Characteristic Phenolic Composition of Single-Cultivar Red Wines of the Canary Islands (Spain)

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ABSTRACT: The detailed phenolic composition of five single-cultivar (Baboso Negro, Listán Negro, Negramoll, Tintilla, and Vijariego Negro) young and aged (vintages 2005−2009) red wines of the Canary Islands has been determined by HPLC-DAD-ESI-MS^n. Despite the total monomeric anthocyanin content decreasing for older wines in each set of single-cultivar wines, the corresponding anthocyanin profiles remained almost unchanged. Although all wine anthocyanin profiles were dominated by malvidin 3-glucoside, their differentiation by grape cultivar was possible, with the exception of Listán Negro. In contrast, the total content of non-anthocyanin phenolics did not appreciably change within vintages but polymerization, hydrolysis, and isomerization reactions greatly modified the phenolic profiles. Aglycone-type flavonol profiles offered the best results for differentiation of the wines according to grape cultivar (Listán Negro and Negramoll; Baboso Negro and Vijariego Negro; and Tintilla). Within flavan-3-ols, the B-ring trihydroxylated monomers ((−)-epigallocatechin and (−)-gallocatechin) and also (−)-epicatechin provided additional cultivar differentiation. Hydroxycinnamic acid derivatives and stilbene profiles were very heterogeneous with regard to both grape cultivar and vintage and did not significantly contribute to wine differentiation, even when structure-type profiles were obtained, with the exception of Tintilla, which always appeared as the most different single-cultivar wines. Finally, most Canary Islands wines showed characteristic high contents of stilbenes, especially *trans*-resveratrol.

KEYWORDS: anthocyanins, flavonols, flavan-3-ols, hydroxycinnamic acid derivatives, stilbenes, phenolic profiles, wines, Canary Islands

■ INTRODUCTION

Wines from the Canary Islands show several peculiarities as they are elaborated with autochthonous grape cultivars that cannot be found elsewhere in the world. Besides, the Canary Islands vineyards have never suffered from phylloxera, the soils are volcanic, and there are many different microclimates.[1]

Canary Islands autochthonous grape cultivars and their wines have been studied with regard to their winemaking potential,[2−4] conventional enological parameters,[5−7] color and other sensory properties,[7−12] volatile composition,[13,14] and trace elements.[15−17] However, few data can be currently found dealing with their phenolic composition, with the exception of some global parameters such as total phenolic or anthocyanins[8,11,18] and single phenolics such as resveratrol.[19] As far as we know, there are no available data on the content of individual nonvolatile phenolic compounds of wines from the Canary Islands. Phenolic compounds play in red wines crucial roles because they are directly involved in sensory properties such as color, bitterness, and astringency, suitability for barrel and bottle aging, and also antioxidant and other health-promoting properties associated with moderate wine consumption.[20−22]

Phenolic profiles have been used for cultivar differentiation of red wines; use of the usual anthocyanin profiles[23] is limited because of the disappearance of monomeric anthocyanins that are involved in many different reactions (oxidation, polymerization, formation of low and high molecular new red pigments)

from the beginning of winemaking and further into wine aging. The anthocyanin-derived new products usually lead to polymerized and nonsoluble compounds that are difficult to analyze. Other phenolic profiles, such as hydroxycinnamic acid derivatives and flavonols, have shown some ability in wine cultivar differentiation.[24,25] The latter compounds are also involved in reactions during wine aging, but their reaction products (mainly hydrolysis products and also ethyl ester derivatives in the case of released hydroxycinnamic acids) can be still analyzed under the same chromatographic conditions used for the original compounds, thus retaining some of the identity of the original grape cultivar.

The aims of this work were to determine for the first time the detailed composition (total content and molar percentages or phenolic profiles) of anthocyanins, flavan-3-ols (monomers and B-type dimers), flavonols, hydroxycinamic acid derivatives, and stilbenes in single-cultivar red wines from the Canary Islands; to compare the obtained results with those of other wines; and, finally, to statistically test the differences within phenolic profiles that could help differentiate these single-cultivar red wines.

Table 1. Grape Cultivar, Origin, and Vintage of Canary Islands Wine Samples

wine sample	grape cultivar	vintage	denomination of origin	island
1	Baboso Negro	2005	El Hierro	El Hierro
2	Baboso Negro	2007	Abona	Tenerife
3	Baboso Negro	2007	Abona	Tenerife
4	Baboso Negro	2007	El Hierro	El Hierro
5	Baboso Negro	2007	Ycoden-Daute-Isora	Tenerife
6	Baboso Negro	2008	Abona	Tenerife
7	Baboso Negro	2008	Abona	Tenerife
8	Baboso Negro	2008	El Hierro	El Hierro
9	Baboso Negro	2008	Ycoden-Daute-Isora	Tenerife
10	Baboso Negro	2009	Abona	Tenerife
11	Baboso Negro	2009	Tacoronte-Acentejo	Tenerife
12	Listán Negro	2007	Valle de Orotava	Tenerife
13	Listán Negro	2007	Valle de Orotava	Tenerife
14	Listán Negro	2007	Ycoden-Daute-Isora	Tenerife
15	Listán Negro	2008	Tacoronte-Acentejo	Tenerife
16	Listán Negro	2008	Tacoronte-Acentejo	Tenerife
17	Listán Negro	2008	Valle de Güimar	Tenerife
18	Listán Negro	2008	Valle de Orotava	Tenerife
19	Listán Negro	2009	Abona	Tenerife
20	Listán Negro	2009	Lanzarote	Lanzarote
21	Listán Negro	2009	Lanzarote	Lanzarote
22	Listán Negro	2009	Lanzarote	Lanzarote
23	Listán Negro	2009	Tacoronte-Acentejo	Tenerife
24	Listán Negro	2009	Valle de Orotava	Tenerife
25	Listán Negro	2009	Valle de Orotava	Tenerife
26	Listán Negro	2009	Valle de Orotava	Tenerife
27	Listán Negro	2009	Valle de Orotava	Tenerife
28	Listán Negro	2009	Valle de Orotava	Tenerife
29	Negramoll	2006	Tacoronte-Acentejo	Tenerife
30	Negramoll	2007	Tacoronte-Acentejo	Tenerife
31	Negramoll	2007	Ycoden-Daute-Isora	Tenerife
32	Negramoll	2008	La Palma	La Palma
33	Negramoll	2008	Tacoronte-Acentejo	Tenerife
34	Negramoll	2008	Tacoronte-Acentejo	Tenerife
35	Negramoll	2008	Ycoden-Daute-Isora	Tenerife
36	Negramoll	2009	Tacoronte-Acentejo	Tenerife
37	Negramoll	2009	Ycoden-Daute-Isora	Tenerife
38	Tintilla	2005	Ycoden-Daute-Isora	Tenerife
39	Tintilla	2006	Tacoronte-Acentejo	Tenerife
40	Tintilla	2007	Ycoden-Daute-Isora	Tenerife
41	Tintilla	2008	Ycoden-Daute-Isora	Tenerife
42	Tintilla	2008	Ycoden-Daute-Isora	Tenerife
43	Tintilla	2009	Tacoronte-Acentejo	Tenerife
44	Tintilla	2009	Tacoronte-Acentejo	Tenerife
45	Tintilla	2009	Tacoronte-Acentejo	Tenerife
46	Tintilla	2009	Tacoronte-Acentejo	Tenerife
47	Tintilla	2009	Ycoden-Daute-Isora	Tenerife
48	Vijariego Negro	2005	El Hierro	El Hierro
49	Vijariego Negro	2006	El Hierro	El Hierro

Table 1. Continued

wine sample	grape cultivar	vintage	denomination of origin	island
50	Vijariego Negro	2008	Abona	Tenerife
51	Vijariego Negro	2008	El Hierro	El Hierro
52	Vijariego Negro	2008	El Hierro	El Hierro
53	Vijariego Negro	2009	Abona	Tenerife
54	Vijariego Negro	2009	Ycoden-Daute-Isora	Tenerife

■ MATERIALS AND METHODS

Wine Samples. The wine samples used for the present study were 54 single-cultivar red wines of the Canary Islands (Spain) produced during the vintages of 2005−2007 (16 samples), 2008 (17 samples), and 2009 (21 samples) and elaborated with five different autochthonous grape cultivars (Table 1). The distribution of samples according to grape cultivar was as follows: Baboso Negro ($n = 11$), Listán Negro ($n = 17$), Negramoll ($n = 9$), Tintilla ($n = 10$), and Vijariego Negro ($n = 7$). All of the samples were provided by the local Denomination of Origin Certification Councils to ensure the geographic origin and the grape cultivar authenticity of the wines. The samples were taken in the months of November and December 2009 (vintages 2005−2008) and January 2010 (vintage 2009), stored at −18 °C, and analyzed in March and April 2010.

Chemicals. All solvents were of HPLC quality and all chemicals of analytical grade (>99%). Water was of Milli-Q quality. Commercial standards from Phytolab (Vestenbergsgreuth, Germany) were used: malvidin 3-glucoside, caffeic and p-coumaric acids, trans-piceid, (−)-epigallocatechin, and (−)-gallocatechin. Commercial standards from Extrasynthese (Genay, France) were used: kaempferol, quercetin, iso-rhamnetin, myricetin, and syringetin; the 3-glucosides of kaempferol, quercetin, isorhamnetin, and syringetin; and procyanidins B1 and B2. Commercial standards from Sigma (Tres Cantos, Madrid, Spain) were used: gallic acid, trans-resveratrol, (+)-catechin, (−)-epicatechin, (−)-epicatechin 3-gallate, and (−)-gallocatechin 3-gallate. Other noncommercial flavonol standards (myricetin 3-glucoside and quercetin 3-glucuronide) were kindly supplied by Dr. Ullrich Engelhardt (Institute of Food Chemistry, Technical University of Braunschweig, Germany). The trans isomers of resveratrol and piceid (resveratrol 3-glucoside) were transformed into their respective cis isomers by UV irradiation (366 nm light during 5 min in quartz vials) of 25% MeOH solutions of the trans isomers. A sample of trans-caftaric acid was kindly supplied by Dr. Vrhovsek (IASMA Research Centre, San Michele all'Adige, Italy). All of the standards were used for identification and quantification by means of calibration curves, covering the expected concentration ranges (usually 0−100 mg/L, with the exception of malvidin 3-glucoside covering a range of 0−1000 mg/L). Vitisin A and hydroxyphenyl-pyranoanthocya-nins were quantified using calibration curves previously obtained in the same chromatographic system.[26] When a standard was not available, the quantification was made using the calibration curve of the most similar compound (with subsequent molecular mass correction): malvidin 3-glu-coside was used for all native grape anthocyanins and also for Mv3glc-cat; vitisin A was used for vitisin B; p-coumaric acid was used for trans- and cis-coutaric acids; flavonol 3-glycosides with nonavailable standard as their corresponding 3-glucoside derivatives.

