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Doctoral thesis

"Research on the authentication of food products from raw materials of plant origin"

Summary

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Chapter I

Aims and objectives of the doctoral thesis

The present doctoral thesis entitled "Research on the authentication of food products from raw materials of plant origin" aims to carry out a study on the application and customization of modern methodologies for the authentication of juices and wines resulting from blueberries and grapes from the central area of Romania. The work focuses on two major lines of research: the first on the documentary study, Chapter I exploring the current state of knowledge, where general notions about blueberry juice, white and red wines were deepened, the second chapter of this first part dealing with advanced techniques for the authentication of food products of plant origin. The second part is the experimental one, which summarizes the application of modern techniques for investigating the chemical composition and fingerprinting of the products under study in order to establish their authenticity. Thus, the polyphenolic components, total anthocyanins and antioxidant activity of blueberry juices and selected white and red wines were evaluated (Chapter III). The volatile profile was established, (Chapter IV) and Chapter V focused on the evaluation of phenolic compounds and the correlations between them and polyphenols, total anthocyanins and antioxidant activity. The evaluation of the mineral profile of the juices and wines was complemented by isotopic analyses leading to the establishment of their authentication benchmarks (Chapter VI). The research and studies were carried out during the years 2021-2025, the blueberry samples coming from the "Afine de cultură Sibiu" Plantation, and the wines from the "Villa Vinea" Mica Winery/Târnavelor Vineyard. The thesis includes 158 pages, 69 figures, 12 tables, 318 bibliographical references, notations and annexes. The aims of this work is to establish a series of authentication criteria for blueberry products grown in the Sibiu area and for white and red wines from the "Villa Vinea" Winery/ Mica Vineyard, Târnavelor Vineyard.

The topic of the doctoral thesis is of major importance in that it establishes for the first time concrete benchmarks for authenticating these products through modern and efficient methods. Studies carried out in the area are very few (Mica), even lacking (Sibiu), so we considered that a major, large-scale investigation on the plantations in the reference areas is necessary for the purpose of authenticating the products, the results obtained contributing to completing the databases at national level.

In order to achieve this goal, a series of studies were required regarding:

- * authentication of blueberry juices and selected wines by establishing the polyphenolic component and antioxidant activity
- * authentication of blueberry juices and selected wines by establishing the volatile profile
- * authentication of blueberry juices and selected wines by establishing representative phenolic compounds
- * authentication of blueberry juices and selected wines taken into work by using multielement analyses and stable isotopes
- * achievement of statistical correlations between compounds and identification of authentication markers in the samples taken into study

Chapter II

Polyphenolic component, total anthocyanins and antioxidant activity evaluation

2.1. Materials and methods

In order to establish the concentration of polyphenols, three blueberry varieties were selected: Spartan, an early variety, with large, aromatic berries; Duke with fruit in mid-July, very prolific; Elliot, a late variety with fruit until mid-September. The fruits harvested from the Sibiu Blueberry Plantation were cold-pressed, resulting in natural juices that were subsequently investigated and noted according to the variety they come from. Three white wine varieties (Chardonnay, Kerner, Gewürztraminer) and three red wine varieties (Merlot, Pinot noir and Fetească neagră) from the 2023 harvest were selected from the "Villa Vinea" winery.

Total polyphenols were determined by the spectrophotometric method using the Folin-Ciocalteu method (Niculescu et al. 2024).

Total anthocyanins were determined by the spectrophotometric method (Niculescu et al. 2024).

The antioxidant capacity of the juices and white and red wines was determined by the DPPH, TEAC, FRAP method (Niculescu et al. 2024).

2.2. Results and discussions of blueberry juices

As can be seen in Table 1, blueberry juices present generous values of polyphenols and anthocyanins. Depending on the variety from which the juice comes, total polyphenols range between 823.34 ± 0.61 mg GAE/L (Duke variety) and 587.12 ± 0.97 mg GAE/L (Spartan variety).

These values can be a benchmark to establish that the juices are authentic and have not undergone external modifications.

Table 1. Variation of total polyphenols, total anthocyanins and antioxidant activity in the three blueberry juices from the Spartan, Duke and Elliot

Analysis	Blueberry juice		
	Spartan	Duke	Elliot
Polyphenols (mg GAE/L)	587.12 ± 0.97	823.34 ± 0.61	729.49 ± 0.78
Anthocyanins (mg C3GE/L)	389.65 ± 0.23	517.62 ± 0.19	416.27 ± 1.36
DPPH (%)	63	72	71
IC ₅₀ (µg/mL)	234.72	111.67	118.27
Antioxidant activity (mmol TE/L)	5.67	7.79	7.66
TEAC (µmol TE/L)	525.4 ± 2.7	612.4 ± 3.1	580.12 ± 1.3
FRAP (µmol TE/L)	631.7 ± 1.9	789.91 ± 1.5	701.0 ± 4.4

Values are expressed as the mean of three determinations $\pm$ standard deviation; mg GAE=milligrams gallic acid equivalent/liter; mg C3GE/L= milligrams cyanidin-3-glucoside equivalent/liter; DPPH=1,1'-diphenyl-2-picrylhydrazyl radical; IC₅₀ (µg/mL)= Antioxidant efficiency expressed in micrograms/milliliter; mmol TE/L=millimoles Trolox equivalents/liter; TEAC (µmol TE/L)=Trolox equivalent antioxidant capacity expressed in micromoles Trolox equivalents/liter, FRAP=iron ion reducing power of antioxidants, expressed in micromoles Trolox equivalents/liter; $p \leq 0.005$

Total anthocyanins accumulate in blueberry juices at values ranging from 389.65 mg C3GE/L to 517.62±0.19 mg C3GE/L, with maximum values being observed in the Duke variety. Regarding the antioxidant activity measured by the DPPH method, it varies between 72% (Duke) and 63% (Spartan). The antioxidant efficiency IC₅₀ for the juice obtained from the Duke variety is maximum, presenting the lowest values (111.67 µg/mL), compared to the other two juices, with the total antioxidant activity reaching a maximum of 7.79 mmol TE/L.

The maximum capacity to neutralize the ABTS⁺ radical belongs to the juice obtained from the Duke variety with a value of 612.4 ± 3.1 µmol TE/L, followed by Elliot juice (580.12 ± 1.3 µmol TE/L) and Spartan (525.4 ± 2.7 µmol TE/L).

Conclusions

- the three blueberry juices are rich in polyphenols, respectively anthocyanins, which gives them a superior antioxidant activity.
- the juice from the Duke variety presents polyphenols in the highest amount, being the variety with the richest chemical composition and antioxidant activity in most of the analyzed indicators, suggesting a superior potential for use in the food and nutritional industry.
- in the context of the analyzed blueberry juice, TEAC provides a standardized measure of antioxidant capacity, showing that the juice from the Duke variety has the strongest antioxidant activity.

2.3. Results and discussions of white wines

In table 2 it is observed that the white wines from Târnavelor /Mica Vineyard/ "Villa Vinea" winery) present a series of specific properties of the area, characteristics that can differentiate them from wines from other regions.

Table 2. Variation of total polyphenols, total anthocyanins and antioxidant activity in the white wine Chardonnay, Kerner, Gewürztraminer

Analysis	White wine		
	Chardonnay	Kerner	Gewürztraminer
Polyphenols (mg GAE/L)	258.72±1.03	228.31±1.11	345.19±1.72
Anthocyanins (mg M3GE/L)	3.85±0.03	4.73±0.04	2.37±0.03
DPPH (%)	19	12	31
IC ₅₀ (µg/mL)	2.72	2.61	1.19
Antioxidant activity (mmol TE/L)	0.52	0.35	0.63
TEAC (µmol TE/L)	205.1±0.5	180.02±0.3	119.6±1.1
FRAP (µmol TE/L)	201.9±0.9	182.31±0.5	101.4±1.2

Values are expressed as the mean of three determinations ± standard deviation; mg GAE=milligrams gallic acid equivalent/liter; mg C3GE/L= milligrams cyanidin-3-glucoside equivalent/liter; DPPH=1,1'-diphenyl-2-picrylhydrazyl radical; IC₅₀ (µg/mL)= Antioxidant efficiency expressed in micrograms/milliliter; mmol TE/L=millimoles Trolox equivalents/liter; TEAC (µmol TE/L)=Trolox equivalent antioxidant capacity expressed in

micromoles Trolox equivalents/liter, FRAP=iron ion reducing power of antioxidants, expressed in micromoles Trolox equivalents/liter; $p \leq 0.005$

Gewürztraminer wine has a high polyphenol content (345.19 ± 1.72 mg GAE/L), suggesting that it is richer in compounds such as flavonoids and phenolic acids. These compounds may contribute to the complexity of aroma and taste. Kerner and Chardonnay wines have lower levels of polyphenols (228.31 ± 1.11 mg GAE/L and 258.72 ± 1.03 mg GAE/L, respectively), which may imply a different aromatic profile or processing that influences the extraction of polyphenols. Anthocyanins are pigments that influence the color of wine, especially for red wines, but also in white wines in lower concentrations. Although Kerner wine has the highest anthocyanin content (4.73 mg M3GE/L), the impact on color in white wines is less obvious, but they may contribute to antioxidant capacity. Gewürztraminer wine has the lowest anthocyanin content (2.37 mg M3GE/L), which could explain the lower values for color-related parameters, but does not directly affect the total antioxidant activity.

The free radical scavenging capacity (DPPH) of Gewürztraminer (23%) shows a high activity, which confirms the contribution of phenolic compounds and other antioxidants. The differences between the wines (Chardonnay – 19%, Kerner – 12%) reflect both the chemical composition and possible variations in the winemaking method.

The total antioxidant activity (mmol TE/L) integrates the effects of all antioxidant compounds: Gewürztraminer wine dominates (0.63 mmol TE/L), confirming that its phenolic profiles provide protection against oxidation. Kerner wine (0.35 mmol TE/L) shows the lowest antioxidant activity, which could be explained by a lower content of polyphenols and specific antioxidants.

Conclusions

In conclusion, the relationship between polyphenols and antioxidant activity can be correlated as follows: Gewürztraminer wine, with the highest polyphenol content, also has the best antioxidant activity according to IC₅₀ and DPPH. This underlines the importance of the amount of polyphenols for antioxidant properties.

Kerner wine, although it has a moderate content of polyphenols, is less efficient in free radical scavenging (DPPH) and shows a low total activity. Although anthocyanins are present in different amounts, they are not the only ones responsible for antioxidant activity. Gewürztraminer wine, with the lowest values for anthocyanins, is the best performing antioxidant due to other active polyphenols. The differences between the TEAC and FRAP vs. DPPH tests show that antioxidant activity depends on the mechanism of action and the interactions between the active compounds. Thus, it can be stated that Gewürztraminer wine stands out as having the best antioxidant properties, suggesting a balanced concentration of effective phenolic compounds. Chardonnay and Kerner wines have different profiles, with advantages in other chemical aspects.

