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The analysis of the chemical composition of the grape seed oil and peel

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Abstract. The increased interest in grapevines and their products, which are universal in terms of taste and healing properties, results from the diverse content of beneficial compounds that have a positive effect on the human body. The valuable chemical composition of grape seed oil, as well as the peel of both white and red grape varieties, supports the importance of using this product not only in food but also in other areas.
Keywords: lipids, oil, fatty acids, aromatic acids, flavonoids, physico-chemical indices, phenolic compounds.

Analiza compoziției chimice a pieliței și a uleiului din sâmburii de vița-de-vie

Rezumat. Interesul sporit pentru vița-de-vie și produsele ei, care sunt universale după însușirile gustative și curative, rezultă din conținutul variat al compușilor utili cu acțiune benefică asupra organismului uman. Compoziția chimică valoroasă a uleiului din sâmburii de struguri, dar și a pieliței soiurilor albe și roșii, argumentează importanța utilizării acestui produs atât în alimentație, cât și în alte domenii.
Cuvinte-cheie: lipide, ulei, acizi grași, acizi aromatici, flavonoide, indici fizico-chimici, compuși fenolici.

1. Introduction

The grapevine has been known in the territories occupied by the Romans since prehistoric times, from the Neolithic period, over 3000 years BC. The cultivation of this vine in our country is confirmed by numerous sources, including archaeologists, paleontologists, as well as in the folklore and ethnography of the native region as part of our people's culture.

The highly favorable natural conditions, as well as people's attachment to this plant, explain the increased interest in cultivating grapevines, which first developed among the Thracians, then among the Greeks and Romans. Evidence of the knowledge of the Getae-Dacians and the development of this culture is seen in the preservation of Dacian-origin words in the Romanian language, such as “butuc” (grapewine), “strugure” (grape), or “răvac” (fermented grape juice drained prior crushing and pressing).

Grapevines are cultivated for their delicious and aromatic grapes, which contain 10-30% sugars (glucose, fructose) with high nutritional, dietary, and healing qualities. Grapes are used in the treatment of liver, kidney, and stomach diseases, as well as tuberculosis. They are used to make juice, compote, jam, fruit paste and others. Grape seeds contain up to 20% of fatty oil, which is used in food and for certain technical purposes. The extract from grape seeds, which is rich in antioxidants, accelerates wound healing and benefits the cardiovascular, skeletal, and immune systems, as well as the cognitive function.

The period of grape development and maturation is characterized by several biochemical processes that produce qualitative and quantitative changes in the composition of the berries, determining the optimal time for harvesting. Both the raw material and the by-products obtained from grape processing must meet the applicable standards.

The grape seed oil is a valuable product with multiple properties and uses. It is one of the most potent oils with antioxidant effects, due to the presence of flavonoids, polyphenols, tannins, anthocyanins, and proanthocyanins.

The most significant stages of analyzing these substances include their extraction from plant sources, separation, purification, and isolation of individual components from crude extracts. Typically, polyphenols are extracted from plant sources using methanol [1], ethanol [2], acetone [3], or mixtures of these solvents with water in various proportions. Good results are also obtained with extractions using mixtures of methanol-water or acetone-water as extractants of proanthocyanidins from plant sources, as these mixtures have enhanced extraction capacity [3, 4]. In the extraction process with solvents such as methanol, ethanol, or acetone, in addition to proanthocyanidins, other substances are also extracted, making the purification procedure of the extract more challenging and reducing the extraction rate of proanthocyanidins [5]. If the extract is accompanied by lipophilic compounds, then non-polar solvents such as petroleum ether and other non-polar solvents are typically used for extraction [6].

It is known that besides water, methanol, or acetone, proanthocyanidins are highly soluble in ethyl acetate, and this solvent exhibits significant selectivity concerning natural products, making it a good alternative in the extraction process of proanthocyanidins from grape seeds [7].

2. Methods and materials used

For the study of the chemical composition of lipids and phenolic compounds from grape seeds and peel there were used the following methods: Soxhlet extractions, gas chromatography (GC), and high-performance liquid chromatography (HPLC). The practical part of the work was carried out in the laboratories of the *Institute of Chemistry* in Chișinău.

