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The influence of pre-fermentative maceration and ageing factors on ester profile and marker determination of Pedro Ximenez sparkling wines

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ABSTRACT

The influence of pre-fermentative maceration and ageing factors on the ester profiles of Pedro Ximenez sparkling wines was evaluated. The pre-fermentative maceration consisted of the skin-maceration of musts at 10 °C for 6 h. The sparkling wines were produced following the Champenoise method. Samples were monitored at 3, 6 and 9 months of ageing on lees. Sparkling wines with pre-fermentative maceration displayed higher contents of ethyl esters of branched acids and cinnamates. Meanwhile, those without maceration showed higher levels of ethyl esters of fatty acids and higher alcohol acetates. The study of statistical interactions elucidated different hydrolytic kinetics and developments in higher alcohol acetates and ethyl esters of branched acids during ageing. The application of a dual criterion based on univariate (ANOVA) and multivariate analyses (OPLS–DA) allowed us to identify new potential volatile markers related to pre-fermentative maceration and ageing time, reported for the first time in sparkling wines.

1. Introduction

Recently, a new wine market paradigm based on product diversification has emerged for winemakers (Pozo-Bayón, Martínez-Rodríguez, Pueyo, & Moreno-Arribas, 2009). This has given consumers a large choice of typologies of wines, different qualities and prices. A good example of the diversification of wine types is sparkling wines. While the worldwide production of still wines has increased by 7% over the 10 last years, that of sparkling wines increased by more than 40% over the same period (OIV. The International Organisation of Vine, 2014). In addition, although the production of sparkling wine is lower than other wines in terms of quantity, the economic impact of this product is very important, due to its high added value and increased production on a global scale (Caliari, Burin, Rosier, & BordignonLuiz, 2014; Torresi, Frangipane, & Anelli, 2011). This increasing interest in sparkling wines is bound to new market segments for sparkling wines, resulting in changes in the global market for this product. Thereby, cava exceeded the exports of champagne in volume terms during 2015 (Institut del Cava., 2015; Le Comité Champagne., 2015) and the production of sparkling wines from Russia, USA, Ukraine, Australia, Hungary or Brazil has rapidly increased in the last few years (OIV, 2014).

Winemakers and the scientific community are searching for new collaborative platforms to enhance the peculiarities and distinctive characteristics of their wines (Caliari et al., 2014; Pozo-Bayón et al., 2009). These distinctive characteristics of the wines are usually given by local or regional grape varieties. In this context, Pedro Ximenez is an autochthonous white grape variety traditionally used for the production of Sherry-type wines in the Montilla–Moriles designation of origin (Andalusia, Spain). The versatility and attitude of this variety have been well proven (comprising the organic production, sun-drying and oxidative and biological ageing) producing many different styles of wines. The grape variety and other factors, such as crop management, ripe-

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ness, and base wine composition, have been well reported to impact on the quality of sparkling wine (Pozo-Bayón et al., 2009; Riu-Aumatell, Bosch-Fusté, López-Tamames, & Buxaderas, 2006). Skin maceration induces compositional modifications as well as the extraction of grape-derived components in grape juices. Furthermore, the traditional or Champenoise method, involving a second fermentation and ageing in contact with lees, also produces compositional changes impacting on the final quality of the product (Pozo-Bayón et al., 2009; Riu-Aumatell et al., 2006).

Skin maceration is usually performed in the production of rosé sparkling wines. Several authors concur with the use of this operation as an oenological practice to improve the quality of sparkling wines from red grape varieties (Martínez-Lapuente, Guadalupe, Ayestarán, & Pérez-Magariño, 2015; Pozo-Bayón et al., 2009). However, to our knowledge, comparative studies have not explored the influence of pre-fermentative strategies on the distinctive aroma styles of sparkling wines, and this requires investigation. In this sense, deepening our understanding of the aromatic impact of this pre-fermentative operation may offer a promising strategy for obtaining sparkling wines with differential aromatic characteristics.

Aroma is considered one of the most decisive quality attributes in wines and a key factor impacting on consumers' preferences and tasting experience (Antalick et al., 2015; Lockshin & Corsi, 2012; Sáenz-Navajas, Ballester, Pêcher, Peyron, & Valentin, 2013). In this sense, the role of ester compounds in wine aroma is a current topic of research. The growing interest in the characterization of wine esters is not only due to their direct sensory contribution but also to complex synergistic interactions affecting aroma perception (Escudero, Campo, Fariña, Cacho, & Ferreira, 2007; Lytra, Tempere, Le Floch, de Revel, & Barbe, 2013). Esters are formed as a result of the reaction of an alcohol with a carboxylic acid functional group. These molecules are mainly synthesized by two mechanisms in wines: during alcoholic fermentation through enzymatic reactions produced by yeasts and during wine ageing by chemical esterification between alcohol and acid functional groups at low pH (Sumby, Grbin, & Jiranek, 2010). Besides the mechanisms of genesis, ester hydrolysis and ester oxidation by hydroxyl radical-related processes could modulate their contents over the winemaking process (Ramey & Ough, 1980). Recent studies have reported that the maturity of grapes, fermentation strategy and ageing factors greatly affect the ester profile of wine and consequently impact on its aroma. In the case of the Pedro Ximenez grapes, the impact of pre-fermentative maceration on cinnamates has not been reported. Moreover, studies focused on the role of ester compounds in sparkling wines modified by skin maceration and ageing are scarce.

