



The Effect of Grape Variety on the Micro- and Macroelement Composition of Grape Seeds

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ABSTRACT

This study aimed to examine the differences between the micro- and macro-element content of the seed of eight different grape varieties, namely 'Italian Riesling', 'Cabernet Franc', 'Pinot Noir', 'Sauvignon Blanc', 'Királyleányka', 'Rhine Riesling', 'Merlot', 'Kékfrankos'. On the basis of the results, there were significant differences between the calcium (Ca), potassium (K), magnesium (Mg), phosphorus (P), iron (Fe), zinc (Zn), manganese (Mn), copper (Cu) and boron (B) content of grape seed varieties. In the case of macroelements, the largest amount of K (Italian Riesling 4239 mg/kg to Cabernet Franc 8646 mg/kg), followed by Ca (Pinot Noir 5435 mg/kg to Királyleányka 7369 mg/kg), P (Sauvignon Blanc 2566 mg/kg to Királyleányka 3470 mg/kg) and finally Mg (Cabernet Franc 1097 mg/kg to Királyleányka 1466 mg/kg) was contained in the seeds of the cultivars studied. Of the microelements, Fe was present in the largest amount (Sauvignon Blanc 23.7 mg/kg to Merlot 59.5 mg/kg) considering the grape varieties. The amounts of the other microelements tested were as follows: Mn from 13.1 mg/kg (Pinot Noir) to 31.3 mg/kg (Királyleányka), Cu from 9.38 mg/kg (Italian Riesling) to 19.1 mg/kg (Cabernet Franc), Zn from 10.9 mg/kg (Kékfrankos) to 16.2 mg/kg (Királyleányka) and B from 9.46 mg/kg (Italian Riesling) to 9.46 mg/kg (Rhine Riesling). Based on the results, the type of grape affects the micro- and macro-elements content of the seed, and the daily consumption of 100g of grape seed meal can significantly contribute to the daily intake of trace elements.

Keywords: by-product, grape seed, minerals, ICP-OES



1. INTRODUCTION

Winemaking is one of the most ancient activities of mankind, and during the process several by-products are generated. These by-products contain substances that may have a beneficial effect on human health. Therefore, they are becoming more widespread in the food industry (Martin et al., 2020), but the chemical composition is influenced by climatic conditions and soil quality (Baglyas & Hajdu, 2024). Grape pomace is a basic by-product of wine production, which includes 20–26% grape seed (Mattos et al., 2017; Kapcsándi et al., 2021). Grape seed contains 2-4% w / w minerals (Licev et al., 1974; Rubilar et al., 2016), and the main macronutrients are calcium, potassium (Ahn & Son, 2012; Mironeasa et al., 2010), phosphorus and magnesium. The main microelements are iron, manganese, and zinc (Tangolar et al., 2009). Minerals play an important role in metabolic processes and are essential parts of some enzymes. They act as catalysts and antioxidants (Rubilar et al., 2016). Adequate calcium intake has a beneficial effect on human health. Reduce hypertensive disorders of pregnancy, plays a role in the regulation of blood pressure, and helps prevent osteoporosis and colorectal adenomas, especially among young people (Cormick & Belizán, 2019). Potassium is an essential nutrient. It is the most common cation in the intracellular fluid, where it plays a key role in maintaining cell function, especially in excitable cells such as muscles and nerves, and sodium helps to regulate osmotic pressure and pH equilibrium (Suzuki et al., 1999). Phosphorus is also essential for life and plays several roles in maintaining cell vitality. Phosphorus is the major structural component of DNA and RNA. The element plays a role in the synthesis of ATP (adenosine 5'-triphosphate) and also in the formation of phospholipids and cell membranes. Phosphorus is essential for the formation and maintenance of bones and teeth in all vertebrates (Childers et al., 2011). Magnesium is the fourth most common cation and has many functions in the human body. It is a cofactor of more than 300 enzymes and regulates several essential functions of the body, such as neuromuscular conduction, muscle and heart muscle contraction, blood glucose, and blood pressure (Bertinato et al., 2015). Furthermore, magnesium plays a role in body energy production, nucleosynthesis, and bone development (Al Alawi et al., 2018; Grober et al., 2015).

