Quality Improvement in Sweet Red Wines Through an Alternative Grape-Drying System

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A sensorial analysis was undertaken and the colour parameters and phenolic profile were measured for two types of Andalusian sweet red wines. Two wines types were studied, i.e. commercial and alternative wines elaborated with musts from grapes obtained by traditional sun drying and by chamber drying under controlled temperatures respectively. Results show that the alternative wines obtained in this study were analytically closer to typical red wines in their lower concentration of browning compounds, a high contribution of red and blue colour, and hence having a more suitable hue than the traditional sweet wines. Furthermore, the alternative wines were the richest in monomeric anthocyanins, flavan-3-ols and flavonols, which give these wines their antioxidant properties. Their sensorial characteristics were accepted by consumers, which means that the alternative grape-drying system improves the quality of sweet red wines relative to those obtained by the traditional method.

INTRODUCTION

Wine quality is influenced by several factors, such us the health of the grapes and their chemical composition. In relation to the last, in addition to the sugar concentration and acidity it is necessary to know the concentrations of phenolic compounds present in the berries, which will depend on various factors such as grape variety (Perez-Magariño *et al*., 2009), maturation degree, culture practices (Downey *et al*., 2006; Petropoulos *et al*., 2011), and environmental factors such as soil (Prado *et al*., 2007) and climate (Jackson & Lombard, 1993).

The importance of the phenolic composition in oenological products and their relation to quality is because these compounds are responsible for the organoleptic characteristics such as bitterness and astringency (Fischer & Noble, 1994; McRae & Kennedy, 2011; Chira *et al*., 2012), as well as for the colour of musts and wines (Glories, 1984; Garcia-Puente Rivas *et al*., 2006; Monagas *et al*., 2006). Moreover, the interest in this chemical family is based on its antioxidant properties (Alen-Ruiz *et al*., 2009; Sun *et al*., 2011), responsible for the "French paradox" and the prevention of cardiovascular diseases and cancer, among others (Vidavalur *et al*., 2006).

To obtain sweet wines, the grapes can be subjected to different processes prior to winemaking, like drying processes to dehydrate the berries, the *off-vine* system, which is the most common. Dehydration is a complex process that increases the sugar content, but induces several changes in the physicochemical characteristics of grape berries. Firstly, the evaporation of water involves significant changes in the cellular structure of the skins, which lose elasticity, increasing the risk of breakage. The raisins therefore are characterised by a loss of firmness and softening of their texture (Rolle *et al*., 2012), which increase their susceptibility to mechanical damage and infection by pathogens (Genovese *et al*., 2007).

On the other hand, grape dehydration leads to important modifications in colour, volatile compounds and phenolic composition (Bellicontro *et al*., 2004; Serratosa *et al*., 2008a). In particular, the phenolic compounds present in the skins are diffused to the pulp due to their structural alterations (Marquez *et al*., 2012b). These compounds participate in several types of reactions, resulting in the disappearance of some of them and the formation of others. Furthermore, because of the cellular damage, the phenolic compounds contained in the vacuoles of the plant cells come into contact with the polyphenol oxidase enzymes in the cytoplasm (Li *et al*., 2008). Consequently, the enzymatic reactions begin in the presence of oxygen and the brown compounds, called melanins, are synthesised. All these reactions induce a colour change in musts and in elaborated wines. Due to changes in the phenolic composition in the grapes during the dehydration process, the final wines obtained also present different concentrations of phenolic compounds.

Natural sun drying is still the most commonly used

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method for dehydrating grapes in the Mediterranean region as a result of the large number of sun hours. In this raisining process, grapes are exposed to sun on mats for five to ten days to increase their sugar content (Serratosa *et al*., 2008b; Ruiz *et al*., 2010; Serratosa *et al*., 2012). This traditional method is widely used in the Montilla-Moriles region (southern Spain) to obtain sweet white wines. However, in the case of sweet red wines, this drying system decreases the quality, mainly due to the loss of the typical red colour of these wines.

Under this premise, the aim of this work was to elaborate sweet red wines by an alternative *off-vine* drying system to improve their quality in relation to other commercial sweet red wines obtained by traditional sun drying and produced in the Montilla-Moriles region. The wines were compared by analysing their sensory profile, colour parameters and phenolic composition.

MATERIALS AND METHODS
Reagents
Methanol, formic acid, hydrochloric acid and acetonitrile were purchased from Merck (Madrid, Spain). Phenolic commercial standards were purchased in 95 to 99% purity from Sigma-Aldrich Chemical Co. (Madrid, Spain) and Extrasynthèse (Genay, France).

Commercial traditional wines
Three samples (a, b, c) of each commercial sweet red wine (w1 and w2) obtained from two different winemakers in the Montilla-Moriles region (southern Spain) were subjected to analyses. These wines were chosen for being the only commercial sweet red wines made from a sun-drying process in the Montilla-Moriles region. The wines were obtained from 15% (v/v) fortified musts by the addition of wine alcohol. W1 and w2 were elaborated with Syrah/Tempranillo and Merlot grapes respectively, which were subjected to a traditional sun-drying process in order to raisin the berries.

