beverages

MDPI

Article

Organic Acids in Varietal Red Wines: Influence of Grape Cultivar, Geographical Origin, and Aging

Jesús Heras-Roger [1,2,*], Carlos Díaz-Romero [1], Javier Darias-Rosales [3] and Jacinto Darias-Martín [1]

[1] Facultad de Farmacia, Campus de Anchieta, Departamento de Ingeniería Química y Tecnología Farmacéutica, Universidad de La Laguna (ULL), 38201 La Laguna, Spain; cdiaz@ull.edu.es (C.D.-R.); jdarias@ull.edu.es (J.D.-M.)
[2] Cátedra de Agroturismo y Enoturismo de Canarias, Instituto Canario de Calidad Agroalimentaria (ICCA-ULL), 38201 La Laguna, Spain
[3] Facultad de Farmacia, Campus de Anchieta, Departamento de Obstetricia y Ginecología, Pediatría y Medicina Preventiva y Salud Pública, Universidad de La Laguna (ULL), 38071 La Laguna, Spain; alu0100881288@ull.edu.es
* Correspondence: jherasro@ull.edu.es

Abstract

Wine organic acids influence their overall quality. This study examines the variability of major acids (tartaric, malic, lactic, citric, acetic, and gluconic) and minor phenolic acids (gallic, protocatechuic, syringic, caftaric, caffeic, cutaric, coumaric, and 2-S-glutathionylcaftaric) in varietal red wines produced from predominantly autochthonous grape cultivars of the Canary Islands. Two hundred and five monovarietal red wine samples were analyzed to assess how the organic acid profiles differed depending on the grape cultivars employed in their production, island of provenance, denomination of origin, and aging, supporting relationships between both genetic and environmental factors. High-performance liquid chromatography and enzymatic methods were used for determining minor and major organic acids, respectively. Many significant differences between grape cultivars, geographical origin, and aging were observed, reflecting the complexity of the composition of the organic acids in red wine and its relationship with viticultural factors. Linear discriminant analysis achieved classification accuracies up to 88.3% by cultivar and 83.4% by island. Correlation and multivariate analyses helped identify compositional patterns and key discriminant acids. This study advances the comprehension of major and minor acid composition and equilibria in red wines and may support future research on quality parameters and regional typicity.

Keywords: major and minor acids; red wine; grape cultivar; aging geographical origin; Canary Islands; multivariate analysis; authenticity

check for updates

Academic Editor: António Manuel Jordão

Received: 30 April 2025
Revised: 13 June 2025
Accepted: 26 June 2025
Published: 2 July 2025

Citation: Heras-Roger, J.; Díaz-Romero, C.; Darias-Rosales, J.; Darias-Martín, J. Organic Acids in Varietal Red Wines: Influence of Grape Cultivar, Geographical Origin, and Aging. *Beverages* **2025**, *11*, 102. https://doi.org/10.3390/beverages11040102

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Organic acids are among the most relevant components of red wine, which contribute to their sensorial characteristics and stability. These acid concentrations highly influence important sensory characters, like the perception of acidity and the color expression of wine pigments, but at the same time they are also fundamental for microbial stability and intervene in the chemical transformations occurring during wine aging [1]. The organic acids found in red wine are commonly divided into two groups according to the abundance: (1) Major organic acids, which can come directly from grapes, such as tartaric, malic, and citric acids, or they can be produced in microbiological transformations, such as

lactic, acetic, and gluconic acids. (2) Minor organic acids can be divided into two groups, hydroxycinnamic acids (caftaric, caffeic, cutaric, coumaric, and 2-S-glutathionylcaftaric acids) and hydroxybenzoic acids (gallic, protocatechuic, and syringic acids). These minor organic acids mostly come from biosynthesis in the plant, but their concentrations change during the wine aging—they protect against oxidation and improve sensory evolution. Understanding the function and behavior of these acids allows to optimize the wine quality and its longevity [2].

Tartaric acid represents the principal organic acid naturally occurring in grapes and is, therefore, the major contributor to the organic acid composition of the resulting wine. It imparts a sharp, tangy flavor and it is essential for maintaining a low pH in the wines, which contributes to microbial stability and enhances color retention by preserving anthocyanins [1]. Tartaric acid is highly stable under typical winemaking conditions and is not significantly metabolized by the dominant microbial populations involved in fermentation. However, under specific spoilage scenarios—such as uncontrolled malolactic fermentation—certain lactic acid bacteria may degrade tartaric acid, leading to "wine illness" and compromising stability and flavor quality [3,4]. Although some *Acetobacter* have also been shown to metabolize tartaric acid under laboratory conditions [5], this is not considered a common phenomenon during standard vinification. Malic acid is involved in the perceived wine acidity and sensorial balance, contributing a tart, green-apple-like freshness to young wines. Citric acid has the lowest concentrations of these major organic acids, and in addition has less concentration than those organic acids formed during fermentation, such as lactic and acetic. Although present in small amounts, citric acid contributes to the wine's acidity profile and aromatic complexity [1].

In the winery, tartaric acid tends to remain relatively stable unless intentionally modified through winemaking interventions, such as acid addition, cold stabilization, or precipitation. By contrast, malic acid in red wines normally undergoes significant transformation, primarily due to malolactic fermentation (MLF), a microbiological process, most notably *Oenococcus oeni*, decarboxylate malic acid into lactic acid and carbon dioxide. This conversion reduces the wine's perceived acidity, enhances microbial stability, and contributes to a rounder, softer mouthfeel [6]. Although tartaric acid is not the main target of MLF, slight reductions in its concentration have been noted during fermentation due to the increase in pH and subsequent precipitation of potassium tartrates [7]. The choice of lactic acid bacteria strain used for MLF shapes the wine's final acid profile. Different strains of *O. oeni* or alternative species, such as *Lactobacillus plantarum*, exhibit distinct malic acid degradation rates and metabolite profiles, which significantly influence the sensorial characteristics [8]. The lactic acid resulting from MLF reduces wine sharpness and contributes to deacidification, resulting in a smoother and rounder mouthfeel.

Acetic acid is the major component of volatile acidity in wine and is produced as a byproduct of yeast metabolism during alcoholic fermentation. It also arises from the activity of spoilage microorganisms belonging to the *Acetobacter* and *Lactobacillus* sensu lato genera during or after fermentation. Gluconic acid is a non-volatile organic acid that is not naturally present in healthy grapes but forms during grape deterioration, through the metabolic activity of filamentous fungi, such as *Botrytis cinerea*, and species of *Aspergillus* and *Penicillium* genera, which oxidize glucose to gluconic acid during grape ripening or spoilage [9].

In terms of minor organic acids, hydroxycinnamic acids (HCAs) and hydroxybenzoic acids (HBAs) are the most prominent phenolic acids, both originating from grape biosynthesis and undergoing transformations during winemaking. HCAs in wines are typically present in two forms: as free acids, such as caffeic, p-coumaric, and ferulic acids, or as tartaric acid esters, notably caftaric, cutaric, and fertaric acids. One derivative of these acids

is 2-S-glutathionylcaftaric acid, which is a product of oxidative reactions between caftaric acid and glutathione. This compound acts as a protective antioxidant, helping to preserve phenolic stability and reduce oxidative browning in wines [10]. HBAs include gallic, syringic, vanillic, and protocatechuic acids, which are generally found in lower concentrations compared to HCAs. HCAs contribute to wine color stability through co-pigmentation [11] and are precursors to volatile phenols, like 4-ethylphenol or 4-vinylphenol, which can positively or negatively impact wine aroma depending on concentration and microbial activity, especially by species of Brettanomyces genus and lactic acid bacteria [12]. Meanwhile, HBAs interact with salivary proteins and may modulate astringency perception through their binding affinity, contributing to mouthfeel sensations in wine [13]. Viticultural practices, such as leaf removal, can influence the concentration of phenolic acids, providing winemakers with tools to shape wine composition and style, while also expressing the distinctive characteristics of the vineyard [14].

Minor phenolic acids, especially HBAs and HCAs, are increasingly recognized as varietal and regional markers due to their biosynthetic regulation and sensitivity to environmental conditions. Their concentrations are genotype-dependent, shaped by the grape's phenylpropanoid metabolism, and are further modulated by terroir-specific factors, such as temperature, altitude, and soil composition [15,16]. As a consequence of the multitude of factors influencing acid composition in red wines, previous studies have demonstrated the potential of profiling organic acids for classifying wines by both grape cultivar and geographical origin. For example, chemometric models based on organic acid profiles have successfully distinguished wines from various international regions, often achieving classification accuracies exceeding 90% [17,18]. While major acids reflect general fermentation and ripening dynamics, minor phenolic acids have shown stronger varietal and regional associations due to their genetic and environmental dependence, making them particularly valuable for origin determination. Nevertheless, prior studies typically involve comparisons across regions separated by thousands of kilometers, which permit a relatively easier differentiation.

In contrast, our study centers on the Canary Islands, an Atlantic archipelago belonging to Spain, located off the northwest coast of Africa. This region presents vineyards at different altitudes, with heterogeneous microclimates, and the continued use of ungrafted traditional vines. While previous studies have examined the mineral composition of Canary wines as a potential marker of origin due to soil influences [19,20], the role of organic acids remains underexplored. Although some studies have quantified the main organic acids [21–23] and a few have investigated phenolic acids in detail [24,25], none have systematically evaluated their potential as markers of geographical origin across the region's broad spectrum of grape cultivars and denominations of origin (DO).

Therefore, this study addresses this gap by providing a detailed characterization of organic acid profiles in an extensive set of single-varietal red wines from the Canary Islands. These organic acids were quantified through chromatographic and enzymatic methods, and factors such as grape cultivar, island of origin, and DO with specific terroir characteristics were considered. Red wines come from various islands and multiple cultivars and vintages to ensure a representative and diverse dataset. Our approach integrates multivariate statistical techniques—including correlation analysis, principal component and factor analysis (PCA and FA), and linear discriminant analysis (LDA)—to identify patterns linking organic acid concentrations with grape cultivar, geographic origin, and aging practices.

This is one of the first comprehensive studies to combine the analysis of both major and phenolic acids for classification purposes in wines made from native grape varieties of the Canary Islands. The findings aim to enhance our understanding of how organic acids

reflect regional wine characteristics and to assess their potential as reliable markers for authentication, wine traceability, and regional identity.

2. Materials and Methods

2.1. Samples

A representative selection of bottled monovarietal red wines was obtained from all DO across the Canary Islands, including a variety of grape cultivars and vintages. The distribution of samples was aligned with the relative scale of red wine production in each region. Tenerife emerged as the major contributor, represented by several DOs, including Abona (DO A), Tacoronte-Acentejo (DO T), Valle de la Orotava (DO O), Ycoden-Daute-Isora (DO Y), and Valle de Güímar (DO G). Moderate contributions came from the islands of La Palma (LP), El Hierro (HI), and Gran Canaria (GC), while Lanzarote (LZ) and La Gomera (GO) were minor contributors to the overall sample set. The autochthonous cultivar Listán Negro (LN) was the most prevalent, followed by Baboso (B), Vijariego (V), Tintilla (T), Castellana (C), Negramoll (N), Listán Prieto (LP), and the international cultivars Syrah (S), Merlot (M), and Rubi Cabernet (R). The wines were also categorized by aging, with the majority classified as young wines ($\leq$2 years), followed by medium-aged wines (3–5 years) and a small number of old wines ($\geq$6 years). For a more detailed overview of the geographical distribution and breakdown of wine samples by aging and grape cultivar, please consult Table S1.

2.2. Analytical Methods

Several analytical methods were employed to characterize the organic acid content and other wine quality parameters related to the acidic profile. All wine measurements were performed in triplicate (n = 3). pH and total acidity were determined using an automated Metrohm potentiometric titrator (Metrohm AG, Herisau, Switzerland), following the OIV standardized methods, OIV-MA-AS313-15 for pH and OIV-MA-AS313-01 for total acidity [26].

L-malic, acetic, L-lactic, citric, and gluconic acids were determined using specific enzymatic methods, measuring the absorbance at 340 nm. These analyses were conducted using specific enzymatic kits (Biosystems, Barcelona, Spain) on the Y15 food and beverage sequential analyzer from the same manufacturer (Biosystems, Barcelona, Spain). The OIV standardized reference methods applied included OIV-MA-AS313-09 for citric acid, OIV-MA-AS313-25 for L-lactic acid, OIV-MA-AS313-26 for L-malic acid, OIV-MA-AS313-27 for acetic acid, and OIV-MA-AS313-28 for D-gluconic acid. Tartaric acid was quantified using an optimized automated version of Rebelein's colorimetric method [27], with specific reagents from TDI (Tecnología Difusión Ibérica SL, Gavà, Spain), analyzed on the Y15 sequential analyzer.

As no official OIV method has yet been standardized for the analysis of phenolic acids, the separation of phenolic compounds was achieved via high-performance liquid chromatography (HPLC), implementing a protocol adapted from the method described by Ibern-Gómez et al. [28], with specific modifications. Analyses were performed using a Waters 2690 Separation Module interfaced with a Waters 996 Photodiode Array Detector (HPLC-DAD, Waters, MA, USA). Chromatograms were recorded primarily at 280 and 320 nm, wavelengths relevant for phenolic detection. Prior to injection, all wine samples were filtered through 0.45 µm membrane filters to remove particulates. Subsequently, 15 µL of each sample was introduced into a Nova-Pak C18 reversed-phase column (3.9 $\times$ 150 mm, 4 µm particle size; Waters), maintained at a constant temperature of 30 °C. The chromatographic separation was conducted under a linear gradient using acidified Milli-Q water (solvent A) and acetonitrile (solvent B), both containing 0.2% trifluoroacetic acid, with a flow rate of 1.5 mL/min.

