A comprehensive study of red wine properties according to variety

J. Heras-Roger, C. Díaz-Romero, J. Darias-Martín *

Chemical Engineering and Pharmaceutical Technology Department, University of La Laguna, 38201 La Laguna, Tenerife, Spain

ABSTRACT

More than 80 properties have been studied in 250 commercial red wines to obtain a reliable description of the characteristics of each variety. Such a large set of data allows the testing of previous assumptions and a thorough investigation about whether varietal discrimination is possible despite the strong influences of ageing and environment.

Even though several studies have been performed regarding how variety influences wine phenolics or colour, only a few count on a large data set. Most studies are performed by applying only one technology or on a limited number of wines. In this work, a heterogeneous wine population is thoroughly analysed by using diverse analytical techniques. Therefore, analysis of variance can be applied and patterns are observable in different parameters like flavonols or anthocyanins in spite of the high heterogeneity of the samples. The study confirms that discriminant analysis can be successful in distinguishing wines according to variety in spite of the influences of winemaking techniques and vintage.

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1. Introduction

Red wine is a complex matrix with a high number of chemicals. This beverage is often considered one of the most important sources of polyphenol (De Nisco et al., 2013). Phenolic compounds contribute to valuable sensory properties such as astringency or wine structure, which are mainly evaluated in wine tasting (Granato, Katayama, & de Castro, 2011). Other important properties perceived during wine tasting such as flavour, acidic taste, alcoholic strength, sweetness or bitterness directly depend on its chemical composition (Blouin & Peynaud, 2003, chap. 4).

Wine metal content normally proceeds from the vineyard but it can be modified by winemaking techniques or oenological practices (De Nisco et al., 2013). Colour is one of the most valuable characteristics in red wine tasting (Granato et al., 2011) and direct relationships between colour quality and wine chemical composition have long been established (Darias-Martín et al., 2002).

Canary wines exhibit interesting properties as many of them are produced with autochthonous varieties and the vineyards have never suffered from phylloxera. Because of these properties, Canary wines have been used to research aspects such as the winemaking potential (Miguel-Tabares, Martín-Luis, Carrillo-López, Diaz-Diaz, & Darias-Martín, 2002) or colour qualities (Darias-Martín, Carrillo-Lopez, Echavarri-Granado, & Diaz-Romero, 2007).

Wine phenolics have been studied for their sensory properties (Granato et al., 2011), their ability to differentiate wine growing regions (Li, Pan, Jin, Mu, & Duan, 2011) or varieties (Gris et al., 2013), but also for the consequences of terroir on their profile (Jiang, Zhang, & Zhang, 2011) and even differences between clones of the same variety (Burin, Costa, Rosier, & Bordignon-Luiz, 2011). The literature indicates that factors like climate, soil, irrigation, grape ripeness, winemaking techniques or ageing among others affect the accumulation of phenolic compounds (Porgalı & Büyüktuncel, 2012). Gallego, Sánchez-Palomo, Hermosín-Gutiérrez, and Viñas (2013) reported that phenolic contents are affected by variety and vintage but phenolic profiles are mainly affected by variety.

The aim of this work is to thoroughly investigate whether grape varieties can be traced in red wines despite high heterogeneity. For this end, red wine characteristics such as oenological properties, colour, sensory characters, phenolic, metallic and acidic content have been evaluated and the influence of the variety has been taken into account. In general, varietal studies are based on exclusively one technology or use a limited number of samples. The

extensive and detailed results obtained herein with diverse techniques allow novel relationships between parameters to be established and reliable testing differences between single-variety red wines.

2. Methods

The 250 wines selected include twelve or more samples of each single variety from international (Syrah, Merlot and Ruby Cabernet) to specific Spanish and Canary cultivars (Listán Negro, Negramoll, Listán Prieto, Tintilla, Baboso, Castellana, Vijariego), but also blended wines. Most samples were young wines (2011–2012 $n = 140$), less than half from 2008–2010 ($n = 77$), and around 15% aged wines (2004–2007 $n = 33$). Wines from nine vintages and seven different Canary Islands were used.

All samples were filtered (0.45 μm) before assessment except for turbidity. Milli-Q water (Millipore, USA) was used for dilutions and blank runs, except when the use of a "synthetic wine" is detailed. Detection and quantification limits were calculated according to the three and ten sigma criterion as all standards presented linear calibration curves within the concentration range ($r \sim 0.99$).

2.1. Conventional parameters

Oenological properties such as free and total sulphur dioxide, pH and titratable acidity, density, glucose + fructose, glycerine, acetaldehyde, ammonia nitrogen, alcoholic strength, turbidity, anthocyanins, Folin Ciocalteu and Total Phenol Index (IPT) were determined following OIV reference methods (OIV, 2014).

Tannin (proanthocyanidins) quantification was based on their transformation to anthocyanins by heating in acid media (Zamora-Marín, 2003, chap. 5). Gelatine Index (G.I.) was obtained following the Glories (1984) procedure.

2.2. Acid profile

Tartaric acid was obtained following a colorimetric sequential technique (Hycel Diagnostics, France) based on its reaction with vanadium salts in acid media ($\lambda = 480$ nm). Acetic, L-malic, L-lactic and gluconic acid were quantified using specific enzymatic methods (TDI, Spain) described as OIV standards (OIV, 2014).

