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Effect of freeze-drying and oven-drying on volatiles and phenolics composition of grape skin

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ABSTRACT

Grape skins are the part of the fruit with the highest amount of volatile and polyphenolic compounds. Volatile compounds give the fruit and other grape derivatives their flavour. Polyphenolic compounds are responsible for the colour of the fruit, juice and wine, and also act as very important natural antioxidant compounds. Dehydration is a method used to prevent the damage of these compounds over time. Nevertheless, in the case of volatile compounds, removing water can cause compound degradation or the evaporation of such compounds. This work studied two drying methods, freeze-drying and oven-drying, at 60 °C, as skin preservation methods. The skins from two grape varieties, Carménère and Cabernet Sauvignon, were dried. Many volatile compounds, which are of interest in the aroma profile, were identified in both varieties as terpenes (linalool, etc.), sesquiterpenes (farnesol), norisoprenoids (vitispirane, etc.), C_6 alcohols (1-hexanol, etc.), etc., and their amount decreased significantly with the oven-drying method, in contrast to the freeze-drying method. Both phenolic compounds, anthocyanins and flavonols, were identified in fresh and dehydrated samples, thus resulting in the freeze-drying method being less aggressive than oven-drying methods.

1. Introduction

In most fruit, the skin is the solid part that contains the highest percentage of volatile compounds, which give the fruit its aroma, and phenolic compounds, which are responsible for the colour. Various authors are currently interested in the study of the chemical composition of this part of the fruit, since it is possible to find a greater richness in chemical compounds, in addition to finding them in greater concentrations. Aubert and Milhet [1] studied the chemical composition of peach skin in comparison with the pulp. They found that the skin contained a 35–78% higher amount of compounds that were of interest with regard to aroma, such as terpenes, C_6 alcohols and norisoprenoids. They obtained similar results with melon skin [2]. A similar situation arises with the grape, since the highest amount of volatile and phenolic compounds is found in the skin, as extensively described in the bibliography [3,4]. This characteristic could be used to enhance aroma and colour in the industry of juices and grape derivatives, since, as they also contain aroma precursors, they would generate a greater aromatic complexity in wines during fermentation. On the other hand, the most abundant phenolic compounds are the anthocyanins and flavonols. The former give red grape derivatives their colour, in addition to being very interesting from a health point-of-view [5]. In the case of red varieties, flavonols, despite playing a smaller role than the anthocyanins with regard to colour (given that they are compounds that generate a yellow colour), are important in the stabilization of anthocyanins through the phenomenon of copigmentation [6], in addition to the undeniable antioxidant contribution that they make to the foods that contain them [7].

Nevertheless, skins have a water content of between 75–80%. Thus, the growth of microorganisms is very favourable, as is the degradation of chemical substances. On the other hand, skins contain a large amount of enzymes, amongst which the polyphenol oxidase enzymes are noteworthy [8]. These specific enzymes cause the oxidation of the phenolic compounds, and can thus influence the browning process.

Due to the type of chemical compounds that the skins contain and the instability that their high water content generates, the need arises to find different methods with which to preserve them, with a view to lengthening their useful life and making vineyard cultivation less season-dependent, such as for example dehydration, in order to keep them preserved over time.

Dehydrated skins generate interest because of their possible use as an ingredient in other foods, providing aromas and colour, as well as their addition to musts from grape harvests that are poor in volatile and phenolic metabolites.

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The aim of this work is to study the effect of two skin dehydration techniques, oven-drying at 60 °C and freeze-drying, on chemical composition from the point-of-view of the volatile and phenolic composition.

2. Materials and methods

2.1. Samples

Two grape varieties, Carménère and Cabernet Sauvignon, from Chile were used. They were supplied by Mostinsa (Mostos Internacionales), collected at optimum ripeness for harvesting. The initial moisture content of the skins was 74.6% and 73.2% dry weight of Carménère and Cabernet Sauvignon varieties, respectively.

2.2. Drying methods

For the freeze-drying process, the Carménère and Cabernet Sauvignon samples were frozen at −78 °C for 12 h and then freeze-dried in a vacuum (2.4×10^{-2} mB) for 24 h. The condenser temperature was −49 °C. The dried material had a moisture content of 5.4% and 5.9%, respectively.

Fresh Carménère and Cabernet Sauvignon skins were oven-dried using a laboratory oven at 60 °C for 24 h. The final moisture content was 5.1% and 5.5%, respectively.

2.3. Extraction and concentration of volatiles

A microscale simultaneous distillation–extraction apparatus (Chrompack, Middelburg, The Netherlands) was used as previously described [9]. An amount of 5 g of grape skins in 40 mL of water with 10 μL of 4-nonanol added as an internal standard was extracted under atmospheric conditions for 2 h using dichloromethane as the extraction solvent. The extracts obtained were frozen at −18 °C for gas chromatography analysis. Two replications of each extraction were performed.