Phenolic acids were identified by comparison of their retention times and UV-visible spectra (200–700 nm) with those of authentic standards, when available (see Table S2). The peak identification procedure involved the following detailed assessment of spectral profiles and chromatographic behavior:

1. Retention times were consistently assessed comparing with data from the literature [16,28–31]. When possible, red wines were directly spiked with standards available to observe the proportional increase in the corresponding peaks.
2. For each peak, the UV-VIS absorption spectrum was compared with the UV-VIS absorption patterns published of the corresponding standards.
3. Peak behavior and elution order were consistent with the literature [16,28–31].

Quantification was carried out using calibration curves constructed within the concentration ranges corresponding to those detected in the wine samples, for compounds with available reference standards. Hydroxybenzoic acids (HBAs) were primarily monitored at 280 nm and quantified using gallic acid as the calibration reference, with concentrations expressed in milligrams of gallic acid equivalents per liter (mg GAE/L). Hydroxycinnamic acids (HCAs), on the other hand, were detected at 320 nm and quantified relative to caffeic acid, with results reported as milligrams of caffeic acid equivalents per liter (mg CAE/L).

The commercial standards used in this study included gallic acid, caffeic acid, p-coumaric acid, ferulic acid, syringic acid, ellagic acid, chlorogenic acid, and vanillic acid, all with purities exceeding 98% (Sigma-Aldrich, Merck KGaA, Darmstadt, Germany). All standards exhibited linear responses, with correlation coefficients (r) between 0.9942 and 0.9999. The phenolic acids identified in the red wine samples, with their respective abbreviations in parentheses, were as follows: gallic acid (Gall), protocatechuic acid (Prot), syringic acid (Syri), caftaric acid (Caft), caffeic acid (Caff), cutaric acid (Cuta), coumaric acid (Coum), and 2-S-glutathionylcaftaric acid (2SGl).

For the quantification of phenolic acid content, the eight identified acids were classified according to their chemical structures. Specifically, they were grouped into HBAs and HCAs. Further subclassification of HCAs was performed, differentiating between those esterified with tartaric acid (TE.HC) and those present in their free form (FR.HC). Subsequently, the total phenolic acid content for each sample was calculated and expressed as the sum of all the individual compounds (TPhe). The calculations carried out were as follows:

$$\text{Hydroxybenzoic acids (HBAs)} = \text{Gall} + \text{Prot} + \text{Syri} \quad (1)$$

$$\text{Hydroxycinnamic acids (HCAs)} = \text{Caft} + \text{Caff} + \text{Cuta} + \text{Coum} + \text{2SGl} \quad (2)$$

$$\text{HCA tartaric esters (TE.HC)} = \text{Caft} + \text{Cuta} + \text{2SGl} \quad (3)$$

$$\text{HCA free from (FR.HC)} = \text{Caff} + \text{Coum} \quad (4)$$

$$\text{Total phenolic acids (TPhe)} = \text{Gall} + \text{Prot} + \text{Syri} + \text{Caft} + \text{Caff} + \text{Cuta} + \text{Coum} + \text{2SGl} \quad (5)$$

To facilitate clarity throughout the manuscript, the following abbreviations are used to refer to grape cultivars, geographical origin, and phenolic acid groups:

- Grape cultivars: LN (Listán Negro), N (Negramoll), LP (Listán Prieto), B (Baboso), V (Vijariego), T (Tintilla), C (Castellana), R (Rubi Cabernet), M (Merlot), and S (Syrah).
- Denominations of origin (DO) from Tenerife: DO A (Abona), DO T (Tacoronte-Acentejo), DO O (Valle de La Orotava), DO Y (Ycoden-Daute-Isora), and DO G (Valle de Güímar).
- Islands: LP (La Palma), HI (El Hierro), GC (Gran Canaria), LZ (Lanzarote), and GO (La Gomera).

- Phenolic acids: Gall (gallic acid), Prot (protocatechuic acid), Syri (syringic acid), Caft (caftaric acid), Caff (caffeic acid), Cuta (cutaric acid), Coum (coumaric acid), and 2SGl (2-S-glutathionylcaftaric acid).
- Phenolic acid groupings: HBAs (hydroxybenzoic acids), HCAs (hydroxycinnamic acids), TE.HC (hydroxycinnamic acids esterified with tartaric acid), FR.HC (free hydroxycinnamic acids), and TPhe (total phenolic acids).

2.3. Statistics

All statistical computations were performed using SPSS software (version 18.0). Group-level differences were examined through one-way analysis of variance (ANOVA), applying a significance criterion of $p < 0.05$. To identify specific pairwise differences among groups, Duncan's multiple range test was conducted as a post hoc procedure. Associations between quantitative variables were evaluated using Pearson's correlation coefficients, enabling the characterization of both positive and negative linear relationships.

To uncover patterns within the dataset and to facilitate dimensionality reduction, principal component analysis (PCA) was employed. In addition, linear discriminant analysis (LDA) was utilized for supervised classification of red wine samples based on qualitative categorical variables. A stepwise selection approach was implemented to determine the most relevant variables contributing to discrimination among groups. Comprehensive analyses incorporating the full variable set were also conducted to assess potential multivariate interactions and the structure of discriminant functions. Classification probabilities were estimated by taking into account the group sizes and the within-group variance–covariance matrix.

3. Results

3.1. Overall Content

The acidity profile presented high variability and a typical balance between total acidity, pH, and the presence of both major organic acids and phenolic acids (Table 1). Acetic acid had a mean of 0.61 g/L, within acceptable sensory thresholds as a byproduct of fermentation. The concentration of citric acid was the lowest, and gluconic acid exhibited significant variability, with concentrations ranging from not detected to 2.29 g/L. The variability in malic acid concentrations was notably high, with a coefficient of variation (CV) of 181%.

Total phenolic acids had a mean concentration of 151.2 ± 33.3 mg/L, with HCAs being the most abundant phenolic acid group, most present as tartaric acids esters. HBAs presented a lower mean concentration, with gallic acid being the most concentrated despite its high variability, with a CV of 58%. Despite the inclusion of these acids as standard spiking compounds, no traces of ferulic acid, ellagic acid, chlorogenic acid, or vanillic acid were detected in the red wine samples analyzed.

Table 1. Acid contents as mean + standard deviation (SD) and range in red wines ($n = 3$).

	Mean ± SD	**Min–Max**
Wine acidity		
pH (pH Units)	3.73 ± 0.18	3.23–4.54
Total Acidity (g tart./L)	5.20 ± 0.73	3.93–7.59
Major organic acids (g/L)		
Tartaric	1.73 ± 1.06	0.06–4.89
Malic	0.37 ± 0.67	<0.02–3.62
Lactic	1.78 ± 1.02	0.07–5.53
Acetic	0.61 ± 0.24	0.15–1.53
Gluconic	0.37 ± 0.42	<0.02–2.29
Citric	0.14 ± 0.10	<0.02–0.46

Table 1. *Cont.*

	Mean ± SD	**Min–Max**
Phenolic acids (mg/L)		
TPhe	151.20 ± 33.3	66.28–246.20
Gall	37.41 ± 21.66	3.23–113.21
Prot	3.29 ± 3.56	0.44–33.83
Syri	13.16 ± 4.76	3.60–30.06
HBAs	53.86 ± 23.91	9.04–140.20
Caft	47.94 ± 15.59	4.42–73.12
Caff	12.23 ± 9.34	0.71–55.35
Cuta	28.62 ± 12.69	3.74–65.85
Coum	7.55 ± 7.25	0.26–51.10
2SGl	0.95 ± 0.70	0.07–4.06
HCAs	97.29 ± 19.17	30.43–155.38
TE.HC	77.52 ± 19.04	26.32–121.18
FR.HC	19.77 ± 14.07	3.37–72.54

Each wine sample was analyzed in triplicate (n = 3).

3.2. Univariate Analysis

Descriptive statistics, including mean concentrations and standard deviations, were calculated for the organic acids and related enological parameters. To assess differences in mean values across groups, one-way analysis of variance (ANOVA) was performed, followed by Duncan's multiple range test for post hoc comparisons. Red wine samples were categorized based on qualitative variables, including grape cultivar, geographical origin in terms of island of provenance or DO, and aging practices, in order to evaluate the influence of these factors on the compositional profile.

3.2.1. Grape Cultivar

Table 2 displays results organized by cultivar. The analysis of variance (ANOVA, $p < 0.05$) was complemented by Duncan's multiple range test to identify statistically significant differences among groups. The corresponding results are presented in Table 2, which summarizes the mean concentrations.

The pH, acidity, and organic acid composition of red wines varied significantly across grape cultivars. pH values of red wines ranged from 3.66 (LP cultivar) to 4.13 (C cultivar), with C exhibiting a significantly higher pH than the rest of the red wines. In accordance with this, C red wines had the lowest total acidity (4.47 g/L). Mean tartaric and citric acid concentrations showed no significant differences. Malic acid exhibited more variability. Red wines from M cultivar had the greatest concentration, with significant differences when compared with N, T, and C cultivars. This suggests possible differences in the completion of malolactic fermentation depending on the cultivar. Mean lactic acid levels were the greatest for C cultivar, followed by red wines from T cultivar, which aligns with enhanced malolactic activity.

Mean acetic acid concentrations had a narrow range, ranging from 0.51 g/L observed in red wines from LN cultivar to 0.85 g/L in red wines from T cultivar. These red wines (T cultivar) showed a mean acetic acid concentration higher than those levels in LP, LN, N, and R cultivars. Mean gluconic acid concentrations varied between the red wines according to the grape cultivar and within each cultivar. Red wines from B cultivar showed the highest mean gluconic acid concentration, with significant differences with respect to the rest, except for M and V. Total phenolic acids were the highest in red wines from N (170.8 mg/L) cultivar, and lowest in R, C, and T (<130 mg/L) cultivars. HBAs and HCAs followed similar patterns, generally showing higher mean concentrations in N and LP than R and T.

Table 2. Mean concentrations and standard deviations of acids as a function of grape cultivars.

