



Article

The Influence of Climatic Conditions Associated with Altitude on the Volatile Composition of Cabernet Sauvignon Wines from Argentina, Spain and Portugal

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Abstract: In addition to winemaking techniques, wine's quality and typicity are linked to the place where the grapes are grown. Climate, soil and the cultivar are major drivers of the terroir's expression. Moreover, climate change is affecting the distribution of grapevine varieties in different wine-growing regions because changes in climatic conditions over the past years is affecting grape production. This study investigated the influence of some terroir parameters on the volatile composition of Cabernet Sauvignon wines. Eight wines from vineyards sited in Argentina, Spain and Portugal with altitudes between 2400 and 77 m above sea level (a.s.l.) with different soils and climatic conditions were selected. The results suggested that the vineyard's place significantly modified the volatile composition of Cabernet Sauvignon wines because all chemical groups of volatiles quantified were affected. Volatile acids, C6 compounds, aldehydes, esters and terpenes showed the highest concentrations at 2400 m a.s.l., where the highest thermal amplitude was observed. In Portugal, where the vineyard studies were sited at lower altitudes (77 m a.s.l.) and under warm climatic conditions, high concentrations of alcohols and lactones were observed. Alcohols also showed high concentrations in wines from vineyards sited at 413 and 155 m a.s.l. (Spain). Principal component analysis showed the positive correlation of Cabernet Sauvignon wines located at higher altitudes with terpenes. On the contrary, wines from grapes grown at lower altitude conditions exhibited a correlation with alcohols and lactones.

Keywords: climatic change; aroma compounds; climatic conditions; vineyard altitude



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1. Introduction

Cabernet Sauvignon stands as one of the most widely cultivated grape varieties for winemaking across the world, with 340,000 ha [1]. Spain has the largest vineyard area in the world, with 955,000 ha in 2022, and Cabernet Sauvignon accounted for 2% of this area (18,851 ha). Argentina, with 207,000 ha, has the seventh largest vineyard surface, with 7% of the Cabernet Sauvignon variety, and Portugal is the ninth in terms of vineyard surface, 193,000 ha, with 1% of Cabernet Sauvignon (1985 ha) [1]. Cabernet Sauvignon is grown in different environmental conditions due to its excellent adaptivity. It is a long-cycle variety with average temperature requirements between 15 °C and 19 °C, and the local environmental conditions can influence the quality of the grape and its physical-chemical and sensory characteristics [2,3]. Cabernet Sauvignon wines tend to have an intense red color and are characterized by fruity, floral and herbal aromas [4].

Climate has the greatest influence on the grapes' and wines' composition and quality. Temperature plays an important role in the growth of vines and fruits, affecting grapes'

and wine's quality [5]. A number of vine-based bioclimatic indices have been proposed with the aim of characterizing viticultural areas and determining the suitability of different grape varieties for cultivation in the environment of a given region [6–9]. One of the most frequently used indices is the Winkler index (or sum of heat in growing degree-days), with a base temperature of 10 °C during the vegetative period of the vine. Another widely used index is the Huglin index, in which the sum of temperature over the temperature threshold of 10 °C is calculated and then summed for all days from the beginning of April to the end of September. The Huglin index can be used to estimate the suitability of specific regions for various grapevine varieties. Another one, the Fregoni Quality Index (FI), takes into account the thermal amplitude during the month of ripening and the number of days with temperatures below 10 °C [8].

Climate change has increased the temperature, and it will continue increasing [10]. The climatic conditions in traditional wine-growing regions were previously characterized by warm temperate conditions, but climate change has increased the temperatures. These changes include an increase in temperature, a greater frequency of heatwaves and a more extensive occurrence of droughts [3]. This situation has significant effects on grapevines' physiology and especially the composition of grape volatiles, which are the compounds responsible for wine's aroma and flavor. Higher temperatures may lead to lower levels of white aromatic grape varieties at equivalent sugar concentrations [11]. Therefore, temperature influences the synthesis and degradation of volatile compounds in grapes. Higher temperatures during ripening can accelerate the breakdown of certain volatile compounds, leading to changes in the aroma profiles. Additionally, warmer temperatures can alter the balance of primary and secondary metabolites in grapes, affecting the development of aromas [12,13].

One strategy for the mitigation of climate change is the cultivation of vines in regions with high latitudes and altitudes [14,15]. Altitude affects temperature and solar irradiation, modifying the mesoclimate. Altitude plays a crucial role in grape cultivation, as it can affect the temperature, sunlight exposure, and soil characteristics. Higher altitudes are correlated with cooler temperatures, which can slow down the ripening process and preserve acidity in grapes, contributing to the freshness and complexity of wines. It was reported by Alessandrini et al. [16] and Falcão et al. [17] how altitude modified the aroma composition of Cabernet Sauvignon and Merlot from different altitudes. Cabernet Sauvignon wines from vineyards at 774 and 1415 m a.s.l. showed differences in 2-methoxy-3-isobutylpyrazine. Wines from 774 m a.s.l. were characterized by red fruit and jam aromas, and those from higher altitudes by bell pepper aromas. Furthermore, a robust negative correlation was noted between vineyards' altitudes and seasonal temperature values. This observation indicated that in the highest vineyards, both winter and summer seasons tend to be cooler [17].

Wine's volatile compounds depend on the grape variety, environmental conditions, soil type, solar radiation, altitude, and viticultural and oenological management [18]. In Malbec wines, the volatile compounds were correlated with altitude and the average minimum temperature in the month of harvest. Alcohols in general and 2-phenylethanol in particular (rose flower flavor), as well as esters ethyl isobutyrate and ethyl isovalerate (associated with floral and fruity aromas), increased in cooler conditions [19]. Terpenes, mainly related to herbal flavors, and norisoprenoids, related to fruity flavors, are more concentrated in warm climates [20].

In the context of climate change, understanding the effect of altitude on volatile compounds will allow us to make decisions according to the type of wine we want to produce. In this sense, the possibility of cultivating grape cultivars at high altitudes with a cooler climate needs to be studied, relating the effects of altitude on the chemical components. It has not been previously studied how volatile compounds vary in wines from three different countries with altitudes ranging from 77 to 2400 m above sea level.

The aim of this work was to evaluate the volatile compounds of Cabernet Sauvignon wines from vineyards of Argentina, Spain and Portugal sited at different altitudes. An anal-

ysis was conducted to assess the effects of altitude and its associated climatic characteristics on the aroma compounds of Cabernet Sauvignon wine

2. Materials and Methods

2.1. Vineyard Conditions and Wines

This study was carried out in eight commercial vineyards of Cabernet Sauvignon. These vineyards were located at different altitudes in different viticultural areas that represent different climatic conditions, namely Jujuy and Mendoza in Argentina, Lisbon in Portugal, and Navarra, Albacete, Lérida and Penedés in Spain (Table 1). The Argentinean and Portuguese climatic data were obtained from the national service of each country and from the station close to the vineyards. In the case of Spain, the data were collected from meteorological stations of each different community. All vineyards were trained via vertical shoot positioning, with short pruning. No relevant vineyard management was applied.

Cabernet Sauvignon wines, all from the 2022 harvest, were produced with grapes grown at the different vineyards selected from Argentina, Spain and Portugal. Wines were vinified by application of the conventional method of red winemaking, without contact with wood. Similar conditions were applied throughout the vinification process.

Wines from different altitudes (meters above sea level, m a.s.l.) and countries were coded as follows:

- Wines from Argentina (AR): altitudes of 2400 m a.s.l. (AR-2400), 1200 m a.s.l. (AR-1200) and 900 m a.s.l. (AR-900);
- Wines from Portugal (PT): an altitude of 77 m a.s.l. (PT-77);
- Wines from Spain (SP): altitudes of 886 m a.s.l. (SP-886), 413 m a.s.l. (SP-413), 240 m a.s.l. (SP-240) and 155 m a.s.l. (SP-155).

