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Fondillón Wine Adulteration by Addition of Other *Monastrell* Wines

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Abstract: Authenticity and traceability are two issues of great importance to quality and food safety in the food industry. For wine producers and authorities, it is essential to know how to detect adulterations because wine is one of the alcoholic beverages most prone to adulteration, as indicated by the European Commission. *Fondillón* is one of the most important naturally sweet Spanish wines and is certainly the core of the Alicante PDO. *Fondillón* is a wine that is prone to be adulteration due to its limited production and high price. The aim of this study was to identify potential markers of *Fondillón* adulteration by mixing it with other *Monastrell* wines. The experimental results showed that *Fondillón* is characterized by high concentrations of acetic acid, furfural, benzaldehyde, vitispirane, and TDN and low concentrations of citric, tartaric, and malic acids; a low total phenolic content; and low values of antioxidant activity.

Keywords: acetic acid; authentication; fraud; fructose; minerals; TDN; vitispirane; volatile composition

Citation: Issa-Issa, H.; Hernández, F.; López-Lluch, D.; Uysal, R.S.; Carbonell-Barrachina, Á.A. *Fondillón* Wine Adulteration by Addition of Other *Monastrell* Wines. *Beverages* **2023**, *9*, 28. https://doi.org/10.3390/beverages9010028

Academic Editors: Stamatina Kallithraka and Matteo Marangon

Received: 13 February 2023
Revised: 4 March 2023
Accepted: 9 March 2023
Published: 20 March 2023

1. Introduction

Traceability and authenticity are two key aspects for both the food and beverages industries because they are associated with the quality and safety of the produced items and the protection of consumers [1]. Traceability is a measure concerning the full control over marketed products from their origin to the production process, storage, and, finally, acquisition by consumers. Traceability increases food safety and is a tool that both producers and consumers can use to obtain all the necessary information to be able to manage any problem more easily and quickly by accessing a product's history [2]. Authenticity is the key to guaranteeing the quality of food and beverages; it is a component of food safety as it helps producers adequately comply with national legislation [3].

Regarding wine, the study of authenticity is a central part of production because wine is one of the most easily imitated food products [4]. Wine is produced following a series of long and complex processes involving physical, chemical, and biological reactions, where every step has a strong influence on the desired quality of the final product [5]. However, it is a very easy product to adulterate due to its chemical features (low pH and high alcoholic content) and its availability throughout the world. In this sense, wine is one of the products with the most complete and complex legislation [6]. In addition, it is also one of the products with the most extensive analytical procedures [7]. Both facts are

directly linked to the fight against the massive quantities of adulterations available in the international wine market.

In particular, when wines are scarce and appreciated, the number of imaginative schemes with which to take advantage of their prestige and price increases. This can result in a lack of consumer confidence, and thus the system must develop new control methods [8]. Wine adulteration is a worldwide problem. In 2021, almost 1,800,000 L of wine and alcoholic beverages was seized in a specific raid led by the European Anti-Fraud Office (OLAF) [9]. Wine fraud costs the EU wine sector an estimated EUR 1.3 billion each year, amounting to around 3% of the total value of sales. These adulterations refer to different types of fraud, such as the (*i*) addition of alcohol, (*ii*) dilution with water, (*iii*) the addition of flavorings, (*iv*) substitution or mixture with lower quality wine, and (*v*) mislabeling (fraud with respect to the origin and the cultivar) [1,10,11].

The authenticity and commercial value of wines are linked to their geographical origin, the grape variety employed, and the year of the harvest. Therefore, the methods currently used to counterfeit wine include (*i*) fraud regarding the geographical region of origin, (*ii*) fraud regarding the grape variety used, and/or (*iii*) fraud regarding the vintage year [12]. This is the case of wines within a Protected Designation of Origin (PDO). These wines are produced using specific grape varieties cultivated in specific geographical regions under controlled growing and production conditions. In this sense, one of the main purposes of PDO Regulatory Councils is the prevention of fraud by guaranteeing the origin and quality of wines [7].

Until recently, tasting by experts was the most widely used method with which to evaluate and certify wine's authenticity. However, this technique is time consuming and too expensive because it requires a highly trained panel to be able to detect some of these types of fraud; thus, a new strategy has been developed that combines the latest analytical technology and advanced mathematical tools. Studies have developed a series of methods used to assess the authenticity of wines, which include the determination of polyphenols, the identification and quantification of odor-active compounds, the determination of minerals, and determination of organic acids and sugars [13,14].

Fondillón, an Alicante PDO wine with a production process constituting at least 10 years of aging and an alcoholic strength of over 16%, which is obtained from overripe on-vine *Monastrell* grapes and is produced without the addition of alcohol, is a perfect candidate for adulteration, which can occur through different methods, but one of the most difficult to identify is its mixing with cheaper *Monastrell* wines, even with those coming from the Alicante PDO. Depending on the season, approximately 2000 to 5000 bottles are sold annually, and this wine has a high price, namely, ~EUR 75 per 700 mL bottle; however, there is no validated methodology to prevent the production and circulation of fraudulent versions of this wine.

Consequently, the aim of this study was to find chemical markers to identify potential instances of the adulteration of *Fondillón* by mixing it with other *Monastrell* wines, which are the closest ones to the sensory profile of this wine. The following parameters have been considered as potential markers and have been evaluated accordingly: sugars, organic acids, minerals, antioxidant activity, and volatile compounds. Another goal of this study was to analyze the authenticity of pure *Fondillón* using gas chromatography and mass spectrometry (GC–MS) combined with chemometrics. For this purpose, two other *Monastrell* wine samples were used to prepare adulterated *Fondillón* samples; measurements of key parameters of these samples were conducted using GC–MS, and the data were evaluated using principal component analysis (PCA).