	V	N	LP	B	T	LN	M	S	C	R
pH (pH Units)	3.75 ^{ab} (0.15)	3.71 ^{ab} (0.16)	3.66 ^{a} (0.18)	3.77 ^{ab} (0.12)	3.85 ^{b} (0.18)	3.69 ^{a} (0.13)	3.74 ^{ab} (0.19)	3.73 ^{ab} (0.25)	4.13 ^{c} (0.33)	3.82 ^{ab} (0.14)
Total Acidity (g Tartaric/L)	5.34 ^{b} (0.81)	5.02 ^{ab} (0.61)	5.13 ^{b} (0.80)	5.64 ^{b} (0.87)	5.56 ^{b} (0.98)	5.01 ^{ab} (0.52)	5.59 ^{b} (0.54)	5.46 ^{b} (0.85)	4.47 ^{a} (0.48)	5.50 ^{b} (0.81)
Tartaric (g/L)	2.32 ^{a} (1.02)	2.35 ^{a} (1.03)	2.10 ^{a} (0.40)	1.49 ^{a} (1.01)	2.06 ^{a} (1.45)	1.56 ^{a} (1.04)	2.31 ^{a} (0.71)	1.53 ^{a} (1.24)	1.36 ^{a} (0.84)	1.40 ^{a} (1.11)
Malic (g/L)	0.56 ^{ab} (0.94)	0.16 ^{a} (0.20)	0.35 ^{ab} (0.44)	0.63 ^{ab} (0.97)	0.17 ^{a} (0.16)	0.31 ^{ab} (0.57)	0.89 ^{b} (1.39)	0.34 ^{ab} (0.53)	0.05 ^{a} (0.03)	0.42 ^{ab} (0.46)
Lactic (g/L)	1.51 ^{ab} (0.67)	1.57 ^{ab} (0.54)	1.33 ^{a} (0.91)	2.33 ^{bcd} (1.37)	2.56 ^{cd} (0.78)	1.53 ^{ab} (0.82)	1.54 ^{ab} (0.85)	1.99 ^{abc} (0.92)	3.19 ^{d} (1.38)	2.17 ^{abc} (0.92)
Acetic (g/L)	0.68 ^{abc} (0.14)	0.62 ^{ab} (0.16)	0.63 ^{ab} (0.20)	0.78 ^{bc} (0.28)	0.85 ^{c} (0.29)	0.51 ^{a} (0.21)	0.66 ^{abc} (0.13)	0.67 ^{abc} (0.09)	0.68 ^{abc} (0.25)	0.61 ^{ab} (0.20)
Gluconic (g/L)	0.50 ^{bc} (0.41)	0.25 ^{ab} (0.19)	0.14 ^{ab} (0.32)	0.73 ^{c} (0.66)	0.13 ^{ab} (0.21)	0.34 ^{ab} (0.32)	0.47 ^{bc} (0.51)	0.17 ^{ab} (0.18)	0.05 ^{a} (0.06)	0.36 ^{ab} (0.43)
Citric (g/L)	0.11 ^{a} (0.08)	0.13 ^{a} (0.10)	0.08 ^{a} (0.07)	0.14 ^{a} (0.12)	0.07 ^{a} (0.09)	0.16 ^{a} (0.09)	0.16 ^{a} (0.17)	0.14 ^{a} (0.10)	0.09 ^{a} (0.05)	0.09 ^{a} (0.09)
Gall (mg/L)	42.42 ^{bcd} (18.66)	53.31 ^{d} (21.24)	31.76 ^{abc} (19.75)	39.14 ^{abcd} (23.32)	47.64 ^{cd} (36.47)	37.43 ^{abcd} (21.15)	33.7 ^{abcd} (8.7)	24.75 ^{ab} (9.39)	24.80 ^{ab} (6.45)	18.20 ^{a} (10.03)
Prot (mg/L)	2.99 ^{a} (1.60)	3.46 ^{a} (1.74)	2.69 ^{a} (1.58)	4.27 ^{a} (5.92)	3.0[1] ^{a} (1.83)	3.27 ^{a} (3.61)	5.21 ^{a} (5.68)	2.78 ^{a} (1.20)	1.63 ^{a} (0.62)	2.37 ^{a} (1.13)
Syri (mg/L)	11.10 ^{a} (3.27)	12.17 ^{a} (3.76)	13.53 ^{a} (4.48)	14.61 ^{a} (5.30)	15.77 ^{a} (7.00)	13.31 ^{a} (4.52)	11.29 ^{a} (4.49)	11.15 ^{a} (5.13)	14.04 ^{a} (6.13)	10.96 ^{a} (2.23)
Caft (mg/L)	57.99 ^{cde} (8.87)	58.95 ^{de} (6.94)	64.61 ^{e} (5.69)	46.81 ^{bcd} (12.95)	26.69 ^{a} (9.85)	48.36 ^{bcd} (14.01)	43.95 ^{b} (8.74)	30.23 ^{a} (17.77)	46.03 ^{bc} (12.0)	24.88 ^{a} (16.97)
Caff (mg/L)	11.46 ^{ab} (7.57)	11.92 ^{ab} (8.90)	7.43 ^{ab} (3.06)	6.82 ^{a} (3.25)	13.42 ^{ab} (10.25)	13.98 ^{ab} (10.43)	16.14 ^{b} (9.11)	12.87 ^{ab} (11.05)	9.82 ^{ab} (3.47)	24.59 ^{c} (11.31)
Cuta (mg/L)	19.16 ^{a} (7.19)	26.40 ^{ab} (4.87)	28.87 ^{ab} (12.47)	18.37 ^{a} (9.16)	20.55 ^{a} (10.94)	35.62 ^{b} (12.02)	24.78 ^{a} (9.49)	28.90 ^{ab} (11.34)	21.97 ^{a} (8.47)	24.33 ^{a} (11.02)
Coum (mg/L)	5.36 ^{a} (3.85)	3.90 ^{a} (2.18)	2.12 ^{a} (1.22)	6.99 ^{a} (9.11)	13.95 ^{b} (6.17)	7.62 ^{a} (6.43)	6.87 ^{a} (2.51)	14.23 ^{b} (7.57)	4.82 ^{a} (4.54)	18.61 ^{b} (14.81)
2SGl (mg/L)	0.97 ^{abc} (0.55)	0.68 ^{ab} (0.40)	0.58 ^{a} (0.57)	1.62 ^{d} (0.96)	1.45 ^{cd} (0.89)	0.74 ^{ab} (0.47)	1.03 ^{abcd} (0.60)	1.23 ^{bcd} (0.62)	0.74 ^{ab} (0.81)	1.26 ^{bcd} (0.47)
TPhe (mg/L)	151.5 ^{abc} (19.77)	170.8 ^{c} (28.50)	151.6 ^{abc} (32.56)	138.6 ^{ab} (34.53)	142.5 ^{abc} (52.95)	160.3 ^{bc} (31.88)	142.4 ^{abc} (26.08)	126.1 ^{a} (17.17)	123.8 ^{a} (27.4)	125.2 ^{a} (14.49)
HBAs (mg/L)	56.51 ^{bc} (21.02)	68.93 ^{c} (23.23)	47.98 ^{abc} (22.54)	58.02 ^{bc} (25.08)	66.42 ^{c} (42.83)	54.00 ^{abc} (22.89)	49.67 ^{abc} (11.12)	38.68 ^{ab} (12.00)	40.5 ^{ab} (9.58)	31.53 ^{a} (12.35)
HCAs (mg/L)	94.94 ^{bcd} (9.37)	101.85 ^{cd} (11.10)	103.61 ^{d} (15.19)	80.60 ^{ab} (16.19)	76.06 ^{a} (17.33)	106.32 ^{d} (17.54)	92.76 ^{bcd} (15.15)	87.46 ^{abc} (13.40)	83.4 ^{ab} (21.3)	93.7 ^{bcd} (19.6)
TE.HC (mg/L)	78.12 ^{cd} (8.10)	86.03 ^{de} (8.78)	94.06 ^{e} (12.43)	66.80 ^{bc} (15.41)	48.68 ^{a} (12.46)	84.72 ^{de} (17.51)	69.76 ^{bc} (12.69)	60.36 ^{ab} (12.68)	68.73 ^{bc} (19.9)	50.48 ^{a} (8.23)
FR.HC (mg/L)	16.82 ^{abc} (10.05)	15.81 ^{abc} (10.51)	9.55 ^{a} (3.52)	13.81 ^{ab} (11.19)	27.37 ^{c} (15.05)	21.60 ^{abc} (14.49)	23.01 ^{bc} (11.27)	27.11 ^{c} (12.79)	14.6 ^{abc} (6.85)	43.20 ^{d} (25.49)

Standard deviations are reported in parentheses. Distinct superscript letters within each row denote statistically significant differences between means at the $p < 0.05$ level. Abbreviations follow Table S1 and acid compounds' abbreviations: Gall: gallic acid; Prot: protocatechuic acid; Syri: syringic acid; Caft: caftaric acid; Caff: caffeic acid; Cuta: cutaric acid; Coum: coumaric acid; 2SGl: 2-S-glutathionylcaftaric acid; TPhe: total phenolic acids; HBAs: hydroxybenzoic acids; HCAs: hydroxycinnamic acids; TE.HC: hydroxycinnamic acid esters of tartaric acid; FR.HC: Free hydroxycinnamic acids. Each wine sample was analyzed in triplicate ($n = 3$).

Notable differences were observed in hydroxybenzoic acids. Even though Prot and Syri acids did not show significant differences according to the cultivar, the mean Gall acid concentration, the major HBA, varied significantly according to cultivar. So, R, S, and C presented lower mean Gall acid concentrations than N and T. Similar results were obtained when the sum of hydroxybenzoic acids was considered.

Hydroxycinnamic acids exhibited a different behavior depending on the phenolic acid considered. Mean Caft concentration was significantly high in LP (64.61 mg/L) and low in M, S, C, B, T, LN, and R (26.69–48.36 mg/L). Mean Coum concentrations clearly distinguished between two groups: a group with mean concentration $\geq$ 13 mg/L and another group with a mean Coum concentration $\leq$ 8 mg/L. According to 2SGl, samples were classified into two groups. B, T, and the three foreign cultivars R, S, and M had mean 2SGl concentrations $\geq$ 1 mg/L, while the rest showed mean concentrations lower than that value. In this same sense, mean Caff was the highest in R, followed by M, LN, and T, whereas B presented the lowest mean concentration. In contrast, mean Caft concentrations from LP, N, and V were higher than those in LN, B, C, and M, and these were higher than R, T, and S. LN cultivar had the highest mean Cuta concentration. When all hydroxycinnamic acids were considered together, LN, LP, and N had significantly higher mean concentrations.

3.2.2. Geographical Origin

Regarding geographical origin, two hierarchical factors were taken into account: the island of provenance and, specifically for samples from Tenerife, the DO within the island.

Island

The analysis of variance (ANOVA) applied to pH, total acidity, and both major and minor organic acids in monovarietal red wines from the Canary Islands indicated statistically significant differences ($p < 0.05$) in mean concentrations based on the island of origin (Table S3). While certain acid-related parameters displayed distinct geographical patterns, others were more homogeneously distributed across regions.

As it can be observed in Table S3, wines from La Gomera Island had the significantly lowest pH. Total acidity and many major acids showed no statistically significant differences. However, mean acetic acid from El Hierro Island was significantly higher than from La Gomera Island; likewise, El Hierro wines had the highest significant gluconic acid mean concentration (0.72 g/L).

Considering the minor HBAs, El Hierro had significantly the highest Gall—the HBAs had a similar behavior to the Gall, as it was the predominant HBA. In addition, El Hierro also showed the highest Prot. In contrast, Syri concentration varied significantly.

With respect to HCAs, mean Caft in La Palma was significantly higher than in Tenerife Island, while Gran Canaria had significantly higher Caff than these from El Hierro, La Gomera, and Lanzarote. Cuta had a similar behavior, presenting also the highest in Gran Canaria Island. The 2SGl in El Hierro Island was higher than in La Gomera, La Palma, and Lanzarote Islands, while Coum did not show significant differences.

Lanzarote had a significant higher mean total HCAs concentration than El Hierro and La Gomera. TE.HC was the highest in Lanzarote, while La Gomera had the lowest TPhe.

Denomination of Origin from Tenerife Island

Phenolic acids exhibited considerable heterogeneity across the DOs from Tenerife Island, contrasting with a relative equilibria in major organic acids (Table S4).

The acid profiles of red wines from the five DOs from Tenerife Island showed both shared patterns and significant differences. DO A had the highest pH value, significantly greater than DO O. Mean total acidity permitted to classify the DO in two different groups. A group with a mean concentration $\geq$ 5.6 that included DO Y and DO G, and a second group with total acidity < 5.6 formed by DO T, DO O, and DO A. No differences were observed in the mean tartaric and lactic acids among the red wines. Malic acid in DO G was significantly higher (nearly three times higher) than in the other Tenerife DOs. Acetic acid was higher in DO Y, DO A, and DO T. Gluconic acid content in DO Y was higher than

in DO O and DO G, and these were higher than in DO A. Mean citric acid in DO A was also the lowest.

In terms of specific phenolic acids, mean Gall in DO Y and DO T was significantly higher than in DO A and DO G. Proto was the highest in DO T. Mean Syri contents were significantly higher in DO Y and DO O than in DO T and DO G. Caft was the highest in DO O and DO Y, while Coum and Caff presented no differences. DO A and DO G showed the lowest TPhe concentrations. Mean HBA concentrations in DO Y and DO T were higher than in DO A and DO G. HCAs and TE.HC exhibited the same pattern. So, DO O was higher than DO Y and DO T (north side of Tenerife), and these were higher than DO A (south of Tenerife Island), while FR.HC (minor fraction or free HCA) showed no differences.

3.2.3. Aging

Acid contents showed distinct patterns according to aging, observing significant differences in several acid parameters (Table S5). No significant differences were found in pH, total acidity, and malic and gluconic acids according to aging. Nevertheless, most of the individual major organic acids showed higher mean concentrations in the oldest wines (≥6 years). Mean tartaric, malic, acetic, gluconic, and citric acid concentrations increased while aging, while an inverse behavior was observed for the lactic acid. Organic acids exhibiting significant differences with respect to aging are shown in Figure 1. The data clearly demonstrated a notable increase in the levels of citric, acetic, and tartaric with aging, while lactic acid concentrations exhibited a corresponding decrease.

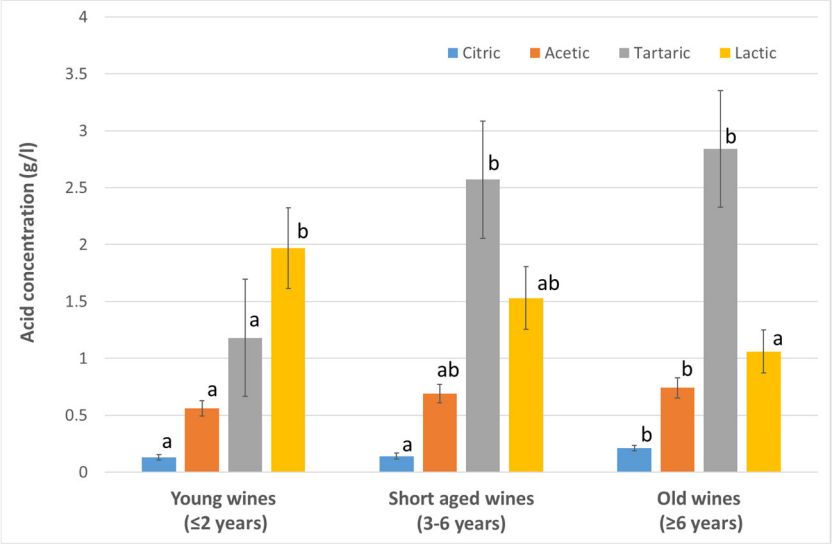


Figure 1. Organic acids' concentrations with significant differences according to wine aging. Different letters indicate significant differences at the $p < 0.05$ level.

In terms of specific phenolics (Table S5), mean Gall and Prot concentrations increased significantly with the aging, in contrast to the mean Syri concentration, which was significantly higher in young wines compared to old wines, suggesting a progressive decrease with aging. With respect to HCAs, Caft, Cuta, and 2SGl showed no significant variation with aging. Interestingly, Caff and Coum presented a notably high mean concentration in short-aged wines (3–5 years of aging).

