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Wine Spirit Ageing with Chestnut Staves under Different Micro-Oxygenation Strategies: Effects on the Volatile Compounds and Sensory Profile

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Abstract: The purpose of this work is to evaluate the wine spirit aged by an alternative process (staves combined with different micro-oxygenation levels) and its comparison with the traditional process (wooden barrels). This evaluation was made by analyzing the volatile compounds and sensory profile of the spirits during 365 days of ageing. The findings confirmed the role played by oxygen in the volatile profile of aged wine spirits. Samples of alternative ageing modalities were well distinguished from those of wooden barrels based on the volatile profile, namely on the concentrations of several volatile phenols. From a sensory point of view, the results are promising with high overall consistency scores obtained from samples of alternative ageing process modalities.

Keywords: wine spirit; chestnut; micro-oxygenation; volatile compounds; sensory profile

1. Introduction

The traditional process for ageing wine spirits consists of keeping them, after the distillation, in wooden barrels for a longer or shorter period of time, from several months to several years. Traditionally, the oak wood, especially from the French region of Limousin (mostly *Quercus robur L.*), is used for making the barrels for the ageing of wine spirits [1]. Nevertheless, the results from several studies [2] revealed the suitability of chestnut barrels for the ageing of wine spirits.

During this time, the interaction between the drink and the wood takes place in an oxidative environment, as the barrel allows very low levels of oxygen to pass through [3]. As consequence several physicochemical reactions occur [4], which promote a deep change on the volatile and sensory profile of the beverage [1,5–7], resulting in their quality increase over the time [5]. In fact, the freshly distilled wine spirit, which is colorless, with floral and fruity notes and slight green notes, acquires great sensory complexity as it ages in wooden barrels, due to the arising of vanilla, dried fruits, smoke, coffee, and spicy odor notes [5–7]. Regarding the volatile composition, the unaged wine spirit (i.e., the distillate) mostly consists of water and ethanol as well as various volatile compounds from different chemical families [1,8,9]. During ageing in wooden barrels, it is enhanced with various volatile compounds derived from wood, such as volatile phenols, phenolic aldehydes, furanic aldehydes and lactones [1,10] which are well correlated with several odor notes of aged wine spirits [11–13] and whose contents increase over time [10,14]. On the other hand, the contents of some volatile compounds derived from the distillate do not seem to change significantly over time [10,14], although other volatiles, such as acetaldehyde, acetic acid, and ethyl acetate, tend to increase due to oxidation and esterification reactions [14,15].

In the last years, alternative ageing processes have been studied, namely the application of wood fragments to the spirits kept in stainless steel tanks. These studies were focused on cider spirits [16], apple spirit [17], grape marc spirits [18,19], and sugar cane spirits [20,21]. Concerning the wine spirits, the research revealed that the fragment size/shape and the kind of wood had a significant effect on the chemical composition of these beverages [8,22,23]. In addition, it has been shown that it was possible to obtain aged wine spirits with sensory quality similar to that of the traditional process, although with a very different chemical composition [8,10].

More recently, the combination of wood fragments with micro-oxygenation (MOX), in an attempt to simulate what is happening in a wooden barrel, has shown that it is possible to accelerate the ageing process in comparison with the conventional process, enabling to obtain higher quality spirits [24,25]. These studies confirmed the importance of oxygen in the ageing process. However, so far, only one mode of micro-oxygenation has been studied under industrial conditions, without achieving a systematic comparison of different oxidative conditions of the medium.

This work intended to comparatively evaluate the same wine spirit aged with alternative process (staves combined with different micro-oxygenation levels) and evaluate its comparison with the traditional process (wooden barrels). This approach was based on the sensory profile and volatile compounds profile of the spirits after an ageing time of 365 days. Besides, some target volatile compounds were quantified during the ageing process to monitoring and understanding the ageing chemistry in different conditions.

2. Materials and Methods

2.1. Reagents

Anhydrous sodium sulfate and ethanol were purchased from Merck (Darmstadt, Germany); dichloromethane was obtained from Honeywell Riedel-de Haën (Steinheim, Germany), and silanized glass wool was supplied by Supelco (Steinheim, Germany).

The ultrapure water was obtained through the arium®comfort I equipment from Sartorius Lab Instruments, Germany.

GC-FID and GC–MS standards: acetic acid was purchased from Riedel-de-Haen (Seelze, Germany); ethyl isobutyrate, ethyl 2-methylbutyrate, ethyl 3-methylbutyrate, ethyl hexanoate, ethyl L-lactate, 1- hexanol, ethyl octanoate, linalool, butanoic acid, 3-methyl butanoic acid, hexanoic acid, guaiacol, 2-phenylethanol, eugenol, 4-ethylphenol, 3,4-dimethylphenol (internal standard), syringol, dodecanoic acid, 4-hydroxy-3-methoxy-benzaldehyde (vanillin), 5-methyl-2-hexanol (internal standard; IS) were purchased from Fluka (Buchs, Switzerland); isoamyl acetate, *trans*-2-hexen-1-ol, *cis, trans*-β-methyl-γ-octalactone, 4-propylguaiacol, 4-methyl-syringol, 4-allyl-syringol were purchased from Aldrich (Steinheim, Germany); 4-ethylguaiacol, DL-malic acid diethyl ester were purchased from TCI (Zwijndrecht, Belgium), ethyl butyrate was purchased from Merck (Darmstadt, Germany). 2-Methyl-1-butanol, 3-methyl-1-butanol, 2-methyl-1-propanol and acetaldehyde were purchased from Fluka (Buchs, Switzerland). The proportion of isomers *cis* and *trans* from β-methyl-γ-octalactone were determined before being used for calibration.

