Research Article

Antioxidant Composition of a Selection of Italian Red Wines and Their Corresponding Free-Radical Scavenging Ability

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This study correlates the antioxidant composition profiles and the overall antioxidant capacities of 36 Italian red wine samples. The samples were fully characterized by chromatographic and spectrophotometric techniques. The overall antioxidant capacity was determined by titrating a solution of the semistable free radical DPPH (1,1-diphenyl-2-picrylhydrazyl) with each wine sample followed by Electron Paramagnetic Resonance (EPR) spectroscopy and then measuring the resulting decrease in DPPH-signal. The antioxidant activities of the samples were expressed as (+)-catechin equivalents and related to their antioxidant composition profiles. Samples with a high polyphenol content showed a high DPPH scavenging ability as well. Seven well-defined groups, mainly constituted by wines coming from the same cultivar, were evidenced by PCA analysis. Alcohol content and pH did not influence the wine DPPH scavenging ability. The most important variables contributing to the wines’ antioxidant power are total flavonoid, total phenol, and proanthocyanidin indices together with fentaric acid, trans-caftaric acid, trans-coutaric acid, and both quercetin glucoside and quercetin glucuronide. EPR is demonstrated to be faster than the other analytical methods (spectrophotometric and chromatographic analyses) to determine the wine overall antioxidant activity.

1. Introduction

Wine has been part of human culture for thousands of years and is an important component of the traditional Mediterranean diet. Although the excessive use of alcohol can lead to serious health problems, a number of studies suggest that moderate consumption of wine (especially red) may provide health benefits. According to the Dietary Guidelines for Americans [1], moderate alcohol consumption is defined as having up to 1 drink (a glass, 150 mL 12% alcohol wine) per day for women and up to 2 drinks (two glasses, 300 mL 12% alcohol wine) per day for men. Positive effects derive from the strong antioxidant properties of polyphenolic compounds [2]. Red wines generally contain higher levels of polyphenols than white ones. These compounds not only contribute to the colour, flavour, astringency, and bitterness of a wine but also serve to fight free radicals in the body that cause disease and ageing. Epidemiological studies pointed out that the consumption of red wine has been shown to increase the body’s antioxidant capacity and is associated with a lower risk of mortality from cardiovascular diseases [3, 4].

There are two major classes of wine phenolics: non-flavonoids and flavonoids. The relative amount and distribution of these compounds depend on a variety of factors such as grape variety, vineyard location, climate, soil type, cultivation practices, harvesting time, production process, and wine ageing [5–8].

The class of flavonoids includes several molecules characterized by their functionalities on the benzene rings. The most important flavonoids in wine are anthocyanidins, flavanols (also known as catechins or flavan-3-ols), and flavonols (including quercetin and myricetin). Proanthocyanidins,
dimers, or oligomers of catechin and epicatechin and their
gallic acid esters are also classified as flavonoids. Red wines
contain wide-ranging concentrations of proanthocyanidins.

The term nonflavonoid usually includes different classes of
substituted phenols. These different congeners can be
grouped as benzoic-based compounds (i.e., vanillic and
gallic acids), benzaldehydes (vanillin and syringaldehyde),
cinnamic acids (p-coumaric, ferulic, and caffeic acids), and
cinnamaldehydes (coniferyl aldehyde and sinapylaldehyde).
These classes can be further subdivided by the number and
type of substituents present.

Ascorbic acid and sulfur dioxide, SO₂, also contribute
to the antioxidant power of wine [9]. These compounds are
naturally present in wine in very low amounts but are often
added as preservatives during the winemaking process.

SO₂ exerts its antioxidant effect by destroying the poly-
phenol oxidase (PPO) enzyme responsible for phenol oxidiza-
tion [10], but it was observed [11] that the content of polyphen-
ols and flavonoids was similar in organic and conventional
red wines as well as their antioxidant activity.

A wide variety of compounds contributes to the antiox-
didant power of wine, making it difficult to determine the
relative contribution of each antioxidant species. Profound
interactions between the compounds may take place, and the
total antioxidant power of a wine may not correspond to the
sum of the antioxidant capacities of each single molecule [12].

Recently, studies performed on grape skins, seeds [13–
15], and wines [16–18] have appeared in the literature. These
studies correlate the overall antioxidant power of the different
wine samples (via EPR determination) with the total amount
of polyphenols, but there is little information about the
interactions within the single class of compounds.