3. Obtained results and discussion

The main substances in the composition of grape peel are:

- Phenolic compounds: anthocyanins, flavonoids, tannins, phenolic acids.
- Aromatic substances with a heterogeneous composition: alcohols, acids, esters, aldehydes, ketones, terpenes, etc.
- Oxidase enzymes (tyrosinases in healthy grapes and laccases in grapes affected by mold), which oxidize anthocyanins and tannins.
- Pectolytic and proteolytic enzymes.

Grape seeds constitute 2-6% of the grape, mature along with their ripening, and have the following chemical composition: 28-40% water, 28% cellulose, 0.8-1.2% nitrogenous substances, 4-6% tannins, 10-25% fatty substances, 2-4% minerals, fatty acids, and other substances. In order to determine the quality indicators of the oils, *Moldova* and *Izabella* grape varieties were analyzed. The fatty substances from grape seeds were determined by extraction with petroleum ether using the Soxhlet apparatus.

Table 1. Physicochemical indicators of grape seed oils.

Name of the variety	Acidity index	Saponification index	Esterification index	Iodine index	Peroxide index
Izabella	1.009	190.47	204.05	121.06	0.185
Moldova	0.505	188.47	195.85	119.73	0.175

The results obtained from the research were compared with the indicators provided in the Technical Regulation for *Edible Vegetable Oils* [9], which demonstrated that all indices meet the quality standards.

The acidity index determines the amount of free fatty acids in the oils, indicates the degree of rancidity and the duration and storage conditions of the oil as well. Fresh lipids usually have a minimal acid content. When pomace and seeds are stored in a moist state or when oil is obtained at high temperatures, the acidity index increases.

The iodine value characterizes the quantity of unsaturated fatty acids in the oil.

The peroxide value indicates the degree of oxidative rancidity of the fat. During the oxidation of fats, various products (peroxides, aldehydes, ketones) are formed, which alter the taste of the oil and give it an unpleasant odor.

The quality of grape seed oil is influenced by the grape variety, the drying and storage conditions of the seeds, as well as their processing technology.

The oil obtained from different varieties differs in physicochemical properties: it was determined that red varieties contain 13.69 - 16.35%, while white varieties contain 12.88 - 20.58% oil. The quantity and quality of oil depend on the soil composition, the ripeness of the grapes, seed quality, and the duration of seed storage. If the seeds are stored for a year, the oil content decreases by 1.45% - 13.55%, so processing should be done within 3 - 4 months after harvest [8].

To identify the chemical composition of seeds from different varieties, the samples were dried and ground, and then the extracts were obtained. Upon analyzing the data by varieties, it was found that the *Aligote* variety has the highest content of (+)-catechin, with a value of 2.640 mg, followed by (-)-*epi*-catechin with 2.574 mg, and chlorogenic acid with 0.247 mg. In descending order, other compounds present in the seeds of this variety include rutin, gallic acid, 3,4-dihydroxybenzoic acid, syringic acid, ellagic acid, quercetin, ferulic acid, resveratrol, 4-hydroxybenzoic acid, p-coumaric acid, while caffeic acid was not detected in the seeds of this variety.

The chemical composition of the seeds of the *Lidia* variety is characterized by an increased amount of (+)-catechin, specifically 0.771 mg, (-)-*epi*-catechin - 0.574 mg, and chlorogenic acid - 0.139 mg. In decreasing order, the sequence continues with syringic acid, rutin, gallic acid, 3,4-dihydroxybenzoic acid, ellagic acid, ferulic acid, quercetin, and 4-hydroxybenzoic acid, resveratrol, p-coumaric acid, and in a quantity of 0.001 mg, caffeic acid was also detected.

