



Effect of Aging Vessel (Clay-*Tinaja* versus Oak Barrel) on the Volatile Composition, Descriptive Sensory Profile, and Consumer Acceptance of Red Wine

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Abstract: Consumers look for unique wines, offering pleasant experiences. Wine producers need to open new markets and are targeting countries with fewer traditions in drinking red and complex wines, such as Poland, Russia and Germany. The use of less popular aging vessels (e.g., clay-*tinajas*) will help in creating unique wines. The aim of this study was to evaluate the effect of the aging vessel on the volatile and sensory profiles and consumer acceptance of red wine in Spain and Poland (model of potential new markets). Three wines were studied: (*i*) *wine A*, aged in a clay-*tinaja* with non-permeable coating); (*ii*) *wine B*, aged in clay-*tinaja* without coating; and (*iii*) *wine C*, aged in oak barrels (control). The key families in the volatile profiles were esters (*wines B* and *C*) and organic acids and terpenes (*wine A*). *Wine A* was described as sour and bitter, *wine B* had a distinctive mineral note, and *wine C* had a complex profile with typical wood notes. Finally, *wines C* and *A* were the preferred ones for Spanish and Polish consumers, respectively. Clay-*tinaja wine A* can be a good option to introduce clay-*tinaja* wines in Polish and similar markets because it is a unique product and fulfills the sensory demands/habits of Polish consumers.

Keywords: affective test; clay amphorae; coating; consumer habits; esters; mineral flavor; organic acids

1. Introduction

Wine consumption has a clear hedonic perspective with consumers looking for highquality wines, presenting unique features, offering pleasant experiences, and being different from those already on the market. This specific demand involves the need for developing new wines based on, among other options, on recovering old producing technologies to fulfil these market requirements. Simultaneously, wineries are trying to open new markets where wine consumption is starting to grow and try to offer products with new, different, and unique attributes. Crucial factors for adding value can be, among others: (*i*) linking the wine to a well-known wine-producing region; (*ii*) mentioning the specific location of the vineyard and how the grapes were cultivated; and (*iii*) ensuring sustainable production



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methods [1]. However, these factors are no longer a way of differentiation but requirements in most wine markets. A quite common strategy for creating value in food products is *appealing to tradition*. In this way, wineries are recovering both local grapes and traditional winemaking methods to produce wines with a unique character and personality [2]. They look for differentiation based on (*i*) the change in the complexity of aromas linked to the use of low-yield local grape varieties, and (*ii*) old or less popular winemaking processes (e.g., aging in clay-*tinajas*). However, research is needed to demonstrate that these differences have a real and objective effect on wine quality and that consumers perceive and/or value them and are willing to pay a proper price for these alternative wines.

Wine aging can be defined as various complex physical (e.g., micro-oxygenation of the wine) and chemical reactions, which will modify the chemical composition of the young wine [3], adding complexity and intensity to its flavor. Different vessels can be used for aging: stainless steel tanks, cement vats, wood barrels (mainly oak), or clay pots. Stainless steel and cement vessels do not significantly affect the wine sensory profile, while, in general, clay and wood affect the wine sensory profile, as it will be explained later. Consequently, the choice of the aging vessel will significantly affect the final sensory profile of the wine.

Aging in wood barrels is the world's most common technique. It changes the color, structure, phenolic profile, and aroma. During aging in the barrel, the wood allows microoxygenation of the wine developing new volatile compounds and the direct contact with the oak (toasted at different intensities) also introduces several volatile and non-volatile compounds into the wine [3], leading to wines with woody, toasted and vanilla notes. On the other hand, clay amphorae or jars were used as storage or transport vessels for many food products (e.g., olive oil, fish, wine, spices, etc.) in ancient times [4,5]. At that time, these vessels had not an aging purpose and their use for storage and transport was avoided due to their fragility. Later, this aging technique was abandoned for many years due to the intense worldwide consumer demand for wood-tasting wines. Recently, wines fermented and/or aged in clay vessels (clay-tinaja wines from now on) are becoming more popular among producers and consumers. Consumers look for these wines as a new experience based on the different sensory profiles, which bring back aromas and flavors that were previously masked by intense use of oak during the aging process [6]. Winemakers have tested clay vessels for fermentation and/or aging in France, Portugal, Italy, Georgia, USA, Slovenia, and Austria [7]. Spain has a wide tradition of using clay-tinajas in winemaking, especially in central regions, such as Castilla La Mancha. In fact, it was the main material used until the middle of the 19th century when concrete started to be used [8] and it stopped being used when stainless steel become popular in the 20th century [9,10].

The goal of aging in clay-*tinajas* is to reproduce the exchange of oxygen that is produced in oak barrels but without transferring tannins and toasted flavors which mask the primary aromas from the local grape varieties being used. Thus, the working hypothesis is that "the resulting wines will present a more pronounced mineral and fresh character and a cleaner taste and flavor" [11]. As a summary, it can be stated that the use of clay *tinajas* should enhance the varietal characteristics of the final wines [1]. These differences can be positive or not depending on whether consumers like clay-*tinaja* wines; however, there are no specific studies linking the changes that winemaking and/or aging in clay-*tinaja* produce into the wine and how they affect consumer acceptance at different countries/markets.

Considering all the above information, the aim of this study was to check the effect of wine aging in clay *tinajas* (with and without non-permeable inner coating) and oak barrels (as control vessels) on the following aspects of the final wines: (*i*) volatile profile, (*ii*) descriptive sensory profile, and (*iii*) consumer opinion of Spanish (a wine-producing country) and Polish (a non-wine producing country) consumers; Spanish wineries are trying to sell their wines in Poland and similar markets, and for them it will be essential to understand this potential new market.

