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Use of Dehydrated Waste Grape Skins as a Natural Additive for Producing Rosé Wines: Study of Extraction Conditions and Evolution

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ABSTRACT: Dehydrated waste grape skins from the juice industry were used as an additive to produce rosé wines. Maceration time, particle size, dosage, alcoholic content, and maceration temperature were first studied in model wine solutions using two different dehydrated waste grape skins. Full factorial experimental designs together with Factor Analysis and Multifactor ANOVA allowed for the evaluation of each parameter according to the composition of color and phenolic and aroma compounds. Higher maceration time favored the extraction of anthocyanins; phenolic compound release was influenced by dosage independent from other factors studied. Rosé wines were produced by direct addition of dehydrated waste grape skins, according to selected parameters in two different white wines, achieving characteristics equivalent to commercial rosé wines. After three months of storage, rosé wine composition was stable.

KEYWORDS: waste grape skins, rosé wine, phenolics, aroma, color

INTRODUCTION

Optimization of food processing based on the reduction of waste has become a mandatory standard within the most developed countries. The European Union in Directive 2008/98/EC[1] stated that "waste prevention should be the first priority of waste management, and that re-use and material recycling should be preferred to energy recovery from waste". According to the previous statement, one of the biggest challenges for grape producing regions is to create alternatives for processing the vast amount of grape waste generated during harvest season. This is important for grape producing countries such as Spain, the fourth largest producer of grapes in the world,[2] and particularly for the Spanish Castilla-La Mancha Region, as it accounts for more than 50% of the country's total vineyard surface where 75% of production is processed by the wine sector and the balance by the juice industry.[3]

Grape wastes are obtained after juice and winemaking processing, with grape marc or grape pomace (mixture of grape skins, seeds, and stalks) as the most abundant residue. Although different grape processing operations aim to extract a maximum of phenolic and aroma compounds in grapes, these are not completely exploited.[4] This fact has led us to study the composition of the different constituents of grape marc and their properties, mainly in the form of extracts. Grape marc extracts and their constituents have received much attention because of the antioxidant capacity derived from the high concentration of flavonoids like catechins and stilbenes as resveratrol, particularly abundant in grape skins and considered as bioactive compounds.[5,6] Several extraction conditions have been studied in order to isolate such phenolic compounds.[7−9] Reuse and recycling winery wastes have been evaluated on a laboratory scale.[5,10,11] However, whole grape processed products are also useful since it has recently been found that quercetin and epicatechin from grape powder attenuate apoptosis (programmed cellular death) in human cells.[12] Although their potential is demonstrated, grape wastes remain underexploited, and disposing of them continues to represent an important issue for producers in terms of economics and environmental impact.

One of the reasons for not exploiting grape wastes is the associated cost of processing implied by extraction-concentration technology. Capability of such technology to deal with a large volume of raw material during a short period of time (harvesting season) is a limiting factor, given the perishable characteristics of grape pomace. On the other hand, applications in the food industry as raw material or as an ingredient are still scarce[13] even though extracts have been applied in cheese, fruits, and fruit juices.[14−16] Recently, Pedroza et al.[17] demonstrated the potential of different dehydrated waste grape skins as a primary source of phenolic and aroma compounds by maceration in model wines, also suggesting the possibilities as a wine or beverage ingredient although further legislation is required by competent authorities.

The aim of this work is to evaluate the release of compounds from dehydrated waste grape skins into wines and assess process parameters for using them as an additive within the wine industry. The use of waste grape skins from the juice concentrate industry has been evaluated, alternatively to most studies on grape wastes which are dedicated to winemaking residues. First, process parameters such as maceration time, dosage, particle size, wine cellar temperature, and alcohol content were tested in model wine solutions. Second, selected parameters were used for producing rosé wines by direct addition of dehydrated waste grape skins. The evolution of color and phenolic and aroma composition from rosé wines was evaluated during storage.

MATERIALS AND METHODS

Waste Grape Skins. Waste grape marc of *Vitis vinifera* [var. Bobal (red)] and a mix of Airén (white variety mixed with an approximately

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30% of an unknown red variety, namely AMIX) was obtained from a juice concentrate factory in Castilla-La Mancha (Julian Soler, Cuenca, Spain) during the 2009 harvest season. Inside the factory, each grape variety was crushed, destemmed, macerated for 3 days, and mechanically pressed to obtain juice. Samples were taken immediately after pressing; grape marcs were collected in plastic bags (60 kg) and frozen at −20 °C. Previous to dehydration, waste grape marcs were thawed at 25 °C. Dehydration was done by conventional oven drying at 60 °C until constant weight (3−5% moisture content) according to Pedroza et al.[17] In order to separate grape skins from stalks and seeds, grape marc was sieved through 3 mm mesh. Residual seeds and stalks of lower particle size were eliminated manually. Dehydrated waste grape skins (DWGS) were then ground in a cutting mill MS 100 (Retsch, GmbH & Co. KG, Denmark) and sieved to different particle sizes (0.5, 1.0, and 2.0 mm).

Chemicals and Standards. Gallic acid, (+)-catechin, caffeic acid, ferulic acid, *p*-coumaric acid, vanillic acid, syringic acid, *cis*- and *trans*-resveratrol, (−)-epicatechin, and quercetin dihydrate from Sigma-Aldrich (Steinheim, Germany) were used as standards for low molecular weight phenolic compound analysis. Malvidin-3-glucoside (Mv-3-G) standard from Extrasynthése (Geneay, France) was used for anthocyanins quantification. D-Limonene, linalool, linalyl acetate, α-terpineol, citronellol, nerol, geraniol, geranyl acetone, nerolidol, farnesol, *trans*-2-hexenal, 1-hexanol, *trans*-2-hexen-1-ol, α-ionone, β-ionone, 2-phenylethanol, and isoamyl acetate supplied by Sigma-Aldrich (Steinheim, Germany) and β-damascenone supplied by Firmenich (Geneva, Switzerland) were used as calibration standards in ethanol−water solution (12% v/v, pH = 3.6, 5 g/L tartaric acid) for volatile analysis. HPLC-grade acetonitrile was from Panreac (Barcelona, Spain).

Dehydrated Waste Grape Skin Extraction Conditions. First, DWGS were infused at 18 °C using a synthetic wine solution (pH = 3.6, 5 g/L tartaric acid, 12% ethanol v/v) according to a 3^3 full factorial design with the following variables: particle size (0.5, 1.0, and 2.0 mm), DWGS dosage (5, 25, and 50 g/L), and maceration time (1, 3, and 9 days). For all experiments, 250 mL amber glass test flasks ISO with plastic screw caps were filled to leave 25 mL of headspace volume. After infusion, solutions were filtered with a strainer to remove DWGS and prepared for the different analyses.

Cellar conditions were then studied by 2^2 full factorial design using temperature (14 and 18 °C) and ethanol content (13% and 14% (v/v)) as variables and using the previously described infusion process according to selected parameters of maceration time, dosage, and particle size. These DWGS-infusions were kept for 1 and 3 months to study the evolution of composition.

Rosé Wine Production by Addition of DWGS to White Wines. Once extraction conditions were selected, DWGS of AMIX were added directly into two different white wines: one young white (YW) wine of Airén (12.5% v/v alcohol) and one oak barrel fermentation (BF) white wine of Airén (12.5% v/v alcohol). YW and BF wines without DWGS were used as control. Final DWGS-rosé wines were then filtered with a strainer to remove skins and stored for 1 and 3 months at 18 °C to evaluate their evolution.

