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Experimental design approach to evaluate the impact of oak chips and micro-oxygenation on the volatile profile of red wines

C. Pizarro *, S. Rodríguez-Tecedor, I. Esteban-Díez, N. Pérez-del-Notario, J.M. González-Sáiz

Department of Chemistry, University of La Rioja, C/Madre de Dios 51, 26006 Logroño, La Rioja, Spain

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ABSTRACT

A chemometric strategy based on combining an experimental design approach and response surface methodology was applied to gain further knowledge on the influence of chip maceration and micro-oxygenation related factors (oxygen doses, chip doses, wood origin, toasting degree and maceration time) on the volatile profile of red wines during the accelerated ageing process. The results obtained indicated that the volatile profile of wines could be modulated by applying different combinations of factor conditions. Thus, these results would be used to obtain wines with specific volatile profiles that would lead to particular olfactory attributes according to consumers' preferences. Moreover, it was shown that combining wood from different origins helped enhance the quality of the elaborated wines. To the best of our knowledge, this is the first time that an experimental design methodology has been applied to simultaneously evaluate the influence of five different ageing parameters on the volatile profile of red wines.

1. Introduction

Oak barrels have commonly been used in red wine maturation due to the benefits that oak wood contact involves. Wood allows a slow and continuous diffusion of oxygen through its pores and the extraction of many compounds (volatile compounds, tannins and phenolic acids), resulting in an improvement in wine quality and an enhancement of its organoleptic characteristics. In particular, the enrichment in aromatic compounds increases aroma complexity, which is highly appreciated in quality red wines (Escalona, Birkmyre, Piggott, & Paterson, 2002). Nevertheless, ageing wine in barrels requires long periods of contact time. This fact, together with the high price of barrels, their limited lifetime, and the large space and maintenance required, make traditional maturation systems a costly and laborious process (Garde-Cerdán & Ancín-Azpilicueta, 2006).

Therefore, the demand for cost-effective and simpler techniques has encouraged the development of alternative ageing systems, such as the use of oak wood pieces, commonly known as oak chips, that accelerate ageing, shortening the time of contact, without decreasing the quality of the wine produced (García-Carpintero, Gómez Gallego, Sánchez-Palomo, & González Viñas, 2011), and leading to sensory properties similar to those of barrel-aged wines (Rodríguez-Bencomo, Ortega-Heras, Pérez-Magariño, González-Huerta, & González-San José, 2008).

However, it should be noted that the oxidative processes that take place in barrels do not occur in tanks (Arfelli, Sartini, Corzani, & Fabiani, 2011; Ortega-Heras, Pérez-Magariño, Cano-Mozo, & González-San José, 2010). In order to imitate the natural uptake of oxygen that occurs in barrels, the addition of controlled doses of oxygen should be considered. This process is called micro-oxygenation and its combination with oak chip maceration has been considered by various researchers (Cejudo-Bastante, Hermosín-Gutiérrez, & Pérez-Coello 2011; Del Álamo, Nevares, Gallego, Fernández de Simón, & Cadahía 2010; Gay et al., 2010). Although the application of micro-oxygenation has been authorised in Europe since 1996 (Gómez-Plaza & Cano-López, 2011), the use of oak wood pieces has been more controversial. This practice has been largely applied for years in certain countries known as "New World" winemaking countries, such as South Africa, Australia and Chile. However, legislation in European Union countries was more restrictive and its application was not authorised until October 2006 (EC (2006)), when the use of pieces of oak wood in winemaking, as well as the designation and presentation of wine obtained by this method, were regulated and approved.

Many factors determine the volatile profile of wines macerated with alternative oenological ageing systems. The amount of wood-related volatile compounds released into the wine depends on the particular characteristics of the wood used (botanical and geographical origin, seasoning, toasting degree) (Frangipane, Santis, & Ceccarelli, 2007), the contact surface (size, amount of chips) and the duration of contact between wood pieces and wine (Cejudo-Bastante et al., 2011; Guchu, Díaz-Maroto, Pérez-Coello, González-Viñas, & Ibáñez, 2006; Ortega-Heras et al., 2010;

* Corresponding author. Tel.: +34 941299626; fax: +34 941299621.
E-mail address: consuelo.pizarro@unirioja.es (C. Pizarro).

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Rodríguez-Bencomo et al. 2008; Schumacher, Alañón, Castro-Vázquez, Pérez-Coello, & Díaz-Maroto, 2013). On the other hand, when micro-oxygenation is applied, the doses of oxygen added have to be individually adapted to each wood product (del Álamo et al., 2010), avoiding excessive amounts that might reduce aromatic complexity and cause undesirable oxidation processes (Arfelli et al., 2011). Although several studies have investigated the combined effect of chips and micro-oxygenation in wine ageing, it should be noted that only Rudnitskaya, Schmidtke, Delgadillo, Legin, and Scollary (2009) have addressed the problem using an experimental design methodology. Their approach aimed to simultaneously evaluate the influence of micro-oxygenation, chips maceration and vintage on phenolic profile. In particular, full factorial design was applied considering micro-oxygenation and the addition of chips at two levels (presence/absence) but without including variations in factors related to doses supplied or duration of treatments or wood properties. Hence, even though micro-oxygenation and chip maceration have been researched in recent years, no studies have focused on experimental design methodology to either evaluate an extended number of influential factors and the possible interaction effects among them or characterize the volatile profile of the wines.

