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Article

General Physicochemical Parameters, Phenolic Composition, and Varietal Aromatic Potential of Three Red *Vitis vinifera* Varieties ("Merlot", Syrah", and "Saborinho") Cultivated on Pico Island—Azores Archipelago

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Abstract: Pico Island is one of the islands of the Azores archipelago located in the North Atlantic Ocean, where there are very specific conditions for vine cultivation. In this context, there is scarce knowledge related to grape ripening under these conditions. Thus, the aim of this study was to evaluate several physicochemical parameters, the phenolic composition, antioxidant capacity, and varietal aromatic potential, of the "Merlot", Syrah", and "Saborinho" grape varieties cultivated on Pico Island over three vintages. The outcomes obtained demonstrated that "Merlot" grapes showed a tendency for significantly higher values of estimated alcohol degree, total phenols, flavonoid and non-flavonoid phenols, total anthocyanins, color intensity, and antioxidant capacity over the three vintages. In addition, for individual anthocyanins, "Merlot" and "Syrah" grapes showed a predominance of acetyl-anthocyanins in relation to *p*-coumaroylated forms, while for "Saborinho" grapes, an oppositive tendency was observed. For varietal aromatic potential, only in the 2021 vintage was it possible to detect significantly different values between the three grape varieties studied. In this case, "Merlot" and "Syrah" grapes showed the significantly highest values. Considering all parameters analyzed, the results obtained for the "Merlot" grape variety seem to show a better adaptation of this variety to the conditions of Pico Island than the remaining two varieties studied.

Keywords: antioxidant capacity; grape ripening; phenolic composition; Pico Island; varietal aromatic potential

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1. Introduction

The Azores archipelago is formed by nine islands of volcanic origin and is part of the central crest of the North Atlantic. These islands are an autonomous region of Portugal located approximately 1500 km west of Europe's mainland coast and about 3900 km from the North America coast (between 36°55′ and 39°43′ Latitude N and 24°46′ and 31°26′ Longitude W). Due to its location, the Azores have a climate with a typical maritime condition and characterized by mild temperatures, high rainfall, and high relative air humidity [1]. This high humidity and cloudy conditions imply that great care is needed in monitoring the risk of fungal attacks in crops, particularly in vines [2]. According to the Köppen classification, the Azores climate falls in the category of warm temperate climates (group C–Csb) with a dry summer to temperate rainy climate with wet seasons [3]. The vineyards on the Azores Islands are typically implanted in volcanic soils. Thus, in general, they accomplish the criteria to be classified in the Andisol Order [4].

Although the Azores Archipelago is made up of nine islands, wine-growing activity is fundamentally concentrated on three islands: Terceira, Graciosa, and Pico. Of these, it is on Pico Island where 95% of Azores wine production is concentrated. Pico viticultural activity began in the 15th century, and today represents an important economic activity. Currently, wine production on this island is around 2700 hL and distributed over a total area of 862 ha, which represents more than 90% of the total vineyard area of all the Azores islands.

The traditional cultivation method, against the roughness of the volcanic terrain, almost with no vegetal soil, is made in "currais", which protects the vines from oceanic winds and humidity. In addition, the grapevine training systems are mainly dependent on the soil type of the vineyard. In fact, traditionally, grapevines are not trellised, and the training system is unique for each plant depending on the area they have available [5]. Thus, vines are planted in the ground to try to protect them from wind and raised at the time of maturation to avoid scalding of the cluster through contact with the black stone. A similar traditional training system is also possible to be found in other European regions with very specific viticultural practices, such as on the Santorini (Greece) and Lanzarote (Canary Islands—Spain) islands [6,7]. However, in the last years, the implementation of new vineyards in different areas of Pico Island has also been carried out through the use of vines with more modern management systems [8].

Pico Island, traditionally, is mostly focused on table white wines using several grape varieties, such as "Verdelho", "Malvasia Fina", "Arinto dos Açores", and "Terrantez do Pico". For red wines, this region has no tradition. Nevertheless, in the last two decades, red wines have showed a slight production increase using several vine varieties, including international varieties, such as "Syrah", "Merlot", and "Cabernet Sauvignon", and also Portuguese varieties, such as "Touriga Nacional", "Castelão", and "Saborinho" [6]. Specifically, in the Azores islands, "Merlot", "Syrah", and "Saborinho" represent, respectively, 30.7, 42.7, and 3.9% of the total red wine-growing area of the Azores. Research using "Saborinho" (or "Tinta Negra"), an autochthonous Portuguese variety, have almost exclusively reported under Madeira Island conditions. Under these conditions, a few studies reported data of the grape phenolic composition [9] and volatile profile of wines produced from this variety [10,11].

"Merlot" and "Syrah" are two of the most widespread red grape varieties of French origin, being cultivated in different wine countries around the world [12]. Thus, they have been widely studied by several authors and under different environmental and soil conditions outside of France, such as Spain [13], Italy [14], Greece [15,16], South Africa [17,18], China [19], Australia [20], the United States [21,22], México [23], Brazil [24], and Argentina [25]. For the Portuguese mainland, several studies have also reported the adaptability of these red grape varieties to different wine regions [26–28]. However, information from these varieties during grape ripening under the specific edaphoclimatic conditions of the Azores archipelago, and particularly on Pico Island, is practically non-existent.

Thus, to deepen the knowledge of the adaptability of several red grape varieties to the climate and soil conditions of Pico Island, the present study aimed to evaluate the physiochemical and phenolic composition of the "Merlot", "Syrah", and "Saborinho" grape varieties during three consecutive vintages. In addition, antioxidant capacity and varietal aroma potential at technical maturation were studied.

2. Materials and Methods

2.1. Grape Varieties and Vineyard Location

One Portuguese ("Saborinho") and two French ("Merlot" and "Syrah") red grape varieties (*Vitis vinifera* L.) were studied at three different ripening stages from an experimental non-irrigated vineyard (established in 2002) with a bilateral cordon-trained system and located at Cabeço do Chão—Madalena (GPS coordinates 38°32′40″ N, 28°29′17.5″ W) on Pico Island—Azores Archipelago, Portugal. The dominant soil types in the vineyard are litholic and lithosols.

For the two French red grape varieties studied, three consecutive growing seasons (2021–2023) were analyzed, while for the Portuguese grape variety, only two growing seasons (2021 and 2023) were considered. This difference resulted from the fact that in 2022, it was not possible to collect samples from the "Saborinho" variety due to grapes having been previously affected by several diseases (namely, downy and powdery mildew).

Grape samples (100 berries) were picked randomly in quadruplicate from 450 different plants of each variety studied. Each grape sample was collected from all possible locations with different height and sunlight exposure. For each growing season, the grape harvest was carried out between 45 and 50 days after veraison. All grape samples were kept frozen at −20 °C until processing.

2.2. Characterization of Climatic Conditions

The Azores archipelago is in the middle of the Atlantic Ocean. Their localization is sufficiently far apart from the continental coasts and, consequently, the air masses that hit these islands reveal a strong increment in properties associated with their maritime route [8].

Specifically for the vineyard studied (Pico Island—Azores), the evolutions of the monthly mean climatic conditions (rainfall, temperature, and relative humidity) for the 2021, 2022, and 2023 vintages are summarized in Figure 1. In general, over the three vintages considered, rainfall occurs throughout the year, including during the last stages of grape ripening (between August and September). However, it was also clear that the 2022 vintage showed lower monthly mean rainfall values (except for January) than 2021 and 2023. For the temperature, the highest monthly mean values were concentrated between July and September. In addition, for the 3 vintages under analysis, the average temperature in these months showed variations between 18.9 and 23.4 °C. Furthermore, February was generally the month with the lowest average monthly temperature (ranging between 13.7 and 14.6 °C). Finally, for relative humidity, this can be considered high throughout the year, where average monthly values varied between 74.3 and 84.6% for the 3 vintages analyzed. For the months corresponding to the grape ripening (between June and September), the average monthly values varied between 77 and 81%.

2.3. Grape Sample Preparation

General physicochemical parameters were measured directly from the must obtained after grape pressing. Phenolic parameters, individual anthocyanins, and antioxidant capacity were determined from an extract previously obtained according to the methodology proposed by Carbonneau and Champagnol [29]. Briefly, grape extracts were obtained by macerating the crushed grapes at 25 °C for 24 h in a pH 3.27 buffer, followed by clarification of the suspension by centrifugation (10 min at 3500 rpm). After, aliquots of each extract were filtered with a Whatman-Cytiva Europe (Velisy-Villacoublay, France) cellulose filter with a pore diameter of 0.45 µm and frozen at −20 °C until processing.

2.4. Enological Parameters and General Phenolic Composition

Basic grape enological parameters such as the weight of 100 berries, estimated alcohol degree, pH, and titratable acidity were analyzed using the analytical methods recommended by the OIV [30]. Total anthocyanins were determined using the SO_2 bleaching method described by Ribéreau-Gayon and Stronestreet [31], while total phenolic compounds were determined by measuring absorbance at 280 nm [32]. Non-flavonoid and flavonoid phenols were determined using the method described by Kramling and Singleton [33]. In brief, the quantification of non-flavonoid phenols is based on the determination of the phenolic content before and after the precipitation of flavonoids through the reaction with formaldehyde, under certain conditions (low pH, room temperature, and darkness). After 24 h, a dilution with distilled water (1:10) is carried out and the absorbance is read at 280 nm on a spectrophotometer. Flavonoid phenols come from subtracting non-flavonoid phenols from total phenols. Color intensity (A420 + A520 + A620) was estimated using the method described by the OIV [30]. For all phenolic and chromatic parameters, a spectrophotometer model Genesys 50 UV-Vis (Thermo Scientific, Ilkirch-Graffenstaden, France) accoupled to VISIONlite Wine Analysis software program version 5.0 (Thermo Fisher Scientific, Waltham, MA, USA) was used. All analyses were performed in triplicate.

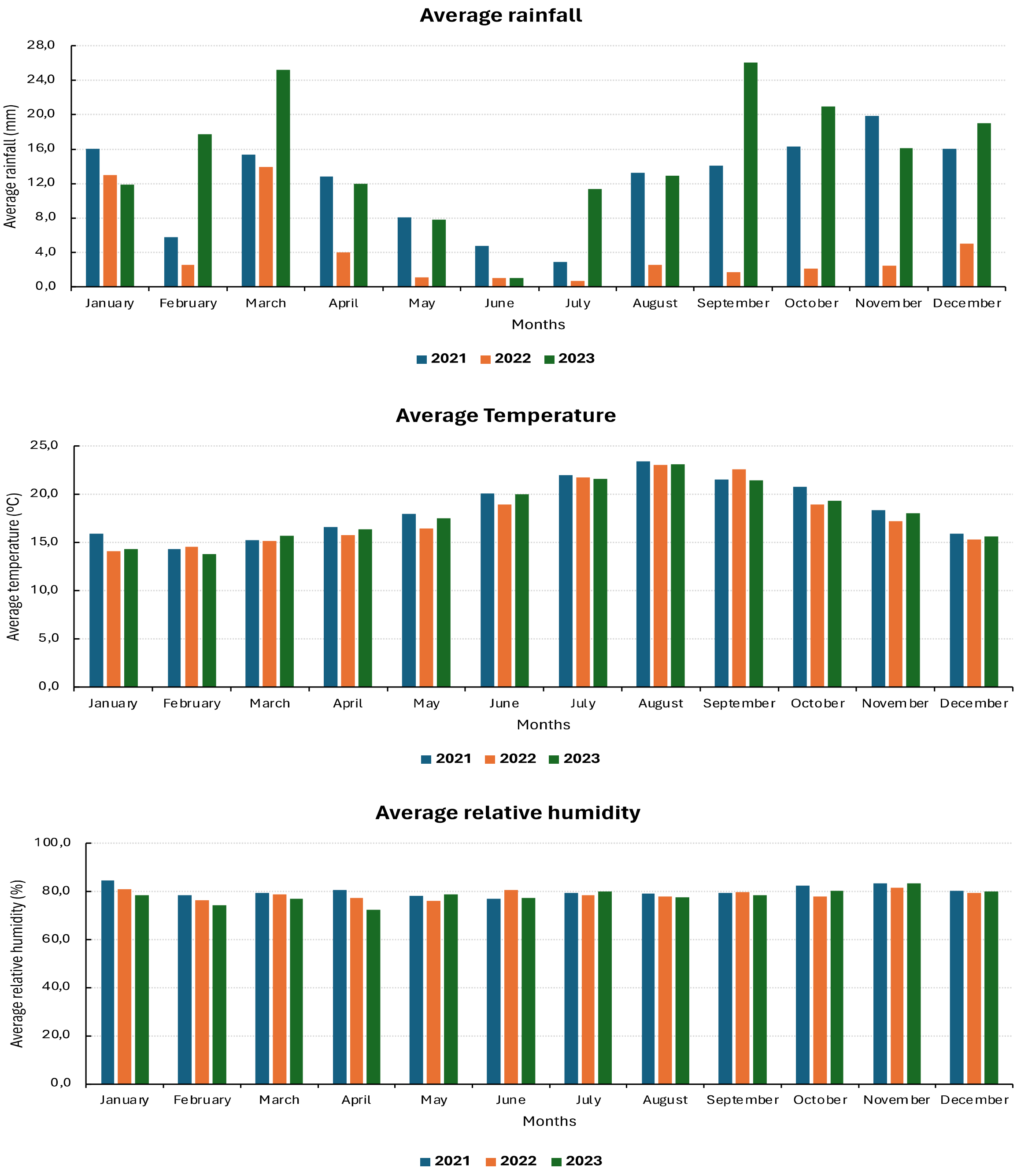

Figure 1. Evolution of monthly mean climatic conditions (rainfall, temperature, and relative humidity) during the 2021, 2022, and 2023 vintages in the vineyard located on Pico Island (Azores archipelago).