2.2. Wine Spirit Samples and Experimental Design

The same wine spirit obtained by column distillation in Lourinhã region (Portugal), at a Portuguese winery (Adega Cooperativa da Lourinhã) was used to fill several vessels corresponding to five modalities with different ageing conditions:

- CB—250 L wooden barrel of chestnut wood;
- CO15—50 L glass demijohns with chestnut staves and micro-oxygenation with a flow rate of 2 mL/L/month during the first 15 days followed by 0.6 mL/L/month until 365 days;
- CO30—50 L demijohns with chestnut staves and submitted to a micro-oxygenation with a flow rate of 2 mL/L/month during the first 30 days followed by 0.6 mL/L/month until 365 days;
- CO60—50 L glass demijohns with chestnut staves and submitted to a micro-oxygenation with a flow rate of 2 mL/L/month during the first 60 days followed by 0.6 mL/L/month until 365 days;
- CN—50 L demijohns with chestnut staves and nitrogen application with a flow rate of 20 mL/L/month (nitrogen modality).

The dissolved oxygen content in each modality was controlled over the time, as described previously [24] and the values are shown in Figure 1.

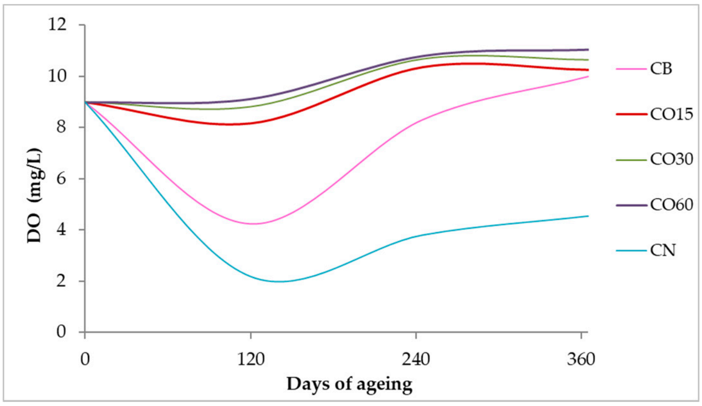


Figure 1. Average dissolved oxygen content in each ageing modality, during the ageing period (adapted from [24]).

Two replicates of each modality were carried out and the chestnut wooden barrel and staves were submitted to medium plus toasting at the cooperage (J. M. Gonçalves, Palaçoulo, Portugal). The number of staves (50 cm length × 5 cm width × 1.8 cm thickness) introduced into the demijohns was planned in order to mimic the surface area to volume ratio of a 250 L barrel (85 cm^2/L).

The supply of pure oxygen (X50S Food, Gasin, Perafita, Portugal) in the 50 L demijohns was done through a multiple diffuser micro-oxygenator (VISIO 6, Vivelys, Viileneuve-lès-Maguelone, France) with ceramic diffusers, at different flow rates according to the ageing modality (O). Pure nitrogen (N) (X50S Food, Gasin, Perafita, Portugal) was supplied during the ageing experiment through a specific apparatus (Gasin, Perafita, Portugal).

All the ten experimental units, located in the cellar of Adega Cooperativa da Lourinhã in similar environmental conditions, were sampled at a middle height and over specific time periods (at 8, 60, 180, 270 and 365 days of ageing) in order to monitor the target volatile compounds: acetaldehyde, linalool, acetic acid and syringol.

At the experiment's conclusion (365 days), the samples were taken for odorant profile screening and sensory evaluation of the wine spirits.

At the beginning of the experiment, a sample of the unaged wine spirit was also taken, and the target and odorant compounds as well as the sensory characteristics were determined. This sample was coded as a control spirit.

2.3. Analysis of Odorant Compounds of Wine Spirits

At the end of the ageing experiment, the analysis was focused on the volatile compounds previously assigned as odorant compounds [11]. These odorant compounds included some major volatile compounds, such as 2-methyl-1-butanol, 3-methyl-1-butanol and 2-methyl-1-propanol, which were quantified by GC-FID in the wine spirit distillate, and several minor volatile compounds that were analysed by GC-FID after previous steps of extraction and concentration.

During the ageing experiment, four target volatile compounds (acetaldehyde, acetic acid, linalool, and syringol) were analyzed.

2.3.1. Quantification of Major Volatile Compounds by GC-FID

Acetaldehyde, 2-methyl-1-butanol, 3-methyl-1-butanol, 2-methyl-1-propanol, and ethyl acetate were determined by GC-FID, following a previously validated method [26]. The samples of 10 mL of each wine spirit distillate, previously added of 1 mL of 5-methyl 2-pentanol (internal standard) were manually injected (1 µL) on Focus GC (Thermo Scientific, Whaltham, MA, USA) chromatograph coupled to a flame ionization detector (FID) and equipped with fused silica capillary column of polyethylene glycol (DB-Wax J & W Scientific, Folsom, CA, USA), 60 m, 0.32 mm i.d., 0.25 µm film thickness. The chromatographic conditions were: injector (200 °C) detector (250 °C); carrier gas hydrogen (3.4 mL/min and split ratio 1:6); oven temperature program: 10 °C/min from 35 °C (8 min isothermal) until 200 °C and held at this temperature for 9 min.

The quantification was done by analyzing hydroalcoholic solutions of the standards in similar conditions.

