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**PHYSICOCHEMICAL CHARACTERIZATION AND ANTIRADICAL ACTIVITY OF MOLDOVAN DRY RED WINES: A CORRELATION STUDY**

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## PHYSICOCHEMICAL CHARACTERIZATION AND ANTIRADICAL ACTIVITY OF MOLDOVAN DRY RED WINES: A CORRELATION STUDY

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**Abstract.** The physicochemical properties, phenolic composition, and antiradical activity of eight Moldovan dry red wines have been investigated to identify the key determinants of their radical scavenging capacity. The results revealed considerable variability in basic physicochemical parameters, phenolic compounds and antiradical activity among the samples, yet remaining compliant with the standards for dry red wines. Total phenolic content varied between 1.40 and 2.27 g GAE/L, with the highest values recorded in Gamay (Beaujolais), Codrinschii, and Saperavi wines. Gamay (Beaujolais) exhibited the highest anthocyanin content (1.256 g M3GE/L) and antiradical activity (1.94 g AAE/L), while Codrinschii wine showed the greatest proanthocyanidin content (0.36 g CE/L). The antiradical activity correlated most strongly with the total phenolic content ( $R^2=0.9854$ ), highlighting its primary role in the radical scavenging capacity of red wines. Anthocyanins ( $R^2=0.5739$ ), proanthocyanidins ( $R^2=0.4717$ ) and free  $SO_2$  ( $R^2=0.4216$ ) also contributed to antiradical activity, showing moderate linear relationships. General compositional parameters, including sugars, titratable acidity, pH, and volatile acidity, showed only weak correlations ( $R^2<0.20$ ).

**Keywords:** red wine, phenolic compounds, antiradical activity, DPPH<sup>\*</sup>, correlation study.

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### Introduction

Wine production represents a major agro-economic sector worldwide, with significant cultural, social, and economic importance at both regional and global levels. According to the FAOSTAT database, global wine production in 2022 reached 27.3 mln tonnes, with Europe accounting for 63% of this total (approximately 17.2 mln tonnes) [1]. Among European producers, Italy, France, Spain, and Portugal dominate the market, while countries with emerging wine sectors, such as the Republic of Moldova, are gaining increasing recognition. In 2022, Republic of Moldova ranked 10<sup>th</sup> in Europe in terms of wine production, with an output of 143,680 tonnes [1].

Beyond production volume, Moldova distinguishes itself through a strong focus on wines derived from autochthonous and newly selected grape varieties, which represent a key component of its cultural heritage and a growing segment of its export-oriented wine industry [2-4]. Recent publications regarding the chemical composition,

phenolic content, and bioactive properties of local grapes and wines display compositional characteristics comparable to well-established European cultivars [5-9]. Moldovan grapes typically exhibit high levels of phenolic compounds, including flavonoids (such as anthocyanins, flavonols, and tannins) and non-flavonoids (such as hydroxycinnamic acids), which play a key role in colour, antioxidant capacity, and organoleptic properties of wines [10,11].

However, while several studies have characterized Moldovan autochthonous wines, correlation studies linking quantitative polyphenolic indices and physicochemical parameters with antiradical activity remain limited in international peer-reviewed literature. Current publications have associated wine phenolic compounds with potential health benefits, mainly due to their antioxidant and anti-inflammatory properties [12]; but the relationship between standard quality parameters and functional properties in local wines is underexplored.

The aim of this study is to characterize the physicochemical parameters and quantitative polyphenolic indices of selected Moldovan dry red wines, and to evaluate their antiradical activity. Through correlation analysis, this research seeks to establish relationships between physicochemical properties, polyphenolic content, and radical scavenging capacity, contributing to the scientific knowledge on Moldovan dry red wines.

## Experimental

### Materials

#### *Wine samples*

The research was carried out at the PI National Institute for Applied Research in Agriculture and Veterinary Medicine (PINIARAVM). Eight dry red wines produced from the grape varieties Codrinschii, Copceac, Feteasca Neagra, Mugurel, Negru de Ialoveni, Gamay (Beaujolais), Pinot Noir and Saperavi, cultivated in the experimental plantations of the PINIARAVM were used. Grapes were harvested in 2020 and processed under microvinification conditions at PINIARAVM. The wine analysis was performed in 2021, after one year of wine maturation.

#### *Description of grape varieties*

Codrinschii is a Moldovan red grape variety obtained from Cabernet Sauvignon × Rara Neagra. It is characterized by medium to late ripening (late September–early October), semi-vigorous growth, and winter hardiness down to  $-23^{\circ}\text{C}$ . Average yield reaches 10–12 t/ha. At technological maturity, sugar content may reach 220 g/L with titratable acidity of 9.0–11.0 g/L. The cultivar is suitable for quality rosé and dry red wines, sparkling wine production, and blending [4].

Copceac is an improved form of Rara Neagra grape variety with medium-late ripening (150–155 days from budburst). The vines exhibit high vegetative vigour and frost-resistant (down to  $-23^{\circ}\text{C}$ ). Yields range from 12–14 t/ha. Sugar accumulation varies between 190–240 g/L, with titratable acidity of 6–9 g/L. It is suitable for the production of dry red and dessert wines with good colour intensity and for blending [4].

Feteasca Neagra is an indigenous grape variety ripening in mid to late September. It exhibits strong vegetative vigour and winter tolerance down to  $-22^{\circ}\text{C}$ . Yield averages 7–10 t/ha. Sugar levels range from 220–230 g/L, with titratable acidity of 5–8 g/L. The variety produces structured dry red wines characterized by balanced tannins, dried plum notes, and good aging potential [4].

