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THE INFLUENCE OF GRAPE SEED DRYING TEMPERATURE ON THE QUALITY OF GRAPE SEED OIL

UTJECAJ TEMPERATURE SUŠENJA SJEMENKI GROŽĐA NA KVALITETU ULJA

Maja ERGOVIĆ RAVANČIĆ, Valentina OBRADOVIĆ**, Josip MESIĆ*, Brankica SVITLICA*, Helena MARČETIĆ*, Krešimir PRTENJAČA*, Svjetlana ŠKRABAL**
**Polytechnic in Požega, Vukovarska 17, 34000 Požega*
***e-mail: vobradovic@vup.hr*

ABSTRACT

As a by-product of the winemaking process, grape seeds have been receiving increased attention worldwide due to a number of beneficial nutritional properties. Moreover, grape seed oil has also been gaining prominence for its high content of unsaturated fatty acids, primarily linoleic acid (C18:2) (72-76%). The objective of this paper was to determine the influence of three different grape seed drying temperatures (20, 40 and 60 °C) on the quality of cold-pressed oils from five different grape varieties (Pinot noir, Pinot blanc, Muscat, Cabernet sauvignon and Graševina). The oils extracted were tested for the acid number (as an indicator of hydrolysis), the percentage of free fatty acids and the peroxide value (as an indicator of autoxidation). The peroxide values of the oil samples considered increased with the increasing drying temperature of grape seeds. The highest peroxide value was observed in the oil samples produced from the Graševina seeds (regardless of the grape seed drying temperature), whereas the Muscat oil samples exhibited the lowest peroxide values. The acid number and the percentage of free fatty acids of the oil samples considered were found to be variety specific and independent of the grape seed drying temperature.

Key words: *drying, grape, oil, grape seed*

REZIME

Sjemenke grožđa se sve rjeđe promatraju kao otpad prilikom proizvodnje vina, a sve češće kao vrlo vrijedna sirovina u mnogim područjima i industrijama, a najčešće se upotrebljavaju za proizvodnju jestivih ulja, kao izvor nutritivno vrijednih vlakana, u farmaceutskoj industriji, za proizvodnu biogoriva itd. Njihova visoka primjena rezultat je velikog udjela mononezasićenih i polinezasićenih masnih kiselina, od kojih je najznačajnija linolna kiselina (C18:2) s udjelom od 72 do 76 %, ovisno o sorti grožđa. Sjemenke grožđa također sadrže određenu koncentraciju visokovrijednih fenolnih spojeva, uključujući flavonoide, karotenoide, fenolne kiseline, tanine i stilbene. Glavni polifenoli identificirani u ulju sjemenki grožđa su katehin, epikatehin, trans-resveratrol i procijanidin B1. Cilj ovog rada bio je utvrditi utjecaj tri različite temperature sušenja (20, 40 i 60°C) sjemenki grožđa na kvalitetu hladno prešanog ulja dobivenog od pet različitih sorata grožđa (Pinot crni, Pinot bijeli, Muškat žuti, Cabernet sauvignon, Graševina). Ovisno o razlikama kultivara, iz sjemenki grožđa mogu se dobiti različiti prinosi ulja. Kako bi se utvrdio utjecaj temperature sušenja sjemenki grožđa na njegovu kvalitetu, svim uzorcima ulja određene su vrijednosti kiselinskog broja koji je jasan pokazatelj hidrolize, postotak slobodnih masnih kiselina, te peroksidni broj, čijom vrijednošću je moguće dobiti uvid u koncentraciju nastalih produkata oksidacije. Vrijednosti peroksidnog broja povećavale su se s porastom temperature sušenja u svim uzorcima. Najviša vrijednost peroksidnog broja zabilježena je kod ulja dobivenog iz sjemenki sorte Graševina neovisno o temperaturi sušenja, dok su kod sorte Muškat žuti zabilježene najniže vrijednosti. Kiselinski broj, kao i udio slobodnih masnih kiselina karakteristični su za svaku sortu i neovisni o temperaturi sušenja.