2.3.2. Quantification of Minor Volatile Compounds by GC-FID

Previous to the analysis by GC-FID, a volume of 100 mL of each wine spirit added of 1.6 mL of 5-methyl-2-hexanol as an internal standard (IS, 81.0 mg/L 50% ethanol solution) and 0.5 mL of 3,4-dimethylphenol (IS, 100 mg/L in ethanol) was extracted with dichloromethane (30, 10 and 10 mL) and concentrated on a rotary evaporator (Büchli rotavapor R114 at 42 ± 0.5 °C, without vacuum) until a volume of about 0.25 mL according to the method previously validated [27]. Each extract was analyzed under the following chromatographic conditions: Agilent Technologies 6890 Series gas chromatograph (Wilmington, DE, USA) coupled to a flame ionization detector (FID) and equipped with a fused silica capillary column of polyethylene glycol (INNOWax of J&W Scientific, Folsom, CA, USA), 30 m, 0.32 mm i.d., 0.25 µm film thickness; injection volume of 0.8 µL; injector and detector temperatures (250 °C); carrier gas hydrogen (2.4 mL/min and split ratio 1:25); oven temperature program: 3.5 °C/min from 35 °C (6 min isothermal) to 55 °C, 7.5 °C/min to 130 °C, 5 °C/min to 210 °C (30 min isothermal). For each sample, the extractions were done in duplicate, and each extract was analyzed in triplicate.

The quantification of minor volatile compounds (acetic acid, linalool, guaiacol, 4-methylguaiacol, eugenol, syringol, 4-methylsyringol, vanillin, acetovanillone, ethyl isobutyrate, ethyl butanoate, isoamyl acetate, trans-2-hexenol, ethyl octanoate, furfural, 5-methylfurfural, butanoic acid, 2-methylbutanoic acid, hexanoic acid, 2-phenylethanol, 4-ethylguaiacol, dodecanoic acid, 5-hydroxymethylfurfural, 4-allylsyringol) was based on calibration curves, which were established by the extraction of hydroalcoholic solutions of standards and their chromatographic analysis under similar conditions.

2.3.3. Analysis by GC/MS

The compounds identification was done by injection of 0.4 µL of each sample on a GC-MS equipment (Magnum, Finnigan Mat, San Jose, CA, USA) with a polyethylene glycol fused silica capillary column (HP-INNOWax of J&W Scientific, Folsom, CA, USA, 30 m, 0.25 mm, 0.25 µm thick), employing helium as carrier gas at 83 kPa pressure; the injector worked with split ratio 1:60 at 250 °C; the transfer line was also at 250 °C; the oven temperature program: 3.5 °C/min of 35 °C (6 isothermal minutes) to 55 °C, 7.5 °C/min to 130 °C, 5 °C/min to 210 °C and kept at this temperature for 30 min. The mass spectrometer worked in the electron impact mode at 70 eV and scanned the mass range of m/z 20–340.

The identities of volatile compounds were carefully confirmed by assessment of Kovats retention index (KI) and by MS fragmentation pattern with those of reference compounds and with mass spectra in the NIST libraries.

2.4. Sensory Evaluation of Wine Spirits

The aged wine spirits samples were assessed by a group of eight tasters according to the procedure previously described [25].

The sensory attributes, previously generated, included sixteen orthonasal aroma attributes (alcohol, fruity, vanilla, wood, rancid, spicy, caramel, toasted, dried fruits, smoke, coffee, sweet, green, tails, glue, and caoutchouc) and twelve gustatory attributes (sweetness, smooth, burning, astringency, roughness, bitter, body, unctuous, flavor complexity, flavor evolution, retronasal aroma, and persistence).

The aged wine spirits samples were diluted with water fifteen days before the tasting session to reduce the ethanol content to 40% v/v, and they were kept in the dark at 20 °C until analysis.

The tasting session was carried out in the Instituto Nacional de Investigação Agrária e Veterinária (INIAV) tasting room with individual white boots, and 30 mL of each sample was assessed in standard wine-tasting glasses (ISO 3591) [28]. The sensory evaluation was done in the morning between 10:00 a.m. and 12:00 a.m., and the tasters evaluated the samples, coded with three random digits, and presented in each session in balanced order to eliminate first-order carryover effects [29].

The tasters were asked to evaluate the sensory attributes with a structured scale (0-no perception to 5-highest perception) and to rate the overall quality of the wine spirits, from 0 to 20. The sensory data were collected by the Tastel software (ABT Informatique, Rouvroy-sur-Marne, France).

2.5. Statistical Analysis of Data

The analytical and sensory data determined in the aged wine spirits samples after 365 days of ageing were submitted to a one-way analysis of variance (ANOVA) to verify the influence of the micro-oxygenation modality on the sensory and volatile composition.

Similar analysis was done at each sampling time with the data of target compounds. The variance homogeneity was assessed (Cochran test); when a statistically significant effect was found ($p < 0.05$) the least significant difference (LSD) test was applied to compare the means.

Heatmaps analysis was performed, firstly, with the volatile compounds and thereafter with the sensory attributes presenting significant effects with the ANOVA. The r value of Pearson correlation was determined for both group of data and correlated using the clustering analysis. On the heatmaps, different colours represent the positive r and negative one.

For all above-mentioned analysis, Statistica version 7.0 software (StatSoft Inc., Tulsa, OK, USA) was used.

3. Results and Discussion

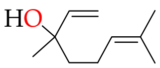
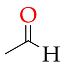
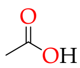
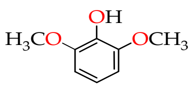
In this study, the effects of different micro-oxygenation strategies on the content of odorant compounds, that is the volatile compounds previously identified as key odorants in aged wine spirits [11], were evaluated. Additionally, acetaldehyde and ethyl acetate were also quantified.