Negru de Ialoveni (Merlot × *Vitis amurensis*) is a medium to late ripening Moldovan grape variety with moderate to strong growth vigour and improved frost and disease resistance. Yield averages 9–12 t/ha. Grape must sugar content reaches 210–230 g/L with titratable acidity of 8–10 g/L. It is intended for dry red and dessert wine production, yielding intensely coloured wines with pronounced structure [4].

Mugurel is a Moldovan interspecific hybrid (*Vitis amurensis* × Muscat of Hamburg) characterized by early ripening, high fertility, and good sugar accumulation. It demonstrates improved ecological adaptability and stress tolerance. The new selected grape variety shows potential for aromatic red wine production and remains under experimental evaluation [4].

Gamay (Beaujolais) is an early to mid-ripening French grape variety with moderate growth vigour and good productivity. Sugar levels range from 190–220 g/L and titratable acidity from 5.5–7 g/L. It is suitable for light-bodied, fruit-driven red wines, particularly under carbonic maceration [13].

Pinot Noir is a French early-ripening grape variety with moderate productivity and sensitivity to frost and fungal diseases. At technological maturity, sugar content ranges from 200–240 g/L and titratable acidity from 6–8 g/L. It produces elegant wines with soft tannins and notable aging potential [14].

Saperavi is a medium to late ripening grape variety, originating from Georgia, with strong growth vigour and good frost tolerance. Sugar accumulation ranges between 200–240 g/L, with titratable acidity of 6–9 g/L. It is suitable for deeply coloured red wines with high tannin content and aging capacity [15].

#### *Reagents*

L-ascorbic acid (AA), (+)-catechin, 4-(dimethylamino)cinnamaldehyde (DMAC), 2,2-diphenyl-1-picrylhydrazyl (DPPH $\bullet$ ), Folin-Ciocalteu reagent were purchased from Sigma-Aldrich. Gallic acid monohydrate (GA) (98.0 %), hydrochloric acid (HCl) (37%), NaOH and H<sub>2</sub>SO<sub>4</sub> titrants were purchased from the local supplier Ecochimie. All reagents were used without further purification.

#### *Equipment*

Absorbance measurements were recorded on a T60U (PG Instruments, UK) spectrophotometer. All samples were analysed in 10 mm quartz cells at room temperature.

The "Mettler Toledo MA 235" pH meter was used for pH determination.

## Methods

### Winemaking technology

Grapes were harvested at technological maturity and processed in 20-kg lots per cultivar. After destemming and crushing, the must was treated with 50 mg/kg SO<sub>2</sub> and inoculated with active dry yeast (LAU) IOC „FIZZ”. Maceration–fermentation was carried out at 30±1°C for 5 days. The fermented pomace was pressed using a vertical screw press, and alcoholic fermentation was allowed to proceed to dryness. Upon completion of alcoholic fermentation, the free SO<sub>2</sub> levels were adjusted to 30 mg/L; after gravitational settling and clarification, obtained dry red wines were subjected to physicochemical analyses.

### Physicochemical analysis

The physicochemical parameters were determined according to standardized methods of the International Organisation of Vine and Wine (OIV).

The determination of sugars was performed using the OIV-MA-AS311-01A, Type IV method [16]

Titrate acidity was determined by OIV-MA-AS313-01 method [17]. Results are expressed as tartaric acid equivalents (g TAE/L).

The volume fraction of ethanol was determined by OIV-MA-AS312-01 method [18].

The mass concentration of volatile acids was determined following the procedure from OIV-MA-AS313-02 method [19]. Results are expressed as acetic acid equivalents (g ACE/L).

Free and total sulphur dioxide were determined by following the OIV-MA-AS323-04B methods [20].

The determination of pH was carried out using the potentiometric method, according to OIV-MA-AS313-15 [21].

### Determination of total polyphenolic content (TPC)

The total phenolic content in wine samples was determined using the slightly modified spectrophotometric method with the Folin-Ciocalteu reagent, and gallic acid used as standard [22]. Briefly, 1 mL of the wine sample was transferred into a 100 mL volumetric flask and diluted with 20 mL of distilled water. Next, 1 mL of Folin-Ciocalteu reagent was added, and after 5 minutes, 10 mL of a 20% Na<sub>2</sub>CO<sub>3</sub> solution was introduced. The solution was then brought to volume with distilled water. The mixture was incubated in the dark at room temperature for 20 minutes, followed by UV-Vis spectrophotometric analysis at a wavelength of 760 nm. For the blank sample, the wine was replaced with distilled water. The results were

expressed as gallic acid equivalents per litre (g GAE/L).

### Determination of the anthocyanin's content (AC)

The anthocyanin content in local wines was determined using the differential pH method, as reported in the literature [23]. In short, 3 mL of appropriately diluted sample was transferred into a 25 mL volumetric flask, followed by 12.5 mL of acidified ethanol (ethanol acidified with HCl, pH 1–2), and 3 drops of 37% HCl. The volume was brought to the mark with distilled water. The resulting mixture was centrifuged at 7000 rpm for 15 minutes. The supernatant was then analysed using a UV-Vis spectrophotometer at a wavelength of 530 nm. The absorbance values obtained were multiplied by the molar extinction coefficient of Malvidin-3-glucoside (1056.7 M<sup>-1</sup>·cm<sup>-1</sup>) [24]. The results were expressed as Malvidin-3-glucoside equivalents per litre (g M3GE/L).

