



Original Research Article

Biogenic amine profiles and antioxidant properties of Italian red wines from different price categories

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ABSTRACT

The most significant and beneficial health properties of wine consumption are related to compounds with high antioxidant capacity like polyphenols, including trans-resveratrol. Red wines are also a source of biogenic amines and sulphites that are detrimental to health. The main aim of this study was to assess whether a direct relationship between potential differences in the health-promoting and health-harmful properties can be found reflected in the commercial value of Italian red wines. Sixty Italian red wines, representative of three retail price categories, were analyzed by chromatographic and spectrophotometric techniques and the results evaluated by Principal Component Analysis. Wines in the category with a higher commercial value were clearly separated from those in the lower price category. In particular, the higher-priced wines showed higher values for trans-resveratrol (3.31 mg/L) and antioxidant capacity ($p < 0.05$), but also of total biogenic amines content, in particular putrescine (10.71 mg/L) and cadaverine (3.23 mg/L) ($p < 0.05$). The lower-priced wines showed a lower polyphenol content (1.35 g/L GAE) and a higher histamine content (1.02 mg/L) ($p < 0.05$). The oenological procedures that lead to wines of higher antioxidant quality cause the natural formation of only putrescine and cadaverine, which are not harmful to human health.

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1. Introduction

Moderate consumption of wine, especially red wine, has been associated with several potential health benefits, such as lower risk of cardiovascular or neurological diseases and anti-cancer properties, because of the antioxidant effect of some wine constituents such as polyphenols, and resveratrol in particular (Shahidi, 2009). On the other hand, red wines are known to be a source of biogenic amines (BA), a class of natural contaminants present both in fermented and non-fermented foods that are formed by decarboxylation of the corresponding amino acids by microorganisms through substrate-specific decarboxylase enzymes. Even if only few countries have adopted legislation on the tolerated contents of BA in wine, the study of BA represents a concern for wine industry. In fact, when normal catabolic routes of amines are inhibited or a large amount of food containing BA is ingested, several physiological changes can occur, such as migraine headaches, nausea, hypo- or hypertension, cardiac palpitations, and anaphylactic shock, and therefore the wine industry is

determined to reduce the presence of BA in wine (Marques et al., 2008).

Another important issue for consumer wine quality perception is the presence of sulphur dioxide (SO₂), an additive used for its antioxidant, anti-oxidase and anti-microbial properties. Nevertheless, it is also a poisonous and allergenic substance, and reported symptoms associated with sulphite sensitivity range widely in intensity and severity and include trouble breathing, skin rashes, and stomach pain (Costanigro et al., 2014). For this reason, European Commission (EC) Regulation No 607/2009 reports that sulphites must be declared on the label if the total SO₂ content in wine is higher than 10 mg/L.

Even though the population of sulphite-sensitive consumers is relatively small, the perception that sulphites may cause negative health effects appears to be very common, which is inducing winemakers to lower the overall amounts of SO₂ in their products (Comuzzo et al., 2013) even in the absence of clear scientific evidence concerning this compound.

The Italian wine market is one of the most important markets in terms of numbers of bottles sold, and the record of €5 billion in exports achieved in 2013 confirms the significant role of foreign demand as an economic factor. The traditional dilemma of whether the leading role in determining the price of Italian wine is the result

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of the label or of chemical/sensory variables is still an open question. Brentari et al. (2011) showed that sensory variables play a marginal role in price formation. The driving factor in price formation is the information that can be inferred from the label, especially if the wine is sold via large-scale distribution. However, “accumulated theoretical and empirical evidence suggests that wine prices depend on quality, reputation, and objective characteristics” (Oczkowski, 2001). But in consumer perception, the concept of quality is strongly related to commercial value (Fanzone et al., 2012), even in the absence of clear evidence.

The relation between phenolic composition and the commercial value of wine has been reported in South American red wines (Granato et al., 2012), and in Chilean, Canadian and American wines (Faustino et al., 2003); and the relation between phenolics composition together with antioxidant capacity in Brazilian (Granato et al., 2010; Lobodanin et al., 2014) and Australian (Yoo et al., 2011) red wines. The effect and relationship with commercial value of phenolic and polysaccharidic composition in Argentinean red wines were studied by Fanzone et al. (2012), and with aroma composition by San Juan et al. (2012). To the best of our knowledge, there are no studies on the total phenolics, trans-resveratrol and antioxidant activity in Italian red wines of different price categories, and this is the first work on the relation of sulphites content and biogenic amines composition to retail wine price.

The main objective of the present work was to compare different Italian red wines belonging to different price categories, in relation to their composition in both health-promoting and harmful chemical parameters, in order to establish the existence of differences linked to their commercial value.