To date, the antioxidant parameters of most wines pro-
duced in Italy have not been fully determined. There are only
a few works regarding Italian wines [19], although one thor-
ough study on wines coming from different zones of Cam-
pania (Italy) has been published [20]. This lack of available
information is unfortunate, since, consequently, wine pro-
ducers do not always take advantage of the commercial value
associated with the antioxidant activity of wine, by making
related claims in advertising.

From a statistical point of view, univariate methods have
usually been applied for determining relationships between
total or individual phenols with the antioxidant properties of
red wines [21, 22]. This one-dimensional approach, however,
fails to determine simultaneous correlations. To overcome
this problem, the use of chemometric methods, which are
intrinsically multivariate in nature, has been recognized as a
valuable tool in wine science, for example, to assure wines’
authenticity and quality [23], to classify their geographical
originality and quality [23], to classify their geographical

value and quality [23], to classify their geographical

2. Materials and Methods

2.1. Reagents. Ultrapure water, calcium oxide, phosphoric
acid 85%, hydrogen peroxide, mixed indicator (pH 5.1), Folin-
Ciocalteu reagent (phosphomolybdic acid and phosphowol-
frameric acid mixture), absolute ethanol, hydrochloric acid
37%, sodium hydroxide solution 1M, methanol (HPLC gra-
fiant grade), sulfuric acid 1N, sodium carbonate, iron sulfate
heptahydrate (FeSO₄·7H₂O), 1,1-diphenyl-2-picrylhydrazyl
(DPPH), quercetin dehydrate, and p-coumaric acid were all
purchased from Sigma-Aldrich (Milan, Italy) and used as
received. Caffeic acid and ferulic acid were purchased from
Extrasynthese (Lyon, France).

2.2. Samples. Thirty-six wines (Table 1) from different Italian
regions were analysed. They were produced in experimental
cellars, where the different steps of the winemaking process
were controlled and traceable. The winemaking procedure
used also allowed for limited and controlled addition of non-
natural antioxidant products. The information about cultivars
is shown in Table 1.

All the chemical and physical determinations were per-
formed in triplicate.

Each sample was coded as indicated in Table 1. Numbers
added at the end of each code identify repetitions of analysis.

2.3. Instrumentation. Determination of anthocyanins, fla-


vones, proanthocyanidins, and total phenols was carried
out using a Jasco V-550 UV-VIS spectrophotometer (Tokyo,
Japan).

The qualitative-quantitative analysis of HCTAs and
flavonoids was performed with HP 1090 Hewlett-Packard
(Palo Alto, California, USA) HPLC liquid chromatograph
-equipped with a Diode Array Detector (DAD).

For EPR determination, a JEOL FA-200 X band EPR
spectrometer (JEOL Ltd., Tokyo, Japan) with a flat cell (JEOL
ES-LC11) was used.

2.4. Analytical Methods. The concentrations of alcohol (OH)
and ascorbic acid (AA), pH, and free SO₂ content were
determined according to the standard procedures reported in
the EEC 2676/90.
Table 1: An overview of the wine samples investigated.