Sample Preparation. Anthocyanin-free flavonol fractions were isolated from diluted red wines (3 mL of wine and 3 mL of 0.1 N HCl) following the procedure previously described[24] using SPE cartridges (Oasis MCX cartridges, Waters Corp., Milford, MA; cartridges of 6 mL capacity filled with 500 mg of adsorbent). The eluate containing flavonols was dried in a rotary evaporator (40 °C), resolved in 3 mL of 25% methanol, and stored at −18 °C until use. These anthocyanin-free fractions were used for the analysis of non-anthocyanin phenolic compounds, with the exception of flavan-3-ols.

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Flavan-3-ol monomers ((+)-catechin, (−)-epicatechin), (−)-epigallocatechin, (−)-gallocatechin, and (−)-epicatechin 3-gallate) and B-type proanthocyanidin dimers (procyanidins B1 and B2) were analyzed in wine extracts obtained by SPE on C18 cartridges (Sep-Pak Plus C18, Waters Corp.; cartridges filled with 820 mg of adsorbent): a mixture of 2 mL of wine with 0.5 mL of a solution of 20 mg/L of (+)-gallocatechin 3-gallate (internal standard) and 6 mL of water was passed through the C18 cartridge previously conditioned with methanol (10 mL) and water (10 mL); after drying of the cartridge under reduced pressure, methanol (15 mL) and ethyl acetate (5 mL) were sequentially added for recovery of adsorbed phenolics; after solvent evaporation in a rotary evaporator (40 °C), the residue was dissolved in methanol (4 mL) and stored at −18 °C until use. For HPLC analysis, 0.50 mL of the aforementioned wine extract was diluted with 2.5 mL of water in a chromatographic vial that was sealed.

Spectrophotometric Measurement of Total Polyphenols and Anthocyanins. Wine samples were diluted 1:10 with 10% (v/v) ethanol in water. To 0.5 mL of diluted wine were added 0.5 mL of 2% HCl in 96% ethanol and 9.1 mL of 1 N HCl and then homogenized. After 15 min, absorbances at 280 nm (total polyphenols) and 520 nm (total anthocyanins) were measured in 1 cm quartz cells using water as blank. Calibration curves were obtained from solutions of different concentrations of gallic acid (total polyphenols) and malvidin 3-glucoside (total anthocyanins). Determinations were performed in duplicate.

HPLC-DAD-ESI-MS^n Analysis of Wine Phenolic Compounds. HPLC separation, identification, and quantification of wine phenolic compounds (namely, anthocyanins and non-anthoctyanin phenolics, with the exception of flavan-3-ols) were performed on an Agilent 1100 series system (Agilent, Germany), equipped with a DAD (G1315B) and LC/MSD Trap VL (G2445C VL) electrospray ionization mass spectrometry (ESI-MS^n) system, coupled to an Agilent Chem Station (version B.01.03) data-processing station. The mass spectra data were processed with the Agilent LC/MS Trap software (version 5.3). Anthocyanins and non-anthocyanin phenolic compounds were separately analyzed following a previously described chromatographic method[24] using both wine samples (anthocyanins) and isolated anthocyanin-free wine fractions (flavonols, hydroxycinnamic acid derivatives, and stilbenes). The samples were injected (50 μL) after filtration (0.20 μm, polyester membrane, Chromafil PET 20/25, Machery-Nagel, Düren, Germany) on a reversed-phase column Zorbax Eclipse XDB-C18 (4.6 × 250 mm; 5 μm particle; Agilent), thermostated at 40 °C. For identification, ESI-MS^n was used in both positive (anthocyanins) and negative (flavonols, hydroxycinnamic acid derivatives, and stilbenes) ion modes, setting the following parameters: dry gas, N$_2$, 11 mL/min; drying temperature, 350 °C; nebulizer, 65 psi; capillary, −2500 V (positive ion mode) and +2500 V (negative ion mode); target mass, m/z 600; compound stability, 40% (negative ion mode) and 100% (positive ion mode); trap drive level, 100%; scan range, m/z 50−1200. For quantification, DAD chromatograms were extracted at 520 (anthocyanins), 360 (flavonols), and 320 nm (hydroxycinnamic acid derivatives and stilbenes). Analyses were performed in duplicate.

With regard to flavan-3-ols (monomers and B-type procyanidins), their HPLC separation, identification, and quantification were performed on an Agilent 1200 series system equipped with DAD (Agilent) and coupled to an AB Sciex 3200 Q TRAP (Applied Biosystems) electrospray ionization mass spectrometry system (ESI-MS). The chromatographic system was managed by an Agilent Chem Station (version B.01.03) data-processing station. The mass spectra data were processed with Analyst MDS software (Applied Biosystems, version 1.5). The samples were injected (100 μL) after filtration (0.20 μm, polyester membrane, Chromafil PET 20/25, Machery-Nagel, Düren, Germany) on a reversed-phase column Zorbax Eclipse XDB-C18 (4.6 × 250 mm; 5 μm particle; Agilent), thermostated at 16 °C. The solvents were water/methanol/formic acid (89:10:1, v/v/v, solvent A) and methanol (solvent B), and the flow rate was 0.5 mL/min.

The linear gradient for solvent B was as follows: 0 min, 1%; 2 min, 1%; 60 min, 23%; 75 min, 70%; 80 min, 95%; 90 min, 95%; 95 min, 1%; 100, 1%. Two MS scan types were used: enhanced MS (EMS) for compound identification, together with matching to authentic standards (chromatographic and spectral characteristics), and multiple reaction monitoring (MRM) for quantification. MS conditions for both scan types were as follows: ion spray voltage, −4000 V; ion source temperature, 450 °C; collision gas, high; curtain gas, 15 psi; ion source gas 1, 70 (arbitrary units); ion source gas 2, 50 (arbitrary units); declustering potential, −35 V; entrance potential, −10 V; collision energy, −30 V; collision cell exit potential, −3 V. The selected mass transitions (m/z pairs) for MRM scan and quantification (in some cases two most intense transitions were available, thus gaining in sensitivity) were for (+)-catechin and (−)-epicatechin, 289−245; for procyanidins B1 and B2, total sum of 577−425 and 577−407; for (−)-epigallocatechin and (−)-gallocatechin, total sum of 305−221 and 305−219; for (−)-epicatechin 3-gallate, 441−289; and for (−)-gallocatechin 3-gallate, total sum of 457−331 and 457−305. Calibration curves for each flavan-3-ol were obtained for calculating the respective molar response factors against (−)-gallocatechin 3-gallate used as internal standard. Analyses were performed in duplicate.

■ RESULTS AND DISCUSSION

Total Polyphenols and Anthocyanins. The content of total polyphenols of Canary Islands red wines was within the usual ranges found for red wines. Tintilla wines and, to a lesser extent, Baboso Negro wines accounted for the highest values (Table 2). Only Tintilla wines showed significant differences in total polyphenols within vintages that can be very likely attributable to differences in difficult to control factors such as climatic conditions. In contrast, the content of total anthocyanins was not significantly different according to grape cultivar origin but was very affected by vintage. The oldest wines had the lowest contents in total anthocyanins, very likely due to the well-known process of wine pigment loss during aging due to polymerization reactions and subsequent precipitation of colorant material.

For a better characterization of the phenolic composition of Canary Islands red wines, a detailed study by HPLC-DAD-ESI-MS^n was performed. Five classes of individual phenolic compounds were investigated, using a combination of sample preparation and chromatographic and detection methods. The following phenolic compounds were analyzed (Figure 1): anthocyanins (monomeric anthocyanins, direct anthocyanin−catechin adducts, and different pyranoanthocyanins); flavan-3-ols (monomers and B-type procyanidin dimers); flavonols (glycosides and aglycones); hydroxycinnamic acid derivatives (tartaric esters, free acids, and ethyl esters); and stilbenes (reveratrol $trans/cis$ isomers and their 3-glucosides).