Sample Characterization. *Conventional Color and Phenolic Content by UV−Vis Spectrophotometry.* General parameters such as color and total phenolic compounds have been measured with a Lambda 25 UV−vis spectrophotometer (Perkin-Elmer, Norwalk, CT). All samples were first filtered through a PVDF Durapore filter of 0.45 μm (Millipore, Bedford, MA). Color was determined following Glories method,[18] measuring absorbance at 420, 520, and 620 nm. Total polyphenol index (TPI) was determined at 750 nm according to Singleton and Rossi[19] and expressed as mg gallic acid equivalents .

Phenolic Compound Determination by HPLC-DAD. Phenolic compound analysis was carried out according to Cozzolino et al.[20] The samples were filtered through a PVDF Durapore filter of 0.45 μm (Millipore, Bedford, MA) and injected into an Agilent 1100 HPLC chromatograph (Palo Alto, CA) equipped with a Phenomenex (Torrance, CA) Synergi 4 μ Hydro-RP column (4 μm particle size, 80 Å pore size, 150 mm × 2.0 mm) at 25 °C. Solvents were: (A) 1% acetonitrile, 1.5% phosphoric acid in water and (B) 20% solvent A, 80% acetonitrile. Gradient elution at a constant flow rate of 0.4 mL/min was as follows: 0 min (14.5% solvent B), 18 min (27.5% solvent B), 20 min (27.5% solvent B), 21 min (50.5% solvent B), 22 min (50.5% solvent B), 26 min (100% solvent B), and 28 min (100% solvent B). The injection volume used was 20 μL. Compound detection was carried out with a diode array detector by comparison with the corresponding UV−vis spectra and retention time of pure standards in the chromatogram. Gallic acid, (+)-catechin, vanillin, syringic acid, and (−)-epicatechin were identified at 280 nm; ferulic acid and caffeic acid were identified at 324 nm; (*trans*)-resveratrol and *p*-coumaric acid were identified at 308 nm; and malvidin-3-G was identified at 520 nm while delphinidin-3-G, cyanidin-3-G, petunidin-3-G, and peonidin-3-G were identified according to the literature[21] and quantified as malvidin-3-G equivalents. Quantification was based on 5-point calibration curves of respective standards ($R^2 > 0.99$) in synthetic wine solution previously described. Data reported represent the mean value of two replicates.

Volatile Compound Determination by SBSE-TD-GC-MS. DWGS extracts (10 mg) were used in duplicate to determine the free volatile fraction[22] by immersing a polydimethylsiloxane coated stir bar [twister, 0.5 mm film thickness, 10 mm length from Gerstel (Mülheim an der Ruhr, Germany)] and stirring at 500 rpm over 1 h at 25 °C. After this time, the stir bar was removed from samples, rinsed with distilled water, dried with cellulose tissue, and finally transferred into thermal desorption tubes for the GC/MS analysis.

Volatile compounds were desorbed from the stir bar in an ATD 400 (Perkin-Elmer, Norwalk, CT) under the following conditions: oven temperature at 290 °C, desorption time 4 min, cold trap temperature −30 °C, and helium inlet flow 45 mL min^{-1}. After this, the compounds were transferred into the Hewlett-Packard 6890 (Palo Alto, CA) gas chromatograph coupled to an Hewlett-Packard 3D mass detector (Palo Alto, CA) with a fused silica capillary column SGE BP21 (stationary phase 30 m length, 0.25 mm i.d., and 0.25 μm film thickness) (Ringwood, Australia). The chromatographic program was set at 40 °C (held for 2 min), raised to 230 at 10 °C min^{-1}, and held for 15 min. Electron impact mode (EI) at 70 eV was used for mass spectrometry analysis. The mass range varied from 35 to 500 u, and the detector temperature was 150 °C. Identification was carried out using the NIST library and standard spectra. Quantification was based on 5-point calibration curves of respective standards ($R^2 > 0.85$) in synthetic wine solution previously described. Data reported represent the mean of two replicates. To avoid matrix interferences between the volatile compounds, the MS quantification was carried out in the single ion monitoring (SIM) mode using their characteristics m/z values.

Statistical Analysis. Factor Analysis and Multifactor ANOVA were carried out in Statgraphics Centurion XVI.I (Warranton, VA). Observations with factor loadings < 0.3 were considered as unimportant[23] and were not included in the analysis. Factor score coefficients were used to identify the compounds having significant influence on the description of variance according to each factor. A Tukey honestly significant difference (HSD) test was used in Multifactor ANOVA. SPSS Statistics 19.0 Software (Chicago, IL) was used to evaluate one-way analysis of variance (ANOVA) of chemical compounds at $p \leq 0.05$. Post hoc Tukey's HSD test was used to distinguish homogeneous subsets of treatments.

RESULTS AND DISCUSSION

Extraction Parameters. Previous work on dehydration of waste grape skins demonstrated that this industrial waste is a source of phenolic and aroma compounds.[8,17] With this in mind,

Table 1. Factor Analysis and Multifactor ANOVA Statistics for the Extraction Parameters of Dosage, Particle Size, and Maceration Time

	factor		
	F1	F2	F3
eigenvalue	7.42	4.83	1.09
variance	49.45	32.20	7.27
variance %	49.45	81.65	88.92
	Factor Score Coefficients		
CI	0.82	0.04	−0.26
shade	−0.07	0.07	0.95
TPI	0.95	−0.01	−0.15
galic acid	0.83	−0.13	0.13
(+)-catechin	0.96	0.03	−0.01
caffeic acid	0.98	0.00	0.06
(−)-epicatechin	0.85	0.06	−0.30
coumaric acid	0.95	−0.11	0.08
ferulic acid	0.87	0.12	−0.05
quercetin	0.92	−0.12	0.08
Dl-3-G	−0.07	0.98	0.06
Cy-3-G	0.03	0.94	0.07
Pt-3-G	−0.03	0.99	−0.01
Pn-3-G	−0.01	0.99	0.00
Mv-3-G	0.00	0.99	−0.03

extraction time (T), particle size (PS), and dosage (D) were studied in a 3^3 full factorial design to ascertain favorable extraction conditions in a synthetic wine solution. A combined exploratory−confirmatory approach of Factor Analysis was used to synthesize the information of the factorial design, thus making the observations easier to comprehend. Multifactor ANOVA was used to detect significant differences and key aspects of experimental conditions.

The independent analysis of AMIX and Bobal DWGS revealed that the extraction behavior of compounds was not influenced by the type of grape skin (data not shown), and then data of both DWGS were used together in the analysis. However, it is important to mention that the composition of fresh grape skin cell wall can influence anthocyanin extractability.[24] Factor score coefficients were useful for identifying the key aspects of variability within data (Table 1). Three factors described 89% of variance: factor 1 (F1) was representative of low molecular weight phenolic compounds (LMWPC) and total polyphenol index (TPI) because of the high factor score coefficients (>0.8); factor 2 (F2) coefficients represented monoglucoside anthocyanins (MA); factor 3 (F3) only described the influence of shade and explained a small amount of variance. Volatile compound factors were not included in the analysis as all of them had factor score coefficients <0.3, indicating a nonsignificant influence on the differentiation of the experimental conditions (data not shown).