2.4. Analysis of volatiles

An Agilent gas chromatograph, model 6890N, coupled to a mass selective detector, model 5973 *inert*, was used to analyze the extracts. An amount of 1 μL of extract was injected in splitless mode on a BP-21 capillary column (50 m × 0.32 mm i.d.; 0.25 μm film thickness). Oven temperature program was: 70 °C (5 min)–1 °C min^{-1}–95 °C (10 min)–2 °C min^{-1}–200 °C (40 min). Injector and transfer line temperatures were 250 °C and 190 °C, respectively. Mass detector conditions were: electronic impact (EI) mode at 70 eV; source temperature: 178 °C; scanning rate: 1 scan s^{-1}; mass acquisition: 40–450 amu.

The identification of the volatile compounds was based on the comparison of their GC retention times and mass spectra with those of Sigma–Aldrich's authentic standards. The compounds for which it was not possible to find references were tentatively identified by comparing their mass spectra with those of Wiley and NBS75K spectra data libraries. A semi-quantitative analysis was carried out assuming a response factor equal to one.

2.5. Extraction of phenolic compounds

An amount of 20 g of fresh grape skins in 150 mL of MeOH/H_2O/HCOOH (50:48.5:1.5) were beaten by a mixer (Moulinex) for 2 min and then centrifuged 2500 × *g* for 15 min. The supernatant were stored at −18 °C until use for HPLC analysis. Two replications of each extraction were performed.

2.6. Isolation of grape flavonols

The anthocyanins present in red grape extract usually cause great interference in the chromatographic separation and identification of flavonols, so solid-phase extraction on MCX cartridges (Waters Corp. Milford, MA; cartridges of 6 cm^3 capacity filled with 500 mg of adsorbent) containing a mixture of reverse-phase and cation-exchanger materials allowed the isolation of grape flavonols.

An amount of 1.5 mL of grape skin extracts were dissolved in 11 mL of 0.1 M hydrochloric acid. The separation procedure was from Castillo-Muñoz et al. [10], previously adapted from González-Manzano et al. [11]. The prepared samples were passed through the MCX cartridges previously conditioned with 5 mL of methanol and 5 mL of water. After washing 5 mL of 0.1 M hydrochloric acid and 5 mL of water, the flavonol fraction was eluted with 3 × 5 mL of methanol. This fraction contained flavonol compounds. Fixed anthocyanins were removed using 3 × 5 mL of ammonia in 80% methanol, and the cationic-exchange material was generated with 3 × 5 mL of 2% hydrochloric acid in 80% methanol. Subsequent conditioning of the cartridge with methanol and water allows its reuse at least four or five times. Flavonol extract was dried in a rotary evaporator (40 °C) and re-solved in 1.5 mL 25% of methanol in water.

2.7. Analysis of phenolic compounds

HPLC separation, identification and quantification of wine phenolic compounds were performed on an Agilent 1100 Series system (Agilent, Germany), equipped with DAD (G1315B) and LC/MSD Trap VL (G2445C VL) electrospray ionization mass spectrometry (ESI-MS^n) system, and coupled to an Agilent Chem Station (version B.01.03) data-processing station. The mass spectra data were processed with the Agilent LC/MS Trap software (version 5.3). The grape skin extracts were injected (50 μL) after filtration (0.20 μm, polyester membrane, Chromafil PET 20/25, Macherey-Nagel, Düren, Germany) on a reversed-phase column Zorbax Eclipse XDB-C18 (4.6 × 250 mm; 5 μm particle; Agilent, Germany), thermostatted at 40 °C. The chromatographic conditions were adapted from the OIV method for analysis of anthocyanins in red wines [12]. The solvents were water/acetonitrile/formic acid (87:3:10, v/v/v, solvent A; 40:50:10, v/v/v, solvent B), and the flow rate was 0.63 mL min^{-1}. The linear gradient for solvent B was: 0 min, 6%; 15 min, 30%; 30 min, 50%; 35 min, 60%; 38 min, 60%; 46 min, 6%. For identification, ESI-MS^n was used employing the following parameters: positive ionization mode; dry gas, N_2, 11 mL min^{-1}; drying temperature, 350 °C; nebulizer, 65 psi; capillary, −2500 V; capillary exit offset, 70 V; skimmer 1, 20 V; skimmer 2, 6 V; compound stability, 100%; scan range, 50–1200 *m*/*z*. For quantification, DAD-chromatograms were extracted at 520 nm and a calibration curve of malvidin 3-glucoside (Phytolab, Vestenbergsgreuth, Germany) was used.

Flavonols were analyzed by injection of the anthocyanin-free flavonol fraction isolated from grape skin extracts, using the same chromatographic equipment and conditions as for anthocyanins, but the solvent were changed to water/acetonitrile/formic acid (88.5:3:8.5, v/v/v, solvent A; 41.5:50:8.5, v/v/v, solvent B) and water/methanol/formic acid (1.5:90:8.5, v/v/v, solvent C) and the flow rate was 0.63 mL min^{-1} (12). The lineal gradient was as follows: (96/4/0)-0 min; (96/4/0)-7 min; (70/17/13)-38 min; (50/30/20)-52 min; (30/40/30)-52.5 min; (0/50/50)-57 min; (0/50/50)-58 min; (96/4/0)-65 min and also positive ionization mode conditions were used. The identification was made as previously described using DAD and MS^n data [10,13]. DAD-chromatograms were extracted at 360 nm for quantification using commercial standards from Extrasynthese (Genay, France): the 3-

glucosides of quercetin, kaempferol, isorhamnetin and syringetin; other non-commercial flavonol standards (myricetin 3-glucoside, quercetin 3-glucuronide, and laricitrin 3-glucoside) were kindly supplied by Dr. Ullrich Engelhardt (Institute of Food Chemistry, Technical University of Braunschweig, Germany). Flavonols for which standards were not available were quantified as their respective 3-glucoside derivative.

