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The impact of cultivar on polyphenol and biogenic amine profiles in Calabrian red grapes during winemaking

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ABSTRACT

In this study, during winemaking, was evaluated the influence of cultivar on bioactive compounds (organic acids, D-(+)-glucose, D-(−)-fructose, biogenic amines (BAs), anthocyanins, polyphenols and flavonoids) and antioxidant activity of Calabrian (Southern Italy) autochthonous grapes (Arvino, Gaglioppo, Greco Nero, Magliocco Canino, Magliocco Dolce and Nocera). Phenolic compounds increased from grapes to wine for all varieties. Arvino grapevine showed the highest DPPH radical scavenging activity, while a promising inhibition of the lipid peroxidation was observed with Greco Nero grapes. BAs were mostly formed during alcoholic fermentation and Arvino always showed the lowest BAs amounts, while Magliocco Canino generally exhibited the highest. Collectively, the results demonstrated that Calabrian autochthonous grapevines were rich in sugars, organic acids and phenolic compounds thus allowing the production of high quality wines.

1. Introduction

Wine is a complex mixture of hundreds of molecules, some of them showing important biological properties, while others are mainly associated with its organoleptic characteristics (Saurina, 2010). Many conditions (i.e. genetic, agronomic, technological, storage, etc.) linked to each other by complex and multifactorial phenomena, affect both profiles and concentrations of bioactive compounds, either in grape or in wine.

Among wine chemical classes, polyphenols and biogenic amines (BAs) have been deeply investigated for their crucial influence on wine quality, safety and nutraceutical features (Rathi & Rajput, 2014).

BAs generally originate in wine by microbial decarboxylation of amino acids and, while high concentrations of the former can cause undesirable physiological effects in sensitive humans, the seconds are precursors of aroma compounds and directly contribute to wine's smell, taste and appearance. BAs can be already present in grape berries or can be formed by the yeast during the alcoholic fermentation (AF). The other alternative in BAs production, is the action of lactic acid bacteria (LAB) involved in the malolactic fermentation (MLF). Ageing or storage of wine can contribute as well in BAs accumulation (Ancín-Azpilicueta, González-Marco, & Jiménez-Moreno, 2008). Also the storage of grapes prior to crushing under non-sterile conditions, can influence BAs concentrations, suggesting that these compounds can be considered indicators of a lack of hygiene during the winemaking process or associated with poor sanitary conditions of grapes.

Some authors reported on the presence of BAs in different wine products (Anli & Bayram, 2009). A wide range of concentration was observed, starting from not-detected up to 130 mg L^{-1} (Ancín-Azpilicueta et al., 2008), with the main amines being generally putrescine (PUT), hystamine (HIS), tyramine (TYR) and cadaverine (CAD). These are mainly the products of microbial decarboxylation of ornithine, histidine, tyrosine and lysine, respectively (Smit, du Toit, & du Toit, 2008), although PUT can also be formed via the arginine deiminase pathway from arginine (Mangani, Geurrini, Granchi, & Vincenzini, 2005). Many other BAs, such as phenylethylamine (PHE), agmatine (AGM), tryptamine (TRY), isoamylamine (ISA), methylamine (MET), and ethylamine (ETH) have also been found in

Abbreviations: AA, antioxidant activity; ABTS, 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid); AF, alcoholic fermentation; AGM, agmatine; BAs, biogenic amines; BHT, butylated hydroxytoluene; CAD, cadverine; DOC, Denominazione Origine Controllata; DOCG, Denominazione di Origine Controllata e Garantita; DPPH, 2,2-diphenyl-1-picrylhydrazyl; ETH, ethylamine; FRAP, Ferric Reducing Ability Power; HIS, histamine; FW, fresh weight; HBA, Total hydroxybenzoic acids; HPLC-DAD, High-Performance Liquid Chromatography-Diode Array Detection; IC_{50}, concentration giving 50% inhibition; IGT, Indicazione Geografica Tipica; ISA, isoamylamine; MET, methylamine; MLA, malolactic fermentation; PCA, principal component analysis; PHE, phenylethylamine; PUT, putrescine; ROS, reactive oxygen species; SPM, spermine; SPD, spermidine; SS, standard scores; TA, Total Anthocyanin Content; TEAC, Trolox equivalent antioxidant capacity; TFC, total flavonoids content; TPC, total phenols content; TRY, tryptamine; TYR, tyramine

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wine (Anli & Bayram, 2009). Finally, polyamines such as, PUT, spermine (SPE) and spermidine (SPD), can also be formed by the metabolisms of plants and thus already present in grapes.

