

THE WINE QUALITY DESCRIPTION OF DIFFERENT ORIGIN EVALUATED BY MODERN CHEMOMETRIC APPROACH

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<https://doi.org/10.55251/jmbfs.9270>

ARTICLE INFO

Received 29. 7. 2022
Revised 16. 10. 2022
Accepted 18. 10. 2022
Published 21. 12. 2022

Regular article



ABSTRACT

The main chemical parameters such as content of sugar (glucose and fructose), organic acid (total acids, malic and tartaric acids), total phenolics and the antioxidant activity in 9 dry white wines with PDO of 3 varieties (Pinot Blanc, Riesling, Sauvignon blanc) from 3 countries (Slovakia, Hungary, Austria) were studied in this work in order to identify possible differences in their quality affected by geographical origin. The wine samples were examined by the FTIR and spectrophotometry methods (TPC and DPPH). As supporting parameters, alcohol and glycerol content were used and sensory evaluation of wines was performed. For the statistical evaluation were used ANOVA and PCA methods. Austrian wines in general, were characterized by high glucose and fructose content, high TPC and antioxidant activity. Higher results of these parameters are characteristic especially for the Austrian varieties Pinot blanc and Sauvignon blanc which originated from the same wine-region in Austria. Sauvignon variety from Slovakia was characterized by higher total acid content, especially in the case of tartaric acid. Statistical evaluation was helpful to show several differences, especially in the case of PCA application. Just Riesling variety from all countries of origin was so similar that it was not possible to be strictly distinguished using PCA. Wines from Hungary (Sauvignon and Pinot blanc) showed higher content of alcohol and glycerol, as they are produced by the sugar fermentation. Wines from Slovakia were evaluated as the best samples among selected ones within their sensory evaluation.

Keywords: grape, wine, quality, PDO, origin, traceability

INTRODUCTION

The price of wine is related to its product and quality (Karabagias *et al.*, 2021). The composition of the wine depends on grape variety, origin, vintage conditions, production etc. Wine is considered to be a product susceptible to adulteration. Traceability systems designed to protect wine quality and origin have obtained the attention of researchers and also food industry. Chemical methods combined with chemometrics can describe wines by applying specific chemical markers.

Traceability under EU law means the ability to track any food, feed or substance that will be used for consumption, through all stages of production, processing and distribution. We can track and record raw materials in the whole supply chain and it could be possible also with use of various devices (e.g. seals, smart phones), to provide confidence in the authentic food product. The wine producer can also use marketing tools to communicate an authentic picture and to reach consumers (Ranaweera *et al.*, 2021).

Ethanol, ethyl acetate, hexanol, ethyl hexanoate, diethyl succinate, nerol oxide, among others, could be used as markers of grape variety, geographical origin, or fraud (Karabagias *et al.*, 2021).

Metabolomics is a method that can support food authentication providing a chemical fingerprint of a biological system, for example in plant-based products. The research based on metabolomics approaches can relate specific food attributes to the region's terroir (Cassago *et al.*, 2021).

Climate is a factor that has important influence on grape growth and development. Vines can be affected by different effects under climate change, but also by grape variety and location (Chacón-Vozmediano *et al.*, 2021). For the grape phenology is important temperature. Then, the change in thermal conditions due to climate change can show to have an influence on phenology and maturity of grape as well as typicity of the wines (Molitor and Junk, 2019).

Local products attract attention that contributes to producer income and region development as well. They can be offered through gastronomy services, innovative production, farm tastings or wine tours. Regional products with the Protected Designation of Origin (PDO) or Protected Geographic Indication (PGI) are connected with the place of origin and producing technologies. The quality of two wine varieties from Slovakia originating from different regions was monitored by the FTIR method at Sauvignon wines, and at Chardonnay wines by the GC-MS

analysis. Processing of results with PCA analysis showed several differences among growing regions (Fikselová *et al.*, 2022). Also study of Kruzlicova and Gruberová (2022) showed ATR FTIR analysis with the chemometric approach to be an effective way, how to discriminate wine categories and to assess of the authenticity of wines (Kruzlicova and Gruberová, 2022).

The aim of this work was to evaluate dry wines with PDO of three different wine varieties which originated from three countries, such as Hungary, Austria and Slovakia mainly by chemical parameters. We suppose that their quality should be comparable within the same variety but can be affected by different factors as well, such as different origin of their production that is important from the consumer and also from research point of view.