Iron is an essential microelement in almost every living organism. It takes part in a number of metabolic processes, such as oxygen transport, deoxyribonucleic acid (DNA) synthesis, and electron transport. One of the main causes of human disease is an abnormal iron metabolism. Improper iron metabolism is responsible for the development of many diseases, such as anemia and, in more severe cases, neurodegenerative diseases (Abbaspour et al., 2014). Manganese is also an essential metal for the human body. This element is needed for proper functioning of the immune system, proper blood sugar levels, blood clotting, regulation of cellular energy, proliferation, digestion, bone growth, and protection against reactive oxygen species (ROS) (Horning et al., 2015). Zinc is one of the most important trace elements in the body. It plays a key role in the growth of microorganisms, plants, and animals. This element is also a cofactor for more than 300 enzymes and is involved in stabilising the structures of many proteins (Chasapis et al., 2012; Vaghari-Tabari et al., 2021).

In this study, grape minerals were compared in eight different grape varieties, which were grown in the northwestern region of Hungary, in the Benedictine Archabbey of Pannonhalma. The experiments aimed to determine the differences between the micro-and macro-element content of each grape varieties.



2. MATERIALS AND METHODS

2.1 Grape seed samples

The samples included in the experiment came from the Benedictine Archabbey of Pannonhalma. In terms of the geological structure of the hills of Pannonhalma, is of Upper Pliocene origin, with slope sediments and a sandy area covered with loess. The area is highly endangered by erosion, the steep slopes, and the original brown earth has mostly been destroyed down to the soil-forming rock, which also affects the state of the vegetation (Pottyondi, 2010). The varieties studied were: 'Italian Riesling', 'Cabernet Franc', 'Pinot Noir', 'Sauvignon Blanc', 'Királyleányka', 'Rhine Riesling', 'Merlot', and 'Kékfrankos'.

2.2 Chemicals

Nitric acid (Iach: ner, Bratislava, Slovakia) and hydrogen peroxide (Molar Chemicals, Halásztelek, Hungary) were used for the digestion method. For calibration, monoelement standards for calcium, potassium, magnesium, and phosphorus, and multielement standards for microelements were purchased from CPAchem (Bogomilovo, Bulgaria). The argon gas required for the operation of the ICP-OES device was procured from Messer Hungarogáz Kft (Budapest, Hungary).

2.3 ICP-OES method

2.3.1 Sample digestion

For the examinations, the grape seeds arrived in dried form from the Abbey. The dried grape seeds were chopped using a coffee grinder (Sencor, SCG 2050RD). 0.4 g of the grape seed samples were weighed in a 90 ml tetrafluoromethoxyl (TFM) digestive vessel. To the weighed samples was added 5 ml of 65% HNO₃ and 1 ml of 30% H₂O₂. The samples were digested in the MLS Mega 1200 microwave digestion system (Milestone, Italy) according to the following programme (time (min)/power (W)): 1/250, 1/0, 8/250, 5/400, 5/650, ventilation time 5 min. After digestion, the samples were diluted to 25 ml and assayed with ICP-OES.

2.3.2 ICP-OES analysis

For the determination of the micro-and macro-element composition of the seeds, an Agilent (Santa Clara, CA, USA) 5110 ICP-OES type equipment was used. The applied ICP-OES programme is shown in *Table 1*. The elements examined and the wavelengths used are shown in *Table 2*. The use of two wavelengths was necessary to avoid possible spectral interference.