When grouping TPhe and HBAs, a significant increase in their mean concentrations according to the aging was observed (Figure 2). Interestingly, FR.HC was significantly higher in short-aged wines, nearly double those in both old and young wines, and no significant differences were observed in HCAs or their tartaric esters (TE.HC) across aging groups.

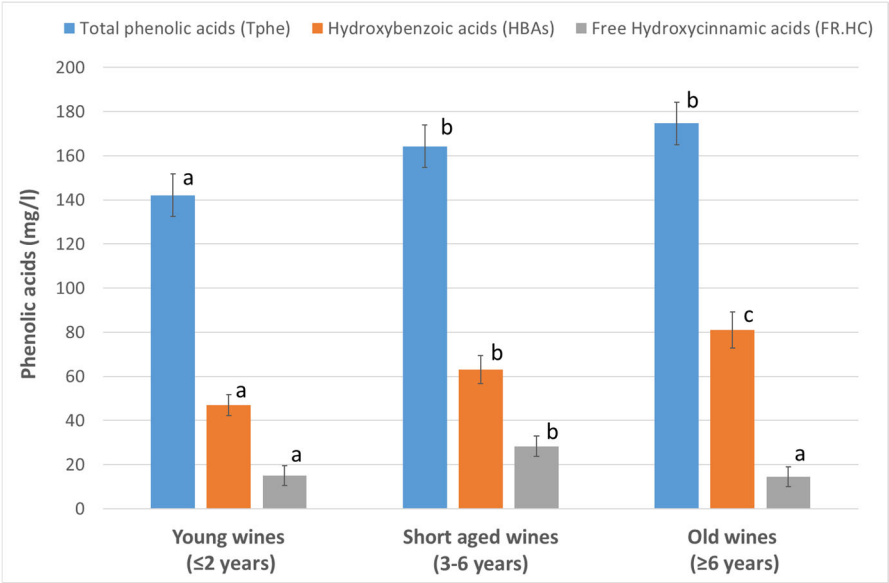


Figure 2. Phenolic acid groups with significant differences according to wine aging. Different letters indicate significant differences at the $p < 0.05$ level.

3.3. Correlations

Relationships between major and phenolic organic acids are exposed in Table 3, including Pearson's correlation coefficient (r) and degree of significance. *P*-values below 0.05 were considered statistically significant. As it could be anticipated, pH showed a moderate and inverse correlation with total acidity ($r = -0.319$, $p < 0.001$), and weaker negative correlations with tartaric, malic, citric, and hydroxycinnamic acids, indicating that as these organic acid concentrations increased, pH tended to decrease. The positive and high correlation between pH and lactic acid is remarkable ($r = 0.586$, $p < 0.001$).

Total acidity positively correlated with many major organic acids, such as malic acid ($r = 0.440$, $p < 0.01$), acetic acid ($r = 0.378$, $p < 0.001$), gluconic acid ($r = 0.376$, $p < 0.001$), and citric acid ($r = 0.236$, $p < 0.001$), supporting its dependence on multiple acid types. In contrast, an inverse correlation was observed with Cuta ($r = -0.241$, $p < 0.01$).

Tartaric acid was positively correlated with Gall ($r = 0.422$, $p < 0.001$), Caff ($r = 0.302$, $p < 0.001$), and TPhe ($r = 0.389$, $p < 0.001$), suggesting links between primary grape acids and phenolic extraction or stability. Malic acid was positively correlated with other major organic acids, such as tartaric, gluconic, and citric acids; in contrast, it was inversely correlated ($r = -0.466$, $p < 0.001$) with lactic acid, which is a consequence of the MLF of red wines.

Among the phenolic acids, there are obviously many significant correlations between parameters obtained by calculation and the phenolic acids utilized in the corresponding calculation. For instance, TPhe were strongly correlated with HBAs and HCAs, and HCAs were correlated with the two chemical species constituents, TE.HC and FR.HC. In addition, Gall showed strong positive correlations with the total phenolic acids ($r = 0.797$, $p < 0.01$), confirming its central role in the overall phenolic composition. The highly significant and inverse correlations observed between Caft and Coum ($r = -0.769$, $p < 0.001$) are noteworthy, which are presented in Figure 3, and those between Caft and 2SGl ($r = -0.516$, $p < 0.001$).

Table 3. Correlations among the acids considered in the red wines.

	pH	T.A.	Tartaric	Malic	Lactic	Acetic	Gluc.	Citric	Gall	Prot	Syri	Caft	Caff	Cuta	Coum	2SGl	TPhe	HBAs	HCAs	TE.HC	FR.HC
pH	1	**−0.319**	**−0.145**	**−0.171**	**0.586**	**0.224**	0.031	**−0.222**	−0.030	**−0.186**	**0.155**	**−0.333**	0.024	−0.103	**0.194**	**0.185**	−0.160*	−0.024	**−0.247**	**−0.334**	0.116
T.A.	*	1	0.128	**0.440**	−0.083	**0.378**	**0.376**	**0.236**	0.116	0.003	−0.084	−0.019	−0.044	**−0.241**	−0.010	**0.285**	−0.045	0.089	**−0.190**	**−0.166**	−0.034
Tartaric	***		1	0.076	**−0.288**	**0.167**	−0.029	−0.088	**0.422**	0.122	−0.102	0.134	**0.302**	−0.092	0.015	0.020	**0.389**	**0.380**	**0.202**	0.049	**0.208**
Malic	***	*		1	**−0.466**	−0.103	**0.255**	**0.436**	0.047	**0.241**	0.054	0.112	0.034	−0.015	−0.110	0.011	0.096	0.089	0.057	0.082	−0.034
Lactic	*		*	*	1	**0.346**	−0.034	**−0.317**	**−0.158**	**−0.233**	−0.029	**−0.350**	**−0.201**	**−0.193**	**0.176**	**0.206**	**−0.383**	**−0.183**	**−0.436**	**−0.408***	−0.042
Acetic	**	*	***		*	1	0.112	**−0.236**	**0.203**	0.048	**−0.185**	−0.103	−0.075	**−0.416**	0.070	**0.249**	−0.097	**0.154**	**−0.361**	**−0.353**	−0.014
Gluc.		*		*			1	**0.355**	**0.208**	0.117	0.067	0.074	−0.072	−0.104	−0.115	**0.349**	0.115	**0.219**	−0.074	0.005	−0.107
Citric	**	**		*	*	**	*	1	**0.157**	**0.214**	−0.002	0.099	0.061	0.111	−0.089	−0.033	**0.210**	**0.173**	**0.149**	**0.154**	−0.005
Gall			*		***	**	**	***	1	**0.170***	**0.221**	0.078	**0.170**	0.023	0.013	0.074	**0.797**	**0.975**	**0.169**	0.082	0.120
Prot	**			**	**			**	***	1	−0.129	−0.028	0.029	−0.073	0.078	0.115	**0.186**	**0.277**	−0.023	−0.067	0.060
Syri	***					**			**		1	0.026	0.073	**0.202**	−0.028	−0.036	**0.376**	**0.379**	**0.179***	**0.155**	0.034
Caft	*				*							1	**−0.286**	−0.063	**−0.769**	**−0.516**	**0.237**	0.072	**0.323**	**0.758**	**−0.586**
Caff			*		**				***			*	1	0.115	**0.429**	−0.127	**0.405**	**0.173**	**0.488**	**−0.162**	**0.885**
Cuta		*			**	*					**			1	**0.194**	**−0.337**	**0.455**	0.050	**0.728**	**0.603**	**0.176**
Coum	**				***							*	*	**	1	**0.279**	0.071	0.018	0.100	**−0.490**	**0.800**
2SGl	**	*			**	*	*					*		*	*	1	**−0.268**	0.077	**−0.563**	**−0.611**	0.060
TPhe	***		*		*			**	*	**	*	**	*	*		*	1	**0.825**	**0.709**	**0.488**	**0.306**
HBAs			*		**	***	**	***	*	*	*		***				*	1	**0.186**	0.095	0.124
HCAs	*	**	**		*	*		***	***		***	*	*	*		*	*	**	1	**0.729**	**0.376**
TE.HC	*	***			*	*		***			***	*	***	*	*	*	*		*	1	**−0.361**
FR.HC			**									*	*	***	*		*		*	*	1

Correlation coefficients (r) are presented above the diagonal, whereas the corresponding *p*-values are shown below. Statistically significant correlations are highlighted in bold. Significance levels are denoted as follows: * $p < 0.001$ (two-tailed), ** $p < 0.01$ (two-tailed), and *** *p*-values between 0.01 and 0.05 (two-tailed). Abbreviations for the compounds are as follows: T.A. total acidity; Gluc.: gluconic acid; Gall: gallic acid; Prot: protocatechuic acid; Syri: syringic acid; Caft: caftaric acid; Caff: caffeic acid; Cuta: cutaric acid; Coum: coumaric acid; 2SGl: 2-S-glutathionylcaftaric acid; TPhe: total phenolic acids; HBAs: hydroxybenzoic acids; HCAs: hydroxycinnamic acids; TE.HC: hydroxycinnamic acid esters of tartaric acid; FR.HC: free hydroxycinnamic acids.

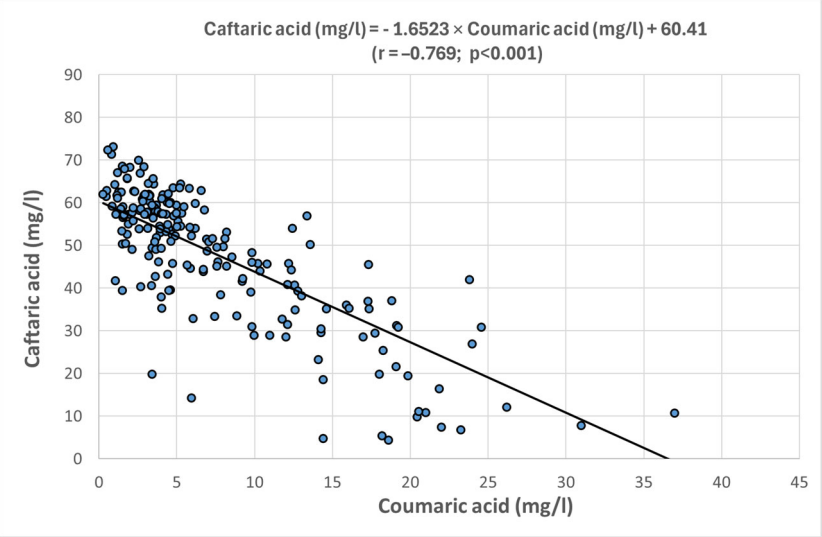


Figure 3. Correlations between Coum and Caft organic acids for all the wines analyzed.

Notably, even though the concentration of 2SGl was introduced in the summative equation employed to calculate HCA content, both parameters (HCA and 2SGl) correlated inversely ($r = -0.563$, $p < 0.001$), suggesting oxidative or binding transformations during wine maturation. This correlation was even higher with TE.HC, in which 2SGl was directly included, as it can be observed in Figure 4.

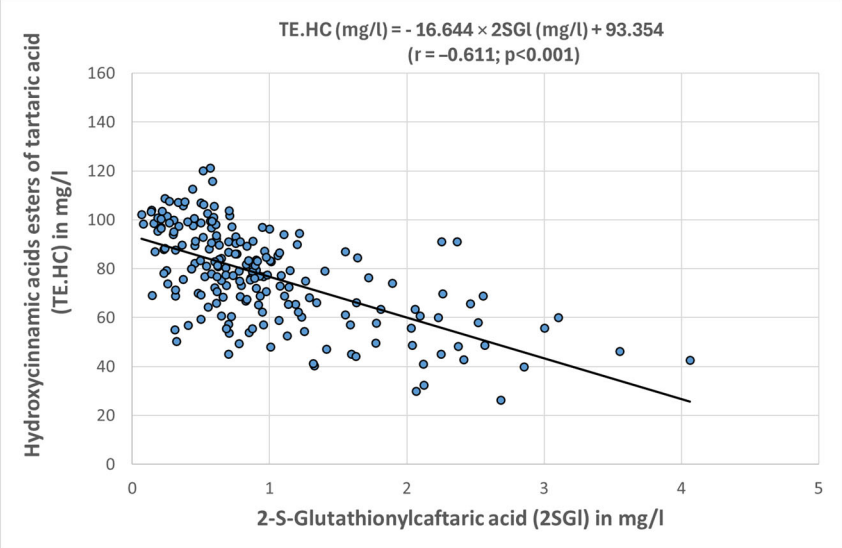


Figure 4. Correlations between 2SGl and TE.HC organic acids for all the wines analyzed.

3.4. Multivariate Analysis

3.4.1. Principal Compound Analysis

Principal component analysis (PCA) was conducted to identify patterns in the dataset and to reduce dimensional complexity associated with organic acid parameters in monovarietal red wines. To enhance factor interpretability, a Varimax orthogonal rotation was applied, which minimized variable overlap across components. This analysis yielded three principal components with eigenvalues equal to or greater than 1, collectively explaining 94.4% of the total variance. The first principal component, accounting for 52.1% of the variance, showed high positive loadings for HCAs and TE.HC, along with a moderate association with Cuta and a notable inverse relationship with 2SGl. The second component

(28.3%) was predominantly defined by HBAs, TPhe, and Gall. The third component (15.1%) captured variation associated with specific HCAs, particularly Caff, Coum, and FR.HC, while exhibiting negative loadings for Caft and TE.HC. Figure 5 presents a biplot of the first two components, which together explained 80.4% of the total variance. This visual representation enables the identification of relationships among variables—compounds positioned in close proximity on the plot are indicative of shared structural or functional characteristics.