A scatter plot (Figure 1) of F1 and F2 using factor scores allows distinguishing between maceration time and dosage levels. Note that LMWPC (F1) extraction is influenced by dosage but not by the extraction time, while extraction of anthocyanins (F2) is influenced by maceration time and not by dosage. Multifactor ANOVA interaction plots (Figure 2) indicate that phenolic

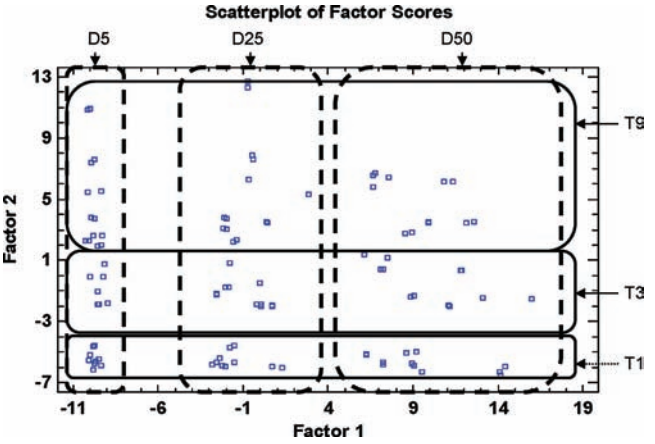

Figure 1. Scatterplot of factor scores from the extraction conditions assay of dehydrated waste grape skins in model wine solutions according to factor 1 (phenolic compounds) and factor 2 (monomeric anthocyanins): D5 = dosage 5 g/L; D25 = dosage 25 g/L; D50 = dosage 50 g/L; T1 = one day of maceration; T3 = three days of maceration; T9 = 9 days of maceration.

compound extraction occurred during the first day of maceration with no significant influence of particle size and maceration time. This observation suggests that phenolic compound extraction is ruled by dosage and that these compounds are not influenced by the integrity of grape skin cells or rehydration. Thermal dehydration pretreatment of waste grape skins could be responsible for such behavior, by affecting cell-wall integrity and thus liberating phenolic acids, catechins, and quercetin. Pinelo et al.[5] made a similar observation on the extraction of phenolic compounds when using water as a solvent. Maceration time did not affect the release of LMWPC, suggesting that most of the compounds quickly solubilize during the first day of maceration, as previously observed by González-Manzano et al.[25] when evaluating similar phenolic compounds from grape skins. These observations are important toward optimization of industrial processes if pigments or phenolic compounds have to be extracted from DWGS into a beverage-like wine.

Anthocyanins were progressively extracted and independent of dosage and particle size (Figure 2). This behavior was contrary to the observation from LMWPC and could be related to the nature and the localization of pigments within the grape skin cells. Our results suggest that most of the anthocyanins in the free noncomplex form were extracted at the juice factory when fresh grapes were crushed, and that the remaining pigments are those with a stronger interaction with cellular traits. The complexity of the compositional changes caused by dehydration on the cell-wall structure/composition as well as the different anthocyanin interactions might be responsible for this behavior. Assuming that mass transfer occurs only from one side of the grape skins surface (the one represented by bigger size hypodermis cells), anthocyanins located between the epidermis and the bigger cells of the hypodermis might be trapped by thermally degraded polysaccharides from cells,[26] with the latter representing a hurdle for mass transfer. Moreover, interaction of anthocyanins with tannins, other anthocyanins, phenolic compounds, and phenolic acids could be prompted by dehydration thus limiting the release of these compounds. Interaction with cell-wall components such as proteins and polysaccharides[5,27] might be slowly disrupted by media conditions (pH, acidity, equilibrium concentration).

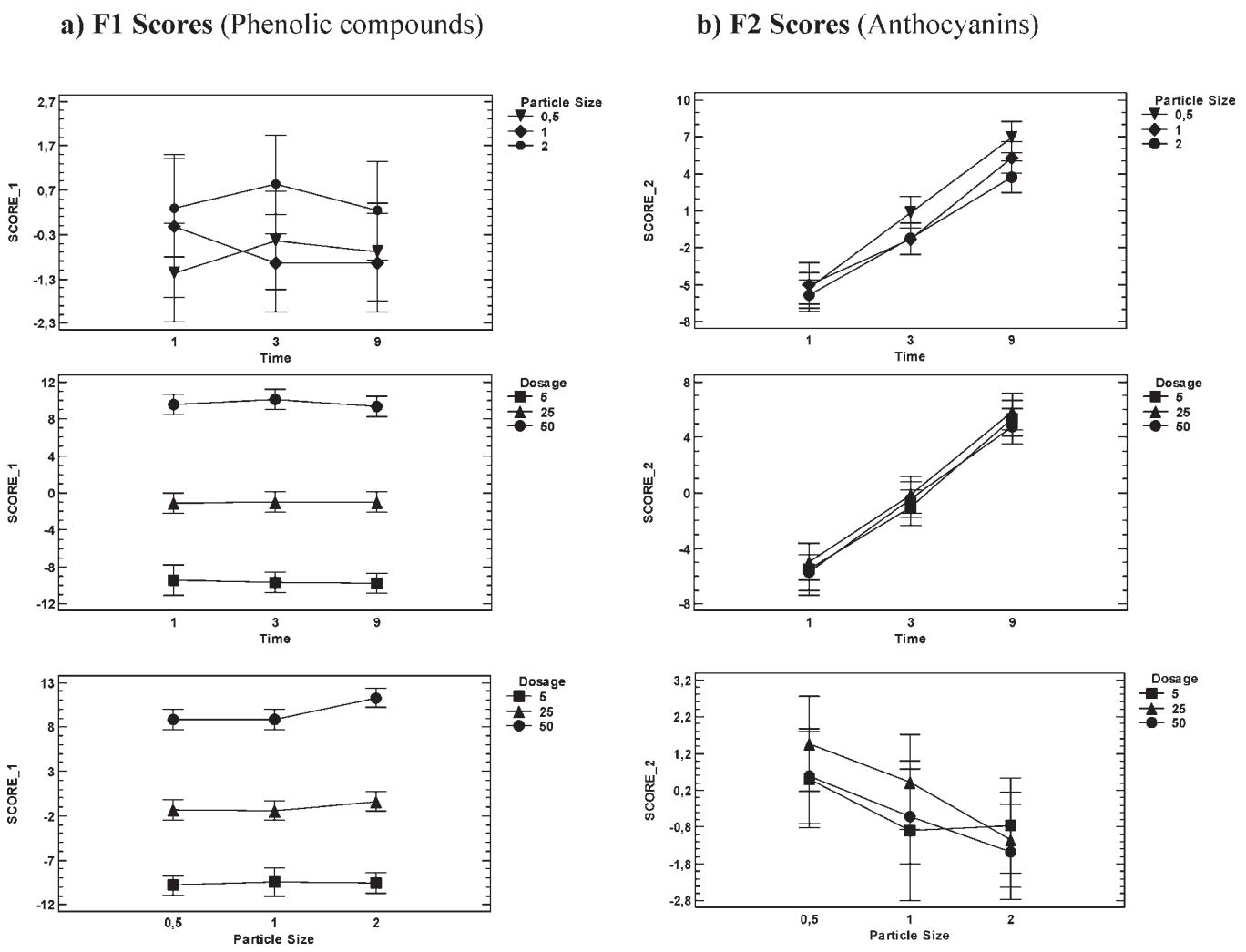

Figure 2. Interaction plots of factor scores from the extraction conditions assay of dehydrated waste grape skins in model wine solutions according to extraction conditions. Score 1 figures represent phenolic compound concentration, and score 2 figures represent anthocyanins. 95% Tukey HSD intervals indicate significant differences between each level. Dosage levels in g/L. Particle size levels in mm. Time levels in days.

