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Biological aging status characterization of Sherry type wines using statistical and oenological criteria

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ABSTRACT

20 chemical compounds were quantified in wines from 6 different biological aging statuses in an industrial "criadera" system. A Conglomerated Analysis (CA) realized with 7 selected compounds allowed the differentiation of wines according to their aging. By a Linear Discriminant Analysis (LDA) the 6 most discriminant compounds were identified and a correct classification of 100% of wine samples was achieved. The wine aging time can be calculated by a 3 compound equation obtained by Multiple Regression Analysis (MRA). The last two models were applied to wines with unknown aging time and their results related obtaining a $R = 0.958$. A kinetic model, based in the glycerol content evolution, allows the calculation of the required time to achieve the specific concentration of a status and the glycerol concentration after a known aging time. These models can help to protect the quality of wines elaborated by the traditional biological aging system.

1. Introduction

The process for the elaboration of biologically aged white wines through the so-called "criaderas" system can be considered as the most important contribution of the South of Spain to the Enology field worldwide. The obtained wines are known as "Fino" wines and are characterized by a light, subtle flavor; a very pale yellow color; a dry, fragrant, slightly bitter taste and a sugar content below 1 g/L. The sensorial properties of Fino wines are also known as "flor" or velum bouquet (López-Alejandre, 2005). The development and conservation of this velum, a yeast biofilm in the wine–air interface, is the principal aim of the industrial biological aging process.

The Fino-type wines are elaborated traditionally in the Andalucia community, fundamentally in the Protected Denomination of Origin (PDO) Jerez–Xerez–Sherry (JXS), Montilla–Moriles (MM) and Condado de Huelva (CH). According with Hidalgo (1999), these grape-growing areas belong to zone V of Winkler's classification, with an effective temperature, considered as the sum of degree-days below 10 °C, exceeding 2597 °C on the complete vegetative cycle grapevines. Palomino-Fino (PF), Pedro Ximenez (PX) and Zalema (ZA) white grapes are the predominant varieties cultivated respectively in the three above mentioned PDOs.

The criaderas system is a dynamic wine-aging technique applied to the elaboration of some special wine types. The process for the elaboration of Fino wine under the action of flor yeasts starts after alcoholic and malolactic fermentations and when the spontaneous stabilization of wine is concluded. Essentially it involves the aging of wines in used American oak casks with 625 L volume that are filled to 5/6 of their capacity in order to facilitate the development of the flor yeasts. Traditionally, the casks have been previously conditioned through grape-musts fermentations or whisky maturation. In this way the oak-flavor extraction, that might otherwise mask the bouquet of Fino wine, is minimized. A typical velum developed by *Saccharomyces cerevisiae* var. *capensis* on the wines containing around 15–15.5% (v/v) ethanol shows a white-ivory color, a thick film of several millimeters and a rough surface (Cortés, Moreno, Zea, Moyano, & Medina, 1998, 1999; Moreno & Peinado, 2012)

Basically, the set of casks in a criadera system is grouped into different scales, so called criaderas, each of which contains wine with the same aging time. The system consists of several rows that are numbered from the floor to the top. The first row, lying directly on the floor of the aging cellar, is called the "solera" and contains wine with the greatest aging time; the row above is the "first criadera" and subsequently the second, third, etc. The year's vintage wine is loaded in the "sobretabla" (the uppermost row) thereby containing the youngest wine. As a general rule, the wineries have from 4 to 5 criaderas, including the solera. The criadera system is a method of fractional blending, where the youngest wines are periodically added and sequentially transferred through the criaderas containing a more aged wine. Before transfer to the next stage, the wine drawn from each oak cask (about 1/4 of its volume) is blended with wine from other casks in the same criadera. The transfer frequency depends on development of the wine,

Abbreviations: AC, Analysis of Conglomerates; CA, Chemical Analysis; CH, Condado de Huelva; DF, Discriminant Function; GC, Gas Chromatograph; GCA, Gas-Chromatography Analysis; JXS, Jerez, Xeres, Sherry; LDA, Linear Discriminant Analysis; MCA, Multiple Comparison Analysis; MM, Montilla–Moriles; MRA, Multi Regression Analysis; MSE, Mean Square Error; PDO, Protected Denomination of Origin; PF, Palomino Fino; PX, Pedro Ximénez; R^2, variability percentage explained; ZA, Zalema.

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as determined by sensory analysis and typically occur about twice a year, but may occur more frequently. In this way, the last step is the obtaining of the commercial wine that is a blend of wines proceeding from different vintages with similar sensorial properties and therefore no dependent from the vintage. It is recommended by the PDOs that up to 40% of wine stored in the solera with a biological aging average of 4 years can be withdrawn for bottling and marketing each year. Nevertheless, the minimum biological aging time must be 2 or 3 years for bottling wines in MM and JXS respectively.

The action of flor yeasts in this dynamic aging system has been characterized extensively by various authors in the lasts decades: Berlanga, Atanasio, Mauricio, and Ortega (2001), Berlanga, Peinado, Millan, Mauricio, and Ortega (2004), Bravo (1995), Cortés et al. (1998, 1999), Domecq (1989), Martínez, Pérez, and Benítez (1997), Martínez, Valcarcel, Pérez, and Benitez (1998), Mauricio, Moreno, and Ortega (1997), Muñoz, Peinado, Medina, and Moreno (2005) and their results have been summarized by Jackson (2008), Peinado and Mauricio (2009) and Moreno and Peinado (2012). Some studies among cited were dedicated to the characterization of the process by multivariate analysis using Principal Component Analysis (PCA), nevertheless no studies were conducted with the aim of classification and establishment of a model for these wines in an industrial system, probably due to the difficulty setting the time of aging to each criadera with some degree of precision. At this respect, Jackson (2008) shows a mathematical equation to calculate the age of wine in each criadera and hence the average age of that withdrawn from the solera. This equation involves factors as: the number of criaderas, number of barrels in each criadera and solera, the annual number of transfers and the volume of wine withdrawn from each criadera and solera.