Ključne riječi: *sušenje, grožđe, ulje, sjemenke grožđa.*

INTRODUCTION

The grape (*Vitis vinifera L.*) is one of the most valued conventional fruits in the world with more than 50 million tons produced every year (*Beres et al., 2017*). As seeds account for 2-5 % of the grape mass, they are considered significant agricultural and industrial waste. Grape seed oil is a highly valuable product obtained from the utilization and valorization of winery waste (*Bjelica et al., 2019*). According to the global grape seed oil market, grape seed oil production is expected to grow worldwide at an approximate rate of 3.7 % over the next five years, and reach USD 450 million in 2024 (compared to USD 360 million in 2019) (*Mahanna et al., 2019*).

Grape seeds are mainly valued for the nutritional properties of grape seed oil, which is rich in unsaturated fatty acids and phenolic compounds (*Sabir et al., 2011; Ma and Zhang, 2017; Coelho et al., 2018*). They contain 8 – 20 % of oil on dry basis. Grape seed oil yields depend on the extraction technique, the type of solvent, the operating conditions employed, the variety of cultivars, and the environmental factors during the grape growing period (*Garavaglia et al., 2016*).

The health benefits of grape seed oil are associated with its composition, which depends on the grape variety, environmental factors and seed maturation. Linoleic acid is the most abundant fatty acid found in grape seed oil, accounting for 60 – 78 % of the total oil composition, followed by oleic acid (10 – 24 %). These essential fatty acids are referred to in the literature as protectors against cardiovascular diseases (*Rubio et al., 2009; Fernandes et al., 2013; Akin et al., 2019*), exerting strong hepatoprotective and neuroprotective effects (*Beres et al., 2017*). Grape seed oil is one of the major sources of vitamin E, containing relatively large amounts of tocopherols and tocotrienols (from 1 to 53.06 mg of vitamin E/100 g of oil) (*dos Santos Freitas et al., 2008; Acevedo-Correa et al., 2018*).

In the food industry, the grape seed oil produced from agricultural and industrial waste is characterized by low production costs, and thus is considered more competitive than some others. It represents a new food source for human consumption to replace animal fat which contains significant amounts of saturated fatty acids and cholesterol (*Duba and Fiori*, *2016; Beres et al., 2017*).

Cold-pressing is a method of oil extraction employing no heat or chemical treatments in order to preserve health-beneficial components such as natural antioxidants and other phytochemicals. Although the yield of cold-pressing is usually lower than that of the refining process, it is often used due to the lack of solvent residues in the oil produced, thus making it safer and more convenient for the production of consumer-desired products (*Shinagawa et al., 2015*). These oils have better sensory and nutritional properties than refined oils (*Lutterodt et al., 2011*).

Fresh grape seeds are highly perishable, and dehydration is a useful means to increase the shelf-life of grape seeds for further use. Therefore, safe storage is necessary in order to avoid deterioration losses (*Johann et al., 2018*). The cold mechanical pressing of dried grape seeds is an environmentally friendly method for extracting oil without chemicals. Dry grape seeds with a moisture content of less than 0.1 g/g dry solids are required for cold-pressing, thus dehydration is a critical processing step (*Roberts et al., 2008*).

The quality of grape seeds, which can be determined by their physical properties, is a key factor in obtaining quality oil. Therefore, the drying of grape seeds can greatly affect their physical properties and, consequently, the quality of grape seed oil. The knowledge of these properties is fundamental for cost reduction, seed conservation, equipment sizing and operating conditions in the main post-harvest operations (*Sridhar and Charles*, *2019*; *de Araujo et al., 2020*). As grape seeds must be dried, drying temperature is one of the most important factors which affect the quality of seeds and oil. However, the industrial drying of grape seeds is characterized by high energy requirements (*Johann et al., 2018*).

The main objective of the present study was to analyze the influence of three different drying temperatures on the quality of cold-pressed oil obtained from five different grape varieties.

The quality of the oils extracted was determined according to the following parameters: the peroxide value, the acid number and the content of free fatty acids.

MATERIAL AND METHOD

This research was conducted in the Polytechnic vineyard and cellar in Požega. The vineyard is situated on the southern slopes of Papuk (a mountain in the Eastern Slavonia region of Croatia, the Kutjevo subregion) at an altitude of 250 m. Ripened grapes of the Pinot noir, Cabernet sauvignon, Pinot blanc, Muscat and Graševina grape varieties were used in the experiment. The pressing of white grape varieties was done immediately after destemming, whereas red grape varieties were pressed after maceration and fermentation. A pneumatic press (Škrlj, PST 16, 400V 50Hz 3PH, capacity 16 hl) was used for all the varieties considered.

