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# The phenolic chemistry and spectrochemistry of red sweet wine-making and oak-aging

M. Figueiredo-González [a], B. Cancho-Grande [a], J. Simal-Gándara [a,*], N. Teixeira [b], N. Mateus [b], V. De Freitas [b]

[a] Nutrition and Bromatology Group, Analytical and Food Chemistry Department, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E-32004 Ourense, Spain
[b] Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal

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ABSTRACT

A natural sweet wine (NSW) was made with dried grapes from *Vitis vinifera* L. cv Garnacha Tintorera. A fortified sweet wine (FSW) was also obtained: the maceration-alcoholic fermentation of Garnacha Tintorera must was stopped by addition of ethanol 96% (v/v). UV/Vis spectrophotometry and HPLC/DAD-ESI/MS were applied to determine, respectively, the evolution of colour and phenolic compounds in Garnacha Tintorera based-sweet wines during aging. In sweet wines, aging decreased a* (red/green), colour saturation and lightness and increased b* (yellow/blue), and hue angle. Most of the phenolic compounds determined, such as anthocyanins, esters of hydroxycinnamic acids, flavan-3-ols monomers, oligomers and polymers decreased in both sweet wines during aging. On the contrary, hydroxybenzoic and hydroxycinnamic acids and vitisins increased after one year of aging. Despite that both terminal and extension subunit compositions show very small changes, mean degree of polymerisation of proanthocyanidins decline slightly as aging progressed in both sweet wines.



## 1. Introduction

Sweet wines are traditionally elaborated in Galicia (the N.W. corner of Spain). The Denomination of Origin (DO) Valdeorras, one of the five DOs in Galicia, wants to promote the production and marketing of new sweet wines. The following red wines were examined in this work. The first one, a naturally sweet wine (NSW) was made with dried grapes *Vitis vinifera* L. cv Garnacha Tintorera; this cultivar is a teinturier variety which has excellent potential to produce wines from raisined grapes. The second one, a fortified sweet wine (FSW); the maceration-alcoholic fermentation of Garnacha Tintorera must was stopped by addition of ethanol 96% (v/v). Additionally, both sweet wines were subjected to aging process in French oak barrels.

The colour changes during wine maturation are usually attributed to anthocyanin polymerisation reactions with other phenolic compounds, such as flavan-3-ol monomers. The formation of these polymeric pigments by direct and/or mediated by acetaldehyde reactions can usually lead to the loss of colouring matter if the polymerised pigments reach high molecular weight (Alañón et al., 2013). The cycloaddition process between anthocyanins and some yeast metabolites such as vinylphenol, pyruvic acid, acetaldehyde leading to more stable pigments, structurally allied to pyranoanthocyanins, is described as other type of reactions established in wines (Atanasova, Fulcrand, Cheynier, & Moutounet, 2002). The formation of these pigments remains in solution and therefore they hardly are lost in the precipitates of colouring matter. Recently, it has been detected the formation of hydroxyphenylpyranoanthocyanins such as pinotin A in wines during the aging process (Rentzsch, Schwarz, Winterhalter, & Hermosín-Gutiérrez, 2007). Instead, Oliveira, De Freitas, Silva, and Mateus (2007) detected a new class of blue anthocyanin-derived pigments isolated from Port wines, namely portisins (formed from anthocyanins–pyruvic acid adducts and vinyl phenols) and a new family of turquoise blue anthocyanin-derived pigments (Oliveira et al., 2010).

The physical and chemical characteristics of wood are also important quality factors in the wine aging process, since they affect the wood-wine interaction phenomena, such as oxygen-diffusion, compound extraction from wood, and oxidation processes in wines (Hernández, Estrella, Dueñas, De Simón, & Cadahía, 2007).

Although the quality of sweet wine is determined essentially by aroma compounds, colour and phenolic compounds are also significant sensory attribute of wines. The preservation of the optimal chromatic characteristics during the aging process is the main problem of this type of dessert wine, more than the maintenance of aromatic compounds. Therefore, evolution of colour and phenolic compounds during aging process was established in Pedro

* Corresponding author.
*E-mail address:* jsimal@uvigo.es (J. Simal-Gándara).

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Ximénez wines (Chaves, Zea, Moyano, & Medina, 2007; López de Lerma, Peinado, Moreno, & Peinado, 2010; Serratosa, Lopez-Toledano, Medina, & Merida, 2011); in Sherry wines (Fabios, Lopez-Toledano, Mayen, Merida, & Medina, 2000; García-Moreno & García-Barroso, 2002; García-Parrilla, Heredia, and Troncoso, 1999; Ortega, Mayen, Merida, & Medina, 2008; Schwarz, Rodríguez, Guillén, & Barroso, 2012); and Port wines (Mateus & De Freitas, 2001; Oliveira, De Freitas, Silva, & Mateus, 2007; Oliveira et al., 2010; Romero & Bakker, 1999).

In order to obtain a good-quality sweet wine, the aim of this work was to evaluate the colour and phenolic composition from different Garnacha Tintorera-red sweet wines during the aging process. By this way, with the understanding of the evolution of colour-responsible phenolic pigments during aging in red sweet wines obtained under different practices, it could be possible to optimise the best conditions to obtain a sweet aged wine based on their colour and taste balance. In addition, this research may also contribute to the listing of technical support information for the others Geographic indications of origin of sweet wines, since it is the first detailed study on Garnacha Tintorera based-sweet wines during the aging process.