<table>
<thead>
<tr>
<th>Cultivar</th>
<th>Code</th>
<th>PCA code</th>
<th>Region</th>
<th>Vintage</th>
<th>Winemaking technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albarossa</td>
<td>A10T</td>
<td>1T(1,2,3)</td>
<td>Piedmont</td>
<td>2010</td>
<td>Traditional</td>
</tr>
<tr>
<td>Albarossa</td>
<td>A10C</td>
<td>2C(1,2,3)</td>
<td>Piedmont</td>
<td>2010</td>
<td>With cryomaceration</td>
</tr>
<tr>
<td>Albarossa</td>
<td>A10MC</td>
<td>3MC(1,2,3)</td>
<td>Piedmont</td>
<td>2010</td>
<td>With hot prefermentative maceration</td>
</tr>
<tr>
<td>Cornarea</td>
<td>C10T</td>
<td>4T(1,2,3)</td>
<td>Piedmont</td>
<td>2010</td>
<td>Traditional</td>
</tr>
<tr>
<td>Cornarea</td>
<td>C10C</td>
<td>5C(1,2,3)</td>
<td>Piedmont</td>
<td>2010</td>
<td>With cryomaceration</td>
</tr>
<tr>
<td>Cornarea</td>
<td>C10MC</td>
<td>6MC(1,2,3)</td>
<td>Piedmont</td>
<td>2010</td>
<td>With hot prefermentative maceration</td>
</tr>
<tr>
<td>Refosco</td>
<td>R10Ve</td>
<td>7Ve(1,2,3)</td>
<td>Veneto</td>
<td>2010</td>
<td>Traditional</td>
</tr>
<tr>
<td>Refosco</td>
<td>R10Ma</td>
<td>8Ma(1,2,3)</td>
<td>The Marches</td>
<td>2010</td>
<td>Traditional</td>
</tr>
<tr>
<td>Refosco</td>
<td>R09Ve</td>
<td>9Ve(1,2,3)</td>
<td>Veneto</td>
<td>2009</td>
<td>Traditional</td>
</tr>
<tr>
<td>Refosco</td>
<td>R09Ma</td>
<td>10Ma(1,2,3)</td>
<td>The Marches</td>
<td>2009</td>
<td>Traditional</td>
</tr>
<tr>
<td>Nero d’Avola</td>
<td>NA10Ve</td>
<td>11Ve(1,2,3)</td>
<td>Veneto</td>
<td>2010</td>
<td>Traditional</td>
</tr>
<tr>
<td>Nero d’Avola</td>
<td>NA10Ma</td>
<td>12Ma(1,2,3)</td>
<td>The Marches</td>
<td>2010</td>
<td>Traditional</td>
</tr>
<tr>
<td>Nero d’Avola</td>
<td>NA09Ve</td>
<td>13Ve(1,2,3)</td>
<td>Veneto</td>
<td>2009</td>
<td>Traditional</td>
</tr>
<tr>
<td>Nero d’Avola</td>
<td>NA09Ma</td>
<td>14Ma(1,2,3)</td>
<td>The Marches</td>
<td>2009</td>
<td>Traditional</td>
</tr>
<tr>
<td>Primitivo</td>
<td>P08</td>
<td>15_(1,2,3)</td>
<td>Apulia</td>
<td>2008</td>
<td>Traditional with ageing in barriques</td>
</tr>
<tr>
<td>Primitivo</td>
<td>P09</td>
<td>16_(1,2,3)</td>
<td>Apulia</td>
<td>2009</td>
<td>Traditional with ageing in barriques</td>
</tr>
<tr>
<td>Primitivo</td>
<td>P10</td>
<td>17_(1,2,3)</td>
<td>Apulia</td>
<td>2010</td>
<td>Traditional with ageing in barriques</td>
</tr>
<tr>
<td>Cabernet s.</td>
<td>CaT101</td>
<td>18_(1,2,3)</td>
<td>Piedmont</td>
<td>2001</td>
<td>Vineyard with canopy management</td>
</tr>
<tr>
<td>Cabernet s.</td>
<td>CaT201</td>
<td>19_(1,2,3)</td>
<td>Piedmont</td>
<td>2001</td>
<td>Grapes with canopy management</td>
</tr>
<tr>
<td>Cabernet s.</td>
<td>CaT301</td>
<td>20_(1,2,3)</td>
<td>Piedmont</td>
<td>2001</td>
<td>Grapes with canopy management</td>
</tr>
<tr>
<td>Cabernet s.</td>
<td>CaT401</td>
<td>21_(1,2,3)</td>
<td>Piedmont</td>
<td>2001</td>
<td>Grapes with canopy management</td>
</tr>
<tr>
<td>Cabernet s.</td>
<td>CaT501</td>
<td>22_(1,2,3)</td>
<td>Piedmont</td>
<td>2001</td>
<td>Grapes with canopy management</td>
</tr>
<tr>
<td>Cabernet s.</td>
<td>CaT601</td>
<td>23_(1,2,3)</td>
<td>Piedmont</td>
<td>2001</td>
<td>Grapes with canopy management</td>
</tr>
<tr>
<td>Cabernet s.</td>
<td>CaT701</td>
<td>24_(1,2,3)</td>
<td>Piedmont</td>
<td>2001</td>
<td>Grapes with canopy management</td>
</tr>
<tr>
<td>Cabernet s.</td>
<td>CaT801</td>
<td>25_(1,2,3)</td>
<td>Piedmont</td>
<td>2001</td>
<td>Grapes with canopy management</td>
</tr>
<tr>
<td>Cabernet s.</td>
<td>CaT901</td>
<td>26_(1,2,3)</td>
<td>Piedmont</td>
<td>2001</td>
<td>Grapes with canopy management</td>
</tr>
<tr>
<td>Uvalino</td>
<td>U06</td>
<td>27_(1,2,3)</td>
<td>Piedmont</td>
<td>2006</td>
<td>Traditional</td>
</tr>
<tr>
<td>Uvalino</td>
<td>U04</td>
<td>28_(1,2,3)</td>
<td>Piedmont</td>
<td>2004</td>
<td>Traditional</td>
</tr>
<tr>
<td>Primitivo</td>
<td>P10M</td>
<td>29M(1,2,3)</td>
<td>Apulia</td>
<td>2010</td>
<td>Traditional with ageing in barriques</td>
</tr>
<tr>
<td>Primitivo</td>
<td>P10SM</td>
<td>30SM(1,2,3)</td>
<td>Apulia</td>
<td>2010</td>
<td>Traditional with ageing in barriques</td>
</tr>
<tr>
<td>Primitivo</td>
<td>P11M</td>
<td>31M(1,2,3)</td>
<td>Apulia</td>
<td>2011</td>
<td>Traditional with ageing in barriques</td>
</tr>
<tr>
<td>Primitivo</td>
<td>P11SM</td>
<td>32SM(1,2,3)</td>
<td>Apulia</td>
<td>2011</td>
<td>Traditional with ageing in barriques</td>
</tr>
<tr>
<td>Gaglioppo</td>
<td>G09nosd</td>
<td>33_(1,2,3)</td>
<td>Calabria</td>
<td>2009</td>
<td>Without seeds in steel</td>
</tr>
<tr>
<td>Gaglioppo</td>
<td>G09sd</td>
<td>34_(1,2,3)</td>
<td>Calabria</td>
<td>2009</td>
<td>With seeds in steel</td>
</tr>
<tr>
<td>Gaglioppo</td>
<td>G09nosdbq</td>
<td>35_(1,2,3)</td>
<td>Calabria</td>
<td>2009</td>
<td>Without seeds in barriques</td>
</tr>
<tr>
<td>Gaglioppo</td>
<td>G09sdqb</td>
<td>36_(1,2,3)</td>
<td>Calabria</td>
<td>2009</td>
<td>With seeds in barriques</td>
</tr>
</tbody>
</table>