Weather conditions were measured with an automated meteorological station located in the vineyards. Temperature, precipitation and different viticultural indices, namely the Winkler Index and Huglin Heliothermic Index, were calculated. The Winkler index (WI) is based on the summation of heat of growing degree-days (GDD) above 10 °C from 1 April to 31 September in the Northern Hemisphere and from 1 October to 31 March in the Southern Hemisphere [9]. In addition, the Huglin index is also used in viticulture to describe the thermal availability in different territories. The Huglin index (HI) relates daily mean temperatures to daily maximum temperatures and a length coefficient in the period from 1 April to 30 September in Northern Hemisphere and from 1 October to 31 March in the Southern Hemisphere [7]. These indices are commonly used in studies of viticulture and climate, helping to define the representative variability of viticulture climates worldwide.

2.2. Chemical Composition of Wines

Basic parameters of the wines (alcohol content, dry matter, reducing sugars, lactic and total acidity, glycerol and pH) were determined using a Y200 autoanalyzer from Biosystems in ICVV (Spain), calibrated according to OIV [21]. Analyses were performed in triplicate.

2.3. Identification and Quantification of the Wines' Volatile Compounds

Extraction was performed using 8 mL of wine with 400 µL of dichloromethane and 4-nonanol (Merck, ref. 818,773, Darmstadt, Germany) as internal standard following the methodology described by Coelho et al. [22]. Volatile compounds were extracted from each of the wines in triplicate.

Table 1. Location, altitude and thermal index of the vineyards.

| Country | Argentina (AR) | | | Spain (SP) | | | Portugal (PT) | |
|--------------------------|------------------------|--------------------|------------------------|--------------|--------------|-------------------|-------------------|--------------|
| Location | Jujuy | Mendoza-San Carlos | Mendoza-Ugarteche | Albacete | Navarra | Penedes | Lérida | Lisbon |
| Altitude (m a.s.l.) | 2400 (AR-2400) | 1200 (AR-1200) | 900 (AR-900) | 866 (SP-866) | 413 (SP-413) | 240 (SP-240) | 155 (SP-155) | 77 (PT-77) |
| Soil type | Sandy loam with gravel | Sandy loam | Sandy loam | Clay loam | Sandy loam | Clay loam | Gravels | Sandy loam |
| Winkler Index | 1742 III | 2048 IV | 1671 III | 2063 IV | 1845 III | 2297 V | 2067 IV | 2064 IV |
| Huglin Index | 2248 Temperate Warm | 3486 Very Warm | 2285 Temperate Warm | 2936 Warm | 2550 Warm | 3348 Very Warm | 3145 Very Warm | 2542 Warm |
| Min Temperature (°C) | 6.9 | 10.2 | 9.2 | 14.3 | 9.0 | 14.6 | 10.6 | 10.9 |
| Max Temperature (°C) | 22.1 | 24.7 | 23.5 | 20.5 | 21.4 | 22.4 | 22.1 | 22.3 |
| Average Temperature (°C) | 14.5 | 17.5 | 16.3 | 8.2 | 15.2 | 18.5 | 16.3 | 16.6 |
| Precipitation (mm) | 733 | 17 | 365 | 375 | 364 | 310 | 373 | 798 |

Altitude is expressed in meter above sea level (m a.s.l.).

Analysis of the volatile composition was performed using an Agilent 7890 gas chromatograph (GC) coupled to an Agilent 7000C triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). Samples were injected in splitless mode. Chromatographic separation was performed on a DB-WAX ultra-inert (30 m, 0.25 mm i.d., 0.25 μ m film thickness; Agilent Technologies, Santa Clara, CA, USA). The temperature of the injector was programmed to ramp from 20 °C to 250 °C at a rate of 180 °C/min. The oven temperature was maintained at 60 °C for 2 min, then rose from 60 °C to 234 °C with a gradient of 3 °C/min and 5 °C/min to 250 °C, and was finally held for 10 min at 250 °C. The carrier gas was helium N60 (Air Liquide, Paris, France), with a flow of 1 mL/min. The detector was set to electronic impact mode (70 eV), with an acquisition range from 29 m/z to 360 m/z , and an acquisition rate of 610 ms. Identification was carried out with Mass Hunter Qualitative Analysis software Version B.07.00 (Agilent Technologies, Santa Clara, CA, USA) using the NIST library and by comparison with the mass spectra and retention index of chromatographic standards (Sigma-Aldrich, Darmstadt, Germany). The compounds were quantified in terms of 4-nonanol equivalents.

2.4. Statistical Analysis

Differences in the volatile composition among wine samples from different countries and altitudes were analyzed using ANOVA and Tukey's honestly significant difference (HSD) test. Principal component analysis (PCA) was performed using chemical groups of volatiles to visualize graphically the distribution of different wines on the basis of the altitude of the vineyards and countries. The relationships between altitude and volatiles were assessed by Pearson correlation analysis. All analyses were performed using the XLSTAT statistical package from Addinsoft (Paris, France, 2022).

3. Results and Discussion

3.1. Climatic Characteristics of the Wine-Growing Regions

The influence of terroir in grape cultivation plays a fundamental role in determining the quality of grapes and wine. The climate is one of the most critical components of the terroir. Factors such as temperature, rainfall and humidity influence grapevines' growth and grape ripening. Table 1 shows the location, altitude, climatic conditions (temperature and precipitation) and climatic index of the vineyards. Vineyards sited at 1200 m a.s.l. (AR), 866 m a.s.l. (SP) and 240 m a.s.l. (SP) showed warmer mean temperatures. The coldest mean temperature was reached at 240 m a.s.l. (AR). This vineyard (AR-2400) showed the highest thermal amplitude, with a maximum temperature of 22.1 °C and a minimum temperature of 6.9 °C. The production of high-quality grapes relies on the daily thermal amplitude, which stems from the lower night-time temperatures typically found in high-elevation plots [23]. In vineyards with lower night temperatures, grapevines have a greater potential to accumulate color and volatile compounds [24]. On the other hand, the highest maximum temperatures were reached by the vineyards in Mendoza (AR-1200 and AR-900) with 24.7 °C and 23.5 °C, respectively. However, the coldest temperature was reached in Albacete (SP-866). With respect to the rainfall, we observed higher levels for PT-77 and AR-2400 (798 mm and 733 mm respectively) and the lowest level was observed for AR-1200 (175 mm).

Regarding the thermal indices, the Winkler index (WI) showed different classes based on the GDD; thus, the vineyards of this study were sited in Classes III, IV and V. In this sense, AR-2400, AR-900 and SP-413 were favorable for high production of standard to good quality table wines (Class III). On the other hand, AR-1200, PT-77, SP-866 and SP-155 were classified as favorable for high production of acceptable table wine quality at best (Class IV). Finally, SP-240 (Class V) was defined by the Winkler index as typically only suitable for extremely high production of fair quality table wine or table grape varieties destined for early-season consumption.

With respect to the heliothermic index (HI), we observed two growing areas classified as very warm, one in Argentina (AR-1200) and two in Portugal (SP, 155 and SP-155). Moreover, three areas were classified as warm, one in Portugal (PT-77) and two in Spain (SP-413 and SP-866). Finally, two areas in Argentina were classified as temperate warm (AR-2400 and AR-900).

Grapevines are grown in regions where temperatures average 13 °C–21 °C during the growing season [25]. These temperature thresholds are predominantly observed in the mid-latitude regions of continents across both hemispheres, including Europe, North and South America, Australia, New Zealand and South Africa. Cabernet Sauvignon is a warm-to-hot climate variety, with growing seasons ranging from 16 °C–20 °C [25]. The temperature variability among vineyards from countries and altitudes included in this study showed average temperatures during the growing season of 14.5 °C–18.5 °C, with the lowest temperature being 6.9 °C and the highest one being 24.7 °C.