2. Materials and Methods

2.1. Wine Samples

Three Spanish wines, coming from the same must, were analyzed to study the effect of the factor "aging vessel". The must was prepared using local grape varieties (80% Mandó and 20% Monastrell) and samples were vinified in stainless steel deposits and then, transferred into clay vessels or French oak barrels. The final wines under analysis were aged under the following conditions: (i) wine A, aged for 6 months in clay-tinajas (4000 L, ovoid shape and buried) with a non-permeable coating consisting of a food-grade epoxy resin (thus, no direct contact of the wine with the clay occurred); (ii) wine B, aged for 6 months in clay-tinajas (4000 L, ovoid shape and buried) without any inner coating (allowing direct contact of the wine with the clay); and *(iii) wine C*, a control wine aged in oak barrels (Bordeaux barrel, 220 L, medium toasted French oak) for 6 months. The selection of wine C as the control one was due to the fact that this is the most popular wine type for most of the consumers worldwide and consumer acceptance is the key issue in this study; however, wine A could have also been selected as a control because a non-permeable inner coating was used, and, thus, no oxygen was entering the wine environment. This is a practical study reproducing winemaking conditions widely available in Spanish wineries, and, thus, the volume of the clay-tinajas (4000 L) and oak barrels (220 L) were different but represent the reality of the Spanish wineries. The same aging time was used in the winemaking of all three wines to avoid the effect of this factor. The "aging vessel" did not influence the basic oenological parameters of the wines under study, where the main composition at the end of the aging period (6 months) was: alcohol content $13.5 \pm 1.2\%$, pH 3.5 ± 0.2 , total acidity 5.35 ± 0.07 g tartaric acid L⁻¹, volatile acidity 0.58 ± 0.03 g acetic acid L⁻¹, free SO₂ $14.3 \pm 0.8 \text{ mg L}^{-1}$, total SO₂ 44.2 ± 1.9 mg L⁻¹, and reducing sugars $3.25 \pm 0.06 \text{ g L}^{-1}$.

2.2. Volatile Compounds

The volatile compounds isolation from the wine matrix was done using HS-SPME (headspace solid-phase micro-extraction) followed by GC-MS and GC-FID (gas chromatography with two types of detectors, mass spectrometry and flame ionization, respectively). Approximately 15 mL of wine, 1.5 g of sodium chloride and 10 μ L of benzyl acetate (internal standard at 1000 mg L⁻¹) were introduced into vials (50 mL) with polypropylene caps and PTFE/silicone septa, and the vial was heated up in a water bath with controlled temperature (50 °C) and automatic stirring. A 50/30 μ m DVB/CAR/PDMS (divinylbenzene/carboxen/polydimethylsiloxane) fiber of 1 cm and high capacity for adsorbing wine-volatile compounds was placed in the vial headspace for 40 min. Desorption of wine compounds from the SPME fiber was done by heating it up for 3 min in the GC injection port.

A Shimadzu GC-17A gas chromatograph (Shimadzu Corporation, Kyoto, Japan) coupled with mass spectrometer (MS) detector, Shimadzu GC-MS QP-5050A was used for the identification of the wine volatile compounds. The separation was done in an SLB-5ms fused silica capillary column of 30 m \times 0.25 mm \times 0.25 µm film thickness, 5% diphenyl, and 95% dimethyl-siloxane (Supelco Analytical, Barcelona, Spain). Helium was used as the carrier gas (1.2 mL min⁻¹) in splitless mode, and chromatographic conditions were: (a) 80 °C; (b) increase of 3.0 °C min⁻¹ from 80 to 170 °C; (c) increase of 25 °C min⁻¹ from 170 to 300 °C and hold for 5.8 min. The working temperatures for the injector and detector were 250 and 300 °C, respectively. Three different methods were used for the identification of the wine volatile compounds: (*i*) retention indices, (*ii*) GC-MS retention times of authentic chemicals, and (*iii*) mass spectra of standards and those of the Wiley spectral library.

Wine volatile compounds were semi-quantified using a Shimadzu GC-17A with a flame ionization detector (FID). The chromatographic conditions used for the GC-FID were those previously described for the GC-MS analysis, injector working at 300 °C. N₂ was the carrier gas at a flow of 1 mL min⁻¹. Benzyl acetate was the internal standard and 10 μ L were added to each sample at a concentration of 1000 mg L⁻¹. Data should be considered

semi-quantitative because no standard curves were done for each one of the wine volatile compounds. Analyses were run in triplicate, and results were expressed as mg L^{-1} .

2.3. Descriptive Sensory Analysis

Eight highly-trained panelists from UMH (Miguel Hernández University of Elche, Orihuela, Alicante, Spain), with over 500 h of experience on wine, aged between 30 and 62 years (4 females and 4 males) evaluated the three wine samples. The panel was trained according to ISO 8586:2012 [12] and it is specialized in alcoholic beverages [13], including wine [14,15] and beer [16]. These three wines were included in a normal session of the panel, in which two quality control parameters, evaluating the panel performance, were also included: (*i*) reproducibility, consisting in evaluating the same sample but at two different sessions, and (*ii*) repeatability, consisting in evaluating the same sample twice in the same session. To validate the panel performance the deviation of these two parameters between the samples must below 20% for all sensory descriptors. The panel worked in the same way as the official panel of the Regulatory Board of the Alicante Protected Designation of Origin (wine), which is certified by the National Accreditation Agency (ENAC) under the ISO 17065 [17].

For the analysis, 25 mL of wine were served in transparent cups and evaluated at 16–18 °C, in normalized sensory booths with white light. Water and unsalted crackers were provided to panelists between samples for palate cleansing.

The attributes under evaluation were alcohol, fruity, floral, vegetable, spicy, animal, mineral and toasted notes (including oak notes) for both odor (o) and flavor (f), basic tastes (sweet, sour and bitter), tactile sensations (astringent), global attributes (aftertaste), and appearance (color intensity). Definitions of the sensory attributes and the reference materials used are described in the lexicon used and previously published by Issa-Issa et al. [15]. The attribute "minerality" was added to this previous lexicon because it is considered essential to describe clay-*tinaja* wines. Minerality is defined as the perception of aromatics (odor) and non-volatile minerals (flavor) commonly associated with a liquid stored in a clay-*tinaja* for several days and resembling wet soil after a rainy day. The volatile compounds behind the odor are those resembling humidity and moisture attributes such as geosmin and regarding the minerality flavor is mainly due to the presence of increased contents of minerals used in the training of the panel were (*i*) distilled water store in a clay-jug (*botijo*) for 2 days: 6 (odor, o) and 8 (flavor, f); (*ii*) *wine* B (Celler del Roure, Moixent, Valencia, Spain): 3 (o) and 6 (f); (*iii*) geosmin, dipped strips using a concentration of 4000 mg L⁻¹ = 6 (o).