MATERIAL AND METHODS

Samples of dry white wines of 3 varieties were used for this research: Riesling (Blanc), Pinot blanc and Sauvignon, each of them originating from Slovakia, Hungary and Austria, with protected designation of origin (PDO) and coming from the 2020 vintage. The overview of the wine samples is given in Table 1.

Table 1 Overview of analysed wines

Sample of wine	Origin	Variety
1	SVK	SB
2	SVK	RR
3	SVK	RB
4	HUN	SB
5	HUN	RR
6	HUN	RB
7	AUT	SB
8	AUT	RR
9	AUT	RB

Note: Variety: RR – Riesling (Blanc), RB – Pinot blanc, SB – Sauvignon blanc. In relation to wine origin: SVK – Slovakia, HUN – Hungary, AUT – Austria.

Wine origin

Slovakia

The Slovak wine-growing region is divided into six wine-growing areas. All Slovak samples originated from the Južnoslovenska wine-growing region. This area is divided into eight districts. Južnoslovenska wine-growing region is characterized by higher degree of homogeneity that affects wine quality. The average altitude of this region is 140 m. The soils are light (sandy) to medium heavy with deeper profile.

Austria

Due to very favorable climatic conditions, Austrian wine-growing areas are mainly located in the east of the country. In Austria, vine is cultivated on a total of 44,912 hectares.

The states of Niederösterreich (27.074 ha), Burgenland (11.772 ha), Steiermark (5.086 ha) and Vienna (575 ha) form their own generic wine-growing regions and combine 17 specific wine-growing regions. Our samples originated from the Steiermark region, just variety Riesling from the Niederösterreich region.

Steiermark is an area of 5,054 hectares, located in the southeast of the country. 20 % of the vines grows on the solid rock of the Eastern Alps. A small part rests on mainly coarse-grained river deposits. The remaining sediments differ in grain size, carbonate content and range through sands, gravels, scree and gravel, sandstones and conglomerates to locally occurring limestones. Southern Steiermark is the highest wine-growing region in Austria.

Niederösterreich region is presented on 27,160 hectares, divided into three climatic regions: the Weinviertel that is situated in the north, the Danube region on the west of Vienna, and Niederösterreich in the southeast (Baláška, 2022).

Hungary

Approximately 73,000 hectares of vineyards in Hungary are spread over almost the entire country. Hungary is divided into 22 wine regions. Our two varieties, Sauvignon blanc and Riesling, originated from the Tolna region. This region is an area of 2420 hectares located on loess soils. Winters in this region are warm and summers are sunny.

Variety Pinot blanc (Fehér burgundi) originated from the Sopron region. It is located in the west of the country; it is an area of 1630 hectares. The climate is rainy, the winter is warm and the summer is cold in this region. The substrate is made of limestone and slate southeast (Baláška, 2022).

Methods

FTIR analyses

Selected chemical parameters in monitored wines such as total acids, tartaric and malic acids, glucose and fructose content and supporting chemical parameters (for the PCA analysis) such as glycerol and alcohol content were performed using the ALPHA Bruker Optik analyser by method described by Jakabová et al (2021).

Method of total polyphenolic content (TPC) determination

TPC was performed by the modified Folin-Ciocalteu method according to Lachman et al. (2003). The gallic acid (3, 4, 5-trihydroxybenzoic acid monohydrate, 99%; Alfa Aesar Thermo Fisher (Kandel) GmbH, Germany) as a standard was diluted with demineralized water to prepare a stock solution. After calibration curve preparation, TPC was expressed as a gallic acid equivalent (GAE).

The wines were injected (50 µl) into 50 ml flasks. Reagent (2.5 ml) of the Folin-Ciocalteu (p.a. purity, Centralchem, Slovakia) was used with distilled water and 5 ml of Na₂CO₃ (p.a. 99%; Centralchem, Slovakia; diluted with deionized water to 20 % solution) was added. Flasks were shaken, filled up to 50 ml volume. They were left at room temperature and measurements were performed by the UV/Vis spectrophotometer (T80 UV/VIS Spectrometer; PG Instruments Ltd., OK Service, Czech Republic), the wavelength 765 nm was used.

Method of antioxidant activity (DPPH method) determination

Brand-Williams et al. (1995) method with small modification was used for determination of the antiradical activity. The DPPH stock solution was prepared (0.025 g DPPH radical, Sigma-Aldrich; Merck KGaA, Darmstadt, Germany) in ethanol (96%, Centralchem, Slovakia) into 100 ml flask. In a glass cuvette, the initial absorbance was measured (515.6 nm). Wine (100 µl) was injected into the cuvette and the mixture was stirred. The cuvettes were left for reaction during 10 min and final absorbance was determined. All parameters were measured spectrophotometrically at 515.6 nm, triplicate measurements per one sample of wine were obtained. The antioxidant activity was expressed as % inhibition of DPPH radical.