3.2. Chemical Parameters of Cabernet Sauvignon Wines

Table 2 shows the chemical composition of Cabernet Sauvignon wines from different altitudes (77 to 2400 m a.s.l.) and countries (Argentina, Portugal and Spain).

The results showed a tendency of the ethanol content to increase by country when the altitude decreased; thus, PT-77 and SP-155 showed the highest values of ethanol (12.7% vol). In Argentina, this tendency was not observed, where the highest level of ethanol was observed at 900 m a.s.l.; however, the lowest level was shown at 1200 m a.s.l. High values of total acidity (5.4 g/L) and lactic acid (1.6 g/L) were shown in Argentina (AR-2400). However, pH in AR-2400 showed the highest value (3.76). High pH values were shown for all wines of Argentina and Portugal. Spain showed the highest total acidity (5.5 g/L) at 866 m a.s.l. (SP-886). As the altitude increased, temperature tended to decrease, typically at a rate of approximately 1.0 °C per 100 m in elevation. Consequently, vineyards situated at higher elevations experienced delayed budburst and flowering [26]. This delay in ripening in vineyards at higher altitudes resulted in higher potential for producing high-quality grapes, characterized by elevated acidity and lower alcohol levels, particularly with the anticipated warmer temperatures in the future. This phenomenon fosters the maximum expression of terroir [26]. Consequently, wines originating from high-altitude vineyards are renowned for their freshness, aromatic complexity, and distinctively high acidity, coupled with a lower alcohol content [23].

3.3. Total Volatile Composition of Cabernet Sauvignon Wines

The total volatile concentration ($\mu\text{g/L}$) of Cabernet Sauvignon wines from vineyards sited at different altitudes and countries is shown in Figure 1. The present findings suggest that altitude significantly modified the volatile composition of Cabernet Sauvignon wines. Altitude is an important determinant of wine's composition and quality [26]. The influence of altitude on the grapes' chemical composition (sugars, acids, some phenolic compounds and volatile organic compounds) has been observed by some authors [16,24]. However, the altitude factor seems to be cultivar-dependent.

Table 2. General physical-chemical parameters of Cabernet Sauvignon wines from Argentina, Spain and Portugal.

| Country | Altitude | Density | Ethanol | Dry Matter | Glucose+Fructose | Total SO ₂ | Free SO ₂ | Lactic Acid | Total Acidity | Glycerol | pH |
|----------------|----------|---------|---------|------------|------------------|-----------------------|----------------------|-------------|---------------|----------|------|
| | | (g/mL) | (% vol) | (g/L) | (g/L) | (mg/L) | (mg/L) | (g/L) | (g/L of TA) | (g/L) | |
| Argentina (AR) | AR-2400 | 0.993 | 12.5 ab | 29 ab | 0.1 | 34 | 3 | 1.6 | 5.4 a | | 3.76 |
| Argentina (AR) | AR-1200 | 0.994 | 12.0 b | 31 ab | 0.1 | 65 | 8 | 1.0 | 4.6 b | 7.7 | 3.63 |
| Argentina (AR) | AR-900 | 0.993 | 12.6 ab | 30 ab | 0.2 | 57 | 14 | 1.3 | 4.9 ab | 7.6 | 3.73 |
| Spain (SP) | SP-886 | 0.993 | 12.5 ab | 28 ab | 0.3 | 66 | 20 | 1.0 | 5.5 a | 6.2 | 3.51 |
| Spain (SP) | SP-413 | 0.992 | 12.4 ab | 24 b | 0.3 | 28 | 1 | 0.6 | 4.9 ab | 7.6 | 3.40 |
| Spain (SP) | SP-240 | 0.994 | 12.6 ab | 34 ab | 0.3 | 45 | 18 | 0.6 | 4.6 b | 6.3 | 3.46 |
| Spain (SP) | SP-155 | 0.994 | 12.7 ab | 34 ab | 0.4 | 70 | 20 | 0.6 | 4.8 ab | 7.0 | 3.41 |
| Portugal (PT) | PT-77 | 0.992 | 12.7 ab | 25 ab | 0.1 | 35 | 7 | 1.0 | 4.8 ab | 7.4 | 3.70 |
| Sig. A | | ns | * | * | ns | ns | ns | ns | ** | ns | ns |
| Sig. C | | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns |

Sig. A and Sig. C indicate significant differences among altitudes and countries, respectively. The ANOVA shows the effect of the altitude (A) and country (C) as follows: *, **, and ns indicate significance at $p < 0.05$, 0.01 and not significant, respectively. Different letters in the same rows indicate significant differences ($p < 0.05$) by altitude according to Tukey's HSD test. Altitude is expressed in meters above sea level (m a.s.l.).

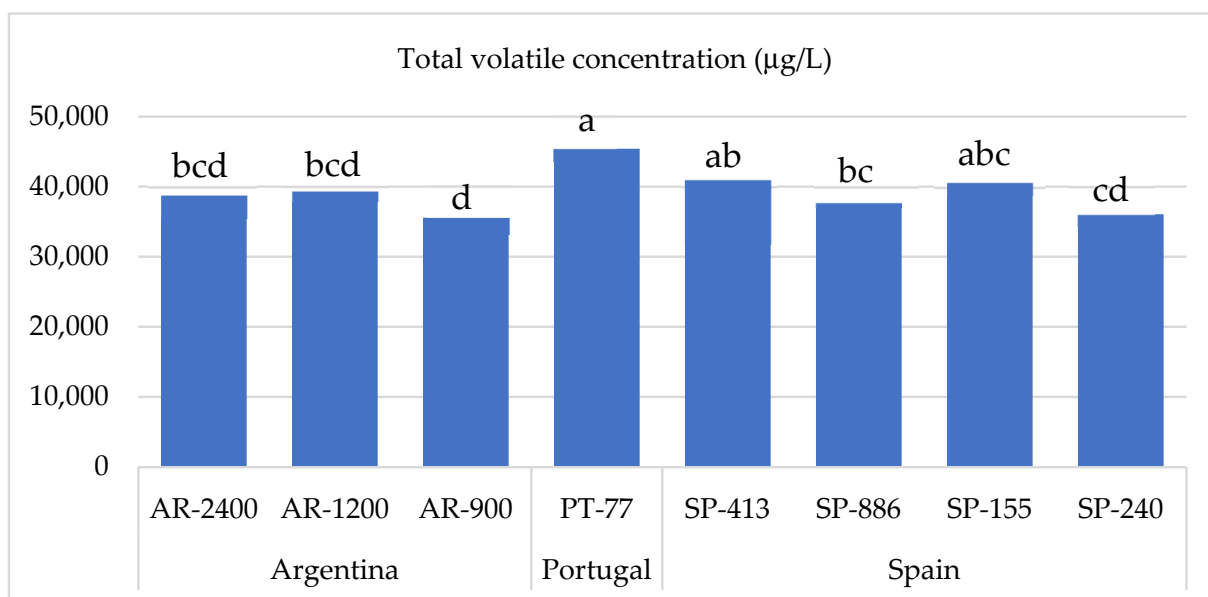


Figure 1. Total volatile concentration ($\mu\text{g/L}$) of Cabernet Sauvignon wines from different altitudes in Argentina (AR), Portugal (PT) and Spain (SP). Different letters indicate significant differences ($p < 0.05$) by altitude according to Tukey's HSD test.