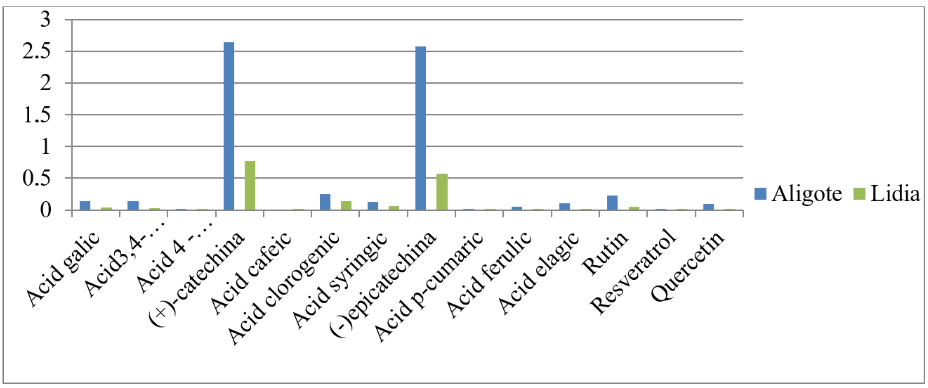

Figure 1. Chemical composition of seeds by grape varieties (mg).

Conducting a comparative study, we reached the conclusion that the grape seeds of the two analyzed varieties contain a significant amount of flavonoids: (+)-catechin and (-)-*epi*-catechin. In the *Aligote* variety, (+)-catechin predominates, followed by (-)-*epi*-catechin and chlorogenic acid. As for the other flavonoids, rutin and quercetin, the difference between the varieties is not as significant, but the *Aligote* variety has the highest content of these two compounds.

The group of hydroxycinnamic acids includes: caffeic acid, chlorogenic acid, *p*-coumaric acid, and ferulic acid. The values for these compounds are also higher in the white variety compared to the red grape variety. An exception is caffeic acid, which is present only in the *Lidia* variety (0.001 mg).

Regarding the derivatives of benzoic acid, the following were analyzed: syringic acid, 3,4-dihydroxybenzoic acid, 4-hydroxybenzoic acid, and gallic acid. For these compounds, no significant differences were observed, except for syringic and gallic acid, which are present in smaller amounts in the red variety.

In comparison to other classes of compounds, grape seeds contain a lower amount of polyphenols, such as resveratrol and ellagic acid, with the red variety having less content of these compounds compared to the white variety.

The seeds of the respective varieties were analyzed in comparison to observe the changes that occur in the chemical composition of the berries over 11 days. In the seeds of the *Aligote* variety there was observed a decrease in the values of all studied flavonoids over time, except for quercetin, which increased by 0.001 mg.

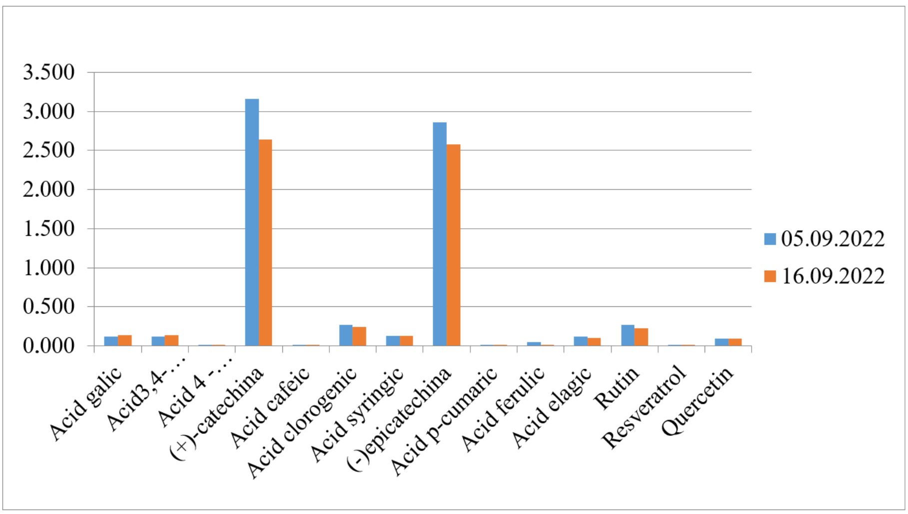

Figure 2. Chemical composition of *Aligote* grape seeds at different time periods (mg).