The determination of total phenol (TP), total anthocyanin (TA), proanthocyanidin (PA), and total flavonoid (TF) indices was performed according to the methods described by Di Stefano et al. [30].

For hydroxycinnamoyl-tartaric acids (HCTAs) and flavonol determinations, chromatographic methods previously reported by Di Stefano and Cravero [31] were used.

HPLC separations were performed using a C18 column ODS Hypersil RP-18 (200 × 2.1 mm, 5 mm) (Thermo Scientific) and the mobile phase gradient reported in Table 2. Solvent A is $1 \times 10^{-3}$ M phosphoric acid and solvent B is methanol. The flow rate was 0.25 mL min$^{-1}$ and the volume injected was 20 μL.

Flavonols were determined registering the chromatogram at 360 nm [32]. In particular, quercetin glucoside (Q1), quercetin glucuronide (Q2), and myricetin (MY) were identified and quantified by the response factor method and reported as an equivalent of quercetin dehydrate.

HCTAs were identified and quantified by the chromatograms registered at 320 nm. The amount of HCTAs was reported as $p$-coumaric acid equivalents for cis- (CC) and trans- (TC) $p$-coumaroyl tartaric acid (cis-, trans-coumaric acid), as caffeic acid equivalents for cis- (CF) and trans- (TE) caffeoyl tartaric acids (cis-, trans-caftaric acid), and as ferulic acid equivalents for trans- (TL) feruloyl tartaric acid (trans-fertaric acid), using the response factor method.
The concentration of cis-feruloyl tartaric acid was too low to be determined.

