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Vine-shoot waste aqueous extract applied as foliar fertilizer to grapevines: Effect on amino acids and fermentative volatile content

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ABSTRACT

The aim of this work was to study the influence of foliar applications of different wood aqueous extracts on the amino acid content of musts and wines from Airén variety; and to study their relationship with the volatile compounds formed during alcoholic fermentation. For this purpose, the foliar treatments proposed were a vine-shoot aqueous extract applied in one and two times, and an oak extract which was only applied once. Results obtained show the potential of Airén vine-shoot waste aqueous extracts to be used as foliar fertilizer, enhancing the wine amino acid content especially when they were applied once. Similar results were observed with the aqueous oak extract. Regarding wine fermentative volatile compounds, there is a close relationship between musts and their wines amino acid content allowing us to discuss about the role of proline during the alcoholic fermentation and the generation of certain volatiles.

1. Introduction

Grape soil fertilization has been used to enhance the quality of grapes and therefore wines. Applications carried out with chemical fertilizers are well known (Bell & Henschke, 2005; Linsenmeier, Loos, & Löhnertz, 2008; Neilsen, Neilsen, Bowen, Bogdanoff, & Usher, 2010; Stockert, Bisson, Adams, & Smart, 2013). The soil addition of nitrogen compounds is important up to certain levels for alcoholic fermentation development, but at the same time may cause other problems. The most important drawbacks for the application of so many fertilizers are: (i) the soil and water pollution (Jurisio, Kisic, Zgorelec, & Kvaternjak, 2012); and (ii) the cost of the treatments and the loss of effectiveness (Yunta, Martín, Lucena, & Gárate, 2013). For this reason, other way to reduce the soil contamination is the application of nitrogen compounds, but as a foliar treatment. The latest is not a substitute for traditional fertilization, but allows nutrients to be absorbed directly by the vine, requiring fewer amounts of fertilizers, for example urea, to get similar results on the grape (Ancín-Azpilicueta, Nieto-Rojo, & Gómez-Cordón, 2013), and consequently the possible pollution can be also reduced.

Other recently approach may be the latest studies based on amino acids treatments. In this case, Garde-Cerdán et al. (2014, 2015) studied the influence of foliar applications of proline, phenylalanine, urea and two commercial nitrogen fertilizers, with and without amino acids in their formulations, on the amino acid content and their effect on the aroma composition of Tempranillo grapes. Khan, Ahmad, Jaskani, Ahmad, and Malik (2012) also studied the effect of foliar amino acid applications in the vineyard, on the growth and physico-chemical characteristics of grapes cv. Perlette.

Some authors, have described how the changes in the grape amino acid content could affect the wine volatile composition (Bell & Henschke, 2005), as phenylalanine, leucine, isoleucine, valine, tyrosine, and methionine for example, seem to be precursors of fermentative volatile compounds (2-phenylethanol, 3-methyl-1-butanol, 2-methyl-1-butanol, isobutanol, tyrosol, and methionol, respectively). However, discrepancies regarding such direct relationship between amino acids and fermentative volatile compounds are nowadays discussed, especially when complex matrices such as wines are studied. It is the case of proline, which until now no direct relationship with the synthesis of volatile

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compounds was described, but it is gaining importance, as its role in the aroma generation could be explained by the synthesis of glutamate (Procopio, Krause, Hofmann, & Becker, 2013).

In recent years, the application of vegetable products in the vineyards underlies significant changes towards a more "*Sustainable Viticulture*". A clear example is the relation between the commercial aqueous toasted oak extracts, applied as foliar fertilizer, and the grape amino acids content of Verdejo grapes (Martínez-Gil, Garde-Cerdán, Martínez, Alonso, & Salinas, 2012a) and their effect on the wine aroma profile. The chemical composition (phenolic and aromatic) of such oak extracts (Pardo-García et al., 2014a) may be compared with the recently research carried out with Airén vine-shoots (Sánchez-Gómez, Zalacain, Alonso, & Salinas, 2014), and for this reason a similar foliar vineyard application could be considered. There is a growing interest in the exploitation of this worldwide agricultural residue, as until now little research is carried out on them (Mendívil, Muñoz, Morales, Juárez, & García-Escudero, 2013; Rayne, Karacabey, & Mazza, 2008; Jiménez, Angulo, Ramos, De la Torre, & Ferrer, 2006) as vine-shoots are usually burnt or throw near vineyards.

Consequently, the aim of this work was to gain insight on the effect of Airén vine-shoot aqueous extracts foliarly applied to grapevines on: must and wine amino acid composition and wine fermentative volatile compounds, since previous studies suggest that these wastes have a potential use as foliar fertilizers in the vineyard. The relationship between the amino acid content and wine fermentative volatile compounds was also addressed when three different foliar treatments were applied.

