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The effect of in-amphorae aging on oenological parameters, phenolic profile and volatile composition of Minutolo white wine

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ABSTRACT

A wine was obtained from cryomacerated *Minutolo* grapes under reductive conditions and aged for 12 months in glass container and in 3 types of amphorae. After aging, wines in glass containers showed the highest alcohol content, volatile acidity, dissolved oxygen, concentrations of aromatics, alcohols, and esters and by the lowest contents of enols and terpenes. They also showed the highest decrease of flavonoids, hydroxycinnamoyl tartaric acids, and procyanidins. Wines in raw amphorae showed the dramatic decrease of flavonoids and flavans reactive with vanillin. The highest antioxidant activity was exhibited by wines in engobe amphorae, while the lowest values were showed by the wines in glass containers and glazed amphorae. Caftaric acid and procyanidin B3 decreased in wine aged under glass while epicatechin mainly reduced in raw amphorae.
According to the Principal Component Analysis, the wines resulted homogeneously grouped as a function of the type of container in which were aged.

1. Introduction

Wine contains different chemical substances that influence the sensory characteristics of the final product. Amount and type of these components can be opportunely modified by managing viticultural practices, winemaking process, aging, and type of containers and closures.

Phenolic compounds are important components of wine. They not only contribute to their sensory profiles, such as color, flavor and astringency (Lee & Jaworsky, 1987), but may also act as antioxidants, with mechanisms involving both free-radical scavenging and metal chelation (Benítez, Castro, Sánchez Pazo, & Barroso, 2002). The composition and concentration of phenolic components in wine depends not only on grape variety and wine-making procedures, but also on the chemical reactions that happen during aging (Peña-Neira, Hernández, García-Vallejo, Estrella, & Suarez, 2000).

A fundamental role in wine sensory profile and consumer preferences is also played by volatile compounds. The aromatic profile of wine is the result of important modifications deriving from esterification, hydrolysis, redox reactions, slow and continuous diffusion of oxygen, spontaneous clarification, and CO_2 elimination (Camara, Alves, & Marques, 2006). As a result of these physical and chemical changes, the volatile fraction is extremely complex, accounting for more than 1000 compounds (Poláková, Herszage, & Ebeler, 2008), which belong to different chemical classes, and cover a wide range of polarities, solubility, and volatility values.

Aging can be made in different containers, such as stainless steel tanks, oak barrels, clay vessels, with the aim of enhancing wine flavor. Stainless steel tanks are inert containers while wood and clay interact with wine. Aging in wood changes color, structure, phenolic profile (Tesfaye, Morales, García-Parrilla, & Troncoso, 2002) and aroma (Callejón, Morales, Silva Ferreira, & Troncoso, 2008) since it is a material enable to make a micro-oxygenation of wine and to release phenolic and aromatic substances while adsorbing other wine components. However, in the case of white wines the aging in oak barrels is not always advantageous since both the oxygen could oxidize the wine and

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the wood deriving components completely mask its sensory characteristics (Ortega-Heras, González-Sanjosé, & González-Huerta, 2007).

In the remote past, clay vessels have been used to store, trade, and serve wine. The most common transport container was amphora. "Qvevri" is the vessel used for the Georgian traditional winemaking procedures, which includes fermentation of grape must on all or part of the grape pomace (skins, seeds, stems) and aging of wine. Lanati et al. (Lanati, Marchi, & Mazza, 2001) studied the Georgian white wines produced according to the ancient technology that employs Kakhetiana amphorae, during fermentation, maceration and aging. They found that the Kakhetian white wines are characterized by dark, almost orange color, which is very different from those of the other white wines. Today the production of in-amphorae wines is becoming interesting but scientific literature concerning this type of aging system lacks. Baiano et al. (2013), Baiano et al. (2013) studied the effects in-amphorae aging on physico-chemical indices and antioxidant compounds of *Falanghina* and *Fiano passito* wines showed that the characteristics of wines were affected both by aging time and types of containers. The aging wines in three types of amphorae (raw, glazed and engobe) showed similar evolution of physical and chemical characteristics, while those stored in stainless steel tanks had a different trend.

The aim of this research was focused on the study of the effects of in-amphorae aging on quality, phenolic profile and volatile composition of an Italian white wine made from *Minutolo* grapes. The study was performed by conventional analysis, gas chromatography and NMR spectroscopy in combination with multivariate statistical analysis.

2. Materials and methods

2.1. Wine samples

Minutolo grapes produced in vineyards of Apricena (Foggia, Italy) were picked early in the morning in the second week of September 2013 and immediately delivered to a pilot plant (Foggia, Italy) made of a crusher-destemmer, 20 stainless steel vats (100 L-capacity), a temperature management system, and 2 wine presses. At harvesting, grapes had the following characteristics: sugar content 18.5 ± 0.4 °Brix; titratable acidity 6.0 ± 0.3 g tartaric acid/L and pH 3.53 ± 0.07.

Grapes were submitted to a winemaking procedure, which included a cryomaceration step and a reductive vinification, according to a previous work (Baiano et al. (2013)). After fermentation, the wines were submitted to a first racking and, after four weeks of decantation, they were transferred into the aging containers. Each vinification was repeated two times, using about 120 kg of grapes for each trial, and every time, 3 samples were withdrawn.