After pressing, the seeds were separated from pulp residues using sieves and dried in a chamber dryer at three different temperatures: 20, 40 and 60 ºC. The drying times of grape seeds at temperatures of 20 ºC, 40 ºC and 60 ºC were 72, 12 and 6 hours, respectively. After drying, the seeds were cleaned manually, in order to remove skin residues and damaged seeds, and stored in bags until pressing. The oil samples were obtained by pressing with a screw press (the KOMET single screw vegetable oil expeller CA 59 G with a 1.1 kW electric motor and a capacity of 3 – 5 kg/h). After pressing, the oils were kept in a dark place for one day at room temperature (for the natural sedimentation of insoluble impurities) and subsequently decanted and used for further analysis.

The water content of grape seeds before and after drying was determined using the AOAC Official Method 925.40 (2000). The oil yield was calculated according to the mass of oil after pressing in relation to the total mass of grape seeds before pressing, and expressed as a percentage of the oil obtained relative to the total mass. The content of free fatty acids and the acid number were determined using the AOAC Official Method 940.28 (1990). A total of 2 g of the oil sample was dissolved in 10 mL ethanol and titrated with a 0.1M NaOH solution using a phenolphthalein indicator until the pink color was reached. The acid value was calculated according to the following equation:

$$\text{Acid value} = \frac{56 \cdot \text{molarity of NaOH} \cdot \text{titration volume}}{\text{the sample mass (g)}}, (\text{-}) \quad (1)$$

The percentage of free fatty acids in the oils extracted was also determined using the AOAC method No. 940.28 and calculated using oleic acid as a factor. The percentage of free fatty acids was calculated according to the following function:

$$\text{Free fatty acid as oleic acid} = 0{,}503 \cdot \text{acid value}, (\%) \quad (2)$$

$$\text{Peroxide value} = \frac{\text{volume of } Na_2S_2O_3 \cdot \text{factor of } Na_2S_2O_3 \cdot 100}{\text{the sample mass}}, (\text{mmol } O_2/\text{kg}) \quad (3)$$

The peroxide value of the grape seed oils considered was expressed as mmol O_2/kg of oil and determined in the following manner: Five grams of each oil sample were mixed with 50 ml acetic acid and chloroform solvent mixture (3:2) and swirled to dissolve. Subsequently, a total of 1 mL of potassium iodide solution was added to the solution. After 1 min in a dark place with occasional swirling, 30 mL of distilled water and 1 mL of starch solution were added. Titration was performed with a 0.01 M sodium thiosulphate solution until the blue color disappeared (*Trajković, 1983*). The peroxide value was calculated using the following equation:

RESULTS AND DISCUSSION

The water contents of grape seeds before and after drying are presented in Table 1. The water contents of grape seeds before drying ranged from 28.86 % in the Pinot blanc variety to 37.94 % in the Muscat variety. The water content of the seeds dried at 20 ºC decreased to approximately one third of its initial value in all the samples examined. The largest decrease of water content was recorded in the Muscat seeds (28.84 %), which had the highest initial moisture content. The drying process at 40 ºC resulted in grape seed water contents of 4.01-5.78 %, which are nearly twice as low as those recorded at 20 ºC (9.10 to 11.72 %). The drying process at 60 ºC did not result in a further water content decease (3.89 to 5.65 %), indicating only slightly lower water contents of grape seeds than those at 40 ºC. The oil yields obtained (expressed as a percentage of oil relative to the total mass of grape seeds) are shown in Table 2. The highest oil yield (14.10 %) was obtained from the Pinot noir seeds dried at 40 ºC, whereas the lowest oil yield was obtained from the Cabernet sauvignon seeds (11.23 %) dried at 20 ºC. As seen in Table 2, the oil yields from all the grape seed varieties considered increased with the increasing drying temperature of grape seeds. As seen in Tables 1 and 2, small differences between the water contents of the seeds dried at 40 ºC and 60 ºC resulted in small differences between their oil yields. When comparing the grape seed oil yields at the same temperature across the grape varieties considered, the Pinot noir seeds had the highest yield at all experimental drying temperatures.