2.4. Results and discussions of red wines

Although the Transylvanian Plateau, with its vineyards, is famous for its white wines, attempts are increasingly being made to acclimatize red varieties, in the context of climate changes observed in recent years. The red wines obtained in these areas are typical, specific due to the microclimate, the soil composition, and generally different factors compared to other vineyards. The analyzed parameters can provide valuable data in validating wines from the area and in detecting possible fraud.

Table 3. Variation of total polyphenols, total anthocyanins and antioxidant activity in the red wine Merlot, Pinot noir and Fetească neagră

Analysis	Red wines		
	Merlot	Pinot noir	Fetească neagră
Polyphenols (mg GAE/L)	2328.34±1.18	2539.19±1.07	2814.22±1.21
Anthocyanins (mg M3GE/L)	423.32±0.73	477.77±0.84	526.33±0.72
DPPH (%)	68	75	84
IC ₅₀ (µg/mL)	228.12	196.45	115.32
Antioxidant activity (mmol TE/L)	7.47	9.32	12.92
TEAC (mmol TE/L)	10.18±0.51	12.02±0.29	13.62±1.16
FRAP (mmol TE/L)	10.97±0.83	12.39±0.47	13.45±1.22

Values are expressed as the mean of three determinations ± standard deviation; mg GAE=milligrams gallic acid equivalent/liter; mg C3GE/L= milligrams cyanidin-3-glucoside equivalent/liter; DPPH=1,1'-diphenyl-2-picrylhydrazyl radical; IC₅₀ (µg/mL)= Antioxidant efficiency expressed in micrograms/milliliter; mmol TE/L=millimoles Trolox equivalents/liter; TEAC (µmol TE/L)=Trolox equivalent antioxidant capacity expressed in micromoles Trolox equivalents/liter, FRAP=iron ion reducing power of antioxidants, expressed in micromoles Trolox equivalents/liter; p≤0.005

The significant difference between Fetească Neagră and Merlot (almost 500 mg GAE/L) suggests that Fetească Neagră wines may be more valuable from a nutritional and oxidative aging point of view. The increase in anthocyanin concentration in Fetească Neagră wine may be correlated with a higher resistance to color degradation and a potential consumer preference for wines from this variety. The ratio between anthocyanins and polyphenols suggests that in Fetească Neagră wine, a higher proportion of total polyphenols is represented by anthocyanins, amplifying their specific contribution to appearance and antioxidant benefits. There is a significant positive correlation between total polyphenols and antioxidant capacity (TEAC, FRAP, DPPH).

Conclusions

- Merlot wine presents the lowest antioxidant profile
- Pinot Noir wine reveals intermediate performances
- Fetească Neagră wine stands out for its chemical and antioxidant superiority, which makes it suitable for the premium market and for consumers interested in health benefits.

Chapter III

Blueberry juices, white and red wines authentication by evaluating the volatile profile

3.1. Materials and methods

In order to determine the volatile compounds, samples of blueberry juices (Spartan, Duke, Elliot), white wines (Chardonnay, Kerner, Gewürztraminer) and red wines (Merlot, Pinot noir and Fetească neagră) were taken into consideration.

The method used was that described by Popescu et al. (2024), by gas chromatography with a mass detector/three quadrupole (Nexis GC-2030 GCMS-TQ8050NX, Shimadzu, Kyoto, Japan).

3.2. Results and discussions of blueberry juices

Following the sum of higher alcohols (Figure 1/a) it is observed that Duke juice has the highest concentration (6266.82 $\mu\text{g/L}$), and the concentrations of volatile fatty acids are very low for all varieties, Duke juice having the lowest value (5.42 $\mu\text{g/L}$).

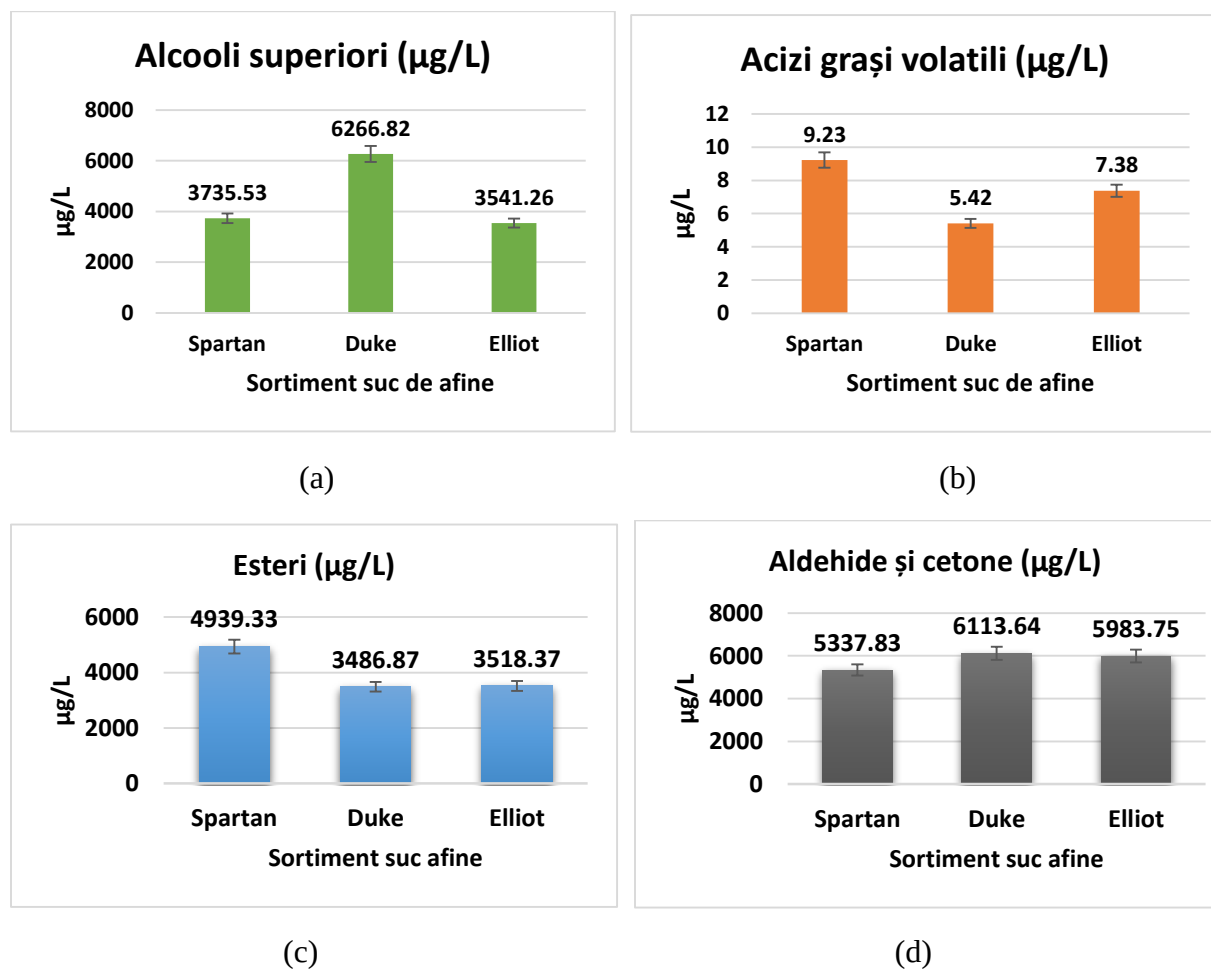


Figure 1. Distribution of volatile compounds for each blueberry juice variety (sums of higher alcohols, volatile fatty acids, esters, aldehydes and ketones)

The amounts of esters obtained suggest the aromatic potential of the juices, with Spartan standing out with the highest concentration (4939.33 $\mu\text{g/L}$); Duke (3486.87 $\mu\text{g/L}$) and Elliot (3518.37 $\mu\text{g/L}$) juices are comparable, but the ester concentrations are significantly lower than in Spartan juice (Figure 1/c). The sum of aldehydes and ketones in Duke juice leads with a high value (6113.64 $\mu\text{g/L}$), which indicates an important contribution to the overall aromatic character, while in Elliot (5983.75 $\mu\text{g/L}$) and Spartan (5337.83 $\mu\text{g/L}$) close values are observed.

Statistically (Figure 2) Duke juice has a smaller dispersion than Spartan juice, suggesting that its profile is more uniform. The median value shows the median concentration of the compounds, while the differences between the medians reflect the overall levels of the compounds.

Thus, it is observed that the medians for Spartan juice are higher than those for Duke juice, suggesting a richer composition for certain categories of compounds. In the presented case, no extreme values (outliers) were recorded, i.e. points outside the whiskers that suggest concentrations significantly different from the rest of the data.

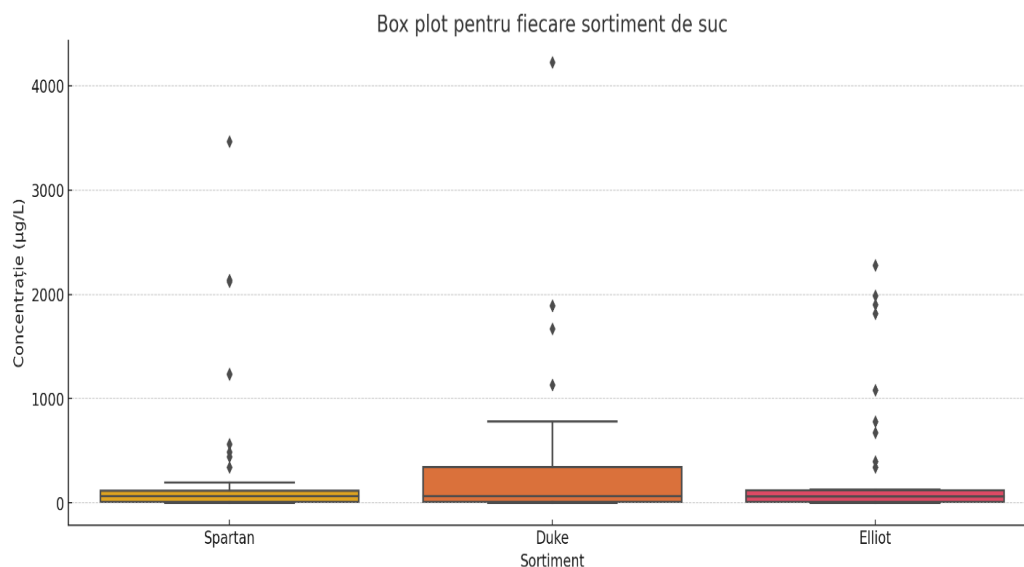


Figure 2. Dispersion representation of the concentrations of the compounds for each assortment (box plot)

The correlation matrix (Figure 3) reflects the degree of linear association between the three juice assortments based on the concentration of volatile compounds.