Anthocyanins. The profiles of monomeric anthocyanins of all the single-cultivar red wines from Canary Islands were clearly dominated by malvidin 3-glucoside (Mv3glc), as usual in $Vitis$ $vinifera$ red wines.[23] This single anthocyanin accounted for its highest molar proportion in Tintilla and Vijariego Negro wines (MV of 74.91 and 75.41%, respectively), the lowest proportions being found in Baboso Negro, Listán Negro, and Negramoll wines (MV of 68.63, 67.55, and 64.74%, respectively) (Table 3). Other nonacylated anthocyanins such as the 3-glucosides of delphinidin, petunidin, and peonidin (Dp3glc, Pt3glc, and Pn3glc, respectively) accounted for molar proportions of <10%: Negramoll wines showed the highest proportions of both Dp3glc and Pt3glc (MV of 8.82 and 9.94%, respectively), whereas Baboso Negro wines showed the highest proportion of Pn3glc

Table 2. Total Polyphenols (mg/L, as Gallic Acid) and Total Anthocyanins (mg/L, as Malvidin 3-Glucoside)[a]

cultivar	vintage		total polyphenols		total anthocyanins	
Baboso Negro	2005−2007 (n = 5)	MV	1699		117.2	a
		SD	340		46.3	
	2008 (n = 4)	MV	1647		168.6	ab
		SD	75		44.7	
	2009 (n = 2)	MV	1793		228.5	b
		SD	825		62.5	
	total (n = 11)	MV	1698	AB	156.1	
		SD	345		61.0	
Listán Negro	2005−2007 (n = 3)	MV	1344		81.1	a
		SD	296		25.8	
	2008 (n = 4)	MV	1199		92.1	a
		SD	83		30.5	
	2009 (n = 10)	MV	1553		256.8	b
		SD	222		71.9	
	total (n = 17)	MV	1433	A	187.1	
		SD	254		102.8	
Negramoll	2005−2007 (n = 3)	MV	1307		68.8	a
		SD	47		20.3	
	2008 (n = 4)	MV	1307		105.0	a
		SD	165		34.9	
	2009 (n = 2)	MV	1418		280.1	b
		SD	180		62.5	
	total (n = 9)	MV	1332	A	131.8	
		SD	132		91.6	
Tintilla	2005−2007 (n = 3)	MV	1557	a	92.1	a
		SD	372		9.7	
	2008 (n = 2)	MV	1194	a	106.9	a
		SD	14		15.6	
	2009 (n = 5)	MV	2523	b	384.0	b
		SD	560		149.6	
	total (n = 10)	MV	1977	B	241.0	
		SD	735		180.9	
Vijariego Negro	2005−2007 (n = 2)	MV	1313		68.2	a
		SD	110		13.0	
	2008 (n = 3)	MV	1527		195.3	b
		SD	135		31.5	
	2009 (n = 2)	MV	1391		239.5	b
		SD	107		36.5	
	total (n = 7)	MV	1427	A	171.6	
		SD	141		77.2	

[a] MV, mean value; SD, standard deviation; a and b indicate significant differences (ANOVA, $\alpha = 0.05$) within wines from different vintages of the same grape cultivar; A and B indicate significant differences (ANOVA, $\alpha = 0.05$) within wines from different grape cultivars.

(MV, 9.28%); Listán Negro wines contained simultaneously high proportions of Dp3glc, Pt3glc, and Pn3glc (MV of 6.28, 7.94, and 5.87%, respectively). Cyanidin 3-glucoside (Cy3glc) was a very minor nonacylated anthocyanin for all of the wines (molar proportions of <1%). With regard to acylated anthocyanins, the acetylated derivative of Mv3glc (Mv3acglc) and the coumaroylated derivatives of Mv3glc and Pn3glc (Mv3cmglc and Pn3cmglc, respectively) were easily quantified in all of the wine samples, and their molar proportions rarely exceeded 5% except for Mv3cmglc (MV ranging within 5.27−6.85%); some significant differences were found within wines grouped by grape cultivar, but they only affected the minor Mv3acglc and Pn3cmglc. Other known acylated anthocyanins were very minor compounds not properly quantifiable, and therefore they were not considered in the anthocyanin profiles. Vintage slightly affected a few individual anthocyanin proportions, as was only
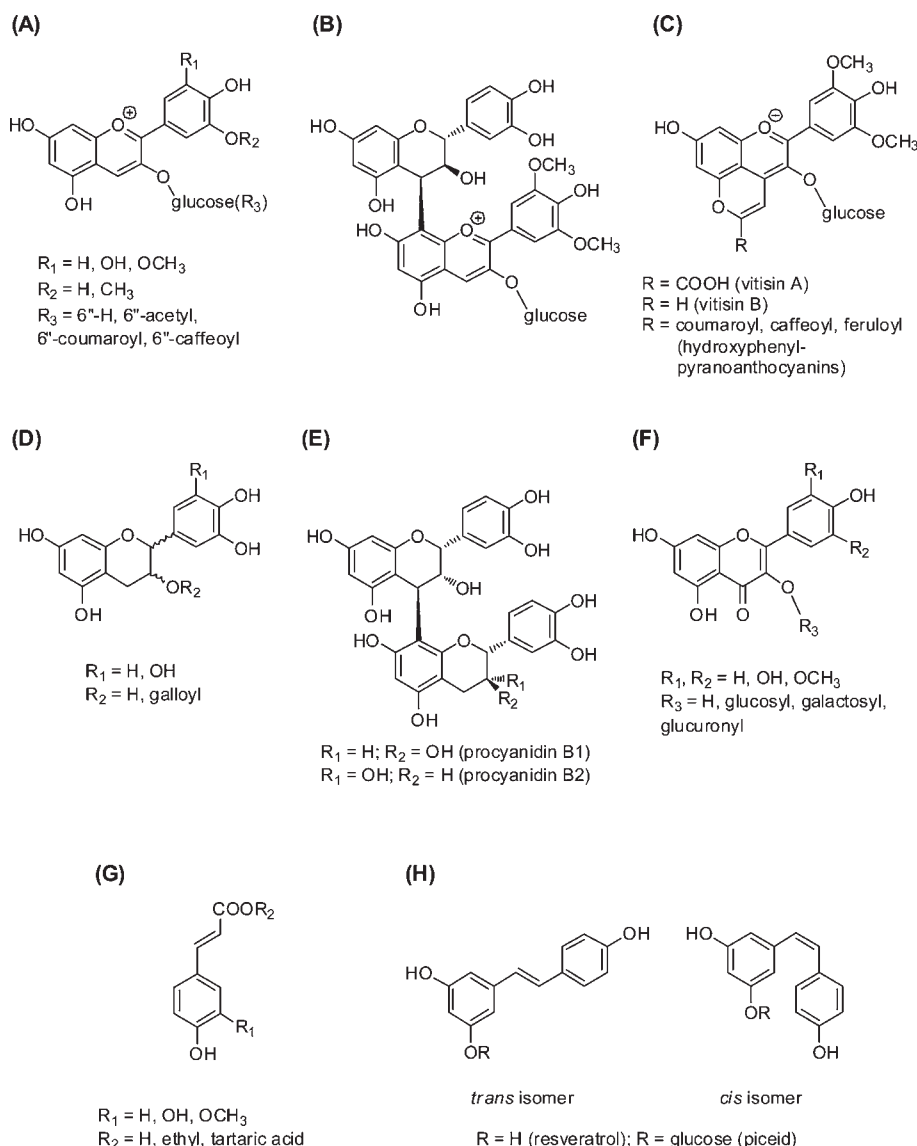
Figure 1. General structures of the classes of phenolic compounds analyzed in Canary Islands red wines: anthocyanins (A); anthocyanin–catechin direct adduct (B); pyranoanthocyanins (C); flavan-3-ol monomers (D); B-type procyanidins (E); flavonols (F); hydroxycinnamic acid derivatives (G); and stilbenes (H).

observed for Dp3glc and Mv3glc in Tintilla wines and Mv3cmglc in Listán Negro wines.

Total concentration of monomeric anthocyanins of red wines from the Canary Islands ranged within usual values for red wines[27−29] and was more affected by vintage than grape cultivar (Table 3), as seen for total anthocyanins (Table 2). It is well established that many viticultural and environmental factors can affect the total anthocyanin content of red grapes and, together with the winemaking technique, the corresponding total anthocyanin content of red wines even for wines of the same grape cultivar and vintage. In addition, grape anthocyanins (monomeric anthocyanins) are involved in reactions just after their transfer to fermenting must that progress over the aging, thus giving rise to new red pigments (namely, anthocyanin–tannin adducts and pyranoanthocyanins) or leading to their disappearance (for instance, by oxidation and precipitation of polymeric matter).[30] Therefore, young red wines (vintage 2009) showed the highest content of total monomeric anthoctyanins,

whatever the grape cultivar considered, whereas wines from the oldest vintages showed lower contents (Table 3).

Finally, some low molecular weight anthocyanin-derived compounds were quantified in these red wines, as the direct condensation product between Mv3glc and (+)-catechin (Mv3glc-cat) and also the pyranoanthocyanins formed by reaction of Mv3glc with pyruvic acid (vitisin A), acetaldehyde (vitisin B), or hydroxycinnamic acids (the so-called hydroxyphenyl-pyranoanthocyanins, HP-pyrant). With the exception of Porto red wines, which reached very high contents of vitisin A because of their special winemaking technique,[31] reported concentrations of vitisin A in Tempranillo and other red wines[26] were similar to those found in the studied Canary Islands wines. With regard to HP-pyrant, the concentrations found in the Canary Islands wines were higher than those reported for Tempranillo wines[26] and reached values as high as found in Pinotage wines.[32] In general, no differences were found within the content of those anthocyanin-derived pigments according to the vintage. However, it is