2. Materials and Methods

2.1. Reagents and Chemicals

The standards for identification of volatile compounds shown in Table S1 were all purchased from Sigma-Aldrich (Steinheim, Germany). The compounds 2,2-diphenyl-1-picrylhydrazyl and 2,2-azinobis-(3-ethylbenzothiazoline acid-6-sulfonic used for the

analysis of the antioxidant activity were supplied by Fisher Scientific (Hampton, NH, USA). The standards for the minerals were purchased from Sigma-Aldrich (Steinheim, Germany).

2.2. Wine Samples

The three wine samples (young, aged/*crianza*, and *Fondillón*) used for this study were kindly provided by Bodegas BOCOPA (Petrer, Alicante, Spain); they were supplied in triplicate from three different batches and taken to the facilities of the Miguel Hernández University of Elche (Orihuela, Alicante, Spain).

The main physicochemical quality parameters (total and volatile acidity; total alcoholic content and reducing sugars) were analyzed following the official methods of the International Organization of Vine and Wine (OIV) (published in accordance with article 15 Commission Regulation (EC) No. 606/2009 of 10 July 2009, which can be found on the OIV website) [15]. The main characteristics of the wines used were as follows: (*i*) young wine—prepared using exclusively *Monastrell* grapes from the 2019 season, with 15% alcohol, total acidity equal to 3.9 g L^{-1} tartaric acid, and volatile acidity equal to 0.4 g L^{-1} acetic acid; (*ii*) aged/*crianza* wine—prepared using exclusively *Monastrell* grapes from the 2017 season, aged for 24 months in total, including 6 months in oak barrels, with 15% alcohol, a content of reducing sugars of 48 g L^{-1}, a total acidity of 4.2 g L^{-1} tartaric acid, and a volatile acidity of 0.7 g L^{-1} acetic acid; and (*iii*) *Fondillón*—prepared exclusively from overripe *Monastrell* grapes from the 1988 season, aged (using the vintage system) for 32 years in old oak barrels and a subsequent 2 years in a bottle, with 21% alcohol, reducing sugars of 40 g L^{-1}, total acidity of 5.3 g L^{-1} tartaric acid, and volatile acidity of 0.7 g L^{-1} acetic acid.

Pure aged/*crianza Monastrell* and young *Monastrell* wine samples were used separately to prepare wine mixtures (*Fondillón*-aged wine and *Fondillón*-young wine) to simulate *Fondillón* adulteration. Both "*Fondillón*–aged" and "*Fondillón*–young" mixed samples were prepared with different *Fondillón* replacement percentages of 0, 30, 50, 70, and 100%.

2.3. Sugars and Organic Acids

For the identification and quantification of sugars and organic acids, an HP 1100 series high-performance liquid chromatography (HPLC) machine (Wilmington, DE, USA) was used, as previously described [16], with slight modifications. For the preparation of the samples, 5 mL of the wines was extracted and centrifuged at 15,000 rpm (28.980 g) and 4 °C for 10 min. Subsequently, the supernatant was filtered through 0.45 µm Millipore filters and stored in amber vials, and 10 µL was then injected into the chromatograph using an elution buffer (0.1% phosphoric acid with a flow rate of 0.5 mL min^{-1}). Organic acids were isolated using a column (Supelcogel TM C-610H 30 cm × 7.8 mm) and a pre-column (Supelguard 5 cm × 4.6 mm; Supelco, Bellefonte, PA, USA). Absorbance was measured at 210 nm with a diode array detector (DAD). Sugars were detected for analysis using a refractive index detector (RID), using the same HPLC conditions (elution buffer, flow rate, and column).

Calibration curves of sugars (glucose and fructose) and organic acids (citric, tartaric, lactic, acetic, and malic acid) were developed in accordance with the proper standards, with a concentration range between 1 and 10 g L^{-1}. The analyses were performed in triplicate and the results were expressed as g L^{-1}.

2.4. Antioxidant Activity (AA), Total Polyphenol Index (TPI), and Chromatic Characteristics

2.4.1. Antioxidant Activity (AA)

For the determination of AA, 3 methods were used: (*i*) FRAP to evaluate the ferric reducing/antioxidant power and (*ii*) DPPH$^{\bullet}$ (2,2-diphenyl-1-picrylhydrazyl) and (*iii*) ABTS$^{\bullet+}$ [2,2-azinobis-(3-ethylbenzothiazoline acid-6-sulfonic) to assess the ability to scavenge free radicals. For the evaluation of FRAP, the method described by Iris and Benzie et al. [17], with slight modifications, was followed, wherein absorbance was measured at 593 nm. The method for the determination of DPPH$^{\bullet}$ was that reported by Katalinic et al. [18], wherein

absorbance was recorded at 517 nm. Finally, the $ABTS^{\bullet+}$ was determined following the method proposed by Re et al. [19], employing a measurement of absorbance at 734 nm.

A UVG1002E UV–vis spectrophotometer (Helios, Cambridge, UK) was used. For the preparation of the sample, 5 mL of wine was extracted; additionally, 5 mL of extractant was added [methanol/water (80:20, *v*/*v*) + 1% HCl] and sonicated for 15 min. Then, the mixture was left to stand overnight at 4 °C. The samples were sonicated again for 15 min and centrifuged for 10 min at 10,000 rpm (12.880 g). The supernatant was collected and placed in amber vials. All analyses were performed in triplicate and results were expressed as mmol Trolox L^{-1}.

2.4.2. Total Polyphenol Index (TPI)

The extract used for the analysis of the antioxidant activity was also used for the quantification of the TPI. Absorbance was measured at a wavelength of 280 nm in a UV–visible spectrophotometer (Helios Gamma, UVG 1002E, ThermoSpectronic Helios, Cambridge, UK) [20]. The TPI was determined after carrying out a 100-fold dilution of the sample. Analyzes were performed in triplicate.