Sensory evaluation of wines

Sensory evaluation of wines was performed in sensory laboratory by the panel consisted of 7 trained evaluators. Wines with a temperature of approximately 10–12 °C were served anonymously in clear glasses. The samples were evaluated by the international system according to O.I.V. The following characteristics (Ailer, 2016) were assessed at the wine samples: appearance, aroma (intensity, purity, harmony), taste (intensity, purity, harmony/quality, persistence) and overall impression of the given sample. By the average value, the wines were classified into the individual categories as it is shown in Table 2.

Table 2 Final wine classification by given points

Points	Category
100 – 87	Excellent
86 – 73	Very good
72 – 57	Good
56 – 41	Satisfactory
40 and less	Deficient

Statistical evaluation

Differences among individual parameters/samples of wines regarding their origin were evaluated by the ANOVA (Kruskal-Wallis with Dunn pairwise test) and Principal component analysis (PCA). All calculations were done with use of the program Jamovi (The jamovi project (2021), R Core Team (2021), Wickham et al. (2018), Patil (2018), Revelle (2019), Kassambara and Mund (2020), Seol (2020)).

RESULTS AND DISCUSSION

The description of geographical origin is one of the primary requirements for wine authenticity (Fikselová et al., 2022).

By applying the Kruskal-Wallis test with Dunn pairwise test, several differences among samples of wines have been shown by their geographical origin.

Glucose, fructose and sucrose are the main components of sugar found in wines and together they represent more than 98%. Sucrose in wine is hydrolyzed to fructose and glucose. The mean fructose content in our wine samples was determined to be the lowest in sample of Pinot blanc from Hungary (0.7 g.l⁻¹) and the highest (3.8 g.l⁻¹) in Austrian wine of Riesling. The average glucose content ranged from 0.8 to 2.8 g.l⁻¹ (Pinot blanc).

Regarding fructose (Fig. 1), statistical evaluation showed differences between AUT and HUN at Pinot blanc (p = 0.02), between AUT and SVK in the case of Riesling (p = 0.026) and statistically significant differences between AUT and HUN were observed at Sauvignon variety (p = 0.026).

No statistically significant difference was determined at the glucose content regarding the different geographical origin of Riesling. Observing the other tested varieties, significant differences between AUT and SVK were observed at Pinot blanc and Sauvignon as well (p = 0.02 (Pinot blanc variety); p = 0.039 (Sauvignon variety)).

Acidity is important parameter in the winemaking process and in final quality of wine. Regarding the total acids in our samples, they ranged from 4.8 to 8.8 g.l⁻¹ (Sauvignon). Statistically significant differences were determined at Pinot blanc between HUN and SVK (p = 0.021). In the case of Riesling no statistically significant differences were observed and in the case of Sauvignon significantly higher results were determined in the case of SVK compared to HUN wines (p = 0.018). Wine acids are responsible for its sensory quality (Robles et al., 2019).

More than 90% of the total concentration of organic acids in wine are represented by malic and tartaric acids. The mean malic acid content ranged from 2 to 3.8 g.l⁻¹ (Pinot blanc). Statistically significant differences at malic acid content were observed in the case of Pinot blanc variety between HUN and SVK (p = 0.02), at Riesling variety between AUT and HUN (p = 0.02), and in the case of Sauvignon between HUN and SVK (p = 0.025).

The mean content of tartaric acid in our wine samples ranged from 1.6 to 3.8 g.l⁻¹. The lowest one was determined at Pinot blanc from Hungary, the highest mean content in sample of Sauvignon originating from Slovakia. By statistical evaluation significantly higher results were determined at tartaric acid content in the case of Pinot blanc and Sauvignon varieties between SVK and HUN (p = 0.022). Significantly the highest tartaric acid was observed in Hungarian wines at Riesling variety (p = 0.02). Tartaric acid is included in the chemical stability of wine.

Grape composition at ripening was evaluated by Chacón-Vozmediano et al. (2021) in relation to climatic variables. Decrease in acidity was observed to be due to the higher temperatures. Anthocyanin content suffered from changes due to temperature variations and water deficits as well.

