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Freeze-dried grape skins by-products to enhance the quality of white wines from neutral grape varieties

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ABSTRACT

Wastes generated by the wine industry (grape marc), mainly residues from white wine vinifications, are an important source of aroma and phenolic compounds. However, grape marcs are highly perishable and seasonal products, so they require an adequate conservation method. In this respect, freeze-drying, versus conventional drying methods, is a good alternative since this technique preserves the quality of the raw material. Specifically, freeze-drying hardly caused losses of characteristic grape variety volatiles, such as terpenes and C_6 compounds, neither increases in the concentration of furan compounds. Furthermore, freeze-dried grape skins obtained from residues did not presented changes in the amounts of phenolic compounds with respect to the fresh skins. On the other hand, skin-contact treatment with Muscat freeze-dried skins enhanced the aroma of white wines made from Airén grapes, a variety considered neutral, without affecting negatively their color. Skin-contact treatment preserved the wine fruity notes, although the only wine that conserved floral notes in its flavor profile was that macerated with freeze-dried skins. Also, these wines were better rated by the assessors than those macerated with Muscat fresh skins.

1. Introduction

Grape waste management is one of the main problems of winery industries, mainly in grape producing countries, such as Spain. According to the International Organization of Vine and Wine (OIV, 2011), Spain ranks first in vineyard area planted, concentrating 50% of it in the Castilla-La Mancha region. Nowadays, there is a growing interest in the exploitation of the residues generated by the wine industry. Once the juice has been extracted, the skin, stalks, and seeds, mixture known as grape marc or pomace, are all redundant. That grape marc, if not treated effectively, can initiate a number of environmental hazards (Spigno & Faveri, 2007).

Furthermore, grape marc is a highly perishable product, and due to the enormous volumes of grape wastes generated during harvest season, the utilization of fresh grape marc is unfeasible, and therefore requires an appropriate method of preservation or appropriate use.

One of the higher value options is the recovery of bioactive plant food constituents, which could be used in other industries, such as pharmaceutical or food industry. In particular, winery wastes are an important source of polyphenols (Alonso, Guillén, Barroso, Puertas, & García, 2002; Makris, Boskou, & Andrikopoulos, 2007). In this regard, the last year's several studies have been realized, with the aim to recover antioxidant phenolics, mainly on pomace deriving from red wine production (Lazze et al., 2009; Pinelo, del Fabbro, Manzocco, Nuñez, & Nicoli, 2005; Spigno & Faveri, 2007), whereas other by-products, such as white vinification solid wastes have been much less studied (Casazza, Aliakbarian, Mantegna, Cravotto, & Perego, 2010; Makris et al., 2007). On the other hand, the high aromatic potential of grapes, concentrated mainly in the skins cannot be forgotten. Specifically, in white vinification, this potential, in many cases, is not sufficiently exploited, since the skins are discarded in the early stages of the winemaking process, becoming part of the grape wastes.

Although polyphenols are highly reactive, their recovery from grape wastes is relatively easier than volatile compounds due to their non-volatile character. The volatility of the compounds responsible for aroma makes their isolation more costly and complex, and the extraction conditions could modify the volatile profile profoundly. In this regard, the drying is one of the methods used to preserve the aromatic potential of the grape skin wastes (de Torres, Díaz-Maroto, Hermosín-Gutiérrez, & Pérez-Coello, 2010; Pedroza, Carmona, Salinas, & Zalacaín, 2011). Different methods of drying have been successfully applied in the food industry, though it must be noted that the changes in volatile product concentration during the drying process depend on different factors, such as the drying method, the biological characteristics of the plants and their volatile composition. For example,

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oven drying and freeze-drying applied to parsley or spearmint lead to significant volatile losses (Díaz-Maroto, Pérez-Coello, & Cabezudo, 2002a; Díaz-Maroto, Pérez-Coello, González-Viñas, & Cabezudo, 2003). However, freeze-dried skins maintained their volatile and phenolic composition in comparison with the original skins, better than those which were oven-dried (de Torres et al., 2010). Freeze-drying is based on the dehydration by sublimation of a frozen product. Due to the absence of liquid water and the low temperatures required, a final product of excellent quality is obtained.

The purpose of this study was first to assess the impact of the freeze-drying process on the aroma and polyphenol potential of white skins obtained from grape wastes, in order to obtain a stable and quality product. Grape wastes were obtained after vinification of white wines from grapes of *Vitis vinifera* var. Muscat, one of the main white aromatic varieties. Freeze-drying was chosen after conducting a preliminary study on the effect of different drying methods (freeze-drying, oven drying at 45 °C and oven-drying at 30 °C) on the aroma quality of white grape skins. Then, the freeze-dried skins were used to improve the aroma of white wines obtained from grapes of *Vitis vinifera* var. Airén, a neutral grape variety and the most representative in the "La Mancha" region, Spain.

2. Materials and methods

2.1. Samples

White vinification by-products of *Vitis vinifera* (var. Muscat) were obtained from the experimental winery of the University of Castilla-La Mancha (Ciudad Real, Spain). They included pomace, a mix of skins and seeds. Seeds were manually separated from skins immediately after receipt, and all skins were stored at −78 ° C until dehydrated.

Frozen Muscat skins were freeze-dried under vacuum (2.4×10^{-2} mB) for 24 h. The condenser temperature was -49 ± 2 °C. The initial moisture content of the fresh skins was 73.5% dry weight, and the dried material had a moisture content of 9.5% dry weight. The freeze-drying conditions were selected in a preliminary study, where fresh Muscat skins were divided in four batches. One batch was refrigerated at 5 °C for analysis in fresh. The other three batches were immediately dried using different drying methods (freeze-drying, oven drying at 45 °C and oven drying at 30 °C). Three replicates of each treatment were performed. The drying conditions employed were previously selected after conducting trials to achieve a percentage moisture content of less than 10% using the shortest possible time.