2.4.3. Chromatic Characteristics

The chromatic characteristics, namely, (*i*) tonality, (*ii*) color intensity, and (*iii*) color density, of the wine samples were analyzed according to the method described in [21]. For this analysis, a spectrophotometer ThermoSpectronic Helios (Cambridge, UK) was used. The Glories color index percentages [22] of red, yellow, and blue were evaluated by measuring absorbances at 420, 520, and 620 nm, respectively.

2.5. Minerals

The concentrations of macro- and micro-elements were determination using an inductively coupled plasma mass spectrometer (ICP-MS): Shimadzu ICPMS-2030 (Shimadzu Scientific Instruments, Inc., Columbia, MD, USA). For the preparation of the samples, 1 mL of wine was diluted to 10 mL with HNO_3 1% (1:10 dilution); then, this portion was passed through 0.45 µm Millipore filters and stored in 15 mL Falcon tubes.

Calibration curves were created with the mineral standards, where for the macro-elements (Ca, Mg, Na, and K) the concentration ranges between 1 and 20 mg L^{-1}, while for the micro-elements (Fe, Cu, Mn, and Zn) the concentration ranges between 0.01 and 0.2 mg L^{-1}. The analyses were performed in triplicate and the results were expressed as mg L^{-1}.

2.6. Volatile Compounds

The volatile profile was determined according to Issa-Issa et al. [23]. The identification and semi-quantification of volatile compounds was carried out using a Shimadzu GC2030 gas chromatograph and a TQ8040 NX triple quadrupole mass spectrometer as detector, as well as GC–MS (Shimadzu Scientific Instruments, Inc., Columbia, MD, USA) with an AOC-6000Plus. For the preparation of the samples, 10 mL of wine was extracted and placed in a 20 mL vial with 10 µL of benzyl acetate used as internal standard (100 mg L^{-1}); finally, 1.5 g of NaCl was added. Volatile compounds were extracted using the HS-SPME technique and a DVB/CAR/PDMS fiber (Supelco, Bellefonte, PA, USA). The sample was then placed in an autosampler at 500 rpm and 40 °C for 20 min. The GC program temperature scheme was as follows: holding at 40 °C for 2 min, followed by a +3 °C min^{-1} increase to 250 °C. The helium pressure was 50.4 kPa, and the flow control mode was linear velocity (at 36.3 cm s^{-1}). The injection temperature was 260 °C, the ion source temperature was 200 °C, and the interface temperature was 250 °C. Helium was used as carrier gas, with a total flow rate of 1.01 mL min^{-1}. Most of the volatile compounds were identified by 3 different methods: (*i*) retention indices of the analyzed compounds, calculated using the C7 to C16 *n*-alkane mix (Sigma-Aldrich, Steinheim, Germany); (*ii*) retention indices of standards; and (*iii*) comparison of the mass spectra obtained with those of the standards and those of the

NIST 14 and Wiley 229 spectrum libraries. All analyses were performed in triplicate and the results were expressed as mg L^{-1}.

2.7. Statistical Analysis

The processing of the results was initially carried out with one-way analysis of variance (ANOVA) followed by Tukey's multiple range test. Differences were considered statistically significant at $p < 0.05$. The software used to perform the statistical analyses was XLSTAT Premium 2016 (Addinsoft, New York, NY, USA).

Subsequently, data analysis of GC–MS measurements was performed using principal component analysis (PCA) with Stand-alone Chemometrics Software (Version Solo 9.1. for Windows, Eigenvector Research Inc., Wenatchee, WA, USA). The data obtained from GS-MS measurements of pure (*Fondillón* ($n = 3$), aged ($n = 3$), and young ($n = 3$)) wines and *Fondillón* samples adulterated with aged ($n = 9$) or young ($n = 9$) *Monastrell* wines at different ratios (30%, 50%, and 70%, *v*/*v*) were used to develop a PCA model. Autoscale pre-processing step was applied to the data while developing the model. Three separate PCA models were constructed. The first PCA model consisted of the three pure wine sample groups (*Fondillón*, aged and young *Monastrell* wines). The second PCA model was created using pure *Fondillón*, aged sample groups, and adulterated *Fondillón* sample groups by addition of aged wine at different ratios 30% ($n = 3$), 50% ($n = 3$), and 70% ($n = 3$). Finally, the last PCA model also incorporated the pure *Fondillón*, young sample groups, and adulterated *Fondillón* sample groups doctored by the addition of young wine at different ratios (30% ($n = 3$), 50% ($n = 3$), and 70% ($n = 3$)). The number of principal components (PCs) for the PCA models was selected by leave-one-out cross validation, where all calibration samples were validated by one. The success of the models was evaluated based on root mean squared error calibration (RMSEC), root mean squared error cross-validation (RMSECV) values, percent per variance, and percent cumulative variance of the PC.