Further rehydration kinetics studies and electronic microscope observations might confirm these postulations.

Although the influence of particle size on mass transfer phenomena is known,[28,29] it seems to have a limited role in the release of anthocyanins and LMWPC under the present experimental conditions. Nevertheless, bigger particle size samples had a not significant higher concentration of phenolic compounds and anthocyanins (Figure 2).

Other extraction methods such as high pressure and temperature (HPTE) and microwave assisted extraction (MAE) have been tested for extracting phenolic compounds from waste grape skins of Pinot Noir grapes.[30] Although there were differences in the nature of samples and extraction conditions, our samples (PS = 1.0 mm, D = 50 g/L, T = 3 days) had similar concentrations in compounds like catechin (65 mg/L) and gallic acid (24 mg/L). This might indicate that conventional solid−liquid extraction methods, such as the one proposed in the present work, are also efficient for releasing compounds, and that different techniques can be chosen in terms of particular compounds. It also proves the importance of dosage and maceration time on the extraction of phenolic compounds.

Selected conditions were established for the cellar condition assay. With one of the objectives being to improve the concentration of bioactive compounds in wines, a dosage of 50 g/L was used to release the maximum concentration of such compounds. A maceration time of three days was selected for allowing a faster process at the winery but still maintaining an important amount of pigments. Since no significant effect of particle size was observed, 1.0 mm was preferred because of the easier separation of small seeds and pedicel/brush residues (manually done in 2.00 mm samples) and also because it was easier to remove them from the wine than the 0.5 mm samples.

Cellar Conditions. To ascertain the effect of typical wine and cellar conditions on the release of compounds from DWGS, temperatures of 14 and 18 °C were evaluated as well as different ethanol concentrations representative of finished wines.

The composition of samples was studied with ANOVA and *post hoc* Tukey's test to identify differences between each condition (month 0 in Tables 2 and 3). The most relevant differences found for cellar temperature were the concentration of quercetin and (+)-cathechin in 18 °C samples of AMIX as well as (−)-epicatechin and quercetin in 18 °C Bobal extracts. Monoglucoside anthocyanins were significantly higher in 14 °C samples of AMIX although such differences were not substantial. Regarding alcohol content, 13% ethanol samples of

Table 2. Composition of Synthetic Wines Macerated with Dehydrated Waste Grape Skins (DWGS) of AMIX at the Different Levels of Cellar Condition Assay [a]

month:	0								1								3							
temp:	14				18				14				18				14				18			
alcohol %:	13		14		13		14		13		14		13		14		13		14		13		14	
Color																								
color intensity	0.12	b	0.15	a	0.15	a	0.15	a	0.18	b	0.20	a	0.21	a	0.21	a	0.16	c	0.19	b	0.20	a	0.20	a
shade	0.96	a	0.94	b	0.97	a	0.97	a	1.12	a	1.22	a	1.39	a	1.36	a	1.41	c	1.34	d	1.61	a	1.54	b
% yellow	45.82	a	45.30	b	45.88	a	45.53	b	41.59	d	43.18	c	48.26	a	47.20	b	49.87	c	47.39	d	53.88	a	52.26	b
% red	47.58	a	48.06	a	47.45	a	47.02	a	37.12	a	35.40	b	34.76	c	34.80	c	35.40	a	35.30	a	33.53	c	33.86	b
% blue	6.60	a	6.64	a	6.67	a	7.46	a	21.29	b	21.42	a	16.97	d	18.00	c	14.72	b	17.31	a	12.59	d	13.87	c
Phenolic Compounds																								
TPI	162.93	d	179.60	a	177.49	c	178.98	b	382.46	c	431.27	a	421.02	b	431.96	a	347.86	d	411.99	a	400.10	c	410.76	b
gallic acid	15.01	c	11.55	d	15.89	a	15.45	b	21.32	b	22.19	a	19.22	c	19.78	c	17.46	d	19.83	a	18.04	c	19.00	b
(+)-catechin	41.77	b	32.47	c	42.79	b	47.17	a	43.53	a	44.27	a	38.26	b	41.08	a,b	32.33	a,b	35.52	a	24.80	c	28.59	b,c
(−)-epicatechin	54.93	a	42.37	b	55.13	a	57.03	a	54.98	b	63.53	a	51.37	b	53.14	b	39.68	b	49.89	a	33.49	d	37.34	c
(*E*)-resveratrol	2.04	a	2.37	a	2.44	a	2.84	a	1.40	a	2.09	a	1.64	a	1.72	a	0.95	a	1.34	a	1.19	a	1.13	a
quercetin	11.11	d	12.39	c	14.54	b	15.46	a	14.74	d	17.96	c	19.48	b	19.96	a	11.43	d	16.31	c	16.44	b	17.59	a
total LMWPC	124.87	b	101.16	c	130.78	a,b	137.94	a	135.96	b	150.04	a	129.96	b	135.68	b	101.85	b	122.88	a	93.96	c	103.66	b
Anthocyanins																								
delphinidin-3-glucoside	2.46	a	2.36	a	2.15	b	2.16	b	1.86	a	1.64	b	0.82	d	0.97	c	0.35	b	0.97	a	0.29	c	0.32	b,c
cyanidin-3-glucoside	2.28	a	2.29	a	2.09	c	2.17	b	1.74	a	1.65	b	1.11	d	1.18	c	0.25	d	1.13	a	0.40	c	0.45	b
petunidin-3-glucoside	3.32	a	3.25	a	3.03	c	3.13	b	2.35	a	2.26	b	1.27	d	1.42	c	0.55	b	1.37	a	0.34	d	0.47	c
peonidin-3-glucoside	6.38	a	6.29	b	5.73	d	6.18	c	3.94	a	3.70	b	2.15	d	2.35	c	0.84	c	2.20	a	0.74	d	0.95	a
malvidin-3-glucoside	15.63	a	15.37	b	14.37	d	15.22	c	10.71	a	10.66	a	6.95	c	7.59	b	3.78	b	6.95	a	3.00	d	3.63	c
total anthocyanins	30.08	a	29.57	b	27.37	d	28.88	c	20.60	a	19.91	b	12.31	d	13.51	c	5.77	b	12.63	a	4.76	c	5.83	b
Terpenoid Volatiles																								
D-limonene	1.30	a	1.41	a	1.11	a	1.53	a	4.87	a	6.71	a	6.56	a	6.24	a	5.34	a	3.62	a	4.81	a	3.30	a
β-ionone	0.27	a	0.30	a	0.29	a	0.32	a	0.17	a	0.14	a	0.15	a	0.14	a	0.11	a	0.13	a	0.11	a	0.06	b

[a] Different letters between samples at each month represent statistically significant differences ($p < 0.05$). Total polyphenol index (TPI) is expressed in mg/L gallic acid equivalents. Low molecular weight phenolic compounds (LMWPC) and anthocyanins are expressed in mg/L. Mv-3-G volatile compounds are expressed in μg/L.