Table 3. Monomeric Anthocyanin Profiles (Molar Percentages) and Concentrations (mg/L) of Total Monomeric Anthocyanins (Tot-Ant, as Malvidin 3-Glucoside), Direct Anthocyanin–Flavanol Adduct (Mv3glc-cat), Vitisin A, Vitisin B, and Total Hydroxyphenyl-pyranoanthocyanins (HP-Pyrant)[a]

cultivar	vintage		Dp3glc	Cy3glc	Pt3glc	Pn3glc	Mv3glc	Mv3acglc	Pn3cmglc	Mv3cmglc	Tot-Ant	Mv3glc-cat	vitisin A	vitisin B	HP-Pyrant
Baboso Negro	2005–2007 (n = 5)	MV	3.76	0.54	6.72	9.07	69.41	4.50	1.24	4.77	38.17 a	1.23	3.67	0.20	8.60
		SD	1.66	0.34	1.67	2.02	4.42	0.61	0.41	1.27	25.42	0.65	1.78	0.14	14.02
	2008 (n = 4)	MV	3.37	0.43	6.37	9.45	68.69	4.19	1.81	5.69	79.87 ab	1.34	6.30	0.36	6.50
		SD	1.13	0.24	1.28	3.50	4.04	0.99	0.36	1.41	13.93	0.93	2.18	0.06	6.45
	2009 (n = 2)	MV	4.57	0.49	7.89	9.48	66.55	3.02	2.15	5.85	118.77 b	0.19	5.75	2.00	3.91
		SD	0.30	0.31	0.15	6.14	6.49	0.47	1.05	0.10	40.08	0.27	4.36	2.27	2.42
	total (n = 11)	MV	3.76 A	0.49 BC	6.81 B	9.28 B	68.63 A	4.12 AB	1.61	5.30	67.99	1.08	5.00 A	0.58 A	6.98 A
		SD	1.30	0.28	1.39	3.02	4.25	0.89	0.60	1.23	38.65	0.80	2.51	1.01	9.74
Listán Negro	2005–2007 (n = 3)	MV	6.97	0.32	8.56	5.92	68.80	3.46	1.06	4.90 a	35.27 a	1.77	3.49	0.51	9.14
		SD	1.56	0.31	0.56	2.99	5.59	0.38	0.41	0.26	13.49	0.76	1.40	0.12	7.64
	2008 (n = 4)	MV	5.48	0.42	7.11	4.97	68.28	4.19	1.37	8.19 b	81.85 ab	2.49	4.43	0.74	4.81
		SD	1.85	0.29	1.64	1.89	3.11	0.89	0.19	1.81	18.09	0.81	1.27	0.29	2.30
	2009 (n = 10)	MV	6.40	0.49	8.09	6.22	66.88	3.44	1.59	6.89 ab	143.73 b	0.88	3.01	1.67	6.53
		SD	1.79	0.37	1.27	1.70	4.14	1.17	0.32	1.87	60.11	0.27	1.13	1.62	2.55
	total (n = 17)	MV	6.28 B	0.44 BC	7.94 B	5.87 B	67.55 A	3.62 AB	1.44	6.85	110.03	1.42	3.43 A	1.25 A	6.59 A
		SD	1.73	0.33	1.31	1.92	4.01	1.02	0.36	1.94	63.82	0.85	1.28	1.33	3.74
Negramoll	2005–2007 (n = 3)	MV	8.24	0.60	9.57	5.17	66.96	3.30	1.05	5.11	23.81 a	1.16	3.40	0.27	8.56
		SD	1.69	0.15	1.04	0.26	3.43	0.38	0.27	0.53	18.11	0.33	1.46	0.13	3.67
	2008 (n = 4)	MV	10.18	0.76	10.91	6.23	62.07	3.60	1.16	5.09	77.45 a	2.42	4.95	1.05	5.40
		SD	3.32	0.51	1.53	1.07	5.56	0.88	0.25	1.23	29.57	1.66	2.69	0.69	3.31
	2009 (n = 2)	MV	6.95	0.40	8.55	5.46	66.75	3.71	1.41	6.76	170.81 b	0.52	4.22	0.85	8.33
		SD	1.80	0.03	1.18	0.20	6.03	1.12	0.30	1.41	82.48	0.18	0.35	0.27	0.05
	total (n = 9)	MV	8.82 C	0.63 C	9.94 C	5.71	64.74 A	3.52 A	1.18	5.47	80.32	1.58	4.27 A	0.75 A	7.10 A
		SD	2.68	0.35	1.52	0.84	5.05	0.71	0.27	1.19	67.15	1.33	1.94	0.57	3.18
Tintilla	2005–2007 (n = 3)	MV	4.85 b	0.17	7.59	3.92	71.73 a	4.45	2.30	5.00	33.61 a	1.06	3.38	0.42	8.81
		SD	0.93	0.18	0.93	0.61	2.47	0.47	2.46	0.94	28.52	0.69	1.25	0.16	6.09
	2008 (n = 2)	MV	2.73 a	0.05	6.38	2.81	77.33 b	3.58	1.14	5.99	70.31 a	0.55	4.47	0.78	12.89
		SD	1.10	0.06	1.48	1.31	2.10	1.50	0.25	0.12	31.30	0.78	0.64	0.52	3.43
	2009 (n = 5)	MV	3.19 a	0.10	6.67	2.32	75.85 ab	4.16	1.61	6.09	206.68 b	0.51	14.03	3.46	17.76
		SD	0.65	0.02	0.64	0.51	2.09	0.20	0.12	0.99	33.87	0.22	7.03	3.34	5.61
	total (n = 10)	MV	3.60 A	0.11 A	6.89 B	2.90	74.91 B	4.13 B	1.72	5.74	127.48	0.68	8.92 B	2.01 B	14.10 B
		SD	1.14	0.10	0.93	0.96	2.99	0.65	1.25	0.95	89.15	0.52	7.17	2.71	6.37
Vijariego Negro	2005–2007 (n = 2)	MV	3.00	0.22	5.64	5.40	76.42	4.62	0.29	4.41	35.68 a	0.46	1.55	0.08	2.85
		SD	0.64	0.31	0.42	0.10	2.03	0.02	0.40	0.17	36.36	0.05	0.18	0.03	1.57

Table 3. Continued

cultivar	vintage		Dp3glc	Cy3glc	Pt3glc	Pn3glc	Mv3glc	Mv3aglc	Pn3cmglc	Mv3cmglc	Tot-Ant	Mv3glc-cat	vitisin A	vitisin B	HP-Pyrant
2008 (n = 3)	MV		2.84	0.31	4.97	6.13	74.90	4.72	0.99	5.14	103.67 b	1.10	5.43	0.80	6.48
	SD		1.94	0.29	1.58	3.22	5.75	0.75	0.24	0.85	16.92	1.05	2.42	0.65	5.50
2009 (n = 2)	MV		2.82	0.17	4.75	5.31	75.17	4.41	1.02	6.35	120.91 b	0.42	5.77	1.88	8.35
	SD		0.03	0.02	0.08	1.71	0.80	0.10	0.20	2.54	16.09	0.32	5.89	1.06	5.69
total (n = 7)	MV		2.88 A	0.25 AB	5.10 A	5.69 B	75.41 B	4.60 B	0.80 A	5.27	89.17	0.72	4.42 A	0.91 A	5.98 A
	SD		1.15	0.22	1.01	2.03	3.51	0.46	0.42	1.40	41.88	0.71	3.41	0.94	4.60

[a] MV, mean value; SD, standard deviation; Dp, delphinidin; Cy, cyanidin; Pt, petunidin; Pn, peonidin; Mv, malvidin; 3glc, 3-glucoside; 3acglc, 3-(6''-acetyl)-glucoside; 3cmglc, 3-(6''-coumaroyl)-glucoside; Mv3glc-cat, direct adduct of the reaction between Mv3glc and (+)-catechin; a and b indicate significant differences (ANOVA, $\alpha = 0.05$) within wines from different vintages of the same grape cultivar; A–C indicate significant differences (ANOVA, $\alpha = 0.05$) within wines from different grape cultivars.
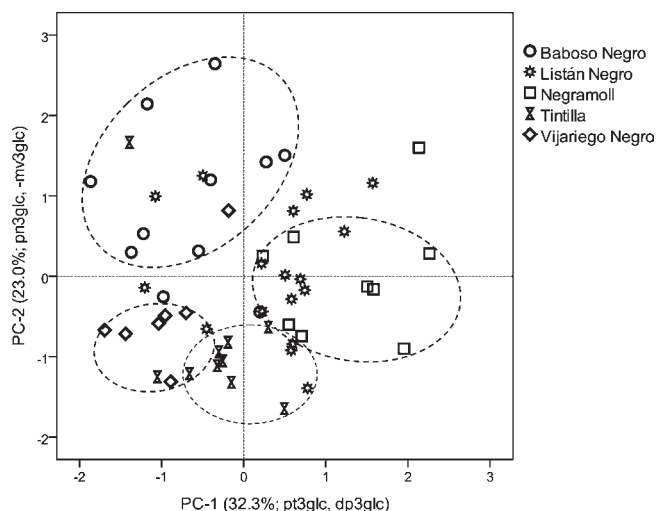
Figure 2. Principal component (PC) analysis applied to monomeric anthocyanin and anthocyanin-derived pigment composition data (Table 3) of single-cultivar red wines from the Canary Islands: plot of wine samples in the space defined by PC-1 and PC-2. For each PC, explained variance and the most correlated variables are indicated (loading absolute values >0.75; a minus sign before the variable abbreviation indicates a negative correlation loading).

remarkable that Tintilla wines reached significantly higher concentrations of both vitisin A and HP-pyrant with regard to the other single-cultivar wines (Table 3).

According to the aforementioned results, it is possible to suggest that the characteristic monomeric anthocyanin profiles of the considered single-cultivar red wines from the Canary Islands did not significantly change within the five-year vintage period studied. Moreover, the differences found within the anthocyanin profiles allowed enough statistical differentiation of four of the five single-cultivar wines by principal component (PC) analysis (Figure 2): Negramoll showed higher proportions of Dp3glc and Pt3glc (PC-1 axis) and a lower proportion of Mv3glc (PC-2 axis) than Tintilla and Vijariego Negro; Negramoll also showed higher proportions of Dp3glc and Pt3glc (PC-1 axis) than Baboso Negro, together with a lower proportion of Pn3glc (PC-2 axis); Baboso Negro showed a higher proportion of Pn3glc and a lower proportion of Mv3glc (PC-2 axis) than Tintilla and Vijariego Negro; the main differences between Tintilla and Vijariego Negro were the higher proportion of Pt3glc (PC-1 axis) for Tintilla and the higher proportion of Pn3glc (PC-2 axis) for Vijariego Negro; unfortunately, the samples of Listán Negro wines overlapped to a great extent with those of the other grape cultivars, in particular with Negramoll.