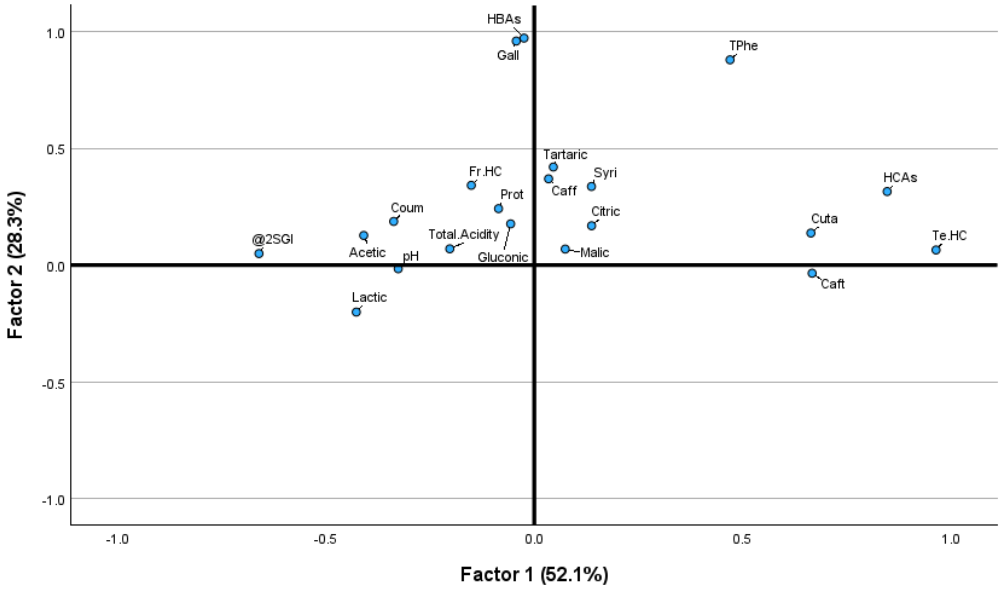


Figure 5. Acids' projection within the factorial space defined by the first two principal components.

Factor 1 primarily separated variables based on phenolic content. It was positively associated with TPhe, HCAs, Caft, Cuta, and TE.HC. Factor 2 was strongly influenced by HBAs, such as Gall, and with TPhe, while also distinguishing lactic acid and 2SGl in the negative quadrant. Compounds such as total acidity, Gluc, citric acid, Caff, and Syri clustered near the origin, indicating moderate influence on both axes. Acetic acid, pH, and lactic acid loaded negatively on Factor 2, with lactic acid distinctly separated, suggesting its variability was less correlated with the major phenolic acids.

This factor analysis was applied to explore the differentiation of red wine samples directly according to cultivar, geographical origin, and aging. Despite this, the distribution of the red wines did not show a clear separation according to the grape cultivar used for its elaboration. However, a subtle trend emerged that indicated some separation among the three aging categories and between some specific islands, such as Lanzarote and Tenerife Islands.

3.4.2. Linear Discriminant Analysis

Linear discriminant analysis (LDA) was applied to the pH, total acidity, and major and phenolic organic acid composition profiles in order to assess the feasibility of classifying samples based on four categorical factors: cultivar, island, DO within Tenerife, and aging. The classification accuracy was evaluated both before and after cross-validation, and the most relevant acids contributing to the discriminant functions (F1 and F2) were identified using both full-variable and stepwise LDA approaches (Table 4).

LDA, based on all acid parameters studied, yielded the highest classification accuracy for grape cultivar, achieving 88.3% correct classification, with a considerable drop to 68.8% after cross-validation. The stepwise model, which retained a reduced subset of discriminant acids, resulted in a lower performance (61.0% originally and 54.5% after cross-validation). The primary contributors to discrimination in the first canonical function

were HCAs, Cuta, and FR.HC, while the second function was mainly influenced by Caft, TE.HC, and Coum. Applying this analysis, Table 5 reveals the entire classification (100% of the red wine samples) for certain cultivars, such as N, LP, T, C, M, and S, while some overlap was observed for autochthonous cultivars, like the most cultivated LN, and other minor cultivars, such as V and B. It is interesting to note that R was correctly classified in 80% of the cases, and its misclassification was produced with M, another well-known international cultivar.

Table 4. Results of LDA for classification according to selected variables.

Classification Factor	LDA Type	Classification Accuracy (% with Cross-Validation)	Variables Contributing to F1 and F2
1. Cultivar			
	All variables	88.3 (68.8%)	F1: HCAs, Cuta, FR.HC F2: Caft, TE.HC, Coum
	Stepwise	61.0% (54.5%)	F1: TE.HC, Cuta, HCAs F2: Caft, FR.HC, Coum
2. Island			
	All variables	83.4% (76.6%)	F1: Caft, Gall, tartaric F2: Gluconic, 2SGl, HCAs
	Stepwise	74.6% (72.7%)	F1: Caft, gluconic, Gall F2: 2SGl, pH, lactic
3. Tenerife DO			
	All variables	69.2% (66.4%)	F1: TPhe, HBAs, TE.HC F2: Gluconic, malic, citric
	Stepwise	61.6% (54.8%)	F1: TPhe, malic, Gall F2: Gluconic, tartaric, citric
4. Wine Aging			
	All variables	86.8% (83.9%)	F1: Tartaric, Gall, HBAs F2: Prot, FR.HC, Caff
	Stepwise	83.4% (78.5%)	F1: Tartaric, TPhe, HBAs F2: Prot, FR.HC, Caff

Table 5. LDA classification results based on cultivar as percentages of assignments.

Original → / ↓ Predicted	LN	N	B	LP	T	C	R	M	V	S
LN	**87.1**	0.0	16.7	0.0	0.0	0.0	0.0	0.0	17.6	0.0
N	3.2	**100.0**	3.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
B	2.2	0.0	**76.7**	0.0	0.0	0.0	0.0	0.0	0.0	0.0
LP	0.0	0.0	0.0	**100.0**	0.0	0.0	0.0	0.0	0.0	0.0
T	0.0	0.0	0.0	0.0	**100.0**	0.0	0.0	0.0	0.0	0.0
C	1.1	0.0	0.0	0.0	0.0	**100.0**	0.0	0.0	5.9	0.0
R	1.1	0.0	0.0	0.0	0.0	0.0	**80.0**	0.0	0.0	0.0
M	4.3	0.0	0.0	0.0	0.0	0.0	20.0	**100.0**	0.0	0.0
V	1.1	0.0	3.3	0.0	0.0	0.0	0.0	0.0	**76.5**	0.0
S	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**100.0**

Predicted cultivars listed in the rows and actual cultivars indicated in the columns. Abbreviations for grape cultivars follow Table S1.

Classification by island after LDA using all variables produced a high accuracy of 83.4% (76.6% after cross-validation), suggesting strong environmental signals embedded in the acid profiles. Moreover, taking into account that in Tenerife Island, five distinct DOs converged, the stepwise model maintained high performance (74.6%, and 72.7% after cross-validation), with the most influential variables including Caft, gallic acid, and tartaric acid for F1, and gluconic acid, 2SGl, and HCAs for F2.

The LDA applied to distinguish among DOs within Tenerife Island showed moderate classification performance, with 69.2% accuracy (66.4% after cross-validation) using all variables, and 61.6% (54.8%) for the stepwise model. Relevant variables included total phenols (TPhe), hydroxybenzoic acids (HBAs), TE.HC, and several organic acids, such as gluconic, malic, and citric acids.

The classification matrix for all the DOs (Table 6) revealed high precision for those winemaking areas, encompassing a complete or almost complete classification according to the island of provenance, such as Gran Canaria (GC, 84.6%), La Gomera (GO, 100%), El Hierro (HI, 88.9%), La Palma (LP, 100%), and Lanzarote (LZ, 100%). However, it was more complex when DOs belonged to the same island and were thus closely related.

Table 6. LDA classification results based on DOs as percentages of assignments.

Original → / ↓ Predicted	DO T	DO O	DO Y	DO G	DO A	LP	HI	LZ	GO	GC
DO T	**62.2**	7.4	11.1	0.0	4.3	0.0	5.6	0.0	0.0	7.7
DO O	11.1	**85.2**	5.6	0.0	2.2	0.0	0.0	0.0	0.0	0.0
DO Y	2.2	0.0	**72.2**	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DO G	0.0	0.0	0.0	**100.0**	2.2	0.0	0.0	0.0	0.0	0.0
DO A	8.9	3.7	5.6	0.0	**87.0**	0.0	0.0	0.0	0.0	7.7
LP	2.2	3.7	0.0	0.0	0.0	**100.0**	0.0	0.0	0.0	0.0
HI	6.7	0.0	0.0	0.0	0.0	0.0	**88.9**	0.0	0.0	0.0
LZ	4.4	0.0	5.6	0.0	4.3	0.0	5.6	**100.0**	0.0	0.0
GO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**100.0**	0.0
GC	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**84.6**

Predicted DO listed in the rows and actual DO indicated in the columns. Abbreviations in Table S1.

The LDA based on aging groups yielded strong classification outcomes, achieving 86.8% accuracy (83.9% after cross-validation) with all variables, and 83.4% (78.5%) using stepwise selection. The major contributors to F1 included tartaric acid, gallic acid, and HBAs, whereas F2 was influenced by Prot, FR.HC, and Caff. According to Table S6, young wines ($\leq$2 years) were very accurately classified (93.6%), while old wines ($\geq$6 years) showed very low or poor classification accuracy (28.6%), with a high rate (71.4%) of misclassification into the short-aged category.

4. Discussion

Section 4 is structured using the same subsections as those presented in the Section 3 to maintain consistency in the organization of the content.

4.1. Overall Content

The pH in our samples was relatively high (3.73 $\pm$ 0.18), probably due to the warm climate of the Canary Islands compared to the temperatures in continental winemaking regions. However total acidity aligned with the reference values reported for red wines [32].

As expected, tartaric acid was the most abundant organic acid, followed by lactic, acetic, and malic acids. This distribution is consistent with general trends observed in previous studies of red wine acidity, where tartaric and lactic acids are typically the most prevalent [32].

Red wines generally exhibit lower total acidity than white wines, a trend observed when comparing our results with previous studies with Canary Island wines [33]. This difference is attributed to the extended maceration period in red winemaking, which promotes the extraction of potassium from grape skins and seeds. The extracted potassium precipitates as potassium bitartrate salts, thereby lowering the measurable acidity in the final wine. Thus, factors such as maceration temperature and duration play a key role in modulating acid retention and balance during fermentation.

According to the literature, grape malic acid content ranges from 1 to 6 g/L at harvest, though its content varies widely depending on grape cultivar, climate, and ripening stage [34]. This agrees with the content observed in our study for those wines not performing MLF (around 3.6 g/L). Malic acid presented a wide range of concentrations from 0.01 to 3.62 g/L. However, most wines (approximately 60%) had malic acid concentrations below 0.5 g/L, deducing that these red wines underwent almost complete MLF. Around 8% had significantly not undergone this process, as their L-lactic acid levels were below 0.5 g/L, while the remaining 32% had gone through a partial phase but had not completed MLF. Although most of the red wines underwent MLF, the differences in the extent of malic acid reduction confirm that the progress of MLF was influenced by various factors, including fermentation temperature, lactic acid bacteria strain, ethanol content, pH, wine acidity, and winemaking practices. These factors varied widely in our study and were consistent with findings from previous research on MLF [35].

Lactic acid concentrations in wine typically range from 0.1 to 2.5 g/L, depending on the extent of MLF and wine type [7], which agrees with our results, with the first quartile in 1.15 g/L and the third quartile in 2.29 g/L, even though some red wines presented anomalously high content above 5 g/L. MLF is associated with the production of minor volatile compounds, such as diacetyl and ethyl lactate, which influence on the aroma profile of the red wines. Diacetyl imparts buttery or butterscotch-like aromas, which in moderation are appreciated but excessive concentrations (typically above 0.2–0.3 mg/L) can be perceived as a flaw, overshadowing varietal characteristics and resulting in an undesirable sensory profile [36].

In grape must, citric acid concentrations generally range from 0.1 to 0.4 g/L, depending on the grape cultivar, environmental conditions, and maturity stage [37], which is in agreement with our results in the final wine (0.02–0.46 g/L). Lactic acid bacteria can metabolize citric acid during MLF, leading to the formation of intermediate compounds, including diacetyl, acetoin, and acetic acid. The acetic acid content in our study agrees with data reported in the literature, with the first quartile at 0.44 g/L and the third quartile at 0.75 g/L. These low concentrations (typically 0.2–0.7 g/L) can contribute to wine complexity and freshness, while excessive contents are perceived as vinegar-like off-flavors and significantly degrade wine quality. Regulatory limits for volatile acidity are generally 1.2 g/L for red wines in the European Union and many other wine-producing regions [38], which were only detected in a minority of the samples from this study.

In terms of gluconic acid, our results agree with the literature, with the third quartile being 0.52 g/L, and in red wines its content is generally below 0.5 g/L, while wines made from Botrytis-affected grapes can reach levels from 1 to 5 g/L or even higher. In our study, values of 2.29 g/L were also detected, indicating this affection was also present in some of the analyzed red wines. Gluconic acid is not metabolized by typical wine yeasts and thus persists through fermentation. Elevated levels have been associated with undesirable effects during aging, such as increased volatile acidity [9].