A structured scale of 10 points was used to quantify the intensity of the wine attributes, where 0 represents no or extremely low intensity and 10 represents extremely high intensity.

2.4. Affective Sensory Analysis

This affective study was conducted using 150 consumers at each of the two locations used (*i*) Sevilla (Spain) and (*ii*) Wrocław (Poland); email and flyers were used for the recruitment process. These two countries (Spain and Poland) were selected to conduct this initial study because the tradition, consumption habits, market and preferences are different. Spain is a big wine producer, but average–low consumer and Poland is a minor wine producer and average/low consuming country. The consumer profile was as follows:

- (i) Spain: 41% and 59% female and male, respectively; 34% (18–24 years old group), 44% (24–39 years old group), 20% (40–59 years old group) and 2% (60–74 years old group). Spanish consumers were used as model for wine drinkers highly accustomed to complex and intense red wine with intense oaky notes [18].
- (ii) Poland: 44% and 56% female and male, respectively; 30% (18–24 years old group), 49% (24–39 years old group), 17% (40–59 years old group) and 3% (60–74 years old group). Polish consumers were selected considering that they are used to drink sour and fresh white wines.

The test questionnaire was developed in Spanish and, then, translated into Polish; finally, back translation from Polish to Spanish was conducted to check the proper translation.

All samples were served in a randomized order labeled with three-digit codes. Information about wine consumption was requested to check that consumers were regular wine drinkers and agreed with the assumptions made when selecting these two countries and consumers. The information obtained was as follows (*i*) Spanish consumers: *frequency of wine consumption*: 4% daily, 33% twice a week, 22% twice a month and 41% on special occasions; *regularity of drinking wine*: 9% weekdays, 83% weekend and 8% all days; (*ii*) Polish consumers: *frequency of wine consumption*: 1% daily, 18% twice a week, 46% twice a month and 35% in special occasions; *regularity of drinking wine*: 8% weekdays, 71% weekend and 21% all days.

Consumers were asked about their satisfaction degree for each of the attributes under study, using a nine-point hedonic scale (1 = dislike extremely; 5 = neither like or dislike; and 9 = like extremely). JAR questions (Just About Right) were used to ask consumers about the intensity appropriateness of each of the main wine attributes. Finally, consumers ranked samples from the least preferred one to the most preferred one.

Research was approved by the ethics committee of *Oficina de Investigación Responsable* (Universidad Miguel Hernández de Elche, Elche, Alicante, Spain) and consumers provided their informed consent prior to participating in the study.

2.5. Statistical Analysis

XLSTAT Premium 2016 (Addinsoft Inc., New York, NY, USA) was the software used to apply one or two-way ANOVA (analysis of variance) and later to Tukey's multiple-range test to the experimental data generated in this study. In the affective study, a two-way ANOVA (aging, factor 1, and country factor 2). Differences were considered statistically significant at p < 0.05.

3. Results and Discussion

3.1. Volatile Profile and Composition

A total of 29 volatile compounds were isolated, identified and quantified in the headspace of the three wines under study, using HS-SPME and GC-MS and GC-FID. These compounds were grouped into 7 chemical families: (*i*) esters (n = 14), (*ii*) aldehydes (n = 5), (*iii*) alcohols (n = 3), (*iv*) acids (n = 4), (v) terpenes (n = 1), (vi) alkanes (n = 1), and (vii) norisoprenoids (n = 1) (Table 1). The most important finding was the predominant role played by the ester family in wines B and C, while acids and terpenes were the most abundant families in *wine* A (Figure 1). This pattern of chemical families seemed to imply that the first two wines (B and C) were more complex and had more intense fruity and sweet flavor notes as compared to the third one (A), which was characterized by high levels of freshness and sourness. This experimental finding is essential to state that the type of inner coating of the clay-*tinaja* (through different micro-oxygenation patterns) plays a key role in determining the final volatile profile of the wine and probably its sensory profile. It will be very interesting to design future studies controlling different levels of micro-oxygenation through the use of different inner coatings and/or clay materials and studying their effects of the wine characterization and quality.