2.8. Statistical analysis

The Student–Newman–Keuls test (SPSS, program 2000) was used to asses the significance of differences among the various treatments.

3. Results and discussion

3.1. Volatile compounds

Ninety-seven volatile compounds were identified in both varieties (Table 1

and Table S1, see supplementary information). The similarity in the volatile composition between both was noteworthy, although the amount found for the different compounds were different.

Both skins had a high number of terpene, sesquiterpene and norisoprenoid compounds, and C_6 derivatives, which are very important with regard to aroma.

Within the terpenic compounds of both varieties, the amount of phytol was of special note [14], but other terpenes were also found that are of sensory interest, such as linalool, α-terpineol, nerol, trans-geraniol, geranyl acetone with floral olfactory notes [4], citral, which contributes a lemon scent, and menthol, as found in other grape varieties [15]. With regard to the dehydrated skins, no significant differences were generally found in the amount of these compounds in the lyophilized skins, but they did exist in the oven-dried skins of both varieties, which indicates that this type of compound is more sensitive to oven-drying.

The total amount of sesquiterpenes found was greater than total amount of terpenes, noting a significant increase in the case of δ-cadinene in the Carménère variety and of farnesol both in the Carménère and Cabernet Sauvignon skins when they were lyophilized, which caused an increase in the total amount of this compound family. The increase of these compounds following dehydration through lyophilization has been described by authors such as Díaz-Maroto et al. [16], who observed an increase in the amount of the sesquiterpenes spathulenol and β-eudesmol in lyophilized laurel leaves, a fact that is attributed to the breaking of the cells in which they are stored, which caused their extraction to be more effective.

In both varieties, the norisoprenoids that were found in the highest amount were the β-damascenone and β-ionone, which together with the β-cyclocitral, vitispirane and methyl-dihydrojasmonate contributed to the floral aroma [4] followed by the 6-methyl-5-hepten-2-one. The presence of 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) was also observed, which smells like kerosene, with a low olfactory perception threshold (20 ppb in wine [17]). This compound has been found in stored wines and is not common in musts, which indicates that it should not be found in the berry. Nevertheless, different authors have noted that the generation of this compound is related to excessive exposure to the sun [18]. With the dehydration, an increase in the total amount of norisoprenoids was observed, caused by the increase in the amount of some of the compounds, like the β-damascenone, in the dehydrated skins of both varieties. The norisoprenoids in the berry are usually found in the bound form. Their increase in the dehydration could be due to various hypotheses. On the one hand, as is the case of the sesquiterpenes, it could be due to the breaking of the cells or organelles that contained these compounds and thus, they would have been more effectively extracted. On the other hand, that during the dehydration process, as the water decreased, the acidity would have increased, giving rise to the hydrolysis of the glycosides, which would cause the release of the aglycones. An increase in this type of compound increases the fruity and floral flavour, which gives the skins greater aromatic potential.

The skins were richer in C_6 alcohols and aldehydes, with the amount being highest in the Carménère variety. In both varieties, the most noteworthy amount were those of 1-hexanol, (E)-2-hexen-1-ol, hexanal and E-2-hexenal, which together with the rest of this family's compounds provide an herbaceous and fresh smell. Of all the compound families, the C_6 alcohols were most sensitive to dehydration through oven-drying, since their amount dropped by around 80% in both varieties, and small drops were noted in the lyophilized skins. The reduction of the rest of the identified alcohols was not so significant, which indicates that it is the small size of the molecule and its polarity that causes the C_6 alcohols to evaporate together with the water in the oven-drying process. This can cause a sensation of reduced freshness and less of an herbaceous aspect in the foods to which this skin is added.

A high amount of acids were found in the skins of both grape varieties, especially in the Cabernet Sauvignon variety, with both experiencing a reduction during the drying processes, primarily in the case of oven-drying at 60 °C.

The rest of the identified aldehydes were of the alkyl-2,4-diene and alkyl-2,6-diene types, and superior saturated aliphatic aldehydes like: nonanal, decanal, etc. They all come from long-chained unsaturated fatty acids [19], and no significant variations were noted in their amount, with the same occurring in the case of the esters.

Within the benzene compounds, a certain number of naphthalene compounds were found that had already been identified by Riu-Aumatel et al. [20] in various fruit juices. In the same way that the norisoprenoids increased during lyophilization, which causes an increase in the total amount of these types of compounds, the oven-dried samples experienced a reduction in the amount of these compounds in both varieties. Regarding other benzenic compounds that are of aromatic interest, such as benzaldehyde, guaiacol, vinyl guaiacol, benzeneethanol, amongst others with floral and sweet aromas [21], no general significant changes were observed, which is interesting with regard to the aromatic potential of the skins.