Similarly, the remarkable variability observed in phenolic acid concentrations aligns with previous studies, which have demonstrated that phenolic acid levels can vary considerably depending on grape composition and processing conditions [39]. Caft is normally the most abundant HCA in both grapes and wines, ranging from 17 to 111 mg/L in commercial red wines [15], which agrees with our results (4.4–73.1 mg/L). In general, its concentration is followed by Cuta at 14–89 mg/L, depending on the yeast strain and fermentation conditions [40], which is similar to the 3.7–65.8 mg/L observed in our study. The concentrations of 2SGl in red wine depend on the wine style and oxidation conditions, with our results being in agreement with the literature [41].

HBAs are normally presented in lower concentrations than HCAs. Gall is typically the most abundant in red wines, with levels often from 30 to over 170 mg/L, depending on the grape cultivar and winemaking practices [42]. This agrees with our results, where the first quartile was 22.4 mg/L and the third quartile was 51.4 mg/L. Syri has concentrations typically between 1.5 and 15 mg/L [43], in agreement with our first quartile at 9.5 mg/L and third quartile at 16.3 mg/L. Prot concentrations can vary significantly across wine styles and regions of production, appearing in concentrations of 0.5 to 99 mg/L [42], which in our study ranged from 0.4 to 33.8 mg/L.

In general, the results of HCA agree with other data published in the literature. Caft was the most abundant HCA, with slightly lower contents compared to previous studies on international commercial red wines [15], as well as 2SGl [10]. On the other hand, Caff and Coum appeared to have higher concentrations than in other regions [15]. Cuta concentrations were within the range of those previously reported [40]. Gall was the most abundant HBA, which agrees with that previously reported [42]. High variability was observed in Prot, as has already been documented in prior research [42].

4.2. Univariate Analysis

4.2.1. Cultivar

The findings of this study highlighted differences in the phenolic profiles of single cultivar red wines, demonstrating the strong influence of grape cultivar on wine chemistry. C cultivar showed significantly the highest pH and the lowest total acidity, standing out as less acidic overall. This probably could be due to advanced MLF, which increases pH and reduces titratable acidity. In fact, C cultivar red wines exhibited the highest lactic acid content and the lowest malic acid levels. This acidic profile might also be related to higher potassium retention in this cultivar compared to others, as has previously been described [19]. It can be hypothesized that the higher potassium content in this cultivar increases wine pH, facilitating the MLF by lactic bacteria. Consequently, red wines from this cultivar may undergo MLF more easily and typically reach a complete conversion, in contrast to red wines produced from other cultivars. Additionally, it is noteworthy that the lactic acid produced was significantly higher, which also indicates a higher initial malic acid concentration in the grapes. In general, the variation in malic and lactic acid concentrations supports differences in MLF extent. C, LN, and N cultivars showed near-complete malic acid degradation and correspondingly high lactic acid levels, suggesting more thorough secondary fermentation. In contrast, red wines from M and B cultivars retained more malic acid, indicating a partial conversion.

Acetic acid remained within acceptable sensory and legal limits across all cultivars. However, its concentration was notably higher in T cultivar, albeit still below spoilage thresholds. Elevated acetic acid can subtly affect aroma and freshness perceptions. The relationship between specific grape cultivars and acetic acid concentrations has been observed in various regions, although the underlying mechanisms are not fully understood. It is suggested that cultivar-specific factors, such as grape nutrient composition, skin

thickness, and susceptibility to microbial activity, may influence acetic acid production during fermentation [44]. These findings support the hypothesis that both grape genetics and microbial dynamics contribute to the modulation of volatile acidity in wine.

The differences observed in gluconic acid concentrations—higher in B cultivar and markedly lower in R cultivar—may reflect variations in grape health and susceptibility to fungal infections. Notably, the elevated levels in B cultivar could be linked to its highly compact bunch architecture, which reduces air circulation between berries, creating a microclimate that favors fungal growth and humidity retention. Compact clusters are more prone to mechanical pressure, skin rupture, and limited fungicide penetration, all of which elevate disease incidence [45]. Some studies confirmed that tight bunch morphology significantly increases susceptibility to Botrytis rot, particularly under humid conditions [46]. Therefore, the presence of high gluconic acid contents in certain cultivars may warrant closer monitoring of the vineyard microclimate, canopy management, and grape bunch structure to minimize fungal risk and ensure final red wine quality.

The phenolic acid profile varied significantly among cultivars, reflecting genetic influences on polyphenol synthesis and accumulation. N and LP cultivars exhibited consistently higher concentrations of total phenolic acids, HBAs, and HCAs, which are associated with enhanced co-pigmentation effects and color stability in red wines [47]. In contrast, R, C, and T cultivars displayed lower TPhe. Interestingly, FR.HC were significantly elevated for T, C, and R, suggesting increased enzymatic hydrolysis of bound esters or greater exposure to oxidative processes during vinification. This could be attributed to variations in grape maturity or vinification practices, as hydroxycinnamic esters are known substrates for enzymatic and oxidative reactions that shape wine aging and browning pathways [48].

While the levels of Prot and Syri remained unaffected by cultivars, the concentration of Gall acid exhibited considerable variation, with T cultivar showing significantly the highest concentrations. Gall is typically more abundant in grape cultivars with thicker skins or higher seed content. In fact, the T cultivar's Spanish name 'Tintilla' is indicative of its thicker and more pigmented skin. Compounds such as Coum and 2SGl helped to distinguish two groups of cultivars. R, S, and T cultivars had higher concentrations of these hydroxycinnamic derivatives, suggesting cultivar-dependent tendencies toward oxidation-related metabolite accumulation, which may relate to stress responses or specific enzymatic pathways. In fact, previous studies [15] highlighted S cultivar with higher levels in relation to other cultivars. This is in line with our results, as S cultivar was in the significant upper group. Caff was found in greatest abundance in R and M cultivars—both non-native grape cultivars from Canary Islands—possibly supporting cultivar differences in phenolic biosynthesis, as foreign cultivars might exhibit distinct phenolic fingerprints [49].

4.2.2. Geographical Origin

The results indicated geographic influences on acidity parameters from red wine across the Canary Islands. While pH values varied significantly among islands, total acidity and primary organic acids (tartaric, malic, lactic, and citric) remained relatively constant. This suggests uniformity in grape ripeness at harvest and similar enological techniques, which are known to stabilize acid composition in finished red wines despite regional climatic differences.

pH variability likely reflects the climatic conditions. Red wines from La Gomera Island showed the lowest pH, indicative of the higher perceived acidity, potentially due to cooler microclimates, which can limit sugar accumulation and preserve organic acids. Interestingly, despite this elevated acidity, red wines from La Gomera also exhibited the lowest concentrations of phenolic acids, possibly connected to lower phenolic extraction or cultivar limitations. Conversely, red wines from La Palma, Gran Canaria, and Tenerife

showed higher levels of certain phenolic acids, which might be connected to increased phenolic production with higher maturation or longer maceration times.

Elevated acetic and gluconic acid levels in red wines from El Hierro Island suggested a higher incidence of microbial activity or oxidative stress, potentially due to greater humidity or specific grape cultivars' susceptibility to fungal infection [46]. The co-occurrence of high gluconic and acetic acid concentrations supports this hypothesis.

Phenolic acid profiles showed more pronounced variability across islands, observing that red wines from El Hierro Island were distinguished by a significantly higher mean concentrations of Gall and Prot. These elevated concentrations may reflect a greater phenolic extraction, the use of autochthonous cultivars, or a vineyard defense response to microbial stress, which is in line with their higher acetic and gluconic acid content.

Red wines from Tenerife and La Palma Islands contained more Prot and Syri, consistent with the literature, supporting that humid and cooler environments promote the biosynthesis of hydroxybenzoic acids in grapes. In contrast, red wines from Gran Canaria showed the highest levels of Caff and Cuta, which might be due to metabolic differences in the cultivars employed there or vinification methods that preserve hydroxycinnamic derivatives, such as reduced oxidation or limited enzymatic activity.

The acid composition of red wines from Tenerife displayed notable variation across DOs from the same island, highlighting the influence of local terroir, grape cultivar, and winemaking practices. The higher pH in DO A (southern part of the island) may be linked to warmer temperatures, which promote acid degradation during ripening, reducing total acidity and increasing pH [50]. Conversely, DO O, known for its cooler and more humid microclimate, produced red wines with lower pH and higher TPhe and HCA concentrations, supporting the idea that cooler conditions favor acid stability [51]. The significantly higher malic acid concentration in DO G may reflect incomplete MLF, a typical trait of wines with high total acidity where bacterial activity is slower. Elevated acetic and gluconic acids in DO Y may signal increased microbial activity.

Regarding phenolic acids, DO O presented the highest levels of Caft and Cuta, suggesting factors favoring accumulation of hydroxycinnamic derivatives. This DO also recorded the highest concentration of TE.HC, indicating potential for greater wine stability and antioxidant capacity. DO Y and DO T also showed robust phenolic profiles, especially in Gall, Prot, and Syri. In contrast, those areas from the south of Tenerife, DO A and DO G, generally had lower TPhe and TE.HC, possibly reflecting differences in sun exposure, or less extractive winemaking techniques.

Overall, these findings suggest that DO designation within Tenerife significantly influenced the wine's acid profile, supporting regional differentiation and the potential for terroir-driven wine typicity.

4.2.3. Aging

Wine aging clearly determined the acid profile. Although pH and total acidity remained stable, the lower tartaric acid concentration in young wines may reflect the production technologies. So, young red wines are typically designed for early consumption, where freshness is prioritized over long-term stability. In contrast, red wines intended for aging often exhibit a higher initial acid content, which helps preserve structure and sensory balance through precipitation and complexation processes that naturally occur during bottle aging. Moreover, in young wines, tartaric stabilization processes using low temperatures to precipitate tartaric salts are relatively more aggressive than those designed for aged wines, which would be naturally stabilized by aging.

The higher lactic acid content in younger red wines is consistent with ongoing or recently completed MLF used to soften wine acidity. Higher acetic acid concentrations in

older wines may arise from slow oxidative processes or microbial activity, particularly from spoilage organisms, such as Acetobacter genus, which can be more active in red wines that are poorly protected or aged under suboptimal conditions. These compounds accumulate gradually and are often responsible for increased volatile acidity in older bottles. The slightly elevated citric acid levels in older wines could result from preferential degradation of other acids or specific microbial metabolic activity, such as by lactic acid bacteria under certain storage conditions [7].

The peak in FR.HC observed in short-aged wines may indicate a transitional state where these compounds are at their maximum extractability prior to polymerization or incorporation into larger phenolic complexes during extended aging. As phenolic compounds evolve, hydrolysis of esters and oxidative condensation reactions reduce the levels of free acids while increasing bound or polymeric forms [39].

From the phenolic acid perspective, older wines exhibited significantly higher levels of Gall and Prot, which is consistent with their release through hydrolysis of galloylated tannins and other complex phenolics during aging. The high HBA content in old wines supports this, as HBAs are degradation products of larger phenolic molecules, such as flavonoids and hydrolyzable tannins. However, this high HBA concentration might also reflect deliberate selection of red wines with initially higher phenolic content for aging, since phenol-rich wines tend to have greater structural integrity and oxidative resilience, making them more suitable for long-term cellaring [42].

In contrast, young wines showed significantly higher Syri concentrations, likely due to recent extraction from grape skins and minimal oxidative degradation. Short-aged wines displayed elevated levels of Caff and Coum, suggesting an intermediate phase where phenolic extraction is still active, but degradation and polymerization have not yet substantially progressed. This pattern reflects the dynamic nature of phenolic evolution in red wines, shaped by both chemical transformation and winemaking decisions, including maceration time, oxygen exposure, and aging conditions [42].

4.3. Correlations

The inverse relationship between pH and total acidity, and its weaker negative associations with tartaric, malic, and citric acids, reflected expected physicochemical behavior in wines, as higher acidity results in lower pH due to greater hydrogen ion concentrations. The positive correlation between pH and lactic acid supports this, as lactic acid is a weaker acid and, therefore, contributes less to pH reduction than the original malic acid.

Several of the statistically significant correlations observed in this study can be explained through known biological and enological mechanisms. For instance, the strong inverse correlation between malic acid and lactic acid ($r = -0.466$) is a direct reflection of the malolactic fermentation (MLF) process, where malic acid is decarboxylated into lactic acid by lactic acid bacteria, reducing the perceived acidity and enhancing wine smoothness. Total acidity's strong correlations with malic, citric, and gluconic acids underline their relevance in shaping the wine's acid profile. The correlation between gluconic and acetic acid ($r = 0.112$) was weak, but it suggests a shared microbial origin, as both compounds are indicative of spoilage. The presence of overripe grapes infected by *Botrytis Cinerea* may elevate the concentrations of both acids. However, it is important to note that acetic acid naturally increases during the aging process due to oxidation reactions and independent acetobacter activity [38].

The correlations between tartaric acid and phenolic acids like Gall, Caff, and TPhe suggest that red wines richer in the primary grape acids also tend to have higher phenolic acids, possibly due to enhanced extraction or preservation under acidic conditions. Lower pH and higher acidity are known to improve phenolic stability during winemaking and

aging [32]. This aligns with the negative correlation between pH and hydroxycinnamic acids obtained, supporting the idea that higher phenolic acid concentrations are associated with greater acidity and color stability, both critical for red wine aging and freshness [3].