3. Results and Discussion

3.1. Sugars and Organic Acids

It is important to remember that the organic acids in wine limit oxidation and, together with ethanol, are responsible for the physicochemical and microbial stability of wine. They also influence its flavor and improve its color, rendering it more stable. The organic acids contained in wine are produced by the oxidation of sugars (e.g., citric, tartaric, and malic acid) or by alcoholic fermentation (e.g., lactic, acetic, and succinic acid) [24]. *Fondillón* contained the lowest concentrations of all organic acids, except acetic acid. All three samples had a similar amount of lactic acid, which is logical as this compound is produced during the lactic fermentation of the *Monastrell* must and remains constant during aging. The decrease in the concentrations of *Fondillón* citric, tartaric, and malic acid reached values of 66.4, 51.1, and 72.2%, respectively, compared to the young wine (Table 1). A similar trend was recently reported by Valcárcel-Muñoz et al. [25], who studied the characterization of Fino and Amontillado Sherries during aging in the criaderas and solera system. These authors reported that the concentration of malic acid (originating from the grapes) decreased significantly because it was consumed by flor yeasts and lactic bacteria; citric acid (which is a component of yeast metabolism during the formation of the flor yeast veil) also showed a decreasing trend during the aging of the oxidative *Monastrell* wines. Tartaric acid, which originated from the (*i*) grapes and (*ii*) was supplemented during the vinification process because *Monastrell* grapes grown under the dried conditions of the Mediterranean vineyards require tartaric acid to be added during the operation of the grape-crushing unit and before the start of fermentation because their pH would otherwise be too high, was precipitated as calcium tartrate and potassium bitartrate during the aging of the wine; thus, the *Fondillón* samples had the lowest concentrations of the studied *Monastrell* wines.

Table 1. Concentration (g L^{-1}) of organic acids and sugars identified in *Monastrell* young, aged and *Fondillón* wines.

Wine Type	Organic Acids					Sugars	
	Citric	Tartaric	Malic	Lactic	Acetic	Glucose	Fructose
	(g L^{-1})						
	ANOVA						
	***	***	***	*	***	***	***
	Tukey Multiple Range Test ‡						
Young	2.50 b	5.15 b	6.95 b	4.73 ab	0.87 b	5.82 b	4.10 b
Aged	3.72 a	6.95 a	9.78 a	5.44 a	0.63 c	6.89 b	3.88 b
Fondillón	0.84 c	2.52 c	1.93 c	4.42 b	1.27 a	7.12 a	6.01 a

* and *** indicate significance at $p < 0.05$ and 0.001, respectively. ‡ Values (mean of three replications) followed by the same letter within the same column are not significantly different ($p > 0.05$) according to Tukey's least significant difference test.

Regarding acetic acid, the opposite trend occurred, with its content increasing after the long aging of *Fondillón*, reaching a value of 1.27 g L^{-1}. This concentration is below the detection threshold for this volatile compound of 3.185 g L^{-1} reported in ice wine, which is also a naturally sweet wine; however, it is above the detection threshold reported for table wine 0.7 g L^{-1} [26]. Acetic acid is formed by the oxidation of ethanol via acetaldehyde and acetyl groups that are present in wood xylans. As reported by Caldeira et al. [27], the same trend occurred in his study on the kinetics of odorant compounds in a wine brandy aged in two aging systems (in barrels and in steel tanks with staves inside); the acetic acid presented a significant increase over time in the studied aging systems. It is important to highlight that the presence of low concentrations of acetic acid is not considered an off-flavor but rather a characteristic attribute of this type of aged-wines [27].

Regarding sugars, these compounds are responsible for the formation of ethanol and other secondary products. The main sugars used by yeasts during alcoholic fermentation are glucose and fructose, which are used to determine the optimal maturity of the grape [28,29]; however, in the current study, the highest sugar concentrations were found in *Fondillón* (Table 1). The increase in sugars may be influenced by the hydrolysis of wood hemicellulose during oxidative aging [30]. In the study carried out by Valcárcel-Muñoz et al. [25], the sugar concentration increased over time due to the transfer of certain compounds such as pentoses, hexoses, and hemicellulose polysaccharides from the wooden barrels to the wine.

3.2. Antioxidant Activity (AA), Total Polyphenol Index (TPI), and Chromatic Characteristics

Previous studies showed a non-consistent behavior of the antioxidant potential of wine as affected by the aging time. Authors such as Echeverry et al. [31] reported that the aging of wine increased its antioxidant potential; however, other authors, e.g., Roginsky et al. [32], found that young wines presented higher values of $ABTS^{\bullet+}$. In the current study, the experimental results showed a global trend, with the antioxidant activity, measured by three methods ($ABTS^{\bullet+}$, FRAP, and $DPPH^{\bullet}$), increasing at the beginning of the aging period but significantly decreasing after the minimum of 10 years of aging required for the preparation of *Fondillón* (Table 2). These results agree quite well with those published by Rivero-Pérez et al. [33], who studied the total antioxidant capacity ($ABTS^{\bullet+}$, $DPPH^{\bullet}$, DMPD, ORAC, and FRAP), the scavenging activity, and biomarkers of oxidative stress of wines and concluded that young wines presented higher values of $ABTS^{\bullet+}$ and $DPPH^{\bullet}$; this behavior occurs in these two specific methods of measuring AA because they have the same antioxidant mechanism, which is a single electron transfer mechanism. In general, during the wine-aging process, the concentrations of phenolic compounds normally show a slow decrease due to adsorption, precipitation, and/or reduction in the degree of polymerization and astringency [34]. The experimental results demonstrate that the *Fondillón* samples had

the lowest content of TPC (Table 2); this trend agreed with that previously reported by Chira et al. [35].

Table 2. Antioxidant activity, total phenolic index, and chromatic characteristics identified in *Monastrell* young, aged and *Fondillón* wines.

Wine Type	ABTS•+	FRAP	DPPH•	Total Phenolic Index	Color Intensity	Tonality	Color Density	Y ¶	R ¶	B ¶
	(mmol Trolox L^{-1})			(mg AG/100 mL Wine)				(%)		
	ANOVA									
	***	***	***	***	***	***	***	***	**	**
	Tukey Multiple Range Test ‡									
Young	2.30 a	7.42 b	2.18 b	285 a	9.13 a	0.60 b	7.88 a	32.4 b	53.9 a	13.7 a
Aged	2.35 a	13.9 a	2.43 a	289 a	8.70 a	0.60 b	7.48 a	32.4 b	53.5 a	14.1 a
Fondillón	1.28 b	3.52 c	1.49 c	221 b	3.92 b	1.87 a	3.62 b	60.1 a	32.2 b	7.73 b

** and *** indicate significance at $p < 0.01$ and 0.001, respectively. ‡ Values (mean of three replications) followed by the same letter within the same row are not significantly different ($p > 0.05$) according to Tukey's least significant difference test. ¶ Y mean yellow color, R mean red color, and B mean blue color.