In the seeds of *Lidia* grape variety, the content of flavonoids and hydroxycinnamic compounds also undergoes changes over time. The derivatives of benzoic acid also decrease in quantity over the 11-day period, except for 3,4-dihydroxybenzoic acid, which increases from 0.152 mg to 0.156 mg. An increase is also observed in the polyphenolic compounds: ellagic acid and resveratrol.

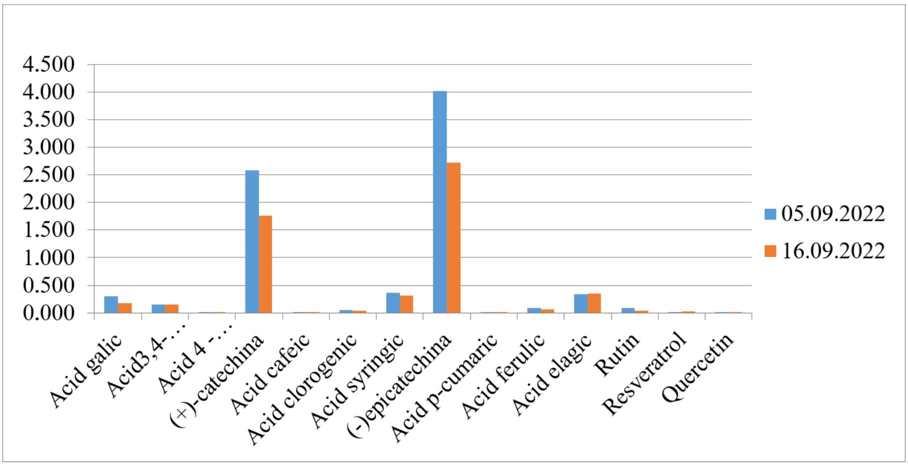

Figure 3. Chemical composition of *Lidia* grape seeds at different time periods (mg).

If the quantity of chemical compounds in the seeds decreases over time, the situation is reversed in the composition of the peel. Observing the evolution of chemical compounds in the peel of *Aligote* grape variety over time, it was noticed that flavonoids: (+)-catechin, (-)-*epi*-catechin, and rutin significantly increase their values, while quercetin, like in the seeds, decreases in quantity. Two representatives of hydroxycinnamic acids, chlorogenic and p-coumaric acids, show decreased values over 11 days, while the other two representatives, caffeic and ferulic acids, exhibit an opposite situation. The derivatives of benzoic acid of this white variety, as the harvest period approaches, concentrate more in the peel, while the polyphenols show the opposite trend.

Performing a comparative analysis of the chemical compounds in the peel of *Lidia* grape variety, it was observed that over 11 days, the peel of red varieties become richer in flavonoids, except for rutin. The content of hydroxycinnamic acids in the peel also increases. The derivatives of benzoic acid decrease quantitatively in the peel, except for syringic acid, which shows an increase. As for the polyphenols in this variety, the values of resveratrol decrease, while the value of ellagic acid remains constant. The study conducted on the peel and seeds of grapes, which includes the extraction and identification of compounds present in these sources rich in antioxidants and essential fatty acids necessary for the body, justifies their separation and use in various fields.

4. Conclusions

(1) The chemical composition of Aligote, Izabela, Moldova, and Lidia grapes was investigated.
(2) The total content of fatty oil in the grape seeds of Moldova and Izabela varieties was determined through extractions with petroleum ether, using a Soxhlet apparatus.
(3) To confirm the quality of the oils, their physicochemical indices were determined, which were similar, since both varieties are red.
(4) Fourteen phenolic compounds were determined in the seeds and peels using the HPLC method.
(5) A decrease in the content of polyphenols was observed in the seeds during the pre-harvest period, while an increase in polyphenol content was observed in the peel during the same period.
(6) Additionally, a difference in the chemical composition between the white and red varieties was observed. The white variety is characterized by a high content of flavonoids, while the red variety has a higher content of polyphenols.

Recomandations: The wine industry represents one of the main branches of our country's economy, but the by-products accumulated after grape processing are not fully utilized. The bioactive components in grapes with antioxidant, antibacterial, anti-inflammatory, cardiovascular, and hepatic protective properties can be used in various fields: food industry, pharmaceuticals, cosmetics, animal husbandry and agriculture.

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