Flavan-3-ols. The main occurring flavan-3-ol monomers in Canary Islands autochthonous single-cultivar red wines were the expected (+)-catechin (49−54%) and (−)-epicatechin (14−21%), together with also important proportions of (−)-gallocatechin (4−11%), low proportions of (−)-epigallocatechin (<3%), and trace proportions of (−)-epicatechin 3-gallate (Table 4). These flavan-3-ol profiles were generally in agreement with previously reported data.[27−29,33] (+)-Catechin predominated in all of the single-cultivar wines, and nonsignificant differences according to grape cultivar were found. The proportion of (−)-epicatechin allowed three levels within wines to be established: highest levels for Tintilla wines; medium levels for Negramoll, Vijariego Negro, and Baboso Negro wines; and lowest levels for Listán Negro

Table 4. Flavan-3-ol (Monomers and B-Type Procyanidin Dimers) Profiles (Molar Percentages) and Total Flavan-3-ol Concentrations (μmol/L)[a]

cultivar	vintage		C		EC		EGC		GC		ECG		PB1		PB2		total flavan-3-ols	
Baboso Negro	2005–2007 (n = 5)	MV	53.11		16.78		0.84		4.24		0.03		15.25		9.74	ab	321.2	
		SD	3.32		1.37		0.31		1.71		0.01		2.06		1.69		100.8	
	2008 (n = 4)	MV	49.42		16.47		1.14		3.57		0.07		17.14		12.19	b	353.0	
		SD	3.29		1.50		0.52		0.76		0.05		1.04		1.19		127.0	
	2009 (n = 2)	MV	52.29		15.90		2.15		5.72		0.20		15.33		8.41	a	518.1	
		SD	3.03		0.35		1.71		4.94		0.24		0.93		2.08		184.4	
	total (n = 11)	MV	51.61		16.50	B	1.19	A	4.26	A	0.07		15.95		10.39	B	368.6	AB
		SD	3.42		1.25		0.81		2.10		0.11		1.73		2.07		134.1	
Listán Negro	2005–2007 (n = 3)	MV	60.04	b	15.34	b	1.59		8.45		<0.01		9.78	a	4.80	a	240.5	a
		SD	2.19		0.48		0.46		2.53		<0.01		1.24		0.51		96.1	
	2008 (n = 4)	MV	57.88	b	12.49	a	1.83		10.62		0.09		12.32	a	4.78	a	220.2	a
		SD	3.19		0.33		1.14		2.62		0.08		1.53		0.49		51.1	
	2009 (n = 10)	MV	50.71	a	13.83	ab	2.53		8.25		0.25		17.94	b	6.48	b	557.0	b
		SD	3.40		1.90		1.02		2.85		0.18		2.54		0.74		163.3	
	total (n = 17)	MV	54.25		13.77	A	2.18	AB	8.88	B	0.16		15.00		5.74	A	413.4	AB
		SD	5.15		1.70		1.01		2.76		0.18		4.08		1.06		210.4	
Negramoll	2005–2007 (n = 3)	MV	55.01		13.96		1.65		9.34		<0.01		13.31		6.72		166.8	a
		SD	1.93		1.62		0.41		0.41		0.01		2.89		1.27		26.9	
	2008 (n = 4)	MV	50.79		15.18		1.87		8.34		0.06		15.46		8.29		174.3	a
		SD	5.22		3.53		0.88		2.70		0.07		5.26		1.59		26.1	
	2009 (n = 2)	MV	46.82		16.52		3.48		10.52		0.17		15.20		7.29		347.8	b
		SD	3.38		0.32		0.63		1.16		0.14		1.71		2.02		89.4	
	total (n = 9)	MV	51.31		15.07	AB	2.16	AB	9.16	B	0.07		14.69		7.55	A	210.4	A
		SD	4.78		2.52		0.98		1.94		0.09		3.73		1.55		86.7	
Tintilla	2005–2007 (n = 3)	MV	49.50		21.52	b	1.18		5.06		nd	a	12.74		9.97		250.5	
		SD	5.10		0.85		0.31		1.05				4.01		2.95		90.5	
	2008 (n = 2)	MV	56.01		21.73	b	1.09		5.08		0.02	a	9.00		7.05		238.8	
		SD	9.80		1.83		0.43		1.31		0.02		7.52		5.86		201.4	
	2009 (n = 5)	MV	48.10		19.50	a	1.30		3.95		0.05	b	16.04		11.04		988.0	
		SD	2.30		0.13		0.64		1.32		0.01		0.98		3.30		412.0	
	total (n = 10)	MV	50.10		20.55	C	1.22	A	4.51	A	0.03		13.64		9.92	B	616.9	B
		SD	5.38		1.33		0.48		1.25		0.03		4.31		3.62		484.5	
Vijariego Negro	2005–2007 (n = 2)	MV	50.96		16.03		1.68		12.05		0.14		12.24		6.88		192.6	
		SD	0.85		1.33		0.39		4.01		0.19		2.67		1.44		101.1	
	2008 (n = 3)	MV	46.61		15.59		2.99		12.30		0.22		14.04		8.23		271.2	
		SD	3.36		0.43		0.87		3.07		0.12		3.95		1.92		44.0	
	2009 (n = 2)	MV	50.95		17.03		3.06		8.47		0.08		13.57		6.82		360.3	
		SD	3.63		1.04		1.41		1.91		0.06		5.68		2.26		163.9	
	total (n = 7)	MV	49.09		16.13	B	2.64	B	11.13	B	0.15		13.39		7.44	A	274.2	A
		SD	3.39		0.98		1.02		3.13		0.12		3.53		1.72		107.3	

[a] MV, mean value; SD, standard deviation; C, (+)-catechin; EC, (−)-epicatechin; EGC, (−)-epigallocatechin; GC, (−)-gallocatechin; ECG, (−)-epicatechin 3-gallate; PB1, procyanidin B1; PB2, procyanidin B2; a and b indicate significant differences (ANOVA, α = 0.05) within wines from different vintages of the same grape cultivar; A−C indicate significant differences (ANOVA, α = 0.05) within wines from different grape cultivars.

wines. In the case of (−)-gallocatechin, the highest propotions were found in Listán Negro, Negramoll, and Vijariego Negro wines, whereas the lowest proportions corresponded to Baboso Negro and Tintilla wines. B-type procyanidins were found in important proportions, procyanidin B1 being always more important than B2 and accounting for proportions close to those found for (−)-epicatechin. However, the proportion of procyanidin B1 did not show significant differences within grape cultivar, whereas the highest proportions of procyanidin B2 were shown by Baboso Negro and Tintilla wines and the lowest by the other wines. With regard to the total flavan-3-ol content, the highest value was found in Tintilla wines and the lowest in
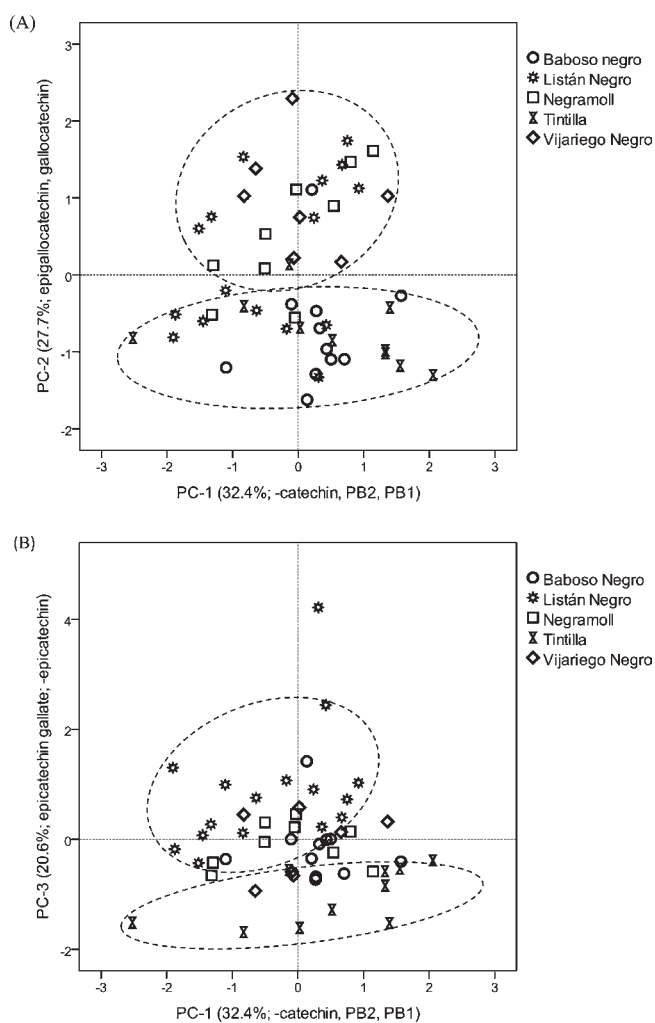
Figure 3. Principal component (PC) analysis applied to flavan-3-ol composition data (Table 4) of single-cultivar red wines from the Canary Islands: plot of wine samples in the space defined by PC-1 and PC-2 (A); plot of wine samples in the space defined by PC-1 and PC-3 (B). For each PC, explained variance and the most correlated variables are indicated (loading absolute values >0.75; a minus sign before the variable abbreviation indicates a negative correlation loading).

Negramoll and Vijariego Negro wines, all of the values ranging within 210−617 μmol/L (61−179 mg/L, as catechin equivalents). Finally, only a few significant differences were found in the flavan-3-ol composition of wines according to vintage (Table 4); the most affected wines were those of Listán Negro, showing in the youngest wines higher amounts of total flavan-3-ols, with lower proportions of both (+)-catechin and (−)-epicatechin and higher proportions of both procyanidins B1 and B2. The latter differences could be attributable to the implication of flavan-3-ols in the well-known polymerization reactions that occur during wine aging, which could suggest a partial conversion of monomers ((+)-catechin and (−)-epicatechin) into dimers (procyanidins B1 and B2).