Wines of Grüner Veltliner and Zweigelt varieties which originated from different geographical regions of Austria and Czech Republic were monitored for their TPC, determined by the Folin-Ciocalteu method, total antioxidant activity by FRAP and DPPH analysis, and phenolic compounds by the use of HPLC/UV-VIS method (Soyollkham et al., 2011). The total content of phenolics was associated with wine colour, mouthfeel, astringency and bitterness (Pokryvková et al., 2020). By Soyollkham et al. (2011) antioxidant activity and the phenolic compounds could

be indicators for identification of wines' geographical origin. The gallic acid was the most represented component; tannic and caffeic acid, quercetin and rutin were intermediate; and the ferulic acid and resveratrol had the lowest effect on the antioxidant activity.

The antioxidant activity of our wines (% inhibition DPPH) was determined to be the highest (74%) at Sauvignon from Austria. The lowest results (32 and 33% DPPH inhibition) were detected in samples of Pinot blanc from HU and SVK. No statistically significant difference at antioxidant activity of our wines was observed in the case of Riesling variety. AUT samples of wines showed significantly higher antioxidant activity compared to HUN at Riesling and Sauvignon varieties ($p = 0.022$).

TPC in our wine samples ranged from 257 mg GAE·l⁻¹ to 435 mg GAE·l⁻¹. The lowest TPC was recorded at Sauvignon variety from Slovakia and the highest in Riesling from Slovakia. Statistically significant differences were observed only at

Riesling variety, significantly higher content of total polyphenols was found to be in SVK samples compared to HUN ($p = 0.022$). The content of total polyphenolics in the Slovak wines was in agreement with the studies on the white wines performed by **Bajčan et al. (2017)** and **Čéryová et al. (2021)**.

Costa et al. (2015) monitored Portuguese grape varieties cultivated at the same time in two wine regions, focused on the influence of region on phenolic substances and antioxidant activity. The highest results were determined in 'Dão' region. Concerning the total antioxidant capacity and superoxide radical scavenger activity, a similar trend was observed. For non-flavonoid phenols, the highest results were found to be in the samples from 'Douro' region. Authors of the study state that the variability of the results is determined by the genetic and environmental factors.

