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Natural Blending as a Novel Technology for the Production Process of Aged Wine Spirits: Potential Impact on Their Quality

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Abstract: The blending of wine spirits (WSs) produced in different ageing conditions is a key operation to impart specific features, enhance complexity, increase the final product's quality and ensure brand consistency over the years, but requires time, labour and experienced blenders. This work aimed to develop a novel technology, natural blending, towards innovation and a more sustainable production process, adding value to the final product. WSs were aged in 250 L barrels and in 1000 L stainless steel tanks with wood staves and micro-oxygenation (MOX), using Limousin oak and chestnut wood simultaneously at a 50:50 ratio (natural blending) and separately; after 18 months of ageing, the last ones underwent the blending operation at the same ratio. All WSs were bottled and thereafter the following traits were analysed: alcoholic strength, acidity, dry extract, total phenolic index, low molecular weight compounds by HPLC method, chromatic characteristics and sensory profile. No significant differences in the physicochemical characteristics and sensory profile between the WSs resulting from the two blending technologies were found. Natural blending did not induce changes in the characteristics imparted by each ageing technology. These findings point to natural blending as a reliable alternative to the blending operation, especially in combination with ageing in tanks with staves and MOX.

Keywords: blending; wine spirit; ageing; oak wood; chestnut wood; chemical composition; colour; sensory profile; innovation; sustainability

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1. Introduction

The aged wine spirit (WS) is a prominent spirit beverage in terms of production worldwide [1], and the main Designations of Origin, such as Cognac, Armagnac and Lourinhã, are located in Europe [2].

Traditionally, its production process comprises four basic stages: winemaking, distillation, ageing in wooden barrels and finishing. In the last one, blending, dilution and filtration operations are carried out [3].

Ageing is a pivotal stage because it affords positive and unique sensory properties to the WS as a consequence of the changes promoted in its chemical composition by multiple physicochemical phenomena involving the distillate and the wood [4].

In the last decades, several studies have been conducted towards more sustainable WS ageing by the traditional technology, searching for the best conditions in terms of type of wood, toasting level and barrel size [5,6] as well as the reuse of barrels [7]. Despite the gains achieved, this technology still has some drawbacks: it is lengthy, and expensive, the barrels take up a lot of space in the cellar, there is a high demand for wood, which is a natural resource with limited availability, and there is great evaporation of WS. Therefore, in recent years, research has been focused especially on alternative aging technologies to meet sustainability criteria (environmental, economic, and social) and their linkages, seeking to balance ecology and prosperity in a lasting way [8]. Indeed, some works were performed resorting to physical treatments [9,10], wood extracts [11–13], and wood fragments added to WS kept in stainless steel tanks, assessing their influence on the physicochemical and sensory characteristics conferred to the aged spirits. Regarding the last solution, wood staves in conjunction with micro-oxygenation (MOX) allowed to reproduce the ageing in barrels but in a faster and more affordable way, using a low amount of wood while guaranteeing the production of high quality WS [14–19]. A residual loss of WS by evaporation was also reported [19,20].

Currently, agro-industry faces a global and more competitive market with consumers increasingly aware of their choices, considering health and environment concerns and responsible consumption [21], and privileging the product's quality and differentiation based on innovation [22] and sustainable processes [23]. Hence, the competitiveness of the beverage industry, associated with a very important and growing world market [24], largely depends on the ability to understand these challenges, and anticipating the development of new processes and high value products. In this context, research in food science plays a key role, providing the industry with new ideas/tools and the scientific basis for their implementation. Thus, besides the ageing stage, other WS' production steps, such as blending, can be explored. In fact, the blending of aged spirit beverages, such as WS [3,25,26], whisky [27–29], rum [30] and sugar-cane spirit [31], from different wooden barrels (e.g., different kinds of wood, toasting level, and ageing time) is a crucial operation to impart specific characteristics, enhance complexity, increase the final product's quality and ensure brand's consistency over the years, but it is time consuming, and requires labour and know-how (experienced blenders) [25,27]. It is worth mentioning that, as far as we know, very few scientific studies have been carried out on the blending of WSs.

The advancement of the cooperage technique and knowledge on the chemical, mechanical and physical properties of the wood used for the ageing of WS (oaks and chestnut, among others) [32,33] already allow the manufacture of mechanically stable barrels, made up of staves from different kinds of wood. In addition, alternative ageing technology using wood staves inserted into stainless steel tanks makes it possible to explore all the desired wood combinations as well as the toasting levels ones. These facts open doors to natural blending as a new technology performed during ageing using different kinds of wood simultaneously, which may contribute to expanding the sustainability of the production process and add value to the final product.

The first approach made to the simultaneous use of Limousin oak wood, traditionally used in the ageing of WSs, and chestnut wood, which has shown high suitability for this purpose [34], was based on experimental units (3000 L stainless steel tanks containing wood staves and 650 L new barrels) using only both kinds of wood (50:50 ratio); that is, barrels of each kind of wood separately and the application of MOX in the tanks were not included due to financial constraints. Therefore, despite the promising results obtained, it was not possible to compare the outcomes of natural blending (provided by the simultaneous use of these botanical species during ageing) with those of the blending operation (commonly performed after ageing). Moreover, the absence of MOX gave rise to a tenuous correlation between chromatic characteristics and chemical composition.

Further investigation was carried out under the R&D Project CENTRO-04-3928-FEDER-000028 in order to obtain robust evidence on the advantages of natural blending vs. blending operation. For this purpose, the same *Lourinhã* wine distillate was aged in 250 L new barrels of Limousin oak wood, chestnut wood, and these two kinds of wood simultaneously (natural blending), in triplicate, as well as in 1000 L stainless steel tanks with staves inside from Limousin oak wood, from chestnut wood, and from both kinds of wood (natural blending), combined with MOX, in duplicate. In each ageing technology, WSs from Limousin and chestnut modalities were mixed at the end of the ageing process (blending operation).

Hence, the aim of this work was to study the quality of the WSs produced by these blending technologies, through a broader analytical approach, involving basic chemical characteristics (alcoholic strength, acidity, and total dry extract), total phenolic index, low molecular weight compounds quantified by HPLC, chromatic characteristics, and sensory profile. Thus, the potential contribution of this novel technology, natural blending, to an innovative and sustainable production process, adding value to the final product, was examined for the first time and comprehensively in this research. Moreover, it concurs to the advancement of scientific knowledge on the blending of WSs.

2. Materials and Methods

2.1. Experimental Design and Sampling of WSs

The 15 experimental units were placed in the cellar of Adega Cooperativa da Lourinhã (Lourinhã, Portugal) in 2017, in the same environmental conditions, and filled with the same freshly distilled wine spirit produced in a column still (alcoholic strength, 77.40 v/v; pH, 5.44; total acidity, 0.13 g acetic acid/hL of absolute ethanol; volatile acidity, 0.11 g acetic acid/hL of absolute ethanol) from this producer.