2.5. HPLC Analysis of Individual Anthocyanins

For the analysis of individual monomeric anthocyanins grouped into 3 main groups (monoglucosides, acetylglucosides, and coumarylglucosides), the equipment used was a high-performance liquid chromatography (HPLC) Dionex Ultimate 3000 Chromatographic System (Sunnyvale, CA, USA) equipped with a quaternary pump Model LPG-3400A, an auto sampler Model ACC-3000, a thermostatted column compartment (adjusted to 25 °C), and a multiple Wavelength Detector MWD-300. The column (250 × 4.0 mm, particle size 5 µm) was a C_{18} Nucleodur (100-5 ec, Macherey-Nagel, Düren, Germany) protected by a guard column of the same material. The solvents were (A) 40% (*v*/*v*) formic acid, (B) pure acetonitrile, and (C) bi-distilled water. The HPLC conditions were based on the original method described by Dallas and Laureano [34]. Thus, the initial conditions were 25% (A), 10% (B), and 65% (C), followed by a linear gradient from 10 to 30% (B), and 65 to 45% (C) for 40 min, with a flow rate of 0.7 mL/min. The injection volume was 40 µL, the detection was made at 520 nm, and a Chromeleon software program version 6.8 (Dionex, Sunnyvale, CA, USA) was used. Individual anthocyanins were quantified by using a calibration curve obtained with diverse standard solutions containing different concentrations of malvidin-3-monoglucoside (Extrasynthese, Genay, France). The chromatographic peaks of anthocyanins were identified also according to reference data previously described by Dallas and Laureano [34]. All measurements were performed in triplicate.

2.6. Determination of Antioxidant Capacity

To determine the antioxidant capacity using the DPPH method, the procedure was based on the original method described by Brand-Williams et al. [35]. Briefly, 0.1 mL of different sample concentrations was added to 3.9 mL of a 2.2-diphenyl-1-pirylhydrazyl (DPPH) methanolic solution (25 mg/L). The DPPH solution was prepared daily and protected from the light, and the absorbance at 515 nm was measured after 30 min of reaction at 20 °C considering methanol as a blank reference. The reaction was carried out under shaking in closed Eppendorf tubes at 20 °C. For the antioxidant capacity using the ABTS method, the conditions described previously by Re et al. [36] were used. This methodology is based on the discoloration that occurs when the radical cation $ABTS^{\cdot +}$ is reduced to ABTS (2,2′-azinobis-3-ethylbenzothiazoline-6-sulfonic acid). This radical was generated by the reaction of a 7 mM solution of ABTS in water with 2.45 mM potassium persulphate (1:1) in darkness at room temperature. The assay was made up of 980 µL of $ABTS^{+}$ solutions and 20 µL of the sample (at a dilution of 1:50 in water). Absorbance measurements at 734 nm were made after 15 min of reaction time. The antioxidant capacity results obtained from the ABTS and DPPH methods were expressed as Trolox equivalents (TEAC mM), using a calibration curve obtained previously. For all measurements, a spectrophotometer model Genesys 50 UV-Vis (Thermo Scientific, Ilkirch-Graffenstaden, France) was used. All measurements were performed in triplicate.

2.7. Determination of Varietal Aroma Potential Index

For determination of the grapes' varietal aroma potential index (IPAv), a commercial IPAv kit (Teknokroma S.A., Barcelona, Spain) was used, following the procedure based on the original method described by Salinas et al. [37] but modified to enable the spectrophotometric determination of the glucose released from the glycosylated aroma precursors by acid hydrolysis [38]. All measurements were performed in triplicate.

2.8. Statistical Analysis

The data are presented as the mean ± standard deviation. The statistical difference between the mean values of the parameters studied was estimated by analyses of variance (ANOVA, one-way). In this research, the Tukey multiple range test ($p < 0.05$) was applied to the data to determine significant differences between grape varieties during ripening. Principal component analysis (PCA) was also used to analyze the data and to study the relationships between the three grape varieties studied for the different parameters analyzed at technical maturation. In this case, the average data obtained for the 3 vintages were considered. Since variables with different scales were used, the PCA analysis was performed with a previous standardization of the initial variables and conducted using a correlation matrix. All analyses were performed using SPSS software version 27.0 (SPSS Inc., Chicago, IL, USA).

3. Results and Discussion

3.1. General Physicochemical Characteristics

The physicochemical parameters of the grape varieties studied during ripening and for the three vintages analyzed (2021 to 2023) are summarized in Table 1. Making a comparative analysis for estimated alcohol degree, in general, “Merlot” grapes showed a tendency for higher values during ripening than “Syrah” and “Saborinho” grapes. This trend was particularly evident at harvest, where during the three vintages, “Merlot” grapes showed significantly higher values for estimated alcohol degree. Thus, at harvest, “Merlot” grapes showed an average value of 10.12% v/v for the three years of the study, while “Syrah” and “Saborinho” grapes showed average values between 9.22 and 9.54% v/v, respectively (although for “Saborinho” grapes, only the results from 2021 and 2023 were considered). Independently of the vintage analyzed, the estimated alcohol degree values obtained were low, compared to the alcoholic potential values that these grape varieties show when cultivated in other wine regions with different edaphoclimatic conditions [22,24,27,28]. However, it is important to consider that besides the vineyards being installed on arable land, on Pico Island, grapevines are traditionally planted in very poor soils (shallow or stony) with very low fertility [5]. On the other hand, the climatic data obtained (Figure 1) allow us to verify that there was always some rain and high humidity in the months corresponding to grape ripening (particularly between August and September), which could also have contributed to these low alcohol content values. Several authors reported that maturation and harvest during rainy months do not favor sugar accumulation in the berries [28]. According to Trujillo et al. [39], table wines produced on the Azores islands are usually characterized by a lower alcoholic degree. In fact, there are several factors that determine grape ripening and, consequently, their composition such as the climate of the vintage, the microclimate associated with the parcel, the cultivar, and the soil type [40]. However, specifically for grape sugar concentration during ripening, there are three main factors that determine their changes: sugar import, sugar metabolism, and dilution in a growing berry. In addition, sugar concentration is affected by the leaf area/fruit weight ratio. Thus, when this ratio is very low, sugar import is reduced more than sugar metabolism and berry water import, resulting in lower sugar concentration in grapes [41,42]. All these facts united could help to explain the low estimated alcohol degree values obtained for the grape varieties studied over the three years analyzed.

Regarding the titratable acidity, in general, a clear decrease in the values was detected during the ripening for the three grape varieties studied (Table 1). At harvest, it was also clear that the “Syrah” grapes for the 2021 and 2023 vintages showed the significantly highest titratable acidity values. The constant high average relative humidity values (around 80%) and mild temperatures (June to September lower than 23 °C) can help to obtain grapes with higher acidity. However, it should be noted that these conditions may also have negative consequences for the phytosanitary characteristics of the grapes. According to Sanderson et al. [43], high rainfall during grape ripening can promote growth of the vines but increase the risk of fungal disease.

Furthermore, it is well known that titratable acidity in grape berries is well correlated to temperature, where total acidity will be reduced as a result of higher temperatures [42]. Nevertheless, previously, several authors reported good adaptation of “Syrah” grapes to different climatic conditions, including warm and cool temperatures [28,44,45]. Finally, at harvest, it was also detected that “Saborinho” showed the lowest titratable acidity values for the vintages considered. Previously, Perestrelo et al. [9] reported higher titratable acidity values (8.6 g/L tartaric acid) for “Saborinho” grapes cultivated under Madeira Island conditions. These results are not in agreement with the values obtained in our study under Pico Island conditions, where the values at harvest ranged between 4.49 and 5.11 g/L for tartaric acid.

Table 1. General physicochemical composition of "Merlot", "Syrah", and "Saborinho" grape berries during ripening over three vintages (2021 to 2023) on Pico Island (Azores archipelago).

Vintages Grape Varieties	Grape Berry Weight (1) (g)			Must Volume (2) (mL)			Estimated Alcohol Degree (%, *v*/*v*)			pH			Titratable Acidity (g/L Tartaric Acid)		
	Days After Veraison														
	21	**37**	**45 ***	**21**	**37**	**45 ***	**21**	**37**	**45 ***	**21**	**37**	**45 ***	**21**	**37**	**45 ***
2021															
Merlot	76 ± 1 ^{a**}	83 ± 1 ^{a}	111 ± 3 ^{a}	56 ± 2 ^{a}	54 ± 2 ^{a}	81 ± 1 ^{a}	9.76 ± 0.04 ^{a}	9.70 ± 0.08 ^{a}	10.70 ± 0.04 ^{b}	3.34 ± 0.01 ^{a}	3.49 ± 0.01 ^{b}	3.66 ± 0.02 ^{b}	12.49 ± 0.40 ^{b}	6.38 ± 0.06 ^{c}	5.25 ± 0.07 ^{b}
Syrah	67 ± 2 ^{b}	62 ± 2 ^{c}	102 ± 1 ^{b}	45 ± 1 ^{c}	49 ± 4 ^{a}	73 ± 2 ^{b}	9.06 ± 0.16 ^{b}	9.29 ± 0.16 ^{b}	9.55 ± 0.07 ^{a}	3.18 ± 0.01 ^{c}	3.34 ± 0.03 ^{c}	3.63 ± 0.02 ^{b}	15.33 ± 0.11 ^{a}	10.86 ± 0.04 ^{a}	8.31 ± 0.04 ^{a}
Saborinho	66 ± 1 ^{b}	69 ± 2 ^{b}	101 ± 2 ^{b}	51 ± 1 ^{b}	51 ± 1 ^{a}	75 ± 1 ^{b}	8.83 ± 0.01 ^{b}	9.00 ± 0.08 ^{b}	9.80 ± 0.14 ^{a}	3.27 ± 0.01 ^{a}	3.63 ± 0.02 ^{a}	3.78 ± 0.01 ^{a}	13.13 ± 0.03 ^{b}	7.75 ± 0.07 ^{b}	5.11 ± 0.01 ^{b}
2022															
Merlot	96 ± 1 ^{b}	142 ± 2 ^{b}	146 ± 1 ^{b}	47 ± 2 ^{b}	88 ± 1 ^{b}	90 ± 1 ^{b}	6.74 ± 0.19 ^{a}	7.30 ± 0.14 ^{b}	9.10 ± 0.21 ^{a}	3.26 ± 0.01 ^{a}	3.50 ± 0.01 ^{b}	3.70 ± 0.01 ^{a}	15.05 ± 0.07 ^{b}	12.60 ± 0.39 ^{b}	6.08 ± 0.04 ^{b}
Syrah	111 ± 2 ^{a}	179 ± 4 ^{a}	190 ± 1 ^{a}	59 ± 1 ^{a}	98 ± 2 ^{a}	119 ± 1 ^{a}	6.20 ± 0.14 ^{b}	7.80 ± 0.01 ^{a}	8.35 ± 0.07 ^{b}	3.25 ± 0.03 ^{a}	3.63 ± 0.02 ^{a}	3.77 ± 0.04 ^{a}	18.50 ± 0.02 ^{a}	8.55 ± 0.07 ^{a}	5.34 ± 0.06 ^{a}
2023															
Merlot	188 ± 2 ^{a}	200 ± 1 ^{a}	209 ± 2 ^{a}	100 ± 1 ^{b}	104 ± 1 ^{b}	109 ± 1 ^{a}	9.25 ± 0.07 ^{a}	10.3 ± 0.14 ^{a}	10.11 ± 0.01 ^{a}	3.53 ± 0.04 ^{a}	3.79 ± 0.01 ^{a}	3.80 ± 0.01 ^{b}	7.55 ± 0.21 ^{b}	7.15 ± 0.35 ^{b}	4.60 ± 0.14 ^{b}
Syrah	183 ± 2 ^{a}	190 ± 1 ^{b}	195 ± 1 ^{b}	110 ± 1 ^{a}	109 ± 1 ^{a}	111 ± 1 ^{a}	8.15 ± 0.06 ^{b}	8.91 ± 0.01 ^{b}	9.19 ± 0.01 ^{c}	3.49 ± 0.01 ^{a}	3.61 ± 0.01 ^{c}	3.81 ± 0.01 ^{b}	10.15 ± 0.07 ^{a}	9.06 ± 0.19 ^{a}	5.81 ± 0.26 ^{a}
Saborinho	121 ± 1 ^{b}	137 ± 2 ^{c}	135 ± 1 ^{c}	93 ± 3 ^{c}	100 ± 2 ^{b}	92 ± 2 ^{b}	8.11 ± 0.01 ^{b}	8.81 ± 0.01 ^{b}	9.29 ± 0.02 ^{b}	3.49 ± 0.04 ^{a}	3.69 ± 0.03 ^{b}	3.96 ± 0.01 ^{a}	7.95 ± 0.06 ^{b}	7.50 ± 0.14 ^{b}	4.49 ± 0.01 ^{b}

(1) Grape berry weight from 100 berries. (2) Must volume extracted from 100 berries. * Technological maturation and harvest (between 45 and 50 days after veraison). ** Different letters for the same vintage and for each data point (in column) indicate the existence of statistical differences (Tukey test, $p < 0.05$); all data express the average of four replicates ± standard deviation.