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Table 3. Composition of Synthetic Wines Macerated with Dehydrated Waste Grape Skins (DWGS) of Bobal at the Different Levels of the Cellar Condition Assay[a]

month:	0								1								3							
temp(° C):	14				18				14				18				14				18			
alcohol:	13		14		13		14		13		14		13		14		13		14		13		14	
Color																								
color intensity	0.16	b	0.14	c	0.19	a	0.20	a	0.20	c	0.18	d	0.22	b	0.23	a	0.14	c	0.14	c	0.18	b	0.20	a
shade	0.64	a	0.60	a	0.62	a	0.62	a	0.76	c	0.78	b	0.87	a	0.87	a	0.89	b	0.85	c	1.00	a	1.01	a
% yellow	35.24	a	34.41	a	34.74	a	34.94	a	30.80	c	28.73	d	32.24	b	32.75	a	43.17	c	42.21	d	45.63	b	45.79	a
% red	55.28	a	57.57	a	56.47	a	56.04	a	40.28	a	36.67	d	37.20	c	37.85	b	48.37	b	49.51	a	45.60	c	45.27	d
% blue	9.49	a	8.01	b	8.79	a,b	9.02	a	28.91	d	34.60	a	30.55	b	29.39	c	8.46	c	8.28	d	8.76	b	8.94	a
Phenolic Compounds																								
TPI	183.84	a	150.14	d	180.08	b	157.99	c	323.93	b	328.85	b	385.74	a	389.02	a	339.93	d	341.16	c	387.51	b	397.63	a
gallic acid	14.75	b	11.16	c	15.20	a	15.18	a	14.06	a	14.38	a	15.38	a	14.83	a	17.07	b	17.33	b	19.20	a	19.61	a
(+)-catechin	38.01	b	29.22	d	40.28	a	35.60	c	31.80	a	31.66	a	24.82	c	28.73	b	33.18	b	34.17	a	33.40	b	33.34	b
(−)-epicatechin	50.44	c	45.85	d	59.42	a	54.13	b	49.34	a	46.07	b	23.45	d	26.60	c	47.21	a	41.23	b	26.85	c	27.24	c
(*E*)-resveratrol	3.03	a	3.27	a	2.47	a	2.83	a	2.39	a	1.65	a	2.28	a	2.71	a	2.00	a	1.45	a	1.52	a	1.50	a
quercetin	7.44	d	7.91	c	9.14	b	10.14	a	10.93	c	8.85	d	12.53	b	13.56	a	10.10	c	9.70	d	12.23	b	13.54	a
total LMWPC	113.67	a,b	97.42	b	126.52	a	117.89	a,b	108.51	a	102.61	b	78.47	d	86.43	c	109.57	a	103.89	a	93.20	b	95.23	b
Anthocyanins																								
delphinidin-3-glucoside	5.10	a	5.04	a	4.70	b	4.75	b	3.83	a	3.96	a	3.24	b	3.30	b	2.79	b	3.23	a	1.62	c	1.64	c
cyanidin-3-glucoside	2.75	a	2.72	a,b	2.59	c	2.67	b	2.50	a	2.53	a	2.36	c	2.41	b	2.01	b	2.23	a	1.59	c	1.61	c
petunidin-3-glucoside	5.93	a	5.88	a	5.57	b	5.88	a	4.54	b	4.66	a	4.16	d	4.25	c	3.47	b	3.95	a	2.52	c	2.54	c
peonidin-3-glucoside	11.20	a,b	10.95	b	10.85	b	11.75	a	7.73	c	8.10	a	7.59	d	7.82	b	6.13	b	6.96	a	4.97	c	5.01	c
malvidin-3-glucoside	25.35	b	25.73	b	25.94	b	27.67	a	19.71	c	20.58	a	19.64	d	20.05	b	15.61	b	17.72	a	13.08	c	13.05	c
total anthocyanins	50.32	a	50.31	a	49.66	a	52.74	a	38.31	b	39.83	a	36.99	d	37.83	c	30.01	b	34.08	a	23.77	c	23.85	c
Terpenoid Volatiles																								
D-limonene	1.18	a	0.84	a	1.11	a	1.78	a	2.96	a	6.78	a	6.75	a	4.10	a	6.03	a	6.57	a	5.51	a	4.50	a
β-ionone	0.28	b	0.37	a	0.37	a	0.35	a	0.18	a	0.20	a	0.19	a	0.21	a	0.10	a	0.09	a	0.05	a	0.10	a

[a] Different letters between samples at each month represent statistically significant differences ($p < 0.05$). Total polyphenol index (TPI) is expressed in mg/L gallic acid equivalents. Low molecular weight phenolic compounds (LMWPC) and anthocyanins are expressed in mg/L. Mv-3-G volatile compounds are expressed in μg/L.

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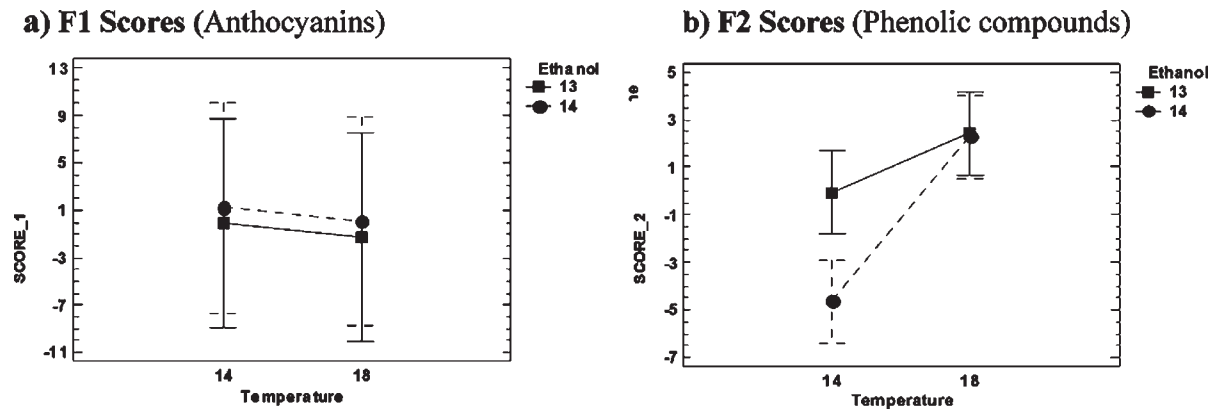

Figure 3. Interaction plot of factor scores after extraction of dehydrated waste grape skins in wine model solutions according to cellar conditions: (a) anthocyanins and (b) phenolic compounds—D-limonene with 95% Tukey HSD intervals. Ethanol content is expresed in % (v/v); temperature in °C.

Bobal had a significantly higher content of (+)-catechin and TPI while 13% samples of AMIX had a higher yellow component.