2.3. Tasting

Sensory qualities and main organoleptic characters were blind evaluated on a 65 wine subset by a professional tasting panel of 10 judges from AOC committees. Tasters considered colour intensity, violet hue, oxidation, acidity, minerality, astringency, and warming feeling on a 0–5 scale.

2.4. Colorimetric properties

Absorbance measurements were performed with a λ25 Perkin–Elmer spectrophotometer (Massachusetts, USA). "Synthetic wine" (12% ethanol, 5 g/l tartaric acid and 3.6 pH) was used for calibrations and dilutions. Wine spectra (380–780 nm) were obtained on a 0.1 cm path length quartz cuvette following the recommendations of the Commission Internationale de L'Eclariage (OIV, 2014). This procedure allows the calculation of wine CIELab values like lightness (L^*), redness (a^*), yellowness (b^*), chroma (C^*), hue (h_{ab}) and saturation (S^*). Colour measurements were performed at wine pH but copigmentation was quantified at 3.6 pH as described by Boulton (1996).

2.5. Metal profile

Potassium, iron, copper, cobalt, and manganese were quantified by atomic absorption spectrometry (AAS) using an air/acetylene flame, magnesium with an acetylene/nitrous oxide flame and sodium by atomic emission spectrometry (AES) following Díaz, Conde, Estévez, Pérez-Olivero, and Pérez-Trujillo (2003). Major elements (Na, K, Mg) were diluted while minor and trace elements (Fe, Cu, Mn, Co) were directly analysed using certified standards as quality control. Instrumental zero, dilutions, and calibrations curves were prepared with an acidified "synthetic wine" (12% ethanol, 5 g/l tartaric acid and 5% nitric acid).

AAS and AES analyses were performed with a Varian Spectraa 55B spectrometer (Agilent Technologies, USA). All chemicals were analytical grade (Panreac, Spain) and working standards were prepared by dilution using cesium chloride (99%) as ionic suppressor (Fluka, Switzerland).

2.6. Phenolic profile

HPLC analyses were pursued on a Waters 2690 Separation System (Massachusetts, USA) with a Photodiode Array Detector (DAD). Samples were injected (15 μL) on a Nova-Pak C18 reversed-phase column (3.9 × 150 mm; 4 μm) thermostated at 30 °C. Chromatographic conditions were adapted from Ibern-Gómez, Andrés-Lacueva, Lamuela-Raventós, and Waterhouse (2002) and chromatograms processed at 280, 320, 365 and 520 nm.

Compounds were identified by their relative retention times and spectral data either compared with available standards or with data previously published under similar conditions (Baiano & Terracone, 2011; Ginjom, D'Arcy, Caffin, & Gidley, 2011).

2.7. Statistical analysis

All measurements were performed in triplicate except for wine tastings whose results are an average of 10 judges' scores. Relationships were considered statistically significant with at least $p < 0.05$ after applying tests with SPSS 17.0 (USA). Correlations were evaluated using Pearson coefficient (r) and one way analysis of variance (ANOVA) was applied. Principal compound analysis (PCA) was used to discriminate between varieties.

3. Results and discussion

3.1. Global analysis

Results from the whole population are summarized in Table 1. All wines met commercial standards but pH and K values were slightly higher than those generally reported (Blouin & Peynaud, 2003, chap. 4). Similarly, Na content was greater than in other areas because of the marine spray from the Canary Islands (De Nisco et al., 2013; Vinkovic, Bojic, Zuntar, Mendas, & Medic-Saric, 2011). Results agree with the literature but the data suggest an increase in Na and K (Moreno et al., 2007).

Tannin levels were higher than those previously reported (Harbertson et al., 2008; Hosu, Cristea, & Cimpoiu, 2014) due to an over quantification as the method is based on anthocyanin–tannin combination reactions and this implies a limited specificity. Anthocyanin content showed unusual variability (30–800 mg/l) because of the high varietal diversity. In this sense, most conventional parameters were diverse due to sample heterogeneity (7 islands, 9 vintages and 10 varieties). As a matter of fact, some wines presented suitable values for ageing (high IPT, Folin-Ciocalteu or G.I.) while others developed typical young wine properties (high hue and copigmentation but low phenol content).

Table 1
Parameters analysed for all wines.