Mansour et al. [26] demonstrated a positive correlation between altitude and the concentrations of anthocyanins and total aroma compounds in Ekşikara and Glera cultivars. Conversely, for other cultivars, such as Merlot and Cabernet Sauvignon, altitude exerts a negative influence on the same components. In the same way, Yue et al. [27] observed that the number of volatile compounds in Cabernet Sauvignon wines increased with altitude, while the total concentrations of the volatiles decreased. Cabernet Sauvignon wine from vineyards at higher altitudes in Brazil were correlated with bell pepper flavor, while wines from lower altitudes were characterized by red fruit and jam flavors [17]. However, other studies showed that the high-temperature conditions and intense sun exposure in summer had a negative impact on the fruity and floral notes in Cabernet Sauvignon wine's aroma [28]. In this study, the highest concentrations of volatiles were found at 77 m a.s.l., 413 m a.s.l. and 155 m a.s.l. However, in our study, no differences were found among altitudes in Argentinian wines. Portugal (PT-77) showed the highest concentration of total volatile compounds due to the high concentrations of γ -butyrolactone (between 1.7 mg/L and 2.1 mg/L). Gamma lactones are indeed recognized as the most significant lactone group in wines. However, it has been noted that γ -butyrolactone does not seem to contribute substantially to the organoleptic profile of wine [29].

3.4. Volatile Composition of Cabernet Sauvignon Wine

Table 3 shows the results of the influence of the vineyards' altitude and country on Cabernet Sauvignon wines' volatile composition, grouped by chemical groups. The chemical groups quantified by GC-MS were acetates, volatile acids, alcohols, C6 compounds, aldehydes, ethyl esters, lactones volatile phenols, terpenes and carbonyl compounds. Alcohols, represented by eight volatile compounds, reached about 70% and 85% of the total volatile content in Cabernet Sauvignon wines, and played a significant role in the determination of the overall aroma of these wines. Esters were the most important chemical group by the number of compounds, represented by 13 compounds, and reaching between 6% to 16% of the total concentration of wines.

Table 3. Volatile composition ($\mu\text{g/L}$) of Cabernet Sauvignon wines from Argentina, Spain and Portugal, grouped by chemical families.

| Volatile Group | Argentina | | | Spain | | | Portugal | | Sig. A | AR | SP | PT | Sig. C |
|--------------------|------------|-------------|------------|-------------|-------------|-------------|-------------|------------|--------|------------|------------|------------|--------|
| | AR-2400 | AR-1200 | AR-900 | SP-886 | SP-413 | SP-240 | SP-155 | PT-77 | | | | | |
| Acetates | 652.8 d | 449.1 f | 421.9 f | 900.7 a | 721.2 c | 842.0 b | 647.3 d | 563.0 e | *** | 507.9 b | 781.6 a | 563.0 b | *** |
| Volatile Acids | 1743.7 a | 770.1 e | 1135.7 cd | 1545.3 b | 1233.5 c | 1035.7 d | 1209.7 c | 1403.7 b | *** | 1216.5 | 1134.6 | 1403.7 | ns |
| Alcohols | 27,226.1 d | 32,566.6 bc | 28,056.3 d | 29,865.3 cd | 34,512.3 ab | 29,805.5 cd | 34,680.8 ab | 36,807.9 a | *** | 29,283.0 b | 32,158.9 b | 38,807.9 a | *** |
| C6 compounds | 875.6 a | 526.1 d | 706.4 b | 537.3 d | 816.2 a | 449.8 e | 235.2 f | 612.5 c | *** | 702.7 | 633.0 | 612.5 | ns |
| Aldehydes | 164.5 a | 145.6 b | 77.2 cd | 13.8 e | 31.5 d | 33.7 d | 14.6 e | 18.9 e | *** | 129.1 a | 32.6 b | 18.9 b | *** |
| Esteres | 6314.3 a | 3378.6 c | 3868.6 b | 2863.2 de | 2567.7 ef | 2406.8 f | 2284.3 f | 3109.3 cd | *** | 4520.5 a | 2487.2 b | 3109.3 ab | ** |
| Lactones | 590.1 b | 324.1 cd | 481.8 bc | 315.1 d | 377.0 cd | 242.4 d | 370.1 cd | 1959.6 a | *** | 465.3 b | 309.7 c | 1959.6 a | *** |
| Volatile Phenols | 820.1 c | 1081.6 ab | 638.4 d | 1163.2 a | 678.7 cd | 972.3 b | 1042.4 ab | 819.2 c | *** | 846.7 | 825.5 | 819.2 | ns |
| Terpenes | 300.4 a | 96.2 c | 101.9 cd | 183.5 b | 42.1 e | 72.9 d | 37.7 e | 88.4 cd | *** | 166.2 | 57.5 | 88.4 | ns |
| Carbonyl compounds | 160.0 c | 21.3 e | 87.5 d | 383.8 a | 15.5 e | 207.5 b | 160.1 c | 16.6 e | *** | 89.6 ab | 111.5 a | 16.6 b | * |

Sig. A and Sig. C indicate significant differences among altitudes and countries, respectively. The ANOVA shows the effect of the altitude (A) and country (C) as follows: *, **, ***, and ns indicate significance at $p < 0.05$, 0.01, 0.001, and not significant, respectively. Different letters in the same rows indicate significant differences ($p < 0.05$) by altitude and country according to Tukey's HSD test. Altitude is expressed in meters above sea level (m a.s.l.).

When the effects of the altitude in different countries on volatile groups were studied, an influence was observed on all chemical groups quantified (Table 3). Most volatile groups showed a significant increase at the highest altitude (AR-2400); thus, volatile acids, C6 compounds, aldehydes, esters and terpenes reached the highest concentrations. Wines from Spain were characterized by a high concentration of acetates, volatile phenols, carbonyl compounds (SP-886) and C6 compounds (SP-413). Wines from Portugal (PT-77) showed the highest concentrations of alcohols and lactones.

The volatile composition of wines from different countries, grouped by chemical family, is also shown in Table 3. Acetates, alcohols, aldehydes, esters, lactones and carbonyl compounds showed differences among wines by countries. Argentinian (AR) wines showed higher concentrations of aldehydes and esters. The highest concentrations of alcohols and lactones were observed in Portuguese wines, and acetates and carbonyl compounds in Spanish wines. No differences among countries were observed for volatile acids, C6 compounds, volatile phenols and terpenes when all altitudes for a country were taken into account.

A principal component analysis (PCA) was applied to visualize the effect of altitude and country on Cabernet Sauvignon wines' volatile composition (Figure 2). The first two principal components accounted for 67.47% of the total variance (38.36% and 29.11% for PC1 and PC2, respectively). The PCA showed that the wines were separated by countries and altitudes on the basis of chemical groups of volatile compounds. PC1 was highly correlated with terpenes, volatile acids, esters, C6 compounds and aldehydes on the positive side, and volatile phenols and alcohols on the negative side. PC2 was characterized by high concentrations of carbonyl compounds and acetates on the positive side and lactones on the negative side.