Table 1. Water contents of grape seeds before and after drying (the results are shown as mean (n = 3) ± SD values)

Variety	Water content of grape seeds, %			
	Before drying	**After drying**		
		20°C	**40°C**	**60°C**
Pinot blanc	28.86 ± 0.82	11.72 ± 0.34	5.78 ± 0.22	5.65 ± 0.18
Muscat	37.94 ± 0.95	9.10 ± 0.45	5.20 ± 0.19	4.80 ± 0.31
Graševina	35.89 ± 0.84	10.55 ± 0.28	4.15 ± 0.31	3.95 ± 0.24
Pinot noir	32.25 ± 0.77	9.32 ± 0.36	4.01 ± 0.27	3.89 ± 0.28
Cabernet sauvignon	33.67 ± 1.21	9.87 ± 0.25	4.36 ± 0.21	4.12 ± 0.23

Table 2. Oil yields after grape seed cold-pressing (the results are shown as mean (n = 3) ± SD values)

Yield after cold-pressing, %			
Variety	**20°C**	**40°C**	**60°C**
Pinot blanc	11.75 ± 0.23	12.57 ± 0.32	12.42 ± 0.52
Muscat	11.72 ± 0.31	12.00 ± 0.39	12.71 ± 0.31
Graševina	12.55 ± 0.32	13.52 ± 0.42	13.24 ± 0.17
Pinot noir	13.10 ± 0.26	14.10 ± 0.18	13.81 ± 0.24
Cabernet sauvignon	11.23 ± 0.44	12.54 ± 0.25	12.87 ± 0.34

Triglycerides and triglycerides are prone to thermal hydrolysis, particularly in the presence of water, thus releasing fatty acids from their ester linkage and increasing the acid number and the free fatty acid content. Therefore, those analytical parameters are frequently used to evaluate the extension of hydrolysis, a very important quality issue.

The acid number is an important aspect of the quality of oil which depends on the amount of free fatty acids in the oil and the degree of oil hydrolysis. Figures 1 and 2 indicate that the acid number and the content of free fatty acids were the highest in the oil obtained from the Pinot blanc grape seeds dried at 20 ºC, i.e. 10.36 and 5.21 %, respectively. This can be accounted for by a longer drying time at 20 ºC compared to the drying time at higher temperatures. Therefore, the duration of grape seed drying should be considered a critical factor for the hydrolysis of oil. Higher grape seed drying temperatures reduced the content of free fatty acids and the acid number. The oils obtained from the red grape varieties considered were found to have lower acid numbers and contents of free fatty acids than the oils obtained from the white grape varieties considered at all experimental drying temperatures. According to the Croatian legislation (*NN, 2019*), the maximum free fatty acid content of cold-pressed oil should not exceed 2 %. As presented in Fig. 2, the oils obtained from the red grape varieties considered (dried at all experimental temperatures) were within the legal limits (*NN, 2019*). Conversely, the oils obtained from the white varieties considered were more sensitive to oil hydrolysis, which resulted in the increased content of free fatty acids. The highest content of fatty acids was observed in the oils obtained from the seeds dried at 20 ºC, particularly from the Pinot blanc and Muscat seeds. The free fatty acids contents of the Muscat oils exceeded the legal limits (2 %) at all experimental drying temperatures. Therefore, the oil obtained from this particular variety should be dried as quickly as possible to avoid excessive hydrolysis. Further research is needed to find the best parameters for this particular variety. The peroxide value is a measure of the concentration of peroxides and hydroperoxides formed during the initial stages of lipid oxidation. It is one of the most frequently used tests for the oxidative rancidity of oil. Peroxide values are usually expressed in milliequivalents of active oxygen/kg of oil and calculated from the iodine released from potassium iodide (*Trajković, 1983*).In the present study, the peroxide values obtained were in accordance with the Croatian legislation which stipulates that the maximum peroxide number of cold-pressed oils should not exceed 7 mmol O_2/kg of oil (*NN, 2019*). On balance, the peroxide values of the oils considered increased with the increasing grape seed drying temperature. However, the peroxide values recorded were found to be lower than those generally recommended for cold-pressed grape seed oil (< 7 mmol O_2/kg oil). The oil obtained from the Graševina seeds had the lowest oxidative stability at all experimental drying temperatures, as well as the highest peroxide content (1,5 mmol O_2/kg, 1,61 mmol O_2/kg and 2,27 mmol O_2/kg at 20ºC, 40ºC and 60ºC, respectively). Unlike the hydrolytic stability which was influenced by the drying time as a critical factor, the drying temperature of grape seeds was the main factor influencing the oxidative stability. The grape seed drying temperatures considered in this research were found to be appropriate for preserving the oxidative stability of cold-pressed grape seed oils.