Concerning the results for pH values, at harvest, the lowest values were found for the two French grape varieties (average values ranged from pH 3.63 to 3.81). On the other hand, "Saborinho" grapes for the two vintages analyzed (2021 and 2023) showed high pH values (varied from pH 3.78 to 3.96). According to Brazão et al. [46], this Portuguese grape variety is characterized by high pH values and low titratable acidity values. It is important to note that, in general, grapes with high acidity are preferred because the organic acids (such as tartaric and malic acids) help to stabilize wine color and contribute to wine mouthfeel. At the same time, higher pH values lead to an increasing risk of microbial infection and, generally, unstable wines. In addition, grapes with higher pH lead to a lower antibacterial activity of SO_2, meaning that higher amounts are needed to successfully protect grape musts and wines from early spoilage and organoleptic alterations [47,48].

3.2. Global Phenolic Parameters

The general phenolic composition of the three red grape varieties studied during ripening is shown in Table 2. Making an overall analysis for total phenols, and flavonoid and non-flavonoid phenols evolution, it was clear there was an oscillation in the values. This tendency occurred during the three vintages considered. However, "Merlot" grapes showed a tendency for higher phenolic values during ripening compared to the remaining two varieties. This trend was particularly evident at harvest over the three vintages. In this case, the content of total phenolic compounds found for this grape variety varied from 473 (2023 vintage) to 1079 mg/L gallic acid equiv. (2021 vintage), while for "Syrah" grapes the values varied from 426 (2021 vintage) to 796 mg/L gallic acid equiv. (2022 vintage). Portuguese grape variety "Saborinho" showed the lowest values at harvest for the two vintages analyzed (varied from 396 to 495 mg/L gallic acid equiv., respectively, for the 2023 and 2021 vintages). It is also important to emphasize the particularly low values found for total phenolic and flavonoid compounds for all three grape varieties studied during grape ripening in 2023. This reduction can be a result of low phenolic biosynthesis and accumulation, and at the same time, a reduced extractability (particularly tannins), due to the bonding of these compounds to other cellular contents. Thus, the extractability of phenolics might have become more difficult in all grape varieties studied. This tendency has already been reported previously by several authors for other grape varieties [49,50].

For non-flavonoid phenols, at harvest, the results between the two French varieties did not show such high differences compared to what was detected for total phenols and flavonoid phenols over the three years. Thus, at harvest, for "Merlot" grapes, the values varied between 109 and 140 mg/L gallic acid equiv., while for "Syrah", the values varied between 110 and 178 mg/L gallic acid equiv. However, again, "Saborinho" grapes showed the lowest values (between 43 and 46 mg/L gallic acid equiv.). Therefore, considering the results obtained for non-flavonoid phenols in "Merlot" and "Syrah" grapes, there is probably a higher degree of adaptation of these two grape varieties to the climate and soil conditions of Pico Island with respect to the biosynthesis and accumulation of non-flavonoid compounds. According to Costa et al. [27], the variability in phenolic content found in grape varieties is a consequence not only of the "terroir" characteristics but also a result of the important role of genetic factors in the biosynthesis of these compounds. However, other authors have also mentioned the impact of climatic conditions such as average temperatures as factors that have an important impact on grape polyphenol accumulation [51,52].

Table 2. General phenolic composition of “Merlot”, “Syrah”, and “Saborinho” grape berries during ripening over three vintages (2021 to 2023) on Pico Island (Azores archipelago).

Vintages Grape Varieties	**Total Phenols (mg/L Gallic Acid Equiv.)**			**Flavonoid Phenols (mg/L Gallic Acid Equiv.)**			**Non-Flavonoid Phenols (mg/L Gallic Acid Equiv.)**			**Total Anthocyanins (mg/L Malvidin-3-Monoglucoside Equiv.)**			**Color Intensity (abs. Units × 10)**		
	Days After Veraison														
	21	**37**	**45 ***	**21**	**37**	**45 ***	**21**	**37**	**45 ***	**21**	**37**	**45 ***	**21**	**37**	**45 ***
2021															
Merlot	1030 ± 2 ^{a**}	1146 ± 1 ^{a}	1079 ± 3 ^{a}	1016 ± 2 ^{a}	1001 ± 1 ^{a}	939 ± 1 ^{a}	14 ± 1 ^{a}	144 ± 1 ^{a}	140 ± 2 ^{a}	810 ± 3 ^{a}	1258 ± 2 ^{a}	1076 ± 2 ^{a}	11.51 ± 0.01 ^{a}	14.33 ± 0.18 ^{a}	12.07 ± 0.03 ^{a}
Syrah	776 ± 4 ^{a}	595 ± 1 ^{b}	426 ± 2 ^{c}	768 ± 5 ^{b}	510 ± 1 ^{b}	314 ± 21 ^{c}	8 ± 1 ^{a}	84 ± 1 ^{b}	112 ± 18 ^{a}	560 ± 1 ^{b}	965 ± 1 ^{b}	752 ± 4 ^{b}	8.59 ± 0.01 ^{b}	10.06 ± 0.10 ^{b}	11.31 ± 0.04 ^{b}
Saborinho	222 ± 13 ^{c}	525 ± 1 ^{c}	495 ± 1 ^{b}	208 ± 10 ^{c}	489 ± 7 ^{c}	452 ± 7 ^{b}	14 ± 3 ^{a}	36 ± 5 ^{c}	43 ± 7 ^{b}	458 ± 1 ^{c}	426 ± 5 ^{c}	453 ± 3 ^{c}	7.62 ± 0.21 ^{c}	7.87 ± 0.08 ^{c}	8.38 ± 0.01 ^{c}
2022															
Merlot	794 ± 7 ^{a}	941 ± 9 ^{a}	971 ± 5 ^{a}	742 ± 11 ^{a}	871 ± 18 ^{a}	861 ± 7 ^{a}	52 ± 4 ^{b}	69 ± 8 ^{b}	109 ± 1 ^{b}	348 ± 3 ^{b}	449 ± 1 ^{b}	689 ± 1 ^{b}	7.35 ± 0.03 ^{a}	8.46 ± 0.43 ^{a}	10.22 ± 0.10 ^{a}
Syrah	700 ± 3 ^{b}	754 ± 6 ^{b}	796 ± 1 ^{b}	582 ± 1 ^{b}	645 ± 4 ^{b}	617 ± 8 ^{b}	117 ± 2 ^{a}	109 ± 2 ^{a}	178 ± 9 ^{a}	435 ± 7 ^{a}	541 ± 1 ^{a}	871 ± 1 ^{a}	3.78 ± 0.01 ^{b}	8.63 ± 0.04 ^{a}	10.14 ± 0.11 ^{a}
2023															
Merlot	411 ± 5 ^{a}	412 ± 1 ^{a}	473 ± 2 ^{a}	216 ± 11 ^{c}	227 ± 3 ^{b}	360 ± 4 ^{a}	195 ± 6 ^{a}	184 ± 2 ^{a}	112 ± 6 ^{a}	568 ± 8 ^{a}	608 ± 5 ^{a}	594 ± 5 ^{a}	7.10 ± 0.16 ^{a}	8.78 ± 0.45 ^{a}	7.68 ± 0.02 ^{a}
Syrah	337 ± 3 ^{b}	304 ± 3 ^{b}	418 ± 20 ^{b}	264 ± 2 ^{b}	209 ± 5 ^{b}	307 ± 20 ^{b}	72 ± 6 ^{b}	95 ± 1 ^{b}	110 ± 1 ^{a}	485 ± 1 ^{b}	494 ± 3 ^{c}	435 ± 5 ^{b}	5.94 ± 0.37 ^{b}	6.61 ± 0.01 ^{b}	6.56 ± 0.04 ^{b}
Saborinho	390 ± 8 ^{a}	410 ± 9 ^{a}	396 ± 7 ^{b}	373 ± 6 ^{a}	369 ± 13 ^{a}	349 ± 7 ^{a}	17 ± 2 ^{c}	41 ± 4 ^{c}	46 ± 1 ^{b}	405 ± 6 ^{c}	460 ± 3 ^{b}	442 ± 2 ^{b}	5.05 ± 0.10 ^{b}	5.57 ± 0.23 ^{b}	6.40 ± 0.21 ^{b}

* Technological maturation and harvest (between 45 and 50 days after veraison). ** Different letters for the same vintage and for each data point (in column) indicate the existence of statistical differences (Tukey test, $p < 0.05$); all data express the average of four replicates ± standard deviation.

The total anthocyanins' evolution during ripening presented in grape skin extracts is also shown in Table 2. During ripening, two different evolutive profiles were found depending on the variety. Thus, for "Merlot" and "Syrah" grapes for the 2022 vintage, anthocyanin content increased progressively until harvest, while for the 2021 and 2023 vintages, a slight decrease as maturation ends was observed. For "Saborinho" grapes, it was not possible to perceive a precise pattern in the two vintages studied. Different anthocyanin evolution profiles during ripening are reported by various authors. Thus, depending on the variety, a continuous anthocyanin increase during the maturation process is described by several authors [27,50,53], while others reported an increase progressively until harvest followed by a decrease as maturation ends [54].

At harvest, for the three vintages studied, there was no clear differentiation between the varieties for total anthocyanin content. Thus, while in the 2021 and 2023 vintages, "Merlot" was the variety with the significantly highest total anthocyanin content (varied between 1079 and 594 mg/L malvidin-3-monoglucoside equiv.), in 2022, it was "Syrah" that showed the significantly highest values (871 mg/L malvidin-3-monoglucoside equiv.). On the other hand, "Saborinho" was the variety with the lowest total anthocyanin content only in 2021 (453 mg/L malvidin-3-monoglucoside equiv.). In the 2023 vintage, the "Syrah" and "Saborinho" varieties showed the significantly lowest values (435 and 442 mg/L malvidin-3-monoglucoside equiv, respectively). Although it was only possible to obtain results for "Saborinho" over two vintages (for reasons already mentioned in the Material and Methods), at harvest, this variety showed the lowest anthocyanin content variation (between 442 and 453 mg/L malvidin-3-monoglucoside equiv., respectively, for the 2023 and 2021 vintages). According to Gladstones [55], grape anthocyanin content is determined by several factors (namely, climatic conditions, cultural practices, and genetic origin) and there is a high variability between varieties even when they are collected on the same site, sharing the same environmental conditions and cultivation practices. Finally, for color intensity (Table 2), in general, its evolution during grape ripening for the three vintages followed the same trend already detected for total anthocyanins. Thus, at harvest, "Merlot" grapes were those that showed phenolic extracts with higher color intensity values (varied between 7.68 and 12.07 abs. units) followed by "Syrah" (varied between 6.56 and 11.31 abs. units). "Saborinho" grapes showed the lowest color intensity values (varied between 6.40 and 8.38 abs. units) for the two vintages studied. However, it is important to note that according to Ortega-Regules et al. [56], highly colored grape must and total anthocyanin content do not necessarily produce high colored red wines. These differences are probably related to the easiness of anthocyanin extraction from grape skins into grape must.

From the data presented about phenolic composition for the three grape varieties studied under Pico Island conditions, several specific red winemaking techniques could be suggested. Thus, for the "Merlot" grape variety that showed in general high phenolic potential, a standard winemaking process is suggested to obtain red wines which express the varietal flavors of this variety. In addition, an increase in the frequency of pumping over can produce a full-body red wine, although the estimated alcohol degree found in "Merlot" grapes was low for the three vintages studied. Conversely, for "Saborinho" grapes, which showed lower polyphenolic potential, a long period of maceration during alcoholic fermentation would be recommended to increase the color and phenolic content in the wines produced.

3.3. Individual Anthocyanin Composition

The individual anthocyanin composition of the skin extracts obtained from the grape varieties during ripening is shown in Tables 3–5. Three different groups of anthocyanins grouped as monoglucosylated, p-coumaroylated, and acetylated were quantified. For "Merlot" and "Syrah" grapes, monoglucosylated was the major anthocyanin group followed in descending order by the acetylated and p-coumaroylated groups. However, for "Saborinho" grapes, after the monoglucosylated group, this variety showed higher content of the p-coumaroylated than the acetylated group.

Table 3. Individual monoglucosylated anthocyanins of "Merlot", "Syrah", and "Saborinho" grape skins during ripening over three vintages (2021 to 2023) on Pico Island (Azores archipelago).