| Code | Volatile Compounds | Chemical Family | Odor Threshold ⁺ (µg L ⁻¹) | Odor Descriptor ‡ | | RT Retention Index | | ANOVA ^٤ – | Wine A | Wine B | Wine C |
|------|-----------------------|--------------------|---|----------------------------------|--------|--------------------|------|----------------------|--|--------|---------|
| | | | | | RT | | | | $\frac{(\mu g \ L^{-1})}{Tukey \ Multiple \ Range \ Test \ ^{\psi}}$ | | |
| | Compounds | | | | (min) | | | | | | |
| V1 | Isoamyl acetate | Esters | 30 | Banana, pear | 3.640 | 879 | 878 | * | 140 b | 205 a | 214 a |
| V2 | Benzaldehyde | Aldehydes | 2000 | Almond, cherry, sweet | 5.282 | 973 | 971 | NS | 7 | 4 | 9 |
| V3 | Ethyl hexanoate | Esters | 14 | Apple, banana, pineapple | 5.719 | 998 | 998 | *** | 73 с | 246 a | 210 a |
| V4 | Hexanoic acid | Acids | 420 | Cheese, fatty, sour | 5.783 | 1001 | 1006 | NS | 27 | 21 | 19 |
| V5 | Hexyl acetate | Esters | 670 | Apple, cherry, floral, pear | 5.938 | 1007 | 1007 | NS | 5 | 5 | 5 |
| V6 | Limonene | Terpenes | 200 | Citrus, herbaceous, sweet | 6.625 | 1033 | 1033 | *** | 228 a | 102 b | 61 c |
| V7 | Benzyl alcohol | Alcohols | 200,000 | Berry, cherry, citrus | 7.072 | 1050 | 1052 | NS | 14 | 13 | 5 |
| V8 | 1-Octanol | Alcohols | 120 | Citrus, fatty, woody, waxy | 7.758 | 1076 | 1076 | NS | 10 | 24 | 18 |
| V9 | Nonanal | Aldehydes | 1 | Apple, coconut, grape | 8.727 | 1109 | 1108 | NS | 11 | 9 | 10 |
| V10 | Phenethyl alcohol | Alcohols | 14,000 | Honey, rose | 9.520 | 1132 | 1130 | ** | 664 b | 733 ab | 934 a |
| V11 | Diethyl butanedioate | Esters | - | Fruity | 11.413 | 1185 | 1188 | ** | 215 b | 510 ab | 569 a |
| V12 | Ethyl octanoate | Esters | 5 | Apricot, floral, pear, pineapple | 11.991 | 1201 | 1200 | ** | 736 b | 1830 a | 1857 a |
| V13 | Octanoic acid | Acids | 500 | Oily | 13.011 | 1226 | 1210 | ** | 708 a | 299 b | 321 b |
| V14 | Isoamyl hexanoate | Esters | - | Apple, green, pineapple | 14.034 | 1250 | 1251 | NS | 3 | 9 | 6 |
| V15 | Phenylethyl acetate | Esters | 250 | Floral | 14.477 | 1261 | 1260 | NS | 28 | 18 | 26 |
| V16 | 2-Decenal | Aldehydes | - | Oily, orange, floral, citrus | 14.921 | 1272 | 1270 | NS | 4 | 9 | 12 |
| V17 | Vitispirane | Norisoprenoid | - | Woody, spicy | 15.532 | 1287 | 1286 | * | 5 b | 83 a | 46 a |
| V18 | Nonanoic acid | Acids | - | Cheese, waxy | 15.791 | 1293 | 1293 | NS | 7 | 8 | 7 |
| V19 | Ethyl nonanoate | Esters | - | Oily, fruity, nutty | 15.993 | 1298 | 1297 | NS | 14 | 11 | 14 |
| V20 | Tridecane | Alkanes | - | Floral | 16.873 | 1318 | 1300 | NS | 5 | 16 | 10 |
| V21 | Methyl decanoate | Esters | - | Oily, fruity | 17.279 | 1328 | 1326 | NS | 2 | 4 | 8 |
| V22 | Isobutyl caprylate | Esters | - | Fruity | 18.090 | 1347 | 1345 | NS | 2 | 9 | 8 |
| V23 | t-2-Undecenal | Aldehydes | - | Fruity | 19.016 | 1368 | 1367 | NS | 1 | 0 | 1 |
| V24 | Ethyl 9-decenoate | Esters | - | Fruity | 19.856 | 1388 | 1390 | ** | 43 b | 63 ab | 122 a |
| V25 | Ethyl decanoate | Esters | 200 | Grape, oily, pear | 20.337 | 1399 | 1397 | ** | 1609 a | 1294 b | 1539 ab |
| V26 | Decanoic acid | Acids | 1000 | Fatty, citrus | 20.588 | 1405 | 1404 | ** | 180 a | 68 b | 86 b |
| V27 | Dodecanal | Aldehydes | - | Herbaceous, floral, sweet | 20.873 | 1412 | 1411 | NS | 18 | 11 | 23 |
| V28 | Isoamyl octanoate | Esters | 125 | Apple, coconut, fruity | 22.324 | 1447 | 1446 | NS | 21 | 21 | 18 |
| V29 | Ethyl dodecanoate | Esters | 1500 | Coconut, creamy, soapy | 28.508 | 1601 | 1598 | ** | 212 a | 126 b | 93 b |
| | TOTAL | | | | | | | | 4990 | 5751 | 6250 |

Table 1. Content of volatile compounds (μ g L⁻¹), retention index and odor descriptors in the studied wines as affected by the type of vessel used for the aging step (*A*: aged in clay-*tinaja* with non-permeable inner coating; *B*: aged in clay-*tinaja* without inner coating; *C*: aged in oak barrels).

† References [24–26]. ‡ Reference [27]. ¥ Reference [28]; Exp. = experimental; Lit. = literature. ξ NS = not significant at p > 0.05; *, **, ***, significant at p < 0.05, 0.01, and 0.001, respectively. ψ Values (mean of 3 replications) followed by the same letter, within the same row, were not significantly different (p > 0.05), according to Tukey's least significant difference test.

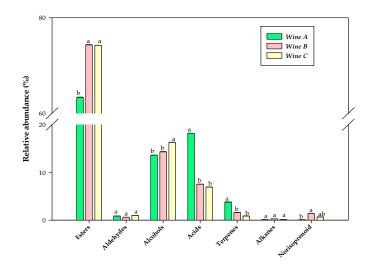


Figure 1. Chemical families in the volatile profiles of the studied wines as affected by the type of vessel used for the aging step. Bars with the same letter, within one chemical family, were not significantly different (p > 0.05), according to Tukey's least significant difference test.

The 4 most abundant volatile compounds found in each wine and their sensory descriptors were: (*i*) wine A: ethyl decanoate, ethyl octanoate, octanoic acid and phenethyl alcohol; (*ii*) wine B: ethyl octanoate, ethyl decanoate, phenethyl alcohol and diethyl butanedioate; and (*iii*) wine C: ethyl octanoate, ethyl decanoate, phenethyl alcohol and diethyl butanedioate. Thus, the predominant volatile compounds in the studied wines were esters (ethyl decanoate and ethyl octanoate) and alcohols (phenethyl alcohol). These compounds have been previously reported as playing a key role in *Monastrell, Tempranillo, Cabernet sauvignon* and *Alicante Bouschet* wines [19–21].