Phenolic compounds play a fundamental role in some sensory properties of grapes and wines (Guerrero, Puertas, Fernández, Palma, & Cantos-Villar, 2010). The main flavonoid compounds present in red wine include several classes, such as flavanols [(*epi*)catechin], flavonols (e.g., myricetin and quercetin) and anthocyanins (e.g., malvidin-3-glucoside), while non-flavonoid compounds present in wine are phenolic acids, phenols and stilbenes (Caridi et al., 2017; Krammerer & Carle, 2009). This class of compounds has been proved to exert important health effects, acting against cancer pathologies (Giovinazzo & Grieco, 2015) as well as reactive oxygen species (ROS) which are considered the main cause of different cardiovascular and neurodegenerative diseases.

The wine sector is a pillar of the Italian economy. Italy is the world's largest wine producer and the second largest exporter by volume after Spain; moreover, approximately one-third of Italy's wines are high quality products boasting the Controlled Appellation (DOC, DOCG and IGT). Although still far from the leading regions, Calabria (southern Italy), has gained attention during last decades, reaching 12 DOCs and 12 IGTs recognitions and hosting 174 grape varieties, 76 of them are unique to the region (IOV, 2016). Mostly used as blending grapes, in recent years, Calabrian indigenous cultivars have gone uphill to produce varietal wines as well, although the complete characterization of both the raw materials and the final products is still lacking. Because the composition of wine is greatly influenced, either by the grape cultivars or by the winemaking techniques, it therefore essential to know the chemical-physical characteristics of each wine, especially the ones obtained from monovarietal grapes.

In this context, the goal of the present study was the characterization of autochthonous Calabrian red grapes and wines (Arvino, Gaglioppo, Greco Nero, Magliocco Canino, Magliocco Dolce and Nocera) that, to the best of author's knowledge, have been never considered elsewhere. The evolution of different classes of bioactive compounds (organic acids, carbohydrates, polyphenols and BAs) and in vitro antioxidant properties of the extracts, estimated using different assays ($ABTS^+$, DPPH•; β-carotene bleaching test and FRAP), was followed during winemaking. Moreover, in order to highlight differences among varieties, principal component analysis (PCA) was also applied to underline possible correlations among samples and different discriminating compounds.

2. Materials and methods

2.1. Chemicals and reagents

D-(+)-glucose, D-(−)-fructose, L-(+)-tartaric acid, L-(−)-malic acid, lactic acid, acetic acid, succinic acid and fumaric acid were purchased from Sigma-Aldrich Chem. Co. (Milwakee, WI, USA). BAs, SPE (tetrahydrochloride), SPD (trihydrochloride), PUT (dihydrochloride), HIM (dihydrochloride), TYR (hydrochloride), PHE (hydrochloride), dansylchloride, perchloric acid (60% w/w), ammonia (30%), ascorbic acid, butylated hydroxytoluene (BHT), β-carotene, chlorogenic acid, 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) solution, 2,2-diphenyl-1-picrylhydrazyl (DPPH), quercetin, sodium acetate buffer, sodium carbonate, sodium nitrite, Folin-Ciocalteau's reagent, Tween 20, potassium persulphate, linoleic acid, propyl gallate and Whatman filters (0.45 μm and 0.20 μm) were purchased from Sigma-Aldrich S.p.a. (Milan, Italy). Ultrapure water was obtained from Milli-Q System (Millipore Corp., Milford, MA, USA). SPE C_{18} cartridrges (0.5 g) were obtained from Supelco Inc. (Bellefonte, PA, USA). Gallic acid, (+)-catechin, caffeic acid (3, 4-dihydroxycinnamic acid), syringic acid (4-hydroxy-3, 5-dimethoxybenzoic acid), rutin (quercetin-3-*O*-rutinoside), *trans*-resveratrol, polydatin and quercetin were supplied by Extrasynthese (Genay-France).