Table 1: ICP-OES program for the determination of macro- and micro-elements

Parameters	Macroelements	Microelements
Read time (s)	5	20
RF power (kW)	1.4	1.4
Stabilisation time (s)	15	15
Viewing mode	radial	axial
Viewing height (mm)	8	-
Nebulizer flow (L/min)	0.75	0.75
Plasma flow (L/min)	12	12
Aux flow (L/min)	1	1

Table 2: Wavelengths used to determine macro- and microelements

Element	λ_1 (nm)	λ_2 (nm)
Ca	315.887	317.933
K	766.491	769.897
Mg	279.553	280.270
P	213.618	214.914
B	249.678	249.772
Cu	324.754	327.395
Fe	234.350	238.204
Mn	257.610	293.305
Zn	206.200	213.857

2.4 Data analysis

The composition of micro- and macro-elements of grape seeds was determined by Microsoft Office Excel from the absorbance values measured for grape seed oils. The equation of the second order least squares analytical curve was fitted to the measurement solutions using the nonlinear least-squares method. All results are expressed as means ($n=3$) \pm standard deviation. Analyses of variance (ANOVA) followed by the Tukey post hoc test were used to compare the significant differences in the data. Differences were considered statistically significant when $p < 0.05$.

3. RESULTS AND DISCUSSION

No significantly different data were found for the elements measured at the two different wavelengths; therefore, the results measured at the primary wavelengths are presented in each case in the evaluations. Results are expressed in mg/kg of dry matter.

3.1 Macro-element content of grape seed samples

As shown in *Table 3*, the grape seed cultivars studied provided different results in macroelement content. Similar differences were observed by Al-Juhaimi et al. (2017) in the macroelement content of variant grape seed varieties. Significant differences were found in the amount of each element studied. In all samples, potassium was present in the highest amount of macronutrients, while magnesium was detectable only in negligible amounts.



Table 3: Results of the macroelement content of the grape seed samples (mg/kg) and standard deviations of data (n=3), different letters (a, b, c, d, and e) denote significant differences ($p \leq 0.05$)

Grape varieties	Ca	K	P	Mg
Merlot	6711 ± 117.8 ^a	7824 ± 325.6 ^a	3202 ± 62.8 ^a	1136 ± 24.9 ^a
Rhine Riesling	6204 ± 132.5 ^b	5333 ± 47.6 ^b	3294 ± 37.0 ^a	1232 ± 13.9 ^b
Cabernet Franc	5864 ± 123.0 ^c	8646 ± 475.9 ^c	3059 ± 83.7 ^b	1097 ± 29.3 ^c
Pinot Noir	5435 ± 101.6 ^d	7200 ± 216.5 ^d	3227 ± 38.6 ^a	1205 ± 16.3 ^d
Italian Riesling	6539 ± 200.1 ^a	4239 ± 146.6 ^e	2733 ± 69.6 ^c	1285 ± 34.6 ^b
Sauvignon Blanc	6311 ± 205.9 ^b	4325 ± 164.2 ^e	2566 ± 134.8 ^c	1252 ± 60.2 ^b
Királyleányka	7369 ± 137.8 ^e	5376 ± 86.1 ^b	3470 ± 68.6 ^d	1466 ± 38.4 ^e
Kékfrankos	6745 ± 230.8 ^a	7642 ± 357.2 ^a	2641 ± 146.6 ^c	1190 ± 64.6 ^a

In the case of calcium, the highest amount was measured in the Királyleányka seeds (7369 mg/kg), while the lowest amount was detected in the Pinot Noir seed (5435 mg/kg).

The potassium content of the seeds of blue grape varieties (Merlot, Cabernet Franc, Pinot Noir, Kékfrankos) is remarkably high compared to the seeds of white grape varieties. The highest amount of potassium was in Cabernet Franc (8646 mg/kg) and the lowest was in the seeds of Italian Riesling (4239 mg/kg). The difference in the potassium content of the two varieties of grapes is 4407 mg/kg, which is not a negligible factor considering the recommended daily allowance (3.51 g) of WHO (2012).

In the case of phosphorus and magnesium, minimal quantitative differences were observed. Phosphorus contents below 3000 mg/kg were measured for Sauvignon Blanc, Kékfrankos, and Olaszrizling. For the other cultivars studied, this value was higher.

