was dried over Na₂SO₄, evaporated under a stream of nitrogen to about 200 µL volume of the extract. From this solution, 1 µL was injected into the GC/MS system. All extractions were performed in triplicate.

2.6. Determination of Volatile Compounds

Analysis of volatile organic compounds [27] from wine samples was performed using a Shimadzu QP 2010 PLUS Mass Spectrometer coupled with Gas Chromatograph (Shimadzu, Japan) equipped with a Carbowax type column from Agilent (30 m × 0.32 mm inner diameter and 0.50 µm film thicknesses). Helium (6.0) was used as carrier gas with a flow rate 1.7 mL/min. The injector, the detector and the interface temperature were set at 220 °C. The column temperature program was conducted as follows: 40 °C was the initial temperature for 5 min, increasing at a rate of 4 °C/min to 220 °C, and holding 220 °C for 15 min. Quadrupole mass detector acquisition was carried out using the positive electronic ionization-mode at the 70 eV, with continuous scanning from 40 to 500 amu. Standard compounds in wines were identified by comparing their relative retention times and mass fragmentation with those of computer matching against a commercial library (National Institute of Standards and Technology and Willey).

2.7. Odor Activity Values (OAVs)

The contribution of each volatile compound to wine aroma was evaluated qualitatively by its associated descriptor and quantitatively by its odor activity values (OAVs). OAVs were calculated using the ratio between total concentration (in µg/L) of each compound in the wine samples, and the odor threshold value (in µg/L) of the compound in water/ethanol solution [28]; threshold values were obtained from information available in the literature [28].

2.8. Statistical Analysis

Univariate analysis was performed using analysis of variance (ANOVA), applying the Tukey multiple range test. Partial least squares regression (PLSR) analysis was also carried out, using the XLSTAT Addinsoft 2014.5.03 version (Addinsoft Inc., NY, USA).

3. Results

3.1. Basic Oenological Parameters

Analysis of basic oenological parameters is presented in Table 2. Alcohol content is high in all samples (above 12.5% *v/v*), with small but significant differences among variants, with a lower value after ageing in barrel. Samples BAR1M–BAR3M aged in non-toasted oak barrels have a higher level of total acidity than samples N1M–N3M and L1M–L3M, probably due to higher oxygen diffusion through barrel wood pores [29]. All tested wine samples reached dryness (less than 4.0 g/L residual sugar—data not shown). Nevertheless, there is a small and not significant difference in the dry-extract and non-reducing dry-extract level between the control wine and aged variants (Table 2). The concentration of extract without sugar is very similar in all samples regardless of the ageing method, as previously showed by other studies [11,30]. Concentration of free and total SO₂ in samples is acceptable for all variants.

3.2. Volatile Profile of White Wines Aged with Non-Toasted and Light-Toasted Oak Chips

Liquid-liquid extraction-gas chromatography-mass spectrometry analysis of Chardonnay white wines after 1, 2 and 3 months of ageing with non-toasted oak chips, light-toasted oak chips and non-toasted oak barrels, identified five chemical groups: higher alcohols, esters, volatile fatty acids, lactones and phenolic compounds. As noted in Table 3, volatile compounds have significant differences depending on the experimental variant.

3.2.1. Alcohols

In our study, the concentration of volatile alcohols varied both depending on the time and type of ageing. Three major alcohols (iso-butanol, isopentyl alcohol and 2-phenylethanol) were quantified in wine samples. Those alcohols showed different trends during ageing. As can be observed in Table 3, the iso-butanol significantly decreased during 3 months of ageing, regardless of the methods, while isopentyl alcohol and 2-phenylethanol have increased concentration. After 3 months of ageing, the major alcohol concentrations were higher, regardless of the method (N3M-142 mg/L; L3M-144 mg/L and BAR3M-143 mg/L). By using LLE-GC-MS analysis were detected and quantified 9 minor alcohols (hexanol, 2,3-butanediol, 3-methylthio-1-propanol, benzyl-alcohol). In the minor group, hexanol was the highest alcohol, and its concentration was dependent on ageing time and significantly dependent on ageing method. As can be observed from Table 3, the non-toasted barrel ageing method favored the concentration of hexanol, which supplied a leafy and grassy note to the wine samples [31]. Also, the minor alcohols had different trends during ageing. Most of them (4 methyl-1-pentanol, 2-nonalol, 1-heptanol, 3 methylthio-1-propanol) decreased after 3 months of ageing. The highest increase was detected for 2,3-butanediol in BAR1M–BAR3M variants (1686–4973 µg/L).

3.2.2. Esters

Individual fruity volatile concentrations obtained in the present research were higher than the bibliographic ranges reported by Gambetta et al. [3] in Italy, or González-Centeno et al. [19], in Greece, but in agreement with those obtained by Cheng et al. [31] in Xianjiang (China). Most of them exhibited concentrations above their olfactory perception threshold, providing the wine with pear, apple, pineapple and/or floral notes [30,31]. Among the ethyl esters of straight-chain fatty acids, ethyl caproate (3120–3240 µg/L) and ethyl octanoate (2122–2362 µg/L) were the predominant ones. Isoamyl acetate, characterized by banana flavor, was the main component among the higher alcohol acetates, with values ranging from 2433 to 2538 µg/L, depending on time and method of ageing. Within this family of esters, it was the only volatile present at above threshold level (30 µg/L).

Table 2. Oenological analyses of white wines aged with oak chips and barrel for 1, 2 and 3 months; analysis of variance (ANOVA) taking as factors time and ageing method. All values are expressed as means \pm SD. Different letters in each row of the same variant are significantly different at the 0.05 level according to ANOVA by Tukey's test. *: $p < 0.05$; **: $p < 0.01$; ***: $p < 0.001$; ns: not significant. CW, N1M, N2M, N3M, L1M, L2M, L3M, BAR1M, BAR2M and BAR3M are the abbreviations for 10 variants of Chardonnay (CW—control wine, N—non-toasted chips, L—light toasted chips, BAR—non-toasted barrel; 1M, 2M and 3M—number of months of ageing).