It is observed that high correlation values (close to 1) appear, which indicates a very similar composition between the assortments, in this case the Spartan and Duke assortments (0.9).

Low or negative values indicate the lack of a strong association, which demonstrates the different composition of the assortments.

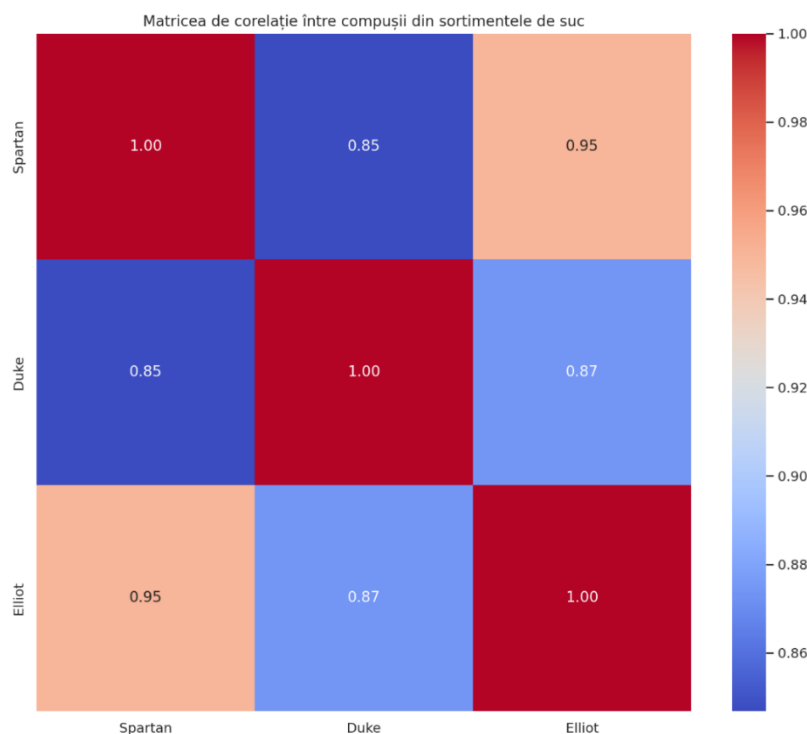


Figure 3. Correlation matrix between juice varieties compounds

Conclusions

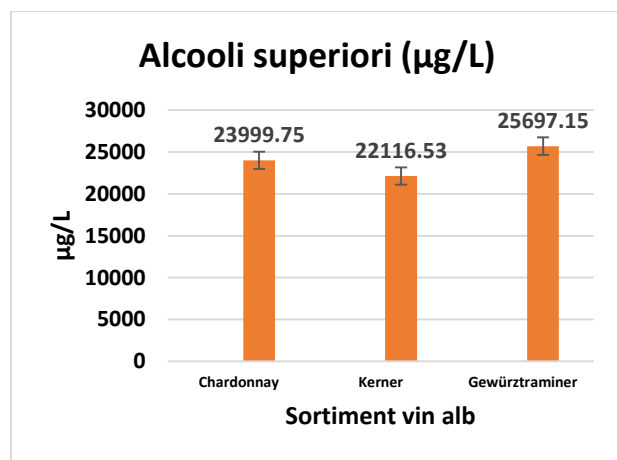
- Duke juice contains the most higher alcohols and ketones, which could enhance its floral aromas
- Spartan juice is the variety richest in esters, which gives it a more fruity olfactory profile
- Duke and Elliot juices have a more complex aldehyde profile, which may give them greener and fresher aromas
- Elliot juice offers a balanced presence of compounds, with an emphasis on aldehydes, which gives it a fresh and slightly citrus character
- terpene compounds contribute to the specific aromatic characteristics of blueberry juices, providing floral, citrus or fresh aromas
- absolute differences from the average show the uniqueness of each variety

3.3. Results and discussions of white wines

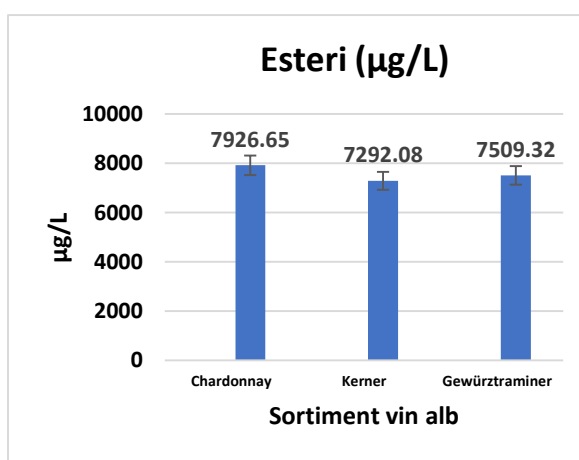
Gewürztraminer wine presents the highest total concentration of higher alcohols (25697.15 $\mu\text{g/L}$), followed by Chardonnay (23999.75 $\mu\text{g/L}$) and Kerner (22116.53 $\mu\text{g/L}$). These compounds contribute significantly to the aromatic complexity and body of the wines. The higher concentrations in Gewürztraminer may explain its distinct aromatic profile. The values for esters are similar between the three varieties, with small differences: Chardonnay wine (7926.65 $\mu\text{g/L}$) shows a maximum concentration. Kerner and Gewürztraminer wines have comparable concentrations, 7292.08 $\mu\text{g/L}$ and 7509.32 $\mu\text{g/L}$. Esters are responsible for the fruity and floral aromas. The higher concentrations in Chardonnay wine may contribute to its characteristic more

fruity notes. It is observed that volatile fatty acids show a maximum concentration in Gewürztraminer wine (5583.38 $\mu\text{g/L}$), followed by Kerner wine (5472.09 $\mu\text{g/L}$) and Chardonnay wine (5139.38 $\mu\text{g/L}$). These compounds influence the taste and microbiological stability of the wines. Gewürztraminer, with higher values, could present a more complex taste balance. Regarding the concentration of aldehydes and ketones, Kerner wine is at a slightly higher concentration (1276.07 $\mu\text{g/L}$), followed by Chardonnay wine (1233.23 $\mu\text{g/L}$) and Gewürztraminer (1219.56 $\mu\text{g/L}$). These compounds contribute to the slightly oxidized notes and unique characteristics of each wine. The differences are relatively small, indicating similar influences in the aromatic profile.

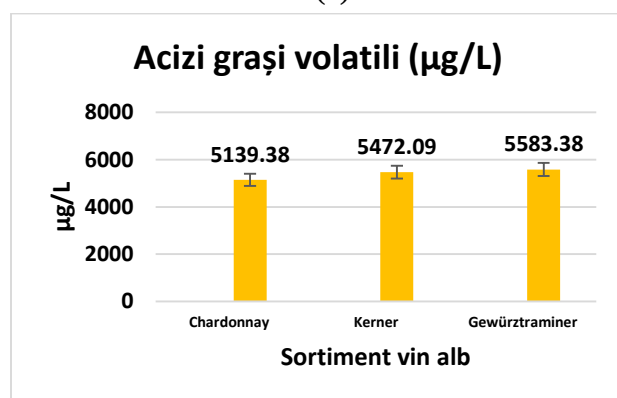
Chardonnay wine presents the highest concentration of lactones (1011.58 $\mu\text{g/L}$), which gives it lactic or caramel notes, while Gewürztraminer wine has intermediate values (866.39 $\mu\text{g/L}$) and Kerner wine the lowest value (543.51 $\mu\text{g/L}$). Lactones are associated with creamy and vanilla characteristics, being more prominent in Chardonnay.



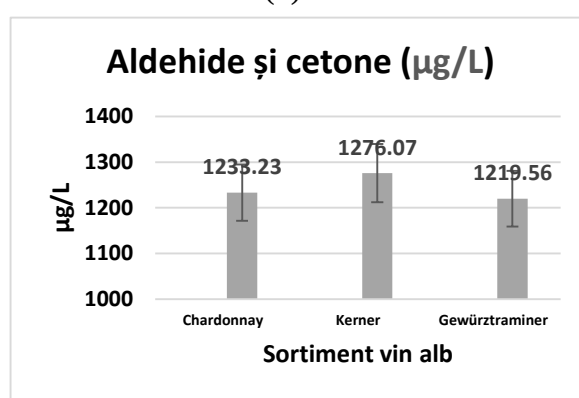
(a)



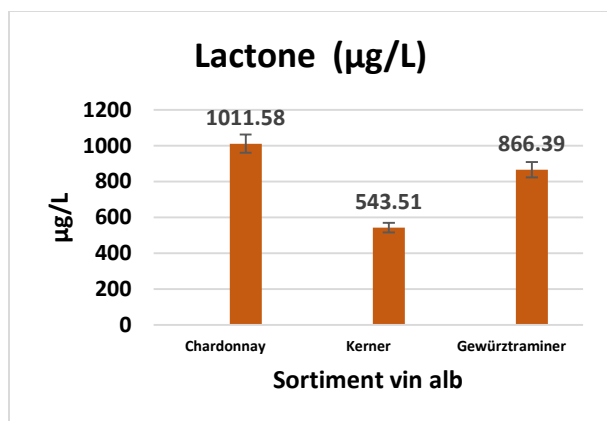
(b)



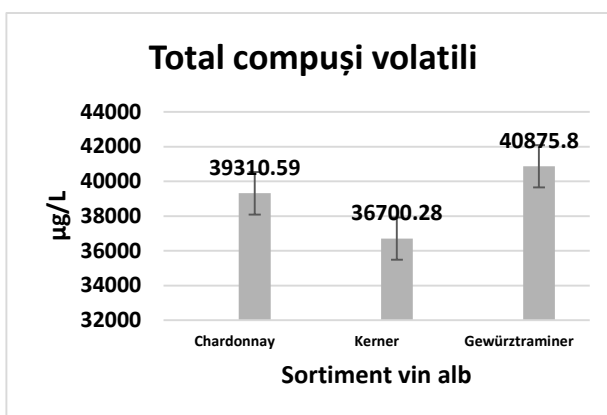
(c)



(d)



(e)



(f)

Figure 4. Total amount of higher alcohols (a), esters (b), volatile fatty acids (c), aldehydes and ketones (d), lactones (e) and the final sum (f) of volatile compounds identified in the white wine varieties Chardonnay, Kerner, Gewürztraminer

Conclusions

- Gewürztraminer wine is distinguished by an intense floral and fruity profile, amplified by higher alcohols and esters.
- Chardonnay wine has a more balanced base between floral and fruity
- Kerner wine focuses on a strong floral character, with a slight acidity, and
- each wine variety has a unique dominant compound that contributes significantly to its distinct character.
- Gewürztraminer wine stands out through higher overall concentrations of aromatic compounds -
- Chardonnay wine offers a creamier profile
- Kerner wine is distinguished by floral balance and acidity

3.4. Results and discussions of red wines

Figure 5 shows the total values of volatile compounds quantified in the three red wine varieties. Thus, higher alcohols (a) were quantified at maximum values in Pinot Noir red wine (49275.68 µg/L), followed by Merlot and Fetească neagră. Esters (b) presented a maximum accumulation in Pinot Noir wine (26289.79 µg/L), followed by Merlot and Fetească neagră. The most significant total values of volatile fatty acids (c) are observed in the case of Merlot red wine where they reach 5984.75 µg/L, with minimum total values being noted in the case of Pinot Noir wine of 5516.32 µg/L. The total of aldehydes and ketones (d) accumulate to a maximum total of 8871.79 µg/L in the case of Pinot noir wine, which confers specific notes to it. Lactones (e) characterize all Pinot noir wine (9064.99 µg/L), being involved in the formation of vanilla, soft, silky aromas. The total of volatile compounds quantified in the three red wines (f) amounts to values that give these wines

remarkable aromatic qualities, ranging between 99018.57 $\mu\text{g/L}$ for Pinot Noir and 81320.35 $\mu\text{g/L}$ for Fetească Neagră.