The experimental units of this trial, carried out on an industrial scale and based on a factorial design (two ageing technologies × two blending technologies), are shown in Figure 1.

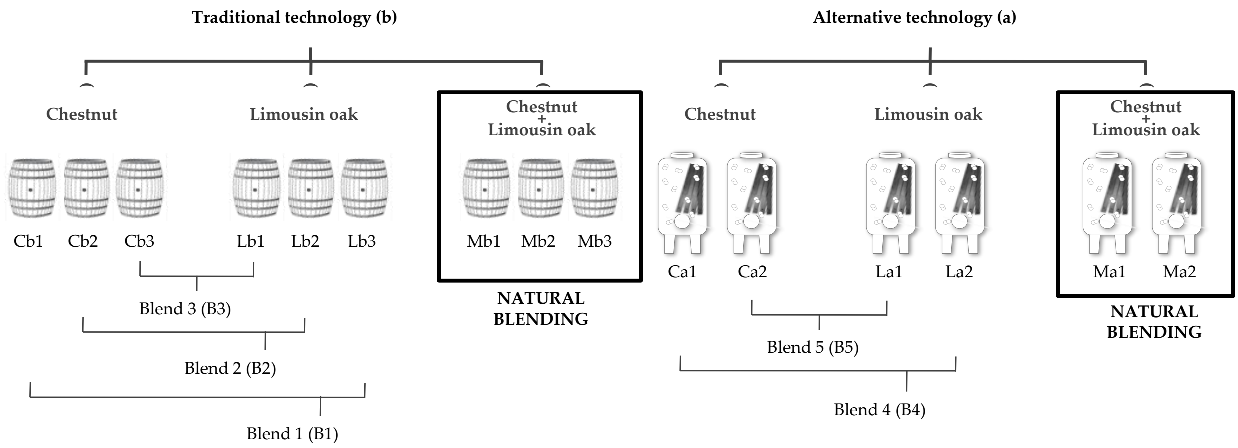

Figure 1. Trial scheme. Blends B1–B3 were produced by blending operation of WSs from chestnut barrels (Cb) and Limousin oak barrels (Lb), at 50:50 ratio, after 18 months of ageing. Mb1–Mb3 were obtained by natural blending of WS (barrels comprising chestnut and Limousin oak staves, at 50:50 ratio, alternatively arranged) during 18 months of ageing. Blends B4 and B5 were produced by the blending operation of WSs from tanks with chestnut staves inside combined with MOX (Ca) and from those with Limousin oak staves inside combined with MOX (La), at 50:50 ratio, after 18 months of ageing. Ma1 and Ma2 were obtained by natural blending of WS (tanks comprising chestnut and Limousin oak staves inside, at 50:50 ratio, alternatively arranged, combined with MOX) during 18 months of ageing.

The 250 L new barrels and the wood staves inserted into the 1000 L stainless steel tanks were made by J. M. Gonçalves cooperage (Palaçoulo, Portugal) from Limousin oak wood (L; *Quercus robur* L.) and chestnut wood (C; *Castanea sativa* Mill.). The medium plus toasting level of both kinds of wood was assured by an accurate control of the wood's temperature: 90 min at an average temperature of 240 °C resorting to a fire of wood scraps for the barrels and to an industrial oven for the staves.

In each ageing technology (b—barrels, traditional; a—tanks with wood staves inside, alternative), the two kinds of wood were used separately (C and L) and simultaneously

(M, 50:50 ratio with staves alternately arranged). The M modalities correspond to the natural blending.

The quantity of staves used in the tanks mimics the surface area/volume ratio of a 250 L barrel (85 cm^2/L). During ageing, MOX was applied to the WSs stored in the tanks, supplying pure oxygen (X50S Food, Gasin, Portugal) at 2 mL/L/month flow rate by a micro-oxygenator with several ceramic diffusers (VISIO 6, Vivelys, France) [14].

After 18 months of ageing, the WSs resulting from the natural blending (Mb1, Mb2, Mb3, Ma1 and Ma2) were bottled.

At the same time, the WSs aged separately in chestnut barrels and in Limousin oak barrels were blended at 50:50 ratio (blends B1, B2 and B3), and those aged separately in tanks with chestnut staves and in tanks with Limousin oak staves were also blended at a 50:50 ratio (blends B4 and B5), as depicted in Figure 1. Barrels and tanks were randomly selected for the blending operation (B1–B5).

Four bottles of each blend were kept in the cellar of Polo de Dois Portos—INIAV at 19 °C and 80% relative humidity for four months. Then they were sampled and analysed; a total of 10 samples were taken: B1, B2, B3, Mb1, Mb2, Mb3, B4, B5, Ma1 and Ma2.

2.2. Chemicals

All solvents used in the basic chemical composition and total phenolic index analyses were analytical grade purchased from Merck (Darmstadt, Germany).

Ellagic acid dehydrate (Ellag), furfural (Furf), gallic acid monohydrate (Gall), 5-hydroxymethylfurfural (HMF), 5-methylfurfural (5Mfurf), syringic acid (Syrg), and vanillin (Vanil) were purchased from Fluka (Buchs, Switzerland). Coniferaldehyde (Cofde), sinapaldehyde (Sipde), syringaldehyde (Syrde) and 4-hydroxybenzaldehyde were purchased from Aldrich (Steinheim, Germany). These commercial standards (of purity over 97%) were used as such. The standard solutions were prepared immediately before use with an hydroalcoholic solution (ethanol/water, 75:25 *v*/*v*). Gradient grade solvents used in HPLC analysis were purchased from Merck (Darmstadt, Germany). Ultrapure water (with conductivity lower than 0.055 μS/cm) was produced by an Arium Comfort I equipment (Sartorius, Göttingen, Germany).

2.3. Basic Chemical Characteristics

The basic chemical characteristics of the WSs resulting from the natural blending and from the blending operation were analysed in duplicate: alcoholic strength, total acidity, fixed acidity, volatile acidity, pH, and total dry extract.

Alcoholic strength was determined by distillation and electronic densimetry [35]; the corresponding results were expressed as a volumetric percentage of ethanol in the WS.

Total acidity, fixed acidity and volatile acidity were assessed by colorimetric titration, colorimetric titration of the water solution of dry extract, and by calculation of the total acidity minus fixed acidity, respectively [36]; the corresponding results were expressed as grams of acetic acid per litre of absolute ethanol.

pH was determined by potentiometry [35] using a potentiometer (micro pH2002, Crison, Barcelone, Spain).

Total dry extract was analysed by gravimetry [35]; the corresponding results were expressed as grams per litre.

2.4. Total Phenolic Index

Total phenolic index (TPI) of the WSs was determined (in duplicate) according to Canas et al. [14]: the WS was diluted with ethanol/water 77:23 *v*/*v*, and thereafter the absorbance measurement was made at 280 nm using a Varian Cary 100 Bio spectrophotometer (Santa Clara, CA, USA) and a 10 mm quartz cell. The TPI calculation was performed by multiplying the dilution factor by the measured absorbance.