The correlation observed between Caft and Coum could be explained due to the former being synthetized from Coum and tartaric acid [52]. On the other hand, the 2SGl is a metabolite that is formed through the reaction of Caft with glutathione [10], which could explain the correlation obtained between both HCAs.

Interestingly, a significant negative correlation between HCAs and 2SGl was observed, despite 2SGl being itself derived from a hydroxycinnamic acid (caftaric acid). This correlation was even more pronounced between the hydroxycinnamic esters of tartaric acid (TE.HC) and 2SGl. This suggests a precursor–product relationship, where the accumulation of 2SGl reflects the oxidative conversion of FR.HC, particularly Caft. As oxidation progresses—either enzymatically or chemically—FR.HC are consumed, and conjugated derivatives like 2SGl increase. Therefore, high levels of 2SGl may indicate greater oxidative processing of HCAs, which could explain the inverse relationship [53].

4.4. Discriminant Analysis

The PCA revealed clear groupings of wine organic acids, reflecting underlying chemical transformations and winemaking processes, such as MLF. For instance, Factor 1 distinguished wines based on total phenolic richness, particularly hydroxycinnamic derivatives like caftaric and cutaric acids, and their tartaric esters (TE.HC). These compounds were closely associated with grape cultivar and winemaking techniques, especially skin contact and oxidative stability [53]. Their strong loading on Factor 1 highlighted their role in defining the phenolic acid identity of red wines. Factor 2 separated hydroxybenzoic acids, such as Gall and Prot, which are known breakdown products of tannins and flavonoids during aging. Their position along the top quadrant suggested association with aged wine profiles and oxidative phenolic transformation. Lactic acid's isolated position in the negative region of Factor 2 reflects its origin from MLF, a microbiological process independent from phenolic evolution.

The proximity of total acidity, pH, gluconic acid, and citric acid near the plot center suggests that these components did not strongly define phenolic acid-based axes, though they remained essential for wine freshness and microbial stability. Notably, 2SGl loaded negatively on both axes, supporting its role as a protective oxidation product rather than a driver of phenolic diversity. Overall, the PCA supports that major organic and phenolic acids contribute differently to wine variability: acids like lactic and acetic acid mark fermentation processes and freshness, while phenolics dominate the variation in aged and structured wines.

Despite the high percentage of variance explained by the first two components (80.4%), the PCA did not result in clearly defined clusters based on cultivar or DO. This suggests that organic acid variability was distributed along continuous gradients, shaped by overlapping factors, such as grape biochemistry, microclimate, and winemaking practices. In this context, the unsupervised nature of PCA limited its ability to discriminate between subtly distinct groups.

The application of LDA to the acid profiles of Canary red wines demonstrated significant discriminatory capacity across different classifications, though the level of success varied depending on the complexity and distinctiveness of the groups. Grape cultivar was the most reliably predicted qualitative variable, especially when all acid variables were included in the model. The high classification accuracy (88.3%) suggests that grape genotype strongly influenced the biosynthesis and accumulation of major organic and phenolic acids, which might serve as effective chemotaxonomic markers. The dominant role of HCAs,

FR.HC, and Caft in the discriminant functions supports their utility as cultivar-specific metabolites. However, the drop in accuracy after cross-validation (68.8%) and the confusion observed for cultivars like LN and V cultivars pointed to overlapping acid profiles or intra-varietal variability. These may be attributed to shared ancestry, clonal variations, or similar vinification practices. Autochthonous Canary grapes are not cultivated in grape nurseries but are reproduced in nature with their own rootstocks, which leads to high clonal heterogeneity when compared to international cultivars.

The interpretation of the canonical discriminant functions provided relevant information about the separation patterns. For cultivar classification, the first function (F1) was driven by variables related to HCA content and structure (e.g., TE.HC and FR.HC), supporting potential varietal control over hydroxycinnamate metabolism. The second function (F2) was more influenced by Caft and Coum, reflecting how specific oxidation and esterification dynamics might differ among cultivars.

Island of provenance also showed robust discriminatory potential, reflecting the influence of climatic factors, such as soil, altitude, and microclimate, which affected acid metabolism in grapes. The consistent performance of the stepwise model (72.7% post-validation) reinforced the notion that a limited set of organic acids—particularly Caft, gallic, and gluconic acids—encapsulate key geographic signals. The inclusion of pH and lactic acid in the discriminant function 2 of the stepwise model may additionally reflect fermentation conditions and microbial activity, which can vary according to geographical origin. DO within Tenerife posed a greater challenge for classification. More modest performance may stem from the homogenizing effect of DO regulations, shared winemaking techniques, and similar cultivars across DOs. For example, Tacoronte-Acentejo (DO T) exhibited more frequent misclassifications, as this region bordered DO O and DO Y on the same island, making their acid profiles tend to be more similar. Nonetheless, the accurate classification of geographically or winemaking distinct DOs (e.g., La Gomera and El Hierro) implied that where differences in viticultural practices or terroir were more pronounced, acid profiles retained sufficient discriminatory power. The relevance of organic acids like malic, citric, and gluconic acid suggests a role for oxidative degradation and MLF processes in DO specific signatures.

In the case of Tenerife Island with five distinct wine regions, the reduced accuracy for DO classification (66.4% post-validation) compared to island classification supports the idea that larger-scale environmental factors (e.g., island-wide climate) generate more distinctive acid signatures than localized DOs, especially when common cultivars and similar practices are shared. This means LDA can help in capturing broad regional typicity more effectively than subtle subregional distinctions.

Our findings are consistent with earlier studies [17,18] that utilized chemometric techniques on organic acid compositions to classify wines with high accuracy. For instance, Huang et al. (2017) [17] successfully applied LDA to differentiate red wines based on tartaric, malic, citric, lactic, acetic, and succinic acid contents, achieving 100% classification accuracy in geographical identification, and over 86% for varietal classification of Cabernet Sauvignon, Merlot, and Pinot Noir wines. Similarly, Tang et al. (2015) [18] used a combination of organic acids and phenolic compounds to classify Chinese red wines and achieved 100% correct classification by region and 96% by grape cultivar using LDA. These high classification accuracies reported in prior work align with our results, particularly in demonstrating the discriminative power of minor acids, such as gluconic, gallic, and hydroxycinnamic acid derivatives (e.g., caftaric and coumaric), which were pivotal in differentiating red wines by cultivar and island origin. Importantly, while earlier research focused on large geographical distances or limited cultivar ranges, our study added novel

insights by showing that LDA retained strong discriminative power even within a relatively small and climatically diverse wine-producing region like the Canary Islands.

It is also important to recognize the limitations of LDA. Its effectiveness depends on the quality of group definitions, balanced sample sizes, and stability of chemical profiles over time. In regions like the Canary Islands, with complex vineyard mosaics and diverse cultivation practices, some overlaps are inevitable. While our study applied cross-validation to assess internal consistency, future studies would benefit from incorporating external validation strategies, such as k-fold cross-validation or the use of independent test subsets, to better simulate real-world predictive performance and minimize potential overfitting. These approaches are particularly relevant in wine authenticity research, where models must generalize across vintages and producers. Longitudinal designs involving multiple harvest years, wineries, or cultivars would also contribute to confirming the robustness of discriminant patterns and enhancing the external applicability and precision of classification models.

Wine aging status was also successfully classified, particularly for younger wines. The biochemical evolution of wine during aging—including acid hydrolysis, esterification, and phenolic polymerization—produced measurable shifts in acid concentrations. The high classification accuracy for young wines (93.6%) reflected their distinctive freshness and higher concentrations of primary acids. The lower accuracy for old wines and their frequent misclassification as short-aged may be due to the convergence of acid profiles during long-term aging, as well as bottle variation and oxidation effects. Notably, tartaric and gallic acids appeared as robust markers of aging stages.

These patterns align with known chemical kinetics of wine aging, where interconversion of phenolics and acid degradation often leads to more homogeneous profiles over time. The reduced classification accuracy of older wines (28.6%) supports the idea that prolonged bottle aging attenuates compositional differences, underscoring the challenges of classifying wines that have undergone extensive chemical convergence.

Collectively, these findings highlighted the efficacy of LDA as a multivariate classification technique for wine profiling. The results support the use of acid composition not only as a tool for wine authentication and traceability but also for understanding the chemical underpinnings of varietal, geographic, and temporal differentiation.

The use of supervised and unsupervised statistical models demonstrated that, while PCA is more focused on structure and acid variability, LDA might be useful for classification and identification. Together, they form a complementary statistical toolkit for wine characterization.

Future work integrating additional metabolomic and environmental data may further refine these models.

5. Conclusions

This study provided a detailed characterization of organic acid profiles in monovarietal red wines from the Canary Islands, demonstrating how grape cultivar, geographical origin, and aging distinctly shaped both the major and minor phenolic organic acid composition. The marked variability observed in acid concentrations, especially among malic, lactic, acetic, gallic, and caftaric acids, revealed the influence of genetic traits, viticultural practices, and winemaking decisions across a uniquely diverse insular landscape.

Differences in acid profiles among grape cultivars reflected the extent and completeness of MLF and suggested cultivar-specific metabolic or microbial interactions. Geographic origin, particularly at the island level, also contributed to significant differentiation in organic acid content, with certain acids (e.g., gallic acid, caftaric acid, and 2-S-glutathionylcaftaric acid) emerging as potential markers of regional identity. Additionally,

phenolic acid variation among DOs within Tenerife revealed subtle but consistent compositional differences that may serve as chemical signatures of local terroir. Aging further impacted the acid profile, especially through increased levels of tartaric and gallic acids in older wines and evolving trends in HBA and HCA.

These results not only support the use of organic acid profiling as a tool for red wine classification and traceability but also open several avenues for future research. First, additional longitudinal studies across vintages could help confirm the stability and robustness of the identified acid markers under varying climatic conditions. Second, integrating acid profiling with other chemical dimensions, such as volatile aroma compounds or elemental composition, could enhance multivariate models for origin authentication and typicity classification. Third, microbial ecology studies are warranted to better understand how native yeast and lactic acid bacteria strains across different islands modulate acid transformations during fermentation and aging. Finally, sensory analysis combined with compositional profiling could clarify the specific contributions of phenolic organic acids to mouthfeel and flavor perception, helping winemakers optimize style and quality.

In practical terms, the findings of this study offer valuable tools for the wine industry in several areas. The identification of acid-based markers can support quality control and certification processes, helping producers ensure consistency and compliance with denomination of origin standards. Wineries can also use these chemical fingerprints to strengthen the branding and market positioning of wines made from native grape cultivars, especially in a context where origin-linked authenticity is increasingly demanded by consumers. Moreover, winemakers may apply insights from acid profiling to guide fermentation management, blending decisions, and aging strategies, ultimately contributing to improved wine typicity, stability, and sensory quality.

In conclusion, this research contributes a foundational dataset on the organic acid composition of varietal Canary Island red wines and underscores the potential of these compounds as biochemical markers of cultivar and geographical identity. As climate change and global markets increasingly challenge traditional wine typicity, such molecular-level insights are essential for preserving and promoting the uniqueness of regional wine heritage.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/beverages11040102/s1. Table S1: Red wine sample distribution with abbreviations employed. Table S2: Phenolic acids quantified by HPLC-DAD. Table S3: Mean and standard deviation (between brackets) of acids according to the island of provenance. Table S4: Acid profile according to the DO from Tenerife Island. Table S5: Results of acids according to aging. Table S6: Correct classification rates (diagonal values) and misclassifications obtained from the LDA employed to differentiate red wines according to aging group.

Author Contributions: Conceptualization, J.D.-M. and C.D.-R.; methodology and formal analysis, J.H.-R.; data curation C.D.-R., J.D.-R., and J.H.-R.; writing—original draft preparation, J.H.-R.; writing—review and editing, C.D.-R.; supervision, J.D.-M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The datasets presented in this article are not readily available due to winemakers and cellars' privacy. Requests to access the datasets should be directed to jherasro@ull.edu.es.

Acknowledgments: We acknowledge Canary Island wineries for their support with the samples.