### Determination of the proanthocyanidin's content (PC)

The content of proanthocyanidins in local wines was determined using the chromophore compound 4-dimethylaminocinnamaldehyde, following the method described previously [25]. The DMAC solution was prepared by dissolving 1 g of DMAC reagent in 25 mL of 37% HCl, followed by dilution with methanol to a final volume of 100 mL. The resulting orange solution was stored overnight at –19°C.

To determine the proanthocyanidin content, 1 mL of appropriately diluted sample was transferred into a 25 mL volumetric flask. Then, 3 drops of glycerol and 5 mL of the DMAC solution were added, and the volume was brought to the mark with methanol. The reaction was allowed to proceed for 7 minutes, after which absorbance was measured using a UV-Vis spectrophotometer at a wavelength of 640 nm. The results were expressed as g catechin equivalents per litre (g CE/L).

### Determination of antiradical activity (ARA)

The method for testing antiradical activity using the free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH<sup>•</sup>) is widely recognized as a simple and accessible approach for evaluating the antiradical capacity of plant extracts, food products, or individual compounds [26]. The transfer of hydrogen atom or electron to the DPPH<sup>•</sup> radical results in a decrease in absorbance at 510–520 nm, which can be measured using a standard UV-Vis spectrophotometer operating in the visible range [26]. To assess the antiradical activity of local wines, the method described by Brand-Williams, W. *et al.* was employed [26].

The concentration of the DPPH<sup>•</sup> solution, prepared in 96% ethanol, was verified daily using a calibration curve. The initial absorbance of the free radical was maintained at approximately 0.03 g/L (absorbance = 1.000 ± 0.020 a.u.). The maximum absorbance of the DPPH radical was observed at 517 nm, with a molar extinction coefficient ( $\epsilon$ ) of 11.858 ± 16 M<sup>-1</sup>·cm<sup>-1</sup>. The use of DPPH<sup>•</sup> method for analysis of grape and wine biologically active compounds was previously reported [27,28]

The radical scavenging activity of wine samples was estimated according to the previously described procedure [26]. To 3.9 mL of DPPH<sup>•</sup> solution, 0.1 mL of appropriately diluted sample was added. The absorbance was recorded after allowing the reaction to proceed in the dark during 60 minutes. Results were expressed in AAE/L (ascorbic acid equivalents per litre).

#### Data analysis

Statistical analysis was performed using one-way ANOVA to determine whether significant differences existed among the wine varieties. When the ANOVA test yielded significant results ( $p < 0.05$ ), Tukey's Honest Significant Difference (HSD) post-hoc test was applied to identify specific pairwise differences between groups. All determinations were performed in triplicate. A  $p$  value of 0.05 was considered significant.

#### Equations and formulas

To determine the IC<sub>50</sub> parameter, the percentage of remaining DPPH<sup>•</sup> at reaction equilibrium was calculated using Eq.(1).

$$\% \text{remaining DPP} = \left( \frac{A_{\text{sample}}}{A_{\text{control}}} \right) \times 100\% \quad (1)$$

where, %remaining DPPH<sup>•</sup> - the percentage of unreacted DPPH<sup>•</sup> at equilibrium;

$A_{\text{sample}}$  - the absorbance of the mixture containing the wine sample after reaching equilibrium;

$A_{\text{control}}$  - the initial absorbance of the mixture at the time zero.

## Results and discussion

The physicochemical parameters of the analysed wine samples are the primary indicators of wine quality and normal maturation processes, and include sugar content, ethanol concentration, titratable and volatile acidity, total and free SO<sub>2</sub> content, and pH. The data for each measured parameter are shown in Table 1. The spectrophotometric analysis performed on eight Moldovan red wine samples revealed notable differences in the total phenolic content (TPC), anthocyanin content (AC), proanthocyanidin content (PC), and antiradical activity (ARA) (Table 2). The variability observed among the wines appears to be associated primarily with grape variety, while also reflecting the influence of vinification practices [29].

#### Physicochemical analysis

The ethanol content of the wines ranged from 12.5% to 15.53% (v/v) (Table 1). The highest ethanol level was observed in Negru de Ialoveni (15.83%), which also exhibited the highest sugar concentration at harvest (283 g/L), indicating that harvested grapes are at an advanced stage of technological maturity. Conversely, Pinot Noir presented the lowest ethanol content (12.5%), correlated with its sugar content at harvest (218 g/L) (Table 1).

The variation of sugar content from grapes to wine is a reliable indicator of wine quality. From Table 1, it is evident that sugar content of the grapes ranged from 218 to 283 g/L, which indicates that the grapes were harvested at medium to advanced technological maturity. Also, alcoholic fermentation was complete in most of the wines, except for Gamay (Beaujolais) (5.6 g/L residual sugar), Mugurel (7.9 g/L), and Negru de Ialoveni (8.1 g/L), where the residual sugar content exceeds 5 g/L, indicating incomplete fermentation. All wines demonstrated a good conversion efficiency of sugars into ethanol, but in these samples, the high initial sugar concentrations (above 260 g/L) likely led to partial inhibition of fermentation.

