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Differentiation between Croatian dessert wine Prošek and dry wines based on phenolic composition

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ABSTRACT

The phenolic composition of the Croatian dessert wine Prošek and dry wines Plavac mali and Pošip produced from the same autochthonous cultivars was investigated to determine which phenolic compounds best discriminate between these wine types. The wines were analyzed by the targeted metabolomic method using UPLC/QqQ-MS/MS. Forty-five (45) phenolic compounds were identified and classified into five groups based on chemical structure: benzoic acid derivatives, cinnamic acid derivatives, flavan-3-ols, stilbenes and flavonols. ANOVA indicated that the grape-drying process heavily influences the complex phenolic composition of Prošek dessert wine, which differs significantly from dry wines produced from the same cultivars. The data was grouped by principal component analysis and linear discriminant analysis to derive a classification function that distinguished dry and dessert wines with 98% accuracy. Principal component analysis separated the samples and showed that 23 phenolic compounds depending to phenolic acids, phenolic aldehydes, flavan-3-ols and flavonols were the compounds that best differentiated the Prošek from the dry wines.

1. Introduction

Recent research has focused on plant bioactive compounds with potential beneficial effects on human health. Phenolic compounds may have the potential to naturally prevent some major diseases such as cancer, cardiovascular and neurodegenerative diseases like Parkinson's and Alzheimer's (Aguilera et al., 2016; Rangel-Huerta et al., 2015; Rodriguez-Mateos et al., 2014; Stefani and Rigacci, 2014). Wine is a rich source of dietary phenols, particularly red wine. Wine contains different classes of flavonoid and non-flavonoid phenolic compounds originating from grapes (Mattivi et al., 2006). The phenolic composition of a wine depends on grape variety, ripeness, cultivation system, sunlight exposure and UV radiation, winemaking process and phenolic reactivity during winemaking and ageing (Lorrain et al., 2011; Bindon et al., 2013; Fulcrand et al., 2006; Song et al., 2015).

Traditional sweet dessert wines produced in winemaking regions where grapes are dried to naturally concentrate sugars are rich in phenolic compounds and demonstrate interesting antioxidant activity (Moreno et al., 2008; Loizzo et al., 2013). The dessert wine Prošek is produced exclusively on the Mediterranean coast of Croatia (Dalmatia) and can be made only from autochthonous cultivars. An important step in Prošek production is the dehydration of grapes prior to vinification by sun drying or under controlled conditions with the temperature below 40 °C. Dehydration increases the sugar concentration and substantially modifies the chemical composition of phenolics due to changes in concentration, chemical modification or degradation (López de Lerma et al., 2014; Sarratosa et al., 2008; De Torres et al., 2010). Water evaporation can cause grape skin deterioration that allows phenolic compounds to migrate from the skin to the pulp, increasing the pulp concentration (Panceri et al., 2013). However, phenols present in grape juice can participate in reactions of enzymatic oxidation and non-enzymatic browning, reducing their concentration (Serratosa et al., 2008).

Recently, attention in Croatia has focused on enological and overall evaluation of wines from native cultivars. Phenolic compounds play an important role in understanding the unique qualities of wines produced from native cultivars (Tamborra et al., 2003; Letaief et al., 2007). Phenolic characterization has highlighted the contribution of these compounds to the structure and overall quality of wine. Total phenolic content has been studied in several commercial Croatian wine samples (Piljac et al., 2005), and several studies have examined flavonoids, phenolic acids, anthocyanins and resveratrol (Herjavec et al., 2007; Rastija et al., 2009; Vinković Vrček et al., 2011). However, none of these studies provided a detailed phenolic profile of Prošek dessert

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Table 1
List of the wine samples produced in three biological replicates.

Variety	Wine type	Vintage	Wine color	Maceration
Plavac mali	dessert	2007	red	+
Plavac mali	dessert	2008	red	+
Pošip	dessert	2008	white	–
Plavac mali	dry	2007	red	+
Pošip	dry	2010	white	–
Plavac mali	dry	2011	red	+

wines. The objectives of this work were (i) to identify and quantify multiple classes of phenolics in Prošek sweet wines using targeted metabolomics methodology (UPLC/QqQ-MS/MS); and (ii) to differentiate the dessert wine Prošek from dry wines made from the same autochthonous cultivars based on their phenolic composition (Villiers et al., 2005). To our knowledge, this in the first comprehensive study on the polyphenol composition of Prošek dessert wines encompassing ANOVA and PCA to classify wine types based on the phenolic composition.