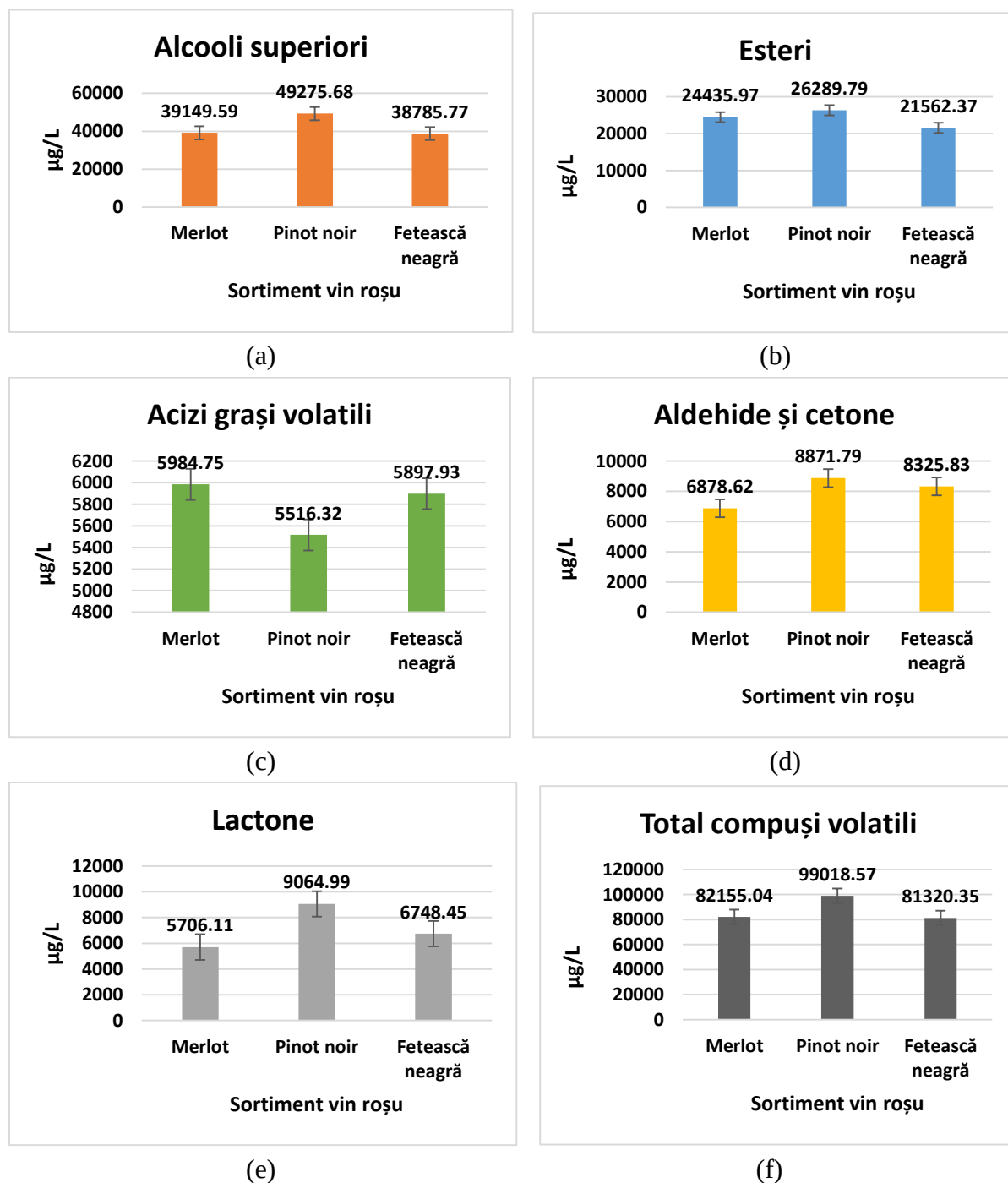


Figure 5. Total amount of higher alcohols (a), esters (b), volatile fatty acids (c), aldehydes and ketones (d), lactones (e) and the final sum (f) of volatile compounds identified in the red wine varieties Merlot, Pinot Noir, Fetească Neagră

Statistically, it was found that Pinot Noir wine has, on average, the highest concentration of volatile compounds, followed by Merlot and Fetească Neagră wines, and the concentrations vary significantly (high standard deviations), which indicates a high diversity of compounds between and within the classes. The minimum distribution appears with a value of 0 and the maximum of over 19,000 µg/L (ethyl acetate for Merlot and Pinot Noir wines). The results of the ANOVA analysis for each class of compounds indicate that all indicate p values > 0.05, which suggests that the differences between the wine varieties (Merlot, Pinot Noir, Fetească Neagră) are not statistically significant for any of the main classes of volatile compounds. This result could be influenced both by the high variability within each class, which dilutes the differences, and by limitations of the data set or the lack of additional factors to be analyzed.

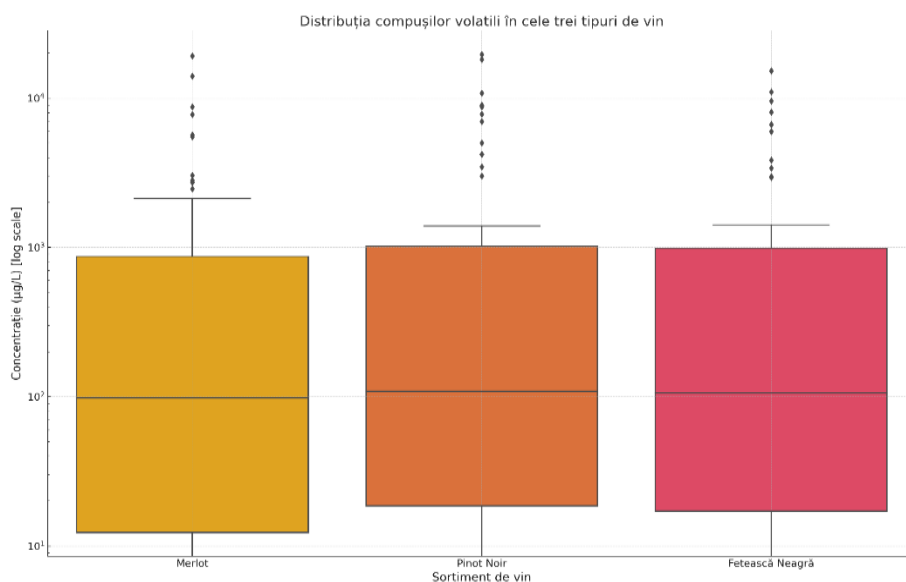


Figure 6. Distribution of volatile compound concentrations for the three wine varieties (Merlot, Pinot Noir and Fetească Neagră)

Conclusions

The results obtained and the general correlations between the volatile compounds identified in the wines lead to the following conclusions:

- Pinot Noir wine is characterized by high concentrations of higher alcohols, esters and lactones, contributing to a rich, floral, fruity and sweet aromatic profile
- Fetească Neagră wine presents high values of compounds that add vegetal, vanilla and creamy texture notes
- Merlot wine stands out for its balance, with more moderate values and lighter fruity notes, complemented by a pleasant acidity.

Chapter IV

Blueberry juices, white and red wines authentication by evaluating of phenolic compounds

4.1. Materials and methods

In order to evaluate phenolic compounds, the samples described in Chapter I were taken into consideration, namely natural juices of the Spartan, Duke and Elliot varieties, the fruits for juice coming from the "Blueberry Plantation of Sibiu". Three varieties of white wine (Chardonnay, Kerner, Gewürztraminer) and three varieties of red wine (Merlot, Pinot noir and Fetească neagră) from the 2023 harvest were selected from the "Villa Vinea" winery. The reagents used in the chromatographic analyses were of HPLC quality or of analytical grade (>99%) and came from Carl Roth GmbH Co. (Karlsruhe, Germany). The identification and quantification of phenolic compounds was achieved by applying the method described by Cristea et al. (2024) slightly modified, using an Agilent 1200 HPLC equipment (Agilent Technologies, CA, USA) coupled with a PDA detector, degasser, automatic quaternary injection pump.

4.2. Results and discussions of blueberry juice

38 phenolic compounds were identified and quantified, compounds that characterize blueberry juices from the Sibiu Plantation. Phenolic acids are characterized by significant concentrations of gallic acid and chlorogenic acid (Figure 7), with the absolute values of ferulic acid, sinapic acid, vanillic acid and trans-cinnamic acid low for all varieties.

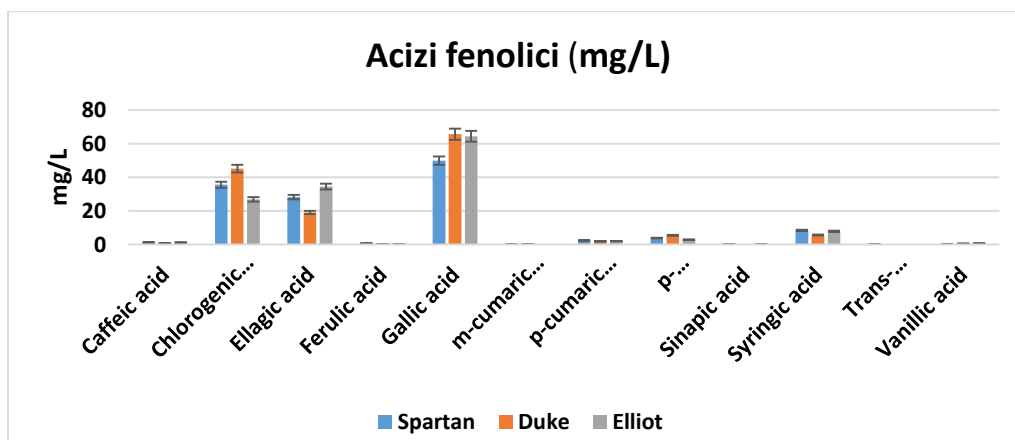


Figure 7. Phenolic acids concentration in the three blueberry juices Spartan, Duke, Elliot

In figure 8 it is observed that flavonols are present in these juices, through rutin which presents a maximum value in the Elliot assortment (12.36 mg/L) and a minimum in Spartan juice (8.75 mg/L).