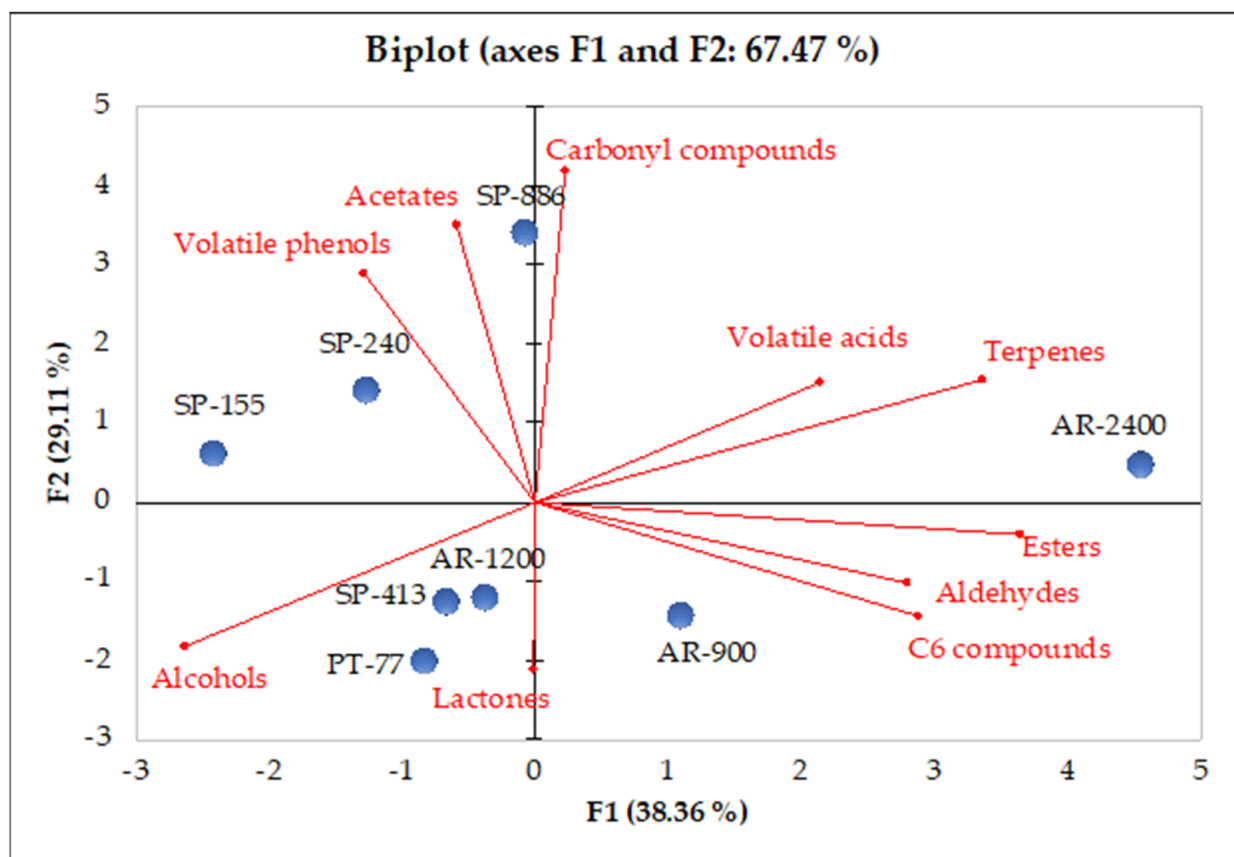


Figure 2. Principal component analysis (PCA) of the volatile composition of wines from Argentina, Portugal and Spain.

In this context, wines from Argentina (AR-2400) sited on the positive side of PC1 and PC2 were characterized by high concentrations of esters, terpenes, aldehydes, C6 compounds and volatile acids; however, AR-900's wines were located on the positive side of PC1 and the negative side of PC2, and were mainly characterized by lactones and C6 compounds. On the other hand, all wines from Spain, Portugal and AR-1200 were grouped on the negative side of PC1. Wines from SP-886 were characterized by carbonyl compounds and acetates, and those from SP-155 and SP-240 by volatile phenols. However, wines from SP-413 and AR-1200 were characterized by high concentrations of alcohols. Finally, the Portuguese wines (PT-77) showed the highest concentration of lactones.

3.5. Cabernet Sauvignon Wine Volatiles by Individual Compounds

Table 4 shows the results of the influence of the vineyards' altitude and country on Cabernet Sauvignon wine's volatiles. Table 4 also shows the results of ANOVA.

In total, 55 volatile compounds were identified and quantified by GC-MS: 3 acetates, 7 volatile acids, 8 alcohols, 4 C6 compounds, 2 aldehydes, 13 esters, 3 lactones, 7 volatile phenols, 7 terpenes and 1 carbonyl compound.

Volatile compounds in wines are derived from the secondary metabolism of grape berries. These volatile compounds can be extracted during the fermentation process from grapes, determining the varietal aroma of wine [30,31]. Additionally, the fermentative aromas of wine, such as higher alcohols and esters, result generally from the volatiles generated during the fermentation process of wine [32]. The release of aroma precursors is possible through yeast and malolactic fermentation, and it depends on the variety, the metabolism, soil and climate conditions.

When the volatile compounds quantified in Cabernet Sauvignon wines from different altitudes were compared, there were differences in most volatile compounds (50 out of 55 compounds), with the exception of one acetate (hexyl acetate), two volatile phenols (4-ethylguaiaicol and 4-ethylphenol) and two terpenes (*a*-terpineol and *cis*-pyran linalool oxide). However, only 27 out of 55 volatile compounds quantified showed differences among wines from different countries.

On the other hand, some volatile compounds were only quantified in the highest altitudes from some countries. Thus, octadecanoic acid (AR-2400), *trans*-pyran linalool oxide (AR-2400), and *cis*- and *trans*-furan linalool oxide (AR-2400) were only quantified in Argentinian wines; ethyl guaiaicol (AR-1200 and PT-77) and *trans*-2-hexen-1-ol (AR-2400) were quantified in Argentinian and Portuguese wines; 4-terpineol was quantified in Spanish wines (SP-240); and *trans*-whiskey lactone (AR-2400, AR-1200, AR-900 and SP-886) and *cis*-pyran linalool oxide (AR-1200 and SP-886) in Argentinian and Spanish wines.

Altitude increased the concentration of most volatile compounds analyzed. In total, 29 volatile compounds showed higher concentrations in Cabernet Sauvignon from Argentina, the country with the highest altitudes in this study.

Among the aroma compounds of Cabernet Sauvignon wines, the group of alcohols showed the highest concentrations in all wines. Alcohols, produced by alcoholic fermentation, are the most abundant chemical group of wine's volatile compounds. Higher levels of alcohols play an important role in aromatic complexity of the wine, with a positive contribution at concentrations below 300 mg/L. The most important alcohols in terms of concentration were phenylethyl alcohol, with highest concentration for wines from PT-77, followed by isoamyl alcohol (SP-413) and isobutyl alcohol (SP-155). Phenylethyl alcohol contributes to the aroma of wine (honey and rose odor) when its concentration is above the detection threshold (14 mg/L) [33]. In our study, phenylethyl alcohol reached a concentration above the detection threshold in all Cabernet Sauvignon wines.

Table 4. Volatile composition ($\mu\text{g/L}$) of Cabernet Sauvignon wines from Argentina (AR), Spain (SP) and Portugal (PT).