As the effect of variables was not clearly elucidated, the composition of solutions was used in factor analysis, describing 81.5% of the variability within 3 factors. In factor 1 (f1), all monomeric anthocyanins had factor score coefficients >0.9 describing 54.1% of variance; factor 2 (f2) highest coefficients (>0.4) were shade, TPI, gallic acid, quercetin, and D-limonene describing 19.5% of variance; factor 3 (f3) highest coefficients were (+)-catechin, (−)-epicatechin, (*E*)-resveratrol, quercetin, and β-ionone describing 7.8% of variance (data not shown). The global effect of experimental conditions was described by a Multifactor ANOVA (Figure 3). No significant differences were found ($p < 0.05$) for temperature and ethanol content in AMIX and Bobal DWGS solutions when using f1 scores (anthocyanins) (Figure 3a). Nevertheless, a trend toward a slightly higher extraction of anthocyanins is noted at 14 °C. A significantly higher extraction of phenolic compounds was observed at 18 °C (Figure 3b) in 14% ethanol samples. However, there were no differences between 13% and 14% ethanol samples at 18 °C.

Evolution of DWGS-infusions was studied after 1 and 3 months of storage under established cellar temperatures and alcohol contents. Overall compositional changes were not attributed to alcohol content and cellar temperature, as Multifactor ANOVA of factor scores revealed no significant differences between variable levels (Figure 4). One month AMIX-14 °C samples had a higher concentration of anthocyanins, gallic acid, (+)-catechin, and (−)-epicatechin, and higher red and blue components (Table 2). The highest average colorant intensity in both DWGS was detected after one month of storage due to the significant increase of the blue component (absorbance at 620 nm). The blue component still provided an important contribution to color in AMIX samples after 3 months. This was associated to the increased concentration of phenolic compounds acting as copigments and causing the shift toward a blue shade.[31] The blue component in Bobal samples after 3 months returned to values similar to those of the initial infusion (month 0) (Table 3). The differences in the initial composition of LMWPC between AMIX and Bobal could be responsible for the loss of blue shade in Bobal samples during storage.

In Figure 4, the absence of significant differences in the 1 and 3 month samples, for both anthocyanins and phenolic compound scores, suggests that the critical period for stabilization occurs throughout the first month of storage. AMIX samples suffered a higher average degradation of anthocyanins (75%) with respect to Bobal (45%) at the end of storage (Tables 2 and 3). Self-association and copigmentation of anthocyanins might explain this behavior as these stabilization reactions are favored in more concentrated solutions.[31]

According to results, degradation of anthocyanins and phenolic compounds is not influenced significantly by common cellar temperatures and typical alcohol content of wines. Amendola et al.[8] suggested "light, oxygen availability, chemical-structure and concentration of anthocyanins and the presence of other phenolic compounds" could be responsible for the compositional changes in grape marc extracts. The thermal dehydration process of waste grape skins could also be related to the degradation of anthocyanins in our samples.

Rosé Wine Production by Infusion of DWGS into White Wines. AMIX-DWGS were infused in two different white wines of cv. Airén: one young wine (YW) with 12.5% v/v alcohol and one oak barrel fermentation wine (BF) with 12.5% v/v alcohol. Previously selected parameters of dosage (50 g/L), maceration time (3 days), and particle size (1 mm) were used with a maceration temperature of 18 °C. AMIX grape skins were preferred since they allow a moderate transfer of pigments into the wine.

Table 4 shows the composition of color and phenolic and aroma compounds of control and rosé wines made with DWGS. Month 0 corresponds to the initial extraction and was used for evaluating differences between control wines and the cellar conditions assay. The color intensity of both YW and BF DWGS-rosé wines at month 0 was within the typical range (0.1−2.0) of other rosé wines.[32] The composition of color components in DWGS-rosé wines was similar in terms of yellow, red, and blue components, indicating that color extraction was not influenced by the type of wine.

A significant contribution from DWGS to rosé wines was observed in terms of phenolic compounds. LMWPC released by DWGS were gallic acid, (+)-catechin, caffeic acid, (−)-epicatechin, coumaric acid, quercetin, and (*E*)-resveratrol (month 0, Table 4). These compounds were extracted to the same extent as in the model wine solution, indicating that composition in final rosé wines could be controlled to fit a certain profile by modifying the process variables, such as increasing dosage and/or maceration time.

A higher concentration of anthocyanins was released in wines (at month 0) in comparison to model wines solutions; e.g., the

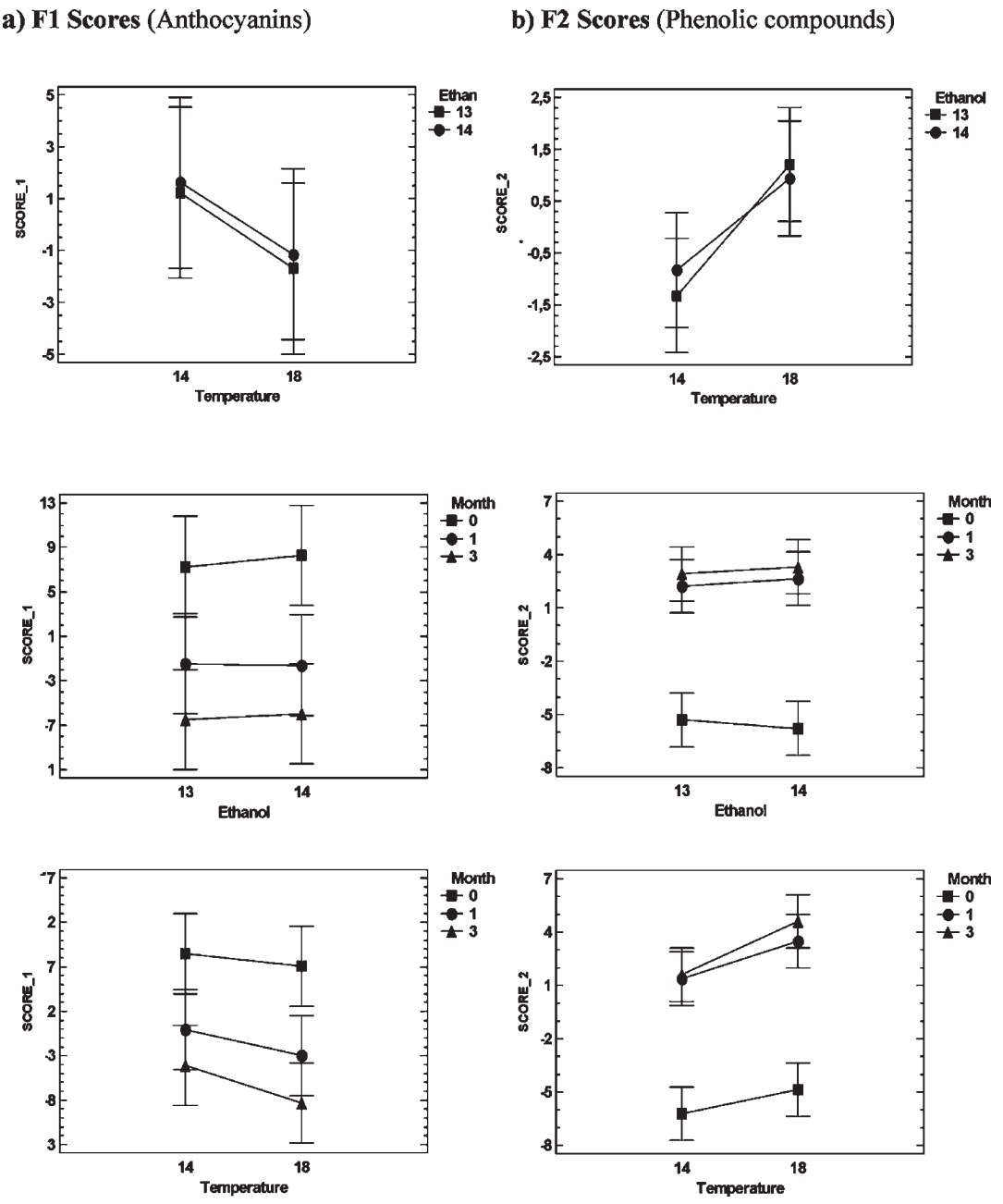

Figure 4. Interaction plots of factor scores representative of Anthocyanin and LMWPC concentration during storage of samples at different wine cellar conditions with 95% Tukey HSD intervals. Ethanol content is expressed in % (v/v); temperature in °C.