A sensory assessment of control and aged spirits was also carried out.

3.1. Evolution of Target Volatile Compounds over the Ageing Experiment

Table 1 exhibits the results of the target volatile compounds over the ageing time and the corresponding graphical representation to clearly show the behavior over the time. These compounds were chosen as targets from a wide set of volatile compounds in wine spirits [1] because they have different origins and different behaviors during the ageing time according to previous research made on alternative ageing technologies without micro-oxygenation [8,10].

Table 1. Concentration (mg/L) of target volatile compounds quantified in the wine spirits sampled from different ageing modalities over the time (8, 60, 180, 270 and 365 days) and ANOVA summary.

		Ageing Time (days)					
		0	**8**	**60**	**180**	**270**	**365**
	Significance level	-	*ns*	*ns*	*ns*	*ns*	*0.008*
Linalool (mg/L) 	*CB*	0.31	0.30	0.27	0.22	0.20	0.14 [a]
	CO15		0.28	0.27	0.24	0.21	0.17 [a]
	CO30		0.29	0.26	0.26	0.23	0.25 [b]
	CO60		0.27	0.24	0.23	0.19	0.25 [b]
	CN		0.28	0.26	0.24	0.20	0.16 [a]
	Significance level	-	*ns*	*ns*	*0.016*	*0.001*	*0.013*
Acetaldehyde (mg/L) 	*CB*	28.90	40.03	61.05	58.82 [a]	43.99 [a]	56.64 [a,b]
	CO15		40.90	51.59	64.84 [b]	59.18 [b]	66.01 [c]
	CO30		43.51	56.75	65.66 [b]	57.39 [b]	60.09 [b,c]
	CO60		46.99	67.93	66.20 [b]	56.80 [b]	59.68 [b]
	CN		43.51	61.05	58.91 [a]	43.10 [a]	51.43 [a]
	Significance level	-	*0.018*	*0.002*	*0.000*	*0.000*	*0.000*
Acetic acid (mg/L) 	*CB*	84.84	153.21 [b]	278.62 [b]	361.03 [c]	381.05 [c]	427.14 [c]
	CO15		141.14 [a]	177.73 [a]	243.14 [b]	257.36 [b]	246.85 [b]
	CO30		136.65 [a]	222.63 [a,b]	227.29 [b]	228.15 [a,b]	245.20 [b]
	CO60		141.61 [a]	197.79 [a,b]	235.89 [b]	247.97 [b]	254.33 [b]
	CN		133.65 [a]	195.48 [a,b]	205.58 [a]	200.83 [a]	218.29 [a]
	Significance level	-	*0.002*	*0.000*	*0.000*	*0.000*	*0.000*
Syringol (mg/L) 	*CB*	0.00	0.14 [a]	0.22 [a]	0.24 [a]	0.27 [a]	0.28 [a]
	CO15		0.27 [b]	1.03 [b]	1.46 [b]	1.50 [b]	1.39 [b]
	CO30		0.25 [b]	1.02 [b]	1.42 [b]	1.37 [b]	1.43 [b]
	CO60		0.27 [b]	1.04 [b]	1.39 [b]	1.42 [b]	1.48 [b]
	CN		0.23 [b]	0.93 [b]	1.34 [b]	1.38 [b]	1.30 [b]

For each compound and for each ageing time, means within the same column followed by different uppercase letters ([a], [b], [c]) are significantly different ($p < 0.05$).

Linalool, a terpenic alcohol proceeding from the grapes [30], is normally present in unaged wine spirits, as can be observed in Table 1, and it is usually linked to a floral, violet odor [11]. The linalool amount of 0.31 mg/L in the control wine spirit sample is according with the values range (0.17–0.50 mg/L found in other wine spirits [10,31]. Conversely, it is lower than the amounts found in distillates made from Muscat wines [32], as the result of high levels of this compound in Muscat grapes [30]. In the present work, the linalool amount was not affected by the MOX strategies until 270 days of ageing. Only at the end of the ageing experiment (365 days) were significantly higher amounts observed in the spirits produced with CO30 and CO60 MOX. The increase in linalool concentration has been ascribed by several authors to the availability of different precursors capable of generating this alcohol during ageing, particularly glycosidic precursors [33] and terpene diols [34]. The acidic hydrolysis of terpene glycosides result in a molecular rearrangement of the monoterpenols, which are then converted into other compounds such as linalool [35,36]. The higher concentration of oxygen in these MOX modalities (CO30 and CO60) resulted in an increase of electron-deficient oxygen species, such as aldehydes and carboxylic acids [24], contributes to reduce the pH of the medium, and may lead to the degradation of terpene glycosides. A slight decrease over the time of the linalool was observed in all the other modalities. A similar decrease was pointed out during an ageing experiment of two years [10]. The non-saturation characteristic of the double bond relates to the capability to participate in addition reactions, which is enabled by the π bond's weak energy. The cyclization product of monoterpes catalyzed in acidic medium, is well known and can produce the two cineoles, by dehydration and direct cyclization or by the production of α-terpineol [36]. On the other hand, the high electronic density at the level of a double bond, as well as the accessibility of electrons π, means that electrophilic reagents (H^+, R^+, among others) would be the primary cause of attacks. Due to its own reactivity, the double bond is a weak point in the carbon chain, and certain reactions, such as oxidation reactions, can lead to a rupture between two double bonded carbons. The linalool concentration presented in freshly distilled wine spirits supposed to be consumed over time, as there is no way to form it in the reaction mixture, given that primarily sources of terpenes are the grapes skins and pulp [35,37,38]. Our findings for this compound might suggest further studies to determine whether it can be used as a marker of the authenticity of the wine distillate, as well as of its ageing time, since the longer it ages, the less linalool in its free state should be present.