Parameter	X ± SD	Parameter	X ± SD
Conventional		*Phenolic compounds* (mg/l)	
Density (g/ml)	0.9941 ± 0.006	Caffeic acid	13.5 ± 10.1
% volume alcohol	13.72 ± 1.2	Gallic acid	41.8 ± 24.0
Glicerine (g/l)	11.0 ± 2.9	Caftaric acid	34.4 ± 19.1
pH	3.74 ± 0.18	Coutaric acid	19.8 ± 8.8
Titratable acidity (g. tart/l)	5.16 ± 0.72	Syringic acid	7.9 ± 2.8
Free SO_2 (mg/l)	16 ± 8	Coumaric acid	9.7 ± 9.8
Total SO_2 (mg/l)	78 ± 34	Protocatechuic acid	4.2 ± 5.2
Glucose + fructose (g/l)	1.9 ± 6.9	Catechin	66 ± 30
Acetaldehyde (mg/l)	16 ± 39	Epicatechin	39 ± 17
Nitrogen ammonia (mg/l)	38 ± 29	Tyrosol	9.8 ± 4.1
Folin-Ciocalteu Index	50 ± 11	Resveratrol	5.1 ± 3.0
Gelatine Index	60 ± 10	2-S-Glutathioncaftaric acid	0.3 ± 0. 2
Tannins (g/l)	2.0 ± 0.8	Rutin	4.3 ± 3.0
Anthocyanins (mg/l)	296 ± 179	Quercetin	2.8 ± 2.5
Turbidity (NTU)	5.6 ± 6.9	Quercetin-3-glucoside	6.2 ± 4.0
IPT (U.A.)	52.7 ± 12.9	Quercetin-3-glucuronide	9.2 ± 4.9
Acids		Myricetin	7.4 ± 4.3
Tartaric acid (g/l)	2.5 ± 1.0	Myricetin-3-glucoside	0.7 ± 3.9
L-lactic acid (g/l)	1.78 ± 1.0	Myricetin-3-glucururonide	0.4 ± 0.3
Acetic acid (g/l)	0.60 ± 0.24	Isorhamnetin	3.6 ± 2.1
L-malic acid (g/l)	0.38 ± 0.71	Isorhamnetin-3-glucoside	2.9 ± 1.8
Gluconic acid (g/l)	0.36 ± 0.42	Laricitrin-3-glucoside	1.6 ± 0.8
Citric acid (mg/l)	140 ± 102	Syringetin-3-glucoside	0.4 ± 0.4
Metals (mg/l)		Kaempferol-3-glucoside	0.3 ± 0.3
K	1428 ± 459	Delphinidin-3-glucoside	10.3 ± 9.0
Mg	129 ± 27	Cyanidin-3-glucoside	2.0 ± 5.1
Na	98 ± 57	Cyanidin-6-acetyl-3-glucoside	3.6 ± 3.0
Fe	1.7 ± 1.0	Petunidin-3-glucoside	11.1 ± 9.7
Mn	1.3 ± 0.7	Petunidin-6-acetyl-3-glucoside	4.3 ± 3.8
Cu	0.2 ± 0.7	Peonidin-3-glucoside	10.0 ± 9.0
Co	0.02 ± 0.01	Peonidin-6-acetyl-3-glucoside	5.6 ± 4.8
Tasting (0–5 scale)		Peonidin-6-coumaryol-3-glucoside	7.6 ± 7.6
Acidity	2.58 ± 0.55	Malvidin-3-glucoside	93 ± 79
Oxidation	1.40 ± 0.76	Malvidin-6-acetyl-3-glucoside	14.1 ± 13.4
Violet Hue	2.23 ± 1.48	Malvidin-6-coumaryol3-glucoside	15.1 ± 12.3
Astringency	2.26 ± 0.63	*Colorimetric characteristics*	
Colour intensity	3.04 ± 0.90	L^* (C.U.)	20 ± 10
Warming feeling	2.56 ± 0.63	C^* (C.U.)	54 ± 11
Mineral perception	1.79 ± 0.71	h_{ab}^* (C.U.)	29 ± 6
Colour		a^* (C.U.)	42 ± 13
Colour intensity (U.A.)	9.0 ± 3.6	b^* (C.U.)	30 ± 12
Hue (A_{420}/A_{520})	0.75 ± 0.16	S (C.U.)	3.5 ± 1.2
A_{420} (U.A.)	3.4 ± 1.3	$X_{COPIGMENTATION}$ (%)	18 ± 11
A_{520} (U.A.)	4.5 ± 2.0	$X_{POLYMERIC\ PIGMENT}$ (%)	41 ± 10
A_{620} (U.A.)	0.9 ± 0.4	$X_{FREE\ ANTHOCYANIN}$ (%)	41 ± 15

Most samples contained low levels of residual ammonia nitrogen. Those with high levels also showed a high acetic acid content and titratable acidity, with their tasting scores being generally low. Atypical turbidity values were obtained for samples from wineries producing non filtered wine. Maximum glucose + fructose and ethanol values were obtained in the case of dessert red wines. In terms of colour, the wines had high cromacity and low oxidized hues.

3.2. Varietal analysis

Phenolic profiles have been used for wine differentiation (Gonzalez-San Jose, Santa-Maria, & Diez, 1990) mainly due to the ability of hydroxycinnamic acids and flavonols to discriminate between varieties (Castillo-Muñoz, Gómez-Alonso, García-Romero, and Hermosín-Gutiérrez (2007)). Jaitz et al. (2010) studied phenol analytical differentiation against fraud in 97 samples achieving acceptable results. Granato et al. (2011) obtained a significant variance in phenolic composition and colour among grape varieties in 73 South American red wines. In the present study, a separation between varieties was achieved in spite of the high variability arising from vintage, ageing, region and winemaking procedure.