2.5. Low Molecular Weight Compounds

Twelve low molecular weight compounds (LMWC) were chosen based on their effectiveness, demonstrated in previous works, in differentiating between aged WSs [4]: ellagic acid, gallic acid, syringic acid (phenolic acids), vanillin, syringaldehyde, coniferaldehyde, sinapaldehyde (phenolic aldehydes), scopoletin, umbelliferone (coumarins), 5-hydroxymethylfurfural (HMF), furfural and 5-methylfurfural (furanic aldehydes).

They were quantified in the WSs by a validated HPLC method [37], using a Lachrom Merck Hitachi system (Merck, Darmstadt, Germany) equipped with a quaternary pump L-7100, a column oven L-7350, a UV-Vis detector L-7400, a fluorescence detector L-7480 (connected to the UV-Vis detector) and an autosampler L-7250, and coupled to HSM D-7000 software (Merck, Darmstadt, Germany) for the management, acquisition and treatment of data. The stationary phase was a 250 mm × 4 mm i.d. LiChrospher RP 18 (5 µm) column (Merck, Darmstadt, Germany). UV detection was carried out at 280 nm for phenolic acids and furanic aldehydes, and at 320 nm for phenolic aldehydes. Fluorescence detection was carried out at 325 nm (excitation)/454 nm (emission) for coumarins. Samples were spiked with 4-hydroxybenzaldehyde (internal standard, 20 mg/L), filtered through 0.45 µm membrane (Filter-Bio, Nantong, China), and analysed by direct injection of 20 µL.

The analysis was performed in duplicate. Calibration curves made with the corresponding commercial standards were used for the compounds' quantification. The results were expressed as mg of compound per litre.

2.6. Chromatic Characteristics

The chromatic characteristics—lightness (L*), chroma (C), chromaticity coordinates (a* and b*) and absorbance at 470 nm—of the WSs were analysed (in duplicate) as described by Canas et al. [14], using a Varian Cary 100 Bio spectrophotometer (Santa Clara, CA, USA) and a 10 mm glass cell. Measurement of transmittance was carried out from 380 to 780 nm (every 5 nm), using a D65 illuminant and a 10° standard observer.

In addition, to complement the colour characterisation of WSs, the total colour difference (ΔE) was calculated, based on the following equation [38]:

$$\Delta E = \sqrt{(L_s^* - L_r^*)^2 + (a_s^* - a_r^*)^2 + (b_s^* - b_r^*)^2} \quad (1)$$

where s is the WS sample and r is the reference; that is, total colour differences of the studied WSs were calculated by comparing their CIELab coordinates with the CIELab coordinates of the wine distillate used to fill the 15 experimental units (L*, 96.30%; a*, 0.39; b*, −3.29). The wine distillate was considered as the reference [39].

2.7. Sensory Analysis

The WSs were assessed by free sorting task analysis since this method has been applied to a wide range of foods and beverages, especially in the development of products and production processes [40].

The samples, previously diluted to an alcoholic strength of 40% *v*/*v*, were presented in a balanced order [41] to a taster panel, selected and trained. The tasting panel was composed of 14 judges (seven females and seven males, aged between 26 and 63 years, non-smokers, with education levels ranging from high school to PhD). Previously and during this trial, training sessions were performed, and different aged WSs were tasted. The sensory session took place in the tasting room of Polo de Dois Portos-INIAV, under natural light and temperature at about 20 °C, around 10 a.m. The 10 WSs samples (30 mL) were provided simultaneously in standard wine-tasting glasses [42] that were coded with three random digits. Firstly, the tasters were asked to sort the samples into groups based on the similarities between their colours. Once this sorting task was completed, the tasters were asked to continue sorting the samples according to the aroma similarities, and thereafter based on the flavour similarities, and finally on the overall quality.

The number of groups, the number of samples in each group and the underlying criteria were freely chosen by each taster, but it was requested that more than one group and fewer groups than the number of samples should be made [40].

For each taster, the results of the sorting task were inserted into distance matrices (colour, aroma, flavour, and overall quality), in which the rows and columns corresponded to the WS samples. For each taster individual matrix, a value of 0 or 1 indicates that the samples were in different groups or in the same group, respectively, as described by Cariou et al. [43]. The matrices of all the tasters for each sensory attribute were summed, resulting in a global matrix of co-occurrences, which depicted the global similarity between the samples.

2.8. Statistical Analysis

The effect of blending (natural blending vs. blending operation), as a fixed factor, on the physicochemical characteristics of the WSs produced by each ageing technology, was assessed by a one-way analysis of variance (ANOVA).

To complement the ANOVA results, a cluster heat map was obtained towards a global analysis of the data, intending to understand their behaviour according to the blending modalities in a visually stimulating and easy-to-interpreted way [44]. For this purpose, the values of Pearson correlation (r values) between modalities and the studied parameters were calculated. Thereafter, the r values were grouped by clustering analysis, using single linkage and Euclidean distance.

Multidimensional scaling analysis (MDS), the most common method used to examine the data from free sorting task analysis [40], was applied to the global matrices of co-occurrences generated in the four sorting tasks (colour, aroma, flavour, and overall quality); it was intended to know if tasters were able to perceive differences between WSs produced by natural blending and by the blending operation in each ageing technology. MDS of the metric type was applied.

Statistica version 7.0 software (Statsoft Inc., Tulsa, OK, USA) was used for all calculations.

3. Results and Discussion

3.1. Effect of Blending on the Basic Chemical Characteristics of WSs

The results of one-way ANOVA for the basic chemical composition of WSs from the natural blending and the blending operation in each ageing technology are shown in Table 1. None of the studied parameters were significantly influenced by the blending technology; that is, the natural blending imparted chemical characteristics similar to those resulting from the blending operation, regardless of the ageing technology. Therefore, the novel blending technology did not affect the WS matrix, which is a positive achievement since the aroma, taste and mouthfeel perception of the alcoholic beverages depend on their ethanol content (expressed by the alcoholic strength), acidity and total dry extract [3,24].

Comparing the WSs from the alternative and traditional technologies, slightly higher alcoholic strength was found in the former (76.31–76.83 vs. 75.82–76.40% *v*/*v*), reflecting lower WS evaporation from tanks than barrels, thus confirming our previous results [19,20], which was not influenced by the kind of blending performed.

In addition, it is worth mentioning that the total dry extract was slightly higher in the WSs from the alternative technology (2.42–2.50 vs. 1.47–1.53 g/L), regardless of the kind of blending, reflecting a better equilibrium extraction/oxidation of wood compounds and therefore contributing to enhance the WS quality [45]. Besides phenolic and furanic compounds (addressed in the next subsection), higher fixed acidity (0.28–0.34 vs. 0.21–0.24 g acetic acid/L AE) observed in the WSs aged by the alternative technology, as well as the presumably higher levels of sugars released from the wood (derived from hemicelluloses and cellulose [46]), may have contributed to this outcome.