Vitispirane was found at low concentration but deserves attention because this norisoprenoid could be formed from the degradation of carotenoid molecules during wine aging [15]. In this way, *wine* A had no measurable content of this compound; the other two wines had low but measurable contents and the compound could be, together with others, responsible for the wine aroma uniqueness due to its low detection threshold, $101 \ \mu g \ L^{-1}$ [22]. Further studies are needed with different aging times to establish the role of this compound in the aging process.

The total content of volatile compounds increased from 4.97 mg L⁻¹ in *wine* A (aged in clay-*tinaja* with non-permeable inner coating allowing no contact between the wine and the clay and avoiding a significant micro-oxygenation of the wine) and 6.26 mg L⁻¹ in *wine* C (aged in oak barrels). A positive relationship between the total content of volatile compounds and the complexity of the wine is expected and will be assayed through the study of the wine descriptive sensory profile.

3.2. Descriptive Sensory Analysis with Trained Panel

Table 2 shows that *wine A* had a flatter profile as compared to the other two wines. It is important to highlight here that this wine was aged in a clay-*tinaja* but with a nonpermeable inner coating; thus, there was no direct contact between the wine and the jar, and the micro-oxygenation of the wine was reduced as compared to a more permeable coating or the use of oak barrels. *Wine C* had the characteristic "toasted" (vanilla) odor and flavor due to the contact with the oak wood of the barrel, which led to a longer aftertaste. However, these toasted notes were not supported by volatile compounds with oak or toasted sensory descriptors (Table 1); however, it is worth mentioning that trace levels of furfural, guaiacol and vanillin were found but could not be quantified due to the short aging time in the oak barrels and perhaps to the use of headspace SPME as the extracting methodology for the volatile compounds. Finally, *wine B* had a mineral odor and flavor and is astringent perhaps due to the migration of minerals (K, Ca, and Mg) from the clay-vessel to the wine. In this way, Blanco [23] reported that there were significantly higher contents of K, Mg and Na (774, 134, and 31.9 μ g L⁻¹, respectively) in wine aged in clay-*tinajas* as compared to wines aged in wood barrels (709, 113, and 30.8 μ g L⁻¹, respectively). In addition, an increase in Na and K contents was observed along the aging time due to an increased time of contact between the wine and the clay. The wines studied [23] were from the same winery as those used in the current study and similar clay-*tinajas* were used in both experiments.

Table 2. Descriptive sensory analysis of the studied wines as affected by the type of vessel used for the aging step (*A*: aged in clay-*tinaja* with non-permeable inner coating; *B*: aged in clay-*tinaja* without inner coating; *C*: aged in oak barrels).

| Attribute | ANOVA ⁺ | Wine A | Wine B | Wine C | | | | | |
|-----------------------------|--------------------|--------|--------|--------|--|--|--|--|--|
| Tukey Multiple Range Test ‡ | | | | | | | | | |
| Appearance | | | | | | | | | |
| Color | ** | 5.0 b | 9.5 a | 8.0 a | | | | | |
| Odor | | | | | | | | | |
| Alcohol | ** | 5.5 ab | 6.0 a | 5.0 b | | | | | |
| Fruity | ** | 5.0 b | 6.0 ab | 7.0 a | | | | | |
| Floral | NS | 2.0 | 2.0 | 2.0 | | | | | |
| Vegetable | ** | 2.5 b | 4.5 a | 3.5 ab | | | | | |
| Spicy | *** | 2.0 b | 4.0 a | 4.0 a | | | | | |
| Animal | NS | 2.00 | 2.50 | 2.50 | | | | | |
| Mineral | *** | 0.5 b | 3.0 a | 0.0 b | | | | | |
| Toasted | *** | 0.0 b | 0.5 b | 4.0 a | | | | | |
| Basic Taste | | | | | | | | | |
| Sweetness | ** | 1.5 b | 2.0 ab | 3.5 a | | | | | |
| Sourness | ** | 6.0 a | 6.5 a | 4.0 b | | | | | |
| Bitterness | *** | 4.0 a | 2.5 b | 1.5 b | | | | | |
| Flavor | | | | | | | | | |
| Alcohol | ** | 5.5 b | 6.5 ab | 7.0 a | | | | | |
| Fruity | ** | 4.5 b | 6.0 a | 6.0 a | | | | | |
| Floral | ** | 2.0 b | 2.0 b | 3.0 a | | | | | |
| Vegetable | *** | 2.0 b | 5.0 a | 4.0 ab | | | | | |
| Spicy | *** | 1.5 b | 2.0 b | 4.5 a | | | | | |
| Animal | NS | 1.0 | 1.0 | 1.0 | | | | | |
| Mineral | *** | 1.0 b | 6.0 a | 1.5 b | | | | | |
| Toasted | *** | 0.5 b | 0.5 b | 4.5 a | | | | | |
| Astringency | ** | 4.5 ab | 5.5 a | 4.0 b | | | | | |
| Aftertaste | *** | 3.5 c | 6.0 b | 7.5 a | | | | | |

 \pm NS = not significant at p > 0.05; ** and ***, significant at p < 0.01 and 0.001, respectively. \pm Values (mean of 8 trained panelists) followed by the same letter, within the same row, were not significantly different (p > 0.05), according to Tukey's least significant difference test.

The attribute "mineral (odor and flavor)" can be considered as the key sensory marker to study the effect of the clay pot on the wine. The intensity of this attribute will be positively linked to the direct contact between the wine and the clay; in this way, if a non-permeable coating is used (as in the case of *wine A*), the wine will have no significant mineral nature and will be equivalent to a wine aged in a stainless-steel deposit. However, if a permeable coating or no coating is used (as in the case of *wine B*), the wine will have relatively high intensities of mineral character, minerality (3.0 and 6.0 in the olfactory and gustatory phases, respectively). Thus, it is essential to report the type of coating used when working or selling clay-*tinaja* wine because this parameter will be clearly reflected in the sensory profile of the wine produced and to be sold or bought.