Alternative vinification
The grapes used were *Vitis vinifera* L. cv. Merlot, Syrah and Tempranillo from the 2009 harvest in the Montilla-Moriles region. A total of about 30 kg of grapes was uniformly distributed in a single layer in several trays (11 to 19 kg/m², depending on the variety), and dried *off-vine* in a Frisol Climatronic chamber at a constant temperature of 40°C and an initial relative humidity of 20%. The drying process was finished when the reducing sugar content reached approximately 31.4°Brix. Once dried, the raisins were crushed in a vertical press similar to industrial models, using a maximum pressure of 300 bar. The resulting musts were fortified to 15% (v/v) with wine alcohol (no. CE 200-578-6, Alcoholes del Sur, SA) and macerated with the skins for 47 h at 25°C. After maceration, the grapes were pressed and the skin residues were removed from the wine. The resulting wines (w3, w4 and w5) were centrifuged at 3 000 rpm, filtered and analysed as described below.

Analytical determinations
°Brix was measured using an Atago Master refractometer (Master Baume 2594, Atago, Japan).

Colour parameters
Spectrophotometric measurements were made with a PerkinElmer (Waltham, MA) Lambda 25 spectrophotometer, using quartz cells with a 1 mm light path. Samples were previously passed through Millipore (Billerica, MA) HA filters of 0.45 µm pore size, and all measurements were corrected for a path length of 1 cm. Absorbances at 420, 520 and 620 nm were measured and the percentages of yellow, red and blue colour were calculated. Hue was calculated as the relationship between absorbance at 420 nm and absorbance at 520 nm. Polymeric pigment colour (PPC) was obtained as the absorbance at 520 nm of 5 mL of sample previously supplied with 15 mg of $NaHSO_3$ and allowed to stand at 25°C for 45 minutes.

Analysis of phenolic compounds
For the extraction and fractionation of anthocyanins, the method proposed by Marquez *et al*. (2012b) was used. A volume of 2 mL of wine was passed through a Sep-Pak C18 cartridge packed with 900 mg of material (Long Body Sep-Pak Plus, Water Associates, Milford, MA) that was previously activated with 5 mL of methanol and washed with aqueous 0.01% (v/v) HCl. The cartridge was successively washed with 10 mL of 0.01% aqueous HCl and 5 mL of ethyl acetate, and the anthocyanins were recovered with 5 mL of methanol acidified to pH 2 with HCl. Anthocyanin samples (fraction 1) were concentrated on a vacuum centrifuge thermostated at 35°C and passed through a filter of 0.45 µm pore size for injection into a P4000 HPLC instrument from Spectra-Physics (San Jose, CA).

Other phenolic compounds were extracted with a combination of two cartridges to ensure effective separation (Marquez *et al*., 2012b). Thus, a volume of 15 mL of wine was adjusted to pH 7 with 0.1 M NaOH and passed through Sep-Pak C18 cartridges previously activated with 5 mL of methanol and washed with distilled water, which was adjusted to pH 7 with NaOH. The cartridges were eluted with 10 mL of water at pH 7. This volume, in addition to the volume obtained as a result of sample run-through prior to elution, was used to determine hydroxybenzoic acids and hydroxycinnamic esters (fraction 2). After preconditioning of the cartridge with 5 mL of water at pH 2, flavan3-ols (fraction 3) were eluted with 40 mL of 16% acetonitrile in water at pH 2. Flavonols (fraction 4) were eluted with 5 mL of ethyl acetate, evaporated to dryness and redissolved in methanol. All collected fractions were concentrated on a vacuum centrifuge thermostated at 35°C and passed through a filter of 0.45 µm pore size for injection into the Spectra-Physics P400 HPLC instrument.

All the phenolic compounds were identified by comparing their retention times with those for standards, recording UV spectra on a Spectra-Physics UV6000LP diode array spectrophotometer and calculating the UV absorbance ratios for samples and standards simultaneously co-injected one at a time (Marquez *et al*., 2012b). Identification was confirmed by HPLC–ESI–MS on an AQA quadrupole mass spectrometer from ThermoQuest Finningan. The instrument was operated in both the negative and positive ion modes. The ion spray voltage was -4 kV and the orifice voltage was -60 V. Mass data were acquired in the scan mode (by

scanning the m/z range 150 to 1066 at 1.2 intervals) and the multiple ion mode (by using mass ranges around specific m/z values).

Each compound was quantified by comparison with a calibration curve obtained from the corresponding standard, except for caftaric, coutaric and fertaric acid, which were quantified as caffeic, *p*-coumaric and ferulic acid respectively; procyanidins were quantified as (+)-catechin; quercetin-3-glucuronide, laricitrin-3-glucoside, syringetin-3-glucoside, isorhamnetin-3-glucoside and isorhamnetin were quantified as quercetin-3-glucoside; kaempferol-3-glucoside and kaempferol-3-glucuronide were quantified as kaempferol; and anthocyanins were quantified as malvidin-3-glucoside.

Statistical procedures

The results for all samples were subjected to principal component analysis (PCA), using the Statgraphics Computer Package v. 5.0 from Statistical Graphics Corp.

Sensory analysis

The wines were assessed for aroma, flavour and colour acceptability by 15 experts in a panel in accordance with ISO 8586-1:1993. The selected tasters were: two professional oenologists (male, 40 to 50 years old) selected by the Quality Regulation Board of the Montilla-Moriles Designation of Origin (Southern Spain), seven oenologists (two male, 45 to 55 years old, and five female, 30 to 40 years old) and six consumers who know the characteristics of typical wines produced in this region.