The discriminant analysis in Fig. 1 considers varieties as grouping variables, and according to the leave-one-out test 90% of all cases were correctly classified. Traditional winemaking varieties from the Canary Islands (Listán Negro and Negramoll) were located close to each other in the figure (Group I). Blended wines are also part of this group. Most grapevines grown in the region are Listán Negro and Negramoll, which normally prevail in "coupages". This is probably the reason why blended wines were statistically similar and were part of Group I. International varieties appeared together forming group II while other traditional varieties were statistically differentiated forming group III and group IV. Listán Prieto was significantly different from the rest and described as particularly astringent in tasting sessions.

Varieties in these groups showed similarities in phenol content and colour. Main Function 1 and 2 parameters were specific phenol compounds (hydroxycinnamic acids, flavonols and anthocyanins), colour characteristics and some conventional properties. These oenological parameters can be partly modified by winemaking practices but some of them revealed significant differences between varieties (e.g., acetic acid, titratable acidity, pH and nitrogen ammonia).

A more detailed study was carried out in order to establish the main differences between grape varieties within the groups of
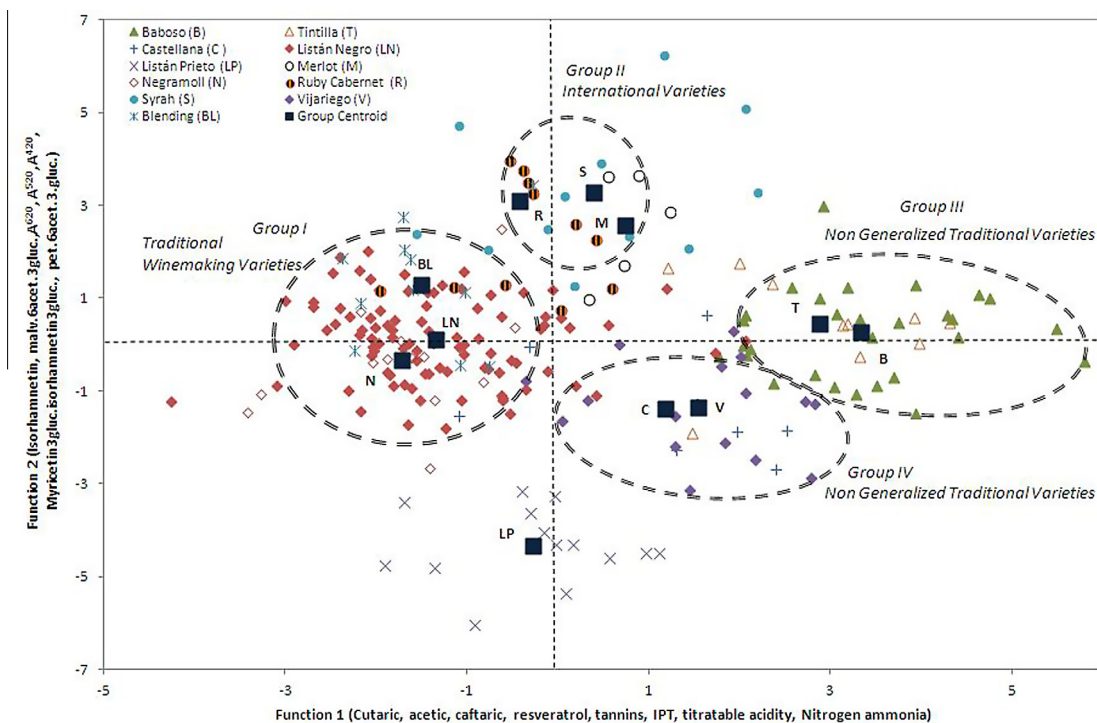
Fig. 1. Red wine discriminant analysis according to variety (LN = Listán Negro; B = Baboso; LP = Listán Prieto; C = Castellana; V = Vijariego; N = Negramoll; S = Syrah; T = Tintilla; R = Ruby Cabernet; M = Merlot; BL = Blending).

parameters considered. Most parameters showed significant differences. Only tartaric and citric acid, acetaldehyde, glucose + fructose, manganese or copper content did not have significant differences between varieties.

3.2.1. Conventional parameters

Some varieties had low pH wines, like Listán Prieto (3.66 ± 0.18) or Listán Negro (3.69 ± 0.10), whereas Castellana and Tintilla (Group III in Fig. 1) presented significantly high pH values (4.13 ± 0.33 and 3.86 ± 0.17, respectively). Geographical origin and other factors influence wine pH, therefore no pH relationship with variety can be confidently established without previously narrowing the geographical factor to a single area but significant trends were observable.

Anthocyanin content was extremely low for Listán Prieto (1545 ± 103 mg/l), Vijariego (169 ± 133 mg/l) and Negramoll (153 ± 78), while international varieties like Syrah (455 ± 213 mg/l) or Ruby Cabernet (508 ± 259 mg/l) and the traditional Tintilla variety (506 ± 288 mg/l) showed high concentrations. In general, blended wines had more equilibrated values than single-varietal wines, avoiding minimum and maximum limits. These wines also developed higher colour indexes and anthocyanin content than most traditional red grape varieties.