Table 1. Average values of basic chemical characteristics and total phenolic index of WSs from natural blending and from the blending operation in each ageing technology.

	p	Alternative Technology				*p*	Traditional Technology					
		Natural Blending		Blending Operation			Natural Blending			Blending Operation		
		Ma1	**Ma2**	**B4**	**B5**		**Mb1**	**Mb2**	**Mb3**	**B1**	**B2**	**B3**
Alcoholic strength (% *v*/*v*)	*0.9999*	76.83 ± 0.01	76.31 ± 0.13	76.49 ± 0.09	76.72 ± 0.24	*1.0000*	76.40 ± 0.14	76.14 ± 0.23	76.30 ± 0.10	75.82 ± 0.39	76.13 ± 0.10	76.36 ± 0.06
Total acidity (g acetic acid/L AE)	*0.9846*	0.65 ± 0.01	0.64 ± 0.01	0.67 ± 0.03	0.65 ± 0.01	*0.9927*	0.66 ± 0.01	0.67 ± 0.01	0.64 ± 0.03	0.65 ± 0.01	0.63 ± 0.04	0.63 ± 0.02
Fixed acidity (g acetic acid/L AE)	*0.5971*	0.28 ± 0.01	0.30 ± 0.01	0.34 ± 0.01	0.30 ± 0.01	*0.8837*	0.21 ± 0.03	0.22 ± 0.02	0.21 ± 0.02	0.23 ± 0.01	0.22 ± 0.01	0.24 ± 0.01
Volatile acidity (g acetic acid/L AE)	*0.8390*	0.37 ± 0.02	0.34 ± 0.01	0.33 ± 0.01	0.35 ± 0.01	*0.8399*	0.45 ± 0.01	0.45 ± 0.01	0.42 ± 0.01	0.41 ± 0.01	0.40 ± 0.02	0.39 ± 0.01
pH	*0.9999*	4.19 ± 0.02	4.17 ± 0.02	4.16 ± 0.01	4.16 ± 0.01	*1.0000*	4.21 ± 0.02	4.21 ± 0.03	4.19 ± 0.05	4.19 ± 0.03	4.22 ± 0.05	4.21 ± 0.02
Total dry extract (g/L)	*0.9939*	2.44 ± 0.02	2.46 ± 0.01	2.50 ± 0.02	2.42 ± 0.02	*0.9991*	1.48 ± 0.01	1.47 ± 0.01	1.51 ± 0.01	1.53 ± 0.02	1.49 ± 0.01	1.47 ± 0.01
TPI	*0.7332*	56.98 ± 0.04	55.86 ± 0.01	63.37 ± 0.09	56.34 ± 0.12	*0.9893*	30.26 ± 0.06	30.78 ± 0.07	30.94 ± 0.16	31.38 ± 0.02	28.91 ± 0.10	30.57 ± 0.04

Results expressed as mean ± standard deviation; $p > 0.05$ indicate no significant differences; AE—absolute ethanol.

3.2. Effect of Blending on the Total Phenolic Index and Low Molecular Weight Compounds Contents of WSs

The results displayed in Table 1 also show a non-significant effect of the blending technology on the TPI of these WSs.

Slightly higher values were exhibited by the WSs produced through the alternative ageing technology than through the traditional one (55.86–63.37 vs. 28.91–31.38). Since TPI reflects the global content of phenolic compounds and furanic aldehydes of the aged WS [47], greater enrichment in these wood derived compounds was promoted by the former, demonstrating that the blending technology did not overlap with the ageing technology [14].

Figure 2 presents the ANOVA results for the total low molecular weight compounds concentration, determined by the HPLC method, of the WSs under study. The outcomes are coherent with those of total dry extract and TPI, confirming that the sum of phenolic compounds (phenolic acids, phenolic aldehydes, and coumarins) and furanic aldehydes concentrations found in the final products resulting from each ageing technology were not significantly influenced by the kind of blending. On the other hand, higher concentrations were associated with the alternative ageing technology (282.17–299.51 vs. 156.72–214.75 mg/L), which is also in agreement with previous reports on these WSs during the ageing process [14,48].

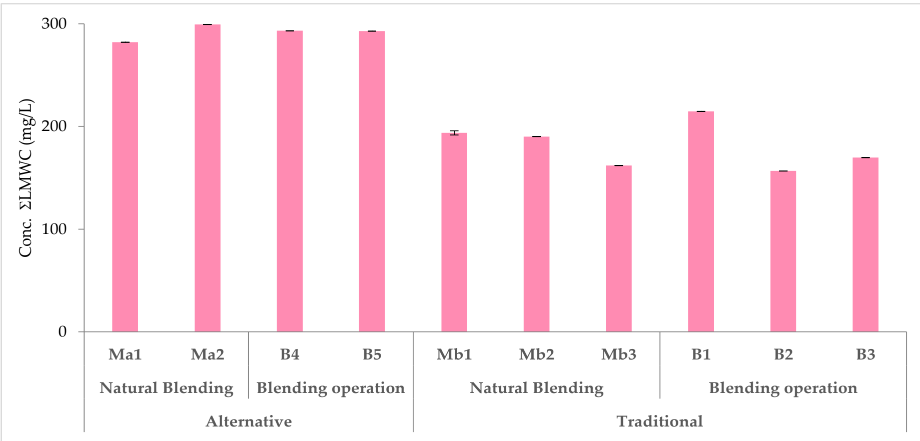

Figure 2. Average values of total low molecular weight compounds concentration of WSs from natural blending and from the blending operation in each ageing technology. Bars not marked with letters indicate non-significant differences between the average values ($p > 0.05$).

Thus, these findings point to the natural blending as a suitable option to reinforce the sustainability of the production process of WSs, together with ageing in stainless steel tanks with wood staves inside and MOX.

Specifically, the results of ANOVA for phenolic acids levels in the studied WSs (Figure 3) reveal that the differences in terms of gallic acid, syringic acid and ellagic acid between WSs obtained by natural blending and by the blending operation were not significant.

Gallic acid was the most plentiful compound within this group of phenolic compounds, as observed during ageing, particularly in WSs that was in contact with chestnut wood [5,14,16]. Since our previous works [5] proved that chestnut wood is richer in gallic acid than Limousin oak, the result now obtained suggests that this kind of wood had a greater effect in the blends than Limousin oak wood, despite the same amount used (50:50 ratio).

Interestingly, the wooden barrels (traditional ageing technology) afforded higher content of gallic acid to the WSs than the alternative technology (54.00–88.75 vs. 30.63–36.83 mg/L), regardless of the blending performed. Indeed, evidence exists that gallic acid is prone to oxidation [16,49,50], and oxidation reactions (subtractive phenomena) prevail over extraction and other additive phenomena, such as the gallotannins' degradation [51], during ageing through the alternative technology by supplying oxygen directly via MOX [14,16]. Therefore, this chemical marker [5] persisted in the aged WSs, even after blending (natural or performed after ageing).