2.5. EPR Measurements. For experiments of free-radical scavenging, 990 µL of a 250 µM DPPH solution in methanol was added to 10 µL of each wine sample. The mixture was then transferred to a flat cell for the analysis of the residual DPPH radicals. The measurements were performed 5, 10, and 15 minutes after the addition of DPPH. The signal areas were evaluated by double integrating the recorded EPR signal in the region between 326 and 330 mT. EPR spectroscopic analyses were carried out under the following conditions: temperature 25°C; magnetic field 329±5 mT; field modulation width 0.1 mT; field modulation frequency 100 KHz; receiver gain 200; time constant 0.03 s; sweep time 30 s; microwave power 4 mW. The percentage ratio of the signal areas of wine and reference samples after 5, 10, and 15 minutes from DPPH addition was calculated. The reference sample was prepared adding 10 µL of a 12% v/v ethanol aqueous solution to 990 µL of the 250 µM DPPH stock solution in methanol. (+)-Catechin was chosen as the reference antioxidant to express the free-radical scavenging activity measured by EPR. Different amounts of a 400 µM (+)-catechin solution in methanol were added to 400 µL of a 250 µM DPPH methanol solution. Methanol was then added to reach the final volume of 500 µL. The obtained samples were 200 µM in DPPH and had a (-)-catechin concentration ranging from 8 to 56 µM. The percentage ratio of the signal areas of (+)-catechin and reference samples after 5, 10, and 15 minutes from DPPH addition was calculated. For (+)-catechin, the reference sample was prepared by adding 100 µL of methanol to 400 µL of the 250 µM DPPH stock solution in methanol. Figure 1 shows the antiradical activity observed for (+)-catechin.

The free-radical scavenging activity of the wines under investigation (T5, T10, and T15) was reported as the equivalent amount of (+)-catechin (mg L⁻¹) necessary to identically quench the EPR signal of DPPH after the same contact time.

2.6. Statistical Analysis. PCA is a pattern recognition method representing objects in a new reference system characterized by variables called Principal Components (PCs) well described elsewhere [33]. Briefly, PCs are orthogonal to each other and are computed hierarchically (the information accounted for by successive PCs is decreasing). Each PC has the property of explaining the maximum possible amount of variance contained in the original dataset. The PCs, which are expressed as linear combinations of the original variables, are used for an effective representation of the system under investigation with a lower number of variables than in the original case. The coordinates of the samples in the new reference system are called scores, while the coefficients of the linear combination describing each PC, that is, the weights of the original variables on each PC, are called loadings.

Principal Component Analysis and all graphical representations were performed using Statistica 7.1 (Dell Statistica, Tulsa, Oklahoma, USA) and Excel 2013 (Microsoft Corporation, Redmond, Washington, USA).

3. Results and Discussion

Thirty-six wines obtained from the 9 cultivars (Table 1) were analysed for the 20 parameters reported in the experimental section. The wines were produced in experimental cellars where the use of chemical additives such as ascorbic acid was avoided, while the SO₂ addition was kept as low as possible.

Samples were produced using grapes grown in different areas of Italy (with a variety of soils and climatic characteristics) and from different cultivars. In this way, the set of samples guarantees adequate heterogeneity of the agronomic and viticulture characteristics.

The entire dataset, obtained analysing each wine sample, is available as supplementary material (in Supplementary Material available online at http://dx.doi.org/10.1155/2016/4565391). As expected, since the wines chosen for the study are very heterogeneous, the experimental values obtained for antioxidant concentrations are spread over a wide range.

In particular, the total phenol index ranged from 765 to 5745 mg L⁻¹ (the average being 2160 mg L⁻¹) [34, 35], the total anthocyanin index from 18 to 687 mg L⁻¹, the total flavonoid index from 810 to 5260 mg L⁻¹, and the proanthocyanidin index from 761 to 6900 mg L⁻¹. The alcohol content ranged between 9.64 and 16.38% v/v. It is important to point out that the majority of SO₂ comes from the addition of potassium metabisulfite to grapes and wine. The wines studied here were
characterised by very low free SO$_2$ values ranging from 0 to 28 mg L$^{-1}$. These analytical results confirmed the claims of cellars who added only the minimum SO$_2$ amount required to preserve the wine, even if higher amounts are allowed by the Italian law. The ascorbic acid concentration was below the detection limit for all the samples measured.

HCTAs (caftaric, coutaric, and fentaric acid) and flavonols (quercetin and myricetin) were present in low concentrations, as expected [36]; even if they were originally present at high concentration in grapes, their amount decreased significantly during fermentation and ageing.

The quenching of DPPH signal is a function of both contact time and the amount of antioxidant compounds added. Figure S1, reported as an example, shows the decrease of the DPPH EPR signal with time after the addition of a given amount of wine. The most common standard employed to quantify the overall antioxidant capacity of wine is (+)-catechin. Noteworthy, kinetics of free-radical quenching of the wines under investigation and (+)-catechin were very similar during the EPR experiment, giving rise to the meaningful T5, T10, and T15 parameters as described in Section 2.5.