2. Materials and methods

2.1. Raw materials

2.1.1. Vine-shoots samples (VS) and their extraction

One hundred kg of Airén white *Vitis vinifera* vine-shoot were sampled from two hundred vines, in Castilla-La Mancha Spanish region, 4 months after the harvest in 2013, by randomized selection. Samples were dried for 72 h at room temperature until a final humidity of 6.5% (g_{water}/100 $g_{of\ sample}$). Dry vine-shoot wastes were ground by a hammer miller (LARUS Impianti, Skid Sinte 1000, Zamora, Spain) to get a homogenous 40-mesh sieve sampling. Samples were kept under vacuum at room temperature (25–27 °C) until their use. Fifty grams of grounded Airén vine-shoot sample were extracted by conventional solid–liquid extraction (CSLE) to get an extract with the highest content in valuable compounds according to Sánchez-Gómez et al. (2014) method.

2.1.2. Commercial oak extract (OW)

A commercial aqueous French oak extract (103 C, Protea France S.A.S.) was chosen for this study. This extract was obtained by macerating French oak chips (*Quercus sessiliflora Salisb*) from natural seasoning, and toasted at a medium intensity level with water at high temperature, as described by Martínez-Gil, Garde-Cerdán, Martínez, Alonso, and Salinas (2011).

2.1.3. Grapevine

White grapes from *Vitis vinifera* variety Airén grown during the year 2013 in Castilla-La Mancha Spanish region, in the Southwest of Spain (altitude of 788 m, latitude 38° 46′60″ N and longitude 1° 19′ W) were used. Grapevines were trained on the traditional bush vines Gobelet system with a row distribution north to south. The annual average temperature was 13.7 °C, with a minimum of −6 °C (November) and a maximum of 37 °C (July and August). The rainfall per year was 200–300 mm.

2.2. Grapevine treatments and winemaking

2.2.1. Extracts treatment

Different extract treatments were applied to the grapevines during veraison. For all treatments, 0.05% (v/v) of adjuvant Fluvius (BASF, Germany) was added, since this is a superficial wetting agent typically used for treatments with foliar herbicide, constituted by an inert mixture of polymers. The vineyards were treated with two different vine-shoot waste extracts, one was applied once at the 7th day post-veraison (VS-100), and the second one was diluted with water at 50% and was applied twice at 7th and 14th days post-veraison (VS-50). Also, a commercial aqueous oak extract was applied once at the 7th day post-veraison (OW), since this formulation showed the higher concentration of volatile compounds according to Martínez-Gil et al. (2011). Each treatment was carried out on 7 plants in the same row, leaving other row with untreated plants between the different applications to avoid contamination. Three hundred mL of each formulation was applied evenly per plant by spraying over leaves. Moreover, the control sampling was carried out on 7 plants that were treated with water and the adjuvant, following the same treatment protocol. The treatments were carried out when the environmental temperature was below 20 °C, at approximately between 7 and 9 a.m. Grapes were harvested on September the 26th at their optimum maturation moment. Before winemaking some berries were randomly separated in order to measure the oenological parameters (°Beaumé, pH and total acidity) and frozen until further analysis.

2.2.2. Winemaking

Grapes resulted from each treatment (approximately 20 kg of grapesfor each treatment) were processed separately. These grapes were destemmed, mixed, homogenized (must and solid parts combined) and processed. Berries were divided and placed into two 30 L stainless steel tanks for maceration at 20 ± 1 °C for one day (two wines from each treatment were obtained).

Then, 150 mg/mL of ammonium bisulfite was added to each must. The next day, skins and seeds of each wine were removed with a traditional vertical hand-press and the free-run musts put back into its tank to finish the alcoholic fermentation. Twenty g/hL of yeast UCLM S377 strain (Springer Oenologie, Maisons-Alfort cedex, France) was inoculated and then added to carry out the alcoholic fermentation, which took place at a temperature of 22 ± 1 °C. The density was measured each two days. After 16 days, the alcoholic fermentation was finished and 4 L of each wine obtained from each treatment was bottled and stored.

2.3. Analytical methods

2.3.1. Oenological classic parameters

Grapes and wines classical parameters such as °Beaumé (°Bé), alcoholic degree (°A), pH, and total acidity (TA) were analyzed by an equipment based on Fourier Transform-infrared spectroscopy (FT-IR Multispec of TDI) using the methods of ECC (1990) as reference.

2.3.2. Determination of free amino acids by HPLC

The amino acids analysis of must, wine, vine-shoot extract and oak extract was performed by the method described by Garde-Cerdán et al. (2014). Briefly, free amino acids were analyzed by reverse-phase HPLC using an Agilent 1100 Series (Palo Alto, USA) equipped with an ALS automatic liquid sampler, a fluorescence detector and a DAD detector. Each sample (5 mL) was mixed with 100 µL of norvaline and 100 µL of sarcosine (internal standards). The mixture was submitted to an automatic precolumn derivatization with *o*-phthaldialdehyde (OPA Reagent, Agilent) and with 9-fluorenylmethylchloroformate (FMOC Reagent, Agilent).