The tasting room was kept at 20°C and had individual booths. Standardised glasses filled with 20 mL of wines were used in accordance with ISO 3591:1992. The glasses were well marked with a code and covered to avoid any loss of organoleptic properties. All the samples were evaluated in a single session, one at a time and with a wait of three minutes between samples. The tasters were instructed in advance about their task and the rules to be followed, and were given a scoring sheet. The evaluation of the quality wines was scored using the scale methods according to ISO

4121:2003, with values of desirable (5 & 6), acceptable (3 & 4) and undesirable (1 & 2).

RESULTS AND DISCUSSION

The commercial sweet red wines obtained from traditional sun-dried grapes (w1 and w2) are currently on the market and widely accepted by consumers. However, the alternative wines from the chamber-dried grapes (w3 to w5) are not commercially available. The first step was to evaluate the sensory differences between them with a view to assessing the customer acceptance potential of the alternative wines. A bottle of each type of wine was used to analyse the aroma, flavour and colour, which were scored on the following acceptance scale: undesirable (scores 1 & 2), acceptable (3 & 4) and desirable (5 & 6). As can be seen in Fig. 1, w1 was judged to have the best aroma (average score 3.9). The other wines received slightly lower scores, but exhibited no significant differences between grape-drying methods. The flavour scores were more different between the wines, with higher values for the alternative wines (3.6 for w5 and 4.4 for w3). Finally, the single property that best differentiated the two wines types was the colour. Thus, the scores for traditional wines (2.2 to 2.8) were substantially lower than those for the alternative ones (3.7 to 4.4). Therefore, these wines could have the potential to compete with the commercial wines and an analytical study consequently was undertaken.

Table 1 shows the contents of the alternative and traditional sweet red wines in low molecular weight anthocyanins, which were identified and quantified by HPLC-DAD-MS. As can be seen, there were qualitative and quantitative differences between the two wine types. Thus, the traditional wines (w1 and w2) did not contain any monomeric anthocyanins. By contrast, the three alternative wines (w3 to w5) contained monomeric glycosylated and acetylglycosylated derivatives of the following anthocyanidins: delphinidin, cyanidin, petunidin, peonidin and malvidin; the coumaroyl glycosides of cyanidin, petunidin, peonidin and malvidin; and malvidin-3-caffeoylglucoside. In addition, the analyses revealed the presence of other anthocyanin derivatives with
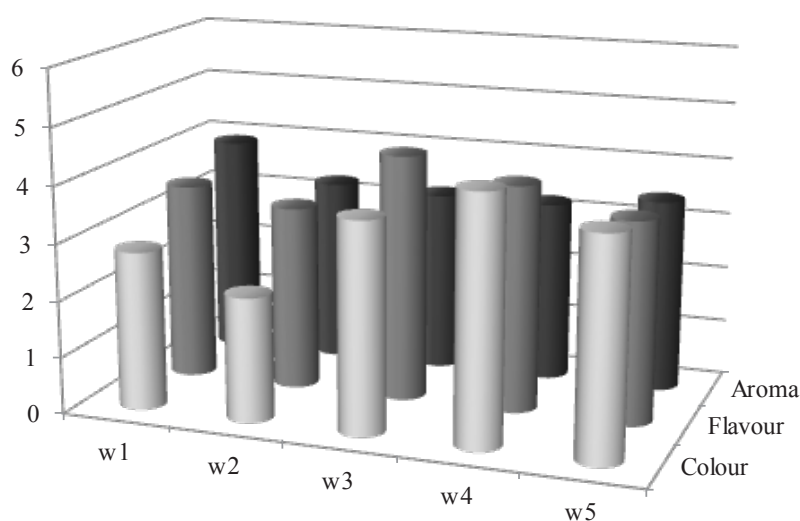

FIGURE 1
Sensorial analysis of the two types of sweet red wines: commercial wines (w1 and w2) and alternative wines (w3 to w5).

TABLE 1

Anthocyanin compound concentrations (mg/L) in the two types of sweet red wines: commercial wines (w1 and w2) and alternative wines (w3 to w5).