3.2.2. Acid profile

Traditionally, wine acids are classified into two groups: one involving those naturally present in grapes and whose concentrations evolve during ripening (mainly tartaric, malic and citric acid) and a second one related to fermentation processes (mostly lactic, acetic and succinic acid). Gluconic acid is normally outside this classification due to its atypical origin. Castellana wines showed significant high L-lactic (3.20 ± 1.37 g/l) and low L-malic (0.05 ± 0.03 g/l) proportions, suggesting a peculiar propensity to complete malolactic fermentations. Baboso wines were characterized by high gluconic acid concentrations (0.73 ± 0.66 g/l), suggest-

ing an exceptional sensitivity of this variety to infection by botrytis. Baboso and Tintilla presented important differences in acetic acid (0.78 ± 0.28 and 0.82 ± 0.28 respectively) when compared to the rest, probably because of their suitability for ageing. Citric acid was low and tartaric content was high for all varieties but no statistical difference was achieved. Fig. 2 shows acid profiles according to variety with a similar pattern to the titratable acidity. Castellana stands out as an atypical variety because of its low titratable acidity but average acid content. Titratable acidity does not consider every acid present in wine as by definition it only represents wine "acid force" until pH 7 is reached, with this variety showing an anomalous behaviour probably due to its peculiar lactic acid content.

3.2.3. Tasting

The sensory panel composed of wine professionals evaluates organoleptic characteristics (data by varieties not shown). As described by Granato et al. (2011) trends observed in colour by the experts agree with analytical laboratory results. Tasters characterized Shiraz wines as having the highest colour intensity and this variety also had the greatest laboratory ICM value, while Negramoll was defined with the lowest violet hues and analytically presented the most evolved hue. The judges gave the lowest acidity scores to the blended wines, and these samples also had the lowest titratable acidity values. The tasters considered that Vijariego wines presented a noticeable warming feeling, with this variety standing out for its high alcohol and glycerine content. In general, Shiraz was considered the most balanced variety while Listán Prieto was characterized by a distinctive astringent taste.

3.2.4. Colorimetric parameters

Red wine colour evolves from bright red to dark red hues during ageing and even though nine vintages were considered some varietal differences were observed in this study (Data not shown). In colour terms, Shiraz stood out from the rest because of its colour
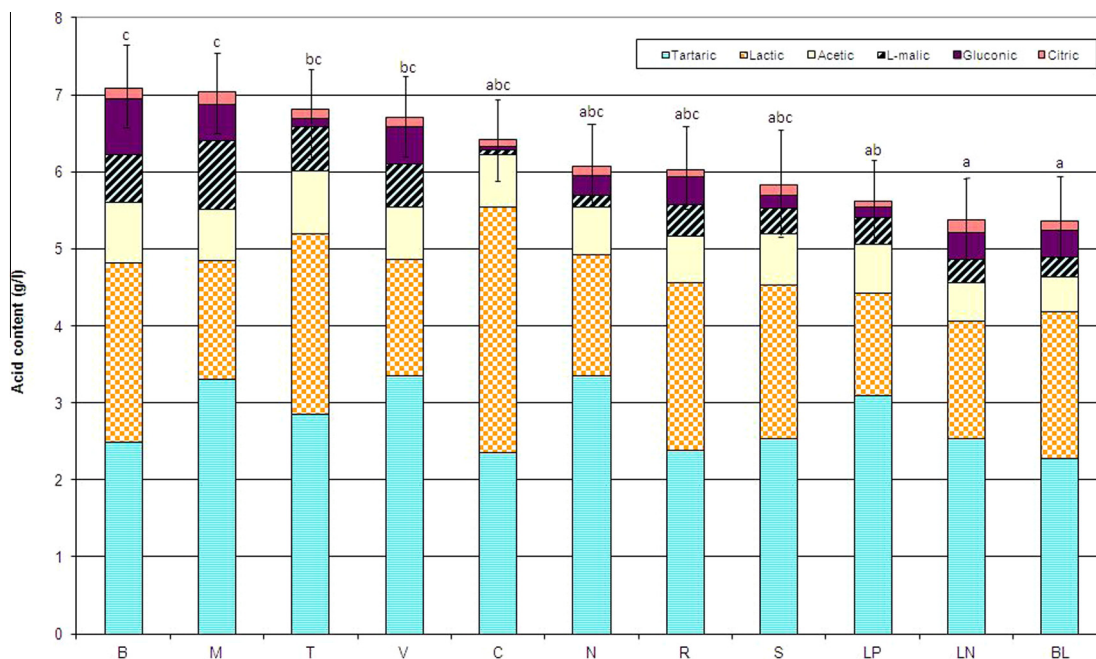
Fig. 2. Red wine acid content by variety. Data are expressed as mean values ± SD. Bars with different letters indicate statistical differences (Duncan Test, $p \leqslant 0.05$). Abbreviations of variety names as in Fig. 1.

intensity (13.1 ± 3.4 U.A.), Tintilla (12.1 ± 3.9 U.A.), Ruby Cabernet (10.2 ± 4.1 U.A.) and Merlot (10.3 ± 0.4 U.A.) also showed high intensity values. In contrast, Negramoll was different to the rest due to its low colour intensity (6.2 ± 2.4 U.A.). The main wine colours were violet and purple red, with Vijariego wines having the highest b^*, h_{ab}, C^* and L^* parameters while Tintilla, Baboso and Castellana had the highest colouring matter for traditional varieties. Red colour (A_{520}) and colour intensity (ICM) were low in varieties with low copigmentation (Vijariego and Castellana) and high in the case of high copigmented varieties (Shiraz and Ruby Cabernet).

