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# CHEMICAL COMPOSITION OF JUISE AND MADZUN (grape molasses) PRODUCED FROM STANUSHINA **GRAPE VARIETY BY TRADITIONAL MEANS**

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### ABSTRACT

In this study, it was analyzing some chemical characteristics and mineral composition of juice and madzun (grape molasses) produced from Stanushina grape variety by traditional method. Madzun (grape molasses) is a natural sweetener widely consumed in the R. N. Macedonia in the past decade and mostly in Eastern Mediterranean countries. It is an important food for humans in terms of mineral content (carbohydrates). Comparative analyses have been conducted to one sample juice (S1) and two (S2, S3) samples madzun. As a result of research: soluble dry matter 29.41 (juice)-82.98% (madzun), total sugar 28.04 (juice)-67.99% (madzun), total phenols 875 (madzun)-1212 mg/L (juice) and HDM (hydroxymethyl furfural) were detected in the range of 5.25 mg/kg (juice) to 723.05 mg/kg (madzun). In the samples, the macro minerals K, Ca and Mg are ranged from 386-640 mg/kg (S1)- 111.7-375 mg/kg (S3) – 375 mg/kg (S1) and 205.5 mg/kg (S2)-297 mg/kg (S1), respectively. Of the microminerals Fe 11.26-15.18 mg/kg, Mn 2.42-4.90 mg/kg, Zn 7.34-17.47 mg/kg and Ba were found between 0.35-0.84 mg/kg. Regarding the content of heavy metals (Pb and Ni), sample C1 and C2 are above the permissible limits for this type of food. Concentration of metals in grapes is influenced by the microregion of origin and type of soil.

## **INTRODUCTION**

Grape molasses is one of the popular and traditional food in North Macedonia for the last 10 years. It is produced in the traditional way and is represented on the market as Grape honey and popularly Madzun. Grape juice and molasses (Mazun) is produced traditional and industrial technique of different flavor, structure and appearance in North Macedonia. Grape molasses composition and structure vary according to grape variety and production process (Abdullah Badem, 2018). Grape molasses are a good energy and carbohydrate source due to its high sugar content (up to 50%-80%) in the form of glucose and fructose; therefore, it easily passes into the blood without digestion (Karababa, E., Develi Isikli, N., 2005). The average energy value of grape molasses is 293 kcal 100 g-1 (Yoğurtçu, H., Kamişli, F., 2006). Phenolic compounds in grape juice and molasses (Mazun) are affected by many factors, such as properties of the varieties, cultivation conditions, the location of the production area and the degree of ripeness of the grape (Kelebek H., at all., 2012). Grape juice and molasses are very rich minerals, especially the contain (+2) valuable iron minerals that can easily be absorbed in the human digestive system (Batu, A., 2006).

### **MATERIAL AND METHODS**

### **RESULTS AND DISCUSSION**

Table 1 Content of total sugars content and simple forms of carbohydrates and soluble dry matter in samples (%)

Sample	Fructose (%)	Glucose (%)	F/G ratio	Sucrose (%)	Maltose (%)	Total sugar (%)	Soluble dry matter (%)
S1 (juice)	14.56	13.48	1.09	<0.1	<0.15	28.04±1.21	29.42±1.27
S2	30.99	28.36	1.09	0.10	0.25	59.70±2.58	84.98±3.67
S3	35.17	32.82	1.07	<0.1	< 0.15	67.99±2.94	80.98±3.49
Min	15.56	13.47	1.07			28.04	29.42
Max	35.17	32.82	1.09			67.99	84.98
Average (S2-S3)	33.08	30.59	1.08			63.84±2.58	82.98±3.58

S1-juice, S2, S3 – madzun (grape molasses-traditional method)