Given the importance of ester compounds and their sensory impact, numerous approaches have been developed to characterize ester compounds in wines (Marquez, Serratosa, Merida, Zea, & Moyano, 2014; Ubeda, Callejón, Troncoso, Peña-Neira, & Morales, 2016). In this sense, headspace solid-phase microextraction (HS-SPME) is a suitable, quick, simple and solvent-free technique. HS-SPME coupled to gas chromatography with mass spectrometry detection (GC–MS) has been widely used for this purpose (Antalick, Perello, & de Revel, 2010; Perestrelo, Barros, Rocha, & Câmara, 2014). This technique can produce a large amount of data for each sample. Therefore, multivariate approaches are used to handle tangled data since the univariate analysis may ignore other interactions found in complex models (Cozzolino, Cynkar, Shah, Dambergs, & Smith, 2009).

The aim of this study was to examine the impact of pre-fermentative maceration and ageing factors on the ester composition of Pedro Ximenez sparkling wines. For that purpose, a novel methodology based on HS-SPME-GC–MS and chemometrics was developed to highlight the potential volatile markers of both factors.

2. Materials and methods

2.1. Wine samples

Sparkling wines were elaborated at IFAPA, Cabra-Priego (37° - 29′ 53″N; 04° 25′ 51″ W) following the traditional or Champenoise method (consisting of a second fermentation of base wines in closed bottles and ageing on lees before disgorging). A 600-kg batch of Pedro Ximenez grapes from the 2014 campaign were harvested at 18.5 19.0 °Brix and divided into two. The first 300-kg batch of grapes (NM samples) was destemmed, crushed and pressed. The grape juices were divided into stainless steel tanks of 50 L. They were corrected, sulfited (at 70 mg L^{-1}) and then alcoholic fermentation was carried out at a controlled temperature of 18 °C, obtaining the NM base wines. The yeast and nutrients used were Pasionviniferm (Agrovin, Spain) at 20 g h L^{-1} and Actimax Bio at 10 g h L^{-1} (Agrovin, Spain), respectively. Next, the base wines were clarified, stabilized and filtered. In the second batch (M), 300 kg of grapes were destemmed, crushed and sulfited (at 50 mg kg^{-1}). Enozym AROME enzyme at a dose of 30 mg kg^{-1} (Agrovin, Spain) was added. Afterwards, a pre-fermentative maceration of the must in contact with the skins was performed for 6 h at 10 °C before pressing. Then, the grape juices were corrected and fermented following the same conditions described for the NM base wines. The tirage liquor consisted of 24 g L^{-1} of sucrose, yeast Viniferm PDM at 20 g hL^{-1} (Agrovin. Spain), Actimax Bio at 15 g h L^{-1} (Agrovin, Spain) and bentonite at 20 g h L^{-1} (Laffort, France). A second fermentation was performed at 15 °C in closed bottles of 0.75 L. The pressure and residual sugars were measured periodically. This fermentation was completed after 11 12 weeks. Then, the sparkling wines were kept at 12 °C and collected at 0, 3, 6 and 9 months of ageing on lees, riddled, disgorged, corked and submitted to analysis. A total of 48 bottles were analyzed. The two treatments (N and NM) were sampled in duplicate at each time (beginning of ageing, 3, 6 and 9 months) for each of the three fermentative tanks.

2.2. Oenological parameters

Ethanol (% vol.), residual sugars, pH, total and volatile acidity were determined following the official analytical methods (OIV, 2014). Optical density at λ = 420 nm was determined using a spectrophotometer (Lambda 25; Perkin-Elmer, Waltham, MA). Total phenolic content was determined by photometric procedure (Folin-Ciocalteu). The results were expressed as mg L^{-1} of gallic acid.

2.3. Chemicals and reagents

HPLC-grade ethanol was obtained from J.T. Baker Chemicals B. V. (Deventer, Holland). Milli-Q water was obtained from a Milli-Q Plus water system (Millipore, Spain). Sigma Aldrich (Madrid, Spain) supplied the sodium chloride, ACS reagent grade (purity ≥99.8%) and standard compounds; ethyl butyrate (≥99%), ethyl hexanoate (≥99%), ethyl octanoate (≥99%), propyl acetate (≥99%), isobutyl acetate (≥99%), isoamyl acetate (≥99%), hexyl acetate (≥99%), phenylethyl acetate (≥99%), ethyl isobutyrate (98%), ethyl 2-methylbutyrate (≥99%), ethyl isovalerate (≥99%), ethyl phenylacetate (98%), ethyl dihydrocinnamate (98%), ethyl cinnamate (98%), methyl hexanoate (≥99%), methyl octanoate