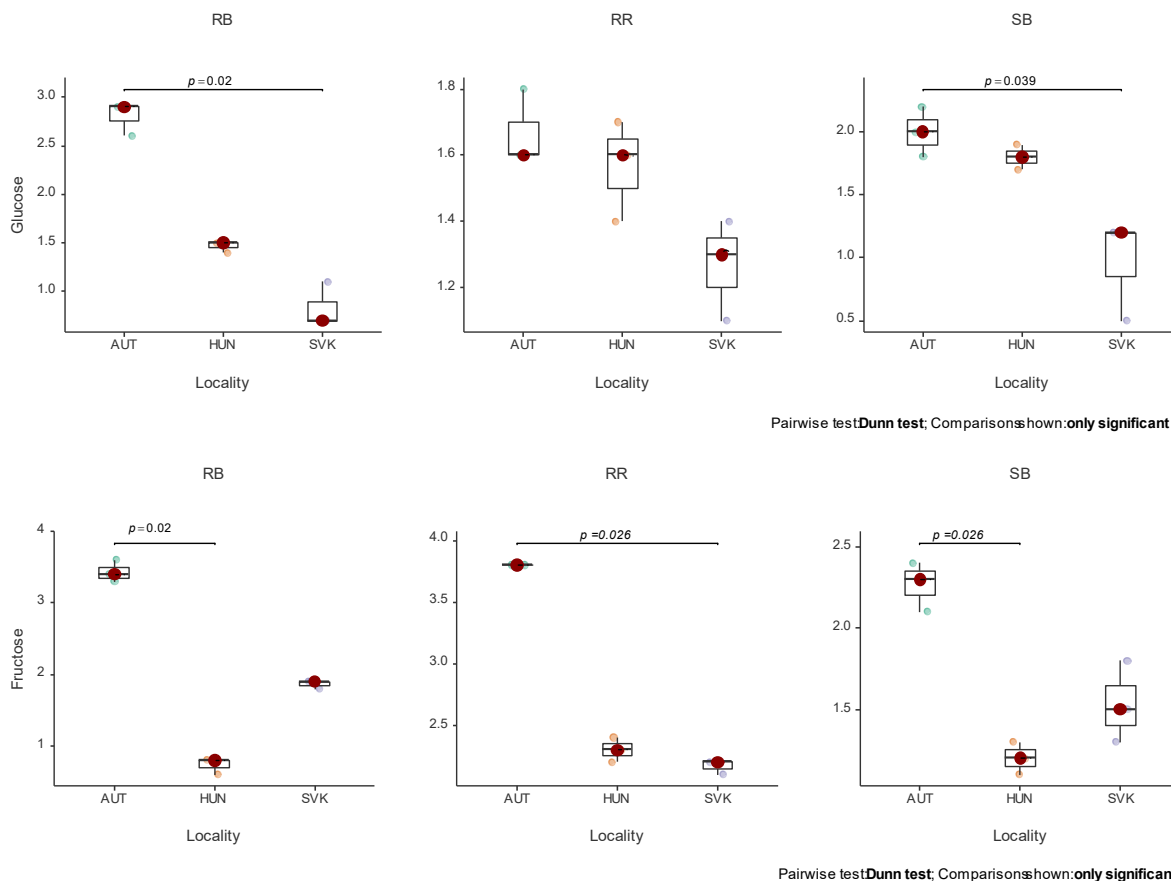


Figure 1 Statistical evaluation of glucose and fructose content in wines by origin using the Kruskal-Wallis test with Dunn pairwise test

Note: Variety: RR – Riesling (Blanc), RB – Pinot blanc, SB – Sauvignon blanc. In relation to origin: SVK – Slovakia, HUN – Hungary, AUT – Austria.

PCA evaluation of wine parameters

Principal component analysis (Fig. 2, 3) was applied to describe the individual wines by their origin. Results of the Bartlett's test indicate that the data was likely factorable (Chi-square (observed = 307.71), Chisquare (critical = 36), $p \leq 0.001$). Kaiser-Meyer-Olkin (KMO) test of sampling adequacy showed middling suitability of the data for complete model (KMO = 0.51). The PCA shows that 72.96 % of the total variation in the variables can be condensed into and explained by the first two principal components (PCs), with eigenvalues of 3.79 and 2.78.

PC1, accounting for 41.18 % of the inertia, contrasted tartaric acid and total acid content with antioxidant activity, content of saccharides (glucose, fructose) and TPC content whereas PC2, explaining 28.94 % of the inertia, reflected the different content of tartaric acid, total acids with alcohol and glycerol.

Our samples of Austrian wines in general could be characterized by high sugar content (fructose, glucose), high results of phenolic substances and antioxidant activity. Higher values of these parameters are characteristic especially for the Austrian varieties Pinot blanc and Sauvignon. Both varieties originated from Steiermark area that is located in the southeast of the country.

The adaptation of grape to the climate and soil may be a differentiating factor regarding its phenolic compound accumulation and subsequent antioxidant activity (**Costa et al., 2015**).

Slovak Sauvignon variety was characterized by higher total acid content, especially in the case of tartaric acid.

Variety Riesling from all countries of origin is similar at the tested parameters and cannot be strictly distinguished using the PCA analysis. However, the samples of

wines originating from Hungary (Sauvignon and Pinot blanc) are characterized by higher content of alcohol and glycerol, which are produced as one of the products in the sugar fermentation process. The production of glycerol at the expense of alcohol increases if fermentation takes place in neutral or weak alkaline environment. For this reason, alcohol and glycerol are far apart on the Y-axis in Fig. 3. High content of glycerol was also determined in wines originated from Slovakia, at Pinot blanc variety.

Wine varieties originated from Slovakia, from the Small Carpathians region were assessed by the FTIR method with an ATR approach by **Kružlicová and Grüberová (2022)** as well. The PCA and linear discriminant analysis were used for the classification of observed wines.

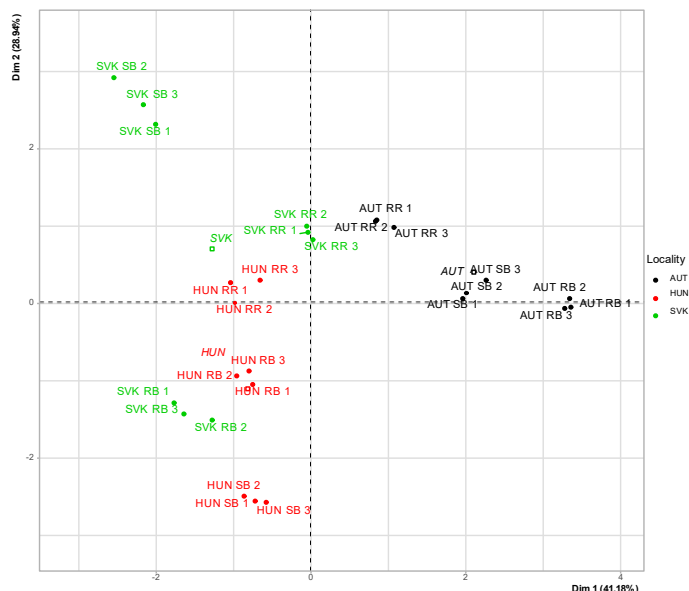


Figure 2 Representation of the wine varieties by their origin by applying the PCA analysis