Variants/Oenologic Parameters	CW	N1M	N2M	N3M	L1M	L2M	L3M	BAR1M	BAR2M	BAR3M	Time	Ageing Method
Ethanol (%v/v)	12.77 \pm 0.03a	12.75 \pm 0.04a	12.69 \pm 0.08ab	12.66 \pm 0.06bc	12.75 \pm 0.04a	12.69 \pm 0.08ab	12.66 \pm 0.06bc	12.62 \pm 0.02bc	12.54 \pm 0.04c	12.55 \pm 0.02c	**	***
Volatile acidity (g/L acetic acid)	0.22 \pm 0.02c	0.24 \pm 0.03c	0.28 \pm 0.02bc	0.31 \pm 0.01b	0.24 \pm 0.03c	0.28 \pm 0.02bc	0.31 \pm 0.01b	0.32 \pm 0.02b	0.41 \pm 0.04a	0.46 \pm 0.02a	***	***
Total acidity (g/L tartaric acid)	7.96 \pm 0.07a	7.86 \pm 0.04ab	7.74 \pm 0.04bc	7.58 \pm 0.08c	7.84 \pm 0.03ab	7.73 \pm 0.04bc	7.58 \pm 0.08c	7.91 \pm 0.04a	7.87 \pm 0.04ab	7.76 \pm 0.07bc	***	**
Dry extract (g/L)	23.60 \pm 0.23a	23.52 \pm 0.35a	23.41 \pm 0.39a	23.37 \pm 0.25a	23.52 \pm 0.35a	23.41 \pm 0.42a	23.36 \pm 0.33a	23.52 \pm 0.31a	23.41 \pm 0.40a	23.37 \pm 0.35a	ns	ns
Non-reducing dry extract (g/L)	22.03 \pm 0.03a	22.01 \pm 0.04a	22.05 \pm 0.04a	21.99 \pm 0.04a	22.06 \pm 0.05a	20.00 \pm 0.03a	21.92 \pm 0.04a	22.04 \pm 0.09a	22.07 \pm 0.12a	20.05 \pm 0.06a	ns	ns
Free SO ₂ (mg/L)	36 \pm 1.00a	33 \pm 0.58ab	32 \pm 0.58bc	31 \pm 1.00c	34 \pm 0.81ab	33 \pm 0.72bc	30 \pm 0.50c	32 \pm 1.42bc	30 \pm 1.15c	27 \pm 1.05d	**	***
Total SO ₂ (mg/L)	120 \pm 0.76bc	123 \pm 2.00ab	124 \pm 1.53a	126 \pm 1.85a	123 \pm 1.44ab	124 \pm 2.08a	126 \pm 1.76a	118 \pm 0.76cd	116 \pm 0.85cd	115 \pm 0.83d	*	***
pH	3.22 \pm 0.02b	3.23 \pm 0.02ab	3.23 \pm 0.01ab	3.24 \pm 0.01a	3.22 \pm 0.02b	3.23 \pm 0.01ab	3.24 \pm 0.02a	3.23 \pm 0.02ab	3.25 \pm 0.03a	3.24 \pm 0.01a	*	ns

3.2.3. Fatty Acids

Nine fatty acids were identified in all wine samples. In the present study, there were significant differences in the fatty acid content between control wine and the wine samples aged with different methods. Furthermore, the concentrations of all kinds of fatty acid detected in the variant N1M-N3M (4728–5071 µg/L) and L1M-L3M (4336–4977 µg/L) were lower compared to variant BAR1M-BAR3M (5035–6540 µg/L).

3.2.4. Lactones

Among lactones, butyrolactone showed the highest concentration and depending significantly on the studied factors, as in the case of pantolactone and 3,4-dimethyl-2(5)-furanone. Thus, for control sample, an amount of 478 µg/L of total lactones was quantified. Regardless of the ageing method, wines in which non-toasted oak chips were added (N1M-N3M) and in non-toasted oak barrel (BAR1M-BAR3M) presented greater butyrolactone concentrations than the corresponding light-toasted chips (L1M-L3M) wines.

3.2.5. Volatile Phenols

The total content of phenolic volatiles in Chardonnay wines, calculated by adding up the individual concentration of each compound, ranged from 365 to 463 µg/L for N1M-N3M wines, from 393 to 505 µg/L for L1M-L3M wines and from 350 to 468 µg/L for BAR1M-BAR3M. Among methods of ageing, light toasting led to the highest values, and non-toasted to the lowest ones. Volatile phenols that resulted from wood toasting, have significantly higher values in the wines of L1M-L3M variants (*p*-vinyl guaiacol—58–65 µg/L, acetovanillone—143–171 µg/L and vanilla 133–139 µg/L), compared to the variants from non-toasted wood.

3.3. Odor Active Odorants

In order to assess the influence of each single volatile compound, the odor activity value (OAV) was calculated. The OAV represents the ratio between the concentration of the compound and its odor threshold. Results in Table 4 show that 17 out of 42 quantified volatile compounds reached a concentration above the odor threshold in at least one variant (OAV >1). For major alcohols, all wine samples presented an OAV >1, with the highest values for isopentyl alcohol, mainly for L1M-L3M sample. The floral aroma supplied by 2-phenylethanol was slowly increased by ageing with OAV higher in aged samples than control wine (1.07). Among minor alcohols, only 2-nonanol and 3-methylthio-1-propanol reached OAV >1 in at least one sample. An important ester present above its threshold in all samples was ethyl hexanoate, which can supply anise and strawberry aromas to a wine [19]. N-amyl acetate was found above its threshold in all samples, which indicates that this compound is a general contributor to the fruity aroma of wines. Interestingly for N-amyl acetate was that it increased the OAV values for L1M-L3M (83.80–86.76) samples, so a fruity character could be highlighted by ageing with light-toasted chips. Among terpenes, only linalool showed OAV >1. Some authors [32] concluded that the high level for terpenes in wines, could explain the floral descriptors. Three of nine fatty acids showed OAV >1 in all variants. The fatty and rancid aroma supplied by isovaleric acid could be easily perceived in non-toasted oak barrel aged sample, due to the low odor threshold of this compound. Butyrolactone and 3,4-dimethyl-2(5)-furanone were lactones with OAV >1. Butyrolactone extracted from non-toasted wood presented higher values of OAV for N1M-N3M (9.77–12.66) and BAR1M-BAR3M (13.17–15.20) samples. For volatile phenols, 4-vinyl guaiacol and vanilla reached OAV >1 in at least one variant. The vanilla scent could be easily perceived in all aged samples, especially in L1M-L3M samples with OAV values between 2.30 and 2.37.