Acetaldehyde, which is linked to a fruity note [13], was present in the unaged wine spirit (Table 1) with an amount of 28.9 mg/L. Indeed, acetaldehyde is a major volatile compound that is produced by yeasts during the wine fermentation process and recovered in the distillate [1], and a by-product of ethanol oxidation metabolism. During the ageing experiment its amount increased over time in all modalities with a slight decrease between 180 and 270 days of ageing. In the first two sampling times (8 and 60 days) there was no significant differences between the five ageing modalities. However, at 180, 270, and 365 days, significant differences between the acetaldehyde concentration in the wine spirits resulting from several ageing modalities was detected (Table 1). The highest amounts were found in wine spirits produced with MOX (CO15, CO30 and CO60) and the lowest ones were found in the wine spirits aged in wooden barrels and with nitrogen. This behavior was expected because the presence of acetaldehyde is related to ethanol oxidation; in more oxidative environments, its higher concentration is not surprising. At the last sampling time, it was possible to discriminate the wine spirit samples proceeding from different alternative modalities based on the acetaldehyde amounts, which were lower in the samples from the nitrogen modality (CN) and higher in CO15 samples. The amount of acetaldehyde found in micro-oxygenation modalities samples should be closely monitored. However, due to its high reactivity even in mild conditions, it is expected that the presence of acetaldehyde will decrease over time. Its reactivity is due to the fact that it has a trigonal carbon electrophile which is attacked by nucleophiles for the formation of a tetrahedral products or intermediates. The most important trigonal electrophiles found in wine spirits include carbonyl groups, which are classified as follows: aldehydes > ketones > esthers > carboxylate ions. This order is easy to understand. The aldehyde ΔE_H has the lowest activation energy for disrupting π stabilization, whereas the carboxylate ion has the highest [39].

Acetic acid derives from the wine distillate, from the oxidation of ethanol via acetaldehyde, and from the acetyl groups found in the wood xylans, an important type of hemicelluloses [40]. Acetic acid is related to vinegar aroma [11,12] and existed in the unaged wine spirit (Table 1). Its concentration increased over the ageing time in accordance with other works [10,14,41,42]; which is associated with ethanol oxidation during ageing [43]. Nevertheless, significant differences in the acetic acid amounts were verified in the wine spirits originated from different ageing modalities. The highest amounts were determined in the samples aged in the wooden barrels while the lowest were determined in samples from nitrogen modality (CN), confirming that its origin is linked to the oxidation of ethanol and acetaldehyde. These results pointed out the oxygen importance in the acetic acid formation and its increase during the ageing process.

Indeed, according to previous studies, acetaldehyde rates are high in very old aged spirits [14] or very old aged wkiskies as result of ethanol oxidation [15], and acetaldehyde oxidation into acetic acid. Esterification between acetic acid and ethanol has been verified by ethyl acetate formation [15]; therefore, ethyl actetate quantification in wine spirits samples at the end of ageing experiment was made (Table 2). The results revealed slightly higher amounts of ethyl acetate in samples aged in wooden barrels and the lowest occurred in the nitrogen modality (CN), while MOX samples presented intermediate values, in accordance with results for acetic acid. However, only the CB modality showed higher concentration of ethyl acetate than the unaged wine spirit, suggesting that ethyl acetate hydrolysis occurred in MOX and CN modalities (Figure S1-Suplementar material).

Table 2. Concentration (mg/L) of odorant compounds quantified in wine spirits sampled from different ageing modalities at the end of the ageing experiment (365 days) and the summary of one-way ANOVA.

Odorant Compound	*Significance Level*	Control	Aged Wine Spirits after 365 Days of Ageing Modality				
			CB	CO15	CO30	CO60	CN
Isobutyl acetate	*0.002*	2.36	1.81 [b]	0.55 [a]	0.0 [a]	0.0 [a]	1.34 [b]
Ethyl hexanoate	*0.009*	1.20	1.89 [c]	1.72 [b]	1.72 [b]	1.80 [b,c]	1.58 [a]
Guaiacol	*0.001*	0.00	0.11 [a]	0.51 [b]	0.45 [b]	0.46 [b]	0.48 [b]
4-Methylguaiacol	*0.004*	0.00	0.05 [a]	0.31 [b]	0.28 [b]	0.25 [b]	0.28 [b]
Eugenol	*0.021*	0.00	0.33 [c]	0.28 [a,b]	0.30 [b,c]	0.28 [a,b]	0.23 [a]
4-Methylsyringol	*0.000*	0.00	0.36 [a]	1.24 [c]	1.24 [c]	1.26 [c]	1.09 [b]
Vanillin	*0.014*	0.00	7.74 [b]	7.52 [b]	7.14 [b]	8.21 [b]	4.97 [a]
Acetovanillone	*0.003*	0.00	0.34 [a]	0.80 [b,c]	0.81 [b,c]	0.97 [c]	0.77 [b]
Ethyl acetate	*0.003*	459.88	472.54 [c]	389.74 [b]	374.85 [a,b]	382.28 [b]	335.22 [a]

For each compound of aged wine spirit samples, means within the same row followed by different upperrcase letters ([a], [b], [c]) are significantly different ($p < 0.05$).