Vintages Grape Varieties	**Delf Gluc** $^{(1)}$			**Cyan Gluc** $^{(1)}$			**Petun Gluc** $^{(1)}$			**Peon Gluc** $^{(1)}$			**Malv Gluc** $^{(1)}$		
	Days After Veraison														
	21	**37**	**45 ***	**21**	**37**	**45 ***	**21**	**37**	**45 ***	**21**	**37**	**45 ***	**21**	**37**	**45 ***
2021															
Merlot	22.0 ± 1.4 ^{a**}	30.5 ± 0.7 ^{b}	26.0 ± 1.4 ^{b}	13.5 ± 0.7 ^{b}	26.5 ± 0.8 ^{b}	12.0 ± 1.4 ^{b}	80.1 ± 1.3 ^{a}	142.5 ± 3.5 ^{a}	103.0 ± 1.4 ^{a}	92.6 ± 5.0 ^{a}	137.0 ± 1.4 ^{a}	231.0 ± 4.2 ^{a}	197.0 ± 7.0 ^{a}	532.5 ± 3.5 ^{a}	403.5 ± 0.7 ^{a}
Syrah	24.5 ± 4.8 ^{a}	36.7 ± 1.8 ^{a}	43.7 ± 1.7 ^{a}	32.0 ± 2.4 ^{a}	40.8 ± 1.2 ^{a}	28.0 ± 2.1 ^{a}	34.5 ± 3.5 ^{b}	122.5 ± 3.5 ^{b}	95.5 ± 2.1 ^{b}	46.5 ± 0.7 ^{c}	77.0 ± 1.4 ^{c}	64.0 ± 1.1 ^{c}	197.0 ± 7.0 ^{a}	398.0 ± 2.8 ^{b}	288.5 ± 6.3 ^{b}
Saborinho	19.0 ± 1.0 ^{a}	33.0 ± 1.4 ^{ab}	47.5 ± 0.7 ^{a}	16.5 ± 2.1 ^{b}	24.5 ± 0.7 ^{b}	14.0 ± 2.8 ^{b}	35.5 ± 0.7 ^{b}	44.5 ± 0.5 ^{c}	25.0 ± 1.4 ^{c}	78.5 ± 0.7 ^{b}	99.0 ± 0.3 ^{b}	89.5 ± 0.7 ^{b}	118.0 ± 2.8 ^{b}	146.5 ± 0.9 ^{c}	134.5 ± 0.6 ^{c}
2022															
Merlot	27.4 ± 1.3 ^{a}	33.9 ± 4.1 ^{a}	18.6 ± 0.6 ^{b}	10.6 ± 1.3 ^{a}	27.8 ± 2.1 ^{a}	15.8 ± 0.9 ^{b}	22.3 ± 0.6 ^{a}	51.2 ± 0.6 ^{b}	40.9 ± 1.3 ^{b}	29.7 ± 3.3 ^{b}	73.2 ± 3.1 ^{a}	104.5 ± 0.7 ^{a}	79.0 ± 1.4 ^{a}	168.5 ± 12.0 ^{b}	248.5 ± 2.1 ^{b}
Syrah	11.2 ± 0.5 ^{b}	17.8 ± 2.1 ^{b}	23.3 ± 1.3 ^{a}	12.9 ± 0.1 ^{a}	19.3 ± 0.8 ^{b}	27.5 ± 1.1 ^{a}	16.0 ± 1.4 ^{b}	32.11 ± 1.3 ^{a}	69.5 ± 2.1 ^{a}	50.7 ± 5.3 ^{a}	64.0 ± 1.4 ^{b}	89.5 ± 0.7 ^{b}	74.3 ± 5.1 ^{a}	216.1 ± 4.0 ^{a}	345.0 ± 5.6 ^{a}
2023															
Merlot	24.1 ± 2.2 ^{a}	23.9 ± 0.7 ^{a}	12.1 ± 1.2 ^{b}	20.8 ± 1.1 ^{a}	17.4 ± 0.6 ^{b}	19.0 ± 0.2 ^{b}	49.7 ± 1.7 ^{a}	57.3 ± 0.7 ^{a}	61.6 ± 0.5 ^{a}	31.8 ± 2.1 ^{c}	111.1 ± 1.3 ^{a}	100.9 ± 0.3 ^{a}	201.5 ± 2.1 ^{a}	289 ± 1.4 ^{a}	313.9 ± 5.6 ^{a}
Syrah	18.9 ± 1.2 ^{ab}	15.0 ± 0.2 ^{c}	27.8 ± 1.1 ^{a}	19.9 ± 0.9 ^{a}	22.2 ± 0.9 ^{a}	30.8 ± 0.8 ^{a}	31.8 ± 1.8 ^{b}	30.7 ± 0.7 ^{b}	50.8 ± 0.7 ^{b}	85.0 ± 0.9 ^{a}	69.9 ± 0.6 ^{b}	70.1 ± 1.6 ^{c}	111.2 ± 1.7 ^{c}	113.6 ± 1.8 ^{c}	126.4 ± 2.1 ^{b}
Saborinho	16.6 ± 1.4 ^{b}	20.0 ± 0.6 ^{b}	11.7 ± 1.1 ^{b}	11.1 ± 0.7 ^{b}	16.1 ± 0.3 ^{b}	8.0 ± 0.3 ^{c}	21.5 ± 1.9 ^{c}	26.1 ± 0.7 ^{c}	10.6 ± 0.5 ^{c}	50.5 ± 0.7 ^{b}	66.1 ± 1.1 ^{b}	82.0 ± 2.3 ^{b}	133.7 ± 4.7 ^{b}	168.1 ± 3.2 ^{b}	121.3 ± 1.1 ^{b}

$^{(1)}$ Individual anthocyanins expressed in malvidin-3-glucoside equivalents (mg/L). * Technological maturation and harvest (between 45 and 50 days after veraison). ** Different letters for the same vintage and for each data point (in column) indicate the existence of statistical differences (Tukey test, $p < 0.05$); all data express the average of four replicates ± standard deviation. Delf gluc, delphinidin-3-glucoside; Cyan gluc, cyanidin-3-glucoside; Petun gluc, petunidin-3-glucoside; Peon gluc, peonidin-3-glucoside; Malv gluc, malvidin-3-glucoside.

Table 4. Individual acetylated anthocyanin derivates of "Merlot", "Syrah", and "Saborinho" grape berries during ripening over three vintages (2021 to 2023) on Pico Island (Azores archipelago).

Vintages Grape Varieties	**Delf Acet-Gluc** $^{(1)}$			**Pet Acet-Gluc** $^{(1)}$			**Peon Acet-Gluc** $^{(1)}$			**Malv Acet-Gluc** $^{(1)}$		
	Days After Veraison											
	21	**37**	**45 ***	**21**	**37**	**45 ***	**21**	**37**	**45 ***	**21**	**37**	**45 ***
2021												
Merlot	7.9 ± 0.1 ^{a**}	16.0 ± 1.4 ^{a}	3.9 ± 0.6 ^{a}	14.8 ± 0.6 ^{a}	19.0 ± 1.4 ^{b}	8.4 ± 0.8 ^{b}	6.3 ± 0.5 ^{b}	20.9 ± 0.1 ^{a}	14.8 ± 1.2 ^{a}	35.2 ± 0.7 ^{a}	115.8 ± 0.3 ^{a}	40.2 ± 0.7 ^{a}
Syrah	3.9 ± 0.6 ^{b}	6.7 ± 1.3 ^{b}	4.2 ± 0.4 ^{a}	14.8 ± 0.6 ^{a}	26.0 ± 1.4 ^{a}	16.1 ± 0.2 ^{a}	3.6 ± 0.4 ^{c}	8.4 ± 0.2 ^{c}	4.1 ± 0.4 ^{a}	14.5 ± 0.7 ^{b}	35.5 ± 0.7 ^{b}	26.5 ± 2.1 ^{b}
Saborinho	1.5 ± 0.4 ^{c}	2.3 ± 0.6 ^{b}	2.2 ± 0.2 ^{b}	0.9 ± 0.1 ^{b}	5.1 ± 0.1 ^{c}	4.4 ± 0.1 ^{c}	9.4 ± 0.3 ^{a}	9.8 ± 0.1 ^{b}	7.4 ± 0.6 ^{b}	9.0 ± 0.4 ^{c}	26.5 ± 2.1 ^{c}	27.8 ± 1.4 ^{b}
2022												
Merlot	5.6 ± 0.3 ^{a}	10.6 ± 0.5 ^{a}	2.4 ± 0.2 ^{b}	4.4 ± 0.4 ^{a}	5.8 ± 0.2 ^{a}	3.1 ± 0.1 ^{b}	3.4 ± 0.6 ^{b}	15.1 ± 0.6 ^{a}	10.6 ± 1.0 ^{a}	20.6 ± 0.4 ^{a}	17.9 ± 1.5 ^{a}	30.5 ± 0.7 ^{a}
Syrah	1.4 ± 0.3 ^{b}	4.3 ± 0.8 ^{b}	5.8 ± 0.1 ^{a}	2.2 ± 0.2 ^{b}	2.9 ± 0.1 ^{b}	9.5 ± 0.2 ^{a}	9.3 ± 0.4 ^{a}	7.8 ± 0.3 ^{b}	4.8 ± 0.2 ^{b}	12.1 ± 2.0 ^{b}	17.9 ± 0.8 ^{a}	26.8 ± 1.3 ^{b}
2023												
Merlot	6.3 ± 1.0 ^{a}	7.1 ± 0.2 ^{a}	1.0 ± 0.2 ^{b}	9.6 ± 0.6 ^{a}	10.7 ± 0.2 ^{a}	9.6 ± 0.2 ^{a}	4.7 ± 0.4 ^{b}	17.6 ± 0.8 ^{a}	7.3 ± 0.5 ^{b}	28.2 ± 1.7 ^{a}	29.0 ± 1.2 ^{ab}	17.2 ± 0.5 ^{b}
Syrah	2.6 ± 0.1 ^{b}	0.5 ± 0.1 ^{c}	7.6 ± 0.4 ^{a}	4.9 ± 0.1 ^{b}	3.8 ± 0.4 ^{b}	10.9 ± 1.0 ^{a}	4.1 ± 0.0 ^{b}	9.9 ± 0.5 ^{b}	3.8 ± 0.4 ^{c}	31.9 ± 0.4 ^{a}	27.9 ± 0.3 ^{b}	30.9 ± 0.7 ^{a}
Saborinho	3.6 ± 0.5 ^{b}	4.3 ± 0.3 ^{b}	1.7 ± 0.1 ^{b}	3.2 ± 0.2 ^{b}	5.3 ± 0.5 ^{b}	2.6 ± 0.4 ^{b}	7.1 ± 0.3 ^{a}	8.4 ± 0.6 ^{b}	9.6 ± 0.1 ^{a}	32.2 ± 2.3 ^{a}	32.0 ± 0.7 ^{a}	27.2 ± 1.4 ^{a}

$^{(1)}$ Individual anthocyanins expressed in malvidin-3-glucoside equivalents (mg/L). * Technological maturation and harvest. ** Different letters for the same vintage and for each data point (in column) indicate the existence of statistical differences ($p < 0.05$); all data express the average of three replicates ± standard deviation. Delf acet-gluc, delphinidin-3-acetylglucoside; Pet acet-gluc, petunidin-3-acetylglucoside; Peon acet-gluc, peonidin-3-acetylglucoside; Malv acet-gluc, malvidin-3-acetylglucoside.

Table 5. Individual p-coumaroyl anthocyanin derivates of "Merlot", "Syrah", and "Saborinho" grape berries during ripening over three vintages (2021 to 2023) on Pico Island (Azores archipelago).

Vintages Grape Varieties	**Pet Coum-Gluc (1)**			**Peon Coum-Gluc (1)**			**Malv Coum-Gluc (1)**		
	Days After Veraison								
	21	**37**	**45 ***	**21**	**37**	**45 ***	**21**	**37**	**45 ***
2021									
Merlot	5.1 ± 0.1 ^{a**}	9.0 ± 0.1 ^{b}	6.0 ± 0.2 ^{a}	11.6 ± 1.2 ^{a}	15.4 ± 1.1 ^{a}	8.6 ± 1.7 ^{a}	11.3 ± 0.3 ^{a}	73.6 ± 3.3 ^{a}	36.3 ± 0.8 ^{a}
Syrah	6.1 ± 1.2 ^{a}	17.1 ± 1.3 ^{a}	6.0 ± 0.1 ^{a}	12.4 ± 0.1 ^{a}	7.8 ± 0.1 ^{b}	6.5 ± 0.6 ^{a}	11.3 ± 0.3 ^{a}	13.5 ± 3.5 ^{b}	35.5 ± 0.7 ^{a}
Saborinho	1.5 ± 0.4 ^{b}	2.0 ± 0.1 ^{c}	6.3 ± 0.1 ^{a}	7.7 ± 0.1 ^{b}	8.9 ± 1.4 ^{b}	10.5 ± 0.4 ^{a}	6.4 ± 0.3 ^{b}	16.9 ± 0.1 ^{b}	26.5 ± 2.1 ^{b}
2022									
Merlot	2.0 ± 0.1 ^{a}	3.3 ± 0.2 ^{a}	2.5 ± 0.4 ^{a}	6.2 ± 0.4 ^{a}	6.6 ± 0.5 ^{a}	5.5 ± 0.6 ^{a}	7.1 ± 1.1 ^{a}	15.9 ± 0.1 ^{b}	20.5 ± 0.7 ^{a}
Syrah	1.8 ± 0.2 ^{a}	4.8 ± 1.1 ^{a}	2.9 ± 0.1 ^{a}	3.6 ± 0.3 ^{b}	5.7 ± 0.4 ^{a}	5.4 ± 0.7 ^{a}	4.6 ± 0.6 ^{b}	18.7 ± 1.0 ^{a}	12.0 ± 0.6 ^{b}
2023									
Merlot	3.9 ± 0.1 ^{b}	4.6 ± 0.1 ^{a}	3.2 ± 0.3 ^{b}	8.3 ± 0.1 ^{a}	10.0 ± 0.4 ^{b}	5.9 ± 0.8 ^{c}	10.8 ± 0.5 ^{b}	12.1 ± 0.4 ^{b}	13.7 ± 0.5 ^{b}
Syrah	5.6 ± 0.1 ^{a}	3.8 ± 0.9 ^{ab}	4.6 ± 0.4 ^{b}	8.2 ± 0.8 ^{a}	8.3 ± 0.2 ^{c}	9.4 ± 0.1 ^{b}	8.9 ± 0.3 ^{b}	15.1 ± 0.8 ^{b}	8.8 ± 0.2 ^{b}
Saborinho	2.7 ± 0.1 ^{c}	2.5 ± 0.1 ^{b}	7.0 ± 0.6 ^{a}	10.0 ± 1.2 ^{a}	13.1 ± 0.6 ^{a}	18.8 ± 5.9 ^{a}	31.4 ± 1.7 ^{a}	22.9 ± 0.8 ^{a}	32.6 ± 3.3 ^{a}

(1) Individual anthocyanins expressed in malvidin-3-glucoside equivalents (mg/L). * Technological maturation and harvest. ** Different letters for the same vintage and for each data point (in column) indicate the existence of statistical differences ($p < 0.05$); all data express the average of three replicates ± standard deviation. Pet coum-gluc, petunidin-3-p-coumaroyl glucoside; Peon coum-gluc, peonidin-3-p-coumaroyl glucoside; Malv coum-gluc, malvidin-3-p-coumaroyl glucoside.