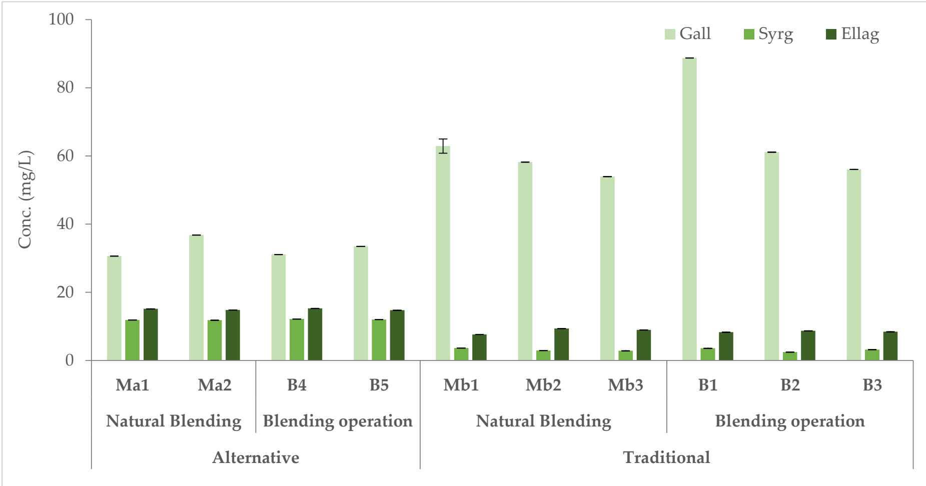

Figure 3. Average values of phenolic acids concentrations of WSs from natural blending and from the blending operation in each ageing technology. Bars not marked with letters indicate non-significant differences between the average values ($p > 0.05$).

Syringic and ellagic acids were more abundant in WSs resulting from the alternative ageing technology than from the traditional one (11.85–12.18 vs. 2.50–3.69 mg/L, and 14.75–15.33 mg/L vs. 7.68–9.37 mg/L, respectively), regardless of the blending technology. Similar behaviour was observed during their ageing process [14,48]. According to studies addressing the role of oxidation reactions in the ageing chemistry [16,51], staves combined with MOX induce more intense extraction of these compounds from the wood as well as degradation of their precursors—lignin for syringic acid, and ellagitannins for ellagic acid—(additive phenomena), but these acids are also less sensitive to oxidation than gallic acid [16].

The natural blending did not change the phenolic acids contents and their proportions, which are important features imparted by the ageing. Indeed, some authors described the relationship between phenolic acids and astringency as well as the relationship between their ethyl esters and astringency and bitterness [52,53]. Furthermore, gallic and ellagic acids are well-known bioactive compounds, conferring antioxidant activity to the aged WS [54].

Figure 4 shows the ANOVA results for phenolic aldehydes levels of WSs according to the blending technology in each ageing technology.

For all the phenolic aldehydes, no significant effect of the blending technology was found in WSs from both ageing technologies. Sinapaldehyde was the main compound of this group, followed by syringaldehyde, coniferaldehyde and vanillin, in the WSs produced. Higher levels were related to the alternative ageing technology compared with the traditional one: 54.09–59.24 vs. 17.16–25.08 mg/L for sinapaldehyde, 21.58–22.30 vs. 7.71–10.43 mg/L for syringaldehyde, 14.93–16.19 vs. 6.48–8.56 mg/L for coniferaldehyde, and 7.58–8.00 vs. 3.43–4.24 mg/L for vanillin. The highest levels observed in WSs resulting from the alternative ageing technology are in accordance with those determined during their ageing [14,48]. Regarding the relation between these compounds, it should be highlighted that the syringyl-type aldehydes (sinapaldehyde and syringaldehyde) prevailed over the guaiacyl-type aldehydes (coniferaldehyde and vanillin), which was consistent with the corresponding ageing results. A similar pattern was also noticed in a recent work on the ageing chemistry [16], in which this behaviour was ascribed to the balance between additive and subtractive phenomena involving lignin and its derivatives, with oxidation reactions being of the utmost significance to explain the lower contents of coniferaldehyde and vanillin (more prone to oxidation than the syringyl-type aldehydes [55]).

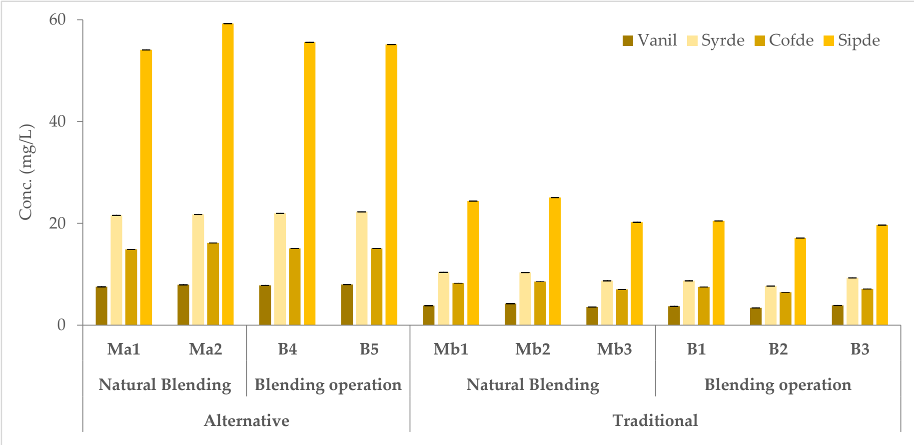

Figure 4. Average values of phenolic aldehydes concentrations of WSs from natural blending and from the blending operation in each ageing technology. Bars not marked with letters indicate non-significant differences between the average values ($p > 0.05$).

Since the natural blending did not affect the phenolic aldehydes contents, its suitability for the WS production process is strengthened. Actually, these compounds contribute to the WS flavour, particularly vanillin, which was positively correlated with the 'vanilla' aroma in WSs produced by the traditional ageing [4,56] and by the alternative one [18], being a remarkable attribute of this spirit beverage and highly appreciated by consumers [57]. Besides, syringaldehyde acts as a bioactive compound [58] and may contribute to the pool of phenolic compounds whose intake, under moderate WS consumption, may have positive health effects [59], as opposed to the harmful effects induced by ethanol [60], thus enhancing the WS' added value.

Concerning coumarins, the ANOVA results attained for the studied WSs (Figure 5) demonstrate that the blending technology had no significant effect on their contents. Quantitatively, scopoletin was the main compound of this group, as previously reported for WSs aged in barrels [4,61].