The different amounts of oxygen in the CN and MOX modalities (Figure 1) could explain the differences in acetaldehyde as well. The acetic acid differences between barrels and the other modalities can be related to differences in wood extraction Thus, further research is needed to understand these differences.

Syringol, which is associated with odor notes of wood, smoke [11], is absent on unaged spirit (Table 1), as observed in other works [8,10]. Its presence in aged wine spirits has been assigned to wood lignin degradation [44]. Its amount increased over the time but the kinectics are quite different according to the ageing modalities (Table 1). In fact, its concentration was always higher in wine spirits proceeding from the MOX modalities (CO15, CO30, CO60) and nitrogen modality (CN) than in those resulting from the wooden barrels (CB). Similar results were previously obtained; with high concentration of syringol found in spirits aged with alternative ageing systems without [10] and with micro-oxygenation [25] in comparison with those aged in wooden barrels. These findings lead us to believe that the degradation of wood lignin can increase in the MOX modalities giving rise to higher concentration of syringol in the beverage. Additionally, since lignins are degraded in contact with alcoholic beverages [45,46], these results suggest a more intense lignin extraction and degradation in MOX and N modalities. Nevertheless, contribution of wood variability and/or the extraction rate of syringol to such a variation should not be excluded [10,47].

3.2. Odorant Compounds of Aged Wine Spirits

At the end of the ageing experiment (365 days), the odorant compounds of the aged wine spirits were quantified. The ethyl isovalerate is not quantifiable and the ethyl-2-methylbutanoate, β-methyl-γ-octalactone, diethyl malate, 4-propylguaiacol and 4-ethylphenol were not detected in these samples. The ANOVA results (Table 2) pointed out a significant effect of the ageing modality on the contents of twelve compounds, which include the four previously mentioned and discussed (linalool, acetic acid, syringol and ethyl acetate). On the other hand, the concentrations of other 17 odorant compounds were not affected (Table S1-Suplementar material).

Regarding isobutyl acetate, which is related to fruity notes [48], higher concentrations were found in samples from wooden barrels (CB) and from nitrogen modality (CN) while in MOX samples the amounts were lower or quite null. These results are not in accordance with those reported by Granja-Soares et al. [25], whose found the highest values of this ester in wine spirits aged through an alternative ageing system (staves combined with micro-oxygenation using a single flow of oxygen; 2 mL/L/month) in comparison with wooden barrels. Since esters are roughly as reactive as carboxylic acids, this reaction is highly reversible. Higher isobutyl acetate concentrations need excess concentration of acetic acid, which was not found in MOX samples. According to Le Chatelier's theory, higher concentration of acetic acid would shift the equilibrium toward ester production, which is confirmed by higher concentrations of isobutyl acetate and acetic acid in samples from wooden barrels (CB) at the conclusion of the ageing experiment (365 days). The concentrations of isobutyl acetate in CO30 and CO60 MOX samples may be indicating that the wide availability of oxygen induces significant chemical content variation over the time, resulting in an increase of electrophilic species, among these phenolic aldehydes and acids such as: syringaldehyde, coniferaldehyde, sinapaldehyde, ellagic, and syringic acid, previously confirmed for the same MOX samples [24]. The presence of these substrates, particularly at higher concentrations, can contribute to the disappearance of isobutyl acetate and other acetates, due to: (i) nucleophilic acyl substitution; (ii) deacetylation processes; (iii) competition with its formation by consumption of direct or indirect building blocks required for the formation of isobutyl acetate (acetic acid, isobutyl alcohol, or pyruvic acid) by reactions with lower activation energies in order to form other, more energetically viable species. In the case of ethyl hexanoate, which is also related with fruity notes [48], the highest concentrations were found in wine spirits from the barrels (CB) and the lowest were found in wine spirits from CN modality. The MOX modalities provided intermediate values. In a previous work [25], the amount of this ester was not influenced by the ageing system, likely due to the higher flow rate of oxygen used.

Guaiacol and 4-methylguaiacol, which are usually related to smoky odor notes [49], behaved similarly to syringol, showing the lowest concentrations in the barrel samples and the highest levels in the other samples (MOX modalities and nitrogen modality). Also for 4-methylsyringol, which is associated with smoke and burned odor notes [11], the lowest concentrations were found in barrel samples, and the highest values were determined in the samples from MOX modalities. The modality with nitrogen (CN) showed an intermediate concentration of 4-methylsyringol.

The behavior of eugenol (4-allylguaiacol), which is well correlated with spicy odor notes [11], was rather different with high concentrations occurring in wine spirit samples from barrels and low concentrations in those obtained under nitrogen modality (CN). The wine spirit samples proceeding from MOX modalities exhibited intermediate values of eugenol.

Some of these results are in agreement with those obtained in previous research work [25] which found significantly higher concentrations of guaiacol, methylguaiacol, 4-methylsiringol, and syringol in wine spirits produced using alternative ageing system (staves and micro-oxygenation) in comparison with those produced by the traditional process (wooden barrels).

The vanillin amounts, generally well correlated with vanilla attribute in aged wine spirits [11], were significantly influenced by the ageing modalities (Table 2) with the lowest amounts on the samples produced under nitrogen (CN). These results confirmed the importance of oxygen in the pathway of vanillin formation during the wood contact. The vanillin is usually available in the wood as result of thermal lignin degradation during the cooperage manufacturing of the barrels or staves, but their presence in wine spirits results from wood extraction, lignin degradation by hydroalcoholysis and by oxidation of coniferaldehyde [4,14].