The suitability of flavan-3-ol profiles of Canary Islands wines for grape cultivar differentiation was poorer than that above-mentioned for their anthocyanin profiles. However, the principal component analysis applied to these data allowed the following grouping and differentiation of the wines: on the one hand,

Baboso Negro and Tintilla showed lower proportions of both (−)-epigallocatechin and (−)-gallocatechin (the B-ring trihydroxylated flavan-3-ol monomers) than those corresponding to Negramoll and Vijariego Negro (Figure 3A); on the other hand, Listán Negro wines showed the lowest proportion of (−)-epicatechin within all of the wines, in particular when compared to Tintilla wines (Figure 3B).

Flavonols. Canary Islands autochthonous single-cultivar red wines contained the same pool of flavonols described for other red wines,[24] consisting of a variable mixture of the original grape flavonol 3-glycosides and their corresponding free flavonol aglycones released from them by hydrolysis in wine. As already described for other red wines, no relationship was found between the hydrolysis degree of flavonol 3-glycosides and the age of a wine.[24] For the aforementioned reasons, the actual flavonol profiles shown by the studied wines were variably distorted, and they were not suitable for characterization of the used grape cultivar. However, the calculation of flavonol profiles on the basis of the common type of flavonoid structure involved in an aglycone and their 3-glycosides (the so-called aglycone-type flavonol profiles) helped to restore the cultivar-related intrinsic information of flavonol profiles lost by hydrolysis (Table 5). Quercetin-type dominated the flavonol profiles (MV range of 43.57−56.18%) followed by myricetin-type flavonols (MV range, of 29.66−33.61%), except for Tintilla wines (MV = 30.34% for quercetin-type and 45.03% for myricetin-type). Laricitrin- and syringetin-type flavonols accounted for lower proportions (MV ranges of 3.97−8.18 and 3.80−13.39%, respectively), and isorhamnetin- and kaempferol-type were minor flavonols (MV not usually higher than 5 or 2%, respectively). These results are in agreement with previously reported data for other red wines.[24] The total flavonol content of wines was not affected by vintage. In contrast, the grape cultivar introduced important differences, and Listán Negro and Negramoll wines almost doubled their content with regard to the other single-cultivar wines (MV ranges of 250−280 and 117−167 μmol/L). The reported MV for other Spanish red wines ranged from 81 μmol/L (Mencía wines) to 274 μmol/L (Syrah wines); the most well-known Spanish red wines (Tempranillo wines) had MV of 189−207 μmol/L.[24]

The aglycone-type flavonol profiles did not substantially change within vintages, and only slight variations were observed for the minor kaempferol-type flavonols in Listán Negro wines and also for quercetin-type flavonols in Tintilla wines (Table 5). Therefore, the aglycone-type flavonol profiles allowed the differentiation of the grape cultivar used in the elaboration of these red wines. In summary, the most characteristic features of the flavonol composition corresponding to the different autochthonous single-cultivar red wines from the Canary Islands were as follows (Table 5): Listán Negro and Negramoll wines simultaneously showed the highest total flavonol content and proportion of quercetin-type flavonols; Baboso Negro wines and, to a lesser extent, Listán Negro and Vijariego Negro wines accounted for the highest proportions of isorhamnetin-type flavonols; and, remarkably, Tintilla wines accounted for the highest proportions of all the B-ring trisubstituted flavonols, namely, myricetin-, laricitrin-, and syringetin-type flavonols. Principal component analysis applied to aglycone-type flavonol profiles and total flavonol content confirmed the aforementioned features and showed three clearly differentiated wine groups (Figure 4): Listán Negro and Negramoll wines; Baboso Negro and Vijariego Negro wines; and Tintilla wines.

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Table 5. Aglycone-Type Flavonol Profiles (Molar Percentages) and Total Flavonol Concentrations (μmol/L)^a

cultivar	vintage		kaempferol-type		quercetin-type		isorhamnetin-type		myricetin-type		laricitrin-type		syringetin-type		total flavonols	
Baboso Negro	2005−2007 (n = 5)	MV	2.17		50.23		5.31		28.45		6.03		7.81		147.49	
		SD	1.53		6.67		0.84		5.81		1.32		2.17		46.54	
	2008 (n = 4)	MV	1.56		47.22		6.10		29.70		6.73		8.70		183.24	
		SD	1.56		5.60		1.12		4.13		1.49		2.67		37.06	
	2009 (n = 2)	MV	0.71		46.64		5.36		34.74		5.98		6.57		182.15	
		SD	0.57		3.81		0.80		4.95		0.26		0.03		49.92	
	total (n = 11)	MV	1.68		48.48	C	5.61	C	30.05	A	6.27	B	7.91	B	166.79	A
		SD	1.42		5.61		0.94		5.18		1.23		2.16		43.24	
Listán Negro	2005−2007 (n = 3)	MV	2.27	b	52.11		4.50		31.74		4.53		4.85		231.92	
		SD	1.05		5.59		0.29		4.10		1.13		1.78		111.90	
	2008 (n = 4)	MV	2.15	b	57.56		4.73		27.15		4.45		3.96		292.71	
		SD	0.81		3.27		0.72		4.12		0.29		0.41		38.84	
	2009 (n = 10)	MV	0.51	a	56.85		4.59		30.04		4.21		3.82		239.14	
		SD	0.48		5.75		1.11		5.42		0.87		1.00		55.94	
	total (n = 17)	MV	1.20		56.18	D	4.61	BC	29.66	A	4.32	A	4.03	A	250.47	B
		SD	1.06		5.33		0.90		4.93		0.79		1.07		64.80	
Negramoll	2005−2007 (n = 3)	MV	2.29		53.83		3.70		32.08		4.20		3.89		272.44	
		SD	1.60		3.86		1.02		3.24		0.79		0.97		67.32	
	2008 (n = 4)	MV	1.61		53.43		4.34		33.42		3.70		3.50		299.50	
		SD	0.87		3.98		0.76		4.82		0.24		0.33		107.65	
	2009 (n = 2)	MV	0.82		52.84		4.91		33.01		4.15		4.28		250.41	
		SD	0.30		5.17		0.41		6.08		0.15		0.34		28.59	
	total (n = 9)	MV	1.66		53.43	D	4.25	B	32.89	A	3.97	A	3.80	A	279.57	B
		SD	1.12		3.63		0.85		4.04		0.50		0.63		77.53	
Tintilla	2005−2007 (n = 3)	MV	0.76		37.30	b	3.00		39.95		7.25		11.74		118.03	
		SD	0.36		5.69		0.81		4.93		0.73		2.53		42.77	
	2008 (n = 2)	MV	0.53		29.68	a	2.96		45.13		9.06		12.65		159.23	
		SD	0.20		2.77		0.21		0.25		1.07		1.96		1.97	
	2009 (n = 5)	MV	0.38		26.44	a	2.07		48.05		8.39		14.67		99.68	
		SD	0.22		1.83		1.01		3.45		0.68		1.46		12.87	
	total (n = 10)	MV	0.53		30.34	A	2.53	A	45.03	B	8.18	C	13.39	C	117.09	A
		SD	0.29		5.85		0.92		4.93		0.97		2.18		32.31	
Vijariego Negro	2005−2007 (n = 2)	MV	3.60		46.34		5.01		28.89		6.07		10.09		106.24	
		SD	1.46		5.08		0.48		5.81		1.17		3.82		71.18	
	2008 (n = 3)	MV	1.79		45.47		5.19		31.85		7.29		8.42		180.08	
		SD	1.21		3.24		0.67		1.84		1.13		2.23		56.71	
	2009 (n = 2)	MV	0.26		37.94		3.41		40.96		7.69		9.74		123.80	
		SD	0.05		9.37		2.40		7.02		0.44		4.25		58.55	
	total (n = 7)	MV	1.87		43.57	B	4.63	BC	33.61	A	7.05	B	9.27	B	142.90	A
		SD	1.64		6.11		1.36		6.48		1.08		2.79		61.23	

^{a} MV, mean value; SD, standard deviation; a and b indicate significant differences (ANOVA, α = 0.05) within wines from different vintages of the same grape cultivar; A−D indicate significant differences (ANOVA, α = 0.05) within wines from different grape cultivars.

Hydroxycinnamic Acid Derivatives (HCAD). The HCAD found in single-cultivar red wines from the Canary Islands were the grape native hydroxycinnamoyl-tartaric acids (caftaric and coutaric acids) and some of their reaction products formed in wine, that is, the respective free hydroxycinnamic acids released by hydrolysis (caffeic and p-coumaric acids) and their subsequently formed ethyl esters (ethyl caffeate and ethyl coumarate). Ferulic acid derivatives could be also detected in these wines as very minor compounds, their quantification not being possible. The chemical hydrolysis of hydroxycinnamoyl-tartaric acids progresses over aging time for an individual wine.[34] However, the hydrolysis degrees found in the studied wines were variable, and no significant differences were appreciated within vintages in any of the single-cultivar red wines (Table 6); the results were similar with regard to the degree of formation of ethyl esters of caffeic and p-coumaric acids. Tintilla wines were characterized by
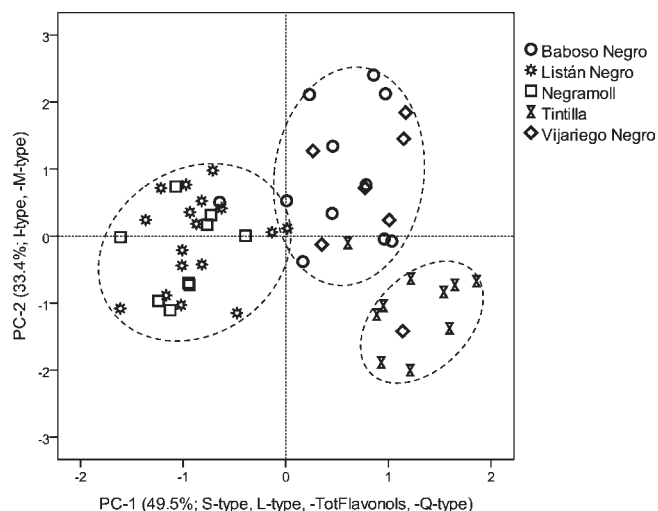
Figure 4. Principal component (PC) analysis applied to flavonol composition data (Table 5) of single-cultivar red wines from the Canary Islands: plot of wine samples in the space defined by PC-1 and PC-2. For each PC, explained variance and most correlated variables (loading absolute values >0.75; a minus sign before a variable abbreviation indicates a negative correlation loading) are indicated. Abbreviations: TotFlavonols, total flavonols; K, kaempferol; Q, quercetin; I, isorhamnetin; L, laricitrin; S, syringetin.

the significantly lowest proportions of both caftaric and coutaric acids, thus suggesting a higher trend to hydrolysis within the Canary Islands red wines; additional supporting evidence of that suggested trend was the significantly highest proportions of released caffeic and *p*-coumaric acids showed by Tintilla wines and, subsequently, significantly highest proportions of ethyl caffeate and coumarate (Table 6).