Table 3. Quantitative analysis of volatile compounds of Chardonnay wine aged with oak chips/barrel. All values are expressed as means ($\mu\text{g/L}$) \pm standard deviation (SD). Different letters in each row of the same variant are significantly different at the 0.05 level according to analysis of variance (ANOVA) by Tukey's test. *: $p < 0.05$; **: $p < 0.01$; ***: $p < 0.001$; ns: not significant. CW, N1M, N2M, N3M, L1M, L2M, L3M, BAR1M, BAR2M and BAR3M are the abbreviations for 10 variants of Chardonnay (CW—control wine, N—non-toasted chips, L—light toasted chips, BAR—non-toasted barrel; 1M, 2M and 3M—number of months of ageing).

Variant/Volatile Compounds	CW	N1M	N2M	N3M	L1M	L2M	L3M	BAR1M	BAR2M	BAR3M	Time	Ageing Method
Isobutanol	47 \pm 0.03a	39 \pm 2.7d	40 \pm 3.8 c	42 \pm 3.5 b	39 \pm 1.7 d	41 \pm 2.3 bc	41 \pm 1.9 bc	38 \pm 2.8 e	38 \pm 2.6 e	41 \pm 2.4 bc	**	***
Isopentyl alcohol	76 \pm 2.1e	83 \pm 4.5c	84 \pm 5.2 bc	83 \pm 5.7 c	85 \pm 4.2 ab	84 \pm 3.2 bc	86 \pm 5.8 a	82 \pm 2.1 d	83 \pm 3.0 c	84 \pm 2.7 bc	*	***
2-phenylethanol	15 \pm 0.3e	16 \pm 2.4 d	17 \pm 2.0 c	17 \pm 2.8c	16 \pm 1.9d	18 \pm 2.5b	17 \pm 2.9c	19 \pm 2.6a	17 \pm 2.1c	18 \pm 2.8 b	*	***
Total major alcohols (mg/L)	138	138	141	142	140	145	144	139	138	143		
Hexanol	564 \pm 5.7de	438 \pm 3.2e	398 \pm 7.8f	865 \pm 6.5b	375 \pm 2.4f	342 \pm 7.8f	1057 \pm 50a	760 \pm 42bc	627 \pm 8.7c	1145 \pm 12.1a	*	***
4-methyl-1-pentanol	22 \pm 0.6b	25 \pm 2.6ab	11 \pm 3cd	12 \pm 0.9cd	31 \pm 1.5a	10 \pm 1.8d	9.7 \pm 0.5d	33 \pm 5.7a	22 \pm 7.8bc	18 \pm 2.8bc	**	**
E-3-hexenol	30 \pm 1.2b	30 \pm 3.5b	16 \pm 3.1c	17 \pm 1.5c	40 \pm 6.6a	41 \pm 3.5a	41 \pm 3.3a	27 \pm 1.2b	24 \pm 3.5 bc	45 \pm 3.4a	*	**
Z-3-hexenol	112 \pm 0.3de	119 \pm 0.4bc	117 \pm 3.7 c	121 \pm 0.2b	111 \pm 2.6e	114 \pm 4.5bc	113 \pm 0.3d	122 \pm 1.3b	124 \pm 2.8a	123 \pm 1.1b	*	*
2-nonanol	173 \pm 9.6a	100 \pm 11b	47 \pm 4.5de	58 \pm 6.8de	115 \pm 3.5b	37 \pm 5.2e	59 \pm 6.8de	98 \pm 2.1c	78 \pm 7.8cd	13 \pm 0.6f	**	***
1-heptanol	124 \pm 1.2e	230 \pm 9.4a	201 \pm 4.9bc	174 \pm 3.1d	240 \pm 35a	150 \pm 22d	136 \pm 6.0c	230 \pm 5.0a	211 \pm 2.6b	182 \pm 3.7c	***	***
2,3-butanediol	301 \pm 35e	507 \pm 24de	1137 \pm 12.9cd	1417 \pm 21c	330 \pm 27e	605 \pm 9.8de	769 \pm 45de	1686 \pm 14.7c	2797 \pm 35.2b	4973 \pm 52a	***	***
3-methylthio-1-propanol	278 \pm 15bc	248 \pm 15bc	250 \pm 25bc	206 \pm 19d	176 \pm 15d	166 \pm 31d	222 \pm 17bc	553 \pm 49a	290 \pm 17b	244 \pm 75bc	***	***
Benzylalcohol	58 \pm 3.5a	44 \pm 2.4c	45 \pm 1.90c	47 \pm 2.2bc	42 \pm 2.6d	49 \pm 2.4b	48 \pm 3.1b	32 \pm 2.4f	34 \pm 2.1e	39 \pm 3.5de	***	***
Total minor alcohols ($\mu\text{g/L}$)	1662	1741	2222	2917	1460	1514	2454	3541	4207	6782		
Linalool	323 \pm 7.8a	59 \pm 4.9c	49 \pm 4.6cd	33 \pm 2.8e	Trace	trace	Trace	83 \pm 7.3b	45 \pm 2.3de	36 \pm 2.3e	***	***
Terpineol	127 \pm 8.7a	11 \pm 2.6c	trace	ND	Trace	trace	Trace	23 \pm 3.6b	10 \pm 0.3c	11 \pm 1.2c	***	***
Trans-geraniol	52 \pm 2.4a	11 \pm 0.5b	ND	ND	ND	ND	ND	14 \pm 2.5b	ND	ND	***	***
Total terpenes ($\mu\text{g/L}$)	502	81	49	33	trace	trace	Trace	120	55	47		
Isobutyric acid	83 \pm 3.7b	81 \pm 2.5bc	51 \pm 4.6de	21 \pm 2.1f	108 \pm 10a	83 \pm 3.1b	39 \pm 4.0e	75 \pm 3.3bc	64 \pm 5.6cd	24 \pm 2.8f	***	***
Hexanoic acid	945 \pm 17e	1267 \pm 21d	1643 \pm 68a	1395 \pm 45c	1640 \pm 96a	1227 \pm 21e	1355 \pm 40c	1574 \pm 96b	1501 \pm 65bc	1016 \pm 10d	***	***
Isovaleric acid	132 \pm 2.1e	156 \pm 9.6d	219 \pm 82bc	ND	163 \pm 9.5d	189 \pm 15bc	190 \pm 15bc	229 \pm 7.4bc	296 \pm 19b	538 \pm 4.4a	**	***
Lactic acid	54 \pm 4.7e	132 \pm 21d	228 \pm 19e	417 \pm 67c	141 \pm 5.8d	192 \pm 32d	108 \pm 10e	431 \pm 17c	808 \pm 75b	1317 \pm 145a	***	***
Octanoic acid	2459 \pm 58c	2377 \pm 165bc	2448 \pm 39c	2653 \pm 72b	2054 \pm 89d	2409 \pm 39c	2442 \pm 54c	2069 \pm 153d	2447 \pm 154c	2866 \pm 75a	**	***
Decanoic acid	957 \pm 26a	449 \pm 56b	227 \pm 25d	125 \pm 9.8e	306 \pm 19cd	117 \pm 10e	124 \pm 13e	441 \pm 41b	274 \pm 30cd	324 \pm 21c	***	***
Malic acid	571 \pm 62a	193 \pm 68c	176 \pm 2.5e	155 \pm 12d	576 \pm 42a	208 \pm 51c	184 \pm 7.2e	372 \pm 356b	205 \pm 24c	165 \pm 59d	**	***
5-oxotetrahydrofuran-2-carboxylic acid	71 \pm 1.9 de	61 \pm 6.3e	83 \pm 3.6 d	91 \pm 6.8cd	103 \pm 14bc	116 \pm 9.8b	126 \pm 32a	36 \pm 4.0f	28 \pm 0.9f	71 \pm 5.2de	**	***
2-oxoapipic	8 \pm 0.7f	12 \pm 1.5de	17 \pm 1.9e	14 \pm 1.7cd	22 \pm 1.6a	19 \pm 1.4ab	17 \pm 1.2b	15 \pm 1.5c	11 \pm 1.8e	12 \pm 1.6de	**	**