On the other hand, for the statically aged wines, the year corresponding to the wine vintage and the aging time is known with precision, existing as an extensive bibliography to the wine aging status identification and discrimination/classification. These studies have been performed in terms of multivariate analysis of the chemical features that can be modified during the aging process, such as pigments composition (Alcalde-Eon, Escribano-Bailón, Santos-Buelga, & Rivas-Gonzalo, 2006; Heredia, Troncoso, & Guzmán-Chozas, 1997); volatile aroma compounds (Lorenzo, Garde-Cerdán, Pedroza, Alonso, & Salinas, 2009; Pereira, Reis, Saraiva, & Marques, 2010; Riu-Aumatell, Bosch-Fusté, López-Tamames, & Buxaderas, 2006; Rodríguez-Nogales, Fernández-Fernández, & Vila-Crespo, 2009), phenolic compounds (García-Parrilla, Heredia, & Troncoso, 1999; Sanza, Escudero, & Torío, 2004; Sun et al., 2011), flavonoids (Huang, Fang, Li, & Pan, 2007) as well as amine, nitrogen compounds and others chemical descriptors (Moreno, Goñi, & Azpilicueta, 2003; Shen, Ying, Li, Zheng, & Zhuge, 2011; Shen et al., 2012).

In the international sherry wine market, the price of wine is usually directly related to its aging time. Therefore, a correct and objective evaluation of wine aging status is of a great commercial and scientific interest for the prevention of adulteration, mislabeling and for a best control of the winemaking process. This study is aimed to the establishment of an objective and easy method for the quality control and to the classification of the wines subjected to biological aging under the traditional criaderas system in the industrial conditions.

2. Material and Methods

2.1. Wine Samples

Fino wine is elaborated in MM from PX grapes, harvested at a potential ethanol content of 15–15.5% v/v, this is an important differentiation factor compared to the fino wines elaborated in JXS, where grapes are harvested with a potential ethanol contents about 12–13%. In this PDO the young vintage wine is added with pure ethanol (95%) of oenological origin to reach a content of 15%, previously to be subjected to biological aging.

Two types of wine samples from the collaborative wineries of the MM were analyzed. The first type was used to establish a model for the classification and also a kinetic model, describing the relationship among aging time and the concentration in some compounds of wines subjected to the industrial biological aging process. This type of samples was constituted by the wines obtained in a great winery with a good established 6 criaderas system, corresponding to 0, 12, 24, 36, 48 and 72 months of aging time. This winery has a quality control system allowing to estimate an error of ± 3 months in the average aging time of the wines in each criadera.

The second type of sample is constituted by three lots of wine samples that were used for the application/validation of the obtained models. The first lot of samples corresponds to 2 commercial wines with an estimated aging time of 60–66 months. The second lot has 10 wine samples obtained from different wineries and with an unknown biological aging time. Finally, the third lot is constituted by 9 wine samples from a small winery with a 3 criaderas system and an estimated aging time of 18, 30 and 48 months with an accuracy of ± 6 months for each one.

The mandatory generic rules for wines subjected to biological aging are established by the of JXS, MM and CH, Regulatory Councils and supervised by the inspectors from each of them. In this sense all wineries must control the ambient moisture to levels higher than 85% and temperature about 15–20 °C over the year. Also, the prevalence of *S. cerevisiae* flor yeasts in the wine surface is periodically controlled through its characteristic ivory color and rough aspect. Particularly, the collaborative winery providing samples to the establishment of classification and kinetic models developed in this work follow these conditions and use oak barrels about 25 years old and a volume capacity of 625 L, filled with wine to 500 L.

To obtain a representative sample of each criadera the following sampling protocol was established: at first time the number of barrels of each criadera is counted and then 1/3 of them was selected. Thus, barrels in alternate columns were selected and a sufficient volume from each of them was removed to reach a final volume of 5 L for each criadera. From this final volume only 3 bottles with a capacity of 0.75 L each, were destined to common oenological analysis, chromatographic analysis and for possible repetitions. Depending on the number of barrels in the criadera, a volume among 50 and 150 mL of wine from each barrel was taken. All the wine samples used to establish the classification and kinetic models for biological aging were analyzed in triplicate and the samples for applications of these models were analyzed once.

2.2. Chemical Analysis

The most important Chemical Analysis (CA) from an oenological point of view are ethanol, titratable acidity, pH and volatile acidity and they were quantified in accordance with the European Union Official Methods (CEE, 1990).

2.3. Gas-Chromatographic Quantification of Major Volatile Compounds and Polyols

Considering the most abundant alcohols (methanol, 1-propanol, isobutanol, isoamylic and 2-phenylethanol), three carbonyl compounds (acetaldehyde, 1,1-diethoxyethane and acetoin), three ethyl esters (ethyl acetate, ethyl lactate and ethyl succinate) and two polyols (glycerol and 2,3-butanediol), thirteen wine aroma compounds were quantified by Gas-Chromatographic Analysis (GCA) using the method of Peinado, Moreno, Muñoz, Medina, and Moreno (2004) and a Model 6890 Gas Chromatograph (GC) from Agilent (Palo Alto, CA). A CP-WAX 57 CB capillary column (60 m long × 0.25 mm i.d., 0.4 μm film thickness) from Varian (Palo Alto, CA) was used and 0.5 μL aliquots from 10 mL of wine or standard samples previously supplied with 1 mL of 1 g/L 4-methyl-2-pentanol as internal standard solution were injected into