Regarding tonality (Table 2), the *Fondillón* samples were characterized by the highest value of the yellow component and the lowest ones of the red and blue components. During aging, there is an increase in the *Y* component and a decrease in the *R* component, which leads to an increase in the wine's tonality, rendering it more brownish.

These results agreed with those reported by Del Fresno et al. [36] in their study on the changes in the phenolic fraction of red wines aged in oak barrels, where they indicated that all the wines studied, after several days of aging, exhibited an increase in absorbance at 420 nm and a decrease in absorbance at 520 nm that corresponded to the *Y* and *R* components, respectively, leading to an increase in tonality.

3.3. Minerals

There are three main sources of metals in wines [37]:

1. Natural source: This is related to the grape variety, its maturity at harvest, and the type of soil and weather conditions during the growth process.
2. Anthropogenic source: This refers to the (external) impurities of the environment that the wine acquires while the grape is growing or during the different winemaking processes (e.g., bottling, aging, etc.).
3. Oenological source: This refers to the different steps of wine production.

The concentrations of some elements can play a very important role in the vinification process; an example is Zn, which, at low concentrations, is important for the proper development of alcoholic fermentation, while other elements such as Fe, Mn, and Cu at higher concentrations can influence the organoleptic profile of the wine [38]. Very high Fe content can cause stabilization problems, causing wine to suffer from oxidation.

In Table 3, Na, Cu, Mn, and Zn from *Fondillón* presented higher concentrations compared to the young and aged *Monastrell* wines. Cu and Mn are involved in changes in the stability of aged wines. During wine storage and maturation, these elements form stable complexes with polyphenols, meloids, and amino acids, leading to the characteristic color, flavor, and final aroma of aged wines [39].

Table 3. Concentration (mg L^{-1}) of micro- and macro-elements quantified in *Monastrell* young, aged and *Fondillón* wines.

Wine Type	Ca	Mg	Na	K	Fe	Cu	Mn	Zn
	(mg L^{-1})				(µg L^{-1})			
	ANOVA							
	**	***	***	**	***	**	***	***
	Tukey Multiple Range Test ‡							
Young	8.88 a	14.2 c	2.87 c	148 a	30 c	Traces b	60 c	10 c
Aged	8.36 b	16.1 a	3.79 b	125 b	170 a	Traces b	60 b	20 b
Fondillón	7.93 c	15.3 b	4.94 a	144 a	140 b	10 a	110 a	40 a

** and *** indicate significance at $p < 0.01$ and 0.001, respectively. ‡ Values (mean of three replications) followed by the same letter within the same column are not significantly different ($p > 0.05$) according to Tukey's least significant difference test.

All the *Monastrell* wines under analysis contained relatively high concentrations of K and Mg, which are elements related to the grape's maturity and, consequently, its sweetness [40]. The Ca concentrations were low compared to those reported in international wines, including Spanish ones, for which Ca ranged from 12 to 241 mg L^{-1} [39]. A similar phenomenon was found for K, which ranged from 338 to 2032 mg L^{-1} in Spanish wines [39].

3.4. Volatile Compounds

Wine is made up of many volatile compounds; some of them come from the grape, some from the yeast and the alcoholic fermentation, and others from the aging of the wine [41]. In fact, during the aging period, some compounds from the oak barrels can be transferred into the wine while others are produced by the reaction of the aroma-precursors, leading to a complex final aromatic profile [42].

To detect a possible *Fondillón* fraud, it is very important to establish possible aging markers that are not present in other younger *Monastrell* wines; these compounds can be considered as indicators and can be used to guarantee and ensure the authenticity of this Alicante wine [43].

A total of 93 volatile compounds of the wines under study (young and aged *Monastrell* wines and *Fondillón*) were identified and quantified (Table S1), with 18 compounds playing a key role in identifying possible adulterations of *Fondillón* (Table 4).

Some of the volatile compounds identified in *Fondillón*, such as furfural (0.60 mg L^{-1}), guaiacol (0.01 mg L^{-1}), and eugenol (0.01 mg L^{-1}), were previously reported by Perestrelo et al. [44] as wood markers. The intensity of the release of these volatile compounds can be controlled by several factors, including the type of barrel, the toasting of the barrel, the time the wine remained in contact with the barrel, etc. As reported by Perestrelo et al. [43], the concentration of furfural shows a tendency to increase during the aging process and is considered a good age marker. This compound can be formed by (*i*) the dehydration of sugars due to the Maillard reaction, (*ii*) the pyrolysis of carbohydrates, and (*iii*) caramelization.

Another key volatile compound was benzaldehyde, which was present in *Fondillón* in a relatively high concentration (0.28 mg L^{-1}) compared to the trace concentrations found in the young and aged/crianza *Monastrell* wines. This trend agreed with the one reported by Castro-Vázquez et al. [45], who reported low benzaldehyde concentrations in young "Tempranillo" wines. In general, benzaldehyde can be considered as a typical aroma of the volatile profile of aged red wines.

Table 4. Concentrations (mg L^{-1}) of the key volatile compounds in *Monastrell* (young and aged) and *Fondillón* wines.