Derivative compounds of furan, pyran and lactones from the browning reactions were determined that generally did not have significant differences in the lyophilized samples, but did in the oven-dried samples, increasing in a more significant manner the furfural amount, although it did not exceed the threshold (3000–23,000 ppb in water [22]).

3.2. Phenolic compounds

In both varieties, flavonoid, anthocyanin and flavonol compounds were determined (Table 2 and Table S2, see supplementary information), finding the same compounds in the two types of grapes, although in different amounts.

In both skins studied the anthocyanin derivatives of the delphinidin, cyanidin, petunidin, peonidin and malvidin anthocyanidins were identified, glycosylated at different glucosides in position 3, showing different acylations. In both varieties, the majority anthocyanins (highest molar percentage) were the malvidin derivatives (malvidin-3-glucoside and malvidin-3-acetylglucoside) [23,24].

The lyophilization process did not generate large drops in the amount of these compounds, with a 15% drop in the Carménère

Table 1
Volatile compounds ($\mu g\,kg^{-1}$) in fresh and dried Carménère skins.

Compounds	$\bar{X} \pm SD$		
	Carménère fresh	Carménère freeze-dried	Carménère oven-dried at 60 °C
Terpenes			
Linalool	$3.1^{a} \pm 0.4$	$3.6^{a} \pm 0.6$	$2.9^{a} \pm 0.3$
Terpinen-4-ol	$7.6^{a} \pm 0.7$	$7.6^{a} \pm 0.1$	$5.6^{b} \pm 0.3$
Menthol	$2.2^{b} \pm 0.0$	$1.5^{c} \pm 0.0$	$2.3^{a} \pm 0.0$
α-Terpineol	$15.2^{a} \pm 0.5$	$16.1^{a} \pm 0.2$	$18.4^{a} \pm 1.5$
E-Citral	$2.1^{b} \pm 0.1$	$2.7^{a} \pm 0.1$	$1.2^{c} \pm 0.1$
Nerol	$10.5^{a} \pm 0.9$	$6.0^{b} \pm 0.4$	n.d.
trans-Geraniol	$15.4^{a} \pm 1.2$	$11.1^{b} \pm 0.4$	$6.6^{c} \pm 1.0$
Geranyl acetone	$32.1^{a} \pm 2.3$	$36.7^{a} \pm 3.5$	$16.7^{b} \pm 0.8$
Geranic acid	$18.7^{a} \pm 2.2$	$21.3^{a} \pm 3.0$	$15.1^{a} \pm 4.0$
Phytol	$119.9^{a} \pm 4.4$	$112.3^{a} \pm 0.3$	$37.8^{b} \pm 2.8$
Total	226.9	218.7	106.6
Sesquiterpenes			
δ-Cadinene	$21.6^{b} \pm 2.1$	$38.5^{a} \pm 2.3$	$16.4^{b} \pm 0.1$
Nerolidol + lilial	$11.8^{a} \pm 1.3$	$9.4^{a,b} \pm 0.7$	$6.5^{b} \pm 0.8$
Cubene + phenol	$20.1^{a} \pm 1.4$	$20.3^{a} \pm 0.9$	$10.9^{b} \pm 1.2$
Pirofarnesyl acetone	$42.5^{a} \pm 1.4$	$41.3^{a} \pm 4.9$	$39.3^{a} \pm 4.5$
Manoyl oxide	$149.2^{a} \pm 1.4$	$134.2^{b} \pm 6.8$	$90.3^{c} \pm 2.2$
Farnesol	$7.2^{c} \pm 0.7$	$14.7^{a} \pm 1.1$	$12.0^{b} \pm 0.5$
Total	252.3	258.4	175.5
Norisoprenoids			
Vitispirane	$9.4^{a} \pm 0.3$	$10.9^{a} \pm 1.0$	$11.8^{a} \pm 1.2$
β-Cyclocitral	$11.3^{b} \pm 0.9$	$17.0^{a} \pm 0.5$	$11.3^{b} \pm 0.8$
1,2-Dihydro-1,1,6-trimethyl-naphthalene (TDN)	$7.8^{b} \pm 0.3$	$8.8^{b} \pm 0.8$	$11.5^{a} \pm 0.4$
β-Damascenone	$47.2^{b} \pm 3.5$	$67.0^{a} \pm 5.0$	$67.7^{a} \pm 3.3$