average concentration of malvidin-3-G in DWGS-rosé wines was 57% higher than that of model wine solutions with a cellar temperature 18 °C and alcohol content 13%. The effect of sulfites from wine could be related to the improvement in the extraction of anthocyanins as this additive favors the extraction of pigments by disrupting the integrity of the grape skin cells.[33] However, the fundamental compositional differences of the wine matrix could modify the equilibrium of the solution toward improved anthocyanin extraction conditions, i.e., higher concentration of copigments, phenolic acids, and mineral ions (K^+, Na^+, Cl^+).[34]

Ribéreau-Gayon et al.[32] reported that rosé wines had a total anthocyanin content between 14 and 160 mg/L; both DWGS-rosé wines had a concentration in that range. This characteristic makes DWGS a versatile tool toward a controlled extraction of pigments, by means of adjusting the maceration time in order to obtain a particular color.

DWGS contributed to the floral profile, characteristic of rosé wines, by releasing volatile compounds such as linalool, geranyl acetone, and β-ionone (Table 4). The former compound was found at a concentration 3 times higher than its odor threshold (0.09 μg/L), and it has been associated with the typicity of other rosé wines.[35]

The volatile composition of wines was modified after the addition of DWGS (Figure 5). β-Damascenone was reduced 50% from the control in both YW + DWGS and BF + DWGS wines. This compound is considered an important odorant because of its low olfactory threshold (0.05 μg/L) and floral descriptor, characteristic of rosé wines. Even after the diminution in its

Table 4. Evolution of Color and Phenolic and Aroma Composition in Young White Wine (YW), Oak Barrel Fermented Wine (BF), and the Corresponding Rosé Wines Made with AMIX Dehydrated Waste Grape Skins at a Cellar Temperature of 18 °C[a]

sample:	control YW						DWGS-rosé YW						control BF						DWGS-rosé BF					
month:	0		1		3		0		1		3		0		1		3		0		1		3	
Color																								
color intensity							0.13	c	0.16	b	0.20	a							0.11	c	0.14	b	0.19	a
shade							0.67	a	0.63	b	0.66	a							0.71	a	0.62	c	0.68	b
% yellow							37.87	a	36.53	b	37.83	a							39.30	a	36.93	c	38.20	b
% red							56.88	b	58.35	a	56.91	b							55.68	c	59.28	a	56.51	b
% blue							5.25	a	5.12	b	5.26	a							5.01	b	3.79	c	5.29	a
Phenolic Compounds																								
TPI	94.46	a	95.55	a	83.25	b	485.56	a	480.50	b	472.98	c	98.29	a	89.13	b	90.90	b	473.53	a	471.48	b	474.90	a
gallic acid	10.57	b,2	10.77	a,2	10.88	a,2	25.14	c,1	27.90	b,1	31.45	a,1	10.98	b,2	11.27	a,2	11.33	a,2	24.73	c,1	29.39	b,1	30.31	a,1
(+)-catechin	11.71	a,2	12.93	a,2	9.88	a,2	86.12	b,1	81.22	c,1	95.69	a,1	11.94	a,2	12.95	a,2	6.34	b,2	81.26	a,b,1	76.57	b,1	91.34	a,1
caffeic acid	2.70	b,2	2.76	a,b,2	2.87	a,2	4.35	a,1	4.31	a,1	5.53	a,1	2.62	b,2	2.16	c,2	2.73	a,2	4.09	a,1	5.02	a,1	5.10	a,1
(−)-epicatechin	13.05	a,2	16.05	a,2	n.d.	b,3	70.65	b,1	82.15	a,1	28.93	c,1	12.17	a,2	15.12	a,2	n.d.	b,3	67.53	b,1	82.93	a,1	62.42	c,1
coumaric acid	0.44	a,2	0.41	a,2	n.d.	b,3	1.13	a,1	1.37	a,1	1.38	a,1	0.38	b,2	0.38	b,2	0.56	a,2	0.99	c,1	1.22	b,1	1.69	a,1
ferulic acid	0.19	a	0.19	a	0.08	b	n.d.		n.d.		n.d.		0.19	b	0.20	a	0.11	c	n.d.		n.d.		n.d.	
(*E*)-resveratrol	n.d.		n.d.		n.d.		2.49	c	3.17	b	3.52	a	n.d.		n.d.		n.d.		2.30	c	2.99	b	3.17	a
quercetin	n.d.		n.d.		n.d.		15.35	b	16.87	a	12.61	c	n.d.		n.d.		n.d.		14.23	b	15.86	a	12.31	c
total phenolics	38.65		43.11		23.71		205.23		216.99		179.11		38.27		42.08		21.06		195.13		213.97		206.33	
Anthocyanins																								
delphinidin-3-glucoside							5.78	a	4.83	b	3.81	c							5.05	a	4.82	b	3.35	c
cyanidin-3-glucoside							6.49	a	5.32	b	3.73	c							5.93	a	5.12	b	3.32	c
petunidin-3-glucoside							8.41	a	6.65	b	4.44	c							7.66	a	6.80	b	3.91	c
peonidin-3-glucoside							16.38	a	13.14	b	8.81	c							14.90	a	12.60	b	7.84	c
malvidin-3-glucoside							34.94	a	28.58	b	19.00	c							32.01	a	27.92	b	16.41	c
total anthocyanins							72.00	a	58.52	b	39.79	c							65.56	a	57.27	b	34.83	c
Volatiles																								
D-limonene	7.10	b,1	5.38	b,1	10.45	a,1	4.88	b,1	9.54	a,1	8.01	a,1	5.40	b,1	5.05	b,1	15.04	a,1	5.11	b,1	6.69	b,1	9.70	a,1
linalol	n.d.		n.d.		n.d.		4.08	b	7.23	a	5.50	b	n.d.		n.d.		n.d.		4.00	a	3.72	a	5.14	a
β-damascenone	3.61	a,b,1	3.91	a,1	2.61	b,1	1.65	b,2	2.01	a,2	1.80	b,2	3.21	a,1	2.10	b,1	2.60	a,b,1	1.47	a,2	1.51	a,2	1.72	a,2
geranyl acetone	n.d.		n.d.		n.d.		0.57	a	1.00	a	0.33	a	n.d.		n.d.		n.d.		0.58	a	0.42	a	0.18	a
(*E*)-whiskylactone	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		9.46	a,1	4.99	b,1	11.62	a,1	6.67	a,1	4.49	a,1	10.87	a,1
β-ionone	n.d.		n.d.		n.d.		0.27	b,1	0.41	a,1	0.25	a,1	n.d.		n.d.		n.d.		0.25	a,1	0.17	a,1	0.23	a,1
(*Z*)-whiskylactone	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		14.54	a,1	10.18	b,1	14.59	a,1	10.40	a,1	9.99	a,1	10.87	a,1
(*E*)-nerolidol	3.49	a,1	3.64	a,1	1.83	b,1	0.60	b,2	0.93	a,2	0.37	b,2	3.24	a,1	2.35	a,b,1	1.67	b,1	0.40	a,2	0.21	a,2	0.42	a,2
farnesol	1.99	a,1	3.31	a,1	3.08	a,1	2.47	a,1	2.00	a,b,2	1.15	b,1	3.14	a,1	2.53	a,1	2.76	a,1	0.80	a,1	0.62	a,1	1.04	a,1