Code	Volatile Compounds	Young	Aged	*Fondillón*
		(mg L^{-1})		
V1	1,1-diethoxyethane	nd	nd	0.13
V6	Furfural	nd	0.09	0.60
V13	1,1-diethoxy-2-methylpropane	nd	nd	0.02
V14	Benzaldehyde	nd	0.01	0.28
V15	1-(1-ethoxyethoxy)-pentane	nd	nd	0.03
V28	Isoamyl butyrate	nd	nd	0.04
V30	Guaiacol	nd	nd	0.01
V31	Ethyl sorbate	nd	nd	0.13
V33	Nonanal	nd	nd	0.11
V39	Diethyl butanedioate	1.86	1.90	2.80
V53	4-Ethylguaiacol	nd	nd	0.02
V55	Vitispirane	0.12	0.22	0.37
V57	trans-Whiskey lactone	0.02	0.05	0.06
V60	cis-Whiskey lactone	0.11	0.09	0.17
V64	Eugenol	nd	0.01	0.01
V65	TDN	0.00	0.04	0.35

nd: not detected.

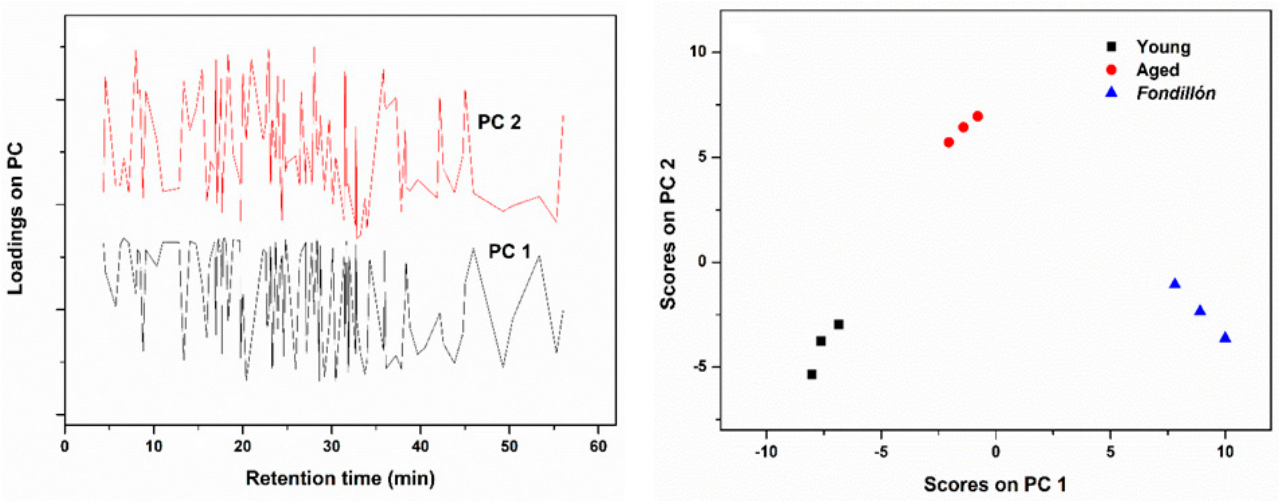
In general, the concentrations of norisoprenoids, such as vitispirane and TDN, increase during the aging of wine (Table 4) and have previously been identified as the odor-active compounds of *Fondillón* [46]. The concentration of TDN in wine can be influenced by four main factors: (*i*) the exposure of the grapes to the sun, (*ii*) the pH, (*iii*) the storage temperature, and (*iv*) the wine's age [47]. This same trend was reported by Marais et al. [48], who concluded that TDN is a key compound because it is responsible for the kerosene-like flavor that develops during the aging process of Weisser Riesling wines. The same trend was reported for vitispirane by Khairallah et al. [49]. Both compounds (vitispirane and TDN) are generated from the decomposition of carotenoid precursors and are released through acid hydrolysis or enzymatic reactions.

Although not in very high concentrations, other compounds, such as 1,1-diethoxyethane; 1,1-diethoxy-2-methyl-propane; and 1-(1-ethoxyethoxy)-pentane, are only present in *Fondillón*. These compounds are formed during fermentation and the concentrations increase during aging, possibly as a result of oxidation, as reported by Versari et al. [44].

3.5. Principal Component Analysis (PCA)

The classification of pure wines and adulterated sample groups was performed using the measurements obtained by the GC–MS chromatogram. The GC–MS chromatograms of the pure wine samples (*Fondillón* + aged/crianza + young) and adulterated *Fondillón* sample groups via the addition of aged *Monastrell* and young *Monastrell* wines are shown in Figure S1a–c. As can be seen in Figure S1a, the chromatograms of pure wines are quite different from each other due to the change in the concentration of volatile compounds. The difference in the chromatogram between *Fondillón* and other wines is most evident for the furfural, benzaldehyde, ethyl hexanoate, phenyl ethyl alcohol, diethyl butanediate, vitispirane, TDN, and ethyl decanoate components. Chromatographic data analyses of the GC–MS measurements of the pure and adulterated sample (*Fondillón* + young *Monastrell* wine and *Fondillón* + aged/crianza *Monastrell* wine) groups were performed separately via PCA. To classify the three pure wine sample groups (young, aged, and *Fondillón*), a PCA model was created using the first two PCs, which explained 50.45% (PC1) and 23.56% (PC2) of the per cumulative data variance. The PCA loading and score plot of the three wine samples are presented in Figure 1a,b. The PCA plot results showed that a good classification was achieved for all the wine sample groups. The explained per variance, cumulative variance, and error values (RMSEC and RMSECV) of the PCA models are given

in Table 5; as can be seen in this table, low error values for RMSEC (0.48) and RMSECV (3.64) were obtained from this PCA model.