Table 1

#### Physicochemical characteristics of grapes at harvest and corresponding dry red wines after fermentation.

Wine samples	Sugars at harvest, g/L	Titratable acidity at harvest, g TAE/L	Ethanol, % Vol.	Sugars g/L	Titratable acidity, g TAE/L	Volatile acidity, g ACE/L	Total SO <sub>2</sub> , mg/L	Free SO <sub>2</sub> , mg/L	pH
Codrinschii	223	8.9	13.12	2.9	8.7	0.26	90	27	3.26
Gamay (Beaujolais)	269	6.5	15.53	5.6	4.7	0.47	129	29	3.77
Copceac	240	5.8	14.11	2.5	5.1	0.42	88	25	3.65
Feteasca Neagra	268	7.7	14.41	4.3	6.8	0.41	78	26	3.42
Mugurel	260	5.6	14.93	7.9	6.1	0.39	71	23	3.55
Negru de Ialoveni	283	4.7	15.83	8.1	4.3	0.48	64	23	3.63
Pinot Noir	218	6.2	12.50	2.7	6.8	0.26	81	22	3.34
Saperavi	247	7.0	14.59	2.2	7.0	0.31	113	28	3.44

TAE: tartaric acid equivalents, ACE: acetic acid equivalents. Values represent means ± standard deviations of three determinations (n= 3).

Titrateable acidity at harvest varied from 4.7 g TAE/L in Negru de Ialoveni to 8.9 g TAE/L in Codrinschii, suggesting differences in grape maturity and varietal characteristics (Table 1). After fermentation, Codrinschii maintained the highest titrateable acidity (8.7 g TAE/L), whereas Negru de Ialoveni showed the lowest (4.3 g TAE/L) (Table 1). Red wines produced from Gamay (Beaujolais) grape variety exhibited a significant decrease in total acidity following alcoholic fermentation, dropping from 6.5 g TAE/L to 4.7 g TAE/L.

Volatile acidity in wines refers to the concentration of volatile acids (primarily acetic, formic, butyric, and propionic acids), but also is an indicator of microbial activity and spoilage. In analysed wines the volatile acidity ranged from 0.26 to 0.48 g ACE/L. Most samples remained below the critical sensory threshold (1.0–0.8 g/L), with Negru de Ialoveni presenting the highest value (0.48 g ACE/L), though still within acceptable limits.

In most samples, the total SO<sub>2</sub> content ranged from 64 to 90 mg/L, while only the red wines produced from the Saperavi (113 mg/L) and Gamay (Beaujolais) (129 mg/L) grape varieties showed higher concentrations, which, however, remain within the permissible limits for dry red wines.

Free SO<sub>2</sub> levels ranged within the technological interval typically recommended for dry red wines (approximately 15–35 mg/L), ensuring adequate protection against oxidative degradation. Sulphur dioxide positively affected the antioxidant properties of wines and, in some cases, its contribution to the overall antioxidant activity of wines is higher than that of naturally occurring antioxidants [30].

The pH values spanned between 3.26 (Codrinschii) and 3.77 (Gamay (Beaujolais)), reflecting the acidity and buffering capacity of each wine (Table 1). Wines with higher acidity, such as Codrinschii and Pinot Noir, correspondingly exhibited lower pH values, which can enhance microbial stability and colour preservation.

#### **Total polyphenolic content**

Total phenolic content (TPC) encompasses a broad range of polyphenolic compounds, including phenolic acids (e.g., gallic, caffeic, and *p*-coumaric acids), flavonoids (such as quercetin and catechin), tannins, and stilbenes (notably resveratrol), which collectively contribute to the antioxidant and antiradical capacity, colour stability, and sensory profile of red wines [31]. Although some degree of interference in the Folin–Ciocalteu assay

appears to be inevitable, studies indicate that the error attributable to SO<sub>2</sub> in red wines is generally 5% [32].

For the analysed local wines, the TPC parameter ranged from 1.40 g GAE/L in Pinot Noir to 2.27 g GAE/L in Gamay (Beaujolais) (Table 2). High TPC is typically associated with improved antiradical potential and stability during storage. Wines such as Gamay, Codrinschii, Copceac, Saperavi, Negru de Ialoveni, and Mugurel displayed values above 1.9 g GAE/L, indicating a rich polyphenolic profile, followed by Feteasca Neagra and Pinot Noir (Table 2). Recent data indicate comparable results for wines obtained from local grape varieties Copceac, Codrinschii and Feteasca Neagra [10]. For comparison, literature data obtained using the Folin–Ciocalteu method show that Feteasca Neagra wines from Romania contain 2.9–3.3 g GAE/L, while the polyphenolic content of Pinot Noir wines range from 1.2 to 6.5 g GAE/L [33]. Slovak Pinot Noir wines were reported to have 1.5–3.3 g GAE/L of total phenolics; Saperavi wines analysed by an Italian–Georgian team showed values around 4.6 g GAE/L [34,35]. These comparisons indicate that Moldovan wines exhibit moderate to relatively high total phenolic contents, influenced not only by winemaking practices but also by regional geographical characteristics.

#### **Anthocyanin's content**

The anthocyanin content (AC) is a parameter of critical importance for defining both the chromatic intensity and hue of red wines. It reflects the concentration of the 3-O-monoglucosides of six major free anthocyanidins: pelargonidin-3-O-glucoside, cyanidin-3-O-glucoside, delphinidin-3-O-glucoside, peonidin-3-O-glucoside, petunidin-3-O-glucoside, and malvidin-3-O-glucoside [36].

Within the framework of the present experimental series, Gamay (Beaujolais) exhibited the highest anthocyanin concentration (1.26 g M3GE/L), registering a value at least twofold higher than those observed for other wine samples (Table 2). The anthocyanin content determined for Saperavi and Negru de Ialoveni was relatively similar, amounting to 0.681 and 0.628 g M3GE/L, respectively. From Table 2, Codrinschii wine sample showed a concentration of 0.511 g M3GE/L. Comparable values were obtained for Copceac (0.476 g M3GE/L) and Mugurel (0.475 g M3GE/L). These were followed by Feteasca Neagra (0.364 g M3GE/L) and Pinot Noir (0.224 g M3GE/L), which presented the lowest anthocyanin levels among the analysed samples.