3.2.5. Metal analysis

To the best of our knowledge, previous metal studies do not consider statistical discrimination according to varieties. Castellana showed high K proportions (>2000 mg/l), which might be related with its pH (>4.10). This peculiar variety had excellent colour parameters and high phenolic content but it was not especially appreciated in the tasting exercises. This is probably due to its atypical acid profile and pH, which could be associated with a particular tendency to absorb K at a greater rate than other varieties. For most minerals, different statistical groups were obtained according to the variety (no data shown). Na contents were generally greater than those from previous studies (González & Peña-Méndez, 2000). No Cu or Mn differences between varieties were observed but significant correlations at 0.01 level between Mg and other metals were obtained, with the relationship with K ($r = 0.485$) and Na ($r = 0.471$) standing out.

3.2.6. Phenolic analysis

Jiang et al. (2011) and Li et al. (2011) reported that terrain had a strong effect on phenolic composition. Porgalı & Büyünktuncel (2012) considered the influence of processing techniques while Heras-Roger, Pomposo-Medina, Díaz-Romero, and Darias-Martín (2014) highlighted the effect of climate. Hosu et al. (2014) focused on the effect of the harvest year and winery of origin in the phenolic profile. Despite the fact the samples in the present study were of many different origins and vintages, it was found that phenolic

compound concentrations varied between varieties when describing three or more groups with significant differences which agrees with Van Leeuw, Kevers, Pincemail, Defraigne, and Dommes (2014). As reported by Gallego et al. (2013), phenolic profiles seem to be mainly affected by grape cultivar even though there are many factors influencing their content.

3.2.6.1. Phenolic acids (detailed data not shown). Hermosín-Gutiérrez, Sánchez-Palomo, and Vicario-Espinosa (2005) suggested cutaric acid can be used to discriminate between varieties but according to the results here this acid would only separate the samples into two groups. Other phenolic acids differentiate three or more groups, for example caftaric acid content classifies samples in five groups with diverse levels.

3.2.6.2. Flavonols. Flavonols show the most significant differences between varieties and their distribution was similar to that described by Castillo-Muñoz et al. (2007). These chemicals were present as a mixture of the original flavonol-3-glycosides of the grapes and their corresponding free flavonol aglycones produced by hydrolysis in wine in agreement with Burin et al. (2011). The hydrolysis phenomenon is the reason why no acceptable flavonol profile according to variety was directly obtained. However, the sum of related flavonoid structures allows information from those flavonol variety profiles lost by hydrolysis to be obtained (Fig. 3). Flavonol composition varies with ageing, but reaction products can be tracked to reconstitute the original variety identity. In agreement with De Nisco et al. (2013), quercetin type flavonols were the most abundant, followed by myricetin and isorhamnetin derivatives. Laricitrin, syringetin and kaempferol associated compounds were minor flavonols with contents not higher than 3% as obtained by Gris et al. (2013).

Pérez-Trujillo, Hernández, López-Bellido, and Hermosín-Gutiérrez (2011) described Listán Negro and Negramoll flavonol content as being double that of other single-variety wines such as Vijariego, Tintilla or Baboso. These tendencies were reproduced in the present study but traditional varietal concentrations were significantly low when compared to international varieties like Shiraz
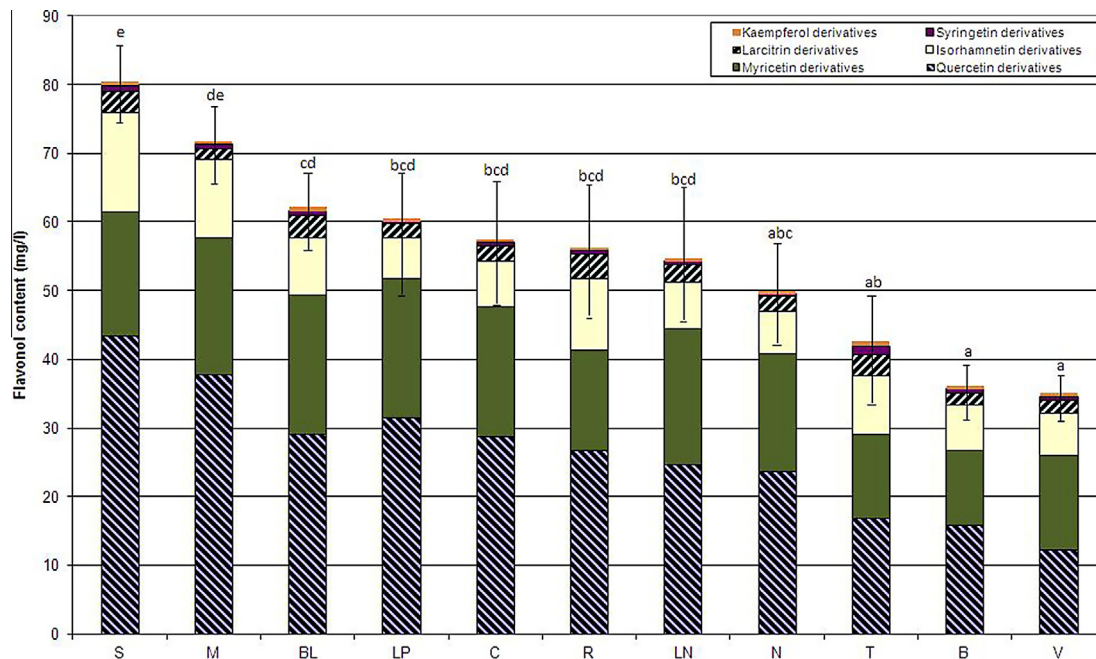
Fig. 3. Flavonol distribution according to variety. Data are expressed as mean values ± SD. Bars with different letters indicate statistical differences (Duncan Test, $p \leqslant 0.05$). Abbreviations of variety names as in Fig. 1.