For all three grape varieties studied, malvidin-3-glucoside was the major individual anthocyanin quantified (Table 3), which is the terminal compound in the process of anthocyanidin biosynthesis. These results agree with previous findings quantified in other grape varieties (including "Syrah" and "Merlot" grapes) cultivated under other climatic and soil conditions [27,28,56–59]. In addition, according to Mori et al. [60], when grape berries are grown under high temperatures, malvidin derivatives (3-glucoside, 3-acetylglucoside, and 3-p-coumaroyl glucoside) present higher resistance to degradation compared to other forms. Ribéreau-Gayon et al. [61] also reported that malvidin derivatives are relatively resistant to oxidation processes and their presence gives stability to the wine during the winemaking process.

At harvest, it was "Merlot" grapes that showed the highest malvidin-3-glucoside values (Table 3) for the 2021 and 2023 vintages (403.5 and 313.9 mg/L malvidin-3-glucoside equiv., respectively), while "Syrah" grapes showed the highest values for the 2022 vintage (345.0 mg/L malvidin-3-glucoside equiv.). It was also "Merlot" grapes that showed the second highest most abundant individual anthocyanin detected (peonidin-3-glucoside) for the varieties studied over the three vintages. Thus, the values of peonidin-3-glucoside for this variety varied between 100.9 and 231.0 mg/L malvidin-3-glucoside equiv., followed by "Saborinho" grapes in which this individual anthocyanin varied between 82.0 and 89.5 mg/L malvidin-3-glucoside equiv. These findings are consistent with the results of González-Neves et al. [62] who detected a higher peonidin content in "Merlot" grape skins. For "Syrah", there was no clear pattern because peonidin-3-glucoside was the second most abundant individual anthocyanin in the 2022 and 2023 vintages, but for the 2021 vintage, it was petunidin-3-glucoside that was the second most abundant form. Previously, other authors have reported peonidin-3-glucoside as the second most abundant non-acylated anthocyanin found in "Syrah" cultivated in China and in several Spanish varieties cultivated in the Galicia region [19,63].

In general, delphinidin-3-acetylglucoside and petunidin-3-p-coumaroyl glucoside were the least abundant individual anthocyanins for all grape varieties studied during the vintages considered (Tables 4 and 5). In addition, cyanidin 3-acetylglucoside, cyanidin 3-p-coumaroyl glucoside, and delphinidin 3-p-coumaroyl glucoside were not detected in all grape varieties studied. Previously, several authors reported that cyanidin derivatives were one of the individual anthocyanin groups with the lowest concentration in grapes [19,27,28,59]. However, in our study, cyanidin monoglucoside showed relatively high values for the three grape varieties studied, even in comparison with the values obtained for delphinidin monoglucoside (Table 3). However, there are authors who reported relatively higher levels of delphinidin and cyanidin derivatives found in "Merlot" grapes [19]. In addition, Segade et al. [63] described similar values between cyanidin and delphinidin derivatives found in the "Brancellao" variety cultivated in the Galicia region (Spain) during two consecutive vintages. Furthermore, previously, Ryan and Revilla [64] reported that the presence of primitive anthocyanins, such as delphinidin-3-glucoside, could be a significant indicator of climatic conditions during grape ripening which probably modulate anthocyanin biosynthesis.

Several authors described the pathways of anthocyanin biosynthesis [65–67]. Briefly, it is assumed that cyanidin-3-glucoside is an initial compound and precursor of delphinidin and peonidin 3-glucosides, which are synthesized by the action of two enzymes ($3'$-hydroxylase and $3'$-O-methyltransferase, respectively). On the other hand, petunidin-3-glucoside is formed with the conversion of delphinidin-3-glucoside by the action of methyltransferase, and it is a precursor of malvidin-3-glucoside which is synthesized by the same enzyme. However, malvidin-3-glucoside could be directly obtained from delphinidin-3-glucoside by the action of methyltransferases. According to Núñez et al. [68], the activities of these enzymes are strongly related to the genetic factors of the grape varieties. Thus, because of the action of the enzymes involved in anthocyanin biosynthesis, the anthocyanin profile could be used for discrimination of the grape varieties. However, it is important to note that environmental conditions may also determine its activity.

Some authors established ratios between some anthocyanins contributing to the identity of red grape varieties and their potential association with cultivation factors [61,69–71]. Thus, at harvest, the ratios between various anthocyanin compounds detected from the three grape varieties studied over the vintages considered are summarized in Table 6.

Table 6. Anthocyanin ratios based on the detected individual anthocyanins at harvest of "Merlot", "Syrah", and "Saborinho" grape skins at harvest over three vintages (2021 to 2023) on Pico Island (Azores archipelago).

	Anthocyanin Ratio			
Vintages Grape Varieties	$\frac{\sum Malv}{\sum Peon}$	$\frac{\sum Coum}{\sum Acet}$	$\frac{\sum Delf}{\sum Peon}$	$\frac{\sum Petun}{\sum Peon}$
2021				
Merlot	$1.88 \pm 0.10^{b*}$	0.75 ± 0.07^{b}	0.11 ± 0.02^{c}	0.46 ± 0.05^{b}
Syrah	4.69 ± 0.31^{a}	0.90 ± 0.08^{a}	0.64 ± 0.09^{a}	1.57 ± 0.07^{a}
Saborinho	1.75 ± 0.05^{b}	1.03 ± 0.04^{a}	0.46 ± 0.07^{b}	0.33 ± 0.01^{c}
2022				
Merlot	2.47 ± 0.09^{b}	0.61 ± 0.03^{a}	0.17 ± 0.03^{b}	0.38 ± 0.03^{b}
Syrah	3.84 ± 0.21^{a}	0.43 ± 0.06^{b}	0.29 ± 0.05^{a}	0.90 ± 0.06^{a}
2023				
Merlot	3.01 ± 0.18^{a}	0.64 ± 0.07^{b}	0.11 ± 0.03^{b}	0.65 ± 0.09^{a}
Syrah	1.99 ± 0.10^{b}	0.42 ± 0.05^{c}	0.24 ± 0.06^{a}	0.79 ± 0.03^{a}
Saborinho	1.64 ± 0.15^{c}	1.42 ± 0.11^{a}	0.12 ± 0.02^{b}	0.18 ± 0.01^{b}

* Different letters for the same vintage and for each data point (in column) indicate the existence of statistical differences (Tukey test, $p < 0.05$); all data express the average of four replicates ± standard deviation. Pet coum-gluc, petunidin-3-*p*-coumaroyl glucoside; Peon coum-gluc, peonidin-3-*p*-coumaroyl glucoside; Malv coum-gluc, malvidin-3-*p*-coumaroyl glucoside.

The first evidence was that the ratios between the various anthocyanins within each variety were not uniform over the vintages. These results demonstrate that in addition to the genetic factor, the variability in environmental conditions will also have influenced the activity of the various enzymes involved in the biosynthesis of the various individual anthocyanins. Thus, "Syrah" showed the significantly highest ratio of ΣMalv/ΣPeon in the 2021 and 2022 vintages (between 3.84 and 4.69), while "Merlot" showed the significantly highest ratio (3.01) in the 2023 vintage. "Saborinho" showed the lowest ΣMalv/ΣPeon ratio values (between 1.62 and 1.75) over the two vintages analyzed. These results suggest that malvidins are the predominant anthocyanins in the "Merlot" and "Syrah" varieties, but its relative weight varies markedly over the years. Thus, these data provide evidence for the influence of environmental factors on anthocyanin biosynthesis. According to Núñez et al. [68], this ratio is related to the flavonoid-$3'$-hydroxylase and o-dihydroxyphenyl-O-transferase enzyme activities.

Another ratio calculated was ΣCoum/ΣAcet, for which "Saborinho" grapes showed the highest values (varied between 1.03 and 1.42). In this case, this tendency demonstrated higher predominance of p-coumaroylated derivates compared to acetyl-anthocyanins derivates, which is related to acetyl and coumaroyl transferase activities. Previously, several authors reported p-coumaroylated derivates as being the second major anthocyanin group [27,28,71]. However, for the "Merlot" and "Syrah" varieties during all vintages analyzed, the ΣCoum/ΣAcet ratio showed values lower than one, which means the predominance of acetyl-anthocyanins in relation to p-coumaroylated forms. Several authors also reported higher acetyl-anthocyanins found in "Pinot Noir" and "Cabernet Sauvignon" cultivated in different countries [28,57,71]. In addition, our findings for "Merlot's" ΣCoum/ΣAcet ratio are similar, as also observed by other authors for this grape variety [71,72].

According to the terminal biosynthetic transformations of anthocyanins in grapes, from cyanidin-3-glucoside and by action of the enzymes 3′-5′-O-methyltransferase or 5′-hydroxylase, there is the formation of peonidins or the sequential formation of delphinidins and petunidins, respectively [66]. Thus, the ∑Delf/∑Peon and ∑Petun/∑Peon ratios allow us to have an idea of the preferential action of each of the enzymes. Among the three grape varieties studied, a clear variation in the values obtained was detected over the vintages. Therefore, "Syrah" showed the significantly highest values for both ratios (varied between 0.24 and 0.64 for the ∑Delf/∑Peon ratio and between 0.90 and 1.57 for the ∑Petun/∑Peon ratio). These results indicate that 5′-hydroxylase and 3′-5-′O-methyltransferase showed high activities in "Syrah" grapes, allowing the accumulation of significantly more delphinidins and petunidins compared with the other two varieties studied. For the remaining two varieties ("Merlot" and "Saborinho"), it was not possible to detect a clear pattern over the years studied. Thus, "Merlot" for the ∑Delf/∑Peon ratio showed the lowest values over the three vintages, but for the ∑Petun/∑Peon ratio, intermediate values were detected. Previous results obtained by other authors showed contradictory results for this grape variety. Thus, Dimitrovska et al. [71] reported high activities of hydroxylase and methyltransferase, allowing the accumulation of significantly more delphinidins and petunidins in "Merlot" grapes, while González-Neves et al. [62] reported higher peonidin content in the skins of this variety.

3.4. Antioxidant Capacity

The data in Figure 2 show the antioxidant capacity quantified in the three grape varieties studied at harvest over the three vintages. Considering the values obtained by the application of the ABTS method, grapes from the "Merlot" variety showed higher values (values varied from 4.18 to 6.25 µmol trolox/L) than "Syrah" (3.80 to 3.64 µmol trolox/L) and "Saborinho" (3.91 to 3.93 µmol trolox/L) over the three vintages. These values were significantly higher for the 2021 and 2023 vintages, while in 2022, the values, although higher, showed no statistical difference compared to the remaining two varieties. A similar tendency was obtained for the values of antioxidant capacity using the DPPH method. However, the differences did not show statistical differences. In fact, it is well known that the antioxidant capacity values could differ based on the method used. According to several authors, this divergence could be explained because ABTS$^+$ and DPPH radicals have different stereochemical structures and a different method of genesis, and thus, they lend, after the reactions with the different individual phenolic compounds, a qualitatively different response to the inactivation of their radical [73,74].

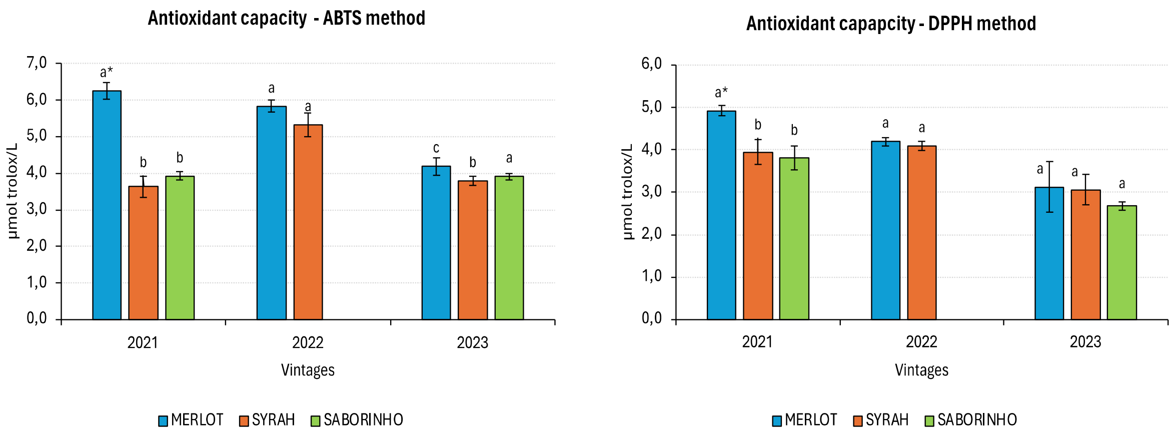

Figure 2. Antioxidant capacity of "Merlot", "Syrah", and "Saborinho" grape varieties at harvest (between 45 and 50 days after veraison) over three vintages (2021 to 2023) in Pico Island (Azores archipelago). * Different letters for the same vintage indicate the existence of statistical differences (Tukey test, $p < 0.05$); all data express the average of four replicates ± standard deviation.