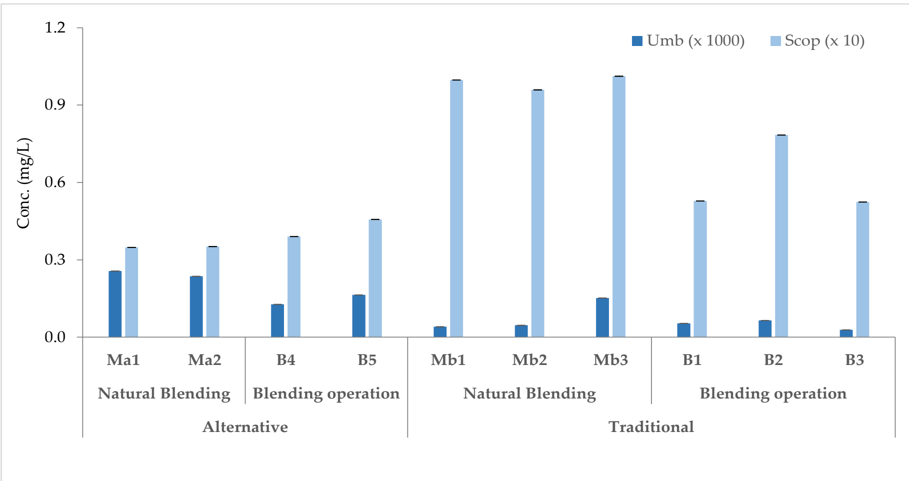

Figure 5. Average values of coumarins concentrations of WSs from natural blending and from the blending operation in each ageing technology. Bars not marked with letters indicate non-significant differences between the average values ($p > 0.05$).

Higher contents of scopoletin were observed in the WSs resulting from the traditional ageing technology (0.052–0.101 vs. 0.035–0.046 mg/L), whereas higher contents of umbelliferone were found in those resulting from the alternative one (0.00013–0.00026 vs. 0.00003–0.00015 mg/L), regardless of the kind of blending. These results suggest different sensitivity towards oxidation for these coumarins because the direct supply of oxygen through MOX (alternative ageing technology) favours the oxidation reactions involving several phenolic compounds [16]. Scopoletin seems to be more prone to oxidation than umbelliferone; for this reason, lower contents existed in the WSs from alternative ageing.

Despite their very low levels in WSs, some sensory attributes, namely bitterness [61], and benefits for human health due to specific biological activities [62,63] have been ascribed to these minority phenolic compounds, and therefore a similar effect as mentioned above for syringaldehyde is plausible.

So, these results also support the appropriateness of natural blending towards a more sustainable WS production.

Figure 6 shows the results of ANOVA for the furanic aldehydes contents in the WSs under study. None of these compounds were significantly influenced by the blending technology, that is, the effects of natural blending and blending operation were similar, regardless of the ageing technology.

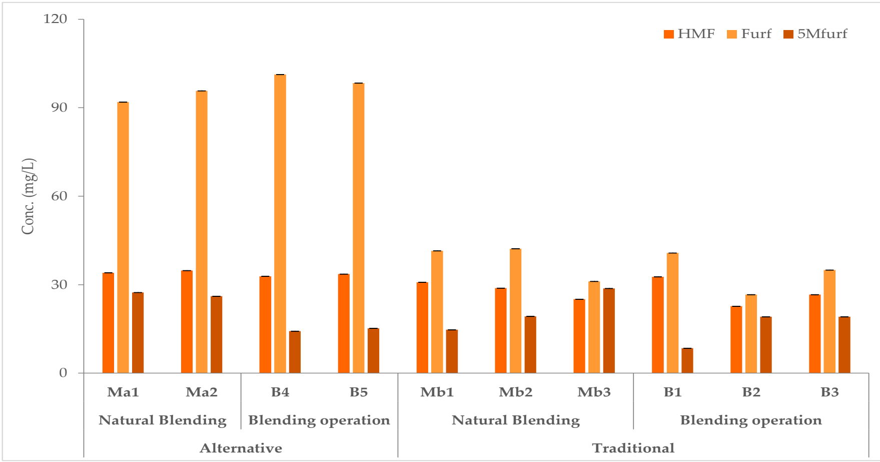

Figure 6. Average values of furanic aldehydes concentrations of WSs from natural blending and from the blending operation in each ageing technology. Bars not marked with letters indicate non-significant differences between the average values ($p > 0.05$).

Among furanic aldehydes, furfural stood out from HMF and 5-methylfurfural due to its higher concentration. Indeed, this aldehyde already exists in the wine distillate [16] as a consequence of the thermal degradation of wine pentoses in the distillation process [64], and greater amounts are also extracted from the wood (in which it exists in the free form due to degradation of hemicelluloses during the heat treatment in cooperage; this polysaccharide is more thermosensitive than cellulose that gives rise to HMF and 5-methylfurfural [65]) by the WS.

Higher furfural concentrations were determined in the WSs produced by the alternative technology than by the traditional one (91.95–101.28 vs. 26.62–42.17 mg/L), as observed during their ageing process [17]. Our work on the ageing chemistry [16] revealed that furfural content mainly depended on the wood extraction and less on the oxidation reactions (triggered by the level of oxygen supplied) and other subtractive phenomena occurring during ageing, which can explain such an accumulation in these WSs. According to Granja-Soares et al. [17], a significant interaction between the ageing technology and kind of wood and a synergistic effect between chestnut wood and the alternative ageing technology were detected. Since chestnut wood promoted greater extraction of furfural, the outcomes of the present work suggest that (i) natural blending did not change this distinctive behaviour, and (ii) chestnut wood had more marked influence on the blends than the Limousin oak wood, despite the same amount used (50:50 ratio).

It should also be emphasized the relationship between furanic aldehydes and the ‘dried fruits’ and ‘caramel’ sensory attributes of these WSs, which were of the utmost importance for their differentiation [17].

Hence, given that the furanic aldehydes contents were preserved by the natural blending, it also preserved the WSs quality and therefore it is a reliable technology for the improvement of the WS' production process.

3.3. Effect of Blending on the Chromatic Characteristics of WSs

Examining the results of ANOVA for the chromatic characteristics of the studied WSs (Figure 7), a similar pattern (non-significant differences) in those produced by the natural blending and by the blending operation in each ageing technology is noted.