3.3. Affective Sensory Analysis

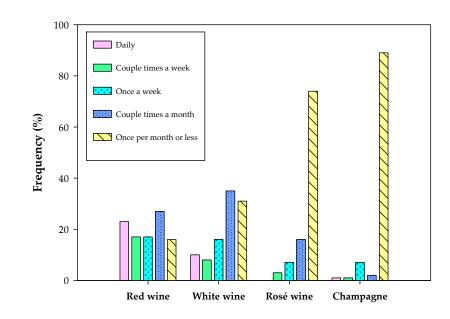
The most relevant finding was that *wine* A, which was the most liked in Poland, was the least liked by Spanish consumers (Table 3). Polish consumers showed a satisfaction degree of ~6.0 for the sweetness, sourness, and astringency of the *wine* A; however, Spanish consumers showed low satisfaction for most of the sensory attributes of this wine, going from its color (4.9) to aftertaste (5.3).

| | Overall | Color | Alcohol (o) ¶ | Fruity (o) ¶ | Sweetness | Sourness | Astringency | Alcohol (f) ¶ | Fruity (f) [¶] | Mineral (f) $^{I\!\!I}$ | Aftertaste |
|-------------------------------------|---------|--------|---------------------|--------------------|----------------|------------------------|-------------|---------------------|-------------------------|-------------------------|------------|
| | | | | | ANOVA Te | est † | | | | | |
| Vessel | * | *** | *** | ** | * | * | * | NS | NS | NS | * |
| Country | * | *** | *** | *** | NS | * | NS | * | * | * | * |
| Vessel \times Country | * | *** | *** | * | * | * | * | * | * | NS | * |
| | | | | Tul | key Multiple R | ange Test [‡] | | | | | |
| Vessel | | | | | | | | | | | |
| Wine A | 5.6 b | 5.5 b | 5.8 b | 5.8 b | 5.3 a | 5.5 a | 5.5 a | 5.8 | 5.6 | 5.3 | 5.6 ab |
| Wine B | 5.8 a | 7.4 a | 6.5 a | 6.1 a | 5.1 b | 5.3 b | 5.1 b | 5.8 | 5.7 | 5.4 | 5.5 b |
| Wine C | 5.8 a | 7.3 a | 6.0 ab | 5.9 b | 5.1 b | 5.2 b | 5.3 ab | 5.7 | 5.6 | 5.5 | 5.8 a |
| Country | | | | | | | | | | | |
| Spain | 5.6 b | 6.3 b | 5.8 b | 5.6 b | 5.2 | 5.1 b | 5.3 | 5.6 b | 5.5 b | 5.3 b | 5.7 a |
| Poland | 5.9 a | 7.1 a | 6.4 a | 6.2 a | 5.1 | 5.6 a | 5.4 | 6.0 a | 5.7 a | 5.5 a | 5.5 b |
| Vessel × Country | | | | | | | | | | | |
| <i>Wine</i> $A \times$ Spain | 5.1 b | 4.9 d | 5.1 c | 5.3 b | 5.0 ab | 5.0 b | 5.2 ab | 5.4 b | 5.3 b | 5.0 | 5.3 b |
| Wine $A \times Poland$ | 6.1 a | 6.1 c | 6.5 ab | 6.2 a | 5.6 a | 5.9 a | 5.9 a | 6.1 a | 5.8 a | 5.6 | 5.9 a |
| <i>Wine</i> $B \times \text{Spain}$ | 5.9 ab | 7.0 b | 6.1 b | 5.9 ab | 5.5 a | 5.4 ab | 5.2 ab | 5.7 ab | 5.8 a | 5.5 | 5.8 ab |
| <i>Wine</i> $B \times Poland$ | 5.8 ab | 7.8 a | 6.8 a | 6.3 a | 4.7 b | 5.3 ab | 5.0 b | 6.0 a | 5.6 ab | 5.4 | 5.2 b |
| <i>Wine</i> $C \times$ Spain | 5.9 ab | 7.0 b | 6.1 b | 5.8 ab | 5.1 ab | 5.0 b | 5.4 ab | 5.7 ab | 5.4 b | 5.3 | 6.0 a |
| Wine $C \times Poland$ | 5.7 ab | 7.5 ab | 5.9 b | 6.0 a | 5.1 ab | 5.4 ab | 5.2 ab | 5.8 ab | 5.7 ab | 5.6 | 5.5 ab |

Table 3. Liking scores of the main attributes of the studied wines as affected by the type of vessel used for the aging step (*A*: aged in clay-*tinaja* with non-permeable inner coating; *B*: aged in clay-*tinaja* without inner coating; *C*: aged in oak barrels).

+ NS = not significant at p > 0.05; *, **, and *** significant at p < 0.05, 0.01, and 0.001, respectively. + Values (mean of 150 consumers) followed by the same letter, within the same column, were not significantly different (p > 0.05), according to Tukey's least significant difference test. \P "o" and "f" mean odor and flavor.

Regarding the effect of the factor "country", it can be seen that Polish consumers liked the studied wines more than the Spanish ones (overall liking) (Table 3), and this liking could be related to the fact that they are not too strong or complex wines (e.g., clear red color, relatively high sour taste, with mineral notes but not too intense and short aftertaste) (Table 2). The preferred wines for the Spanish and Polish consumers were *wine* C (46%) and *wine* A (39%), respectively. In general, Spanish consumers prefer more complex types of red wine with notes of vanilla, spices, and wood [18], while Polish consumers prefer softer red wines because they are basically sour and soft white wine drinkers. These trends are clearly seen in data represented in Figure 2, in which it can be seen that 23% of the Spanish consumers drink red wine daily as compared to only 1% of the Polish ones; on the other hand, 18% of the Polish consumers recognized drinking white wine daily as compared to only 10% of Spaniards.