β-Ionone	$32.8^{a} \pm 1.3$	$41.3^{a} \pm 1.2$	$42.2^{a} \pm 4.0$
Methyl-dihydrojasmonate	$12.1^{b} \pm 1.8$	$23.7^{a} \pm 3.0$	$16.2^{b} \pm 1.3$
6-Methyl-5-hepten-2-one	$10.2^{b} \pm 0.8$	$18.2^{a} \pm 2.0$	$8.6^{b} \pm 0.2$
6-Methyl-3,5-heptadien-2-one	$2.3^{a,b} \pm 0.4$	$2.9^{a} \pm 0.1$	$1.7^{b} \pm 0.0$
Total	133.2	189.9	171.0
C6 Alcohols and aldehydes			
1-Hexanol	$346.1^{a} \pm 15.7$	$331.4^{a} \pm 19.2$	$9.4^{b} \pm 0.1$
(E)-3-Hexen-1-ol	$6.8^{a} \pm 0.4$	$10.1^{a} \pm 2.3$	n.d.
(Z)-3-Hexen-1-ol	$14.0^{a} \pm 2.2$	$15.7^{a} \pm 0.9$	n.d.
(E)-2-Hexen-1-ol	$254.6^{a} \pm 34.9$	$228.2^{a} \pm 2.2$	$6.4^{b} \pm 0.8$
(Z)-2-Hexen-1-ol	$4.3^{a} \pm 1.1$	$2.9^{a} \pm 0.1$	n.d.
Hexanal	$400.7^{a} \pm 53.2$	$369.3^{a} \pm 19.5$	$129.2^{b} \pm 9.3$
E-2-Hexenal	$438.2^{a} \pm 39.7$	$352.4^{b} \pm 10.5$	$84.2^{c} \pm 8.5$
Total	1464.6	1310.0	229.1
Alcohols			
3-Octen-1-ol	$24.2^{a} \pm 2.3$	$29.2^{a} \pm 1.3$	$11.1^{b} \pm 2.5$
Heptanol	$5.3^{b} \pm 0.1$	$7.1^{a} \pm 0.1$	n.d.
2-Ethyl-1-hexanol	$8.7^{b} \pm 0.3$	$12.2^{a} \pm 0.2$	$5.7^{c} \pm 0.6$
3-Methoxy-1-butanol	$17.0^{a} \pm 2.7$	$18.6^{a} \pm 0.8$	$17.3^{a} \pm 1.0$
1-Octanol	$35.3^{b} \pm 2.6$	$41.8^{a} \pm 1.9$	$28.5^{c} \pm 0.7$
2,6-Dimethyl-cyclohexanol	$2.3^{b} \pm 0.3$	$3.3^{a} \pm 0.1$	$2.1^{b} \pm 0.2$
1-Nonanol	$11.3^{a} \pm 3.6$	$16.7^{a} \pm 0.7$	$18.6^{a} \pm 0.1$
1-Dodecanol	$24.7^{a} \pm 1.1$	$14.0^{b} \pm 0.0$	$14.1^{b} \pm 1.7$
Tetradecanol	$10.1^{a} \pm 1.1$	$9.9^{a} \pm 1.5$	$8.4^{a} \pm 1.0$
Pentadecanol	$17.3^{a} \pm 2.4$	$14.4^{a} \pm 1.8$	$21.2^{a} \pm 2.1$
1-Octadecanol	$45.4^{a} \pm 1.8$	$46.4^{a} \pm 4.0$	$39.0^{a} \pm 4.0$
Total	201.5	204.8	158.6
Acids			
Propanoic acid	$3.1^{a} \pm 0.1$	$2.4^{b} \pm 0.0$	$1.3^{c} \pm 0.2$
Butanoic acid	$2.3^{a} \pm 0.2$	$1.7^{a} \pm 0.7$	$1.2^{a} \pm 0.1$
Pentanoic acid	$4.7^{a} \pm 0.0$	$5.1^{a} \pm 0.6$	$3.1^{b} \pm 0.4$
Hexanoic acid	$194.0^{a} \pm 43.4$	$247.0^{a} \pm 8.3$	$65.7^{b} \pm 9.6$
2-Ethyl-hexanoic acid	$15.7^{a} \pm 1.6$	$15.7^{a} \pm 2.4$	$13.7^{a} \pm 2.0$
Heptanoic acid	$19.4^{a} \pm 0.3$	$20.9^{a} \pm 1.5$	$15.8^{a} \pm 2.6$
3-Hexenoic acid	$14.1^{a} \pm 0.1$	$13.9^{a} \pm 2.0$	$4.7^{b} \pm 0.5$
Octanoic acid	$71.8^{a} \pm 6.3$	$81.7^{a} \pm 1.6$	$58.5^{b} \pm 0.1$
Nonanoic acid	$166.6^{a} \pm 15.2$	$181.0^{a} \pm 0.9$	$150.6^{a} \pm 6.1$
Decanoic acid	$53.0^{a} \pm 3.8$	$59.6^{a} \pm 5.3$	$48.8^{a} \pm 5.2$
(Z)-Octadecanoic acid	$15.9^{a} \pm 3.0$	$13.1^{a} \pm 1.4$	$8.8^{a} \pm 1.6$
Dodecanoic acid	$208.0^{b} \pm 12.6$	$280.6^{a} \pm 2.9$	$111.5^{c} \pm 5.7$
(Z,Z)-9,12-Octadecanoic acid	$534.4^{a} \pm 36.5$	$201.3^{b} \pm 7.1$	$153.0^{b} \pm 30.0$
Pentadecanoic acid	$35.8^{a} \pm 4.0$	$41.3^{a} \pm 8.5$	$35.0^{a} \pm 3.6$
Total	1338.8	1165.2	671.5

Table 1 (*Continued*)