The mineral composition of 11 grape seeds was described by Al Juhaimi et al. (2017). The seed samples' phosphorus contents ranged from 2 277.65 mg/kg (Papaz karası) to 3 232.42 mg/kg (Chardonnay). Furthermore, the calcium contents of grape seeds ranged from 5 115.58 (Chardonnay) to 8 036.76 mg/kg (Ada Karası), with the potassium contents varying from 4 347.80 (Cabernet Sauvignon) to 9 492.60 mg/kg (Gamay). Additionally, the samples' magnesium contents ranged from 1 249.18 mg/kg (Ada Karası) to 2 073.90 mg/kg (Alfons Lavallé). Our findings are consistent with these results.

3.2 Microelement content of grape seed samples

Based on the results presented in *Table 4*, it can be clearly stated that the highest amount of microelement was iron (Fe) in the tested samples. The lowest iron content was obtained in the case of Italian Riesling (25.8 mg/kg), while the highest amount of the same element was observed in the seeds of the Merlot variety (59.5 mg/kg). Compared to the article published by Canizo et al. (2018), we were able to detect almost the same amount of microelements in the case of the examined grape seeds. In the case of white grape varieties, we were able to identify less iron than in the case of blue grapes, although Királyleányka stands out from other seeds with its iron content of 54.1 mg/kg. In the case of blue grape varieties, the iron content of Sauvignon Blanc (23.7 mg/kg) was significantly lower than the other varieties.



Table 4: Results of the microelement content of grape seed samples (mg/kg), and standard deviations of the data (n=3), different letters (a, b, c, d, e, f, and g) denote significant differences ($p \leq 0.05$)

Grape varieties	Fe	Zn	Mn	Cu	B
Merlot	59.5 ± 1.179a	14.9 ± 0.216a	19.5 ± 0.330a	17.4 ± 0.205a	14.4 ± 0.125a
Rhine Riesling	32.7 ± 0.450b	16.0 ± 0.624b	16.1 ± 0.189b	11.9 ± 0.082b	16.1 ± 0.205b
Cabernet Franc	48.0 ± 1.438c	12.0 ± 0.327c	16.8 ± 0.419c	19.1 ± 0.741c	15.0 ± 0.411a
Pinot Noir	47.8 ± 1.084c	12.4 ± 0.125c	13.1 ± 0.216d	14.2 ± 0.189d	15.9 ± 0.283b
Italian Riesling	25.8 ± 0.909d	13.8 ± 0.287d	28.4 ± 0.698e	9.83 ± 0.131e	9.46 ± 0.195c
Sauvignon Blanc	23.7 ± 2.061d	14.0 ± 0.531d	27.0 ± 1.322f	10.2 ± 0.125f	9.89 ± 0.215d
Királyleányka	54.1 ± 1.126e	16.2 ± 0.591b	31.3 ± 0.826g	12.1 ± 0.094g	11.0 ± 0.125e
Kékfrankos	55.0 ± 2.428e	10.9 ± 0.624e	17.4 ± 0.713c	18.9 ± 0.490c	14.7 ± 0.499a

Significant differences in the amount of zinc content were also observed in the tested varieties. However, the difference between the highest amount of zinc (Királyleányka 16.2 mg/kg) and the lowest (Kékfrankos 10.9 mg/kg) was only 5.3 mg/kg.

In the case of manganese, a notable difference was observed in the seeds of three grape varieties. The highest amounts were detected in the seeds of Királyleányka (31.3 mg/kg), Italian Riesling (28.4 mg/kg) and Sauvignon Blanc (27 mg/kg). The difference between the highest and lowest measured values is more than 18 mg/kg, which is quite large considering the recommended daily allowance of manganese (2.3 mg is recommended for adult men and 1.8 mg for women (Trumbo et al., 2001).

For copper, three outstanding values were observed, in the case of the varieties Cabernet Franc (19.1 mg/kg), Kékfrankos (18.9 mg/kg) and Merlot (17.4 mg/kg).

There were no large differences in the boron content of the samples tested. However, three varieties, namely Italian Riesling (9.46 mg/kg), Sauvignon Blanc (9.89 mg/kg), and Királyleányka (11 mg/kg) contained significantly smaller amounts of boron.