A valuable compound is also quercetin-3-glucoside whose value is significantly higher in Spartan juice (14.88 mg/L) compared to Duke and Elliot juices, and kaempferol-3-glucoside presents the highest concentration in Elliot juice (3.77 mg/L) and the lowest in Duke juice (1.08 mg/L).

From the point of view of flavanols, it is observed that (+)-catechin is most abundant in Duke juice (31.12 mg/L) and lowest in Spartan juice (17.24 mg/L), epicatechin follows a similar pattern, with the highest value in Duke juice (10.22 mg/L), and epicatechin-gallate is highest in Spartan juice (6.76 mg/L).

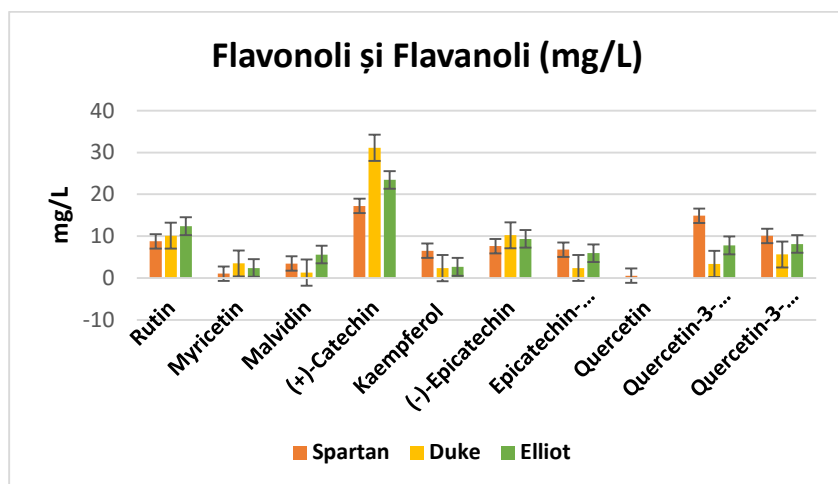


Figure 8. Flavonol and flavanol concentration in the three blueberry juices Spartan, Duke, Elliot

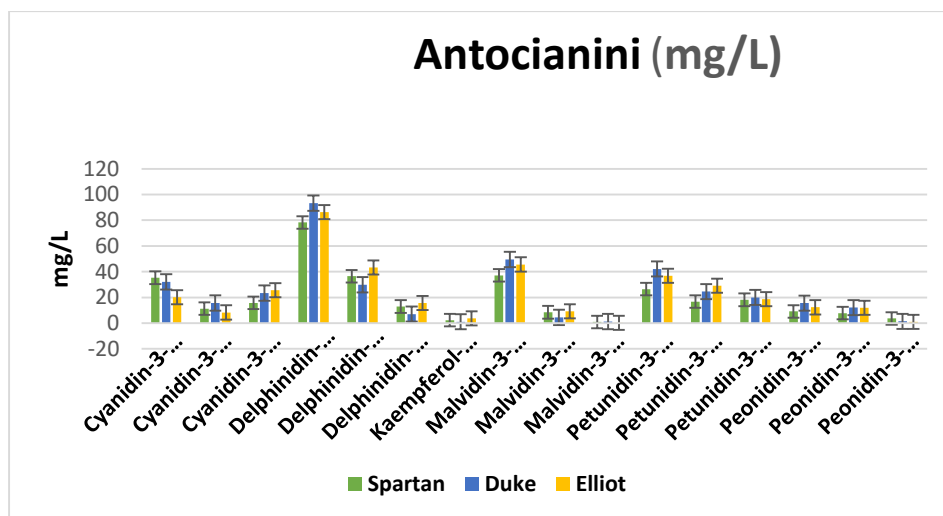


Figure 9. Anthocyanin concentration in the three blueberry juices Spartan, Duke, Elliot

Anthocyanins (Figure 9.) are notable for their generous values, especially delphinidin-3-glucoside, which is the most concentrated compound in this class, with the maximum value in Duke juice (93.24 mg/L) and the minimum in Spartan juice (78.28 mg/L). Cyanidin-3-glucoside has the highest value in Spartan juice (35.35 mg/L) compared to the other varieties, and Malvidin-3-glucoside has the highest values in Duke juice (49.54 mg/L). Duke juice has the highest total concentration of phenolic compounds (643.08 mg/L), followed by Elliot juice (626.87 mg/L) and Spartan (564.50 mg/L).

Conclusions

-Duke juice excels in most phenolic compounds, having maximum concentrations in many of the substances analyzed, with high concentrations of anthocyanins and flavanols, which makes it ideal for antioxidant benefits and intense color.

-Elliot juice has more balanced values, but stands out for ellagic acid and certain anthocyanins, such as delphinidin-3-galactoside.

-Spartan juice has lower values compared to the other two varieties, but remains competitive in the case of specific compounds, such as quercetin-3-glucoside.

4.3. Polyphenols, antioxidant activity, total anthocyanins and phenolic compounds correlation in blueberry juices

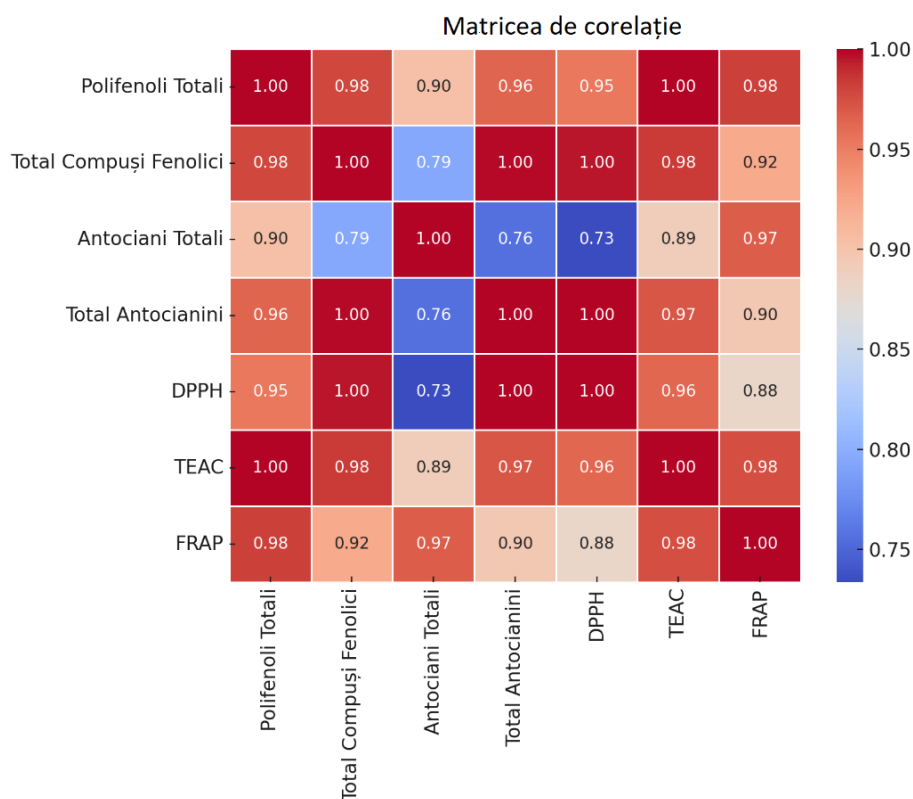


Figure 10. Correlation matrix of polyphenols, antioxidant activity, total anthocyanins and phenolic compounds in blueberry juices

There is a very strong correlation between total polyphenols and total phenolic compounds, as well as between antioxidant activity (DPPH, TEAC, FRAP) and total phenolic compounds. In the correlation matrix, values closer to 1 indicate a strong correlation between the variables, with the link between total polyphenols, anthocyanins, antioxidant activity and phenolic compounds being relevant. Duke juice has the highest concentrations of polyphenols, anthocyanins and antioxidant

activity, and Spartan juice the lowest. The individual values of phenolic compounds and anthocyanins are consistent with the total values of polyphenols and antioxidant activity, confirming a positive correlation between these data sets.

4.4. Results and discussions of white wines

When comparing the wine varieties, it can be stated that Gewürztraminer wine presents the highest total concentrations of phenolic acids (89.15 mg/L) which gives it a superior aromatic complexity, supported by the variety and quantity of phenolic acids, suggesting a more complex profile that can influence its body, taste and sensory qualities (Figure 11). Chardonnay wine, on the other hand, although it has fewer total phenolic acids than Gewürztraminer wine, still presents a relatively high concentration of important compounds, such as trans-caftaric acid and caffeic acid, which contribute to its characteristic aroma and oxidative stability, suggesting a balance between structure and freshness.

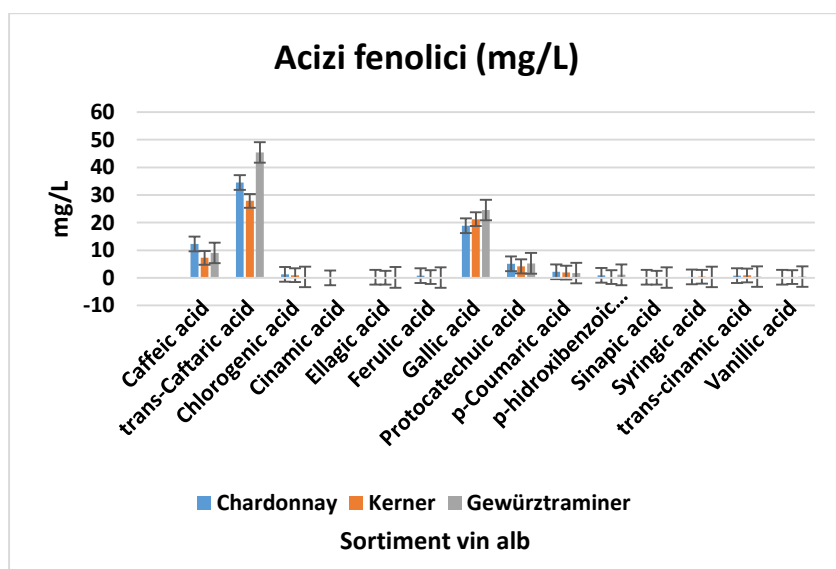


Figure 11. Concentrations of phenolic acids identified in the three white wines (Chardonnay, Kerner and Gewürztraminer)

From the point of view of flavonoids and non-flavonoids, it can be stated that Chardonnay wine presents the richest and most balanced profile, with the predominance of antioxidant compounds such as myricetin and quercetin. Gewürztraminer wine presents the lowest total concentrations, but with a high level of (-)-epicatechin (3.17 mg/L), which influences the aromatic structure. The lower flavonoid profile is compensated by the high concentration of other phenolic compounds. In the three wines, (+)-catechin and (-)-epicatechin are the most present compounds, directly influencing the astringency and taste structure.