Compounds	$\bar{X} \pm$ SD		
	Carménère fresh	Carménère freeze-dried	Carménère oven-dried at 60 °C
Aldehydes			
E-2-Heptenal	$25.7^{a} \pm 3.5$	$74.3^{b} \pm 7.4$	$20.5^{a} \pm 3.9$
Nonanal	$164.3^{a} \pm 25.6$	$271.2^{a} \pm 52.2$	$197.9^{a} \pm 5.9$
2-Octenal	$16.8^{b} \pm 2.3$	$35.6^{a} \pm 2.9$	$14.5^{b} \pm 2.4$
3-(Methylthio)-propanal	$2.4^{a} \pm 0.3$	$2.4^{a} \pm 0.1$	$3.2^{a} \pm 0.6$
(E,E)-2,4-Heptadienal	$9.9^{a,b} \pm 2.9$	$14.2^{a} \pm 0.0$	$4.6^{b} \pm 0.6$
Decanal	$40.3^{b} \pm 4.8$	$59.1^{b} \pm 1.6$	$98.8^{a} \pm 3.6$
(E)-2-Nonenal	$24.1^{a} \pm 2.0$	$33.7^{a} \pm 0.7$	$32.2^{a} \pm 0.2$
(E,Z)-2,6-Nonadienal	$19.9^{a,b} \pm 0.2$	$24.9^{a} \pm 3.0$	$13.8^{b} \pm 1.7$
Undecanal	$9.2^{a} \pm 2.3$	$12.5^{a} \pm 0.3$	$9.3^{a} \pm 0.1$
2,4-Nonadienal	$5.2^{a} \pm 1.1$	$5.8^{a} \pm 0.2$	$4.2^{a} \pm 0.6$
Dodecanal	$20.0^{a} \pm 6.7$	$13.6^{a} \pm 1.2$	$11.8^{a} \pm 1.5$
(E,Z)-1,4-Decadienal	$10.4^{a} \pm 1.6$	$12.4^{a} \pm 1.2$	$5.3^{b} \pm 0.4$
2,4-Decadienal	$20.6^{a} \pm 3.9$	$26.0^{a} \pm 2.3$	$12.1^{b} \pm 1.1$
Tetradecanal	$11.5^{a} \pm 0.6$	$6.1^{a} \pm 7.7$	$6.9^{a} \pm 1.1$
Total	380.4	591.6	434.9
Esters			
Butyl Butanoate	$17.6^{b} \pm 1.6$	$33.5^{a} \pm 4.7$	$26.3^{a,b} \pm 4.3$
Isopropyl miristate	$3.6^{a} \pm 0.2$	$7.0^{b} \pm 1.1$	$5.2^{a,b} \pm 0.2$
Methyl hexadecanoate	$41.1^{a} \pm 4.2$	$39.1^{a} \pm 9.8$	$34.8^{a} \pm 4.8$
Ethyl hexadecanoate	$18.9^{a} \pm 2.9$	$19.2^{a} \pm 3.8$	$16.1^{a} \pm 0.3$
Ethyl octadecanoate	$22.8^{b} \pm 2.8$	$49.1^{a} \pm 1.5$	$16.4^{c} \pm 0.2$
(Z,Z,Z)-9,12,15-Ethyl octatridecanoate	$24.0^{b} \pm 1.1$	$45.5^{a} \pm 7.0$	$20.0^{b} \pm 3.9$
Total	128.0	193.4	118.7
Benzene derivatives			
Benzaldehyde	$19.5^{b} \pm 0.8$	$28.0^{a} \pm 1.3$	$22.4^{b} \pm 1.2$
1,2,3,4-Tetrahydro-1,1,6-trimethyl-naphthalene	$3.5^{b} \pm 0.1$	$5.3^{a} \pm 0.5$	$2.7^{b} \pm 0.1$
Ethyl-Benzaldehyde	$2.5^{a} \pm 0.5$	$2.9^{a} \pm 0.1$	$1.5^{b} \pm 0.2$
1,2-Dihydro-1,5,8-trimethyl-naphthalene	$3.9^{b} \pm 0.0$	$5.5^{a} \pm 0.6$	$6.4^{a} \pm 0.1$
Guaiacol	$16.1^{a} \pm 1.4$	$15.5^{a} \pm 0.5$	$12.8^{a} \pm 0.1$
Benzyl alcohol	$70.7^{a} \pm 15.4$	$81.0^{a} \pm 6.1$	$32.6^{b} \pm 5.0$
2,3-Dimethylanisol	$2.7^{a} \pm 0.7$	$2.4^{a} \pm 0.4$	$1.9^{a} \pm 0.1$
2-Phenyl ethanol	$98.8^{b} \pm 8.1$	$117.4^{a} \pm 5.5$	$47.0^{c} \pm 1.6$
2,6-Dimethyl-naphthalene	$3.5^{a} \pm 0.8$	$4.6^{a} \pm 0.6$	$3.6^{a} \pm 0.4$
1-Ethyl-3,5-diisopropyl Benzene	$6.8^{a} \pm 0.3$	$9.1^{a} \pm 1.2$	$8.9^{a} \pm 0.4$
1-(Butylthio)-3-methyl-benzene	$7.4^{b} \pm 2.1$	$4.7^{b} \pm 3.7$	$13.0^{a} \pm 1.5$
Vinyl guaiacol	$21.9^{a} \pm 3.5$	$24.6^{a} \pm 3.1$	$15.7^{a} \pm 0.8$
1,6-Dimethyl-4-(1-methylethyl)-naphthalene	$7.3^{b} \pm 0.7$	$36.7^{a} \pm 6.3$	$6.0^{b} \pm 1.5$
Siringol	$13.9^{b} \pm 2.0$	$19.8^{a} \pm 0.1$	$11.4^{c} \pm 1.1$
Benzoic acid	$7.2^{a} \pm 0.9$	$6.5^{a} \pm 1.0$	$3.0^{b} \pm 0.1$
Benzophenone	$19.4^{b} \pm 0.6$	$28.8^{a} \pm 0.4$	$8.1^{c} \pm 0.4$
Benzyl benzoate	$5.4^{a} \pm 0.3$	$7.3^{a} \pm 0.3$	$6.7^{a} \pm 1.5$
Total	310.4	399.4	203.54
Furan and pyran derivatives			
2-Penthylfurane	$23.0^{a} \pm 2.8$	$29.4^{a} \pm 3.2$	$21.7^{a} \pm 2.0$
5-Methyl-2(3H)-furanone	n.d.	n.d.	$9.0^{a} \pm 2.5$
Furfural	$61.8^{b} \pm 5.7$	$89.6^{b} \pm 1.5$	$412.4^{a} \pm 63.8$
1-(2-Furanyl)-ethanone	n.d.	$3.4^{b} \pm 0.1$	$21.3^{a} \pm 5.2$
5-Methylfurfural	n.d.	$2.8^{b} \pm 0.3$	$15.6^{a} \pm 2.7$
2-Propyltetrahydropyrane	$3.9^{a} \pm 0.2$	$5.2^{a} \pm 0.1$	$4.0^{a} \pm 0.5$
γ-Nonalactone	$15.4^{a} \pm 2.1$	$26.8^{a} \pm 4.5$	$20.1^{a} \pm 1.7$
2,3-Dihydro-benzofurane	$17.0^{a} \pm 2.2$	$17.4^{a} \pm 0.6$	$4.4^{b} \pm 0.1$
Total	121.1	174.5	508.6