| | | w1 | | | w2 | | | w3 | | | w4 | | | w5 | | |
		w1a	w1b	w1c	w2a	w2b	w2c	w3a	w3b	w3c	w4a	w4b	w4c	w5a	w5b	w5c
Anthocyanins	Delphinidin-3-glc	nd	nd	nd	nd	nd	nd	5.00	4.94	4.91	5.59	5.59	5.40	7.40	7.12	6.99
	Cyanidin-3-glc	nd	nd	nd	nd	nd	nd	5.23	5.22	5.24	6.64	6.55	6.43	5.44	5.54	5.52
	Petunidin-3-glc	nd	nd	nd	nd	nd	nd	8.10	8.32	7.98	9.57	9.40	9.28	11.9	11.7	11.6
	Peonidin-3-glc	nd	nd	nd	nd	nd	nd	24.1	23.9	23.7	40.1	38.8	38.0	12.0	12.1	11.6
	Malvidin-3-glc	nd	nd	nd	nd	nd	nd	81.2	78.9	81.9	80.9	77.0	75.9	77.6	76.3	73.1
	Delphinidin-3-acetylglc	nd	nd	nd	nd	nd	nd	nd	nd	nd	5.43	5.59	5.56	6.35	6.72	6.04
	Cyanidin-3-acetylglc	nd	nd	nd	nd	nd	nd	4.54	4.74	4.55	5.15	4.83	4.92	4.84	4.92	4.57
	Petunidin-3-acetylglc	nd	nd	nd	nd	nd	nd	5.60	5.71	5.49	6.34	6.03	6.05	5.74	5.34	5.33
	Peonidin-3-acetylglc	nd	nd	nd	nd	nd	nd	8.25	7.44	8.16	13.7	13.0	13.1	6.28	6.11	6.07
	Malvidin-3-acetylglc	nd	nd	nd	nd	nd	nd	24.4	23.9	24.3	29.0	27.8	28.1	9.57	9.73	9.56
	Cyanidin-3-coumaroylglc	nd	nd	nd	nd	nd	nd	4.48	4.37	4.28	5.15	5.33	5.12	4.29	4.25	4.26
	Petunidin-3-coumaroylglc	nd	nd	nd	nd	nd	nd	4.51	4.35	4.54	4.99	5.08	4.88	5.84	5.79	6.12
	Peonidin-3-coumaroylglc	nd	nd	nd	nd	nd	nd	5.07	5.47	4.93	7.31	7.22	7.14	4.80	4.93	5.06
	Malvidin-3-coumaroylglc	nd	nd	nd	nd	nd	nd	7.05	7.37	7.05	11.3	10.7	10.6	12.2	12.4	12.1
	Malvidin-3-caffeoylglc	nd	nd	nd	nd	nd	nd	6.26	6.20	6.23	7.18	7.33	6.99	8.03	8.27	8.31
Anthocyanin derivatives	A-type vitisin Mv-3-acetylglc	nd	nd	nd	nd	nd	nd	1.09	1.22	1.28	nd	nd	nd	2.79	3.21	2.44
	B-type vitisin Mv-3-glc	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.328	0.240	0.321	0.923	0.833	0.781
	B-type vitisin Pn-3-acetylglc	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.30	1.27	1.09	nd	nd	nd
	Mv-3-glc-methylmethyne-(epi)catechin	nd	nd	nd	nd	nd	nd	0.915	1.02	0.869	0.809	0.813	0.755	0.624	0.678	0.688
	Mv-3-glc-methylmethyne-(epi)catechin	nd	nd	nd	nd	nd	nd	0.625	0.730	0.834	0.740	0.811	0.814	0.678	0.667	0.698
	Mv-3-glc-methylmethyne-(epi)catechin	nd	nd	nd	nd	nd	nd	0.457	0.387	0.454	0.547	0.510	0.523	0.605	0.611	0.742

* a, b, c indicate three samples of each sweet red wine

nd = non detected, glc = glucoside, acetylglc = acetylglucosides, coumaroylglc = coumaroilglucoside, caffeoylglc = caffeoylglucosides, Mv = malvidin

pyranoanthocyanin structures and malvidin-3-glucoside and (epi)catechin adducts bonded via a methylmethyne bridge. The complete absence of anthocyanins in the traditionally made wines does not necessarily mean that no anthocyanins were extracted. In fact, cellular damage of the grapes as a result of dehydration caused the diffusion of coloured compounds from the berry skin to the pulp in all grape-drying processes, and this may occur to a greater or lesser extent depending on the drying system. Therefore it is reasonable to assume that monomeric anthocyanins were extracted during the drying of the grapes and, subsequently, that they could take part in various reactions such as degradation, polymerisation and, possibly, browning.

The most likely polymerisation reactions in the sweet red wines could involve the monomeric anthocyanins and tannins to form coloured compounds of high molecular weights, increasing the temporal stability of their colour (Soto-Vazquez *et al*., 2010). The formation of these products was studied via polymeric pigment colour (PPC). As can be seen in Fig. 2, the traditional wines, which did not contain monomeric anthocyanins, exhibited greater amounts of polymeric pigments. This could confirm that monomeric anthocyanins are involved in the polymerisation reactions, leading to the formation of coloured compounds. The PPC values for the alternative wines also indicate the formation of pigments, albeit to a lesser extent than in the traditional wines.

The abovementioned monomeric anthocyanins could also take part in browning reactions. To this end, the absorbances of the wines at 420 nm (A420) were measured. As can be seen in Table 2, the traditional wines exhibited a much higher browning index than the alternative wines, without significant differences between them. All wines had been made according to the same winemaking process, except for the grape-drying step. Consequently, the sun drying must have substantially enhanced the synthesis of brown compounds, which absorb at this wavelength. Thus, the A420 values for the traditional wines were approximately double (w2) and triple (w1) those of the all alternative wines (w3 to w5). These results are consistent with others previously found by Serratosa *et al*. (2008a) in musts from

sun-dried and chamber-dried Pedro Ximenez grapes. The increased progress of browning in the traditional wines can be ascribed to several factors. On the one hand, sun drying takes longer (seven to 10 days) than the time used for the alternative wines (two to three days).

On the other hand, sun-dried grapes are subject to abrupt temperature changes, where the berry surface can reach high temperatures at midday (Serratosa *et al*., 2008b) because the temperature can reach 40 ºC around midday (Lopez *et al*., 1988), whereas nocturnal values frequently fall below 18°C and are accompanied by dew. A constant temperature was utilised in the chamber-drying process.