Table 3. Cont.

Total fatty acids (µg/L)	5280	4728	5071	4792	4645	4336	4977	5035	5634	6540		
N-amyl acetate	2483 ± 12cd	2433 ± 12d	2487 ± 40cd	2471 ± 8 cd	2581 ± 42bc	2514 ± 11bc	2603 ± 31a	2462 ± 41cd	2508 ± 36bc	2548 ± 52bc	**	***
Hexylacetate	536 ± 13a	474 ± 31bc	463 ± 35c	423 ± 21e	486 ± 23b	479 ± 13bc	465 ± 28c	452 ± 19cd	416 ± 13e	421 ± 22de	*	*
Ethyl hexanoate	3151 ± 76c	3165 ± 96b	3213 ± 43d	3120 ± 27bc	3193 ± 36b	3160 ± 62b	3141 ± 58c	3240 ± 22a	3103 ± 93d	3128 ± 71bc	***	***
Ethyl lactate	395 ± 15f	1031 ± 59bc	766 ± 38cd	849 ± 75 cd	1179 ± 54b	616 ± 58e	659 ± 78e	1010 ± 64bc	954 ± 87bc	2122 ± 72a	***	***
Ethyl octanoate	2271 ± 12b	2148 ± 34bc	2322 ± 32a	2297 ± 46b	2177 ± 54bc	2362 ± 59a	2214 ± 26c	2122 ± 27bc	2131 ± 12c	2184 ± 68b	***	ns
Phenethyl acetate	334 ± 15d	487 ± 15bc	530 ± 30b	586 ± 21a	476 ± 19bc	490 ± 23bc	517 ± 45b	374 ± 38c	357 ± 41cd	506 ± 11bc	ns	***
Diethyl malate	142 ± 23g	222 ± 29c	286 ± 29a	219 ± 20c	169 ± 32f	162 ± 9.8f	202 ± 18e	256 ± 54b	299 ± 32a	282 ± 49a	**	***
Diethyl succinate	115 ± 21d	283 ± 32ab	270 ± 38b	244 ± 25c	285 ± 41ab	265 ± 21b	240 ± 28c	269 ± 29b	286 ± 21ab	294 ± 72a	**	***
Trimethylene acetate	431 ± 25a	363 ± 12e	341 ± 50f	358 ± 6.2e	276 ± 36c	287 ± 24cd	273 ± 5de	369 ± 35e	360 ± 42e	399 ± 28b	***	***
Ethyl-4-hydroxybutanoate	275 ± 14b	296 ± 25a	149 ± 13d	171 ± 14c	281 ± 26ab	117 ± 12e	150 ± 14d	285 ± 46a	224 ± 20cd	154 ± 32d	**	***
Total esters (µg/L)	10133	10902	10827	10738	11103	10452	10464	10839	10638	12038		
Butyrolactone	344 ± 41b	443 ± 37ab	369 ± 27ab	342 ± 29ab	228 ± 21c	260 ± 14.5bc	208 ± 14c	532 ± 18a	466 ± 12ab	461 ± 10ab	**	*
Pantolactone	12 ± 0.3b	trace	trace	trace	11 ± 3.2b	trace	Trace	trace	trace	44 ± 3.6a	*	*
3,4-dimethyl-2(5)-furanone	122 ± 12a	65 ± 6.7bc	43 ± 3.5cd	52 ± 4.2cd	84 ± 9.6b	33 ± 3.2de	42 ± 9.2cd	71 ± 2.1bc	69 ± 7.0bc	51 ± 5.7cd	***	***
Total lactones (µg/L)	478	508	412	394	323	293	250	603	535	556		
p-vinyl guaiacol	18 ± 2c	26 ± 3.6b	28 ± 3.2b	31 ± 2.4b	58 ± 12a	61 ± 12a	65 ± 13a	26 ± 6.4b	29 ± 3.1b	33 ± 4.2b	*	***
Methyl-hydroxycinnamate	77 ± 6.3a	32 ± 4.5b	16 ± 1.2d	12 ± 1.3e	21 ± 4.7c	14 ± 1.1de	11 ± 0.9e	26 ± 2.4bc	13 ± 1.4e	12 ± 1.2e	***	***
Acetovanillone	61 ± 0.8e	157 ± 21b	122 ± 24d	119 ± 12d	171 ± 35a	167 ± 19a	143 ± 15c	162 ± 32ab	139 ± 21cd	121 ± 11d	***	**
2,3-hydroxybenzofurane	156 ± 5.4a	114 ± 1.6c	63 ± 5.9e	79 ± 1.8de	116 ± 3.1c	44 ± 1.2f	33 ± 1.4f	127 ± 6.3b	99 ± 8.5d	56 ± 2.1ef	***	*
Vanillin	39 ± 3.5e	134 ± 2.1c	136 ± 1.9bc	133 ± 1.7c	139 ± 2.1ab	138 ± 1.8b	141 ± 2.3a	127 ± 1.4d	126 ± 1.1d	128 ± 1.9d	*	**
Total volatile phenols (µg/L)	351	463	365	374	505	424	393	468	406	350		