At harvest, the higher antioxidant capacity obtained for “Merlot” grapes compared to the others two varieties studied confirms the tendency observed for the general phenolic composition already described. In fact, correlations between antioxidant activity and total polyphenolic content from different grape varieties have been reported previously by several authors [28,75,76]. High correlations between anthocyanin content from different Spanish grape varieties and antioxidant activity is reported by Vilanova et al. [77], while other authors also reported high correlations for “Merlot” and “Cabernet sauvignon” grapes between antioxidant activity and total phenolic content and other individual phenolic compounds [78].

3.5. Varietal Aroma Potential Index

The varietal aroma potential index is a parameter that is an integral measure of glycosylated aroma precursors that include mostly volatile aglycones, such as terpenes, phenols, C_{13}-norisoprenoids, and alcohols. Figure 3 shows the varietal aroma potential index results of the grape varieties studied at harvest over the three vintages. Only in the 2021 vintage was it possible to detect significant differences between the three grape varieties studied. Thus, the “Merlot” and “Syrah” varieties showed the significantly highest values for the varietal potential index (IPAV values of 9.99 and 10.93, respectively) compared to “Saborinho” (IPV values of 7.9), which means that these two varieties of French origin that reached harvest for the 2021 vintage, came from grapes with higher glycosylated aroma precursors. For the remaining two vintages (2022 and 2023), no significant differences were detected between the grape varieties, with IPAV values ranging between 8.23 and 9.91 for all grape varieties. According to Pardo-García et al. [79] grapes with high IPAV values are related to grapes with an abundant aglycones content that could be released progressively during winemaking over time, inducing positive effects on wine aroma. Independently of the vintage, the results obtained for the three grape varieties studied under the Pico Island conditions showed similar values already obtained by Serrano de la Hoz et al. [38] for the “Airén” and “Macabeo” varieties cultivated in the La Mancha denomination of origin (Spain), but lower values when compared with the results obtained for the “Tempranillo” variety cultivated in the Rioja denomination of origin (Spain). Campayo et al. [80] reported, at technological maturity for the “Bobal” red variety, IPAV values between 10.18 and 13.58, having also obtained some differentiation depending on the harvest year. Several authors reported the aroma precursor’s synthesis increase during grape ripening [81–83], but their contents are determined by several factors, such as grape variety [82,84,85], agronomic practices [38,84,86], and environmental conditions [38].

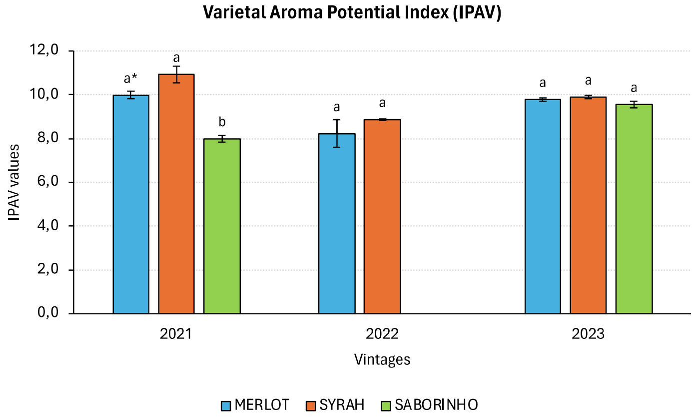

Figure 3. Varietal aroma potential index (IPAV) of “Merlot”, “Syrah”, and “Saborinho” grape varieties at harvest (between 45 and 50 days after veraison) over three vintages (2021 to 2023) on Pico Island (Azores archipelago). * Different letters for the same vintage indicate the existence of statistical differences (Tukey test, $p < 0.05$); all data express the average of four replicates ± standard deviation.

3.6. PCA Applied to Grape Varieties Characterization

A Principal Component Analysis (PCA) was used to better understand the adaptability of the different varieties studied to Pico Island conditions over the three vintages analyzed on general physicochemical characteristics, global phenolic composition, individual anthocyanins (monoglucosylated; acetylated; p-coumaroyl derivatives), antioxidant capacity, and the varietal aroma potential index of grape berry at technological maturity. The PCA was carried out to obtain a reduced number of linear combinations of the variables that explain the greater variability in the data. Thus, a PCA was calculated using the following 27 initial variables: individual anthocyanins (12); anthocyanins' ratios (4); global phenolic parameters (5); general physicochemical composition (3); antioxidant capacity (2); and varietal aroma (1). The corresponding loading plots that established the relative importance of each variable are shown in Figure 4.

The PCA showed that the first two principal components (PCs) explained 64.3% of the total variance. The projections of the analyzed variables in the PCs are the weighted sum of the original variables and are shown in Figure 4A. The first PC (PC1, 35.0% of the variance) was strongly correlated with the following variables: individual monoglucosylated and acetylated anthocyanins (except for peonidin-3-glucoside, peonidin-3-acetylglucoside, and malvidin-3-acetylglucoside); three anthocyanin ratios (ΣMalv/ΣPeon, ΣDelf/ΣPeon, and ΣPetun/ΣPeon); the varietal aroma potential index (IPAV); titratable acidity; and non-flavonoid phenols. However, it was negatively correlated with pH, two individual p-coumaroyl anthocyanins (peonidin and petunidin 3-p-coumaroyl glucosides), and one anthocyanin ratio (ΣCoum/ΣAcet). The second PC (PC2, 29.3% of the variance) was positively correlated with antioxidant capacity, total phenols, flavonoid phenols, color intensity, total anthocyanins, and the remaining individual anthocyanins.

Figure 4B gives a spatial distribution of the three grape varieties and vintages at harvest in relation to the different parameters considered. After a cluster analysis, three different groups were formed. The grouping was carried out according to each grape variety. One group was formed by the "Syrah" variety for all vintages (2021 to 2023). These grape samples were positioned on the positive side of the PC1 axis and characterized by the high content of cyanidin-3-glucoside and petunidin-3-acetylglucoside and high ΣMalv/ΣPeon and ΣPet/ΣPeon ratios for the 2021 vintage. On the other hand, for the 2022 vintage, these grape samples were associated with high delphinidin-3-acetylglucoside content, IPAV values, and ΣDelf/ΣPeon ratio. For the 2023 vintage, a high association with delphinidin-3-glucoside content was detected.

Another group was comprised of the "Saborinho" grape samples and was located on the negative side of the PC1 axis. These grape samples were positively related with two individual p-coumaroyl anthocyanins (petunidin and peonidin, for the 2021 and 2023 vintages, respectively) and a high ΣCoum/ΣAcet ratio for the 2023 vintage. Finally, a last group was formed by "Merlot" grape samples. These samples were positioned on the positive side of the PC2 axis for the 2021 and 2022 vintages and on the negative side for the 2023 vintage. Thus, for the 2021 vintage, these samples were positively related to total flavonoid phenols, malvidin-3-acetylglucoside, and peonidin-3-glucoside, while for the 2022 vintage, they were related to malvidin 3-p-coumaroyl glucoside. However, for the 2023 vintage, "Merlot" grape samples were not related to any of the initial variables analyzed.

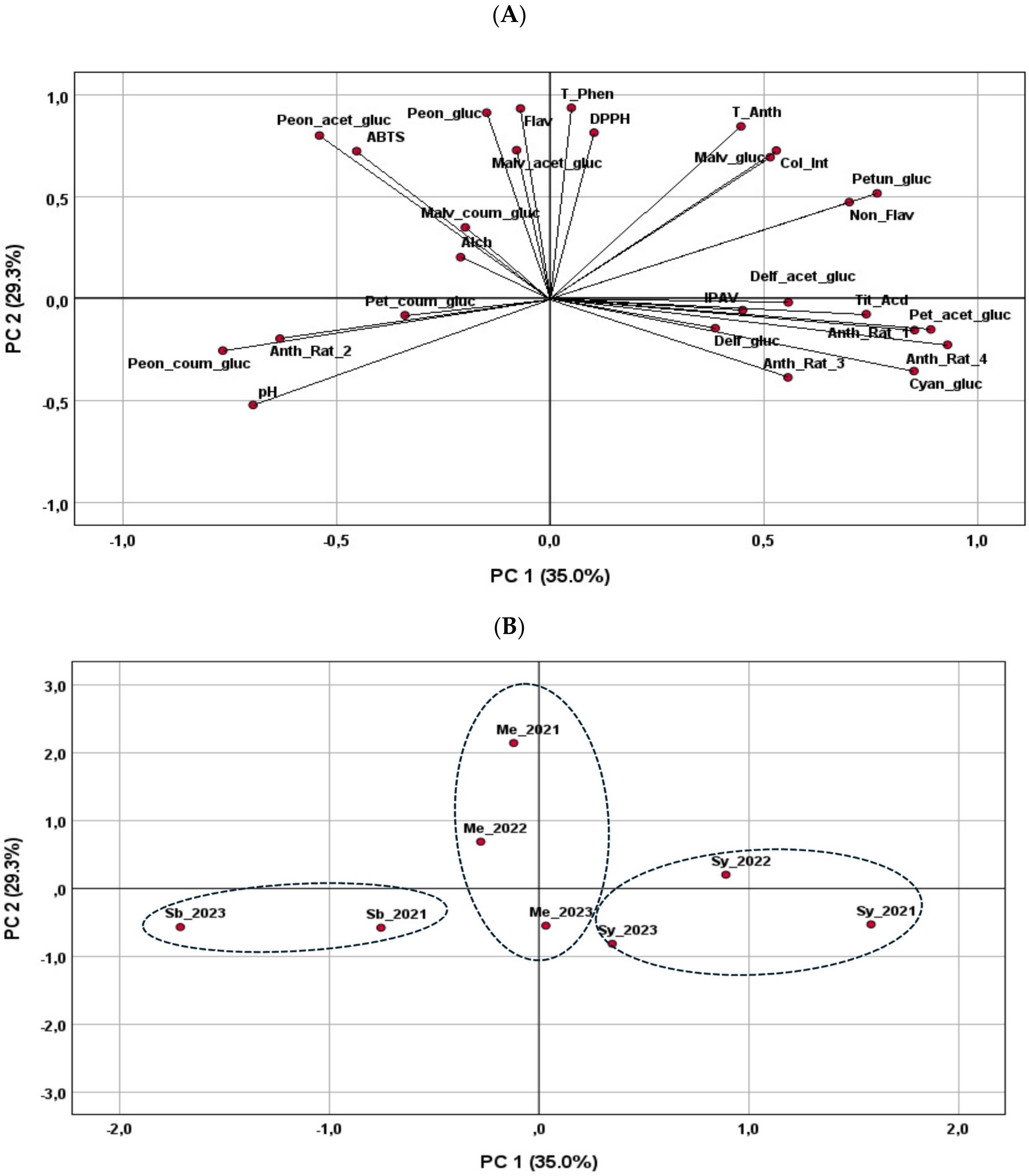

Figure 4. Principal component analysis (PCA; PC1 and PC2) for the different variables and grape varieties at harvest over three vintages. (**A**) Projection of variables; (**B**) projection of grape variety samples. (**A**) Projection of variables: *physicochemical parameters* (Alch—estimated alcohol degree; pH; Tit_Ac—titratable acidity); *global phenolic parameters* (T_Phe—total phenols; Flav—flavonoid phenols; Non_Flav—non-flavonoid phenols; T_Anth—total anthocyanins; Col_Int—color intensity); *individual anthocyanins* (Delf_gluc—delphinidin-3-glucoside; Cyan_gluc—cyanidin-3-glucoside; Petun_gluc—petunidin-3-glucoside; Peon_gluc—peonidin-3-glucoside; Malv_gluc—malvidin-3-glucoside; Delf_acet_gluc—delphinidin-3-acetylglucoside; Pet_acet_gluc—petunidin-3-acetylglucoside; Peon_acet_gluc—peonidin-3-acetylglucoside; Malv_acet_gluc—malvidin-3-acetylglucoside; Pet_coum_gluc—petunidin-3- *p*-coumaroyl glucoside; Peon_coum_gluc—peonidin-3-*p*-coumaroyl glucoside; Malv_coum_gluc—malvidin-3-*p*-coumaroyl glucoside); *anthocyanin* ratios (Anth_Rat_1—∑Malv)/∑Peon; Anth_Rat_2—∑Coum/∑Acet; Anth_Rat_3—∑Delf/∑Peon; Anth_Rat_4—∑Petun/∑Peon); *antioxidant capacity* (ABTS—ABTS method results; DPPH—DPPH method results; *varietal aroma potential* index (IPAV results). (**B**) Projection grape variety samples: *grape varieties* (Me—Merlot; Sy—Syrah; Sb—Saborinho); vintages (2021; 2022; 2023).