| Volatile Compounds | Altitud (A) | | | | | | | Sig. A | Country (C) | | | Sig. C | |
|--------------------------------|-------------|-------------|-------------|-------------|-------------|--------------|-------------|------------|-------------|----------------|------------|------------|---------------|
| | AR-2400 | AR-1200 | AR-900 | SP-886 | SP-413 | SP-240 | SP-155 | | PT-77 | Argentina (AR) | Spain (SP) | | Portugal (PT) |
| Isoamyl acetate | 238.1 e | 214.2 e | 219.4 e | 599.6 a | 448.3 c | 538.8 b | 417.3 c | 295.7 d | *** | 223.9 b | 501.0 a | 295.7 b | *** |
| Phenylethyl acetate | 73.8 e | 67.9 e | 67.4 e | 174.1 a | 98.5 d | 160.8 b | 119.2 c | 120.6 c | *** | 69.7 b | 138.1 a | 120.6 a | *** |
| Diethyl malate | 340.9 a | 167.0 bc | 135.1 de | 127.0 de | 174.4 b | 142.3 cd | 110.7 e | 146.6 cd | *** | 214.3 a | 138.6 b | 146.6 ab | * |
| Isobutanoic acid | 54.3 c | 71.1 a | 55.0 c | 63.5 b | 73.3 a | 38.1 d | 42.7 d | 67.1 ab | *** | 60.1 | 54.4 | 67.1 | ns |
| Butyric acid | 23.0 ab | 17.8 cd | 25.8 a | 22.7 ab | 25.9 a | 14.1 e | 15.6 de | 19.6 bc | *** | 22.2 | 19.6 | 19.6 | ns |
| 2+3-methylbutyric acid | 115.3 d | 204.0 c | 293.2 b | 175.1 c | 328.0 a | 136.4 d | 142.7 d | 337.1 a | *** | 204.2 b | 195.6 b | 337.1 a | * |
| Hexanoic acid | 405.1 a | 246.1 c | 385.5 a | 387.4 a | 413.8 a | 251.9 bc | 295.1 b | 389.2 a | *** | 345.6 | 337.0 | 389.2 | ns |
| Octanoic acid | 425.9 c | 208.0 e | 327.2 d | 664.6 a | 322.3 d | 474.2 bc | 518.3 b | 463.1 c | *** | 320.4 a | 494.8 a | 463.1 ab | ** |
| Decanoic acid | 25.4 f | 23.0 f | 49.0 e | 232.0 a | 70.3 d | 121.0 c | 195.3 b | 127.5 c | *** | 32.5 b | 154.6 a | 127.5 a | *** |
| Octadecanoic acid | 694.8 | - | - | - | - | - | - | - | - | 694.8 | - | - | - |
| Isobututyl alcohol | 751.4 ab | 746.0 ab | 549.9 c | 720.5 b | 787.3 ab | 527.1 c | 836.7 a | 501.1 c | *** | 682.4 ab | 717.9 a | 501.1 b | * |
| 1-butanol | 44.1 b | 64.3 a | 65.2 a | 34.1 c | 45.6 b | 39.7 bc | 24.9 d | 34.1 c | *** | 57.9 a | 36.1 b | 34.1 b | *** |
| Isoamyl alcohol | 9196.2 bc | 9123.9 bc | 8609.7 c | 8597.5 c | 11,532.2 a | 8311.3 c | 10,315.9 ab | 9194.8 bc | *** | 8976.6 | 9689.2 | 9194.8 | ns |
| 3-methyl-1-pentanol | 35.6 cd | 39.2 bc | 38.4 bc | 37.2 bc | 55.3 a | 35.0 cd | 32.0 d | 41.3 b | *** | 37.7 | 39.9 | 41.3 | ns |
| 2.3 butanediol | 36.3 b | 36.7 b | 54.8 a | 34.4 b | 49.5 a | 22.5 c | 34.4 b | 27.5 bc | *** | 42.6 ab | 33.5 b | 57.1 a | ** |
| Methionol | 146.3 b | 220.2 a | 207.6 a | 54.6 d | 95.3 c | 97.6 c | 118.7 bc | 109.1 c | *** | 191.4 a | 91.5 b | 109.1 b | *** |
| Benzyl alcohol | 442.1 a | 135.2 cd | 255.6 b | 162.0 c | 99.6 de | 121.3 de | 86.9 e | 441.9 a | *** | 277.6 b | 117.4 c | 441.9 a | *** |
| Phenylethyl alcohol | 16,574.1 e | 22,201.0 bc | 18,275.2 de | 20,225.1 cd | 21,847.3 bc | 20,651.2 bcd | 23,238.3 b | 26,428.4 a | *** | 19,016.8 c | 21,490.5 b | 26,428.4 a | *** |
| 1-hexanol | 838.0 a | 505.0 cd | 675.0 b | 477.8 d | 789.8 a | 409.9 e | 224.8 f | 571.5 c | *** | 672.7 | 475.6 | 571.5 | ns |
| Trans-3-hexen-1-ol | 16.7 bc | 12.1 e | 15.4 cd | 19.2 a | 17.6 b | 15.1 d | 6.2 f | 13.2 e | *** | 14.7 | 14.5 | 13.2 | ns |
| Cis-3-hexen-1-ol | 15.5 c | 9.0 d | 13.6 c | 40.2 a | 8.8 d | 24.9 b | 4.3 e | 23.7 b | *** | 12.7 | 19.5 | 23.7 | ns |
| Trans-2-hexen-1-ol | 5.5 a | - | 2.4 b | - | - | - | - | 4.2 a | *** | 3.9 | - | 4.2 | ns |
| Furfural | 160.7 a | 110.3 b | 74.9 c | 10.4 e | 26.7 d | 29.7 d | 11.7 e | 13.7 e | *** | 115.3 a | 19.6 b | 13.7 b | *** |
| Benzaldehyde | 3.9 cd | 35.3 a | 2.3 f | 3.4 de | 4.8 b | 4.0 c | 2.9 ef | 5.1 b | *** | 13.8 | 3.7 | 5.1 | ns |
| Ethyl butyrate | 121.1 a | 83.4 d | 111.9 ab | 117.1 a | 121.1 a | 91.7 cd | 100.9 bc | 71.8 e | *** | 105.5 a | 107.7 a | 71.8 b | ** |
| Ethyl 2-methylbutyrate | 20.0 d | 30.1 b | 35.4 a | 10.1 f | 18.8 d | 13.2 e | 7.8 g | 22.8 c | *** | 28.5 a | 12.5 b | 22.8 a | *** |
| Ethyl-3-methylbutyrate | 42.5 c | 50.8 b | 62.2 a | 21.5 e | 46.4 bc | 28.0 d | 19.0 e | 31.8 d | *** | 51.9 a | 28.7 b | 31.8 b | *** |
| Ethyl hexanoate | 307.9 a | 145.9 e | 293.8 a | 291.4 a | 274.6 ab | 182.1 de | 208.5 cd | 241.1 bc | *** | 249.2 | 239.2 | 241.1 | ns |
| Hexyl acetate | - | - | - | 4.6 | 1.8 | 3.6 | - | - | ns | - | 3.3 | - | - |
| Ethyl lactate | 4442.7 a | 2306.6 b | 2418.7 b | 1737.2 c | 1527.3 cd | 1532.0 cd | 1352.1 d | 1769.3 c | *** | 3056.0 a | 1537.2 b | 1769.3 b | *** |
| Ethyl octanoate | 153.4 ab | 98.2 bc | 144.7 abc | 202.7 a | 82.3 c | 102.8 bc | 135.4 abc | 192.4 a | *** | 132.1 | 130.8 | 192.4 | ns |
| Ethyl β -hydroxybutyrate | 120.2 a | 51.1 cd | 51.7 cd | 45.6 de | 66.6 b | 57.6 c | 72.6 b | 42.6 e | *** | 74.3 | 60.6 | 42.6 | ns |
| Isoamyl lactate | 333.3 a | 140.1 bc | 177.7 b | 90.6 d | 100.3 cd | 87.1 d | 78.7 d | 101.2 cd | *** | 217.0 a | 89.2 b | 101.2 b | *** |
| Ethyl methyl succinate | 181.4 a | 82.1 b | 77.2 b | 48.6 cd | 24.9 e | 55.0 c | 34.8 de | 27.9 e | *** | 113.6 a | 40.9 b | 27.9 b | *** |
| Ethyl decanoate | 6.0 d | 12.0 c | 15.9 b | 11.9 c | 5.9 d | 3.9 d | 7.3 d | 31.5 a | *** | 11.3 b | 7.3 b | 31.5 a | *** |
| Methyl vanillate | 44.1 a | 19.0 b | 19.2 b | 17.6 b | 11.6 c | 16.8 b | 11.0 c | 18.0 b | *** | 27.4 a | 14.2 b | 18.0 ab | *** |
| Ethyl vanillate | 541.6 a | 359.4 c | 460.2 b | 264.1 de | 285.9 d | 233.0 e | 256.1 de | 559.0 a | *** | 453.8 b | 259.8 c | 559.0 a | *** |
| γ -butyrolactone | 561.3 b | 295.1 d | 460.0 bc | 275.2 d | 354.9 cd | 231.4 d | 343.6 cd | 1936.3 a | *** | 438.8 b | 301.3 c | 1936.3 a | *** |
| Whiskey lactone (trans) | 17.5 b | 6.2 c | 4.8 c | 18.1 a | - | - | - | - | *** | 9.5 | 18.1 | - | ns |
| γ -Nonalactone | 11.3 d | 22.8 b | 16.9 c | 21.7 b | 22.0 b | 11.0 d | 26.6 a | 23.3 b | *** | 17.0 | 20.3 | 23.3 | ns |