Table 4. Odor activity values of compounds reaching a concentration above the odor threshold (OAV > 1) in, at least, one variant. CW—control wine, N—non-toasted chips, L—light toasted chips, BAR—non-toasted barrel; 1M, 2M and 3M—number of months of ageing; ODT—olfactory detection threshold.

Volatile Compounds	Odor Descriptor	ODT (mL or µL)	References	CW	N1M	N2M	N3M	L1M	L2M	L3M	BAR1M	BAR2M	BAR3M
Iso-butanol (mg/L)	Bitter, fusel, alcohol	40	[27]	1.17	0.97	1.00	1.05	0.97	1.02	1.02	0.95	0.95	1.02
Iso-pentyl alcohol (mg/L)	Fusel	30	[32]	2.53	2.76	2.80	2.76	2.83	2.80	2.86	2.73	2.76	2.80
2-phenylethanol (mg/L)	Roses	14	[33]	1.07	1.14	1.21	1.21	1.14	1.28	1.21	1.35	1.21	1.28
2-nonanol (µg/L)	green creamy, citrus, cheese, fruity	58	[34]	2.98	1.72	0.81	1.00	1.98	0.63	1.01	1.68	1.34	0.22
3-methylthio-1-propanol (µg/L)	Boiled potato, rubber	500	[32]	0.55	0.49	0.50	0.41	0.35	0.33	0.44	1.10	0.58	0.48
Linalool (µg/L)	Floral, citrus	25	[33]	12.92	2.36	1.96	1.32	Trace	trace	trace	3.32	1.80	1.44
Iso-butyric acid (µg/L)	Fatty, butter, cheese	50	[32]	1.66	1.62	1.02	0.42	2.16	1.66	0.78	1.5	1.28	0.48
Isovaleric acid (µg/L)	Fatty, rancid, sweaty	33.4	[33]	3.95	4.67	6.55	-	4.88	5.65	5.68	6.85	8.86	16.10
Octanoic acid (µg/L)	Rancid, cheese, harsh	500	[33]	4.91	4.75	4.89	5.30	4.10	4.81	4.88	4.13	4.89	5.73
N-amyl acetate (µg/L)	Banana	30	[32]	82.76	81.10	82.9	82.36	86.03	83.80	86.76	82.06	83.60	84.93
Ethyl hexanoate (µg/L)	Apple, anise, strawberry	5	[32]	630.2	633.0	642.6	624.0	638.6	632.0	628.2	648.0	620.6	625.6
Ethyl octanoate (µg/L)	Pineapple, pear	2	[32]	1135	1074	1161	1148	1088	1181	1107	1061	1065	1092
Phenethyl acetate (µg/L)	Floral	250	[27]	1.33	1.94	2.12	2.34	1.90	1.96	2.07	1.49	1.43	2.02
Butyrolactone (µg/L)	Caramel, Sweet	35	[32]	9.82	12.66	10.54	9.77	6.51	7.43	5.94	15.20	13.31	13.17
3,4-dimethyl-2(5)-furanone (µg/L)	Caramel	19	[35]	6.42	3.42	2.26	2.73	4.42	1.74	2.21	3.74	3.63	2.68
p-vinyl guaiacol (µg/L)	Clove, smoke, spice	40	[27]	0.45	0.65	0.70	0.77	1.45	1.53	1.63	0.65	0.73	0.83
Vanillin (µg/L)	Vanilla, sweet	60	[35]	0.65	2.23	2.27	2.22	2.37	2.30	2.35	2.12	2.10	2.13

3.4. Multivariate Analysis

Figure 1 shows the chemical analysis results of the Chardonnay wines overlaid over the studied variants, with the wines projected on to that space. According to PLSR analysis, the distance between the variable and the center of the circle shows the interpretive degree of the principal components to the variable. The PLSR was established to determine the influence of methods and duration of ageing on volatile compounds.