4. Conclusions

This study is one of the first reports related to the adaptability of the three red varieties studied based on the very specific conditions of Pico Island in the Azores archipelago.

Considerable variations were observed between vintages for most of the parameters studied. However, despite this variability, the results obtained demonstrated that the "Merlot" variety showed a tendency for significantly higher values for most of the parameters analyzed, namely, estimated alcohol degree, phenolic content, and antioxidant capacity values compared to the "Syrah" and "Saborinho" varieties over the three vintages studied. Nevertheless, for varietal aromatic potential, the three varieties studied did not allow us to obtain a clear trend of possible differentiation between them, although in the 2021 vintage, the two varieties of French origin ("Syrah" and "Merlot") showed significantly higher values compared to the "Saborinho" variety. On the other hand, carrying out a detailed analysis of the ratios between the various anthocyanin groups, the results also seem to indicate that each variety did not show uniform behavior over the vintages. These results demonstrate that in addition to the genetic factor, the variability in environmental conditions for each vintage can also determine the activity of the various enzymes involved in the biosynthesis of the various individual anthocyanins.

Finally, from a global point of view, it is important to note that the adaptation degree of the three red grape varieties studied for the environmental conditions of Pico Island may be a differentiating factor with respect to the main characteristics of these grape varieties compared to the characteristics of the same varieties but grown in other wine regions. The way such differences manifest themselves both in the red wines produced will also be noteworthy. Nevertheless, the outcomes obtained in our research need to be treated with caution because variables such as vintage or harvest date could influence the relative values of the parameters analyzed. In this case, the high variability in climatic conditions that are experienced annually on these islands could be a determining factor.

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References

1. Eiras-Dias, J.E.; Paulos, V.; Mestre, S.; Martins, J.T.; Goulart, I. The grapevine varieties of Azores region. *Ciência Téc. Vitiv.* **2006**, *21*, 99–112.
2. Zorman, M.; Lopes, D.J.H.; Martins, J.O.; Prendes, C.; Lorenzo, C.D.; Cabrera, R. Incidence of downy mildew *Plasmopara viticola* (Berk. Et Curtis ex. de Bary) Berl. Et de Toni in Terceira Island, Azores. *Rev. Ciênc. Agrár.* **2008**, *31*, 134–138. [CrossRef]
3. Azevedo, E.B. Pico Island—Climate Overview. In *Pico Island Natural History Handbook*; Victor-Hugo, F., Ed.; Observatório Vulcanológico e Geotérmico dos Açores: Ponta Delgada, Azores, Portugal, 2014; pp. 1–7.
4. Soil Survey Staff. *Keys to Soil Taxonomy*, 12th ed.; USDA Natural Resources Conservation Service: Washington, DC, USA, 2014.
5. Drumonde-Neves, J.; Franco-Duarte, R.; Lima, T.; Schuller, D.; Pais, C. Association between grape yeast communities and the vineyard ecosystems. *PLoS ONE* **2017**, *12*, e0169883. [CrossRef] [PubMed]

6. Heras-Roger, J.; Díaz-Romero, C.; Darias-Martín, J.; Rios-Mesa, D. Characterization of red wines from Macaronesia. In *Grapes and Wines—Advances in Production, Processing, Analysis and Valorization*, 1st ed.; Jordão, A.M., Cosme, F., Eds.; InTechopen: Rijeka, Croatia, 2018; Volume 1, pp. 225–252. [CrossRef]
7. Xyrafis, E.G.; Gambetta, G.A.; Biniari, K. A comparative study on training systems and vine density in Santorini Island: Physiological, microclimate, yield and quality attributes. *OENO One* **2023**, *57*, 141–152. [CrossRef]
8. Madruga, J.; Azevedo, E.B.; Sampaio, J.F.; Fernandes, F.; Reis, F.; Pinheiro, J. Analysis and definition of potential new areas for viticulture in the Azores (Portugal). *Soil* **2015**, *1*, 515–526. [CrossRef]
9. Perestrelo, R.; Lu, Y.; Santos, S.A.O.; Silvestre, A.J.D.; Neto, C.P.; Câmara, J.S.; Rocha, S.M. Phenolic profile of Sercial and Tinta Negra *Vitis vinifera* L. grape skins by HPLC–DAD–ESI-MS^n: Novel phenolic compounds in *Vitis vinifera* L. grape. *Food Chem.* **2012**, *135*, 94–104. [CrossRef]
10. Perestrelo, R.; Fernandes, A.; Albuquerque, F.F.; Marques, J.C.; Câmara, J.S. Analytical characterization of the aroma of Tinta Negra Mole red wine: Identification of the main odorants compounds. *Anal. Chim. Acta* **2006**, *563*, 154–164. [CrossRef]
11. Perestrelo, R.; Silva, C.; Câmara, J.S. Madeira wine volatile profile. A platform to establish Madeira wine aroma descriptors. *Molecules* **2019**, *24*, 3028. [CrossRef] [PubMed]
12. Anderson, K.; Aryal, N. Where in the world are various wine grape varieties grown? Evidence from a new database. *Bull. l'OIV* **2013**, 461–484.
13. Ortega-Regules, A.; Romero-Cascales, I.; Ros García, J.M.; Bautista-Ortín, A.B.; López-Roca, J.M.; Fernández-Fernández, J.I.; Gómez-Plaza, E. Anthocyanins and tannins in four grape varieties (*Vitis vinifera* L.). Evolution of their content and extractability. *OENO One* **2008**, *42*, 147–156. [CrossRef]
14. Cincotta, F.; Verzera, A.; Prestia, O.; Tripodi, G.; Lechhab, W.; Sparacio, A.; Condurso, C. Influence of leaf removal on grape, wine, and aroma compounds of *Vitis vinifera* L. cv. Merlot under Mediterranean climate. *Eur. Food Res. Technol.* **2022**, *248*, 403–413. [CrossRef]
15. Kallithraka, S.; Aliaj, L.; Makris, D.P.; Kefalas, P. Anthocyanin profiles of major red grape (*Vitis vinifera* L.) varieties cultivated in Greece and their relationship with in vitro antioxidant characteristics. *Int. J. Food Sci. Technol.* **2009**, *44*, 2385–2393. [CrossRef]
16. Kyraleou, M.; Kallithraka, S.; Theodorou, N.; Teissedre, P.-L.; Kotseridis, Y.; Koundouras, S. Changes in tannin composition of Syrah grape skins and seeds during fruit ripening under contrasting water Conditions. *Molecules* **2017**, *22*, 1453. [CrossRef]
17. Hanlin, R.L.; Downey, M.O. Condensed tannin accumulation and composition in skin of Shiraz and Cabernet Sauvignon grapes during berry development. *Am. J. Enol. Vitic.* **2009**, *60*, 13–23. [CrossRef]
18. Hunter, J.J.; Volschenk, C.G.; Novello, V.; Pisciotta, A.; Booyse, M.; Fouché, G.W. Integrative effects of vine water relations and grape ripeness level of *Vitis vinifera* L. cv. Shiraz/Richter 99. II. grape composition and wine quality. *S. Afr. J. Enol. Vitic.* **2014**, *35*, 359–374. [CrossRef]
19. Shi, P.B.; Yue, T.X.; Ai, L.L.; Cheng, Y.F.; Meng, J.F.; Li, M.H.; Zhang, Z.W. Phenolic compound profiles in grape skins of Cabernet Sauvignon, Merlot, Syrah and Marselan cultivated in the Shacheng area (China). *S. Afr. J. Enol. Vitic.* **2016**, *37*, 132–138. [CrossRef]
20. Gouot, J.C.; Smith, J.; Holzapfel, B.; Barril, C. Single and cumulative effects of whole-vine heat events on Shiraz berry composition. *OENO One* **2019**, *53*, 171–187. [CrossRef]
21. Brillante, L.; Martínez-Lüscher, J.; Kurtural, S.K. Applied water and mechanical canopy management affect berry and wine phenolic and aroma composition of grapevine (*Vitis vinifera* L., cv. Syrah) in Central California. *Sci. Hortic.* **2018**, *227*, 261–271. [CrossRef]
22. Gomes da Silva, A.P.; Sabbatini, P.; Vander Weide, J.; Medina-Meza, I.G. Influence of early leaf removal on flavonoid accumulation and antioxidant capacity in Merlot (*Vitis vinifera* L.) berry components. *ACS Food Sci. Technol.* **2023**, *3*, 1457–1470. [CrossRef]
23. Franco-Bañuelos, A.; Contreras-Martínez, C.S.; Carranza-Téllez, J.; Carranza-Concha, J. Total phenolic content and antioxidant capacity of non-native wine grapes grown in Zacateas, México. *Agrociencia* **2017**, *51*, 661–671.
24. de Oliveira, J.B.; Egipto, R.; Laureano, O.; de Castro, R.; Pereira, G.E.; Ricardo-da-Silva, J.M. Climate effects on physicochemical composition of Syrah grapes at low and high altitude sites from tropical grown regions of Brazil. *Food Res. Int.* **2019**, *121*, 870–879. [CrossRef] [PubMed]
25. de Rosas, I.; Deis, L.; Baldo, Y.; Cavagnaro, J.B.; Cavagnaro, P.F. High temperature alters anthocyanin concentration and composition in grape berries of Malbec, Merlot, and Pinot Noir in a cultivar-dependent manner. *Plants* **2022**, *11*, 926. [CrossRef]
26. Cosme, F.; Ricardo-da-Silva, J.M.; Laureano, O. Tannin profiles of *Vitis vinifera* L. cv. red grapes growing in Lisbon and from their monovarietal wines. *Food Chem.* **2009**, *112*, 197–204. [CrossRef]
27. Costa, E.; Cosme, F.; Jordão, A.M.; Mendes-Faia, A. Anthocyanin profile and antioxidant activity from 24 grape varieties cultivated in two Portuguese wine regions. *J. Int. Sci. Vigne Vin.* **2014**, *48*, 51–62. [CrossRef]
28. Costa, E.; Cosme, F.; Rivero-Pérez, M.D.; Jordão, A.M.; González-SanJosé, M.L. Influence of wine region provenance on phenolic composition, antioxidant capacity and radical scavenger activity of traditional Portuguese red grape varieties. *Eur. Food Res. Technol.* **2015**, *241*, 61–73. [CrossRef]
29. Carbonneau, A.; Champagnol, F. *Nouveaux Systèmes des Culture Intégrale du Vignoble*; Internal Report of Programme AIR-3-CT93; Institute Agro-Montpellier—Viticulture and Enology: Montpellier, France, 1993.
30. OIV. *Compendium of International Methods of Wine and Must Analysis*; International Organisation of Vine and Wine: Paris, France, 1994.
31. Ribéreau-Gayon, P.; Stronestreet, E. Le dosage des anthocyanes dans le vin rouge. *Bull. Soc. Chim.* **1965**, *9*, 2649–2652.
32. Ribéreau-Gayon, P.; Peynaud, E.; Sudraud, P. *Science et Techniques du vin Tome 4*; Dunod: Paris, France, 1982.
33. Kramling, T.E.; Singleton, V.L. An estimate of the nonflavonoid phenols in wines. *Am. J. Enol. Vitic.* **1969**, *20*, 86–92. [CrossRef]