The data obtained for Feteasca Neagra are in agreement with previously published results for wines derived from this grape variety [37]. Similarly, Taran, N *et al.* reported comparable anthocyanin concentrations in local wines produced in 2017 from Pinot Noir, Saperavi, and Feteasca Neagra grape varieties [38]. Using the same spectrophotometric procedure, Romanian researchers reported anthocyanin concentrations of 526.3 mg/L in Feteasca Neagra and 477.7 mg/L in Pinot Noir wines, values comparable to those obtained in the present study [39]. Kononenko, E.I *et al.* reported the anthocyanin content of 292 mg/L in Saperavi wine, which is markedly lower than the value of 681 mg/L determined in the present work [40]. In addition, although based on a different analytical method, a French research group reported elevated anthocyanin levels and a high total phenolic index in Gamay (Beaujolais) wines [41].

#### **Proanthocyanidin's content**

Regarding proanthocyanidins, compounds associated with astringency, mouthfeel, and long-term stability, the concentration ranged from 0.18 g CE/L in Feteasca Neagra to 0.36 g CE/L in Codrinschii (Table 2). Elevated concentrations of proanthocyanidins were observed in most of the analysed wines (Table 2), which may contribute positively to their structure and aging potential. Wines Pinot Noir and Feteasca Neagra presented slightly lower values, indicating a lighter tannin profile. Proanthocyanidins, also known as condensed tannins, are oligomeric or polymeric flavonoids composed mainly of catechin, epicatechin, and their gallate derivatives [42]. The data obtained previously on the content of catechin and epicatechin in local dry wines of Feteasca Neagra, Copceac, Codrinschii and Saperavi grape varieties are in alignment with the results from Table 2 [37]. Casassa, L.F. *et al.* reported proanthocyanidin concentrations ranging from 112 to 778 mg/L in Pinot Noir wines from the

Edna Valley AVA, California, a range that includes the value obtained in the present study [43]. Consistent with the findings of the present study, Romanian authors also observed higher proanthocyanidin levels in Pinot Noir wines compared to Feteasca Neagra; however, these values were determined using the vanillin assay, which may limit direct comparability [33].

The statistical groupings support the notion that varietal origin, along with the winemaking technology, plays a critical role in determining the polyphenolic profile of red wines. Among the evaluated cultivars, Gamay (Beaujolais) consistently exhibited the highest levels of total phenolics, anthocyanins, and proanthocyanidins, suggesting superior antioxidant potential and favourable sensory attributes. In contrast, Feteasca Neagra and Pinot Noir displayed significantly lower concentrations across all measured parameters.

#### **Antiradical activity**

Although recent data indicate a growing body of research on the redox and antioxidant properties of wines from the Republic of Moldova [44-46], this topic remains insufficiently explored, particularly in the case of local and newly developed grape cultivars. Therefore, this study reports the data on the antiradical activity of Moldovan dry red wines, determined *via* the DPPH method (Figure 1).

Expressed as ascorbic acid equivalents (g AAE/L), the antiradical activity ranged from 1.23 g AAE/L in Pinot Noir to 1.94 in Gamay (Beaujolais) wines (Figure 1). According to the statistical analysis, samples of Codrinschii (1.62 g AAE/L), Copceac (1.71 g AAE/L), Feteasca Neagra (1.54 g AAE/L), Mugurel (1.68 g AAE/L), Negru de Ialoveni (1.69 g AAE/L) and Saperavi (1.72 g AAE/L) showed comparable high antiradical activity, indicating a significant capacity of these wines to neutralize free radicals (Figure 1).

Table 2

**Total phenolic content, anthocyanins and proanthocyanidins in analysed dry red wines.**

<i>Wine samples</i>	<i>Total phenolic content, g GAE/L</i>	<i>Anthocyanin content, g M3GE/L</i>	<i>Proanthocyanidin content, g CE/L</i>
Codrinschii	1.98 ± 0.11 <sup>ab</sup>	0.511 ± 0.03 <sup>bc</sup>	0.36 ± 0.01 <sup>a</sup>
Gamay (Beaujolais)	2.27 ± 0.41 <sup>a</sup>	1.256 ± 0.42 <sup>a</sup>	0.25 ± 0.01 <sup>b</sup>
Copceac	1.92 ± 0.23 <sup>ab</sup>	0.476 ± 0.07 <sup>bc</sup>	0.23 ± 0.03 <sup>b</sup>
Feteasca Neagra	1.77 ± 0.02 <sup>b</sup>	0.364 ± 0.03 <sup>cd</sup>	0.18 ± 0.02 <sup>c</sup>
Mugurel	1.92 ± 0.14 <sup>ab</sup>	0.475 ± 0.09 <sup>bc</sup>	0.23 ± 0.00 <sup>b</sup>
Negru de Ialoveni	1.94 ± 0.07 <sup>ab</sup>	0.628 ± 0.24 <sup>ab</sup>	0.27 ± 0.03 <sup>b</sup>
Pinot Noir	1.40 ± 0.05 <sup>c</sup>	0.224 ± 0.10 <sup>d</sup>	0.22 ± 0.02 <sup>c</sup>
Saperavi	1.96 ± 0.20 <sup>ab</sup>	0.681 ± 0.12 <sup>ab</sup>	0.25 ± 0.01 <sup>b</sup>