or Merlot. Tsanova-Savova and Ribarova (2002) characterized flavonol differences as markers of grape variety but according to Blouin and Peynaud (2003, chap. 4) flavonol content mainly depends on sunshine intensity, grape skin thickness and technological processes. Previous studies considered technological possibilities (Darias-Martín, Carrillo, Díaz, & Boulton, 2001) and climate (Heras-Roger et al., 2014), while the differences observed in this case can probably be explained by the diverse grape skin thickness, as flavonols accumulate in the skin of red grapes and they are different for each variety. This finding agrees with Gris et al. (2013),

who considered that flavonol content is influenced by variety and vintage.

3.2.6.3. Flavanols. Fig. 4 shows epicatechin and catechin results according to variety. Tintilla stood out because of its high concentration which is nearly double that of other varieties. This profile agrees with previously reported data (Porgalı & Büyüktuncel, 2012; Pérez-Trujillo et al., 2011; Van Leeuw et al., 2014) because catechin predominated for all single-variety wines and epicatechin established groups with significant differences.
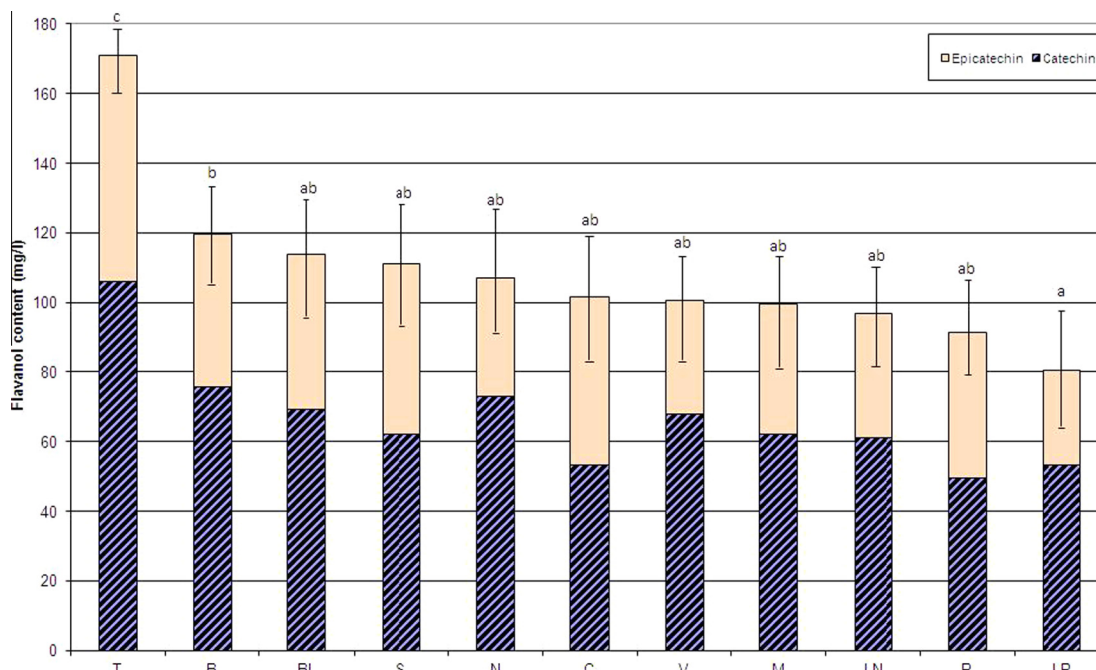

