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Effect of enzyme additions on the oligosaccharide composition of Monastrell red wines from four different wine-growing origins in Spain

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ABSTRACT

The release of oligosaccharides during winemaking depends on the grape skin cell wall degradation, which can be facilitated by the use of enzymes. Oligosaccharide quantities and composition in wine could be influenced by the "terroir" effect. Monastrell wine was elaborated from grapes from four different "terroirs" (Cañada Judío, Albatana, Chaparral-Bullas and Montealegre). Monastrell wines were also treated with β-galactosidase enzyme addition and commercial enzyme addition.

The results showed significant differences in the Monastrell wine oligosaccharide fractions, according to the geographical origin of grapes. A higher quantity of oligosaccharides was found for three out of four terroirs studied when commercial enzymes were added. The use of commercial enzyme modified the Arabinose/Galactose and the Rhamnose/Galacturonic acid ratios in Cañada Judío and Albatana terroirs wines, and it modified the (Arabinose + Galactose)/Rhamnose ratio in Cañada Judío, Albatana and Chaparral-Bullas terroirs wines. Therefore, the "terroir" impacts the effect of commercial enzyme treatment on wine oligosaccharide composition.

1. Introduction

Polyphenols, polysaccharides and proteins are the main macromolecules of wines. They have been thoroughly studied, due to their importance for wine technological and sensory properties. In contrast, oligosaccharides have only recently been shown to occur in wine and much less studied. These natural molecules can be found in important medicinal, food, agricultural applications, play a role in plant defence responses (Darvill & Albersheim, 1984; Elleuch et al., 2011; Qiang, YongLie, & QianBing, 2009) and behave as dietary fibres and prebiotics (Gibson & Roberfroid, 1995; Hopkins & Macfarlane, 2003; Macfarlane, Steed, & Macfarlane, 2008). Concerning their significance for wine quality, some oligosaccharides have physicochemical properties such as chelation of cations (Cescutti & Rizzo, 2001). Oligosaccharide fractions from red wines were first isolated and characterised by Ducasse, Williams, Meudec, Cheynier, and Doco (2010). The Carignan and Merlot wines investigated in this study contained rather large concentrations (approximately 300 mg/L) of oligosaccharides structurally related to plant cell wall polysaccharides (Ducasse et al., 2010). The oligosaccharide structures detected by MS spectrometry include short chains of galacturonic acid with a degree of polymerization between 2 and 6, and as a short chain of rhamnogalacturonan-oligomers constituted by the repeats of rhamnose and galacturonic acid, arising from smooth regions or hairy regions of pectin, respectively, but also 4-OMe-oligo-glucuronoxylan oligosaccharides produced from hemicellulose (Ducasse et al., 2010). Recently, similar structures have been isolated from other wines by Bordiga et al (2012). These authors have isolated and characterised forty-five complex free oligosaccharides in red and white wines, Grignolino and Chardonnay, respectively. The concentrations were around 100 mg/L in both wines, and the oligosaccharides corresponded to hexose-oligosaccharides, xyloglucans, and arabinogalactans, that may be the natural byproduct of the degradation of cell wall polysaccharides.

In red wine winemaking the use of enzymes is now expanding into various more targeted applications beyond the classic press

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yield and clarification purposes. The main use of commercial pectinolytic enzyme preparations is to enhance the extraction of anthocyanin pigments and other desirable phenolics into the juice or red wine during maceration. The permeability of the grape skin cell walls to polyphenols can be increased by enzymes, that can help the partial hydrolysis of cell wall polysaccharides. Enzyme treatments have been shown to modify the wine polysaccharide composition (Ayestaran, Guadalupe, & León, 2004; Doco, Williams, & Cheynier, 2007; Guadalupe, Palacios, & Ayestaran, 2007). They produce an increase of RG-II and a decrease of PRAGs in red wine, along with a particular modification of AGPs, with loss of their terminal arabinose residues (Doco et al., 2007). Studies on the effect of enzymes on wine oligosaccharides are scarce (Bordiga et al., 2012; Ducasse et al., 2010; Ducasse et al., 2011). Ducasse et al. (2011) observed differences in the total oligosaccharide concentration between Merlot wines treated with enzymes; in most cases, enzyme treated wines contained lower amounts of oligosaccharides than the control. Qualitative differences were also found in oligosaccharide composition between enzyme-treated and control Merlot wines.

A terroir can be defined as a grouping of homogeneous environmental units, or natural terroir units, based on the typicality of the products obtained (Laville, 1993). This word is particularly associated with the local production of wine (Barham, 2003), and implies a link between the wine and the area of this production. For example, the "terroir" characteristics could influence on phenol profiles in wines from different wine-growing regions, as several authors detected (Li, Pan, Jin, Mu, & Duan, 2011; Rastija, Srečnik, & Medić-Šarić, 2009). The soil and climate are the main elements of the French notion of "terroir", but the concept also includes human factors that may affect production in different ways (Morlat, 2005).