Therefore, in order to overcome the limitations encountered in the literature, the present study aimed to propose a comprehensive multivariate approach, in order to examine in detail the influence of micro-oxygenation and chip maceration on the volatile profile of red wines. The multivariate methodology presented was based on combining statistical experimental design and response surface methodologies to simultaneously investigate the most representative factors involved in the ageing procedure, as well to evaluate the possible synergistic effects between them.

All in all, the main strength of the proposed approach lies in gaining a full insight into the release of wood-related compounds from oak wood to wine under different experimental conditions, as well as their influence on final sensorial perception. To our knowledge, this is the first time that the simultaneous effect of five essential factors controlling the accelerated ageing process on the evolution of the volatile profile of wines has been comprehensively studied using an experimental design methodology.

2. Material and methods

2.1. Chemicals and standard solutions

Furfural, 5-methylfurfural, furfuryl alcohol, eugenol, vanillin, acetovanillone, syringaldehyde, whiskey lactone, *m*-cresol, *p*-cresol, 4-ethylphenol (4-EP), 4-vinylphenol (4-VP), 4-vinylguaiacol (4-VG), 4-methyl-2-pentanol (internal standard) and 3-*tert*-butyl-4-hydroxyanisole (BHA) were purchased from Aldrich Chemie (Steinheim, Germany). Guaiacol and *cis*-isoeugenol were supplied by Fluka (Buchs, Switzerland). The purity of all the standards ranged from 98% to 99%. The solvents methanol and absolute ethanol were purchased from Scharlau (Barcelona, Spain) and dichloromethane was supplied by Aldrich Chemie (Steinheim, Germany). Ultrapure water was obtained from a Milli-Q system (Millipore, Bedford, MA).

Individual stock standard solutions of each compound were prepared in dichloromethane at a concentration level of 10 mg/mL. Subsequently, work solutions were prepared by diluting different amounts of each stock standard solution. BHA solution was prepared by diluting the compound in methanol to a concentration of 7.9 mg/mL. Internal standard solution contained 4-methyl-2-pentanol at a concentration of 32 μg/mL in dichloromethane. Standard and work solutions were stored in darkness at 4 °C.

2.2. Wine samples and alternative aging system

The red young single-variety wine used in this study was elaborated from the native Spanish *Vitis vinifera* Tempranillo grape variety and supplied by Bodegas Riojanas S.A. (Cenicero, La Rioja, Spain) whose wines are protected by the Qualified Designation of Origin Rioja.

The oak pieces used in this study were commercial products supplied by Dolmar, S.L. (Haro, La Rioja, Spain). A total of eight different types of oak chips were considered including two different origins at four different toasting degrees. As regards their origin, American chips were from Northern Appalachian Forests in Pennsylvania and Ohio, and French chips from Forests of Central France. The different toasting intensities considered for each kind of wood were: medium (M), medium plus (M+), heavy (H) and heavy plus (H+).

The wines in contact with the oak chips were aged using an SAEn 5000 micro-oxygenation system (PARSEC, Florence, Italy) equipped with six stainless steel tank units (145 l capacity and 2 m in height) individually connected to remote control units that enable temperature and oxygen doses to be controlled throughout the process. Temperature was set and kept at 18 °C and different oxygen doses were supplied, depending on the experiment. Samples were taken from each tank after 1, 2, 3, 4 and 5 weeks and at the end of the maceration period (Week 6). A control sample was also taken just before ageing started (Week 0). Samples were bottled and stored at 4 °C until analyses were performed.

2.3. Sample preparation

Volatile compounds were extracted according to the procedure described by López, Aznar, Cacho, & Ferreira, 2002. LiChrolut® EN cartridges (200 mg, 3 ml standard PP-tubes) for solid-phase extraction (SPE) were purchased from Merck (Darmstadt, Germany) and extraction was carried out in an extraction manifold with 20 positions, from Waters (Milford, MA). Cartridges were activated with 4 ml of dichloromethane, 4 ml of methanol and 4 ml of water–ethanol mixture (12% v/v). Subsequently, fifty millilitres of wine containing 25 μl of BHA solution were passed through SPE cartridges at constant flow (2 ml/min). The cartridges were dried using a stream of air. Retained analytes were desorbed by elution with 1.3 ml dichloromethane. Twenty-five microlitres of internal standard solution were added to the resulting extracts. Then, vials were hermetically capped and stored at −20 °C until gas chromatography coupled to tandem mass spectrometry (GC–MS/MS) analyses were performed. All the extractions were performed in triplicate.

2.4. Chromatographic conditions

Chromatographic analyses were performed with a Varian 3800 gas chromatograph (Walnut Creek, CA,) equipped with a CombiPAL autosampler (CTC Analytics, Zwingen, Switzerland) and connected to an ion-trap mass spectrometer (Varian Saturn 2200). Compounds were separated using a CP-WAX 52-CB column (30 m × 0.25 mm I.D., 0.25 μm film thickness) purchased from Varian. Helium was used as carrier gas with a flow rate of 1 ml/min. Oven temperature was programmed as follows: initially temperature was maintained at 35 °C for 5 min, subsequently raised to 150 °C at a rate of 2 °C/min and finally raised to 250 °C at a rate of 4 °C/min and maintained for 10 min. Injection was performed in splitless mode for 1 min and then the split was set at 40 mL/min. An inlet of 3.4 mm I.D. was used and injector temperature was fixed at 270 °C. The manifold, GC–MS interface and ion trap temperatures were kept constant at 60, 280 and 200 °C, respectively. Mass spectra were performed in electron impact mode (EI) at 70 eV. Precursor ions were isolated using a 3 amu isolation