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Volatile and phenolic composition of red wines subjected to aging in oak cask of different toast degree during two periods of time

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ABSTRACT

Volatile aroma compounds of Fetească neagră wines, aged for 1.5 and 3 months in oak barrels with different toast degree, have been analyzed using stir bars sorptive extraction and gas chromatography coupled to mass spectrometry. Principal components analysis of the volatile aroma permits wine differentiation according to the toast degree of the barrels used and also according to aging time. Wine fingerprints were obtained using the aromatic series. Cluster analysis showed that the differences among wines due to the toast degree of the barrels become progressively larger with aging time. Regarding phenolic families, flavonols and flavanols increased with aging time, whereas polymeric compounds decreased due to the precipitation phenomenon. The wines aged in light toast barrels were those with the higher phenolic concentration. The toast degree and the aging time influence significantly the aroma and phenolic composition of the aged wines. Sensory analysis indicated that wines aged for 3 months show the best valuation, highlighting those aged in barrels with medium toast degree. All these changes must be taken into account by the winemaker in order to produce wine with the best quality.

1. Introduction

Aging of red wines in oak barrels is an ancient art steeped in tradition aimed at improving wine quality and complexity contributing to the enhancement of its sensory characteristics (structure, astringency and persistence) and increased stability. Barrel contact modifies wine composition due to the compounds that are extracted from wood, such as volatile compounds.

Qualitative and quantitative volatile compounds extracted from oak barrels depends on several factors, including the botanical and geographic origin of the wood, the degree of the oak toast, the rate of release of the volatiles (mainly influenced by the contact time between wine and wood) and by the numbers of reuse of the oak barrels (Cadahía, Fernández de Simón, & Jalocha, 2003; Crump, Johnson, Wilkinson, & Bastian, 2015; Li et al., 2015).

During barrel production, the oak pass through several processing stages which influence the final wine aroma and flavor. After being split, the wood is submitted to a drying process to ensure the mechanical resistance of the barrels. In order to give form to the barrels the wood is heated. Usually, three types of toasting are used: light, medium and medium plus. This stage is considered one of the most important because its influence on the chemical composition of oak wood. The thermal treatment causes degradation of some components which produces numerous volatile compounds. When the lignin degrades volatile phenols such as guaiacol, aromatic aldehydes such as vanillin and syringaldehyde are generated. Also, the degradation of hemicelluloses produces furanic compounds such as furfural and 5-methyl furfural (Chatonnet, Cutzach, Pons, & Dubourdieu, 1999; Garde-Cerdán & Ancín-Azpilicueta, 2006).

During aging, the phenolic composition of the wine is also modified due to copigmentation, condensation and polymerisation phenomena and also, because some phenolics, mainly ellagitannins, are released to the wine (García-Puente Rivas, Alcalde-Eon, Santos-Buelga, Rivas-Gonzalo, & Escribano-Bailón, 2006). The ellagitannins act as regulators of oxidation, accelerating condensation between flavanols and between flavanols or tannins with anthocyanins. In addition, the ellagitannins can also form flavano-

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ellagitannins or anthocyano-ellagitannins compounds (Moreno & Peinado, 2012). These reactions modify the astringency of the wine. Wine color is also modified from an initial purple-red hue typical of young red wines to a brown-red hue, characteristic of aged wines (García-Estévez, Alcalde-Eon, Le Grottaglie, Rivas-Gonzalo, & Escribano-Bailón, 2015).

The differences among wines from the same winemaking region, harvested in the same year, at the same ripe stage and subjected to the same pre-fermentative and fermentative treatments, but aged in barrels with different toast degree and during different periods of time should be addressed in order to helps the winemakers to classify the wines according to its analytical composition. In the last years, the analytical techniques have come a long way, allowing simultaneous determination of a wide range of analytes. On the other hand, more comprehensive data mining and data analysis have been developed. Both facts, allows to obtain a better grape, must and wine discrimination and classification. In this sense, the use of Gas Chromatography (GC), coupled to Mass Spectroscopy (MS), in combination with analyte enrichment techniques, as is the Stir-Bar-Sorptive Extraction (SBSE), is revealed as a powerful integrated platform for the analysis of the volatile compounds present in grape, must or wine samples (Arbulu et al., 2013; Gómez García-Carpintero, Sánchez-Palomo, Gómez Gallego, & González-Viñas, 2012; Vararu, Moreno-García, Zamfir, Cotea, & Moreno, 2016; Zalacain, Marín, Alonso, & Salinas, 2007). In this sense, the volatile profile of wines and the use of aromatic series is a useful tool allowing an objective and rapid control and classification of wine and derivates (Lopez de Lerma, Bellincontro, Mencarelli, Moreno, & Peinado, 2012; López de Lerma & Peinado, 2011; Noguerol-Pato, Sieiro-Sampredro, González-Barreiro, Cancho-Grande, & Simal-Gándara, 2014; Peinado, Moreno, Bueno, Moreno, & Mauricio, 2004).