Different letters (a, b, c) in the same row indicate statistical differences at the 0.005 level according to the Student–Newman–Keuls test.

variety and 22% in the Cabernet Sauvignon variety. Oven-drying did cause greater drops. The amount dropped 35% in the oven-dried samples in the Carménère variety and 39% in the Cabernet Sauvignon variety, with regard to the initial anthocyanins.

In the flavonol family, myricetin, quercetin, kaempferol, laricitrin, syringetin and isorhamnetin derivatives were determined in both grape varieties, and myricetin glucoside was found in greater proportion, as was the glucuronic and the glucoside of quercetin. The greatest drops in these compounds were found in the Carménère variety, both in the lyophilized skins as well as in the oven-dried skins, in comparison with the results of the Cabernet Sauvignon variety. The amount of these compounds dropped by 35% in the lyophilized skins and 43% in the oven-dried skins in the Carménère variety in comparison with 20% and 25%, respectively, in the Cabernet Sauvignon variety. Both the anthocyanins and the flavonols are stored in the cellular vacuoles. However, as confirmed by Chism and Haard [25], phenolic compounds are often found in the external areas of the vacuoles. Thus, if the cellular structure deteriorates during the drying process, the compounds stored outside of the organelles are more sensitive to degradation, which should have been more marked in the case of flavonol compounds of the Carménère variety.

Table 2
Phenolic compounds (mg kg^{-1}) in fresh and dried Carménère skins.