Iron concentrations in grape seeds varied from 29.96 mg/kg (Narince) to 73.82 mg/kg (Sangiovese), according to Al Juhaimi et al. (2017). Based on literature data the manganese contents of the grape seeds ranged from 2.08 (Ada Karasi) to 11.59 mg/kg (Cinsaut), while the zinc contents of the seeds varied from 8.27 (Narince) to 15.93 mg/kg (Semillon). The seeds' copper contents varied from 8.62 mg/kg (Narince) to 15.28 mg/kg (Chardonnay) (Rubilar et al., 2016). Compared to the article published by Canizo et al. (2018), we were able to detect almost the same amount of microelements in the case of the examined grape seeds. The zinc and copper contents of grape seeds were found to be between 16.5 and 18.5 µg/g and 9.0 and 13.0 µg/g, respectively, while the manganese content was reported to be between 15.7 and 20.3 µg/g. Regarding grape seeds, a number of literary sources (Tangolar et al., 2009; Lachman et al., 2013; Oprea et al., 2022) report comparable element contents. Consuming about 100 g of dried, grounded grape seeds daily can significantly contribute to the intake of elements required for the body's proper functioning, as demonstrated by the presented results and the publications in the literature (Yang et al., 2010).



4. CONCLUSION

Based on the results, it can be concluded that the type of grape clearly influences the element content of the seeds. The samples examined came from the same production area, so the influence of the environment was minimal. Individual plants received similar plant protection treatments during cultivation. After evaluating the results and comparing the data in the literature, it can be said that even small amounts of grape seeds have significant physiological effects. Consumption of approximately 100 g of grape seed per day can already contribute significantly to the intake of the necessary elements for the proper functioning of the body. The use of grape seeds in the food industry (even to produce functional foods) is recommended due to their outstanding element content. Consuming of these seeds can contribute to the development of a balanced diet.

A szőlőfajta befolyásoló hatása a szőlőmag mikro- és makroelem összetételére

ÖSSZEFOGLALÁS

A vizsgálat célja nyolc különböző szőlőfajta, nevezetesen 'Olaszrizling', 'Cabernet Franc', 'Pinot Noir', 'Sauvignon Blanc', 'Királyleányka', 'Rajnai rizling', 'Merlot' és 'Kékfrankos' magjának mikro- és makroelem-tartalma közötti különbségek vizsgálata volt. Az eredmények alapján statisztikailag igazolt különbségeket mértek az egyes szőlőmag fajták kalcium (Ca), kálium (K), magnézium (Mg), foszfor (P), vas (Fe), cink (Zn), mangán (Mn), réz (Cu) és bór (B) tartalmában. A makroelemek közül a legnagyobb mennyiségben a káliumot (Olaszrizling 4239 mg/kg - Cabernet Franc 8646 mg/kg), majd a kalciumot (Pinot Noir 5435 mg/kg - Királyleányka 7369 mg/kg), a foszfort (Sauvignon Blanc 2566 mg/kg - Királyleánykára 3470 mg/kg), végül magnéziumot (Cabernet Franc 1097 mg/kg - Királyleánykára 1466 mg/kg) tartalmaztak a vizsgált szőlőfajták magjai. A mikroelemek közül a legnagyobb mennyiségben a vas volt jelen (Sauvignon Blanc 23,7 mg/kg - Merlot 59,5-mg/kg). A többi vizsgált mikroelem mennyisége a következő volt: mangán 13,1 mg/kg-tól (Pinot Noir) 31,3 mg/kg-ig (Királyleányka), réz 9,38 mg/kg-tól (Olaszrizling) 19,1 mg/kg-ig (Cabernet Franc), cink 10,9 mg/kg-tól (Kékfrankos) 16,2 mg/kg-ig (Királyleányka), bór pedig 9,46 mg/kg-tól (olaszrizling) 9,46 mg/kg-ig (rajnai rizling). Az eredmények alapján a szőlőfajta befolyásolja a magok mikro- és makroelem tartalmát, továbbá napi 100 g szőlőmagliszt fogyasztása jelentősen hozzájárulhat az ajánlott napi ásványianyag bevitelhez.

Kulcsszavak: melléktermék, szőlőmag, ásványianyagok, ICP-OES



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