The aim of this work is to apply SBSE–GCMS, and statistical tools for the objective differentiation of Feteasca neagra wines aged for 1.5 and 3 months in oak barrels with three different toast degree. Also, phenolic fractions of the wines have been analyzed and sensory analyses have been carried out.

2. Material and methods

2.1. Fermentation and aging conditions

Feteasca neagra red grapes (*V. vinifera*), from North-East Romania winemaking region, were harvested in their optimal ripening stage. Stalking and crushed bunches, were subjected to maceration–fermentation process at 10–12 °C, for 7 days. At this point, sulphur dioxide was added to a final concentration of 60 mg/L. After this, grapes were pressed and the juice obtained was added to the fermentation tank. At the end of the alcoholic and malolactic fermentation, the wine was transferred to three new barrels from *Quercus robur* oak species with different toast degree: Light Toast (LT); Medium Toast (MT); Medium Plus Toast (MT+). Free sulphur dioxide was adjusted at 35 mg/L. The wines were aged during 1.5 and 3 months.

2.2. Analytical parameters

pH, reducing sugars, titratable acidity, sulphur dioxide and volatile acidity were quantified by the official European Union methods (CEE., 1990). Ethanol was determined by oxidation with dichromate (Crowell & Ough, 1979).

Absorbance at 420, 520 and 620 nm were measured in a Perkin Elmer Lambda 25 spectrophotometer, after filtering the samples through a HA-0.45 μm paper (Millipore, Milford, MA).

2.3. Major aroma compounds

Major volatile compounds were quantified with a gas chromatograph HP 6890 Series II equipped with a capillary column with molten silica CP-WAX 57 CB (50 m in length, 0.25 mm in internal diameter and 0.4 μm in coating thickness) and a Flame ionization detector. Chromatographic conditions and sample preparation were those described by (Peinado, Moreno, Muñoz, Medina, & Moreno, 2004). Identification and quantification of the major volatile compounds was carried out by using standards submitted to the same treatment as the analyzed samples.

2.4. Minor aroma compounds

2.4.1. Extraction of minor aroma

Aroma extraction was carried out according to (Tredoux et al., 2008) with minor changes. Stir bars (0.5-mm film thickness, 10-mm length, Gerstel GmbH, Mülheim an der Ruhr, Germany) coated with PDMS were used. The wine samples were diluted tenfold with a hydroethanolic solution (12% ethanol (v/v) and pH 3,5). The stir bars were placed in a 10 mL glass headspace vials containing 10 mL of the diluted sample and 0.1 mL of ethyl nonanoate (0.4464 mg/L) as internal standard. The vials were sealed with a Teflon-coated crimp cap and they were stirred at 1500 rpm at 25 °C for 100 min. After removal from the wine sample, the stir bars were softly dried with lint-free tissues and then transferred into glass thermal desorption tubes for GC/MS analysis.

2.4.2. Determination of minor aroma

The glass thermal desorption tubes were introduced into a GC/MS equipped with a Gerstel TDS 2 thermodesorption system. The stir bars were heated to release and transfer the extracts into a cooled injection system/programmed temperature vaporizer (CIS 4 PTV) containing a tenax adsorption tube. The thermal desorption was carried out with a temperature program from 35 °C, ramped at 120 °C min^{-1} to 280 °C and held for 10 min; the helium flow rate was 3 mL/min. The CIS injector was held at 25 °C for the total desorption time and then ramped at 12 °C s^{-1} in splitless mode to 280 °C and held for 7 min.

The GC was fitted with an Agilent-19091S capillary column 30 m × 0.25 mm i.d., 0.25 μm film thickness. Helium was used as carrier gas with a column flow rate of 1 mL min^{-1}. The GC oven temperature was programmed as follows: 50 °C for 2 min, ramped at 4 °C min^{-1} to 190 °C, held for 10 min. The mass detector was used at 1850 V in the scan mode and the studied mass range spanned values from 39 to 300 amu. Retention times, spectral libraries supplied by Wiley (version 7 N) and pure chemical compounds obtained from Merck, Sigma–Aldrich, Riedel de Haën, and Fluka were used for identification, confirmation and preparation of standard solutions of the volatile compounds. Each compound was quantified from its calibration curve, which was obtained by using standard solutions of known concentrations previously subjected to the same treatment as the samples in conjunction with the target and qualifier ions selected for each compound by the Hewlett–Packard Chemstation (Palo Alto, CA).

2.5. Fractionation of phenolic compounds and enzymatic determination

Prior to assay, ethanol was removed from wine samples on a rotary evaporator and the initial volume was re-established with distilled water. The procedure used to obtain the phenolic fractions was carried out according to (Kim & Lee, 2001). Phenolic compounds were fractionated by using tC-18 SepPak columns. The phenolic acids, and their respective esters (fraction 1), were eluted with 5 mL