White wines were obtained from grapes of *Vitis vinifera* var. Airén (a neutral white grape variety, the majority in Castilla-La Mancha). Laboratory fermentations were performed in 3 L vessels. One of them contained only Airen must, the other one had Airen must with 500 g of fresh Muscat skins (25%), and the last one had 145 g of freeze-died Muscat skins (25%). After 15 h at 18 °C (Sánchez-Palomo, González-Viñas, Díaz-Maroto, Soriano Pérez, & Pérez-Coello, 2007) skins were removed, and all the samples were inoculated with *Saccharomyces cerevisiae* (CECT no. 10835). Fermentations were conducted at 18 °C in duplicate.

When fermentation was finished, wines were centrifugated (5000 rpm, 8 °C, 15 min) and stored under refrigeration until their analysis.

OIV (1990) Official methods were used for wine conventional analytical data.

2.2. Analysis of volatile compounds of fresh, oven dried and freeze dried Muscat grape skins

A microscale simultaneous distillation–extraction apparatus (Chrompack, Middelburg, The Netherlands) was used as previously described (Godefroot, Sandra, & Verzele, 1981) to extract skin volatile compounds. An amount of 5 g of Muscat grape skins in 40 mL of water with 10 μL of 4-nonanol solution (0.5 g/L) 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.

One microliter (1 μL) of the extract was injected in splitless mode (0.5 min) for analysis into an Agilent Technology 6890 N Network GC System equipped with an Agilent Technology 5973 inert mass selective detector. The column used was a BP-21 capillary column (60 m × 0.25 mm × 0.25 μm). The injector temperature was 250 °C, and the oven temperature was programmed as follows: 70 °C (5 min) first ramped at 1 °C/min to 95 °C (10 min) and then ramped at 2 °C/min to 200 °C (40 min). The carrier gas was helium at 1 mL/min flow rate, and the MS operated in the electron impact mode with electron energy of 70 eV, ion source temperature of 178 °C and scanning from 40 to 450 a.m.u.

The identification was based on comparison of the mass spectra with those provided for authentic standards and by the NBS75K and Wiley A libraries. Response factor of each volatile compound was calculated by injection of commercial standards. For compounds which commercial standards was not available, the response factors of compounds with similar chemical structures were used (*cis*-furan-linalool oxide for *trans*-furan-linalool oxide, *cis*-pyran-linalool oxide and *trans*-pyran-linalool oxide; linalool for 2,6-dimethyl-3,7-octadiene-2,6-diol, 2,6-dimethyl-1,7-octadiene-3,6-diol and 3,7-dimethyl-1,7-octanediol; β-damascenone for vitispirane; (*E,E*)-2,4-decadienal for (*E,Z*)-2,4-decadienal; guaiacol for vinylguaiacol; and furfural for 2-pentyl furan).

2.3. Analysis of volatile compounds of control and macetated wines

For the analysis of the major volatile compounds, 1.5 mL of wine sample were spiked with 90 μL of 2-pentanol as internal

Table 1
Concentrations of volatile compounds (μg/Kg) extracted from fresh and different dried Muscat skins.

Compounds	RI	Fresh Muscat skins	Freeze-dried Muscat skins	Oven-dried Muscat skins at 45 °C	Oven-dried Muscat skins at 30 °C
		$\overline{X} \pm SD$	$\overline{X} \pm SD$	$\overline{X} \pm SD$	$\overline{X} \pm SD$
Hexanal	1084	$535.8^{a} \pm 29.3$	$414.5^{b} \pm 39.1$	$77.7^{c} \pm 10.6$	$106.2^{d} \pm 7.6$
E-2-Hexenal	1215	$687.4^{a} \pm 63.3$	$546.7^{b} \pm 56.8$	$67.5^{c} \pm 6.5$	$94.3^{d} \pm 8.4$
1-Hexanol	1353	$87.2^{a} \pm 23.3$	$42.6^{b} \pm 4.2$	$4.5^{c} \pm 0.3$	$0.0^{d} \pm 0.0$
Furfural	1447	$0.0^{a} \pm 0.0$	$5.7^{b} \pm 0.8$	$227.7^{c} \pm 28.5$	$202.0^{c} \pm 14.6$
5-Methylfurfural	1540	$0.0^{a} \pm 0.0$	$0.0^{a} \pm 0.0$	$6.3^{b} \pm 0.9$	$4.1^{c} \pm 0.6$
Linalool	1570	$2959.7^{a} \pm 461.5$	$3055.2^{a} \pm 618.4$	$2185.2^{a} \pm 300.0$	$2022.6^{a} \pm 351.6$
Hotrienol	1620	$592.5^{a} \pm 150.9$	$616.4^{a} \pm 2.3$	$528.7^{a} \pm 107.8$	$539.6^{a} \pm 109.5$
α-Terpineol	1646	$595.8^{a} \pm 23.7$	$569.4^{a} \pm 45.9$	$549.2^{a} \pm 64.1$	$502.2^{a} \pm 57.5$
Nerol	1824	$332.3^{a} \pm 18.6$	$281.1^{a} \pm 56.2$	$183.1^{b} \pm 38.7$	$194.6^{b} \pm 21.3$
trans-Geraniol	1849	$1125.2^{a} \pm 52.9$	$1056.3^{a} \pm 189.6$	$599.5^{b} \pm 96.0$	$558.4^{b} \pm 77.4$

Different superscripts (a, b, c, d) in the same row indicate statistical differences at the 0.05 level according to the Student–Newman–Keuls test.
RI, retention index (BP-21, 0.25 μm).