## 2. Materials and methods

### 2.1. Sweet wines

Red grapes of *Vitis vinifera* L. cv Garnacha Tintorera were harvested in Valdeorras (Ourense, N.W. Spain). Two vinification experiments were performed at the experimental cellar belonging to DO Valdeorras Regulatory Council:

(a). Garnacha fortified sweet wine (NSW)

This wine is a naturally sweet wine made with Garnacha Tintorera grapes harvested and dehydrated in 2011 such as follows. Red grapes were harvested at optimum ripening stage, and were left in plastic boxes for 3 months to carry out the drying process in order to concentrate sugars under natural conditions of temperature and relative humidity. Bunches of grapes were placed in a single layer in each box and checked weekly, removing the spoiled grapes manually for the purpose of getting the best conditions of raisining. In December, at first, the grapes were crushed in the traditional manner. Then the pressing of the resulting paste was completed using a hydraulic press of 25 kg and the must was placed in a metallic fermentation vessel (25 L). After 24 h, *Saccharomyces cerevisiae* Fermol Super 16 (AEB Group) yeasts were inoculated. One week later, the alcoholic fermentation began and it lasted one month at room temperature (around 18–20 °C). At the end of the fermentation, the wine was subjected to aging process during one year in French oak barrels

(b). Garnacha fortified sweet wine (FSW)

This wine is a fortified sweet wine made with Garnacha Tintorera grapes harvested at 2011 such as follows. Red grapes were crushed again in the traditional manner and placed in a metallic fermentation vessel (25 L) to which was added $SO_2$ at a 40 mg $L^{-1}$concentration. After 24 h, *S. cerevisiae* commercial yeasts were inoculated. When it reached an alcohol content of 7.5° of alcohol, the maceration-alcoholic fermentation was stopped by addition of ethanol 96% (v/v). Afterwards this wine was subjected to aging process during one year in French oak barrels.

### 2.2. Characterisation of the colour fraction

Colour measurements were taken after centrifugation of the wines for 15 min at 3000 rpm and using quartz cells of 1 mm path length.

#### 2.2.1. Colorimetric indexes

Absorbances at 420, 520, 620 nm were measured to assess the wine colour by chromatic parameters such as % red, % yellow and % blue, colour intensity (CI), tonality (T), according to Glories (1984).

#### 2.2.2. CIELAB space

The wine colour was also assessed by the CIELAB space (OIV, 2000). CIELab colour parameters were determined by measuring the transmittance of the must every 10 nm over the visible spectrum (from 380 to 770 nm), using the illuminate $D_{65}$ (daylight source) and 10° standard observer (perception of a human observer). The parameters that define the CIELab space are: rectangular coordinates such as red/green colour component ($a^*$), yellow/blue colour component ($b^*$) and lightness ($L^*$); and the cylindrical coordinates such as chroma ($Cab*$) and hue angle (hab).

### 2.3. Characterisation of the phenolic content

#### 2.3.1. Analytical standards, reagents and materials

Malvidin-3-*O*-glucoside chloride, catechin, epicatechin, resveratrol, and gallic, 3,5-dihydroxybenzoic, protocatechuic, vanillic, syringic, *p*-coumaric and caffeic acids were purchased from Sigma Aldrich (St. Louis, MO, USA). B1, B2, B4, B6, C1, B3, B5, B7, B8, and B2-gallate were previously isolated in the laboratory. Individual stock solutions of each compound were prepared in methanol. Different working standards solutions were prepared by appropriate dilution in 12% (v/v) ethanol in water and then stored in dark vials at −80 °C.

Solvents (water, methanol, acetone and ethyl acetate) of HPLC grade and other inorganic reagents (formic, hydrochloric, acetic, trifluoroacetic and ascorbic acids, phloroglucinol, sodium acetate anhidro, sodium hydroxide and sodium bisulphite) were purchased from Sigma Aldrich.

The sorbent material used for SPE was: Oasis MCX cartridges (500 mg, 6 mL size) from Waters Corp (Milford, MA, USA); Strata-X-A 33u Polymeric Strong Anion sorbent (60 mg, 3 mL size) and Strata C18-E (2 g, 12 mL size) from Phenomenex (Torrance, CA, USA) and gel TSK Toyopearl HW-40(S) (250 × 25 mm) from Tosoh, Japan.

#### 2.3.2. Extraction procedures

Extraction of these groups of polyphenols was performed according to procedures described by Figueiredo-González, Regueiro, Cancho-Grande, and Simal-Gándara (2014).

*2.3.2.1. No flavonoids.* Ethanol of wine samples were previously evaporated under a stream of nitrogen and reconstituted with water. 3 mL of the reconstituted wine (adjusted to pH 7 with sodium hydroxide) was loaded into a MCX cartridge previously activated with 5 mL of methanol followed by 5 mL of water. The sorbent was washed with 5 mL 0.1 M hydrochloric acid followed by 5 mL of water. The no flavonoid fractions were eluted with 15 mL of methanol. The eluate was evaporated down (35 °C, 10 psi) and and then reconstituted in 12% (v/v) EtOH. The ethanolic extract was passed through a filter of 0.45 μm pore size prior to HPLC/DAD-ESI/MS analysis.

*2.3.2.2. Anthocyanins.* Ethanol of wine samples were previously evaporated under a stream of nitrogen and reconstituted with water. 2 mL of the reconstituted wine was loaded into a Strata C18 cartridge, previously activated with 10 mL of methanol followed by 10 mL of water. The sorbent was dried by blowing $N_2$ for 30 min. After washing with of 20 mL of ethyl acetate, the anthocyanin fraction was eluted with 30 mL of 0.1% (v/v) trifluoroacetic acid in methanol. The eluate was evaporated down (35 °C, 10 psi)