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

References

1. Chidi, B.S.; Bauer, F.F.; Rossouw, D. Organic acid metabolism and the impact of fermentation practices on wine acidity: A review. *S. Afr. J. Enol. Vitic.* **2018**, *39*, 1–15. [CrossRef]
2. Mairata, A.; Pou, A.; Martínez, J.; Puelles, M.; Labarga, D.; Portu, J. Organic mulches slightly influence the wine phenolic profile and sensory evaluation. *Food Chem.* **2024**, *457*, 140045. [CrossRef] [PubMed]
3. Grainger, K. *Wine Faults and Flaws: A Practical Guide*; Wiley Online Library: Hoboken, NJ, USA, 2021.
4. Sponholz, W. Wine spoilage by microorganisms. In *Wine Microbiology and Biotechnology*; CRC Press: Boca Raton, FL, USA, 1993; pp. 395–420.
5. Kim, J.; Choi, S.; Hong, Y.; Kim, D.; Lee, W.; Rhee, C.; Park, H. Isolation and characterization of tartaric acid-degrading bacteria from Korean grape wine pomace. *Food Sci. Preserv.* **2008**, *15*, 483–490.
6. Volschenk, H.; Van Vuuren, H.; Viljoen-Bloom, M. Malic acid in wine: Origin, function and metabolism during vinification. *S. Afr. J. Enol. Vitic.* **2006**, *27*, 123–136. [CrossRef]
7. Kučerová, J.; Široký, J. Study of changes organic acids in red wines during malolactic fermentation. *Acta Univ. Agric. Silvic. Mendel. Brun.* **2011**, *5*, 145–150. [CrossRef]
8. Mendes Ferreira, A.; Mendes-Faia, A. The role of yeasts and lactic acid bacteria on the metabolism of organic acids during winemaking. *Foods* **2020**, *9*, 1231. [CrossRef]
9. Hausinger, K.; Lipps, M.; Raddatz, H.; Rosch, A.; Scholten, G.; Schrenk, D. Automated optical grape-sorting of rotten grapes: Effects of rot infections on gluconic acid concentrations and glycerol/gluconic acid ratios in must and wine. *J. Wine Res.* **2015**, *26*, 18–28. [CrossRef]
10. Bouzanquet, Q.; Barril, C.; Clark, A.C.; Dias, D.A.; Scollary, G.R. A novel glutathione-hydroxycinnamic acid product generated in oxidative wine conditions. *J. Agric. Food Chem.* **2012**, *60*, 12186–12195. [CrossRef]
11. Heras-Roger, J.; Díaz-Romero, C.; Darias-Martín, J. What gives a wine its strong red color? Main correlations affecting copigmentation. *J. Agric. Food Chem.* **2016**, *64*, 6567–6574. [CrossRef]
12. de Lima, A.N.; Magalhães, R.; Campos, F.M.; Couto, J.A. Survival and metabolism of hydroxycinnamic acids by *Dekkera bruxellensis* in monovarietal wines. *Food Microbiol.* **2021**, *93*, 103617.
13. Ferrer-Gallego, R.; Hernández-Hierro, J.M.; Brás, N.F.; Vale, N.; Gomes, P.; Mateus, N.; De Freitas, V.; Heredia, F.J.; Escribano-Bailón, M.T. Interaction between wine phenolic acids and salivary proteins by saturation-transfer difference nuclear magnetic resonance spectroscopy (STD-NMR) and molecular dynamics simulations. *J. Agric. Food Chem.* **2017**, *65*, 6434–6441. [CrossRef] [PubMed]
14. Bubola, M.; Rusjan, D.; Lukić, I. Crop level vs. leaf removal: Effects on Istrian Malvasia wine aroma and phenolic acids composition. *Food Chem.* **2020**, *312*, 126046. [CrossRef] [PubMed]
15. Lima, A.; Oliveira, C.; Santos, C.; Campos, F.M.; Couto, J.A. Phenolic composition of monovarietal red wines regarding volatile phenols and its precursors. *Eur. Food Res. Technol.* **2018**, *244*, 1985–1994. [CrossRef]
16. Baiano, A.; Terracone, C. Varietal differences among the phenolic profiles and antioxidant activities of seven table grape cultivars grown in the south of Italy based on chemometrics. *J. Agric. Food Chem.* **2011**, *59*, 9815–9826. [CrossRef] [PubMed]
17. Huang, X.; Jiang, Z.; Tan, J.; Li, R. Geographical origin traceability of red wines based on chemometric classification via organic acid profiles. *J. Food Qual.* **2017**, *2017*, 2038073. [CrossRef]
18. Tang, K.; Ma, L.; Han, Y.; Nie, Y.; Li, J.; Xu, Y. Comparison and chemometric analysis of the phenolic compounds and organic acids composition of Chinese wines. *J. Food Sci.* **2015**, *80*, C20–C28. [CrossRef]
19. Heras-Roger, J.; Díaz-Romero, C.; Darias-Rosales, J.; Darias-Martín, J. Volcanic Terroirs: Exploring Minerals in Canary Red Wine. *Beverages* **2024**, *10*, 107. [CrossRef]
20. Alonso González, P.; Parga Dans, E.; Hernández González, M.M.; Arribas Blázquez, P.; Acosta Dacal, A.C.; Pérez Luzardo, O. Unveiling terroir: Evaluating the magnitude of the heterogeneity and its main drivers in the Canary Islands wines. *Cogent Food Agric.* **2024**, *10*, 2334997. [CrossRef]
21. Díaz Romero, C.; Tort, S.; Díaz, E.; Pérez-Trujillo, J.P. Chemical characterization of bottled sweet wines from the Canary Islands (Spain). *Acta Aliment.* **2003**, *32*, 247–256. [CrossRef]
22. Díaz, C.; Conde, J.; Méndez, J.; Pérez Trujillo, J. Chemometric studies of bottled wines with denomination of origin from the Canary Islands (Spain). *Eur. Food Res. Technol.* **2002**, *215*, 83–90. [CrossRef]
23. Díaz, C.; Conde, J.E.; Claverie, C.; Díaz, E.; Trujillo, J.P.P. Conventional enological parameters of bottled wines from the Canary Islands (Spain). *J. Food Compos. Anal.* **2003**, *16*, 49–56. [CrossRef]
24. Pérez-Trujillo, J.P.; Hernández, Z.; López-Bellido, F.J.; Hermosín-Gutiérrez, I. Characteristic phenolic composition of single-cultivar red wines of the Canary Islands (Spain). *J. Agric. Food Chem.* **2011**, *59*, 6150–6164. [CrossRef] [PubMed]
25. Darias-Martín, J.J.; Andrés-Lacueva, C.; Díaz-Romero, C.; Lamuela-Raventós, R.M. Phenolic profile in varietal white wines made in the Canary Islands. *Eur. Food Res. Technol.* **2008**, *226*, 871–876. [CrossRef]

26. Master, O.; Patronage, O. *Compendium of International Methods of Wine and Must Analysis*; International Organisation of Vine and Wine: Dijon, France, 2024.
27. Almela, L.; Lázaro, I.; Lopez-Roca, J.M.; Fernandez-Lopez, J.A. Tartaric acid in frozen musts and wines. Optimization of Rebelein's method and validation by HPLC. *Food Chem.* **1993**, *47*, 357–361. [CrossRef]
28. Ibern-Gómez, M.; Andrés-Lacueva, C.; Lamuela-Raventós, R.M.; Waterhouse, A.L. Rapid HPLC analysis of phenolic compounds in red wines. *Am. J. Enol. Vitic.* **2002**, *53*, 218–221. [CrossRef]
29. Ginjom, I.; D'Arcy, B.; Caffin, N.; Gidley, M. Phenolic compound profiles in selected Queensland red wines at all stages of the wine-making process. *Food Chem.* **2011**, *125*, 823–834. [CrossRef]
30. Meng, J.; Fang, Y.; Qin, M.; Zhuang, X.; Zhang, Z. Varietal differences among the phenolic profiles and antioxidant properties of four cultivars of spine grape (*Vitis davidii* Foex) in Chongyi County (China). *Food Chem.* **2012**, *134*, 2049–2056. [CrossRef]
31. Hernández, T.; Estrella, I.; Carlavilla, D.; Martín-Álvarez, P.J.; Moreno-Arribas, M.V. Phenolic compounds in red wine subjected to industrial malolactic fermentation and ageing on lees. *Anal. Chim. Acta* **2006**, *563*, 116–125. [CrossRef]
32. Lima, M.M.; Choy, Y.Y.; Tran, J.; Lydon, M.; Runnebaum, R.C. Organic acids characterization: Wines of Pinot noir and juices of 'Bordeaux grape varieties'. *J. Food Compos. Anal.* **2022**, *114*, 104745. [CrossRef]
33. Darias-Martín, J.; Socas-Hernández, A.; Díaz-Romero, C.; Díaz-Díaz, E. Comparative study of methods for determination of titrable acidity in wine. *J. Food Compos. Anal.* **2003**, *16*, 555–562. [CrossRef]
34. Frioni, T.; Collivasone, R.; Canavera, G.; Gatti, M.; Gabrielli, M.; Poni, S. Identifying the best parameters to determine genotype capability to retain adequate malic acid at harvest and in final wines. *OENO One* **2023**, *57*, 247–256. [CrossRef]
35. Mendoza, S.N.; Canon, P.M.; Contreras, Á.; Ribbeck, M.; Agosin, E. Genome-scale reconstruction of the metabolic network in Oenococcus oeni to assess wine malolactic fermentation. *Front. Microbiol.* **2017**, *8*, 534. [CrossRef] [PubMed]
36. Bartowsky, E.J.; Francis, I.L.; Bellon, J.R.; Henschke, P.A. Is buttery aroma perception in wines predictable from the diacetyl concentration? *Aust. J. Grape Wine Res.* **2002**, *8*, 180–185. [CrossRef]
37. Grigoryan, B.; Mikayelyan, M. The investigation of bioactive compounds in the Charentsi grape variety and its derived wines. *Bioact. Compd. Health Dis.* **2023**, *6*, 303–314. [CrossRef]
38. Vilela-Moura, A.; Schuller, D.; Mendes-Faia, A.; Silva, R.D.; Chaves, S.R.; Sousa, M.J.; Côrte-Real, M. The impact of acetate metabolism on yeast fermentative performance and wine quality: Reduction of volatile acidity of grape musts and wines. *Appl. Microbiol. Biotechnol.* **2011**, *89*, 271–280. [CrossRef]
39. Hornedo-Ortega, R.; González-Centeno, M.R. Phenolic Compounds of Grapes and Wines: Key Compounds and Implications in Sensory Perception. In *Chemistry and Biochemistry of Winemaking, Wine Stabilization and Aging*; IntechOpen: London, UK, 2021; Chapter 1.
40. Petropulos, V.I.; Ricci, A.; Nedelkovski, D.; Dimovska, V.; Parpinello, G.P.; Versari, A. Influence of Yeast Strains on Phenolic Composition and Antioxidant Activity of Vranec wines. In Proceedings of the XXIII Congress of Chemists and Technologists of Macedonia, Ohrid, Republic of Macedonia, 8–11 October 2014; p. 80.
41. Vallverdú-Queralt, A.; Verbaere, A.; Meudec, E.; Cheynier, V.; Sommerer, N. Straightforward method to quantify GSH, GSSG, GRP, and hydroxycinnamic acids in wines by UPLC-MRM-MS. *J. Agric. Food Chem.* **2015**, *63*, 142–149. [CrossRef]
42. Vichapong, J.; Santaladchaiyakit, Y.; Burakham, R.; Srijaranai, S. Cloud-point extraction and reversed-phase high performance liquid chromatography for analysis of phenolic compounds and their antioxidant activity in Thai local wines. *J. Food Sci. Technol.* **2014**, *51*, 664–672. [CrossRef]
43. Zhang, B.; Liu, R.; He, F.; Zhou, P.; Duan, C. Copigmentation of malvidin-3-O-glucoside with five hydroxybenzoic acids in red wine model solutions: Experimental and theoretical investigations. *Food Chem.* **2015**, *170*, 226–233. [CrossRef]
44. Zgardan, D.; Mitina, I.; Sturza, R.; Mitin, V.; Rubtov, S.; Grajdieru, C.; Behta, E.; Inci, F.; Haciosmanoglu, N. A survey on acetic acid bacteria levels and volatile acidity in several wines of the Republic of Moldova. *Biol. Life Sci. Forum* **2023**, *26*, 79.
45. Zyprian, E.; Richter, R.; Rossmann, S.; Theres, K.; Töpfer, R. Molecular Analysis of Bunch Architecture in Grapevine. In Proceedings of the XII International Conference on Grapevine Breeding and Genetics, Bordeaux, France, 15–20 July 2018; pp. 327–330.
46. Kocsis, M.; Csikász-Krizsics, A.; Szata, B.E.; Kovács, S.; Nagy, A.; Mátai, A.; Jakab, G. Regulation of cluster compactness and resistance to Botrytis cinerea with β-aminobutyric acid treatment in field-grown grapevine. *Vitis* **2018**, *57*, 35.
47. Jensen, J.S.; Demiray, S.; Egebo, M.; Meyer, A.S. Prediction of wine color attributes from the phenolic profiles of red grapes (*Vitis vinifera*). *J. Agric. Food Chem.* **2008**, *56*, 1105–1115. [CrossRef] [PubMed]
48. Oliveira, C.M.; Ferreira, A.C.S.; De Freitas, V.; Silva, A.M. Oxidation mechanisms occurring in wines. *Food Res. Int.* **2011**, *44*, 1115–1126. [CrossRef]
49. Palade, L.M.; Popa, M.E. Polyphenol fingerprinting approaches in wine traceability and authenticity: Assessment and implications of red wines. *Beverages* **2018**, *4*, 75. [CrossRef]
50. Ramos, M.C.; de Toda, F.M. Variability in the potential effects of climate change on phenology and on grape composition of Tempranillo in three zones of the Rioja DOCa (Spain). *Eur. J. Agron.* **2020**, *115*, 126014. [CrossRef]

51. Naczk, M.; Shahidi, F. Phenolics in cereals, fruits and vegetables: Occurrence, extraction and analysis. *J. Pharm. Biomed. Anal.* **2006**, *41*, 1523–1542. [CrossRef]
52. Honisch, C.; Osto, A.; de Matos, A.D.; Vincenzi, S.; Ruzza, P. Isolation of a tyrosinase inhibitor from unripe grapes juice: A spectrophotometric study. *Food Chem.* **2020**, *305*, 125506. [CrossRef]
53. Cheynier, V. Phenolic compounds: From plants to foods. *Phytochem. Rev.* **2012**, *11*, 153–177. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.