[a] Different letters between the type of wine represent statistically significant differences ($p < 0.05$), and different numbers represent statistically significant differences between control and DWGS-rosé wine. Total polyphenol index (TPI) is expressed in mg/L gallic acid equivalents. Low molecular weight phenolic compounds (LMWPC) and anthocyanins are expressed in mg/L. Mv-3-G volatile compounds are expressed in μg/L.

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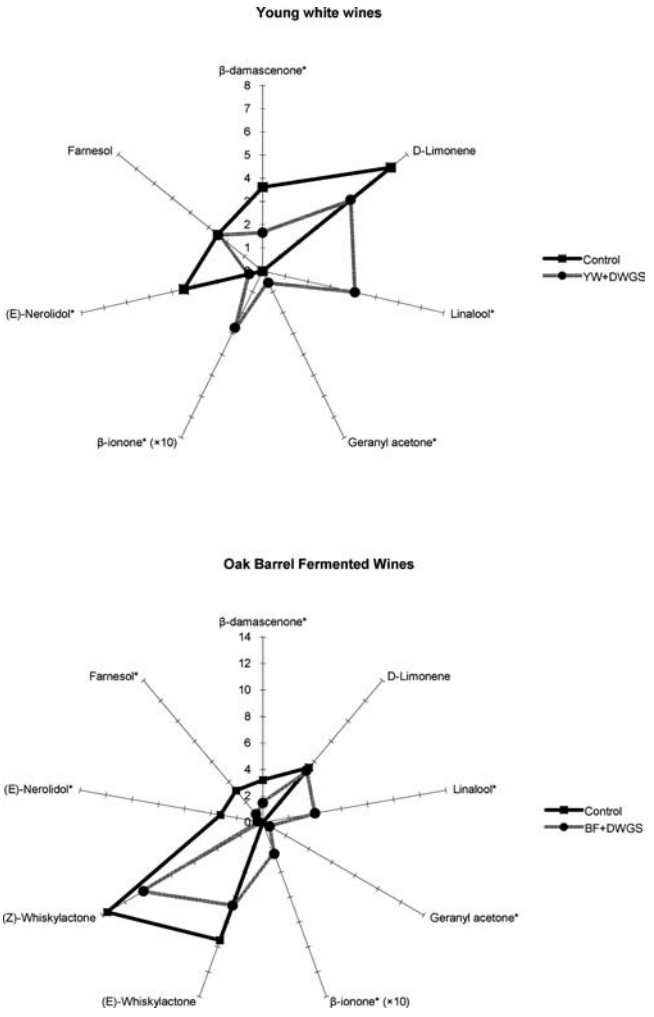

Figure 5. Volatile profile (μg/L) of control young and oak barrel fermented wines and corresponding DWGS-rosé wines.
Statistically significant differences ($p < 0.05$) in compounds are indicated by the asterisk.

concentration, it remained 30 times higher than its olfactory threshold. (*E*)-Nerolidol and isoamyl acetate also reduced their concentration after addition of DWGS, compared to control wines. These volatiles were initially present at a concentration below their corresponding olfactory threshold. However, they were not completely eliminated from wines; thus, their contribution to particular aromatic series and/or to overall aroma could possibly remain.[36] The concentration of whiskylactones in BF DWGS-rosé wines was not significantly different from that of control wines, suggesting that the particular wood notes from BF wine were not altered (Figure 5). Volatile compound evolution after 3 months was in most cases similar to that of control wines or remained without important changes (Table 4); thus, it was considered stable.

The evolution of wines was followed after 1 and 3 months. The TPI increased more than 5 times after the addition of DWGS with respect to control wines. This increase could be attributed to the release of tannins and other phenolic complexes. The percentage of red color reached a maximum value of 59% after 1 month of storage, and low degradation (3%) was observed after 3 months. Blue color remained (5%) almost without variation after 3 months of storage. Slight changes in shade and percent of yellow were considered as indicators of low color degradation (Table 4). As color is one of the factors determining quality in rosé wines, the use of DWGS for rosé production might be considered a good strategy for avoiding premature color degradation reactions that started at grape crushing. The improved concentration of (+)-catechin, (−)-epicatechin, (*E*)-resveratrol, and quercetin might play a important role in the preservation of color particularly during the first month. Note that the concentration of (*E*)-resveratrol in rosé wines was higher than the average concentration reported for red wines (1.5 mg/L)[37] and that after 3 months it remained almost unchanged. This compound was more stable in wine than in synthetic wines highlighting the influence of wine matrix.

Degradation of anthocyanins was progressive and not accentuated during the first month of storage as observed in wine model solutions. Also, the degradation of malvidin-3-glucoside was lower in DWGS-rosé wines (45%) than in model wine solutions (79%) and other rosé wines after 3 months of bottling (70%).[38] The premature degradation of traditional rosé wines, which starts at grape crushing, might explain such differences. Improved concentration of phenolic compounds acting as antioxidants as well as longer maceration times to increase anthocyanin content could be involved in the preservation of anthocyanins in DWGS-rosé wines by means of multiple interactions (self-association, copigmentation). Since the composition of wine seems to play a significant role in the release of compounds from DWGS and the evolution of rosé wines, further research using different white wines might clarify stability aspects of the process.

The present study demonstrates the potential of dehydrated waste grape skins as a raw additive for releasing a valuable amount of pigments, bioactive compounds, and aromas into wines. The experimental conditions of dosage; particle size, and maceration time in model wine solutions led to an improved understanding of the release of color and phenolic and aroma compounds from dehydrated waste grape skins. Maceration time was the factor regulating anthocyanin release while dosage was particularly important for low molecular weight phenolic compounds extraction. Cellar conditions of temperature and alcohol content had a minor influence on the behavior of extraction. Rosé wines produced with dehydrated waste grape skins prove to be stable and to have a composition similar to typical rosé wines. Moreover, the use of DWGS can be considered a good strategy for avoiding premature oxidation in rosé wines. The absence of an extraction-concentration process step of waste grape skins is also an advantage in terms of economics, handling, and storage, demonstrating DWGS as a potential tool for enological applications. The simplified extraction method applied in our experiment is of interest for other beverages such as reduced alcohol content wines, carbonated drinks, and other foods looking to improve their composition and organoleptic profile.

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