Table 4. Cont.

| Volatile Compounds | Altitud (A) | | | | | | | | Sig. A | Country (C) | | | Sig. C |
|----------------------------|-------------|---------|---------|---------|----------|---------|---------|---------|--------|----------------|------------|---------------|--------|
| | AR-2400 | AR-1200 | AR-900 | SP-886 | SP-413 | SP-240 | SP-155 | PT-77 | | Argentina (AR) | Spain (SP) | Portugal (PT) | |
| Guaiacol | 10.6 a | 10.2 a | 7.9 bc | 7.4 c | 4.9 d | 7.0 c | 6.3 cd | 9.6 ab | *** | 9.6 a | 6.4 b | 9.6 a | *** |
| 4-Ethylguaiaicol | - | 74.9 | - | - | - | - | - | 6.5 | ns | 74.9 | - | 6.5 | ns |
| 4-Ethylphenol | 8.5 | 221.5 | - | - | - | 3.8 | 5.8 | 19.0 | ns | 115.0 | 4.8 | 19.0 | ns |
| 2-Methoxy-4-vinylphenol | 37.2 d | 18.4 e | 27.7 de | 116.9 a | 26.1 de | 86.1 b | 37.0 d | 63.0 c | *** | 27.8 b | 66.5 a | 63.0 ab | * |
| 2,6-Dimethoxyphenol | 52.4 b | 50.0 bc | 41.5 c | 56.1 b | 50.1 bc | 52.2 b | 47.4 bc | 70.2 a | *** | 48.0 b | 51.5 b | 70.2 a | *** |
| 4-2-Hydroxyethylphenol | 662.1 bc | 642.3 c | 488.7 d | 939.0 a | 575.5 cd | 774.0 b | 918.2 a | 617.9 c | *** | 597.7 b | 801.6 a | 617.9 ab | ** |
| 3,4,5-Trimethoxyphenol | 49.4 c | 64.4 b | 72.5 a | 43.9 c | 22.3 e | 49.2 c | 27.7 de | 33.1 d | *** | 62.1 a | 35.8 b | 33.1 b | *** |
| 3-Oxo- α -ionol | 122.9 b | 81.4 d | 93.1 c | 173.3 a | 39.8 f | 65.7 e | 27.5 g | 82.9 d | *** | 99.1 | 76.6 | 82.9 | ns |
| Cis-furan linalool oxide | 145.5 | - | - | - | - | - | - | - | - | 145.5 | - | - | - |
| Trans-furan linalool oxide | 16.9 | - | - | - | - | - | - | - | - | 16.9 | - | - | - |
| 4-Terpineol | - | - | - | - | - | 1.5 | - | - | - | - | 1.5 | - | - |
| α -terpineol | 11.4 | 9.2 | 8.8 | 5.2 | 2.3 | 5.8 | 10.2 | 5.5 | ns | 9.8 | 5.9 | 5.5 | ns |
| Trans-pyan linalol oxide | 3.6 | - | - | - | - | - | - | - | - | 3.6 | - | - | - |
| Cis-pyan linalol oxide | - | 5.6 | - | 5.0 | - | - | - | - | ns | 5.6 | 5.0 | - | ns |
| Acetoina | 160.0 c | 21.3 e | 87.5 d | 383.8 a | 15.5 e | 207.5 b | 160.1 c | 16.6 e | *** | 89.6 ab | 191.8 a | 16.6 b | * |

Sig. A and Sig. C indicate significant differences among altitudes and countries, respectively. The ANOVA shows the effect of the altitude (A) and country (C) as follows: *, **, ***, and ns indicate significance at $p < 0.05$, 0.01, 0.001, and not significant, respectively. Different letters in the same rows indicate significant differences ($p < 0.05$) by altitude and country according to Tukey's HSD test. Altitude is expressed in meters above sea level (m a.s.l.).

The ethyl and methyl ester group was the second most abundant group of volatiles in terms of the concentration of volatiles in all wines. All esters, with exception of ethyl 2-methylbutyrate, hexyl acetate and ethyl decanoate, showed the highest concentrations in Argentinian wines, mainly at the highest altitude (AR-2400). Esters are the most important group of aroma compounds in wines. Esters are mainly enzymatically synthesized by yeasts during alcoholic fermentation and lactic acid bacteria during malolactic fermentation [34]. These compounds are responsible for the fruity aroma of the wine and play a decisive role in the sensory characteristics of young wines [33].

Regarding the acetates, phenylethyl acetate and isoamyl acetate showed higher concentrations at the highest altitude in Spain (SP-886). These compounds give wines strawberry-fruity and banana odors, respectively [16].

Most of the lactones are formed as a result of yeast's activities. In our study, γ -butyrolactone showed the highest concentration in all wines studied. Among the altitudes, the lowest altitude (PT-77) showed the highest value of this compound.

Among the volatile acids, octadecanoic acid, which was only quantified in AR-2400, showed the highest concentration of all the acids quantified. Hexanoic and octanoic acids were quantified in all wines, with differences among different altitudes. Thus, the highest concentrations of hexanoic acid were shown in Argentina (AR-2400 and AR-900), Spain (SP-886 and SP-413) and Portugal (PT-77). However, SP-886 reached the highest concentration of octanoic acid. With the exception of octadecanoic acid at 2400 m a.s.l. (AR-2400) and octanoic acid at 886 m a.s.l. (SP-886), volatile acids were below the threshold. In agreement with our results, a previous study on Cabernet Sauvignon wines from China reported higher concentrations of fatty acids in wines but below the flavor threshold [35].

On the other hand, C6 compounds in grapes contribute to a typical green leaf or herbaceous aroma [36]. Previous reports showed that C6 compounds are generated in the plant in response to environmental conditions [37,38]. Grapes in cool-climate regions usually reach higher C6 aldehyde concentrations, whereas warm-region grapes usually have higher terpene concentrations [39]. In our study, four C6 compounds were quantified, where 1-hexanol exhibited the highest concentration in all altitudes and countries. Moreover, higher concentrations were shown in AR-2400 and SP-413 wines. In a correlation analysis, hexanal was negatively correlated with high temperatures in four varieties, namely Riesling, Victoria, Muscat Hamburg and Cabernet Sauvignon [40]. Hexanal, 2-hexanol, (Z)-3-hexenol and (E)-2-hexenol in Cabernet Sauvignon from five Chinese regions were closely associated with the minimum and maximum temperature, average relative humidity, sunshine duration and frost-free days, suggesting that these compounds might comprise a signature for distinguishing the volatile profiles of grape berries from different regions [41].

Terpenoid compounds contribute to the floral aroma in wines and can be used for characterization of the variety [42]. It is known that terpene compounds belong to the secondary plant constituents from acetyl-coenzyme A (CoA). They are present at low levels; however, they contribute to wine's aroma because their low odor thresholds [43]. In total, seven terpenes were quantified in Cabernet Sauvignon wines, mainly in AR-2400, where the thermal amplitude was higher. Only 3-oxo-a-ionol and α -terpineol were quantified in all wines studied. The highest concentration of 3-oxo-a-ionol was found for SP-886, followed by AR-2400 (the locations with lower average temperatures). In general, most studies on the monoterpenes have underlined the benefit of higher temperatures during ripening but also their negative effect on the fruits' metabolism whenever they are excessively high [44]. Grapes in warm regions were reported to have higher terpene concentrations than those in hot regions [45]. An elevated temperature (>35 °C) could inhibit the accumulation of terpenes [46].