(**a**) (**b**)

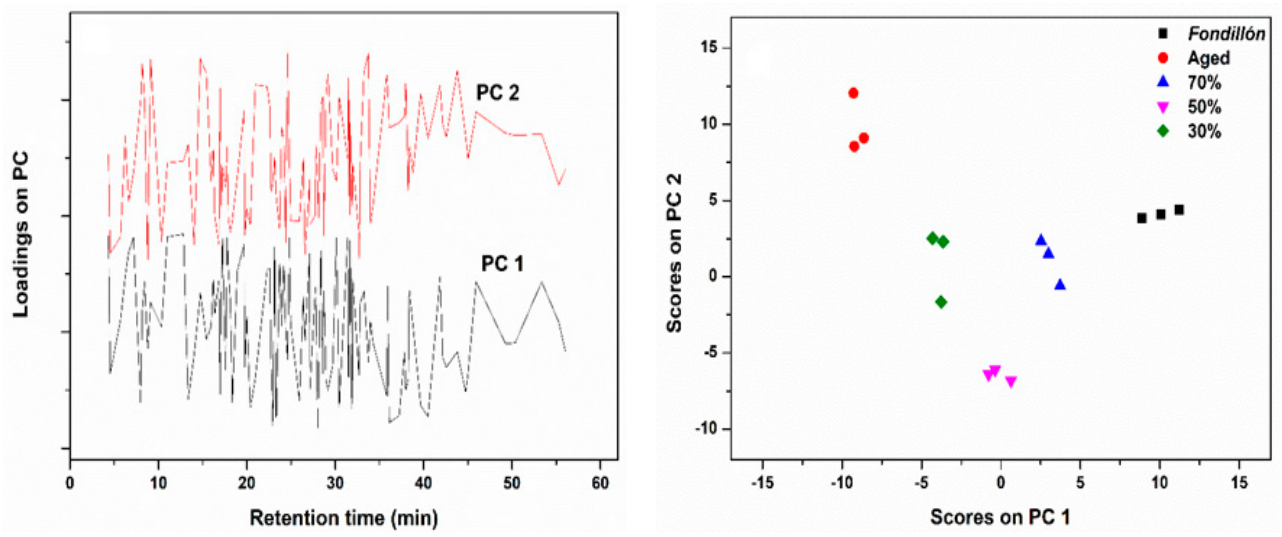
Figure 1. Principal component analysis (PCA) loading (**a**) and score plot (**b**) of GC–MS measurements of pure *Monastrell Fondillón*, aged, and young wines.

Table 5. The per cumulative variance of the principal components (PCs), root mean square error calibration (RMSEC), and root mean square error cross-validation (RMSECV) values of the principal component analysis (PCA) models formed using the *Monastrell* (young and aged) and *Fondillón* wines.

Wine Type	PCs	Variance (%)		RMSEC	RMSECV
		This PC	Cumulative		
Young/Aged—*Fondillón*	1	50.45	50.45	0.48	3.64
	2	23.60	74.01		
Fondillón—Aged	1	33.12	33.12	0.62	2.16
	2	26.78	59.90		
Fondillón—Young	1	40.29	40.29	0.65	1.84
	2	16.10	56.39		

The second PCA model was developed for the adulterated *Fondillón* sample groups prepared by the addition of *Monastrell* aged/crianza wine. Using the first two PCs, the model was constructed for the separation of five sample groups (pure *Fondillón*, 70% *Fondillón*, 50% *Fondillón*, 30% *Fondillón*, and pure aged/crianza *Monastrell* wine). The PCA loading and score plot of the pure and adulterated sample groups is presented in Figure 2a,b.

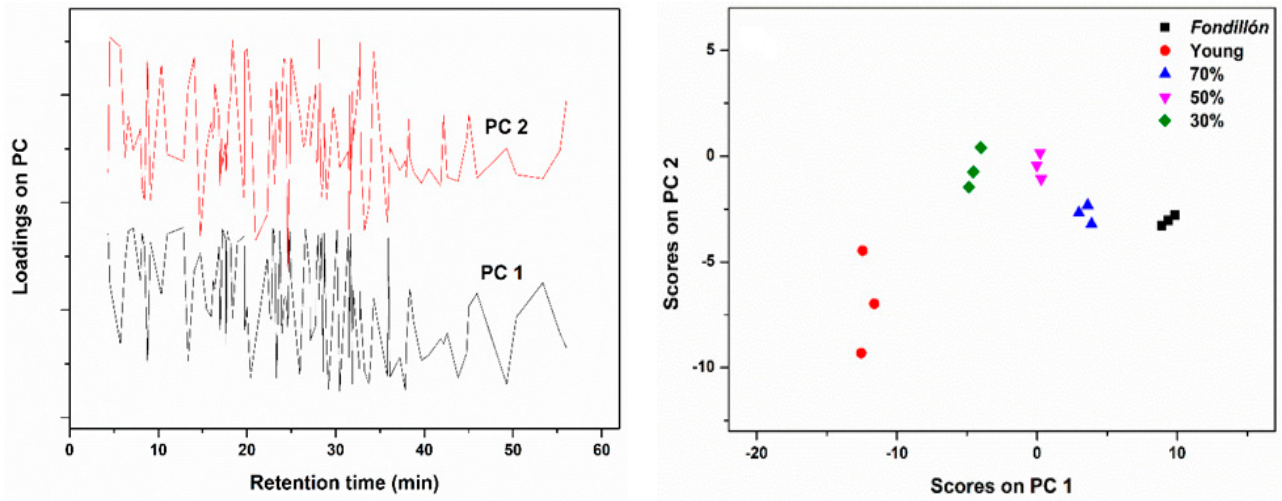
The explained per PC variance, total variance, RMSEC and RMSECV values of the PCA model are listed in Table 5. The explained per PC variance values for PCs 1 and 2 were 33.12 and 26.78, respectively, and low error values (0.62 and 2.16) were also obtained for RMSEC and RMSECV, respectively. As can be seen from the figure, the classification of the each of the sample groups (pure and adulterated) has been achieved. The loading plots (Figure 2a) of PC1 and PC2 show that the main differences among the chromatograms were found in the region of the retention times between 5–10 min (furfural and isoamyl acetate), 10–20 min (benzaldehyde, ethyl hexanoate, and limonene) and 20–30 min (phenyl ethyl alcohol, diethyl butanedioate, and vitispirane), and 30–40 min (TDN, ethyl decanoate, and isoamyl octanoate).