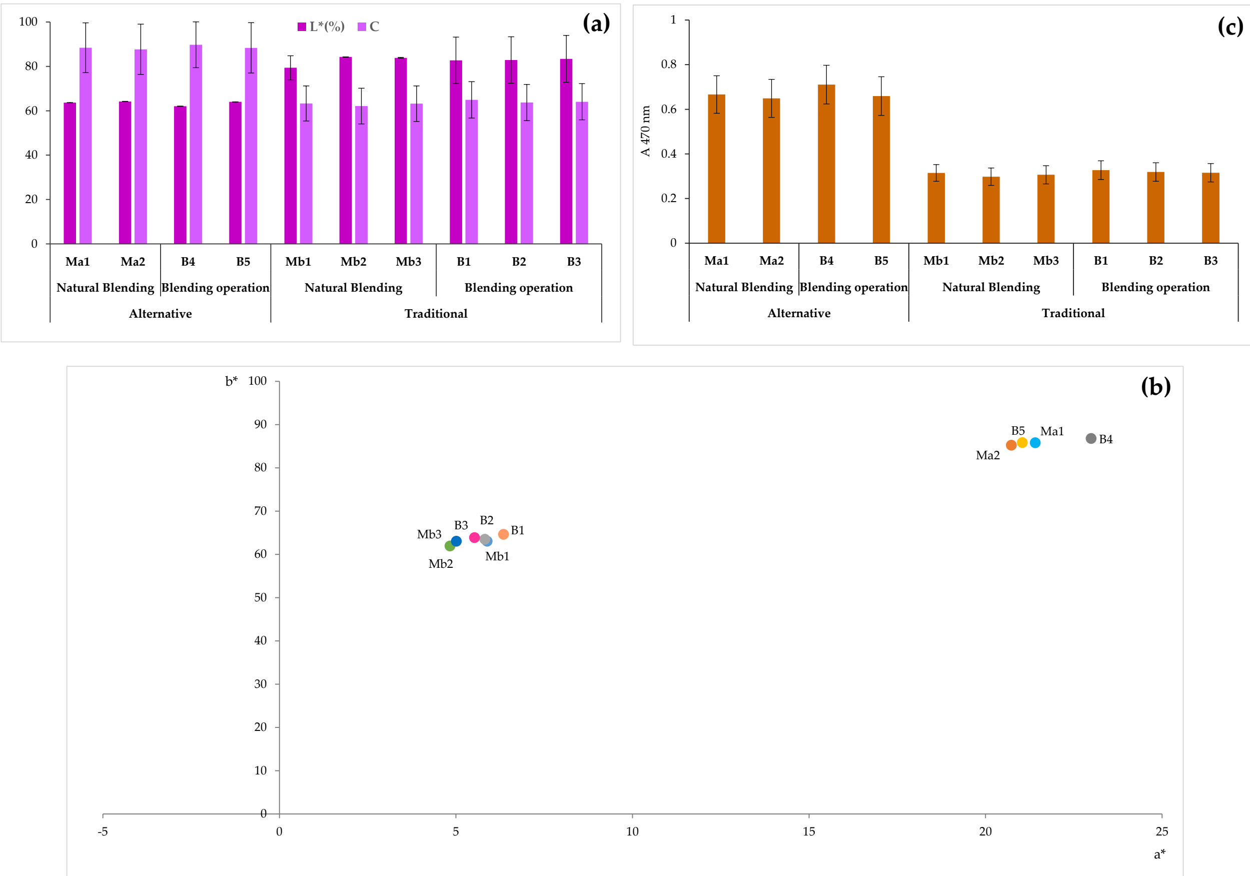

Figure 7. Average values of chromatic characteristics of WSs from natural blending and from the blending operation in each ageing technology: (**a**) lightness and chroma; (**b**) chromaticity coordinates; (**c**) absorbance at 470 nm. Bars and circles not marked with letters indicate non-significant differences between the average values ($p > 0.05$).

Lightness (L*) depicts the grey scale in each colour, varying from fully transparent/bright (100%) to fully opaque/dark (0%) [66]. The WSs resulting from blending in alternative ageing technology exhibited lower lightness than those from blending in the traditional technology (62.02–64.22 vs. 79.36–84.24%), thus having more opaque/darker colour (Figure 7a).

Chroma (C) corresponds to the colourfulness assessed in relation to brightness; a direct relationship exists between the intensity of the colour perceived by the human eye and the chroma [66]. The WSs produce by the alternative ageing technology showed higher chroma than those from the traditional one, regardless of the blending technology (87.70–89.73 vs. 62.11–64.91), and therefore, they had more intense colour (Figure 7a).

Regarding the chromaticity coordinates, a* takes positive and negative values for reddish and greenish colours, respectively, while b* takes positive and negative values for yellowish and bluish colours, respectively [66]. All the WSs displayed a combination of reddish (a* > 0) and yellowish (b* > 0) colours that correspond to amber/orange colours

(Figure 7b). Interestingly, considering these two parameters, the WSs are not grouped according to the blending technology, but rather as clusters of each ageing technology. Indeed, the alternative ageing technology induced a faster development of colour (higher intensities of reddish and yellowish colours) than the traditional one: a* (20.74–22.99 vs. 4.84–6.35) and b* (85.21–86.74 vs. 61.92–64.60).

In addition, the absorbance at 470 nm reflects the complementary colour, brown [67]. As for the CIELab parameters, the WSs resulting from blending in alternative ageing technology had a more intense brown hue than those from blending in the traditional technology (0.65–0.71 vs. 0.30–0.33)—Figure 7c.

The outcomes are consistent with those attained during the ageing of WSs from each ageing technology [14]. In the chemistry underlying the colour evolution over the WS ageing stage [14,19], oxygen and the kind of wood play a pivotal role, which is boosted by the MOX applied to WS kept in stainless steel with wood staves inside. Under these conditions, greater extraction of phenolic compounds and furanic aldehydes from the wood, more intense reactions encompassing their precursors, and the succeeding ones, namely oxidation reactions, involving mineral elements (iron and copper), are triggered and promote a faster colour development (associated with lower lightness, higher chroma, and more intense amber and brown colours).

Complementarily, the results obtained for the total colour difference (ΔE) are in accordance with those of CIELab, showing a non-significant effect of the blending technology, as expected. The average ΔE values of the WSs resulting from the natural blending and blending operation in each ageing technology (96.74 vs. 97.97, alternative; 67.57 vs. 68.78, traditional) differ only by about 1.5 units. This small deviation means that the WSs developed a similar colour, regardless of the kind of blending performed. Comparing the WSs from the alternative and traditional ageing technologies, higher average ΔE values (with about 29 more units) were found in the former, pointing to a more evolved colour for the same ageing time.

Hence, the natural blending respected the colour imparted by each ageing technology to the WSs, and particularly that engendered by the alternative one, which was distinctive, and the WSs looked older, even with the same ageing time (18 months). Besides the innovation and sustainability underlying the WSs production by this blending technology combined with the alternative ageing, their more evolved colour is a valuable factor (the first intrinsic sensory property detected by the consumer that also allows foreseeing other sensory perceptions of this spirit drink) [24,66] that can drive the consumer's preference for these kinds of spirits.

3.4. Global Assessment of WSs' Physicochemical Characteristics

To complete the physicochemical assessment, a global analysis was supported by a cluster heat map to associate patterns to the blending technologies under study (Figure 8).

The heat map clearly divided the WSs into two groups based on the ageing modalities (traditional and alternative); no separation of WSs according to the blending technology was made. These results are in line with and reinforce the ANOVA outcomes.