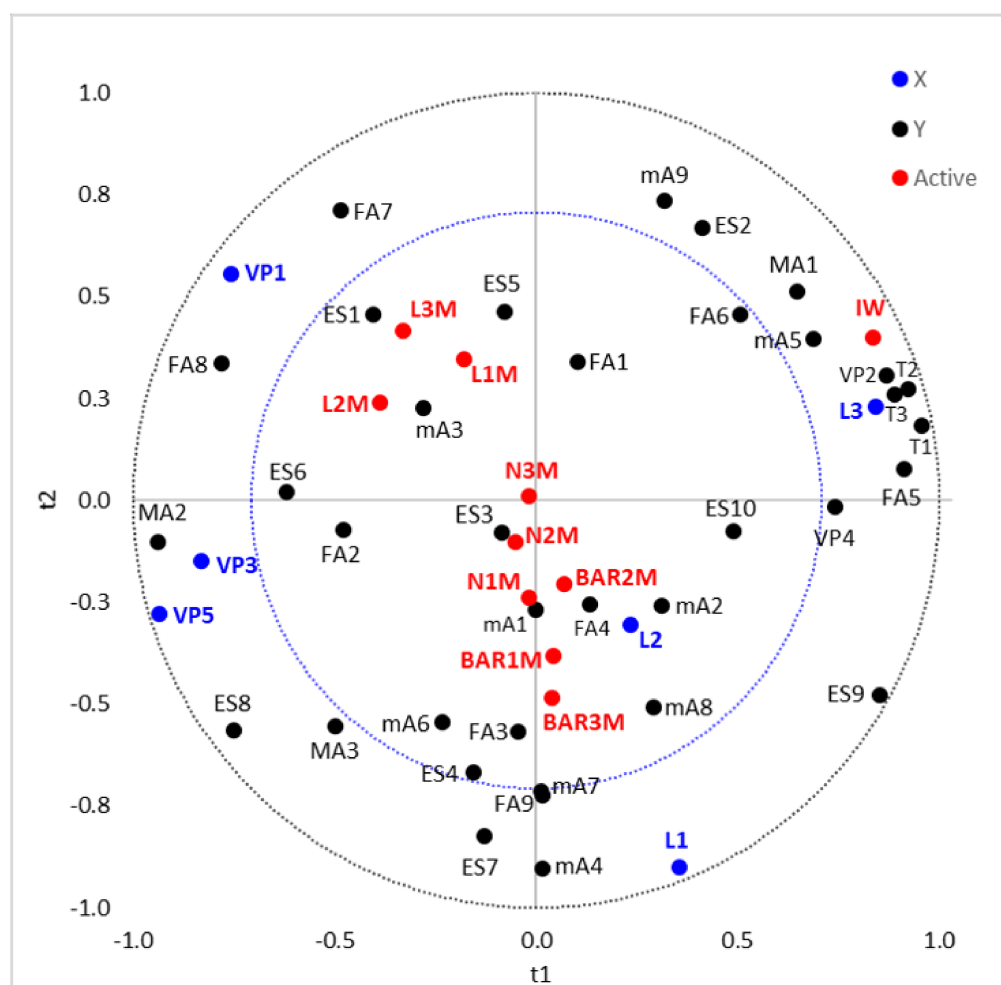


Figure 1. Partial least squares regression (PLSR) analysis, chemical data and the correlation of Chardonnay wines between ageing method and time (t1, chemical components of control wine; t2, chemical components released from wood). CW, N1M, N2M, N3M, L1M, L2M, L3M, BAR1M, BAR2M and BAR3M are the abbreviations for 10 variants of Chardonnay (CW—control wine, N—non-toasted chips, L—light toasted chips, BAR—non-toasted barrel; 1M, 2M and 3M—number of months of ageing). MA1 (iso-butanol), MA2 (isopentanol), MA3 (2-phenylethanol), mA1 (1-hexanol), mA2 (4-methyl-pentanol), mA3 (E-3-hexenol), mA4 (Z-3-hexenol), mA5 (2-nonanol), mA6 (1-heptanol), mA7 (2,3-butanediol), mA8 (3-methylthio-1-propanol), mA9 (benzyl-alcohol), T1 (linalool), T2 (terpineol), T3 (trans-geraniol), FA1 (iso-butyric acid), FA2 (hexanoic acid), FA3 (isovaleric acid), FA4 (octanoic acid), FA5 (decanoic acid), FA6 (malic acid), FA7 (5-oxotetrahydrofuran-2-carboxylic acid), FA8 (2-oxoapipic), FA9 (lactic acid), ES1 (N-amyl acetate), ES2 (hexyl-acetate), ES3 (ethyl hexanoate), ES4 (ethyl lactate), ES5 (ethyl octanoate), ES6 (phenethyl acetate), ES7 (diethyl malate), ES78 (diethyl succinate), ES9 (tri-methylene acetate), ES10 (ethyl-4-hydroxybutanoate), L1 (butyrolactone), L2 (pan-tolactone), L3 (3,4-dimethyl-2(5)-furanone), VP1 (*p*-vinyl guaiacol), VP2 (methyl-hydroxycinnamate), VP3 (acetovanillone), VP4 (2,3-hydroxybenzofurane), VP5 (vanillin).