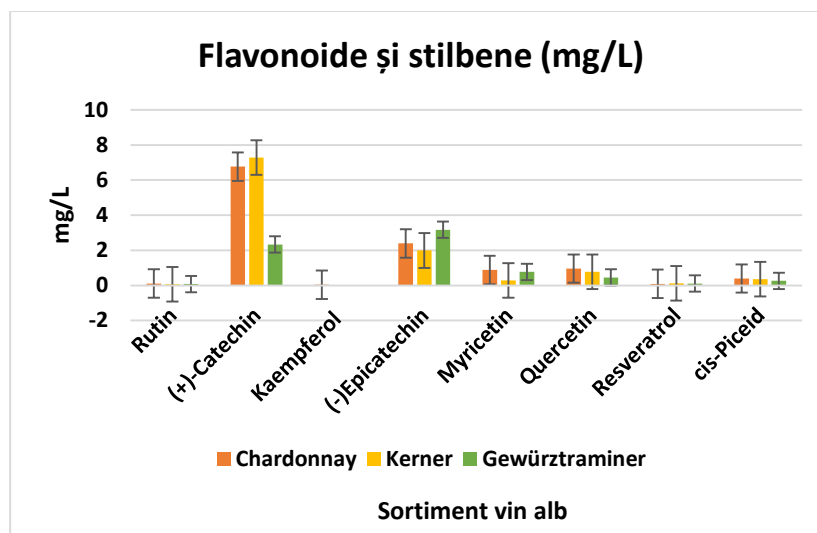


Figure 12. Flavonoids and non-flavonoids identified and quantified in Chardonnay, Kerner and Gewürztraminer white wines

Conclusions

- Chardonnay wine presents a high concentration of trans-caftaric acid and caffeic acid, which gives it a complex phenolic profile, with a high content of (+)-catechin, influencing the taste sensations.
- Kerner wine presents lower values of most phenolic compounds, which suggests a more subtle character, with a high concentration of (+)-catechin suggesting a slight astringency sensation.
- Gewürztraminer wine is rich in gallic acid and trans-caftaric acid, which suggests a superior antioxidant activity despite having the lowest concentrations of catechin, on the other hand it has a significant content of other phenolic acids.

4.5. Polyphenols, antioxidant activity, total anthocyanins and phenolic compounds correlation in white wines

Comparing the values of total polyphenols with those of phenolic compounds by Pearson correlation analysis results in a strong positive correlation with trans-caftaric acid (0.99) the strongest predictor of total polyphenols and (-)-epicatechin (0.99), an essential flavonoid, important in wine structuring. Polyphenols show a moderate correlation with total phenolic compounds (0.90) confirming their contribution to the global level of polyphenols and with vanillic acid (0.78) which is a derivative of benzoic acid, known for its antioxidant properties. They show a strong negative correlation with (+)-catechin (-0.98) this denotes a possible competition between catechins and other polyphenols in the extraction process and chlorogenic acid (-0.85) a result that could be related to the different metabolism of wines. Total polyphenols are strongly correlated with caftaric acid and epicatechin, suggesting that these compounds contribute significantly to the total polyphenol content of wines.

Total anthocyanins show a strong negative correlation with trans-caftaric acid (-0.99) suggesting an antagonistic effect in extraction and (-)-epicatechin (-0.99), resulting in a possible interaction between these compounds.

Total anthocyanins lead to a positive correlation with (+)-catechin (0.96) indicating a link between catechins and pigment stability and chlorogenic acid (0.78) which could influence the color shades of the wine and to a moderate negative correlation with total phenolic compounds (-0.94) confirming that anthocyanins do not contribute significantly to the total phenols.

Antioxidant activity measures the ability of wine to neutralize free radicals, showing a strong positive correlation with total phenolic compounds (0.99) confirming their importance in antioxidant activity and (-)-epicatechin (0.95) a strong antioxidant flavanol, a moderate correlation with caffeic acid (0.45) and vanillic acid (0.49) both compounds being known for their antioxidant properties.

A moderate negative correlation is shown with quercetin (-0.53) which may indicate an interaction with other antioxidant molecules and cis-piceid (-0.58) a derivative of resveratrol, possibly affected by oxidative processes.

The most significant correlations are between trans-caftaric acid and total anthocyanins, (-)-epicatechin and total anthocyanins, as well as between total phenolic compounds and antioxidant activity. Many other phenolic compounds have strong correlations, but are not statistically significant, which suggests high variability or external influences.

4.6. Results and discussions of red wines

Figure 13 demonstrates that in Merlot wine gallic acid (38.71 mg/L) is the dominant compound, in Pinot Noir wine syringic acid (11.21 mg/L) dominates, and in Fetească Neagră wine gallic acid (24.33 mg/L) is also the main compound. This graph provides a clear visual representation of the maximum concentrations for each wine type and the compound that contributes the most to their chemical characteristics.

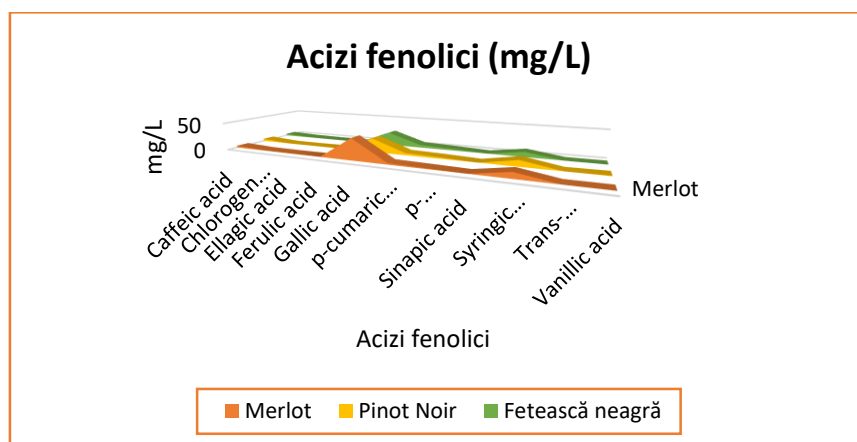


Figure 13. Phenolic acids identified and quantified in Merlot, Pinot Noir and Fetească Neagră red wines

Flavonoids (Figure 14) are notable for significant concentrations of (+)-catechin and (-)-epicatechin. The highest concentrations of (+)-catechin are in Fetească Neagră wine (239.25 mg/L), followed by Pinot Noir wine (201.28 mg/L) and Merlot wine (147.33 mg/L).

This compound is crucial for tannins, contributing to the structure and astringency. Similarly, (-)-epicatechin is more abundant in Fetească Neagră wine, suggesting a more pronounced tannic profile. Pinot Noir wine and Fetească Neagră wine are rich in quercetin-3-glucoside (39.88 mg/L and 40.01 mg/L). These compounds may contribute to color intensity and stability over time. Fetească Neagră wine accumulates the highest content of malvidin-3-glucoside (126.31 mg/L), followed by Pinot Noir wine (98.04 mg/L) and Merlot wine (73.9 mg/L). Malvidin is an essential anthocyanin pigment, associated with the intense color of red wines.

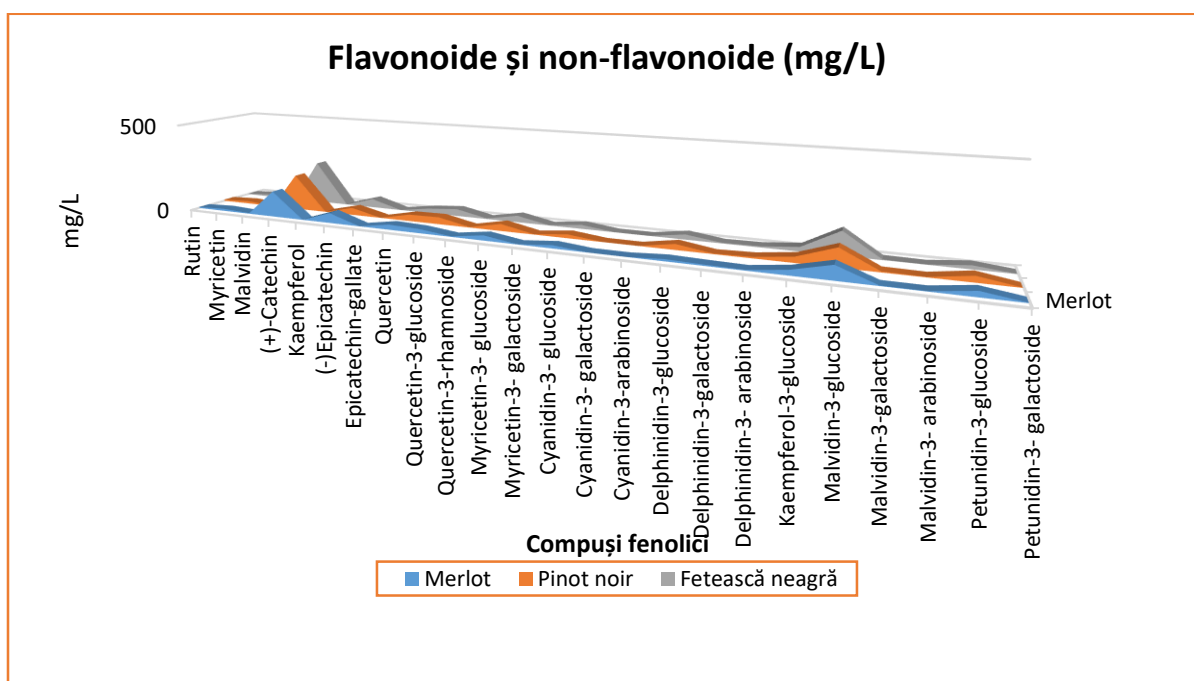


Figure 14. Flavonoids and non-flavonoids quantified in red wines Merlot, Pinot Noir, Fetească neagră

Statistically, a strong correlation between flavonoid compounds such as (+)-catechin and (-)-epicatechin suggests that they are similarly influenced by factors such as environmental conditions and processing methods. A negative correlation (close to -1) suggesting an inverse association, these negative correlations are observed between epicatechin-gallate and the rest of the compounds and suggest that it is present in very low concentrations and is affected differently from other compounds. A correlation close to 0 indicating a weak or non-existent relationship refers to rarely encountered compounds such as cyanidin-3-arabinoside and cyanidin-3-galactoside that show weak or negative correlations with other compounds, indicating a high variability of these compounds between wines, possibly influenced by biological or technological factors.