The acetovanillone, which also results from lignin degradation [4] and also presents vanilla-like odor notes [50] was also significantly influenced by the ageing modalities (Table 2) with the lowest amount in wine spirits aged in wooden barrels and the highest amounts were observed in wine spirits from CO60 modality. The samples from other modalities exhibited intermediate values of this compound.

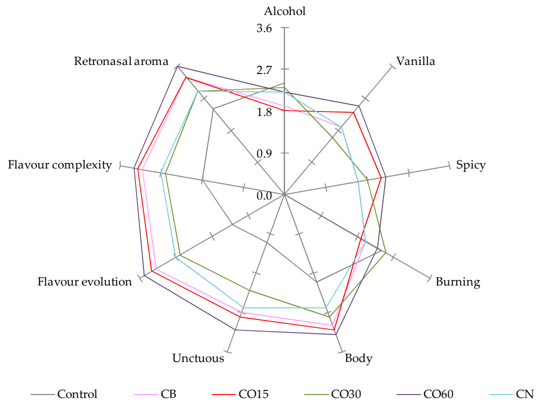
Although the MOX modalities (CO15, CO30 and CO60) were designed to reproduce and accelerate reactions occurring in wooden barrels (CB), the obtained results suggest that the reactions were not the same. These differences may be due to several factors that will need to be further explored. As predicted, the dissolved oxygen levels in MOX modalities were higher than those observed in the wooden barrel (Figure 1). Given that the oxygen dissolved in a wooden barrel is always the result of a balance between the oxygen that passes through the wood and the oxygen that is consumed in the reactions [51], lower levels of dissolved oxygen in the CB than in MOX modalities may indicate a higher consumption or a lower oxygen entry through the barrel. Some results, such as those of acetaldehyde (in a lower content in spirits from wooden barrels), suggest a lower availability of oxygen in the wooden barrels and its lower consumption in oxidation reactions. Nevertheless, other results such as the acetic acid concentration, which is dependent on acetaldehyde oxidation and its extraction from the wood, and whose contents have often been higher in wine spirits from the wooden barrel, suggest a potential higher consumption of oxygen in the barrels, as well as greater extraction. On the other hand, the results of several volatile phenols and acetovanillone seem to indicate higher extraction in wine spirits aged in the alternative modalities. The extraction of compounds from wooden barrels results from the impregnation of the liquid in the staves [52], which is governed and influenced by several driving forces [51]. In our experimental design, in which the arrangement of the staves in relation to the liquid is very different in the barrels and in the demijohns, it could be assumed that the impregnation took place in a different way and contributed to the observed differences.

3.3. Sensory Results

Concerning the sensory outcomes, the ANOVA output showed that the ageing modalities had a major effect on nine sensory attributes. The results for each ageing modality and control sample (without ageing) are shown at Table 3, combined with the equivalent spider graphics in order to better illustrate the differences between modalities. Other sensory attributes (fruity, wood, rancid, caramel, toasted, dried fruits, smoke, coffee, sweet, green, tails, glue and caoutchouc, sweetness, smooth, astringency, roughness, bitter, and persistence) were not significantly affected by the ageing modality. Also, the overall quality of the aged wine spirits was significantly affected by the ageing modality.

The intensities of vanilla, spicy, unctuous, flavor evolution, flavor complexity, and retronasal aroma increased with ageing process in accordance with previous research [5] and were significantly higher in the wine spirits from CO60 modality, while the lowest values were detected in samples proceeding from nitrogen modality and/or from CO30 modality. The intermediate intensities were found in the samples from the CB and CO15 modalities. Since these sensory attributes are positively correlated with the overall quality [5], the samples from CO60 and CO15 modalities were classified as having the highest overall quality, while the samples from CO30 and CN modalities were rated as having the lowest overall quality. The overall quality of the aged wine spirit samples from the barrels presented intermediate values.

Table 3. Sensory attributes intensity (average values) determined by the sensory panel in the wine spirits sampled from different ageing modalities at the end of the ageing experiment (365 days) and the ANOVA summary.



Sensory Attribute	*Significance Level*	Control	Aged Wine Spirits after 365 Days of Ageing Modality				
			CB	CO15	CO30	CO60	CN
Alcohol	*0.048*	2.4	1.9 [a]	1.8 [a]	2.3 [b]	2.2 [a,b]	2.2 [a,b]
Vanilla	*0.010*	0.0	1.9 [a,b]	2.3 [b,c]	1.6 [a]	2.5 [c]	1.9 [a,b]
Spicy	*0.009*	0.0	1.6 [a]	2.1 [b]	1.8 [a,b]	2.2 [b]	1.6 [a]
Burning	*0.041*	2.4	2.0 [a]	1.9 [a]	2.5 [b]	2.3 [a,b]	2.0 [a]
Body	*0.014*	2.0	3.0 [b,c]	3.1 [b,c]	2.8 [a,b]	3.2 [c]	2.6 [a]
Unctuous	*0.000*	1.1	2.7 [b]	2.8 [b]	2.2 [a]	3.1 [c]	2.6 [b]
Flavor evolution	*0.000*	1.3	3.2 [b]	3.3 [b]	2.6 [a]	3.5 [b]	2.7 [a]
Flavor complexity	*0.001*	1.8	3.1 [b]	3.2 [b]	2.6 [a]	3.3 [b]	2.7 [a]
Retronasal aroma	*0.002*	2.4	3.3 [b]	3.3 [b]	2.9 [a]	3.6 [b]	2.9 [a]
Overall quality	*0.001*	-	14.5 [b,c]	14.6 [c]	13.1 [a]	15.1 [c]	13.6 [a,b]

For each sensory attributte of aged wine spirit samples, means within the same row followed by different upperrcase letters ([a], [b], [c]) are significantly different ($p < 0.05$).