The main analytical parameters involved in the differentiation of WSs from the traditional ageing technology and from the alternative one, regardless of the blending technology, were (i) pH, gallic acid, scopoletin, lightness (L*) and volatile acidity that exhibited positive correlations with the ageing in barrels; and (ii) umbelliferone, ferulic acid, ellagic acid, sinapaldehyde, coniferaldehyde, syringaldehyde, vanillin, furfural, total phenolic index, syringic acid, chroma (C), chromaticity coordinates (a* and b*), absorbance at 470 nm, total dry extract, fixed acidity and alcoholic strength that showed positive correlations with the ageing in stainless steel tanks using wood staves and MOX.

The results also reveal the peculiar behaviour of 5-methylfurfural and HMF, as well as of total acidity, which did not present a marked trend according to the ageing technologies.

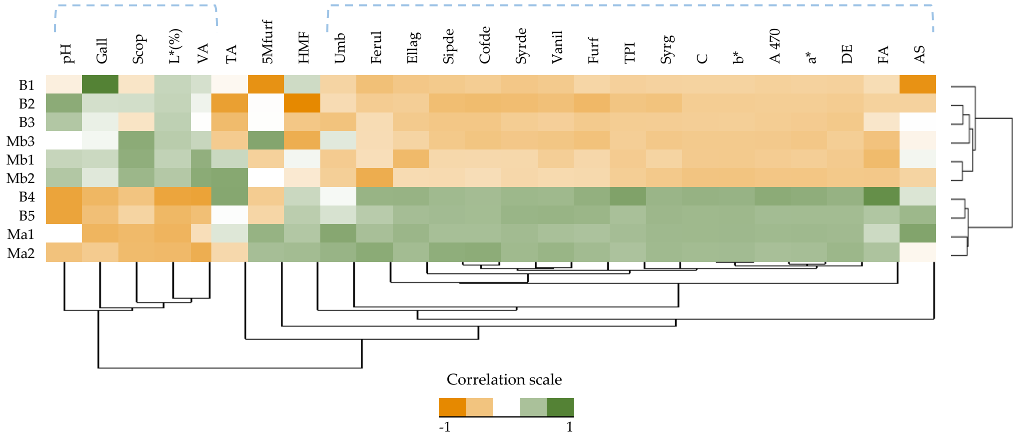

Figure 8. Heat map plotting of physicochemical characteristics and blending modalities of WSs in each ageing technology. Gall—gallic acid; Scop—scopoletin; L*—lightness; VA—volatile acidity; TA—total acidity; 5Mfurf—5-methylfurfural; HMF—5-hydroxymethylfurfural; Umb—umbelliferone; Ferul—ferulic acid; Ellag—ellagic acid; Sipde—sinapaldehyde; Cofde—coniferaldehyde; Syrde—syringaldehyde; Vanil—vanillin; Furf—furfural; TPI—total phenolic index; Syrg—syringic acid; C—chroma; a* and b*—chromaticity coordinates; A 470—absorbance at 470 nm; DE—total dry extract; FA—fixed acidity; AS—alcoholic strength.

3.5. Effect of Blending on the Sensory Profile of WSs

The free sorting task analysis is based on grouping together the samples with perceived sensory similarities. In this experiment, the tasters categorised/gathered the WSs according to their colour, flavour, taste, and overall quality.

The results of MDS for the studied WSs are shown in Figure 9, revealing the lack of differentiation (proximity) between the sensory profiles of WSs produced by the natural blending and by the blending operation in each ageing technology. Conversely, two different clusters (distance), including the WSs from the two ageing technologies, were clearly established. These outcomes corroborate the aforementioned results of the physicochemical analyses, showing that natural blending is an adequate technology for the WSs production because it afforded sensory profiles similar to those resulting from the blending operation.

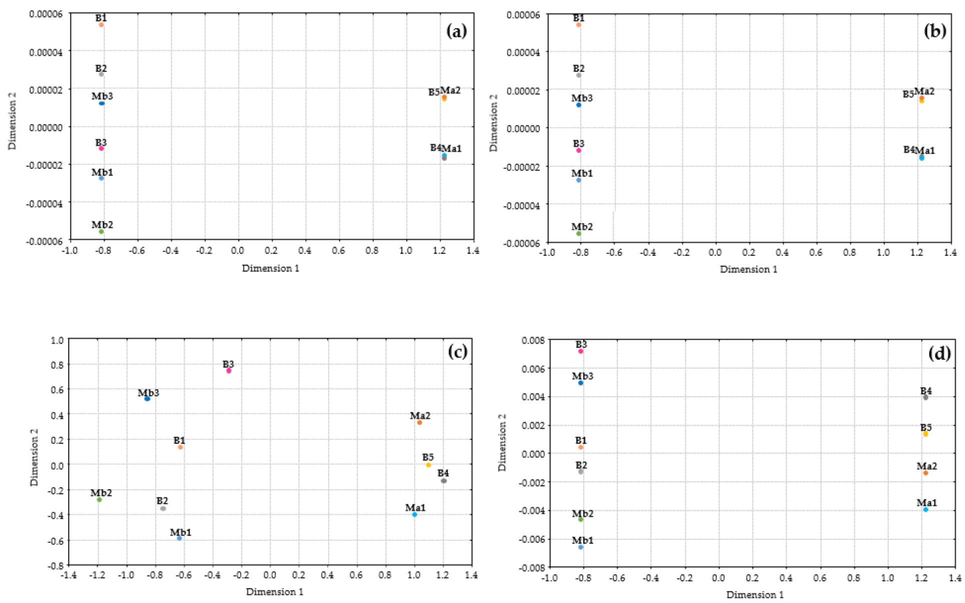

Figure 9. Projection of the WSs from natural blending and from the blending operation of each ageing technology in two-dimensional MDS plots: (**a**) colour; (**b**) flavour; (**c**) taste; (**d**) overall quality.

4. Conclusions

This first study provides key information on natural blending, an innovative technology associated with the WSs' ageing process by using Limousin oak wood and chestnut wood simultaneously.

No significant differences on the physicochemical features (alcoholic strength, total acidity, fixed acidity, volatile acidity, pH, total dry extract, phenolic and furanic composition assessed by HPLC, and chromatic characteristics) and on the sensory profile between the WSs obtained by natural blending and by the blending operation were observed. In addition, the natural blending did not promote changes in the characteristics imparted by each ageing technology. These findings point to natural blending as a reliable substitute of the blending operation, contributing to expanding the sustainability of the production process of this spirit beverage, especially in combination with the alternative ageing technology. Indeed, this kind of blending performed during the ageing process allows to overcome the drawbacks of the blending operation (requirements of time, labour and experienced blenders), thus, lower production costs are expected, while assuring the WSs' *lato sensu* quality.

Further studies are planned to extend the scope of the novel blending technology.

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