Conclusions

- Fetească Neagră wine is distinguished by higher levels of specific acids (chlorogenic and ellagic), which can influence color intensity and aromatic stability.
- Merlot wine is characterized by a high content of phenolic acids, such as gallic acid and moderate levels of flavonoids, presenting a balanced profile, with high antioxidant potential.
- Pinot Noir wine stands out for a greater diversity of flavonoids, such as delphinidin-3-glucoside and quercetin-3-glucoside, with complex aromas, supported by a balance between tannins and anthocyanins.

4.7. Total polyphenols, total anthocyanins, antioxidant activity and phenolic compounds correlations in red wines

The most important correlations (Pearson) that may have an influence on the quality of wines were calculated between total polyphenols and phenolic compounds. Thus, between total polyphenols and malvidin-3-glucoside an extremely strong correlation is observed (0.999), towards p-coumaric acid a very strong correlation (0.989), towards (+)-catechin (0.985) and towards p-hydroxybenzoic acid (0.965) strong correlations are observed. In contrast, moderate correlations are observed with chlorogenic acid (0.524), ellagic acid (0.504), syringic acid (-0.669), rutin (-0.621), malvidin (0.564) and weak correlations with myricetin (0.354), (-)-epicatechin (-0.407) and quercetin (-0.340), significant negative correlation with gallic acid (-0.869). A higher level of gallic acid seems to be associated with lower levels of total polyphenols. Catechin and p-coumaric acid contribute significantly to the total polyphenol level, while gallic acid may have an opposite effect. Antioxidant activity forms very strong positive correlations with (+)-catechin (0.991) and p-coumaric acid (0.968) and strongly negative with gallic acid (0.398). Catechin and p-coumaric acid are closely correlated with antioxidant activity, which confirms their major role in the antioxidant protection of wines. Antioxidant activity is positively correlated with catechin and p-coumaric acid, which confirms their essential role in antioxidant protection. The negative correlation with IC₅₀ indicates that a higher antioxidant capacity is associated with lower IC₅₀ values, and gallic acid shows a negative correlation, which suggests that its high presence may be associated with antioxidant degradation of wine.

Conclusions

- The total phenolic compounds are strongly correlated with all three variables, confirming their importance in red wines.
- This analysis indicates that grape variety selection and winemaking methods that optimize the level of catechins and p-coumaric acid can improve both the phenolic content and the antioxidant capacity of the wine.
- The variety selection and the winemaking process should be oriented towards maximizing catechin and p-coumaric acid and limiting the oxidation of anthocyanins to obtain a more stable and antioxidant-rich wine.

Chapter V

Mineral and isotopic profile evaluation of blueberry juices, white wines and red wines

5.1. Results and discussions on the mineral profile of blueberry juices

The values of macroelements and microelements identified in the three juices were statistically analyzed, establishing correlations between the different concentrations. Descriptive statistics for the concentration of compounds in the blueberry juice varieties show that the macroelements (mg/L) have an average for Spartan juice of 659.14 mg/L, for Duke juice of 847.43 mg/L, and for Elliot juice of 788.56 mg/L. The standard deviation (variation of values) was for Spartan juice of 1000.74, for Duke juice of 1256.38, and for Elliot juice of 1158.45. The minimum and maximum values calculated were for Spartan juice between 5.62 mg/L - 2306.99 mg/L, for Duke juice between 10.52 mg/L - 2966.02 mg/L and for Elliot between 12.93 mg/L - 2759.97 mg/L. Microelements expressed in µg/L showed an average of 210.51 for Spartan juice, 213.79 for Duke juice and 182.04 for Elliot. The standard deviation The calculated standard was 335.86 for Spartan, 342.46 for Duke juice and 289.05 for Elliot juice. Minimum and maximum values were presented by Spartan juices (1.27 - 1157.80), Duke 0.56 - 1175.83 and Elliot (0.93 - 1001.24). Percentage differences for macroelements are observed in the elements Na, K, and Ca which have the highest percentage variation in Duke juice, which suggests a high concentration compared to the average of the three varieties. Mg and Mn are more concentrated in Elliot juice, and Fe is noted by a significantly higher concentration also in Duke juice. The concentrations of microelements Al, Cd, and Zn are the highest in Spartan juice, exceeding the general average. Duke juice dominates in the case of Cr, Cu, and Pb, having positive variations compared to the other varieties, and Elliot juice presents the highest concentrations of Li and Ni. As dominant elements, Duke juice presents the most significant concentrations for most macroelements (Na, K, Ca, Fe and total macroelements), and Elliot juice for Mg and Mn. Spartan juice accumulates the highest concentrations of Al, Ba, Cd, Co, and Zn (microelements), Duke juice dominates in Cr, Cu, Pb, and total microelements, and Elliot juice has the highest levels of Li and Ni.

Conclusions

- The three juices are very similar, which suggests a possible similarity in their elemental characteristics and the fact that they come from the same area.
- The differences between the varieties are relatively small, which confirms the similarity of element concentrations, but there is a subtle separation that may reflect specific differences in certain chemical elements.
- The determined values are within the norms established by the legislation in force.

5.2. Isotopic ratios and elemental concentrations correlations in blueberry juices

The correlation between isotopic ratios and elemental concentrations can provide information about the relationship between the chemical and isotopic composition of the samples. For $\delta^{13}\text{C}$ VPDB and the major elements (macroelements) the $\delta^{13}\text{C}$ values are very close (-27.32, -27.45, -

27.18), indicating a low variation in the carbon source. The Duke variety has the lowest $\delta^{13}\text{C}$ value (-27.45) and the highest concentrations of K, Ca and Fe, which could indicate a link between nutrient consumption and carbon isotopic composition. The relationship between $\delta^{18}\text{O}$ VSMOW and macroelements indicates gradually increasing $\delta^{15}\text{N}$ values (1.24 $\rightarrow$ 1.76 $\rightarrow$ 2.25). Elliot juice ($\delta^{15}\text{N}$ = 2.25) has the highest values for Mn, Ni and Li, which could reflect an interaction between the absorption of these microelements and the nitrogen cycle. It is noted that in the case of $\delta^{13}\text{C}$ VPDB the relationship with macroelements and microelements is almost linear, but the differences between juices are small.

Duke juice, with the lowest $\delta^{13}\text{C}$ value, has higher concentrations of macro and microelements. For $\delta^{18}\text{O}$ VSMOW the relationship with macroelements (blue) and microelements (red) varies. Spartan juice ($\delta^{18}\text{O}$ positive) has the highest concentration of microelements. And in the case of $\delta^{15}\text{N}$ VPDB the values increase with the concentrations of macroelements (purple) and microelements (brown). Elliot juice, with the highest $\delta^{15}\text{N}$, has the highest total concentrations.

Conclusions

- The relationship between isotopic ratio and macroelements leads to Duke juice, which presents the highest total concentration of macroelements (2966.02 mg/L), with more pronounced negative values for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, suggesting a more isotopic "light" environment for carbon and oxygen.
- Spartan juice presents higher values for $\delta^{18}\text{O}$ and the most significant concentration of Al, which could suggest links between the water source and the distribution of elements.

5.3. Results and discussions on the mineral profile of white and red wines

The concentration of macroelements in white wines varies quite a lot, even significantly in some cases. Sodium varies between 49.23 mg/L (Kerner) and 57.45 mg/L (Chardonnay) with this one presenting the highest concentration. Potassium (K) has high values, between 245.67 mg/L (Gewürztraminer) and 301.21 mg/L (Kerner), which indicates a significant contribution to the minerality of the wines. Calcium (Ca) has relatively constant values, between 39.75 mg/L (Kerner) and 48.33 mg/L (Gewürztraminer).

A variation between 104.39 mg/L (Kerner) and 121.21 mg/L (Gewürztraminer) is observed for magnesium (Mg), iron (Fe) has a lower concentration (0.99 - 1.23 mg/L), while copper (Cu) varies between 0.67 mg/L and 0.75 mg/L. The total values of macroelements for white wines are between (517.49 mg/L) for Chardonnay wine, 496.59 mg/L for Kerner wine and 469.69 mg/L for Gewürztraminer wine.

In the analyzed red wines, sodium (Na) presents lower values than in white wines, between 37.89 mg/L (Fetească Neagră) and 48.91 mg/L (Pinot Noir). For potassium (K) the concentrations are much more significant than in white wines, between 629.12 mg/L (Merlot) and 731.11 mg/L (Fetească Neagră).

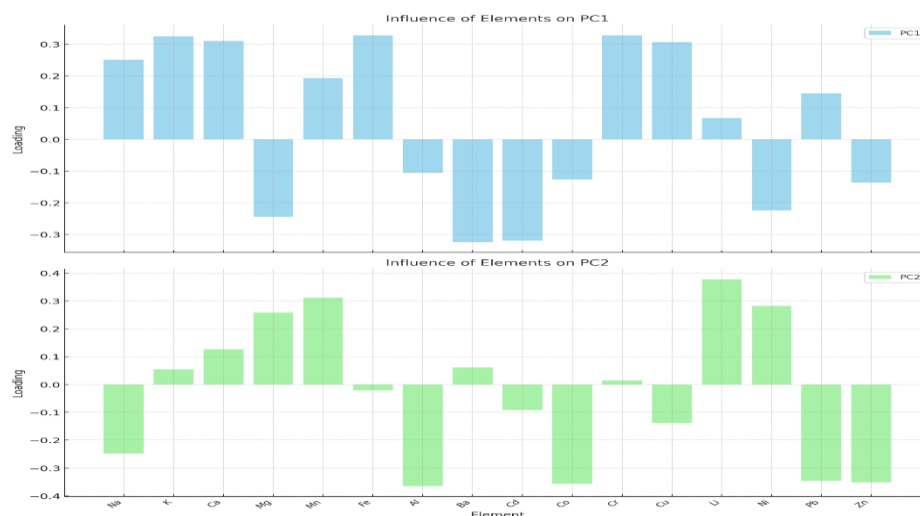


Figure 15. Influence of macro and microelement concentrations on white and red wines

The concentration of microelements in white wines varies for aluminum (Al) between 178.93 $\mu\text{g/L}$ (Kerner) and 204.35 $\mu\text{g/L}$ (Chardonnay), this element contributing to the formation of their astringency. Silver (Ag) shows relatively similar concentrations, between 4.21 $\mu\text{g/L}$ (Gewürztraminer) and 5.02 $\mu\text{g/L}$ (Kerner), indicating low levels, and arsenic (As) accumulates at lower values than in red wines, between 1.95 $\mu\text{g/L}$ (Chardonnay) and 2.64 $\mu\text{g/L}$ (Gewürztraminer). Zinc (Zn) shows significant values in white wines, with high concentrations ranging between 2708.73 $\mu\text{g/L}$ (Kerner) and 3121.04 $\mu\text{g/L}$ (Gewürztraminer), the element contributing to the stability of the wine. Chardonnay wine has the highest total concentration (4494.07 $\mu\text{g/L}$), followed by Gewürztraminer wine (4369.3 $\mu\text{g/L}$) and Kerner wine with 4027.87 $\mu\text{g/L}$. The concentration of microelements in red wines is notable for aluminum (Al) where the values are slightly higher than in white wines, between 403.31 $\mu\text{g/L}$ (Fetească Neagră) and 453.28 $\mu\text{g/L}$ (Pinot Noir). Zinc (Zn) has high concentrations, between 2788.85 $\mu\text{g/L}$ (Pinot Noir) and 3020.22 $\mu\text{g/L}$ (Merlot), contributing to the antioxidant properties of the varieties. Arsenic (As) concentrations are higher than in white wines, between 4.12 $\mu\text{g/L}$ (Pinot Noir) and 5.25 $\mu\text{g/L}$ (Merlot), and vanadium (V) is relatively constant, varying between 203.43 $\mu\text{g/L}$ (Merlot) and 223.20 $\mu\text{g/L}$ (Fetească Neagră). The total of microelements indicates Merlot wine as having the most significant total concentration (4821.68 $\mu\text{g/L}$), followed by Fetească Neagră (4775.72 $\mu\text{g/L}$) and Pinot Noir with 4669.53 $\mu\text{g/L}$.