Note: Variety: RR – Riesling (Blanc), RB – Pinot blanc, SB – Sauvignon blanc. In relation to origin: SVK – Slovakia, HUN – Hungary, AUT – Austria.

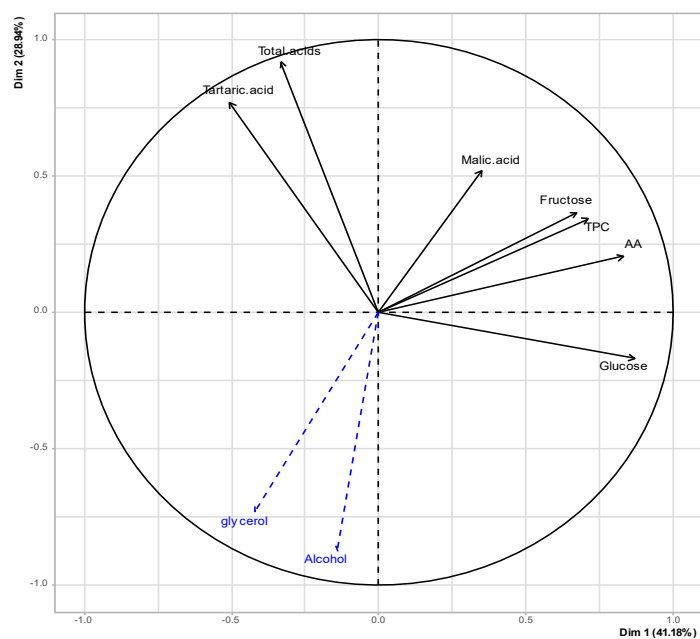


Figure 3 Representation of the main and supplementary (alcohol, glycerol) parameters by the PCA evaluation

In our previous study (Fikselová et al., 2022) we used several chemical parameters in order to separate wines by their geographical origin. We did recommendation to combine them with the PCA or other appropriate statistical method in region separation.

The current tendency in food frauds is getting increased at the expense of consumer. Multidimensional data analysis with advanced analytical methods, e.g. FTIR, gives an interesting instrument for analysis of many parameters at the same time, giving similarities as well as differences within the observed data set (Kružlicová and Grúberová, 2022).

It could be also an important marketing point that the chemical fingerprint is highly associated with the product's quality. The development and description of the product's chemical parameters can give more confidence for consumers. Differences within the quality of selected products can have significant competitive and advertisement advantage. Metabolomics has been demonstrated as significant potential for the marketing of the products (Cassago et al., 2021).

Sensory evaluation of wines

We performed also sensory evaluation of given wines as it is very important for their quality and preferences for the consumer. The results of sensory evaluation

indicate that as the best individual sample was classified Pinot blanc from Slovakia (82 points and it is classified as “very good”). As the worst evaluated sample (58 points) was sample of Riesling from Hungary (category “satisfactory”). Among selected varieties, Pinot blanc received the best rating (73 p.), followed by the Riesling with an average score of 69 points from all three countries. The lowest score, but comparable to the Riesling (68 points) was given to the Sauvignon blanc variety.

Regarding their origin, Slovakia achieved the highest average score (77 points) among all countries. It was followed by Austria with an average number of points of 70 and the lowest average score (63 points) was recorded at wine samples from Hungary. Slovak wines were thus the best sensorically evaluated samples significantly exceeding the samples of wines from the other countries.

CONCLUSION

Using multivariate statistical methods (PCA) was useful tool to find several differences among 3 varieties which originated from three different countries (localities). It is important from the research but also consumer point of view. On the other side there were some cases in which no statistically difference was detected e.g. at antioxidant activity and total acidity at Riesling variety. We can recommend to use the PCA to find typical markers for locality and quality of wines combined with other statistical and/or chemometrical methods as well.

Acknowledgments: This work was funded by the grant VEGA no. 1/0239/21 and the grant APVV-19-0180.

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