Compounds	Carménère fresh $\bar{X} \pm SD$	mol%	Carménère freeze-dried $\bar{X} \pm SD$	mol%	Carménère oven-dried at 60 °C $\bar{X} \pm SD$	mol%
Anthocyanidins						
Delph.-3-glc	29.4$^{a} \pm 0.4$	7.3	23.7$^{b} \pm 0.5$	6.9	10.9$^{c} \pm 0.1$	4.1
Cyan.-3-glc	5.8$^{a} \pm 0.1$	1.4	4.6$^{b} \pm 0.4$	1.3	2.7$^{c} \pm 0.1$	1.0
Petun.-3-glc	25.8$^{a} \pm 1.0$	6.4	17.3$^{b} \pm 0.4$	5.0	13.3 $^{c} \pm 0.5$	5.0
Peonid.-3-glc	29.4$^{a} \pm 0.6$	7.3	18.6$^{b} \pm 0.8$	5.4	18.0$^{b} \pm 0.6$	6.8
Malv.-3-glc	166.0$^{a} \pm 1.2$	41.0	143.3$^{b} \pm 4.1$	41.7	123.8$^{c} \pm 0.2$	46.7
Delph.-3-acglc	7.6$^{a} \pm 0.3$	1.9	8.1$^{a} \pm 0.1$	2.4	4.1$^{b} \pm 0.1$	1.5
Cyan.-3-acglc	1.3$^{b} \pm 0.0$	0.3	1.0$^{c} \pm 0.0$	0.3	1.9$^{a} \pm 0.0$	0.7
Petunid.-3-acglc	7.6$^{a} \pm 0.5$	1.9	8.1$^{a} \pm 0.3$	2.4	5.3$^{b} \pm 0.7$	2.0
Delph.-3-cuglc	3.0$^{a} \pm 0.1$	0.7	2.9$^{a} \pm 0.1$	0.8	0.9$^{b} \pm 0.0$	0.3
Peonid.-3-acglc	7.3$^{a} \pm 0.0$	1.8	7.0$^{a} \pm 0.1$	2.0	4.4$^{b} \pm 0.3$	1.6
Malv.-3-acglc (trans)	79.9$^{a} \pm 3.0$	19.7	68.7$^{b} \pm 1.6$	20.0	60.2$^{c} \pm 0.6$	22.7
Peonid cafeoate.-3-gluc	1.7$^{a} \pm 0.0$	0.4	1.6$^{b} \pm 0.0$	0.5	1.1$^{c} \pm 0.1$	0.4
Malv. cafeoate-3-gluc	4.9$^{b} \pm 0.4$	1.2	5.4$^{b} \pm 0.1$	1.6	6.3$^{a} \pm 0.1$	2.4
Petunid.-3-cuglc	2.1$^{a} \pm 0.0$	0.5	2.1$^{a} \pm 0.0$	0.6	0.8$^{b} \pm 0.0$	0.3
Malv.-3-cuglu (cis)	1.2$^{a} \pm 0.0$	0.3	1.0$^{b} \pm 0.0$	0.3	0.4$^{c} \pm 0.0$	0.2
Peonid.-3-cuglc	4.5$^{a} \pm 0.0$	1.1	3.7$^{b} \pm 0.0$	1.1	1.4$^{c} \pm 0.0$	0.5
Malv.-3-cuglu (trans)	27.9$^{a} \pm 1.1$	6.9	26.6$^{a} \pm 0.3$	7.7	9.9$^{c} \pm 0.2$	3.7
Total	405.4		343.4		265.2	
Flavonols						
Myricetin-glucuronide	0.3$^{a} \pm 0.0$	0.9	0.1$^{b} \pm 0.0$	0.6	0.1$^{b} \pm 0.0$	0.7
Myricetin-galactoside	0.9$^{a} \pm 0.0$	2.8	0.6$^{b} \pm 0.1$	2.8	0.4$^{b} \pm 0.1$	2.2
Myricetin-glucoside	6.3$^{a} \pm 0.0$	20.2	4.7$^{b} \pm 0.0$	22.8	3.5$^{c} \pm 0.0$	19.7
Quercetin-galactoside	1.1$^{a} \pm 0.0$	3.4	0.7$^{b} \pm 0.0$	3.3	0.5$^{c} \pm 0.0$	3.0
Quercetin-glucuronide	7.0$^{a} \pm 0.0$	22.2	3.3$^{b} \pm 0.1$	16.3	2.9$^{c} \pm 0.1$	16.2
Quercetin-glucoside	7.1$^{a} \pm 0.1$	22.7	4.4$^{b} \pm 0.1$	21.6	4.0$^{c} \pm 0.0$	23.0
Laricitrin-glucoside	2.1$^{a} \pm 0.0$	6.7	1.8$^{b} \pm 0.0$	8.9	1.6$^{c} \pm 0.0$	9.3
Kaempferol-galactoside	0.3$^{a} \pm 0.0$	1.0	0.2$^{b} \pm 0.0$	1.1	0.2$^{c} \pm 0.0$	0.9
Kaempferol-glucuronide	0.2$^{a} \pm 0.0$	0.6	0.2$^{a} \pm 0.6$	0.9	0.1$^{a} \pm 0.0$	0.8
Kaempferol-glucoside	2.5$^{a} \pm 0.1$	8.0	1.6$^{b} \pm 0.0$	7.8	1.3$^{c} \pm 0.1$	7.6
Isorhamnetin-galactoside	0.1$^{a} \pm 0.0$	0.3	0.1$^{a,b} \pm 0.0$	0.3	0.0$^{c} \pm 0.0$	0.3
Isorhamnetin-glucoside	1.6$^{a} \pm 0.1$	5.1	1.0$^{b} \pm 0.0$	5.0	0.9$^{b} \pm 0.0$	5.3
Syringetin-galactoside	0.1$^{b} \pm 0.0$	0.2	0.1$^{a} \pm 0.0$	0.4	0.1$^{b} \pm 0.0$	0.3
Syringetin-glucoside	1.9$^{a} \pm 0.0$	5.9	1.7$^{b} \pm 0.1$	8.3	1.9$^{a} \pm 0.0$	10.7
Total	31.4		20.4		17.6	

Different letters (a, b, c) in the same row indicate statistical differences at the 0.005 level according to the Student–Newman–Keuls test.

4. Conclusions

The lyophilized skins maintained their volatile and phenolic composition in comparison with the original skins, better than those which were oven-dried. Thus, they could be a good option for use in the food industry in order to enhance the aroma and colour of musts from poor grape harvests and other foods, in addition to increasing their functional properties due to the antioxidant potential of the polyphenols.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.aca.2009.10.005.

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