Fig. 4. Flavanol distribution by variety. Data are expressed as mean values ± SD. Bars with different letters indicate statistical differences (Duncan Test, $p \leqslant 0.05$). Abbreviations of variety names as in Fig. 1.
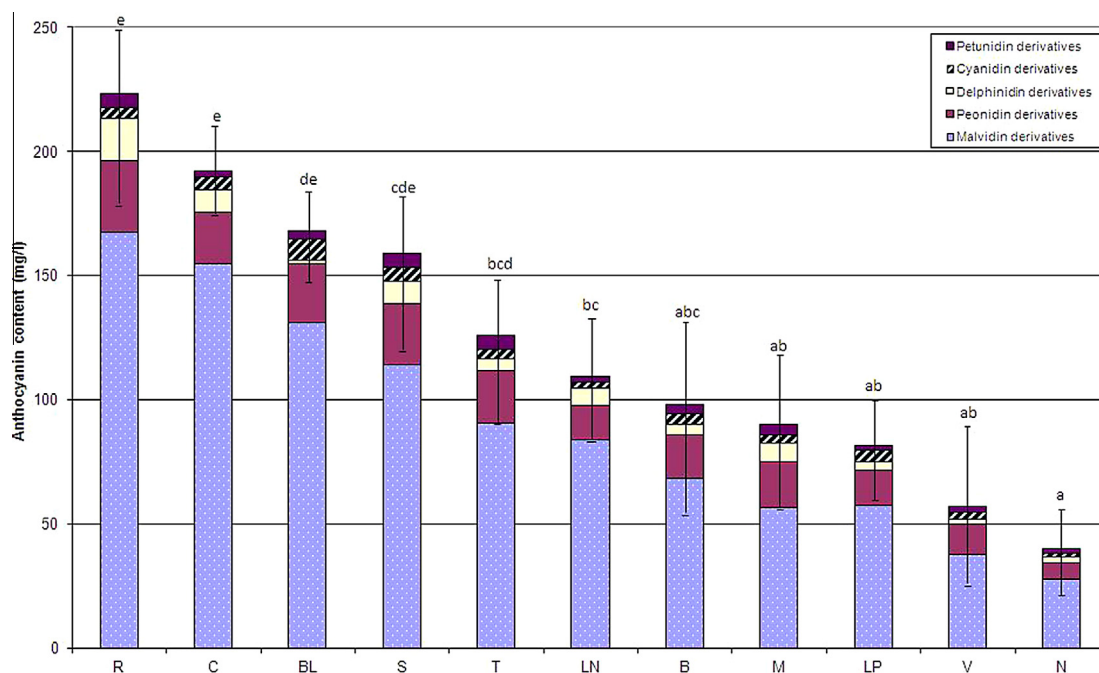
Fig. 5. Monomeric anthocyanins according to variety. Data are expressed as mean values ± SD. Bars with different letters indicate statistical differences (Duncan Test, $p \leqslant 0.05$). Abbreviations of variety names as in Fig. 1.

3.2.6.4. Anthocyanins. Red wines differentiation by using monomeric anthocyanin profiles is limited because of their progressive disappearance during wine ageing (García-Beneytez, Revilla, & Cabello, 2002). Various anthocyanin reactions occur from the beginning of winemaking and continue during ageing. These molecules participate in oxidation and polymerization reactions in order to form new pigments. Fig. 5 describes monomeric anthocyanin variety profile according to the main aglycon involved without glycosylated or acetylated differentiation. Trends by variety were in agreement with the global anthocyanin pattern obtained by direct spectrophotometric measurements in acid conditions (A_{520}).

The most concentrated anthocyanins were malvidin derivatives but the rest varied significantly between varieties. Mitić, Souquet, Obradović, and Mitić (2012) reported that the Merlot variety had the highest anthocyanin content in their study, but according to the results here most Canary traditional varieties as well as the other international varieties showed a higher concentration than the Merlot variety. In agreement with Pérez-Trujillo et al. (2011), some differentiation in anthocyanin profiles between varieties can be achieved in spite of the instability of these chemicals. The present results support the assumptions of Gris et al. (2013) about the influence of variety and vintage in the wine anthocyanin content.

4. Conclusions

Red wine differences by variety are mainly observed in phenolic profiles, colour intensity, sodium and potassium content. Discriminant analyses allow the tracking of grape varieties despite large variations in winemaking techniques, ageing influences or geographical heterogeneity. Analytical profiles obtained for international varieties are grouped and separated from traditional grapes, with autochthonous varieties forming different groups. One of these groups corresponds to the most commonly used traditional varieties which includes blended wines. Listán Prieto is clearly differentiated from the rest.

Baboso wines show high gluconic acid and flavanol content while Ruby Cabernet stands out because of its high anthocyanin level. Tasters and colour analytical measures show that Shiraz wines have the greatest red colour intensity. This variety also presents the highest flavonol level and the greatest copigmentation percentage, suggesting copigmentation influences on colour are as important as the anthocyanin content naturally present in the wine for the final colour.

Vijariego and Negramoll show the weakest red colour, colour density, copigmentation and total anthocyanins. Shiraz wines were given the best scores in terms of overall quality by the tasting panel, whereas Listán Prieto is characterized by a strong astringency in agreement with the highest analytical tannin concentration. Hydroxycinnamic acids and flavonols show interesting variety differentiation features but some routinely used winemaking parameters such as acetic acid, pH, colour or titratable acidity were also surprisingly good variety markers. Finally, the results here show that grape varieties can be traced in red wines mainly through the flavonol and anthocyanin profile despite large sample heterogeneity. Furthermore, the results obtained here, with a large set of data, allow the direct discrimination between varieties in a winery using common and reliable parameters.

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