34. Dallas, C.; Laureano, O. Effects of pH, sulphur dioxide, alcohol content, temperature and storage time on colour composition of a young Portuguese red table wine. *J. Sci. Food Agric.* **1994**, *65*, 477–485. [CrossRef]
35. Brand-Williams, W.; Cuvelier, M.E.; Berset, C. Use of a free radical method to evaluate antioxidant activity. *LWT Food Sci. Technol.* **1995**, *28*, 25–30. [CrossRef]
36. Re, R.; Pellegrini, N.; Proteggente, A.; Pannala, A.; Yang, M.; Rice-Evans, C. Antioxidant activity applying an improved ABTS radical cation decolorization assay. *Free Radic. Biol. Med.* **1999**, *26*, 1231–1237. [CrossRef]
37. Salinas, M.R.; Serrano de La Hoz, K.; Zalacain, A.; Lara, J.F.; Garde-Cerdán, T. Analysis of red grape glycosidic aroma precursors by glycosyl glucose quantification. *Talanta* **2012**, *89*, 396–400. [CrossRef]
38. Serrano de la Hoz, K.; Carmona, M.; Zalacain, A.; Alonso, G.L.; Salinas, M.R. The varietal aroma potential index (IPAv): A tool to evaluate the quality of grape and wines, white and red. In Proceedings of the 37th World Congress of Vine and Wine, Mendoza, Argentina, 9–14 November 2014.
39. Trujillo, J.P.P.; Conde, J.E.; Pont, M.L.P.; Câmara, J.; Marques, J.C. Content in metallic ions of wines from the Madeira and Azores archipelagos. *Food Chem.* **2011**, *124*, 533–537. [CrossRef]
40. Van Leeuwen, C.; Roby, J.-P.; de Rességuier, L. Soil-related terroir factors: A review. *OENO One* **2018**, *52*, 173–188. [CrossRef]
41. Dai, Z.W.; Vivin, P.; Robert, T.; Milin, S.; Li, S.H.; Génard, M. Model-based analysis of sugar accumulation in response to source–sink ratio and water supply in grape (*Vitis vinifera*) berries. *Funct. Plant Biol.* **2009**, *36*, 527–540. [CrossRef] [PubMed]
42. Van Leeuwen, C.; Destrac-Irvine, A.; Gowdy, M.; Farris, L.; Pieri, P.; Marolleau, L.; Gambetta, G.A. An operational model for capturing grape ripening dynamics to support harvest decisions. *OENO One* **2023**, *57*, 505–522. [CrossRef]
43. Sanderson, M.G.; Teixeira, M.; Fontes, N.; Silva, S.; Graça, A. The probability of unprecedented high rainfall in wine regions of northern Portugal. *Clim. Serv.* **2023**, *30*, 100363. [CrossRef]
44. Clímaco, P.; Cunha, J.P. Exigences thérmiques de quelques cépages cultives dans la region de l’Estremadura. *Ciência Téc. Vitiv.* **2006**, *21*, 67–74.
45. Gordillo, B.; Rodríguez-Pulido, F.J.; Mateus, N.; Escudero-Gilete, M.L.; González-Miret, M.L.; Heredia, F.J.; De Freitas, V. Application of LC-MS and tristimulus colorimetry to assess the ageing aptitude of Syrah wine in the Condado de Huelva D.O. (Spain), a typical warm climate region. *Anal. Chim. Acta* **2012**, *732*, 162–171. [CrossRef]
46. Brazão, J.; Sun, B.; Caldeira, I.; Baeta, F.; Amaral, J.; Eiras-Dias, J. Wines’ caracterisation of eight minority Portuguese grapevine varieties. *Ciência Téc. Vitiv.* **2023**, *38*, 21–34. [CrossRef]
47. Payan, C.; Gancel, A.-L.; Jourdes, M.; Christmann, M.; Teissedre, P.-L. Wine acidification methods: A review. *OENO One* **2023**, *57*, 113–126. [CrossRef]
48. Lafon-Lafourcade, S.; Peynaud, E. Sur l’action antibactérienne de l’anhydride sulfureux sous forme libre et sous forme combinée. *OENO One* **1970**, *8*, 187–203. [CrossRef]
49. Gao, Y.; Fangel, J.U.; Willats, W.G.T.; Vivier, M.A.; Moore, J.P. Dissecting the polysaccharide-rich grape cell wall changes during winemaking using combined high-throughput and fractionation methods. *Carbohydr. Polym.* **2015**, *133*, 567–577. [CrossRef] [PubMed]
50. Rouxinol, M.I.; Martins, M.R.; Salgueiro, V.; Costa, M.J.; Barroso, J.M.; Rato, A.E. Climate effect on morphological traits and polyphenolic composition of red wine grapes of *Vitis vinifera*. *Beverages* **2023**, *9*, 8. [CrossRef]
51. Chorti, E.; Guidoni, S.; Ferrandino, A.; Novello, V. Effect of different cluster sunlight exposure levels on ripening and anthocyanin accumulation in Nebbiolo grapes. *Am. J. Enol. Vitic.* **2010**, *61*, 23–30. [CrossRef]
52. Deloire, A.; Rogiers, S.; Šuklje, K.; Antalick, G.; Zeyu, X.; Pellegrino, A. Grapevine berry shriveling, water loss and cell death: An increasing challenge for growers in the context of climate change. *IVES Tech. Rev. Vine Wine* **2021**. [CrossRef]
53. Torchio, F.; Cagnasso, E.; Gerbi, V.; Rolle, L. Mechanical properties, phenolic composition and extractability indices of Barbera grapes of different soluble solids contents from several growing areas. *Anal. Chim. Acta* **2010**, *660*, 183–189. [CrossRef] [PubMed]
54. Jordão, A.M.; Correia, A.C. Relationship between antioxidant capacity, proanthocyanidin and anthocyanin content during grape maturation of Touriga Nacional and Tinta Roriz grape varieties. *S. Afr. J. Enol. Vitic.* **2012**, *33*, 214–224. [CrossRef]
55. Gladstones, J. *Viticulture and Environment*; Trivinum Press Pty Ltd.: Adelaide, Australia, 2021; Volume 1, ISBN 978-0-9945016-0-8.
56. Ortega-Regules, A.; Romero-Cascales, I.; López-Roca, J.M.; Ros-García, J.M.; Gómez-Plaza, E. Anthocyanin fingerprint of grapes: Environmental and genetic variations. *J. Sci. Food Agric.* **2006**, *86*, 1460–1467. [CrossRef]
57. Lorrain, B.; Chira, K.; Teissedre, P.-L. Phenolic composition of Merlot and Cabernet-Sauvignon grapes from Bordeaux vineyard for the 2009-vintage: Comparison to 2006, 2007 and 2008 vintages. *Food Chem.* **2011**, *126*, 1991–1999. [CrossRef] [PubMed]
58. Theodorou, N.; Nikolaou, N.; Zioziou, E.; Kyraleou, M.; Kallithraka, S.; Kotseridis, Y.; Koundouras, S. Anthocyanin content and composition in four red winegrape cultivars (*Vitis vinifera* L.) under variable irrigation: Anthocyanin content and composition under variable irrigation. *OENO One* **2019**, *53*, 39–51. [CrossRef]
59. Budić-Leto, I.; Mucalo, A.; Ljubenkov, I.; Zdunić, G. Anthocyanin profile of wild grape *Vitis vinifera* in the eastern Adriatic region. *Sci. Hortic.* **2018**, *238*, 32–37. [CrossRef]
60. Mori, K.; Goto-Yamamoto, N.; Kitayama, M.; Hashizume, K. Loss of anthocyanins in red-wine grape under high temperature. *J. Exp. Bot.* **2007**, *58*, 1935–1945. [CrossRef] [PubMed]
61. Ribéreau-Gayon, P.; Glories, Y.; Maujean, A.; Dubourdieu, D. Phenolic compounds. In *Handbook of Enology: The Chemistry of Wine: Stabilization and Treatments*; Wiley: Hoboken, NJ, USA, 2006; Volume 2, pp. 141–204. [CrossRef]

62. González-Neves, G.; Franco, J.; Barreiro, L.; Gil, G.; Moutounet, M.; Carbonneau, A. Varietal differentiation of Tannat, Cabernet-Sauvignon and Merlot grapes and wines according to their anthocyanic composition. *Eur. Food Res. Technol.* **2007**, *225*, 111–117. [CrossRef]
63. Segade, S.R.; Orriols, I.; Gerbi, V.; Rolle, L. Phenolic characterization of thirteen red grape cultivars from Galicia by anthocyanin profile and flavanol composition. *J. Int. Sci. Vigne Vin* **2009**, *43*, 189–198. [CrossRef]
64. Ryan, J.-M.; Revilla, E. Anthocyanin composition of Cabernet Sauvignon and Tempranillo grapes at different stages of ripening. *J. Agric. Food Chem.* **2003**, *51*, 3372–3378. [CrossRef] [PubMed]
65. Roggero, J.P.; Coen, S.; Ragonnet, B. High performance liquid chromatography survey on changes in pigment content in ripening grapes of Syrah. An approach to anthocyanin metabolism. *Am. J. Enol. Vitic.* **1986**, *37*, 77–83. [CrossRef]
66. Pomar, F.; Novo, M.; Masa, A. Varietal differences among the anthocyanin profiles of 50 red table grape cultivars studied by high performance liquid chromatography. *J. Chromatogr. A* **2005**, *1094*, 34–41. [CrossRef]
67. Carreño, J.; Almela, L.; Martínez, A.; Fernández-López, J.A. Chemotaxonomical classification of red table grapes based on anthocyanin profile and external colour. *LWT Food Sci. Technol.* **1997**, *30*, 259–265. [CrossRef]
68. Núñez, V.; Monagas, M.; Gomez-Cordovés, M.C.; Bartolomé, B. *Vitis vinifera* L. cv. Graciano grapes characterized by its anthocyanin profile. *Postharvest Biol. Technol.* **2004**, *31*, 69–79. [CrossRef]
69. Otteneder, H.; Marx, R.; Zimmer, M. Analysis of the anthocyanin composition of Cabernet Sauvignon and Portugieser wines provides an objective assessment of the grape varieties. *Aust. J. Grape Wine Res.* **2004**, *10*, 3–7. [CrossRef]
70. Karn, A.; Diaz-Garcia, L.; Reshef, N.; Zou, C.; Manns, D.C.; Cadle-Davidson, L.; Mansfield, A.K.; Reisch, B.I.; Sacks, G.L. The genetic basis of anthocyanin acylation in North American grapes (*Vitis* spp.). *Genes* **2021**, *12*, 1962. [CrossRef] [PubMed]
71. Dimitrovska, M.; Bocevska, M.; Dimitrovski, D.; Murkovic, M. Anthocyanin composition of Vranec, Cabernet Sauvignon, Merlot and Pinot Noir grapes as indicator of their varietal differentiation. *Eur. Food Res. Technol.* **2011**, *232*, 591–600. [CrossRef]
72. González-Neves, G.; Gómez-Cordovés, C.; Barreiro, L. Anthocyanic composition of Tannat, Cabernet Sauvignon and Merlot young red wines from Uruguay. *J. Wine Res.* **2001**, *12*, 125–133. [CrossRef]
73. Wang, C.C.; Chu, C.Y.; Chu, K.O.; Choy, K.W.; Khaw, K.S.; Rogers, M.S.; Pang, C.P. Trolox-equivalent antioxidant capacity assay versus oxygen radical absorbance capacity assay in plasma. *Clin. Chem.* **2004**, *50*, 952–954. [CrossRef] [PubMed]
74. Villaño, D.; Fernández-Pachón, M.S.; Troncoso, A.M.; García-Parrilla, M.C. Influence of enological practices on the antioxidant activity of wines. *Food Chem.* **2006**, *95*, 394–404. [CrossRef]
75. Xu, C.; Zhang, Y.; Cao, L.; Lu, J. Phenolic compounds and antioxidant properties of different grape cultivars grown in China. *Food Chem.* **2010**, *119*, 1557–1565. [CrossRef]
76. Samoticha, J.; Jara-Palacios, M.; Hernández-Hierro, J.; Heredia, F.J.; Wojdyło, A. Phenolic compounds and antioxidant activity of twelve grape cultivars measured by chemical and electrochemical methods. *Eur. Food Res. Technol.* **2018**, *244*, 1933–1943. [CrossRef]
77. Vilanova, M.; Rodríguez, I.; Canosa, P.; Otero, I.; Gamero, E.; Moreno, D.; Talaverano, I.; Valdés, E. Variability in chemical composition of *Vitis vinifera* cv. *Mencía* from different geographic areas and vintages in Ribeira Sacra (NW Spain). *Food Chem.* **2015**, *169*, 187–196. [CrossRef]
78. Panceri, C.P.; Gomes, T.M.; De Gois, J.S.; Borges, D.L.G.; Bordignon-Luiz, M.T. Effect of dehydration process on mineral content, phenolic compounds and antioxidant activity of Cabernet Sauvignon and Merlot grapes. *Food Res. Int.* **2013**, *54*, 1343–1350. [CrossRef]
79. Pardo-García, A.I.; De La Hoz, K.S.; Zalacain, A.; Alonso, G.L.; Salinas, M.R. Effect of vine foliar treatments on the varietal aroma of Monastrell wines. *Food Chem.* **2014**, *163*, 258–266. [CrossRef] [PubMed]
80. Campayo, A.; García-Martínez, M.M.; Sánchez-Martínez, J.F.; Salinas, M.R.; Alonso, G.L.; Serrano de la Hoz, K. Spraying ozonated water on Bobal grapevines: Effect on grape quality. *Food Res. Int.* **2019**, *125*, 108540. [CrossRef] [PubMed]
81. Sefton, M.A.; Francis, I.L.; Williams, P.J. Free and bound volatile secondary metabolites of *Vitis vinifera* grape cv. Sauvignon Blanc. *J. Food Sci.* **1994**, *59*, 142–147. [CrossRef]
82. Peyrot des Gachons, C.; Tominaga, T.; Dubourdieu, D. Measuring the aromatic potential of *Vitis vinifera* L. Cv. Sauvignon blanc grapes by assaying S-cysteine conjugates, precursors of the volatile thiols responsible for their varietal aroma. *J. Agric. Food Chem.* **2000**, *48*, 3387–3391. [CrossRef]
83. He, L.; Ren, Z.-Y.; Wang, Y.; Fu, Y.-Q.; Li, Y.; Meng, N.; Pan, Q.-H. Variation of growth-to-ripening time interval induced by abscisic acid and synthetic auxin affecting transcriptome and flavor compounds in Cabernet Sauvignon grape berry. *Plants* **2020**, *9*, 630. [CrossRef]
84. Hernandez-Orte, P.; Concejero, B.; Astrain, J.; Lacau, B.; Cacho, J.; Ferreira, V. Influence of viticulture practices on grape aroma precursors and their relation with wine aroma. *J. Sci. Food Agric.* **2015**, *95*, 688–701. [CrossRef]
85. Jeffery, D.W. Spotlight on varietal thiols and precursors in grapes and wines. *Aust. J. Chem.* **2016**, *69*, 1323–1330. [CrossRef]
86. Koundouras, S.; Hatzidimitriou, E.; Karamolegkou, M.; Dimopoulou, E.; Kallithraka, S.; Tsialtas, J.T.; Zioziou, E.; Nikolaou, N.; Kotseridis, Y. Irrigation and rootstock effects on the phenolic concentration and aroma potential of *Vitis vinifera* L. cv. Cabernet Sauvignon grapes. *J. Agric. Food Chem.* **2009**, *57*, 7805–7813. [CrossRef]