One hypothesis to explain the differences in the formation of brown compounds might not be due to the temperature value, but the use of temperature changes or constant temperature. So a high temperature results in the continuous evaporation of water from the berries, which hinders oxygen penetration through their skins. However, when the temperature falls, the water evaporation stops and atmospheric oxygen again penetrates the skin, as the solubility is more favourable at low temperatures. The constant temperature (40°C) used in the chamber-drying process facilitates the sustained evaporation of water from the pulp, thereby completely hindering the penetration of gases (particularly oxygen). The fact that oxygen is required by many browning reactions may account for its different progression in the two types of processes. On the other hand, the undesirable browning reactions potentially occurring in red wines therefore could be non-enzymatic (Maillard reaction, autoxidation, etc.) and enzymatic types through the action of polyphenol oxidases (PPOs) on phenolic compounds. However, Maillard reactions would not be favoured, since the temperature never reached 50°C during the process (Rivero-Perez *et al*., 2002). As a result of the anthocyanin compounds being involved in the browning reactions, the wines exhibiting the greatest levels of browning were those without monomeric anthocyanins.

Despite the absence of monomeric anthocyanins, the traditional wines exhibited measurable values of A520, which, however, were lower than those of the alternative wines (Table 2). These values in the traditional wines
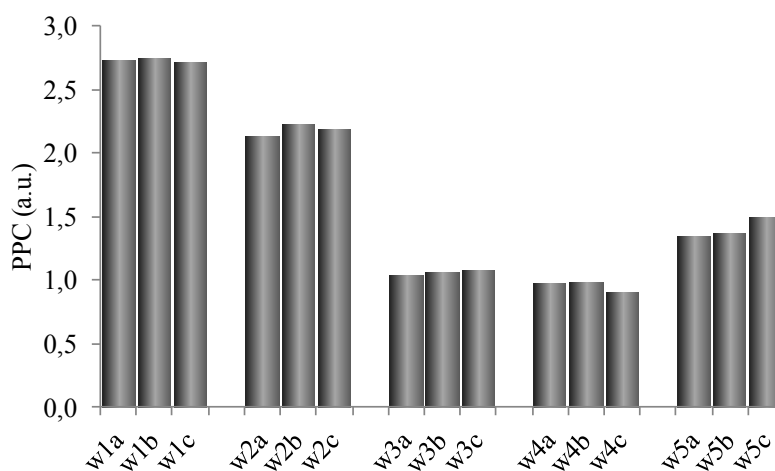

FIGURE 2
Polymeric pigment colour (PPC) in the two types of sweet red wines: commercial wines (w1 and w2) and alternative wines (w3 to w5).

must have been the result of the contribution of polymeric pigments absorbing at 520 nm and the high concentration of brown compounds, which absorb maximally at 420 nm but also, less strongly, at 520 nm.

Wine hues (A420/A520) are shown in Fig. 3. As can be seen, this parameter greatly exceeded unity in the traditional wines (> 2.43), suggesting that brown hues clearly exceeded red ones. On the other hand, the alternative wines had hue values less than unity (< 0.732), exhibiting a typical red colour not present in the traditional wines. Therefore, the use of an alternative grape-drying method may improve the quality of sweet red wines.

Colour differences between the wines were also observed in their percentages of yellow, red and blue. As can be seen in Table 2, and contrary to the expectations for red wines, % yellow prevailed in the commercial wines (64.6 to 68.9%), where it considerably exceeded % red (23.6 to 26.6%). On the other hand, % red prevailed in the three alternative wines (> 51%). Finally, % blue was the least in all the wines (7.63 to 10.1%).

In relation to the anthocyanin concentrations in the alternative wines (Table 1), glycosylated derivatives were the major compounds, with slight differences between them. Specifically, peonidin-3-glucoside was found at concentrations from 11.6 mg/L in w5c to 40.1 mg/L in w4a. With respect to the acetyl glycosylated derivatives, that of delfinidin was not found in any w3 samples. The peonidin derivative was again the compound that differed most

markedly between wines, possibly as a result of the different grape varieties used. Finally, the coumaroyl glycosylated derivatives were found at very low concentrations relative to the previous compounds.

In addition to these anthocyanins, the alternative wines contained pyranoanthocyanin compounds and adducts of malvidin-3-glucoside and (epi)catechin bonded by a methylmethyne bridge. Although all were found at very low concentrations (less than 1 mg/L in most cases), their presence in sweet red wines is interesting, since they protect them from pH changes and decolourisation by SO_2 (Fulcrand *et al.*, 1998; Escribano-Bailon *et al.*, 2001; He *et al.*, 2010). Furthermore, these compounds increase the temporal colour stability (Bakker *et al.*, 1993). The alternative wines were not subjected to fermentation, so pyruvic acid or acetaldehyde, which are indispensable for anthocyanin derivative formation, were not produced by the yeasts. The presence of these two compounds has been ascribed to various enzymatic reactions during grape drying in a controlled-temperature chamber (Marquez *et al.*, 2012a). As a result of the presence of these compounds, colour stabilisation in the sweet red wines from chamber-dried grapes could be assumed to be an additional quality factor for these alternative wines.

The non-flavonoid fraction of the wines included four hydroxybenzoic acids, three hydroxycinnamic acids and the tartaric esters of the latter (Table 3). In relation to the hydroxybenzoic acids, gallic, vanillic and syringic acids were present in the five types of wines, whereas protocatechuic acid

TABLE 2
Colour parameters in the two types of sweet red wines: commercial wines (w1 and w2) and alternative wines (w3 to w5).