Gaglioppo and Cornarea wines showed the highest antioxidant activity, while Nero d’Avola and Cabernet showed the lowest one. For the Cabernet wines (produced in 2001), this fact can be explained by the ageing effect, which leads to a drastic depletion of the polyphenol content. In general, samples with a high polyphenol content showed a high DPPH scavenging ability as well.

The experimental data clearly indicate profound differences among the samples, and finding correlation in the dataset appears to be a complex task especially by the classical univariate approach. Therefore, PCA analysis was performed on the complete dataset in which the variables were autoscaled to eliminate their inhomogeneity. The scree plot in Figure 2 shows that the first PC (PC1) explains about 61% and the second PC (PC2) about 15% of the total variance contained in the original dataset. Therefore, the successive PCs can be considered as not statistically significant.

In Figure 3, the score plot obtained for the first two PCs is reported in which the samples of the same cultivar have the same colour code. The first two PCs allow effective separation of the samples into different classes. Results from three sample replicates proved to be very similar, indicating excellent repeatability for all parameters examined.

In particular, seven well-defined groups can be identified (Figure 3), mainly constituted by wines coming from the same cultivar. The exceptions are Nero d’Avola and Refosco, whose data partially overlapped.

Accurate interpretation of the parameters leading to this grouping of the samples requires the loading plot information reported in the histogram of Figure 4 that represents the weights of the original variables on each PC.

Many of the variables studied show negative weights on PC1. In particular, the variables related to the EPR analyses and the proanthocyanidin, the total flavonoid, and the total phenol indices are located at high negative weights. Moreover, a lower but still significant contribution is also present for quercetin glucoside, quercetin glucuronide, and transcatafcaric acid, which have a lower negative weight. pH is the only variable placed at a positive weight on PC1, but its value is not so high.

Within the first PC, the EPR values and the content of polyphenols have the same sign, indicating that there is a strong correlation between them and that they account for the same information. For those reasons, the meaning of “antioxidant power” can be assigned to the macrovariables PC1. This macrovariable distinguishes very well between Gaglioppo and Cornarea (which have a high antioxidant capacity) from Cabernet sauvignon, Refosco, and Nero d’Avola. Figure 3 clearly illustrates the antioxidant activity attribute of the cultivars under study, showing their position along the PC1 axis. Antioxidant power increases, in fact, when moving from the right to the left side of the figure. In detail, the samples placed in the negative part of the PC1 are characterized by high values of the variables having negative weight on this PC and by low values of the ones having positive weight. The opposite is true for the samples placed in the positive part of PC1.

It is important to note that the antioxidant power of the Gaglioppo samples is much stronger than that of all the other
the wine samples derives from the use of grapes with a high alcohol content in sugar content (such as very mature grapes); this leads to a final product with a relatively high pH (low acidity). Indeed, Primitivo and Uvalino are both wines with a high alcohol content and low acidity, since they were made with very ripe grapes. Despite the low amounts of SO$_2$ found in all the samples, this variable allows PC2 to highlight differences among the biological samples Primitivo and Uvalino with respect to Refosco, Nero d’Avola, Albarossa, and Cornarea that stem from microwinemaking processes. In the latter winemaking procedure, slightly more SO$_2$ is required to prevent oxidation, because of the small volume of grapes used.

4. Conclusions

In this work, 36 wine samples were fully characterised by chromatographic and spectrophotometric techniques, and their antioxidant activities were evaluated by DPPH-EPR assay. The EPR measure is quite fast and does not require any sample pretreatment.

The resulting dataset was subjected to multivariate PCA analysis. The loading plot shows that the most important variables contributing to the wines’ antioxidant power are total flavonoid, total phenol, and proanthocyanidin indices together with tartaric acid, trans-caftaric acid, trans-coumaric acid, and both quercetin glucoside and quercetin glucuronide. From the score plot, it is possible to observe that PC1 can distinguish the seven different cultivars on the basis of their antioxidant capacity so that the meaning of “antioxidant power” can be assigned to the macrovariable PC1. On the other hand, PC2 is able to point out some differences among the samples arising from variations in pH, alcohol, and free SO$_2$. The observed differences among samples could not be evidenced with the classical univariate approach.

Additional Points

The authors studied 36 wines produced with grapes from different cultivars and areas of Italy. Red wines were assessed using spectrophotometric and HPLC determinations. Antioxidant power of red wine was tested with DPPH assays.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

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References