According to Baiano et al. (2013), Baiano et al. (2013), wines were stored for 12 months in three types of earthenware amphorae: raw, glazed, and engobe. The wine stored in glass containers was used as a control.

2.2. Conventional analyses of wine

Wines were analyzed before the transfer into the aging containers and each two months during 12-months of aging. Alcoholic strength at 20 °C (expressed as % vol.), titratable acidity (expressed as g of tartaric acid/L), volatile acidity (g acetic acid/L), density (g/L), dry extract (g/L), and free and total sulphur dioxide (mg/L) were determined according to the EEC Regulation 2676, 2676/1990. The residual sugar content was measured through a Digital Wine Refractometer (WM-7, ATAGO, Tokyo, Japan) and expressed as °Brix. Dissolved oxygen (mg/L) was measured by using a LDO-HQ10 portable oxygen meter (Hach, Düsseldorf, Germany). The evaluation of the redox potential (EH) was performed with a CyberScan pH 510 (Eutec Instruments, Nijkerk, Netherlands) equipped with an encapsulated Ag/AgCl electrode (Crison, Lainate, MI, Italy). The EH were expressed in mV. pH values were measured with a CyberScan pH 510 (Eutec Instruments, Nijkerk, Netherlands) calibrated with buffer solution at pH 4.00 and 7.00 (Crison, Lainate, MI, Italy).

2.3. Determination of phenolic compounds, phenolic profile, and antioxidant activity

The total phenolic content was measured at 765 nm through an UV-visible spectrophotometer (Cary 50 SCAN; Varian, Palo Alto, CA) according to the Folin-Ciocalteu method as reported by Singleton and Rossi (1965). Results were expressed as gallic acid equivalents (mg/L of wine). A calibration line was built on the basis of solutions of known and increasing concentrations of gallic acid (Extrasynthèse, Genay, France). The various phenolic classes were analyzed according to the methods of Di Stefano et al. (Di Stefano, Cravero, & Gentilizi, 1989) and Di Stefano and Cravero (1991). When necessary, the extracts were opportunely diluted with aliquots of the extraction solution. The results were expressed as mg per L of wine.

The phenolic profiles of wine were analyzed by HPLC-DAD-ESI-MS/MS. The chromatographic analyses were performed according to the method described by Crupi et al. (2012), with some changes. A Capillary HPLC 1100 Series system, equipped with a degasser, quaternary pump, thermostated column compartment, diode array detector and MSD Trap XCT Plus in a series configuration (Agilent Technologies, Palo Alto, California, U.S.A.) coupled with an ESI interface was used. The reversed stationary phase employed was a Poroshell 120 SB-C18 2.7 μm (150 × 2.1 mm i.d., Agilent Technologies) thermostated at 40 °C. The following gradient system was used with water containing 1% formic acid (solvent A) and acetonitrile (solvent B): 0 min, 0% B; 2 min, 5% B; 10 min, 13% B; 25 min, 15% B; 30 min, 22% B; 50 min, 22% B; 55 min, 95% B; 65 min, 95% B; 66 min, 5% B; stop time to 66 min followed by washing and re-equilibrating the column. The flow was maintained at 0.2 mL/min; sample injection was 8 μL. Diode array detection was between 250 and 650 nm, and absorbance was recorded at 280, 313, 350 and 520 nm. Both positive and negative electrospray mode were used for ionization of molecules with capillary voltage of 3500 V and a skimmer voltage at 40 V. The nebulizer pressure was 40 psi and the nitrogen flow rate was 8 L/min. Temperature of drying gas was 350 °C. The monitored mass range was from *m/z* 50 to 1200. Wine samples were filtered through a 0.45 μm syringe Cellulose Acetate filter prior to HPLC injection. Identification was achieved by combining different information: elution pattern, UV-Vis and MS spectra, MS/MS fragmentation patterns and with the help of structural models already hypothesized in the literature. Quantification was made using the external standard method. The calibration curves were obtained by injection of standard solutions under the same conditions used for the samples and over the range of concentrations observed. All phenolic compounds were expressed in (+)-catechin equivalents (CE, mg/L; $R^2 = 0.9945$).

The evaluation of the antioxidant activity was made through the 1,1-diphenyl-2-picrylhydrazyl (DPPH) (Brand-Williams, Cuvelier, & Berset, 1995), and 2,2-azinobis-(3-ethylbenzothiazoline)-6-sulfonic acid (ABTS) (Re et al., 1999) assays and the results were expressed as mmol of Trolox equivalents/L of wine.

2.4. Determination of volatile composition

Volatile composition of wine was analyzed by head-space solid phase microextraction hyphenated with gas chromatography – mass spectrometry (HS-SPME-GC-MS). The chromatographic analysis were performed according to the method described by Canuti et al. (2009) and Tao et al. (Tao, Li, Wang, & Zhang, 2008), opportunely modified. For HS-SPME-GC-MS analyses, wine samples (5,0 mL) were transferred into a 20 mL glass headspace vials containing 1 g of NaCl; 2,5 μL of a octan-3-ol internal standard solution (83 mg/L^{-1} in ethanol) were added to each vial. The mixtures were carefully shaken to dissolve NaCl and then left to equilibrate 1 h in the dark at room temperature before the analysis.