Monastrell, also known internationally as the French name of Mourvedre, is the main wine grape cultivar in Southern Spain but, there is no information about the oligosaccharide composition of Monastrell wines. An influence of terroir on wine polysaccharide composition has been demonstrated (Apolinar-Valiente et al., 2013). This factor could also influence in oligosaccharide quantities and composition in wine depending on the cell wall "degrability", although it has not been studied. Moreover, the interaction between this effect and that of enzyme treatments which could facilitate the grape skin cell wall degradation has not been investigated either. The aim of this work was to study the effect of different winemaking techniques (classical winemaking, addition of β-galactosidase and commercial enzyme, separately) on the oligosaccharide fractions in Monastrell wines from four different "terroirs" (Cañada Judío, Albatana, Chaparral-Bullas and Montealegre).

2. Materials and methods

2.1. Samples

Grapes from *Vitis vinifera* cv. Monastrell, cultivated near Murcia (S. E. Spain), were harvested at commercial maturity over vintage 2008 from four different origins (Cañada Judío, Albatana, Chaparral-Bullas and Montealegre).

The geographical information about vineyard plots is: Cañada Judío (1°21′37.02″O Longitude; 38°33′15.84″N Latitude; 450 m. Altitude); Albatana (1°27′49.78″O Longitude; 38°32′28.56″N Latitude; 693 m. Altitude); Chaparral-Bullas (1°40′59.06″"O Longitude; 38°02′38.24″N Latitude; 432 m. Altitude); and Montealegre (1°17′42.82″O Longitude; 38°46′39.85″N Latitude; 771 m. Altitude).

Cañada Judío terroir plot is close to Jumilla village, and is composed by dolomites, loams, limestone and sandstorm. Albatana vineyard is closer to Albatana village, and its terroir is composed by gravel, conglomerates, sand and slime. Evaporites, vulcanites, sandstones, clay and limestones can be found in Chaparral-Bullas terroir, near Cehegín village. Montealegre vineyard is closer to Montealegre del Castillo village, and sand, clay, gravel, mud and gypsum form its terroir.

Climate information of different terroir plots was obtained in weather stations between September 2007 and October 2008. Supplementary Table 1 shows climatic parameters: monthly mean temperature, monthly pluviometry, monthly maximum and minimum mean temperatures, monthly mean relative humidity, monthly maximum and minimum relative humidity, monthly mean wind speed and monthly maximum wind speed. Used instrumental equipment was: HMP45AC thermohigrometer (Vaisala, Helsinki, Finland), 05103-5 wind anemometer (Young Company, Michigan, USA), and different pluviometer models: PCP-214 (Geónica, Madrid, Spain), 4.4031.30.006 (Thies-CLima, Göttingen, Germany) and ARG-100 (Campbell Scientific Ltd., Loughborough, UK.

The maturity control of grapes from four studied terroirs (Cañada Judío, Albatana, Chaparral-Bullas and Montealegre) was carried out in triplicate. Berry sampling was done weekly from veraison to harvest, on 50 vines per treatment. Groups of five to six berries from different parts of the cluster and from different clusters on the same vine were sampled randomly. Berry samples (ca. 300 g), collected from all vines of the same treatment, were placed in plastic bags and stored in ice during the transport from the field to the laboratory, where enological analysis were determined. Grape analysis involved the traditional flesh measurements (°Brix, pH and total acidity) and total anthocyanins content. Total soluble solids (°Brix) were measured using a digital refractometer (Atago RX-5000; Atago Co., Ltd, Tokyo, Japan). Titratable acidity and pH were measured using an automatic titrator (Metrohm, Herisau, Switzerland) with 0.1 N NaOH. The anthocyanin content of the solution (total anthocyanins) was chemically assayed by measuring the absorbance of the samples at 520 nm at pH 3.6.

The physical–chemical characteristics of the grape berry samples from Cañada Judío, Albatana, Chaparral-Bullas and Montealegre were (respectively) as follows: weight of a hundred grape berries: 191.5, 190.7, 198.4 and 197.5 g; °Brix: 24.8, 24.8, 25.2 and 20.3; pH: 3.8, 3.8, 4.1 and 3.5; total anthocyanins content: 1161, 1245, 799 and 943 mg/L; % skin: 17, 18, 14 and 14.

2.2. Preparation of samples

2.2.1. Control trials

Three 90 kg lots of Monastrell grapes from four different terroirs (Cañada Judío, Albatana, Chaparral-Bullas and Montealegre) were destemmed and crushed, using a crusher/destemmer unit (Gamma 30, Zambelli Enotech, Italy) and distributed into 100 L stainless steel tanks to yield triplicate control lots named JUCO, ALCO, BUCO and MTCO. At the same time, sodium metabisulfite (8 g/100 kg grape) was added. This basic winemaking process was followed in all the wines.

2.2.2. Commercial enzyme addition trials

The same process as in the control was followed in triplicate except that a commercial enzyme was added to the tanks (5 g/100 kg) and the resulting wines were named JUCE, ALCE, BUCE and MTCE. The company (Agrovin Company, Alcázar de San Juan, Spain) which produces the commercial enzyme (Enozym Vintage) provided the following information on the enzyme: polygalacturonase activity, 546.6 IU/g; pectinesterase activity, 7.3 IU/g; pectin lyase activity, 2.8 IU/g; and β-glucanase activity, 179.6 IU/g.