Because of the hydrolysis and esterification reactions suffered to variable extents by HCAD in wines, we also calculated the proportions of HCAD based on the type of hydroxycinnamic acid involved in their structure (caffeic- and coumaric-type) to reflect the original composition of grapes (Table 6). As reported for other single-cultivar red wines,[34] caffeic-type HCAD were the predominant, Vijariego Negro wines accounting for the significantly highest proportion (MV of 75.01%), followed by Listán Negro and Negramoll wines (MV of 70.48 and 72.30%, respectively), Baboso Negro wines (MV of 67.39%), and Tintilla wines (MV of 57.41%). The reverse order was obviously found for the coumaric-type HCAD proportions (Tintilla wines showed the significantly highest MV, 42.59%, the other wines ranging within 24.99—32.61%). The vintage generally did not affect caffeic- and coumaric-type proportions, and only slight, but significant, differences were shown by Listán Negro wines.

With regard to the total content of HCAD in the studied red wines, no significant differences within vintage were generally observed, except for Baboso Negro wines, which did not show a clear trend of evolution (Table 6). However, significant differences within wines were associated with the grape cultivar. Listán Negro and Negramoll wines accounted for the highest concentrations of HCAD (MV of 622 and 560 μmol/L, respectively), followed by Vijariego Negro, Baboso Negrom and Tintilla wines (MV of 518, 412, and 277 μmol/L, respectively). The HCAD concentration levels of Listán Negro and Negramoll wines reached values similar to those reported for Garnacha wines, which are generally considered to be one of the single-cultivar

wines having highest HCAD contents.[34] It is important to bear in mind that hydroxycinnamic acids are involved in the formation of copigmentation complexes that promote anthocyanin extraction during winemaking and stabilize anthocyanins in young red wines[35] and also in reactions giving rise to stable anthocyanin-related red pigments in aged red wines, the so-called hydroxyphenyl-pyranoanthocyanins.[30,34]

All of the aforementioned results regarding HCAD composition of Canary Islands red wines were submitted to principal component analysis, resulting in a separate grouping of the Tintilla wine samples on the basis of their characteristic proportions of caffeic-type (the lowest within all wines) and coumaric-type (the highest within all wines) HCAD, but not for the other single-cultivar red wines (data not shown).

Stilbenes. Stilbenes based on resveratrol were found in Canary Islands single-cultivar red wines, that is, the *trans* and *cis* isomers of both resveratrol and its 3-glucoside (piceid). The distribution of these stilbenes varied mainly according to grape cultivar, and vintage exerted little effect (Table 7). Piceid is the naturally occurring form of resveratrol found in grape and is partially hydrolyzed during winemaking,[36,37] giving rise to the less soluble resveratrol. Most of the wines contained the original grape *trans*-piceid in mean value molar percentages ranging within 24.29—31.10%, although Tintilla and Baboso Negro wines showed lower percentages (8.14 and 18.43%, respectively). The degree of piceid hydrolysis in the studied wines was significantly higher in Tintilla wines (67.59% of total piceid, considering both *cis* and *trans* isomers). The literature usually reports on only *trans*-resveratrol content, but we have found that *trans*-resveratrol accounted for molar percentages not higher than one-third of the stilbene pool in the considered wines (MV range of 16.08—31.24%), showing some significant differences according to grape cultivar (Negramoll and Vijariego Negro wines showed the lowest and highest proportions, respectively). In addition, the *cis* isomers of resveratrol and piceid were usually the main forms found in the stilbene pool of studied wines (Table 7), accounting for joint proportions of 44.48—67.03%, with three of the five single-cultivar wine types showing *cis* isomer proportions of >50%. It is important to remark that the health benefits associated with resveratrol have been deduced from studies developed using *trans*-resveratrol, and little is known about similar effects of *cis*-resveratrol.

The mean values of total amount of stilbenes showed significant differences according to grape cultivar (Table 7): Negramoll wines accounted for the highest content (139 μmol/L) and Vijariego Negro wines for the lowest content (82 μmol/L), the other three single-cultivar wines ranging within 95—131 μmol/L. The mean value for the content of *trans*-resveratrol in Canary Islands red wines, mainly Listán Negro wine samples, has been reported to be 2.89 mg/L.[19] However, we are now reporting mean values for *trans*-resveratrol (deduced from total stilbene content and molar proportion of *trans*-resveratrol shown in Table 7) in Listán Negro wines that doubled this amount (6.0 mg/L), and similar contents were found for the other single-cultivar wines (4.7—6.5 mg/L). The mean value for *trans*-resveratrol in red wines has been reported to be 1.9 ± 1.7 mg/L, reaching values as high as 5.1 mg/L in some Canadian wines, whereas reported mean values of *trans*-piceid in red wines were 5.4 ± 4.8 mg/L.[38] The contents found for *trans*-piceid in our wines (deduced from total stilbene content and molar proportion of *trans*-piceid shown in Table 7) ranged within 1.6—7.3 mg/L. Therefore, it can be suggested that most of the red wines from the Canary Islands can be described as high-resveratrol content wines.

Table 6. Hydroxycinnamic Acid Derivative (HCAD) Profiles (Molar Percentages), Hydroxycinnamic Acid-Type Profiles (Molar Percentages), and Total HCAD Concentrations (μmol/L)[a]

cultivar	vintage		caftaric acid		coutaric acid		caffeic acid		coumaric acid		ethyl caffeate		ethyl coumarate		caffeic-type		coumaric-type		HCAD	
Baboso Negro	2005−2007 (n = 5)	MV	42.89		18.57		21.37		12.63		2.29		2.26		66.55		33.45		424.34	ab
		SD	22.34		9.26		19.42		11.24		0.98		0.35		4.13		4.13		54.68	
	2008 (n = 4)	MV	48.04		22.08		16.98		8.51		1.88		2.51		66.90		33.10		349.35	a
		SD	11.31		7.32		12.13		4.69		0.76		0.70		2.57		2.57		46.59	
	2009 (n = 2)	MV	59.13		25.59		10.01		2.26		1.35		1.66		70.49		29.51		506.80	b
		SD	0.38		0.80		3.42		1.33		0.37		0.55		2.67		2.67		87.28	
	total (n = 11)	MV	47.71	B	21.12	B	17.71	AB	9.25	A	1.97	B	2.24	B	67.39	B	32.61	C	412.07	B
		SD	16.61		7.62		14.66		8.55		0.84		0.57		3.45		3.45		77.80	
Listán Negro	2005−2007 (n = 3)	MV	53.67		25.34		12.91		5.83		1.14		1.11		67.72	a	32.28	b	565.10	
		SD	8.72		5.93		8.78		4.44		0.71		0.83		0.68		0.68		93.50	
	2008 (n = 4)	MV	57.21		27.12		10.14		4.10		0.75		0.68		68.10	a	31.90	b	678.06	
		SD	7.48		2.69		7.10		2.45		0.15		0.28		1.57		1.57		75.92	
	2009 (n = 10)	MV	57.23		23.28		14.32		3.81		0.70		0.66		72.25	b	27.75	a	616.73	
		SD	12.19		5.43		12.55		4.13		0.45		0.63		2.54		2.54		177.33	
	total (n = 17)	MV	56.60	BC	24.55	B	13.09	AB	4.24	A	0.79	A	0.74	A	70.48	C	29.52	B	622.05	C
		SD	10.27		5.01		10.53		3.71		0.46		0.60		2.99		2.99		145.85	
Negramoll	2005−2007 (n = 3)	MV	50.91		22.96		17.65		6.56		1.01		0.91		69.56		30.44		579.12	
		SD	9.66		1.92		8.58		3.90		0.58		0.37		1.88		1.88		47.43	
	2008 (n = 4)	MV	48.08		19.43		22.53		8.21		0.91		0.85		71.52		28.48		578.17	
		SD	16.71		7.59		17.54		5.75		0.49		0.34		3.87		3.87		59.92	
	2009 (n = 2)	MV	34.17		12.24		39.14		12.67		0.77		1.02		74.08		25.92		493.24	
		SD	21.77		6.50		21.07		7.63		0.07		0.35		0.77		0.77		1.12	
	total (n = 9)	MV	45.93	B	19.01	B	24.60	BC	8.65	A	0.91	A	0.91	A	71.44	C	28.56	B	559.61	C
		SD	15.28		6.73		16.20		5.41		0.43		0.31		3.10		3.10		57.66	
Tintilla	2005−2007 (n = 3)	MV	31.29		13.83		26.13		21.76		2.61		4.38		60.03		39.97		344.74	
		SD	11.73		3.87		7.61		7.28		0.22		0.83		4.26		4.26		72.72	
	2008 (n = 2)	MV	13.77		7.70		37.20		29.59		3.14		8.60		54.11		45.89		270.05	
		SD	3.55		0.40		2.90		5.44		0.13		1.55		6.58		6.58		17.29	
	2009 (n = 5)	MV	18.84		11.79		35.22		23.83		3.09		7.22		57.15		42.85		239.30	
		SD	20.47		11.69		19.51		10.08		0.99		2.42		4.60		4.60		63.96	
	total (n = 10)	MV	21.56	A	11.59	A	32.89	C	24.36	B	2.95	C	6.64	C	57.41	A	42.59	D	277.08	A
		SD	16.35		8.32		14.33		8.29		0.71		2.40		4.80		4.80		73.19	
Vijariego Negro	2005−2007 (n = 2)	MV	62.72		18.90		11.55		3.84		1.72		1.28		75.98		24.02		489.75	
		SD	0.28		1.27		0.32		0.13		0.82		0.36		0.77		0.77		36.23	
	2008 (n = 3)	MV	64.23		21.20		8.13		4.14		1.31		0.98		73.68		26.32		512.59	
		SD	4.03		1.53		2.31		0.34		0.15		0.01		1.86		1.86		148.03	
	2009 (n = 2)	MV	65.63		19.69		8.95		3.09		1.46		1.18		76.04		23.96		554.22	
		SD	4.27		0.98		2.06		2.04		0.53		0.62		1.68		1.68		74.63	
	total (n = 7)	MV	64.20	C	20.11	B	9.34	A	3.76	A	1.47	B	1.12	A	75.01	D	24.99	A	517.96	C
		SD	3.14		1.53		2.21		0.98		0.44		0.32		1.81		1.81		95.76	

[a] Et, ethyl ester; a and b indicate significant differences (ANOVA, $\alpha = 0.05$) within wines from different vintages of the same grape cultivar; A−D indicate significant differences (ANOVA, $\alpha = 0.05$) within wines from different grape cultivars.