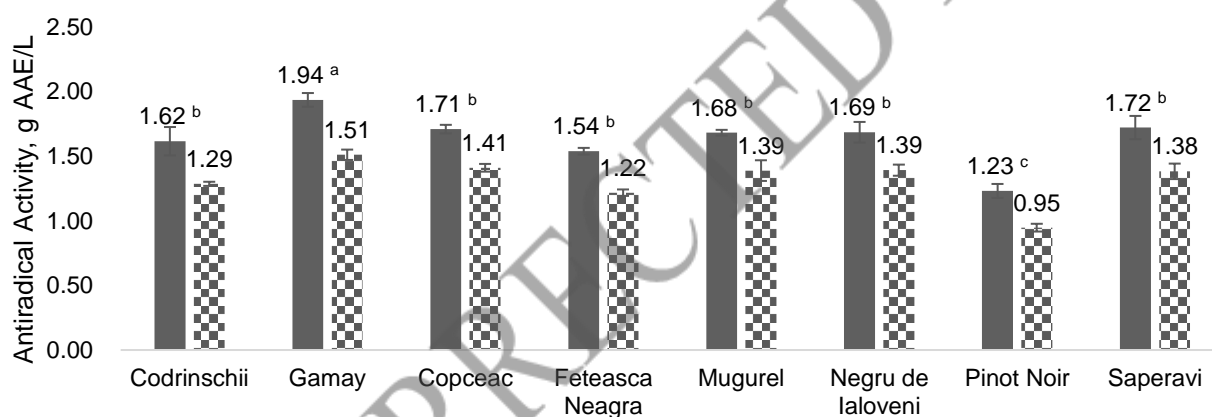
GAE: gallic acid equivalents, M3GE: malvidin-3-glucoside equivalents, CE: catechin equivalents. Values represent means ± standard deviations of three determinations (n= 3). Different letters within the same column indicate statistically significant differences between wine varieties (Tukey HSD test, p<0.05). Varieties sharing at least one letter are not significantly different from each other.

On the other hand, Pinot Noir wine exhibited lower antiradical activity, which correlates with the data on the total phenolics ( $1.40 \pm 0.05$  g GAE/L) and anthocyanin's ( $0.224 \pm 0.10$  g M3GE/L) content (Table 2). For comparison, Mlček, J. et al. reported antioxidant activity values ranging from 3.7 to 4.7 g/L AAE in Czech Pinot Noir wines [47]. Tauchen, J. *et al.* observed that Pinot Noir exhibited lower DPPH radical-scavenging activity than Saperavi, a finding consistent with the results of the present study [48]. Furthermore, Feteasca Neagra wines analysed in Romania showed antioxidant activity values between 1.6 and 2.5 g/L AAE, exceeding the values determined in the present work [49].

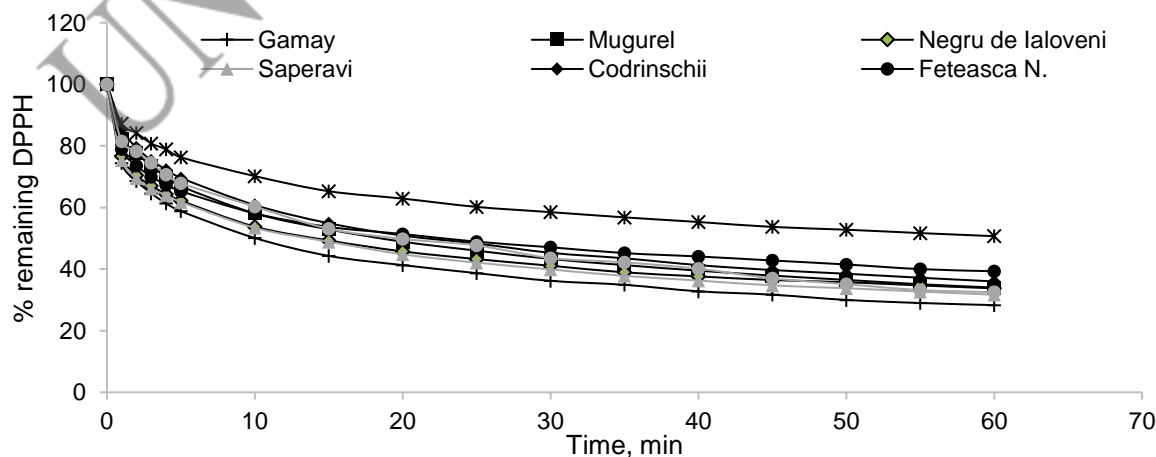
The checkered pattern bars in Figure 1 represent the antiradical activity of the wines after excluding the contribution of free SO<sub>2</sub>, thereby allowing assessment of its specific role in the overall DPPH radical-scavenging capacity. The

comparison between total activity and the activity calculated without free SO<sub>2</sub> indicates that this parameter contributes measurably to the antioxidant response of the wines [30]. Based on the obtained data, free SO<sub>2</sub> accounts for approximately 12% of the total DPPH radical neutralization, demonstrating that, although phenolic constituents remain the primary contributors to antiradical activity, free sulphur dioxide exerts a non-negligible additional effect in the reaction system.

The kinetics of DPPH radical scavenging activity for the analysed wine samples revealed significant variation in antioxidant behaviour over time (Figure 2). All wines demonstrated a rapid initial decrease in DPPH• absorbance during the first 10–15 minutes, indicative of fast-reacting antioxidant compounds such as anthocyanins, catechins, and other low-molecular-weight phenolics.



**Figure 1.** Antiradical activity of the analysed local red wines against DPPH•, expressed as ascorbic acid equivalents (AAE). The checkered pattern bars indicate the antiradical activity of the wine excluding the contribution of free SO<sub>2</sub>. Different letters within the same column indicate statistically significant differences between wine varieties (Tukey HSD test,  $p < 0.05$ ).