2.2. Samples

A total of 18 samples (six berries, musts and wines) of autochthonous Calabria *Vitis vinifera* red grape varieties (Arvino, Gaglioppo, Greco Nero, Magliocco Canino, Magliocco Dolce and Nocera) were collected in September 2016 from a local producer (Azienda Agricola Donna Fidelia, Belvedere Marittimo, Cosenza, Italy). To limit variability of data and to emphasise the effect of grape variety, in this study grapes, musts and wines were provided from the same factory and were harvested, stored and processed in the same way.

Grapes, harvested at technological maturation, were grown in the same vineyard undergoing the same agronomic practices to eliminate possible variations due to different soils, climatic conditions and viticulture procedures and vinified under the same controlled processes to avoid variations during the winemaking. Each grape varieties (50 kg) were destemmed, crushed and pressed and subjected to spontaneous AF. The fermentation-maceration process was carried out at a maximum temperature of 25 ± 2 °C and lasted 7 days. Wines were then run off and maintained at controlled wine cellar temperature for undergoing spontaneous MLF. After 1 month, wine samples were separated from lees, added with SO_2 (10 g hL^{-1}) and then analyzed. In a standard procedure 0.5 kg of grapes and 250 mL of must and wine were collected for each variety in triplicate. All samples were immediately frozen with liquid nitrogen and stored at − 80 °C. The pH of each sample was measured before analysis. A microprocessor pH meter (Hanna Istruments, Eboli (SA), Italy), equipped with a combined glass-calomel electrode, was employed for pH measurements.

2.3. Polyphenols ultrasound extraction procedure

For the ultrasound assisted experiments, an ultrasonic water-bath (Branson model 3800-CPXH, Milan, Italy) was used. Sample (50 g) was mixed with 200 mL of ethanol/water (50:50 v/v) and an ultrasonic frequency of 40 kHz for 30 min was applied. After being extracted, the mixture was filtered under vacuum through Whatman filter, and the solvent was removed with a rotary vacuum evaporator. Each extraction was performed in triplicate.

2.4. Determination of D-(+)-glucose, D-(−)-fructose and organic acids

The sugars level in grape, must, and wine extracts was performed using a Knauer high liquid chromatography system (Asi Advanced Scientific Instruments, Berlin, Germany) equipped with a Knauer HPLC-Pump K-120 (Asi Advanced Scientific Instruments, Berlin, Germany), a Rheodyne injection valve with loop of 20 μL and a Smartiline RI detector 2300. Elution was obtained on a VARIAN Meta Carb H Plus column (300 mm × 7.8 I.D., 5 μm). The column temperature was 55 °C and the flow rate was 0.25 mL min^{-1}. The mobile phase consisted of 0.01 N H_2SO_4 solution.

The HPLC analyses of organic acids were performed on a Knauer (Asi Advanced Scientific Instruments, Berlin, Germany) system equipped with two pumps Smartiline Pump 1000, a Rheodyne injection valve (20 μL) and a photodiode array detector UV/VIS equipped with a semi-microcell. Separation was obtained using an Acclaim OA column (250 mm × 4.0 I.D., 5 μm) at T = 30 °C. The mobile phase consisted of 100 mM Na_2SO_4 (pH = 2.65 with methanesulfonic acid) and the flow rate was 0.6 mL min^{-1}. Stock solutions of each standard, in different diluted concentration ranging from 0.2–2 g L^{-1}, were prepared in ultra-pure water provided by a Milli-Q system (Millipore Co., Bedford, MA). All solutions were filtered through 0.45 mm glass-microfiber GMF Whatman chromatographic filter (HAWP Millipore Co., Bedford), before analysis.

The data related to the concentration of D-(+)-glucose, D-(−)-fructose and organic acids are reported in Table 1.