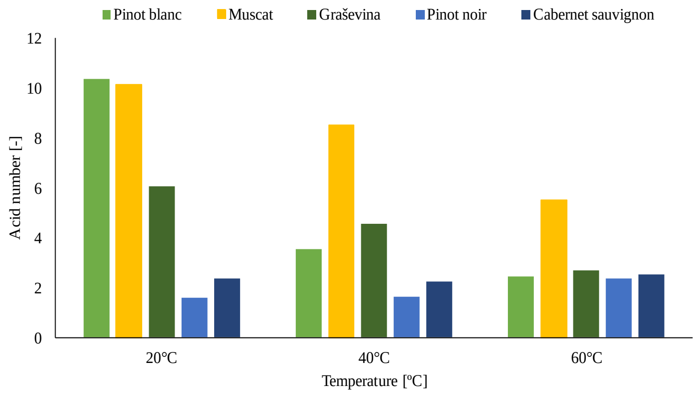

Fig 1. Acid number of the grape seed oils from five different grape varieties dried at three different temperatures (the results are shown as mean (n = 3) ± SD values)

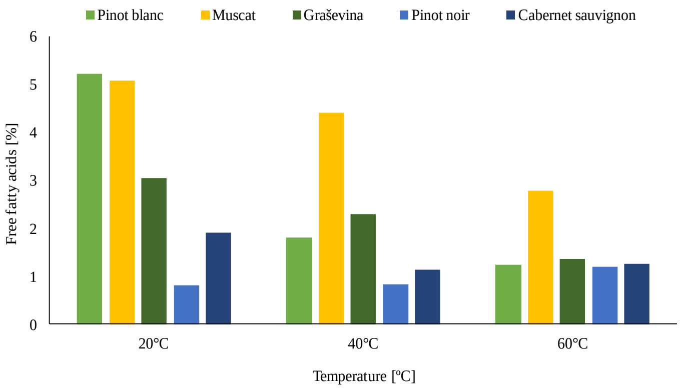

Fig 2. Free fatty acids content of the grape seed oils from five different varieties dried at three different temperatures (the results are shown as mean (n = 3) ± SD values)

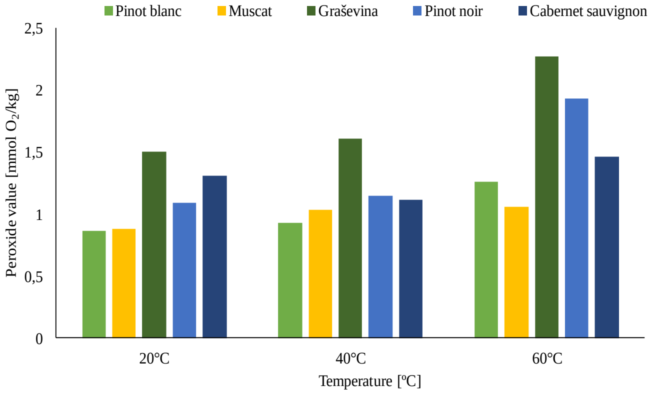

Fig 3. Peroxide values of the grape seed oils from five different grape varieties dried at three different temperatures (the results are shown as mean (n = 3) ± SD values)

CONCLUSION

Higher grape seed drying temperatures were found to be more effective in reducing the water content of grape seeds in shorter drying times and producing higher oil yields. Moreover, the oils obtained from the seeds dried at higher temperatures showed better stability against hydrolysis. Prolonged drying times were found to increase the free fatty acids content of grape seed oil. The oils obtained from the red grape varieties considered had better stability against hydrolysis than that of the white grape varieties considered. Accordingly, the drying parameters of the white grape varieties considered, especially the Mucat grape variety, require further research in order to produce stable oil.

The peroxide values of the grape seed oil samples examined increased with an increase in the drying temperature of grape seeds. However, the results obtained were within the legal limits. The Graševina seed oil was found to be the most sensitive to oxidation.

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