**Figure 2.** Time-dependent decrease of % remaining DPPH in studied wine samples.

Among the studied wines, Gamay (Beaujolais) showed the highest radical scavenging efficiency, with the % of remaining DPPH• dropping to 28.3% after 60 minutes, indicating a fast antiradical response (Figure 2). This result aligns with the data on the total phenolic and anthocyanin content (Table 2). Comparable percentages of remaining DPPH• were obtained for Saperavi (31.7%), Copceac (32.5%), Negru de Ialoveni (33.7%), Mugurel (34.0%), Codrinschii (36.1%) and Feteasca Neagra (39.3%) wines (Figure 2). Pinot Noir exhibited moderate antiradical performance, with 67% of remaining DPPH• in solution after 60 minutes, correlating with its notably low phenolic and anthocyanin content (Table 2).

The decay pattern observed across all samples is generally characterized by a steep initial slope followed by a gradual plateauing phase. This suggests the presence of both fast- and slow-reacting antiradical compounds, highlighting compositional diversity in the phenolic profiles of the wines.

The IC<sub>50</sub> values, which represent the concentration of wine required to inhibit 50% of DPPH radicals, expressed as mg wine *per* mg DPPH•, are represented in Table 3. The lowest IC<sub>50</sub> value was recorded for Gamay (63.09), indicating the highest antiradical activity, followed closely by Copceac (65.27), Saperavi (72.1), Mugurel (72.09), Negru de Ialoveni (74.32), Codrinschii (75.34) and Feteasca Neagra (81.12). These results are consistent with the high total phenolic and anthocyanin contents observed in these samples, which are known contributors to antiradical property. The Pinot Noir wine sample showed higher IC<sub>50</sub> value of 103.42 - this indicating on a relatively moderate antiradical potential, which correlates with the data from Tabel 2 and Figures 1 and 2.

The positive correlations observed between TPC, AC, PC and ARA confirm the critical role of polyphenolic compounds for the antiradical properties of red wines (Figures 3(a), 3(b)

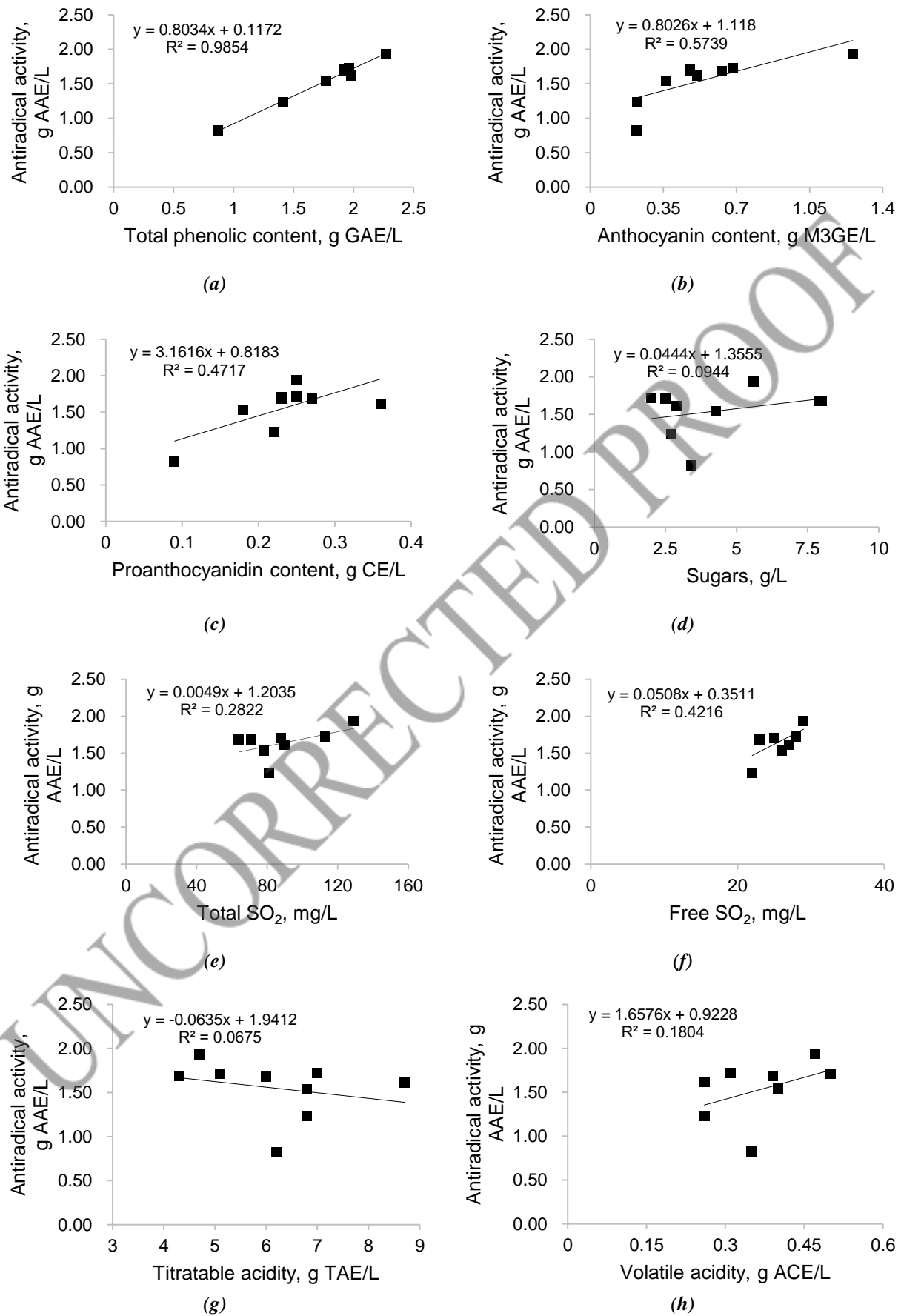
and 3(c)). Notably, Figure 3(a) illustrates a very strong correlation between total phenolic content and the antiradical activity, with a coefficient of determination  $R^2= 0.9854$ . These results are consistent with existing literature, which attributes the antioxidant, antiradical and health-promoting effects of red wines largely to its polyphenolic constituents [50,51]. As anticipated, antiradical activity showed also positive correlations with anthocyanin content ( $R^2= 0.5739$ ) and proanthocyanidin content ( $R^2= 0.4717$ ), suggesting their role in antiradical capacity. Among the non-polyphenolic parameters, the SO<sub>2</sub> content showed positive correlations with ARA (Figure 3(e) and 3(f)). Notably, free SO<sub>2</sub> exhibited a markedly stronger association ( $R^2= 0.4216$ ) compared to total SO<sub>2</sub> ( $R^2= 0.2822$ ), indicating that the active form of SO<sub>2</sub> contributes more significantly to antiradical activity. These findings, together with the varietal differences observed, emphasize the combined importance of grape variety and winemaking technology in determining the antiradical properties and potential health benefits of local wines.