	w1			w2			w3			w4			w5		
	w1a	w1b	w1c	w2a	w2b	w2c	w3a	w3b	w3c	w4a	w4b	w4c	w5a	w5b	w5c
A420 (a.u.)	9.06	9.03	9.10	5.81	5.84	5.83	3.02	3.06	3.02	2.78	2.79	2.79	2.87	2.85	2.87
A520 (a.u.)	3.09	3.08	3.14	2.39	2.40	2.40	4.13	4.18	4.11	4.55	4.54	4.56	3.92	3.90	3.91
A620 (a.u.)	1.00	1.01	1.04	0.790	0.786	0.797	0.797	0.811	0.795	0.702	0.702	0.708	0.755	0.747	0.752
% Yellow	68.9	68.8	68.5	64.6	64.7	64.6	38.0	38.0	38.1	34.6	34.8	34.6	38.1	38.0	38.1
% Red	23.5	23.5	23.6	26.6	26.6	26.6	52.0	51.9	51.9	56.6	56.5	56.6	51.9	52.0	51.9
% Blue	7.63	7.72	7.83	8.79	8.71	8.83	10.0	10.1	10.0	8.74	8.75	8.79	10.0	9.97	9.97

* a, b, c indicate three samples of each sweet red wine
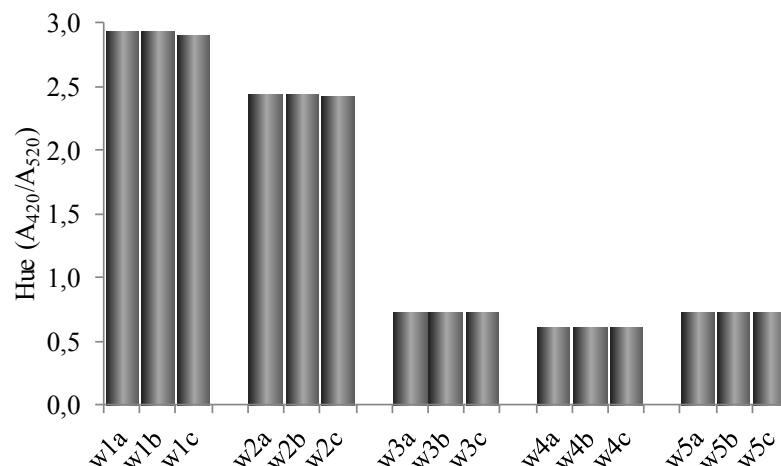

FIGURE 3
Hue (A420/A520) in the two types of sweet red wines: commercial wines (w1 and w2) and alternative wines (w3 to w5).

TABLE 3
Non-anthocyanin phenolic compound concentrations (mg/L) in the two types of sweet red wines: commercial wines (w1 and w2) and alternative wines (w3 to w5).

		w1			w2			w3			w4			w5		
		w1a	w1b	w1c	w2a	w2b	w2c	w3a	w3b	w3c	w4a	w4b	w4c	w5a	w5b	w5c
Hydroxybenzoic acids	Gallic acid	21.4	27.1	25.1	16.2	18.0	17.7	32.9	30.5	30.7	29.5	28.9	29.7	21.5	23.5	23.4
	Protocatechuic acid	31.9	31.6	31.4	0.0	0.0	0.0	4.19	4.20	4.35	0.00	0.00	0.00	0.00	0.00	0.00
	Vanillic acid	10.2	11.1	12.0	12.5	10.1	10.5	4.36	4.07	4.24	9.12	8.93	9.01	6.23	7.20	7.08
	Syringic acid	22.5	22.2	25.1	16.4	16.6	16.2	11.2	11.2	10.7	7.38	9.06	8.23	11.2	12.2	10.9
Hydroxycinnamic acids	Caffeic acid	3.94	4.47	4.30	3.91	4.05	3.08	nd	nd	nd	nd	nd	nd	nd	nd	nd
	p-Coumaric acid	5.60	5.98	6.15	3.34	2.94	2.55	nd	nd	nd	nd	nd	nd	nd	nd	nd
	Ferulic acid	0.520	0.573	0.427	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Esters of hydroxycinnamic acids	c-Caftaric acid	4.36	4.64	4.38	3.92	3.93	3.79	2.56	2.56	2.59	3.28	3.55	3.77	5.10	5.67	5.45
	t-Caftaric acid	0.00	0.00	0.00	6.40	7.29	6.36	1.72	1.71	1.69	4.43	4.60	5.09	4.45	4.82	4.45
	c-Coutaric acid	4.03	4.09	4.08	3.90	3.38	3.26	1.33	1.58	1.56	1.46	1.43	1.55	1.99	2.17	1.98
	t-Coutaric acid	4.47	4.41	4.28	3.91	4.13	3.64	1.39	1.43	1.34	1.01	1.12	1.09	2.05	2.23	2.20
	c-Fertaric acid	1.64	2.11	2.01	1.53	1.66	1.41	0.233	0.232	0.244	1.76	1.85	1.86	2.64	2.74	2.52
	t-Fertaric acid	1.06	1.38	0.97	1.51	1.12	1.44	0.380	0.380	0.434	0.439	0.497	0.496	1.05	1.25	1.42
Flavan-3-ol and Procyanidins	(+)-Catechin	1.78	1.56	1.65	1.57	1.59	1.62	79.7	78.1	80.3	76.0	70.9	78.1	83.1	93.4	83.1
	(-)-Epicatechin	4.54	4.60	4.76	nd	nd	nd	23.6	22.0	31.4	42.2	40.3	43.6	42.9	42.8	44.1
	Procyanidins B1 + B3	nd	nd	nd	nd	nd	nd	14.2	13.0	15.7	7.37	7.88	7.72	8.89	8.81	9.91
	Procyanidins B2 + B4	4.12	3.68	4.05	3.46	3.09	3.64	15.3	17.6	15.9	14.5	16.9	15.3	10.1	9.50	10.4
	B2-3-*O*-gallate dimer	9.77	9.53	9.53	10.8	10.1	9.97	11.2	13.3	12.2	6.16	5.09	4.41	11.8	10.2	11.3
	B2-3-*O'*-gallate dimer	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.61	1.36	1.28	5.33	4.74	4.59
	B1-3-*O*-gallate dimer	nd	nd	nd	nd	nd	nd	6.20	5.59	6.50	nd	nd	nd	4.17	4.73	4.84
Flavonols	Miricetin-3-glc	nd	nd	nd	nd	nd	nd	0.301	0.301	0.284	0.459	0.405	0.367	0.358	0.300	0.287
	Quercetin-3-glucur + Quercetin-3-galac	nd	nd	nd	nd	nd	nd	4.98	4.59	4.73	5.29	4.90	5.52	4.55	4.21	4.23
	Quercetin-3-glc	nd	nd	nd	nd	nd	nd	5.24	4.90	5.01	7.62	7.17	7.91	8.52	7.76	7.66
	Laricitrin-3-glc	nd	nd	nd	nd	nd	nd	1.16	1.13	1.05	1.58	1.46	1.53	2.10	1.86	1.90
	Kaempferol-3-glc	nd	nd	nd	nd	nd	nd	1.03	1.00	1.04	0.657	0.623	0.690	2.44	2.19	2.04
	Isorhamnetin-3-glc + Kaempferol-3-glucur	nd	nd	nd	nd	nd	nd	4.86	4.49	4.64	11.8	11.0	12.7	1.44	1.33	1.39
	Syringetin-3-glc	nd	nd	nd	nd	nd	nd	4.08	3.79	3.85	5.52	5.12	5.60	2.58	2.41	2.36
	Myricetin	nd	nd	nd	0.050	0.043	0.038	0.267	0.252	0.229	0.441	0.440	0.399	nd	nd	nd
	Quercetin	0.736	0.694	0.827	1.92	1.89	1.97	1.99	1.82	1.95	2.65	2.55	2.81	0.886	0.805	0.930
	Laricitrin	0.293	0.229	0.259	0.472	0.437	0.503	nd	nd	nd	nd	nd	nd	nd	nd	nd
	Kaempferol	0.275	0.258	0.261	0.627	0.558	0.661	0.487	0.541	0.533	0.469	0.507	0.467	0.705	0.729	0.845
	Isorhamnetin	0.497	0.415	0.467	0.585	0.501	0.629	0.507	0.534	0.500	1.50	1.40	1.57	nd	nd	nd
	Syringetin	0.608	0.545	0.611	0.263	0.243	0.264	nd	nd	nd	nd	nd	nd	nd	nd	nd