(A)

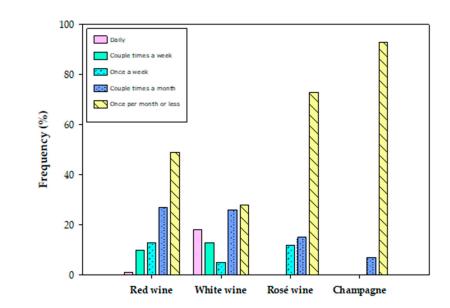


Figure 2. Consumer habits regarding wine consumption in Spain (A) and Poland (B).

The mean value of the overall liking for the studied wines in Spain and Poland was ~6.0 (5.6 and 5.9, respectively), meaning that the wines were liked "slightly". Although it must be considered that in affective studies, consumers tend to concentrate their opinions into the middle section of the scale avoiding extreme values; this means, that a value of 6.0 implies high satisfaction degree by consumers. However, the trends for the satisfaction degree were different for consumers in these two countries and agreed with the behaviors already described for the preference data. There is a general rule for affective tests "consumers like what they are used to drink"; this rule is supported by the fact that Spanish and Polish consumers preferred *wine C* (the strongest studied wine having oaky and vanilla notes) and *wine A* (soft red wine with important sour and fruity notes), respectively, as mentioned before.

The key drivers for choosing their favorite wine for the Spanish consumers (*wine C*) were fruity (22%) and alcohol (15%) flavor notes and sweetness (22%), while for the Polish consumers, they were color (34%) and aftertaste (33%).

4. Conclusions

The goal of this study was to compare the opinion of Spanish (a wine-producing country) and Polish (a non-wine producing country) consumers towards wine with different aging techniques to determine if they affect consumer acceptance and if this acceptance is related to what consumers are used to drinking. It has shown how the aging in clay-tinajas and oak barrels affected the volatile and sensory profiles and consumer acceptance of red wine in Spain and Poland. Furthermore, the research aimed to answer four questions: (*i*) which chemical properties affect the sensory profile of a wine during its aging period? (*ii*) is the aging type affecting the consumer perception and opinion of wine? (*iii*) which of these perception differences can be related to cultural and wine tradition? and (iv) does it make any sense to introduce new aging ways if consumption patterns are converging? The results obtained showed that the predominant volatile family composition was acids (e.g., octanoic acid) and terpenes (limonene) for wine A and esters (ethyl octanoate and diethyl butanedioate) and for wine B and wine C. Wine A was described as sour and bitter, with these attributes being highly attractive to Polish consumers, as they are used to find the high intensity of these attributes in their daily consumed white wines. *Wines B* and *C*, mainly the second one, were the preferred ones for Spanish consumers, and this preference was linked to high intensities of color, alcohol and fruity flavor notes and long aftertaste. The use of coating and its nature (permeable or non-permeable) is essential because it will allow, or not, direct contact between the wine and the clay vessel; the attribute "mineral" will be completely dependent on the use of this inner coating. In some cases, this minerality gets confused with astringency by consumers because both attributes generate a drying sensation in the mouth. Red wines without oaky or mineral notes (e.g., wine A) were highly appreciated in Poland because of their sourness and freshness, which are highly familiar for them because they are very much used to drink white wines. Finally, new wines prepared using old aging methods (e.g., clay-tinaja) can represent a real opportunity as consumers clearly identified the different sensory profiles of these wines. In this way, it has been demonstrated that clay-tinaja wine A (non-permeable inner coating) can be a good option to the Polish market because it is a unique product (made with traditional and old clay-tinajas) but having a sensory profile close to that expected and demanded by Polish consumers.

Author Contributions: H.I.-I. run the volatile profile and composition, sensory data, conducted part of the statistical analysis and writing the manuscript; M.C.-L. helped with statistical analysis and the descriptive sensory analysis with trained panel; A.N. helped with the consumer research in Poland; L.L. helped with the volatile profile and composition and the descriptive sensory analysis with trained panel; M.C. prepared the samples and helped with the physico-chemical analysis; P.C.-G. prepared the samples and helped with consumer research in Spain; Á.A.C.-B. revision and final approval of the manuscript and helped with the sensory analysis with trained panel; D.L.-L. coordinated, interpretation of data and manuscript revision. All authors have read and agreed to the published version of the manuscript.