Regarding the phenol volatiles, 4-ethylguaiacol, 4-ethylphenol, 4-methylguaiacol, vinylphenols, guaiacol, eugenol and vanillin are the most common found in wines [47,48]. The metabolic activity of yeasts and oak maturation can increase the amount of volatile phenols in wine [48]. In this study, seven volatile phenols were quantified in Cabernet

Sauvignon wines, where 4-2-hydroxyethylphenol reached the highest concentration. Wines from SP-886 and SP-155 exhibited significant higher concentrations, with 0.94 mg/L and 0.92 mg/L, respectively, of this compound. Three wines (AR-2400, AR-1200 and PT-77) were associated with high concentrations of guaiacol. Guaiacol is a product of lignin degradation and it is commonly found in wines that have been aged in oak and also in the leaves of some grape red varieties [49–52].

3.6. Correlation between the Wines' Volatile Composition and Vineyards' Altitude

With the aim of correlating the volatile composition of Cabernet Sauvignon wines with the vineyards' altitude, regression analyses were performed. Table 5 shows the results of the Pearson's correlation coefficients between the individual volatile compounds quantified in wines with the altitude and climatic data (mean, maximum and minimum temperature and rainfall) of the vineyards in 2022.

Table 5. Correlation coefficients (Pearson's correlation) between volatile compounds and the altitude and climatic data of the vineyards.

| Volatile Compound | Altitude | Average Temp | Max Temp | Min Temp | Rainfall |
|-----------------------------------|--------------|--------------|----------|----------|----------|
| Isoamyl acetate | −0.454 | 0.052 | −0.747 | 0.770 | −0.258 |
| Phenylethyl acetate | −0.499 | 0.388 | −0.671 | 0.886 | −0.048 |
| Diethyl malate | 0.846 | −0.444 | 0.000 | −0.643 | 0.502 |
| Octanoic acid | −0.198 | 0.188 | −0.791 | 0.572 | 0.276 |
| Octadecanoic acid | 0.818 | −0.444 | −0.084 | −0.567 | 0.539 |
| 1-butanol | 0.395 | −0.234 | 0.728 | −0.366 | −0.374 |
| Methionol | 0.375 | −0.174 | 0.911 | −0.530 | −0.228 |
| Benzyl alcohol | 0.436 | 0.278 | 0.019 | −0.437 | 0.896 |
| Phenylethyl alcohol | −0.733 | 0.716 | 0.019 | 0.270 | 0.089 |
| Trans-2-hexen-1-ol | 0.514 | 0.097 | 0.044 | −0.578 | 0.881 |
| Furfural | 0.908 | −0.471 | 0.500 | −0.660 | 0.135 |
| Benzaldehyde | 0.202 | 0.079 | 0.719 | −0.079 | −0.455 |
| Ethyl butyrate | 0.455 | −0.838 | −0.488 | −0.295 | −0.072 |
| Ethyl 2-methylbutyrate | 0.287 | 0.038 | 0.743 | −0.492 | −0.027 |
| Hexyl acetate | −0.214 | 0.044 | −0.615 | 0.789 | −0.308 |
| Ethyl lactate | 0.938 | −0.425 | 0.184 | −0.649 | 0.450 |
| Isoamyl lactate | 0.908 | −0.479 | 0.182 | −0.702 | 0.442 |
| Ethyl methyl succinate | 0.944 | −0.484 | 0.224 | −0.536 | 0.297 |
| Ethyl decanoate | −0.278 | 0.778 | 0.146 | −0.003 | 0.503 |
| Methyl vanillate | 0.891 | −0.310 | 0.058 | −0.502 | 0.539 |
| Ethyl vanillate | 0.441 | 0.217 | 0.273 | −0.616 | 0.764 |
| γ-butyrolactone | −0.238 | 0.743 | −0.009 | −0.132 | 0.775 |
| Whiskey lactone (trans) | 0.792 | −0.367 | −0.272 | −0.084 | 0.178 |
| 4-Ethylguaiacol | 0.188 | 0.117 | 0.744 | −0.077 | −0.438 |
| 4-Ethylphenol | 0.210 | 0.098 | 0.747 | −0.091 | −0.430 |
| 2-Methoxy-4-vinylphenol | −0.222 | 0.394 | −0.628 | 0.824 | 0.089 |
| 2,6-Dimethoxyphenol | −0.218 | 0.733 | −0.285 | 0.235 | 0.613 |
| Cis-furan linalool oxide | 0.845 | −0.458 | −0.087 | −0.585 | 0.556 |
| Trans-furan linalool oxide | 0.848 | −0.460 | −0.087 | −0.587 | 0.558 |
| Trans-piyan linalool oxide | 0.848 | −0.460 | −0.087 | −0.587 | 0.558 |

Values in bold are different from 0 with a significance level of alpha = 0.05. Volatile compounds in bold are correlated with the vineyard's altitude.

Considering the relationship between altitude and volatile compounds, a significant correlation ($R^2 > 0.700$) was observed between altitude and 12 volatile compounds, all of which had positive correlations, with exception of phenylethyl alcohol ($R^2 = -0.733$). Four of these volatile compounds (furfural, ethyl lactate, isoamyl acetate and ethyl methyl succinate) showed the highest correlations with altitude ($R^2 > 0.900$). Correlations ($R^2 > 0.700$) were also observed between volatile compounds and the average, maximum and minimum temperature and rainfall. The study performed by Lu et al. [40] showed that γ-terpinene, terpinen-4-ol, cis-furan linalool oxide and trans-piyan linalool oxide were all negatively

correlated with high temperatures in four varieties (Riesling, Victoria, Muscat Hamburg and Cabernet Sauvignon).

The altitude allows an important daily thermal amplitude, mainly due to the lower nighttime temperature [52]. The production of high-quality grapes depends on the daily thermal amplitude resulting from the lower night-time temperatures usually associated with high elevation plots. Grapevines that are cultivated in vineyards with low night temperatures have a higher potential for containing color and volatile compounds [23]. The temperature variability among vineyards, countries and altitudes included in this study showed high thermal amplitudes in the growing season of 2022, with the lowest temperature at 6.9 °C and the highest one at 24.7 °C. Daily thermal amplitude favors the production of high-quality grapes for winemaking, because ripening occurs slowly. In this sense, Falcão et al. [17] related the later phenology and longer duration of phenological events in Cabernet Sauvignon grapevines with an increase in elevation. Thus, high altitudes produce aromatic wines [52]. Differences in the grapevines' response at dissimilar altitudes have been reported by some workers in different viticultural areas [53]. Gutierrez-Gamboa et al. [23] concluded that altitude is the most effective strategy to delay the ripening of grapes and to ensure that this ripening takes place at lower temperatures.

4. Conclusions

Climatic conditions associated with altitude have an influence on secondary metabolism in the grapevine. In this work, we demonstrated the effects of some parameters of terroir on the volatile components of Cabernet Sauvignon wines from three different countries, Argentina, Spain and Portugal. This work has provided detailed information on the volatile profiles of Cabernet Sauvignon wines from distinctive wine regions and altitudes, and revealed the effect of such climates on the volatile composition. In total, 50 out of the 55 volatiles quantified showed differences among wines from vineyards sited at different altitudes. The contents of the volatile chemical groups (including volatile acids, C6 compounds, aldehydes, esters and terpenes) in the conditions of vineyards sited at 2400 m a.s.l. in Argentina were the highest versus the other altitude conditions and countries. Terpenes and esters, volatiles associated with wine's quality, showed the highest concentrations at the highest altitude. The high thermal amplitude shown at the highest altitude induced the production of the most volatiles compounds in Cabernet Sauvignon wines. In summary, our study indicated the relationship between climatic parameters associated the vineyards' altitude and the volatile content of wines. Therefore, a new scenario for producing high-quality Cabernet Sauvignon wines has opened in the actual situation of climatic change. High altitudes, because their climatic conditions offer better for growing wine grapes, could be better for wine with the highest volatile composition.

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