Conclusions

- Red wines generally have higher concentrations of aluminum, arsenic and barium, which contribute to body and structure.
- White wines have high concentrations of zinc and copper, which can give them a distinct freshness.

- The varieties richest in microelements are the Chardonnay variety for white wines, and the Merlot variety for red wines.
- Red wines have higher concentrations of macroelements than white wines, which contribute to the differences in taste, minerality and structure.
- Fetească Neagră and Chardonnay wines are the richest varieties in macroelements, suggesting a greater potential for aromatic complexity and longevity.
- Red wines are also richer in microelements that contribute to structure and complexity, such as aluminum and arsenic. White wines excel through high concentrations of zinc, giving them freshness.
- Chardonnay and Merlot wines are the most complex varieties in terms of microelements.
- White wines often undergo more intensive technological treatments before fermentation, explaining the differences for sodium and copper.
- Red wines, due to prolonged contact with the skins, accumulate more elements such as potassium, manganese and iron. High levels of sodium and copper contribute to freshness and a mineral taste in white wines, while potassium, manganese and iron give robustness, color stability and aging potential to red wines.
- The differences reflect not only the chemical composition of the grapes, but also the technological adaptations for each type of wine. These can be adjusted to optimize quality and meet market demands.

5.4. Isotopic ratios and elemental concentrations correlation in white and red wines

- Adulterated (adulterated or diluted) wines can be detected by discrepancies between isotopic values and elemental concentrations.
- For example, adding water from a different source would alter the $\delta^{18}\text{O}$ ratios, and unusually high values for Na, K or other elements may signal soil contamination or the use of inappropriate fertilizers.
- Evaluating the results obtained, it can be stated that water stress and soil mineralization contribute to the formation of the ratios between $\delta^{13}\text{C}$ and the level of elements such as Mg and K. The relationships established indicate an impact of environmental conditions on isotopes and the accumulation of macroelements.
- $\delta^{18}\text{O}$ seems to be linked to water sources and mineral inputs such as Na and Ca, establishing its provenance.
- The correlations can be used to trace the origin of wines and growing conditions (water supply, fertilization) by establishing traceability and authentication of wines, where the isotopic ratios $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ can be used to identify the geographical region and climatic conditions in which the grapes were grown.
- This is relevant in the certification of the origin of wines (e.g. Designation of Controlled Origin - DOC). The mineral profile of wines (Na, K, Mg, Ca) reflects the soil composition and agricultural practices of a specific region, providing a unique chemical “fingerprint”.

Chapter VI

Final conclusions

Final conclusions on authentication of blueberry juice quality

- blueberry juices are rich in polyphenols, respectively anthocyanins, which gives them superior antioxidant activity
- volatile compounds identified in juices lead to the conclusion that higher alcohols and ketones could intensify floral aromas, and aldehydes can provide greener and fresher aromas. Terpene compounds contribute to specific aromatic characteristics by providing floral, citrus or fresh aromas. Esters provide a more fruity olfactory profile, with slightly citrus characters, all of these elements contributing to establishing keys to authenticating the juices subjected
- Duke juice excels in most phenolic compounds, having maximum concentrations in many of the substances analyzed, with high concentrations of anthocyanins and flavanols, which makes it ideal for antioxidant benefits and intense color.
- the individual values of phenolic compounds and anthocyanins are consistent with the total values of polyphenols and antioxidant activity confirming a positive correlation between these data sets, the resulting relationships being a solid premise for the authentication of blueberry juices
- the three juices show similarity in their elemental characteristics by coming from the same area.
- the relationship between the isotopic ratio and macroelements leads to Duke juice, which presents the highest total concentration of macroelements, with more pronounced negative values for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, suggesting a more isotopic "light" environment for carbon and oxygen. Spartan juice presents higher values for $\delta^{18}\text{O}$ and the most significant concentration of Al, which could suggest links between the water source and the distribution of elements. These identified relationships contribute to establishing the authenticity of blueberry juices from the Sibiu area.

Final conclusions regarding the authentication of white and red wines

- polyphenols quantified in white wines can be considered authentication markers for the three varieties Chardonnay, Kerner, Gewürztraminer, the values obtained being corroborated with their antioxidant activity. Gewürztraminer wine stands out as having the best antioxidant properties, suggesting a balanced concentration of polyphenols, while Chardonnay and Kerner wines present different profiles, with advantages in other chemical aspects
- volatile compounds in white wines present particularities that are specific to the three wines from the area. Making a comparison between the three wines, the dominant compound for each wine is a superior alcohol that can lead to a characterization of each wine separately. Chardonnay wine has a more balanced base between floral and fruity, Kerner wine focuses on a strong floral character, with a slight acidity and Gewürztraminer wine presents the most intense aromatic profile, with both floral and fatty influences.
- white wines have high concentrations of sodium, zinc and copper, which can give them a distinct freshness, with a slight mineral taste (specific to each variety)

-red wines stand out for their chemical and antioxidant superiority. Polyphenols present values that can constitute authentication markers through correlations that are statistically significant and that confirm the close relationship between them, anthocyanins and antioxidant activity

-Pinot Noir wine is characterized by high concentrations of higher alcohols, esters and lactones, contributing to a rich, floral, fruity and sweet aromatic profile; it presents a greater diversity of concentrations of individual phenolic acids, flavonoids, as well as delphinidin-3-glucoside and quercetin-3-glucoside, with complex aromas, supported by a balance between tannins and anthocyanins, which contributes to a distinct, personalized aromatic profile

-Fetească Neagră wine presents high values of compounds that add vegetal notes, vanilla and creamy texture; this wine is very rich in flavonoids and anthocyanins, including malvidin-3-glucoside, offering intensity in color, structure accentuated in tannins and a complex aromatic potential specific to the variety from the area

-Merlot wine stands out for its balance, with more moderate values and lighter fruity notes, complemented by a pleasant acidity, characterized by a high content of phenolic acids, such as gallic acid, and moderate levels of flavonoids, with high antioxidant potential, being able to be discriminated without reservations in comparison with the same variety from another region

-phenolic compounds in the three wines are strongly correlated with total polyphenols, total anthocyanins and antioxidant activity, the resulting statistical data establishing the specific ratios for each variety in particular. These ratios are specific only to these wines, from this area, being generally unique.

-red wines present higher concentrations of elements than white wines, which contributes to the differences in taste, minerality and structure; they have in general higher concentrations of aluminum, arsenic and barium, which contribute to body and structure - red wines, due to prolonged contact with the skins, accumulate more elements such as potassium, manganese and iron, and potassium, manganese and iron give robustness, color stability and aging potential to these wines

-analysis of correlations between isotopes and elemental concentrations leads to the establishment of traceability and the authentication of wines from the geographical region studied.

The isotopic ratios $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ establish the climatic conditions in which the grapes were grown, which is relevant in certifying the origin of the wines. The mineral profile of the wines (Na, K, Mg, Ca) reflects the soil composition and agricultural practices in the studied region, providing a unique chemical "fingerprint".

Falsified (adulterated or diluted) wines can be detected by discrepancies between the isotopic values and elemental concentrations established through these studies. $\delta^{13}\text{C}$ analysis can be used to assess the impact of increasing temperatures and drought on the metabolism of grapevines in the area, allowing the selection of resistant varieties, and the concentrations of elements such as K and Mg can guide the application of fertilizers to optimize wine yield and quality. Correlations between isotopes and mineral elements allow the establishment of the authenticity of the studied wines, linked to terroir, in marketing strategies, and organic wines can demonstrate specific isotopic and elemental values, indicating sustainable agricultural practices.

Chapter VII

Personal contributions and prospects for further research

Personal contributions

- a series of complex analyses were carried out for the first time for blueberry juices from the Sibiu Blueberry Plantation and for white and red wines from the "Villa Vinea" Winery/Mica /Târnavelor Vineyard, in order to establish their authenticity.
- modern techniques and methodologies were applied to authenticate products from plant-based raw materials, achieving multiple statistical correlations
- correlations were established between polyphenolic components, their antioxidant activity and the phenolic compounds involved
- specific markers were identified for these products, achieving a complex analytical profile
- the aromatic and compositional profile of blueberry juices and wines was achieved in order to identify counterfeits on the market
- the relationship between elemental compounds and the isotopic ratio of juice samples from cultivated blueberries from Sibiu and white and red wines from the "Villa Vinea" /Mica /Târnavelor Vineyard was established in order to establish the area-specific profile necessary for their authentication

Perspectives for further research

- research in the field of authenticating wines from the region can continue with other current methods and techniques, enabled by the legislative norms in force
- a series of chemical correlations can be established between wines other wines from the region can be studied
- a series of methods for amplifying aromatic components can be addressed in order to improve the ratio between the compounds
- tests can be carried out with several types of yeast strains in order to establish a personalized and authentic model
- through improved working methods, more phenolic compounds can be detected, which can characterize the wines from the area
- volatile compounds that are currently difficult to detect can be quantified by approaching ultra-sensitive methods and improved laboratory techniques
- the wines under study can be compared with other wines from the same assortment, but from other areas in order to establish specific and unique characteristics
- genetic fingerprints can be established through molecular methods on both wines and juices
- a series of technological parameters and procedures can be optimized in order to obtain top products
- land improvements can be made in order to optimize soil quality, knowing that it has a well-defined role in forming the profile of a wine
- research can continue in the area by examining other assortments of wines or juices

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