2. Materials and methods

2.1. Chemicals

Methanol, acetonitrile (HPLC grade), perchloric and hydrochloric acid, Folin–Ciocalteu reagent, 2,2-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), 2,2-diphenyl-1-picrylhydrazyl (DPPH), potassium persulfate, (+/–), gallic acid (GA), trans-resveratrol and sodium carbonate were from Sigma Chemical Co. (St. Louis, MO, USA), while ethanol was purchased from Fluka (Milan, Italy). Distilled water was purified using a Milli-Q system (Millipore, Bedford, MA, USA).

The eleven biogenic amines studied were: ethylamine (ETA), methylamine (MEA), histamine (HIS), serotonin (SER), spermine (SPM), spermidine (SPD), agmatine (AGM), putrescine (PUT), β -phenylethylamine (β -PEA), cadaverine (CAD), and tyramine (TYM), all of which were supplied by Supelco, Bellefonte, PA, USA as well as the derivatizing agent dansyl chloride and the internal standard 1,7-diaminoheptane (IS).

2.2. Red wine samples

Sixty commercial wines in glass bottles (0.75 L) were collected directly from local markets and wine shops. The samples were all

labelled PDO and were produced from four single red grape varieties: Montepulciano D'Abruzzo and Dolcetto D'Alba, that are among the top 15 wines in market share, with 2.7% and 1.8%, respectively; Primitivo di Manduria and Syrah of Sicily that are representative of territories with traditional wine-production history. For each grape variety, 15 samples belonging to different brands were purchased, 3 bottles for each brand; characteristics are summarized in Table 1. The samples were distributed in three sets of 20 wines on the basis of price criteria: <4 € (low price segment), between 4–7 € (medium price segment), >7 € (high price segment). Wines were stored in darkness at 15–20 °C and each bottle was opened immediately before analysis. All analyses were carried out from September to November 2013.

2.3. Analytical procedures

Free and total sulphur dioxide, pH, ethanol content, were determined by the European official method, as reported in European Commission Regulation (EC) No 2676/1990. The pH values were measured by a pH-meter HI110 model (Hanna Instruments, Ann Arbor, MI, USA). Spectrophotometric determinations were performed with a PerkinElmer 554 UV–Vis spectrophotometer (PerkinElmer Instruments, Waltham, MA, USA) with 1-cm path length cuvettes.

2.3.1. HPLC analysis

HPLC chromatographic separations were developed in a system consisting in a LC-10 ATVP binary HPLC pump with a RF-10AXL fluorescence detector and a CT 10AS oven (Shimadzu, Kyoto, Japan). The injector was fitted with a 20 μ L loop. The chromatographic data were collected and processed using Class-VP software (Shimadzu).

Biogenic amines were determined by HPLC and pre-column derivatization with dansyl chloride, as reported by Preti et al. (2015). Briefly, 25 mL of wine previously added with IS, was acidified by HClO₄ 10.3 M to reach a final acid concentration of 0.2 M and then 1 mL derivatized by adding 200 μ L of NaOH 2 M, 300 μ L of saturated NaHCO₃ solution, and 2 mL of dansyl chloride solution (10 mg/mL in acetone). After shaking, samples were left in the dark at 45 °C for 60 min. The final volume was adjusted to 5 mL by adding acetonitrile. The dansylated amine solution obtained was filtered 0.22 μ m (Polypro Acrodisc, Pall Gelmann Laboratory, Ann Arbor, MI, USA) and injected into the chromatograph.

The analytical column was a 100 \times 4.6 mm i.d. Kinetex C18 column (particle size 2.6 μ m), with KrudKatcher C18 (all supplied by Phenomenex, Torrance, CA, USA). Analytical column temperature was kept at $T = 50$ °C. The chromatographic conditions were as follows: a linear gradient was from 65% acetonitrile to 75% acetonitrile in 3.5 min and then increased to 100% acetonitrile in 9 min, and then kept for 2 min for a total run time of 11 min at a constant flow rate of 0.6 mL/min. Fluorescence detection was set at 320 nm for excitation and 523 nm for emission. Identification of the biogenic amines was based on their retention times. The calibration curves, i.e. the peak area versus concentration, were

Table 1
Characteristics of the Italian red wine samples.

PDO wine	Provenance (lat./long./alt. m.a.s.l.)	Tag	Year (no of samples)
Montepulciano D'Abruzzo	Central Italy (42°21'58" N/13°23'40" E/563)	M	2007 (4), 2009 (4), 2010 (4), 2012 (3)
Dolcetto D'Alba	Northern Italy (44°33'56" N/8°07'28" E/252)	D	2007 (3), 2009 (3) 2010 (2), 2011 (3), 2012 (4)
Primitivo di Manduria	Southern Italy (40°28'18" N/17°36'45" E/15)	P	2008 (4), 2010 (3), 2011 (4), 2012 (4)
Syrah of Sicily	Southern Italy (37°33'35" N/14°08'21" E/40)	S	2007 (2), 2008 (2), 2009 (3), 2011 (4), 2012 (4)

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