glucur, glucuronide; galac, galactoside; glc, glucoside
nd = non detected

was present only in the three w1 wines. The concentrations of gallic acid ranged from 16.2 mg/L (w2a) to 32.9 mg/L (w3a), without any significant differences in terms of the drying method or grape variety. On the other hand, differences in the concentrations of vanillic and syringic acids were found relative to the vinification methods, since both compounds exhibited somewhat higher concentrations in the w1 and w2 type wines (traditional wines).

The hydroxycinnamic acids caffeic, *p*-coumaric and ferulic were found in w1 and w2 wines, although none was detected in the alternative wines (Table 3). The low concentrations of the three acids in w1 and w2 (below 7 mg/L) suggest that the difference in the alternative wines depended on the initial raw material. The concentrations in berry phenolic compounds and in the resulting wines are known to depend on the grape variety, cultural practices and environmental factors (Downey *et al*., 2006; Petropoulos *et al*., 2011).

The tartaric esters of the three hydroxycinnamic acids were detected in all the wines. As can be seen in Table 3, caftaric and coutaric acids were present at higher concentrations than fertaric acids, the *cis* isomers of which generally prevailed over the *trans* isomers. Caftaric acids were found at concentrations from 2.56 to 5.67 mg/L, without differences in terms of the grape-drying method. Finally, the coutaric acid concentrations in the traditional wines were above 3.26 mg/L and exceeded those in the alternative wines.

The low molecular weight flavan-3-ol compounds are especially important in red wines because their polymerisation reactions lead to tannins, which are responsible for the astringency in the wine (McRae & Kennedy, 2011). The alternative wines (w3 to w5) were found to contain much higher concentrations of flavan-3-ols and procyanidins than the traditional wines (w1 and w2). The latter only contained (+)-catechin and (–)-epicatechin monomers, procyanidins B2 and B4, and B2-3-*O*-gallate dimer. Both monomers were present at very low concentrations (approximately 1.6 mg/L for (+)-catechin and 4.6 mg/L for (–)-epicatechin) relative to the alternative wines, where they exceeded 25 mg/L and reached levels of up to 44 mg/L for (–)-epicatechin and 93 mg/L for (+)-catechin. Similarly, the combined concentration of the two procyanidins (B2 + B4) in the traditional wines was below 4 mg/L and much lower than in the alternative wines (up to 17.6 mg/L). The alternative wines also contained procyanidins B1 and B3, which were absent from the traditional wines. As a result of the low concentrations of the abovementioned flavanols in the traditional wines, B2-3-*O*-gallate dimer was the major component, with concentrations at the same level as those in the alternative wines. However, the latter also contained B2-3-*O'*-gallate and B1-3-*O*-gallate dimers. The fact that the flavan-3-ol fraction in the alternative wines contained many more compounds and at higher concentrations than those in the traditional wines suggests that these compounds become important substrates of polymerisation and/or degradation reactions during the sun drying of grapes or during their subsequent vinification. The traditional wines, with a lower concentration of these compounds, therefore exhibited a much higher browning index than the alternative wines.