In contrast to phenolic compounds and free SO<sub>2</sub>, the correlation analysis revealed low coefficients of determination between antiradical activity and general compositional parameters of the wines, including sugars ( $R^2= 0.0944$ ), titratable acidity ( $R^2= 0.0675$ ), volatile acidity ( $R^2= 0.1804$ ) (Figure 3(d), 3(g) and 3(h), respectively), and pH ( $R^2= 0.1736$ ) (not presented). Sugars and acidity-related indicators are integral components of the wine matrix, contributing to its physicochemical stability, sensory profile, and overall balance. However, their low  $R^2$  values imply that they do not exert a major direct influence on the DPPH radical-scavenging activity under the conditions applied. While pH and acidity may indirectly affect the redox behaviour of certain compounds through modifications of ionization state or reaction environment, their contribution appears secondary [52].

Table 3

The IC<sub>50</sub> values for analysed dry red wines.

Sample	$y = ax + b$	$R^2$	IC <sub>50</sub> (mg/mg)
Codrinschii	$y = 0.6050x + 4.4171$	0.9841	75.34
Gamay (Beaujolais)	$y = 0.7238x + 4.3379$	0.9901	63.09
Copceac	$y = 0.6412x + 4.1756$	0.9872	71.45
Feteasca Neagra	$y = 0.5767x + 3.2179$	0.9905	81.12
Mugurel	$y = 0.6344x + 4.2632$	0.9862	72.09
Negru de Ialoveni	$y = 0.6377x + 2.6045$	0.9947	74.32
Pinot Noir	$y = 0.4633x + 2.0874$	0.9942	103.42
Saperavi	$y = 0.6365x + 4.1097$	0.9831	72.11



**Figure 3. Correlations among Moldovan's dry red wines antiradical activity and total phenolic content (a), anthocyanin content (b), proanthocyanidin content (c), sugars content (d), total  $\text{SO}_2$  (e), free  $\text{SO}_2$  (f), titratable acidity (g) and pH (h).**

## Conclusions

The results of this study show that local red wines produced from eight grape varieties exhibit distinct physico-chemical parameters and polyphenolic content, while remaining within the standard limits for dry red wines. Gamay (Beaujolais), Codrinschii and Saperavi wines showed the highest total phenolic content (1.96–2.27 g GAE/L). Anthocyanin content was notably higher in Gamay (Beaujolais) (1.256 g M3GE/L) followed by Saperavi (0.681 g M3GE/L) and Negru de Ialoveni (0.628 g M3GE/L). Gamay (Beaujolais) and Saperavi showed the greatest antiradical activity (1.94 and 1.72 g AAE/L, respectively), followed closely by Copceac (1.71 g AAE/L). Wines Feteasca Neagra and Pinot Noir exhibited the lowest values for total phenolic content (1.77 and 1.40 g GAE/L, respectively) and antiradical activity (1.54 and 1.23 g AAE/L, respectively). The highest proanthocyanidin content was observed in Codrinschii (0.36 g CE/L) and in Negru de Ialoveni (0.27 g CE/L) wines, both produced from indigenous grape varieties.

Correlation analysis demonstrated that antiradical activity was strongly associated with total phenolic content ( $R^2=0.9854$ ) and moderately associated with anthocyanins ( $R^2=0.5739$ ), proanthocyanidins ( $R^2=0.4717$ ), and free  $\text{SO}_2$  ( $R^2=0.4216$ ). Weak relationships were observed between antiradical activity and general compositional parameters, including sugars, titratable acidity, pH, and volatile acidity. These findings indicate that the radical-scavenging capacity of the studied wines is predominantly governed by specific reactive constituents, particularly polyphenolic compounds and, to a lesser extent, free sulphur dioxide, whereas the broader physicochemical matrix exerts only a limited influence.

Overall, the findings characterize the physicochemical parameters and quantitative polyphenolic indices of the investigated Moldovan dry red wines and demonstrate statistically significant relationships between polyphenolic content and radical scavenging capacity, contributing to the current knowledge of their compositional and antiradical properties.

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