With regard to differences in stilbene composition of the studied Canary Islands red wines, there was little effect of vintage within a type of single-cultivar wine, due to the wide ranges in which these compounds were found (Table 7). The exception was Tintilla wines, which showed significant differences within vintages for all of the measures with the exception of *trans*-resveratrol. Tintilla wines showed unique features associated with stilbene composition: these wines accounted for high content of total stilbenes, and they showed the highest degree of hydrolysis (highest proportion of resveratrol-type stilbenes) and the highest degree of *cis* isomerization (highest

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Table 7. Stilbene Profiles (Molar Percentages), Summation of Proportions of Glycosylated (Σ Piceid) and Non-glycosylated Resveratrol (Σ Resveratrol), Summation of Proportions of _trans_ (Σ _trans_) and _cis_ (Σ _cis_) Stilbene Isomers, and Total Stilbene Concentrations (μmol/L)[a]

cultivar	vintage		_trans_ piceid		_cis_ piceid		_trans_ resveratrol	_cis_ resveratrol		Σ piceid		Σ resveratrol	Σ _trans_		Σ _cis_	total stilbenes	
Baboso Negro	2005−2007 (n = 5)	MV	14.93		28.23		24.27	32.56		43.17		56.83	39.20		60.80	88.37	
		SD	9.64		12.58		6.79	15.37		21.17		21.17	5.90		5.90	36.87	
	2008 (n = 4)	MV	19.51		37.44		18.56	24.49		56.95		43.05	38.07		61.93	79.21	
		SD	2.45		4.69		2.15	5.36		4.30		4.30	4.17		4.17	14.31	
	2009 (n = 2)	MV	25.02		36.45		22.53	16.00		61.47		38.53	47.55		52.45	143.78	
		SD	6.40		12.54		1.34	4.80		6.14		6.14	7.74		7.74	20.06	
	total (n = 11)	MV	18.43 B		33.07		21.88 AB	26.62 A		51.51 B		48.49 A	40.31 B		59.69C	95.12	AB
		SD	7.64		10.35		5.23	12.14		15.97		15.97	6.18		6.18	35.26	
Listán Negro	2005−2007 (n = 3)	MV	28.14		24.37		25.68	21.81		52.51		47.49	53.82		46.18	116.20	
		SD	12.08		8.02		12.48	7.89		19.50		19.50	0.56		0.56	51.18	
	2008 (n = 4)	MV	30.28		26.91		22.06	20.76		57.18		42.82	52.33		47.67	158.91	
		SD	3.20		2.72		4.70	5.25		2.98		2.98	7.08		7.08	28.47	
	2009 (n = 10)	MV	32.31		32.91		17.52	17.25		65.22		34.78	49.84		50.16	124.73	
		SD	8.15		6.31		7.40	7.26		8.34		8.34	10.63		10.63	26.04	
	total (n = 17)	MV	31.10 C		29.99		20.03 AB	18.88 A		61.09 B		38.91 A	51.13 CD		48.87AB	131.27	B
		SD	7.77		6.74		8.09	6.83		10.80		10.80	8.70		8.70	33.48	
Negramoll	2005−2007 (n = 3)	MV	26.50		29.37		22.53	21.60		55.87		44.13	49.03		50.97	126.21	
		SD	6.07		4.98		6.34	4.94		10.93		10.93	2.19		2.19	26.05	
	2008 (n = 4)	MV	31.58		35.88		13.21	19.34		67.45		32.55	44.79		55.21	143.77	
		SD	3.44		3.33		3.72	1.48		3.10		3.10	4.75		4.75	46.33	
	2009 (n = 2)	MV	34.74		34.79		12.14	18.33		69.53		30.47	46.88		53.12	147.68	
		SD	3.74		8.97		13.88	1.17		12.72		12.72	10.14		10.14	63.02	
	total (n = 9)	MV	30.59 C		33.47		16.08 A	19.87 A		64.05 B		35.95 A	46.67 BC		53.33BC	138.78	B
		SD	5.14		5.48		7.93	2.99		9.60		9.60	5.14		5.14	39.53	
Tintilla	2005−2007 (n = 3)	MV	12.92 b		20.04 b		27.83	39.20 a		32.97 b		67.03 a	40.75 b		59.25a	87.75	a
		SD	8.05		5.31		3.24	9.71		12.76		12.76	5.50		5.50	19.35	
	2008 (n = 2)	MV	0.49 a		7.10 a		25.40	67.02 b		7.59 a		92.41 b	25.88 a		74.12b	66.60	a
		SD	0.69		3.27		7.93	3.97		3.96		3.96	7.24		7.24	29.09	
	2009 (n = 5)	MV	8.32 ab		33.69 c		22.81	35.18 a		42.01 b		57.99 a	31.13 ab		68.87ab	151.24	b
		SD	1.78		4.99		3.88	9.84		6.63		6.63	5.33		5.33	16.88	
	total (n = 10)	MV	8.14 A		24.28		24.83 B	42.76 B		32.41 A		67.59 B	32.97 A		67.03D	115.26	AB
		SD	6.04		11.80		4.62	15.25		15.68		15.68	7.64		7.64	42.45	
Vijariego Negro	2005−2007 (n = 2)	MV	30.76		21.09		31.72	16.43		51.85		48.15	62.48 b		37.52a	50.06	
		SD	3.98		4.31		1.51	1.84		0.33		0.33	2.47		2.47	4.66	
	2008 (n = 3)	MV	19.62		24.77		30.48	25.13		44.38		55.62	50.10 a		49.90b	74.51	
		SD	16.41		6.41		14.09	9.02		22.71		22.71	3.95		3.95	43.05	
	2009 (n = 2)	MV	24.82		28.87		31.88	14.43		53.69		46.31	56.70 ab		43.30ab	126.56	
		SD	1.08		0.28		2.85	3.65		0.81		0.81	3.93		3.93	24.58	
	total (n = 7)	MV	24.29 BC		24.89		31.24 C	19.59 A		49.18 B		50.82 A	55.52 D		44.48A	82.40	A
		SD	10.84		5.19		8.27	7.58		13.88		13.88	6.33		6.33	41.86	

[a] a−c indicate significant differences (ANOVA, α = 0.05) within wines from different vintages of the same grape cultivar; A−D indicate significant differences (ANOVA, α = 0.05) within wines from different grape cultivars.

proportion of _cis_ isomers). In fact, Tintilla wines were the only samples that separately grouped when stilbene composition data were submitted to principal component analysis (data not shown).

In summary, wine age strongly transformed the chemical structure of different phenolic compounds of single-cultivar Canary Islands red wines. Monomeric anthocyanin content significantly decreased for the oldest wines of the same grape cultivar, but their corresponding anthocyanin profiles remained almost unchanged within different vintages. Although all of the anthocyanin profiles were dominated by malvidin 3-glucoside, wine differentiation according to grape cultivar was possible for four of the five single-cultivar wines studied. In contrast, total

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content of non-anthocyanin phenolics did not appreciably change within vintages, but the implication of such compounds in different reactions (polymerization, hydrolysis, and isomerization) greatly modified the phenolic profiles. Flavonol profiles based on the type of flavonoid structure (the so-called aglycone-type flavonol profiles) offered the best results for grape cultivar differentiation of the wines. With regard to flavan-3-ols, the B-ring trihydroxylated monomers (($-$)-epigallocatechin and ($-$)-gallocatechin) and also ($-$)-epicatechin provided additional grape cultivar differentiation. In contrast, hydroxycinnamic acid derivatives and stilbene profiles were very heterogeneous with regard to both grape cultivar and vintage and did not significantly contribute to wine differentiation, even when structure-type profiles were obtained. Within the autochthonous single-cultivar red wines of the Canary Islands, Tintilla wines showed the most different features regarding practically all of the phenolic contents and profiles. These results suggest that the aforementioned singularity of Tintilla wines is linked to the grape cultivar instead environmental or cultivation conditions, because the sampled wines belonged to two different Denominations of Origin and five different vintages (Table 1).

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■ ABBREVIATIONS USED

MV, mean value; SD, standard deviation; Dp, delphinidin; Cy, cyanidin; Pt, petunidin; Pn, peonidin; Mv, malvidin; 3glc, 3-glucoside; 3acglc, 3-(6''-acetyl)-glucoside; 3cmglc, 3-(6''-coumaroyl)-glucoside; Mv3glc-cat, direct adduct of the reaction between Mv3glc and (+)-catechin; HP-pyrant, hydroxyphenyl-pyranoanthocyanins; HACD, hydroxycinnamic acid derivatives.

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