In Figure 1, the volatile compounds of the control wine can be used to distinguish the aroma compounds of the aged wines. Control wine (unaged) is well related to alcohols such as iso-butanol (MA1), 2-nonanol (mA5), and to the terpenes: linalool (T1), terpineol (T2) and trans-geraniol (T3). Esters like hexyl-acetate (ES2), fatty acids like malic acids (FA6) and lactones like 2,4-dimethyl-2(5)-furanone were also related to the control Chardonnay wine. Those compounds are specific for fresh wines. The wines that pass through the maturation process are related to the esters, fatty acids, lactones and volatile phenols [36,37]. As can be seen from Figure 1, the wines aged in non-toasted medium (chips and barrel) appear as grouped against the wines aged with light toasted chips. This finding is similar with other research by Calugar et al. [13], for Muscat Ottonel wines. The non-toasted barrel ageing is correlated with lactones that came from untreated wood—butyrolactone (L1) and pantolactone (L2). The non-toasted medium is also related to esters such as ethyl lactate (ES4), ethyl caproate (ES3), and carboxylic acid, as lactic acid (FA9), octanoic acid (FA4) and isovaleric acid (FA3). The majority of volatile phenols quantified in this research, came from the thermal treatment of wood and are correlated with wines aged with light-toasted chips. In a study, Farrel et al. [38], stated that vanillin (VP5), *p*-vinyl guaiacol (VP1) and acetovanillone (VP3) are volatile phenols which come from the thermal degradation of wood.

4. Discussion

The diversity of oak products allows winemakers to achieve different results according to the expected outcome and consumer preferences. Exposure to oak wood may cause unbalanced flavor profiles with strong oak aromas if the maturation period is longer [30].

4.1. Basic Parameters of Chardonnay Aged Wines

During wood contact, basic parameters of wines were affected. The decrease of alcohol content could be the result of the evaporative loss of ethanol and its diffusion through the staves, which are higher than that of water during ageing [29]. The increase in titratable acidity is due to the rise in volatile acidity; during the first months this rise could indicate the extraction of carboxylic, phenolic and volatile acids from the wood as suggested by Aiken and Noble, [39]. According to Towey and Waterhouse [40], the pH and ethanol of wines also influenced the amount of volatiles extracted from oak products. It has been stated that the characteristics of the wine itself may also be very important during the ageing process, since pH, ethanol and acidity may have a direct influence on ethanolysis of wood components. Some contradictory results have been found. Garde-Cerdán et al. [41,42] stated that the extraction of furanic aldehydes, oak lactones, phenolic aldehydes and alcohols was influenced by the wine alcohol content, the wine pH being less significant, whereas Ortega-Heras et al. [43] did not find significant correlations between wine ethanol content and the levels of any of the volatile compounds studied.

4.2. Volatile Compounds in Chardonnay Aged Wine

The method of ageing influences the amount of chemical compounds at different times of the process. During ageing, specific compounds are transferred to wines as a result of prolonged contact with oak chips [30]. When employing the oak alternatives, the main factors to be considered are the amount and surface area (shape and size) of the materials used. In this respect, chip and barrel-aged wines differ in their content of a range of volatiles, such as vanillin, guaiacol or furfurals [3].

Louw et al. [44] states that young unoaked Chardonnay wines can be discriminated (with 74% correctly classified) by using the following eight volatile compounds: 2-phenylethanol, decanoic acid, diethyl succinate, ethyl hexanoate, ethyl decanoate, ethyl octanoate, hexyl acetate and 1-propanol. In general, alcohols can be the product of sugar fermentation and amino acid metabolism through yeasts. Higher alcohols have a significant impact on the fruity aroma of wine [45]. The major alcohols (iso-butanol, isopentyl alcohol and 2-phenylethanol) varied both depending on the time and type of ageing with different

trends. However, at the end of the maturation period, the major alcohol concentrations were higher, regardless of the method. Also, the concentrations of the minor alcohols group were dependent on ageing time and method. The non-toasted barrel ageing method favored the concentration of hexanol, which supplied a leafy and grassy note to wine samples [31]. Generally, 2,3-butanediol is not expected to affect the sensory qualities of wine appreciably, but some authors [46] noted a bitter taste in variants with a concentration over 700 mg/L of this compound in wines samples. In our research, the higher concentration of 2,3 butanediol in the BAR variant wine sample could be explained by enzymatic reduction of diacetyl and acetoin in this compound under malolactic fermentation which could occur in barrels [47].

Overall, the time and method of ageing, significantly influenced the concentration of major and minor alcohols in wine samples, with higher amount for the variant aged in the non-toasted barrel. Increased amounts of higher alcohols during ageing can be caused by acid-catalyzed ester hydrolysis [48].

The esters chemical family contribute to the fruity character of wines and are one of the predominant chemical groups [49]. In this research, the impact of ageing duration and method on the Chardonnay wines concentration of esters was investigated. Most of them exhibited concentrations above their olfactory perception threshold, providing the wine with pear, apple, pineapple and/or floral notes [30,31]. During ageing, the esters had interesting trends; most of them have increased in concentration compared with the control wine and only hexyl acetate and trimethylene acetate decreased after ageing. Ethyl fatty acid esters are considered to be very important for the aroma of wines. The concentration of ethyl lactate progressively increases during malolactic fermentation [46]. This result is beneficial for the wine bouquet due to its fruity, buttery or creamy aromas, also contributing to the sensations of roundness in the mouth [46,50]. Overall, the ageing process, regardless of the method, slightly increased the amount of esters. Even more, after 1, 2 and 3 months of ageing, the concentrations of esters were nearly similar for the same time period of ageing among methods of ageing.

The fatty acids chemical group of volatile compounds is produced by yeast and bacteria during fatty acid metabolism. Volatile fatty acids can contribute to the complexity of the wine bouquet even if they are present under threshold levels. They have a negative effect on wine aroma when above their thresholds [51]. Some acids, such as iso-butyric acid and decanoic acid are not associated with wine quality, but they play an important role in the complexity of the aroma [52]. In the present study, there were significant differences in the fatty acid content between control wine and the wine samples aged by different methods. Decreased acid concentrations could be caused by the loss of volatile acids and esterification reactions between alcohols and acids during the ageing process [53]. Also, Vivas et al. [54] explained that the increase in volatile acidity in wine in contact with oak wood is mainly due to two reasons: firstly, the acidity may increase or decrease as a result of the chip roasting process, and secondly, may be due to acetic metabolism (i.e., acidic bacteria in wine).