(**a**) (**b**)

Figure 2. Principal component analysis (PCA) loading (**a**) and score plot (**b**) of GC–MS measurements of adulterated *Fondillón* samples via the addition of *Monastrell* aged wine.

Finally, another PCA model with the first two PCs was created for the classification of the adulterated *Fondillón* sample groups by the addition of pure, young *Monastrell* wine (pure 100% *Fondillón*, 70% *Fondillón*, 50% *Fondillón*, 30% *Fondillón*, and pure young wine). Figure 3a,b demonstrate the PCA loadings and score plots of the all the pure and adulterated sample groups. As can be seen in Table 5, low RMSEC (0.65) and RMSECV (1.84) values were obtained. The explained per PC variance values for PC1 and PC2 were determined to be 40.16 and 16.10, respectively. The main chromatographic contributions observed in the loadings of PC1 and PC2 (Figure 3a) were in the regions of the retention times between 4–10 min (isoamyl alcohol, furfural, and 1-Hexanol), 10–20 min (benzaldehyde, ethyl hexanoate, and limonene), 20–30 min (diethyl butanedioate, vitispirane, and ethyl nonanoate), 30–40 min (TDN and ethyl dodecanoate), and 40–50 min (ethyl tetradecanoate).



(**a**) (**b**)

Figure 3. Principal component analysis (PCA) loadings (**a**) and score plot (**b**) of GC–MS measurements of *Fondillón* samples adulterated by the addition of *Monastrell* young wine.

As a result, firstly, based on the difference in the concentration of volatile components, the pure *Fondillón* wine was successfully differentiated from the other pure wine (aged and young) samples. Then, adulterated *Fondillón* sample groups could be distinguished from each other in the different regions of the PCA score plot. This study demonstrated that measurements of volatile compounds can be used to determine the adulteration of *Fondillón* by the addition of cheaper types of wine. To the best of our knowledge, regarding wine studies, *Fondillón* adulteration and volatile compound analysis of *Fondillón* have not been carried out using the method applied herein.

4. Conclusions

To summarize the results and identify the main markers of potential *Fondillón* adulteration using *Monastrell* wines, it can be stated that *Fondillón* is characterized by:

- ✓ Relatively high concentrations of Cu (~10 μg L^{-1}), Mn (~110 μg L^{-1}), Zn (~40 μg L^{-1}), and Na (~4.5 g L^{-1});
- ✓ Relatively high concentrations of fructose (~6.0 g L^{-1}) and acetic acid (>1.0 g L^{-1});
- ✓ Relatively high concentrations of the following volatile compounds: 1,1-diethoxyethane (~10 mg L^{-1}), furfural (~0.6 mg L^{-1}), benzaldehyde (~0.3 mg L^{-1}), vitispirane (~0.3 mg L^{-1}), and TDN (~0.3 mg L^{-1});
- ✓ Relatively low concentrations of the following volatile compounds: ethyl octanoate (≤2.5 mg L^{-1}) and ethyl decanoate (≤2.0 mg L^{-1}).

Thus, if a sample marketed under the name *Fondillón* does not fulfill all the above-listed criteria it is likely an adulterated sample and deserves further study by a trained sensory panel to finally certify its authenticity or adulteration. One drawback of this study is that it was conducted using wine samples from only one winery, but these preliminary statements will be further studied in *Fondillón* samples from as many Alicante wineries as possible (n = 5–8) to build a robust mathematical model that clearly classifies whether a sample being commercialized as *Fondillón* is a real *Fondillón* or a fake *Fondillón*.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/beverages9010028/s1, Table S1: Concentrations (mg L^{-1}) of volatile compounds in *Monastrell* (young and aged) and *Fondillón* wines; Figure S1: Plot of GC–MS chromatogram of (a) pure *Monastrell Fondillón*, aged and young wines, and adulterated *Fondillón* by the addition of (b) aged *Monastrell* wine and (c) young *Monastrell* wine. Supplementary references [50–53].

Author Contributions: H.I.-I.: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Original draft, and Visualization. R.S.U.: Data curation, Writing—review and editing. D.L.-L.: Conceptualization, Validation, Writing—review and editing, Funding acquisition, Supervision. F.H.: Resources, Methodology. Á.A.C.-B.: Conceptualization, Methodology, Validation, Writing—review and editing, Visualization, Funding acquisition, Supervision. All authors have read and agreed to the published version of the manuscript.

Funding: The authors thank Generalitat Valenciana (Conselleria de Innovación, Universidades, Ciencia y Sociedad Digit) for funding the research group "Food Quality and Safety, CSA" through the project REF. AICO/2021/326.

Data Availability Statement: Data will be made available on request.

Acknowledgments: The authors also thank Bodegas BOCOPA for sharing all the wines used in this study and all the information related to their production and traceability. Reyhan Selin Uysal thanks The Scientific and Technological Research Council of Turkey (TUBITAK) (TUBITAK-BIDEB 2219, International Postdoctoral Research Fellowship Program) for providing their postdoctoral fellowship.

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

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