In relation to flavonols, the traditional wines only

contained the aglycones myricetin, quercetin, laricitrin, kaempferol, isorhamnetin and syringetin, all at very low concentrations. As can be seen in Table 3, quercetin was the major component in this fraction, with concentrations from 0.694 to 1.97 mg/L. The alternative wines contained the aglycones myricetin, quercetin, kaempferol and isorhamnetin, as well as flavonol glycosides at much higher concentrations. The absence of flavonol glycosides and the presence of aglycones in wine are usually indicators of ageing, because under wine acid conditions, the glycosides are gradually hydrolysed to free aglycones (Jeffery *et al*., 2008). If flavonol glycosides, naturally present in the grapes, had been hydrolysed, the aglycone concentration should have been higher than it was in the commercial wines. Therefore, the degradation of this phenolic fraction must be considered as a potential cause of their substantially decreased concentrations. Also, the concentration of aglycones may have been further reduced by their low solubility in ethanol solutions such as wine, causing the formation of colourless crystals or yellow precipitates, detracting from the wine stability (Jeffery *et al*., 2008).

The analytical properties of the two types of wine were compared via principal component analysis (PCA), using the colour parameters and the concentrations of the different phenolic fractions. Fig. 4 shows the plane defined by the first two principal components (PCs), which jointly explained 93.1% of the overall variance in the process. The plane contains the scores or eigenvalues of the samples and the eigenvectors of the variables considered in the multivariate analysis. PC1, which accounted for 82.3% of the variance, clearly discriminated between wines obtained by different grape-drying methods. Thus, the wines from sun-dried grapes exhibited negative scores for this component, and those from chamber-dried grapes exhibited positive scores. The former exhibited higher hue values, higher contents of polymeric pigments, increased contributions of yellow (%yellow) and the presence of hydroxycinnamic acids. By contrast, the alternative wines exhibited greater contributions of %red and %blue, and increased concentrations of monomeric anthocyanins, flavan-3-ols and flavonols.

In conclusion, the alternative wines are therefore analytically closer to typical red wines by their lower concentration of browning compounds, a high contribution of red and blue, and hence a more suitable colour than the commercial traditional wines. Also, the alternative wines were richer in phenolic compounds, particularly in monomeric anthocyanins, which give these wines their colour and are responsible for their antioxidant properties (Sun *et al*., 2011). In addition, the sensory properties of the alternative wines are likely to be highly acceptable for consumers. Based on previous works (Serratosa *et al*., 2008a), chamber drying has some other advantages over sun drying. Thus, controlled drying allows the use of grapes of variable ripening status in order to shorten the drying time needed to obtain raisins of similar sweetness and to increase must yield. A preliminary study confirmed that the alternative drying system was economically viable from a commercial point of view. Also, the controlled conditions of the chamber-drying process exclude the development of toxin-producing fungi, which is highly likely to occur during sun-drying of grapes (Serratosa
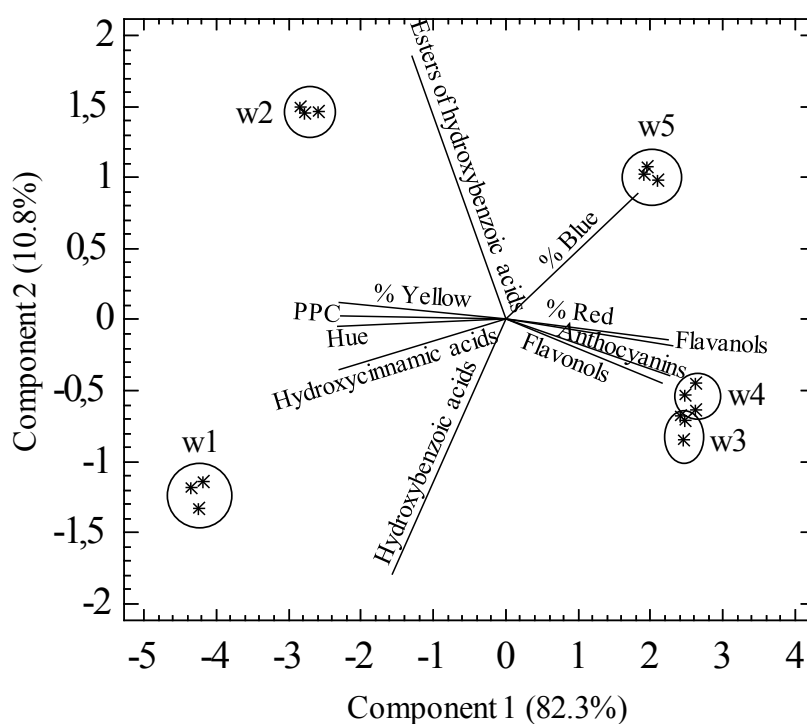
FIGURE 4

Principal component analysis of commercial (w1 and w2) and alternative sweet red wines (w3 to w5). Biplot representation of eigenvalues and eigenvectors.

et al., 2010). On the whole, the alternative winemaking process based on controlled chamber drying improved the quality of sweet red wines relative to commercial wines obtained by the traditional method.

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