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

References

- 1. Díaz, C.; Laurie, V.F.; Molina, A.M.; Bücking, M.; Fischer, R. Characterization of selected organic and mineral components of qvevri wines. *Am. J. Enol. Vitic.* **2013**, *64*, 532–537. [CrossRef]
- 2. Bene, Z.; Kállay, M. Polyphenol contents of skin-contact fermented white wines. Acta Aliment. 2019, 48, 515–524. [CrossRef]
- Baiano, A.; Mentana, A.; Quinto, M.; Centonze, D.; Longobardi, F.; Ventrella, A.; Agostiano, A.; Varva, G.; De Gianni, A.; Terracone, C.; et al. The effect of in-amphorae aging on oenological parameters, phenolic profile and volatile composition of Minutolo white wine. *Food Res. Int.* 2015, 74, 294–305. [CrossRef]
- 4. Foley, B.P.; Hansson, M.C.; Kourkoumelis, D.P.; Theodoulou, T.A. Aspects of ancient Greek trade re-evaluated with amphora DNA evidence. *J. Archaeol. Sci.* 2012, *39*, 389–398. [CrossRef]
- Romanus, K.; Baeten, J.; Poblome, J.; Accardo, S.; Degryse, P.; Jacobs, P.; De Vos, D.; Waelkens, M. Wine and olive oil permeation in pitched and non-pitched ceramics: Relation with results from archaeological amphorae from Sagalassos, Turkey. J. Archaeol. Sci. 2009, 36, 900–909. [CrossRef]
- 6. Martins, N.; Garcia, R.; Mendes, D.; Costa Freitas, A.M.; da Silva, M.G.; Cabrita, M.J. An ancient winemaking technology: Exploring the volatile composition of amphora wines. *LWT* **2018**, *96*, 288–295. [CrossRef]
- 7. Picuno, P. Use of traditional material in farm buildings for a sustainable rural environment. *Int. J. Sustain. Built Environ.* **2016**, *5*, 451–460. [CrossRef]
- 8. Martínez-Ferreras, V.; Capelli, C.; Cabella, R.; Prieto, X.N. From Hispania Tarraconensis (NE Spain) to Gallia Narbonensis (S France). New data on Pascual 1 amphora trade in the Augustan period. *Appl. Clay Sci.* **2013**, *82*, 70–78. [CrossRef]
- 9. Estreicher, S.K. A brief history of wine in Spain. *Eur. Rev.* **2013**, *21*, 209–239. [CrossRef]
- 10. Fuentes, J.M.; Gallego, E.; García, A.I.; Ayuga, F. New uses for old traditional farm buildings: The case of the underground wine cellars in Spain. *Land Use Policy* **2010**, *27*, 738–748. [CrossRef]
- 11. Baiano, A.; Varva, G.; De Gianni, A.; Viggiani, I.; Terracone, C.; Del Nobile, M.A. Influence of type of amphora on physico-chemical properties and antioxidant capacity of 'Falanghina' white wines. *Food Chem.* **2014**, *146*, 226–233. [CrossRef]
- International Organization of Standardization. ISO 8586:2012. Sensory Analysis—General Guidelines for the Selection, Training and Monitoring of Selected Assessors and Expert Sensory Assessors. Available online: https://www.iso.org/standard/45352.html (accessed on 8 May 2021).
- 13. Issa-Issa, H.; Ivanišová, E.; Noguera-Artiaga, L.; Kántor, A.; López-Lluch, D.; Kačániová, M.; Szumny, A.; Carbonell-Barrachina, Á.A. Effect of the herbs used in the formulation of a Spanish herb liqueur, Herbero de la Sierra de Mariola, on its chemical and functional compositions and antioxidant and antimicrobial activities. *Eur. Food Res. Technol.* **2019**, 245, 1197–1206. [CrossRef]
- 14. Issa-Issa, H.; Guclu, G.; Noguera-Artiaga, L.; López-Lluch, D.; Poveda, R.; Kelebek, H.; Selli, S.; Carbonell-Barrachina, Á.A. Aroma-active compounds, sensory profile, and phenolic composition of Fondillón. *Food Chem.* **2020**, *316*, 126353. [CrossRef]
- 15. Issa-Issa, H.; Noguera-Artiaga, L.; Sendra, E.; Pérez-López, A.J.; Burló, F.; Carbonell-Barrachina, A.A.; López-Lluch, D. Volatile Composition, Sensory Profile, and Consumers' Acceptance of Fondillón. *J. Food Qual.* **2019**, 2019, 1–10. [CrossRef]
- 16. Zapata, P.J.; Martínez-Esplá, A.; Gironés-Vilaplana, A.; Santos-Lax, D.; Noguera-Artiaga, L.; Carbonell-Barrachina, Á.A. Phenolic, volatile, and sensory profiles of beer enriched by macerating quince fruits. *LWT* **2019**, *103*, 139–146. [CrossRef]
- 17. International Organization of Standardization. ISO/IEC 17065:2012. Conformity Assessment—Requirements for Bodies Certifying Products, Processes and Services. Available online: https://www.iso.org/standard/46568.html (accessed on 8 May 2021).
- Sáenz-Navajas, M.P.; Ballester, J.; Pêcher, C.; Peyron, D.; Valentin, D. Sensory drivers of intrinsic quality of red wines. Effect of culture and level of expertise. *Food Res. Int.* 2013, 54, 1506–1518. [CrossRef]
- 19. Lorenzo, C.; Pardo, F.; Zalacain, A.; Alonso, G.L.; Rosario Salinas, M. Complementary effect of Cabernet Sauvignon on Monastrell wines. J. Food Compos. Anal. 2008, 21, 54–61. [CrossRef]
- 20. Moreno-Olivares, J.D.; Paladines-Quezada, D.; Fernández-Fernández, J.I.; Bleda-Sánchez, J.A.; Martínez-Moreno, A.; Gil-Muñoz, R. Study of aromatic profile of different crosses of Monastrell white wines. *J. Sci. Food Agric.* **2020**, *100*, 38–49. [CrossRef]
- Noguerol-Pato, R.; González-Álvarez, M.; González-Barreiro, C.; Cancho-Grande, B.; Simal-Gándara, J. Evolution of the aromatic profile in Garnacha Tintorera grapes during raisining and comparison with that of the naturally sweet wine obtained. *Food Chem.* 2013, 139, 1052–1061. [CrossRef]
- Ziegler, M.; Wegmann-Herr, P.; Schmarr, H.G.; Gök, R.; Winterhalter, P.; Fischer, U. Impact of Rootstock, Clonal Selection, and Berry Size of *Vitis vinifera* sp. Riesling on the Formation of TDN, Vitispiranes, and Other Volatile Compounds. *J. Agric. Food Chem.* 2020, *68*, 3834–3849. [CrossRef]
- 23. Blanco, M. Characterization of Terracotta Wines; Universidad Miguel Hernandez: Alicante, Spain, 2015.

- 24. Ferreira, V.; López, R.; Cacho, J.F. Quantitative determination of the odorants of young red wines from different grape varieties. *J. Sci. Food Agric.* 2000, *80*, 1659–1667. [CrossRef]
- 25. Gómez-Míguez, M.J.; Cacho, J.F.; Ferreira, V.; Vicario, I.M.; Heredia, F.J. Volatile components of Zalema white wines. *Food Chem.* **2007**, *100*, 1464–1473. [CrossRef]
- 26. Jiang, B.; Xi, Z.; Luo, M.; Zhang, Z. Comparison on aroma compounds in Cabernet Sauvignon and Merlot wines from four wine grape-growing regions in China. *Food Res. Int.* 2013, *51*, 482–489. [CrossRef]
- 27. Sigma-Aldrich. Flavors & Fragrances; Sigma-Aldrich: Saint Louis, MO, USA, 2012.
- 28. National Institute of Standards and Technology (NIST). NIST Chemistry Webbook. Available online: https://webbook.nist.gov/ chemistry/ (accessed on 8 May 2021).