2. Material and methods

2.1. Wine samples

Experimental dry wines Plavac mali of vintages 2007 and 2011 and Pošip (2010) (Table 1) from the principal Croatian autochthonous cultivars, red Plavac mali and white Pošip, were selected. All wines were made from grape samples from the germplasm collection at the Institute for Adriatic Crops and Karst Reclamation in Split in the wine-producing area of Croatia, Dalmatia. The wines were produced using micro-scale vinification in three biological replicates as part of an evaluation of the enological properties of autochthonous cultivars maintained in the germplasm collection at IAC. The original technology for making Prošek wine involves drying the grapes, but commercial wines produced by different methods are currently on the Croatian market. To equalize the production conditions of samples and facilitate direct comparison, we produced (in IAC) experimental Prošek dessert wines from both Plavac mali and Pošip grape samples from the wine-producing area of Dalmatia (Pelješac and Korčula, respectively; more details about grape sampling and experimental winemaking are included in online Supplementary information 1).

2.2. Experimental winemaking

Table 1 presents the list of wine samples produced for this study; the process is described below.

2.2.1. Prošek dessert wines

Approximately 400 kg of grapes were dried in a greenhouse equipped with a system for temperature control and ventilation (maximum daily temperature 40 °C) until the berries reached ~ 32 Brix. The dried fruit was destemmed, crushed, sulfited and divided into three containers for alcoholic fermentation using the commercial yeast strain EC1118 (*Saccharomyces bayanus*, Lallemand Inc, Montreal, Quebec, Canada). Fermentation of Plavac mali was carried out with five days of skin contact, while fermentation of Pošip was done without skin contact. The pomace was pressed in a hydraulic press at < 2 bar. The must was put in 25 L glass vessels, where alcoholic fermentation continued. The first racking was done at ~ 30 days and the second six months after the beginning of fermentation. After the second racking, wines were sulfited to 50 mg/L free sulfur dioxide (SO_2) and bottled. The wines were stored at the experimental winery until analysis.

2.2.2. Dry wines

Approximately 50 kg of grapes was destemmed, crushed, sulfited to 25 mg/L free sulfur dioxide (SO_2) and stored in a 10 L stainless steel vat. Micro-scaled fermentations were carried out using the commercial strain EC1118 in three replicates. Red pomace from Plavac mali was punched down twice daily until it remained submerged during the six-day maceration. The wine was then pressed and transferred to a stainless tank at 20 °C. Fermentation of white Pošip grapes was done without skin contact. At the completion of fermentation, the wine was racked and sulfited to 50 mg/L (SO_2). Malolactic fermentation was not performed.

2.3. Ultra high-performance liquid chromatography

Samples were analyzed by targeted metabolomics using ultra high-performance liquid chromatography coupled with triple-quadrupole mass spectrometers (UPLC/QqQ-MS/MS). Methods for identifying and quantifying non-colored phenolic compounds were as described (Vrhovšek et al., 2012; Arapitsas et al., 2012). Wine was filtered with a 0.2 µm PTFE filter prior liquid chromatography with a Waters Acquity UPLC system (Miliford, MA, USA) coupled to a Waters Xevo TQMS in ESI ionization mode. The separation of the phenolic compounds was achieved on a Waters Acquity HSS T3 column 1.8 µm, 100 mm × 2.1 mm (Miliford, MA, USA) kept at 40 °C. In the end, 2 µL were injected in the instrument by an auto-sampler at the temperature of 6 °C. Data were processed by the Waters MassLynx 4.1 and Target Lynux software.

Basic chemical parameters were determined according to reference OIV methods for wine analysis (OIV, 2005).

2.4. Chemicals and reagents

Methanol and acetonitrile were of LC–MS grade and were purchased from Sigma-Aldrich (St. Louis, MO, USA). Formic acid was also purchased from Sigma-Aldrich. Milli-Q water was used for the chromatography. The chemical standards were obtained from different suppliers or isolated as described in Vrhovšek et al., 2012.

2.5. Data analysis

Statistical analysis used average values of triplicate determinations. The data matrix was constructed from the analytical data obtained for wines, with rows representing wine samples (two varieties, two different wine types and four different vintage years – objects) and columns representing chemical measurements (45 phenolic compounds – variables). Autoscaling was used to produce variables with zero means and unit standard deviation (De Villiers et al., 2005). To establish which compounds differed significantly among wines, univariate characterization based on Fischer's weight (F) was conducted using one-way ANOVA. For multivariate analysis, factor analysis (FA) and principle component analysis (PCA) were used. FA and PCA present unsupervised pattern recognition techniques that seek to summarize and explain key feature of the data. Factorial analysis was used to reduce the initial set of 45 phenolic parameters to 23. Varimax rotation was performed on the reduced dataset to obtain maximum information from the extracted PCs. Linear discriminant analysis (LDA) was used to evaluate the efficiency of wine separation based on type. LDA is a supervised pattern recognition technique whit the task of inferring a function from labeled training data. The training data were wines types, including only the significant phenolic components, and the validation set was the starting data set of wines with all observed phenolic compounds included (see Supplementary material, Table S1 for all 45 phenolic parameters). All statistical data analysis was performed using STATISTICA, version 8.1 (Statsoft Inc., Tulsa, OK, USA).