As expected, the lactones showed the highest concentration in wine samples treated with non-toasted wood (non-toasted chips and barrel). This could be explained by the fact that some lactones are found in non-toasted wood, and thermal treatment degraded those compounds. Lactones add caramel and sweet flavor to wines [38].

Unlike the expected behavior, for ageing methods in/with non-toasted wood, total phenol volatiles content was similar for both methods, for the three ageing durations. It could be stated that, at least the first three months of ageing in non-toasted barrels are similar with ageing with non-toasted chips, regarding this chemical family. Regardless of the ageing method, wines which underwent the wood ageing presented greater vanillin concentrations, than the corresponding control wine. In our experiments, no control of MLF was conducted (no culture of bacteria and no inhibitors were added), so the increasing of vanilla volatile compounds in wood aged wine could under gone as the capacity of lactic bacteria (spontaneous MLF) to convert vanillin glycoside pre-cursors present in oak

wood [55,56]. Spillman et al. [21] states that *p*-vinylguaiacol is a fermentation product rather than a compound derived from oak contact, formed through decarboxylation of natural grape components ferulic and *p*-coumaric acids by *S. cerevisiae* enzymatic activity. The concentration of 4-vinyl-guaiacol in our Chardonnay wine samples could indicate that this compound formed mainly during the fermentation period, but was also extracted from toasted wood products.

Overall woody aroma of barrel-aged wines results from different chemical compounds naturally present in oak wood, originated in the toasting process and/or formed as a consequence of the wood-wine interaction. Gambetta et al. [3] described furfurals, 5-methylfurfural, cis- and trans-whiskey lactones, guaiacol, eugenol and vanillin as odorants derived from oak wood contact, or formed during ageing. The statistical test of the experimental data disclosed that the time and the ageing method significantly impact the oak wood volatiles concentration of the studied wines.

4.3. Odor Activity Values

Among all the compounds present in Table 3, not all of them present an odor activity value OAV >1 (Table 4), which is normally taken as the value required for a compound to be a likely contributor to the specific aroma. The OAVs based on threshold values in a specific matrix (e.g., neutral white wine or 10% *v/v* aqueous ethanol) act merely as a guide when determining the importance of a compound to wine aroma, due to a significant effect of the matrix [3]. The highest OAV was exhibited, among all samples, by ethyl octanoate characterized by pineapple and apple notes, specific for Chardonnay wines [19]. Ethyl hexanoate and N-amyl acetate are fruity aroma contributors with concentrations above their threshold in all samples, mainly in wine samples treated with light-toasted chips. The method of wine ageing using non-toasted wood products, could preserve the floral character of Chardonnay wines. These results were in accordance with those presented previously by Calugar et al. [11], on Muscat Ottonel wines. Regarding the fatty acids, the rancid aroma supplied by isovaleric acid could be easily perceived in the non-toasted oak barrel aged sample, due to the low odor threshold of this compound. The spicy and condiment aroma could be highlighted by L1M-L3M samples, where light toast of chips increased the amount of *p*-vinyl guaiacol extracted by wine. The compounds that give wines a vanilla and roasted note (vanillin—VP5, *p*-vinyl guaiacol—VP1 and acetovanillone—VP3) are related to the light toasted chips in our study. For short periods of maturation, Chardonnay wines can obtain almost the same qualities if aged with non-toasted chips and non-toasted barrel, from the volatile point of view, but with more efficient cost, from the economical point of view. The PLRS analysis shows that wine samples treated with the French non-toasted oak chips aged for 1 or 2 months have similar wine volatile profiles with those from Romanian non-toasted oak barrels. Some differences between non-toasted variants were observed when the wines were aged for 3 months. Chardonnay is not dominated by a distinct varietal compound as in other varieties like Sauvignon blanc or Muscats. The typicity concept for Chardonnay wines needs more comprehension and requires deeper study, because this is a variety that can express itself in a multitude of profiles. Understanding Chardonnay typicity requires multidisciplinary studies that analyze a number of variables responsible for the final product, rather than a one-directional focus [3]. Nevertheless, the use of oak barrel alternatives, in particular, offers an economic means of imprinting the desirable aroma compounds from oak without the time or expenses associated with ageing wine in oak barrels [57].

It is not easy to distinguish products obtained by aging with chips from those obtained traditionally (barrel aged) from a sensory point of view. The distinction of the two different products is possible through laboratory investigation techniques: analytical methods allow expanding the compositional differences between the two wine products. Among the analytical techniques used, the spectroscopic ones are certainly those that, combined with multivariate statistics techniques, allow to obtain the best results in this field, for commercial purposes and, if necessary, for the control of fraudulent activities [58].

5. Conclusions

This work is the first study on volatile compounds of young and short matured Chardonnay wines from Romania. The method and time of ageing have a significant influence on basic wine parameters and on the volatile composition. The non-toasted medium (chips and barrel) ageing is correlated with lactones, esters (ethyl lactate and ethyl caproate) and fatty acids (isovaleric and lactic acids). The majority of volatile phenols were quantified in wines aged with light-toasted chips. The oak chip method of ageing the Chardonnay wines could be a useful tool to obtain wines as a viable alternative to the traditionally made Chardonnay wines. The amount of chips used in this study (4 g/L) was selected in order to avoid an excessive impact of the wood character in wines that could produce a negative effect on tasting. For short periods of maturation, Chardonnay wines can obtain almost the same wine aged with non-toasted chips and non-toasted barrels, from the chemical point of view, but with more efficient cost, from the economic point of view. For white wines, the use of oak chips could avoid the oxidation of aromatic volatile compounds that could be produced during barrel ageing, and impart oak notes to wines without decreasing the fresh and fruity characteristics. This approach would enable diversification on the market and increase the range of products on offer to the consumer.

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