3.4. Multidimensional Approach of the Similarity/Dissimilarity of Aged Wine Spirit Samples

Based on the previous results, the variables that significantly influenced the variability were used for to a multidimensional analysis through heatmap and PCA to help evaluating the relationship between the sensory and the chemical results, and to assess if the set of variables (sensory and chemical) could be helpful to discriminating the samples from different ageing modalities.

Figure 2 depicts two heatmaps illustrating the multifactorial relationship between volatile compounds or sensory attributes and the different aged wine spirits at 365 days of ageing.

Regarding the volatile compounds, the heatmap clustered three groups of wine spirit modalities: barrel (CB), nitrogen modality (CN) and a group consisting of MOX modalities (CO15, CO30 and CO60). The wine spirit aged in the modalities CO15, CO30 and CO60 have a quite similar volatile composition but with the aforementioned variation showed by the ANOVA results.

This result confirms the influence of the different oxidative media in the aged wine spirit's volatile composition. The cluster of CO15, CO30, and C060 seems to also be related to higher levels of some volatile compounds, such as volatile phenols, acetovanillone, and vanillin.

It was also possible to identify two important subgroups responsible for the observed differences in the studied modalities. The first subgroup comprises the ethyl hexanoate, acetic acid, ethyl acetate, eugenol, vanillin and acetaldehyde and the second one includes guaiacol, syringol, 4-methylguaiacol, 4-methylsyringol, and acetovanillone.

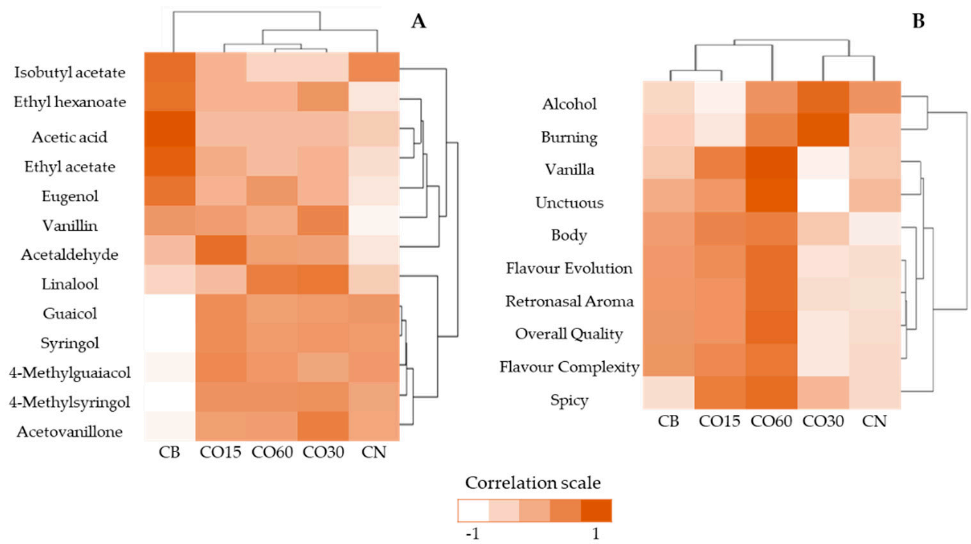


Figure 2. Heatmaps of volatile compounds (**A**) and sensory characteristics (**B**) of wine spirits and ageing modalities at 365 days of ageing.

Concerning the sensory analysis, three groups were observed: the first one contains CN and CO30; the second one contains CO15 and CO60; the last one comprises aged spirits from the wooden barrels (CB). Interestingly, these results are in acordance with the clusters obtained for the phenolic profile of the same wine spirits [24].

The cluster formed by CO15 and CO60 is related to the highest intensities of several sensory attributes, such as vanilla, spicy, flavor evolution, body, unctuous, flavor complexity, and overall quality. The samples of CO30 and CN are grouped together and are related to burning and alcohol odor notes, which are usually associated with younger aged wine spirits [5]. The CB samples presented an intermediate profile, which is more similar to the group formed by CO15 and CO60.

These results are in accordance with previous ANOVA results, and showed that the best results, regarding the overall quality of the aged wine spirits, were obtained with a high flow rate of micro-oxygenation at modality CO60. Since those samples presented high intensity of several gustatory attributes usually associated with non-volatile compounds, such as body and unctuous [53,54], further research is required to evaluate the effect of MOX strategies in other compounds such as elagitanins, lignins, and sugars.

4. Conclusions

Different modalities of alternative ageing (chestnut staves combined with micro-oxygenation) were compared with the traditional ageing process in wooden barrels, regarding the volatile and sensory profile of the aged wine spirits. The results confirmed the influence of oxygen on the volatile composition of aged wine spirits. Regarding the comparison of the ageing processes, there was a great differentiation of the volatile composition between samples from alternative ageing processes and those from the traditional process in wooden barrels, with volatile phenols being one of the groups of compounds responsible for this differentiation. In terms of the sensory overall quality of the aged wine spirits, the best results were obtained in one of the modalities of the alternative ageing process, in which the oxygen flow was applied over a longer period of time, 2 mL/L/month during the first 60 days followed by a flow rate of 0.6 mL/L/month until the end of the experiment, 365 days.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/app11093991/s1, Figure S1: Mechanism of acid catalyzed ethyl acetate hydrolysis, Table S1: Amounts (mg/L) of odorant compounds quantified in the wine spirits from different ageing modalities at the end of the ageing experiment (365 days) and the summary of one-way ANOVA.

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