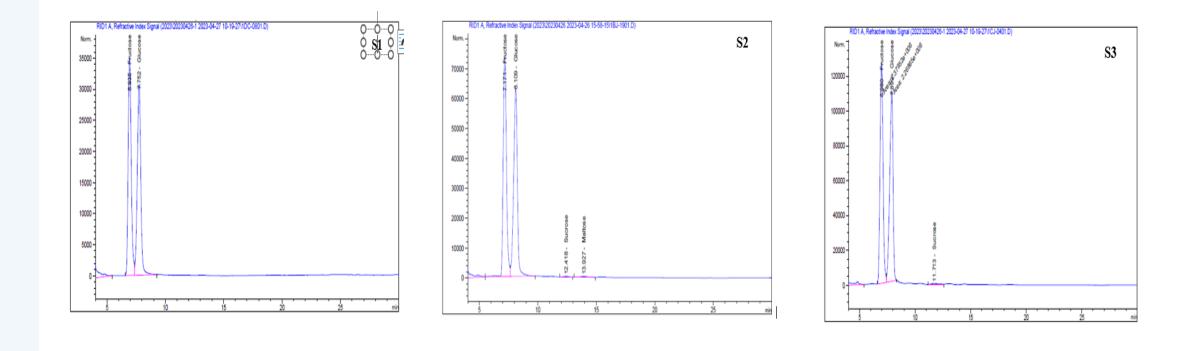
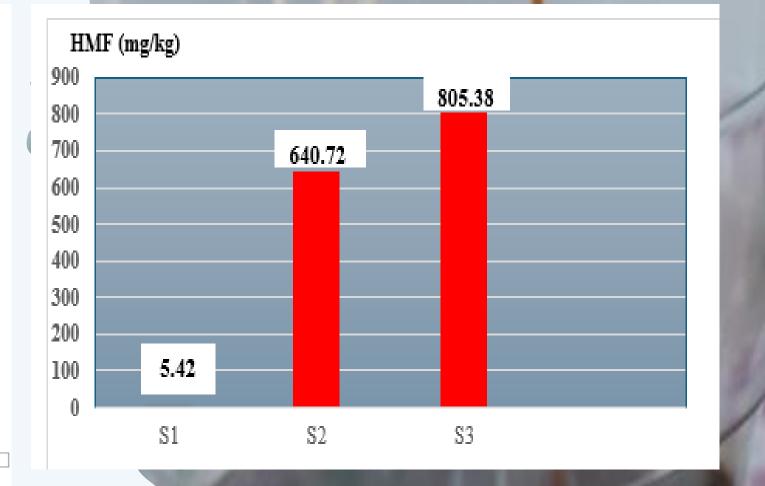


Figure 1 HPLC chromatograms of individual sugars in samples

Table 2 Content of total phenols, total acids, pH value and HMF in samples

Sample Element				
-	Total	Total	pН	HMF
	phenols	acids		(hydroxymethyl
	(mg/L)	(g/L)		furfural)
				(mg/kg)
S1	1212±6.66	$4.63{\pm}0.04$	$3.45 \pm 0.01$	5.24±0.41
S2	$1114 \pm 2.89$	$3.92{\pm}0.02$	$4.43 \pm 0.03$	640.72±51.25
S3	875±5.20	$9.50{\pm}0.01$	$3.73 \pm 0.03$	805.38±64.43
Min	875	4.63		5.24
Max	1212	9.50		805.38
Average	994.5	6.35	4.08	723.05
(S2/S3)				



**1** sample grape juice pasteurized and **2** sample grape molasses (madzun) produced from Stanushina grape variety. The grape juice (S1), and grape molasses/madzun (S2,S3) samples were collected from a local producers in Tikvesh vine region.



The total sugar content of grape juice and molasses samples was determined according to Official Method 929.09 (AOAC 2005).

Identification and quantification of sugar contents (separately: glucose, fructose, sucrose and maltose) in juice and molasses samples were determined by High-Performance Liquid Chromatography (HPLC, version 1, SOP 728), according to the Harmonized Methods of the **International Honey Commission, 2009.** 

S1-juice, S2, S3 – madzun (grape molasses-traditional method)

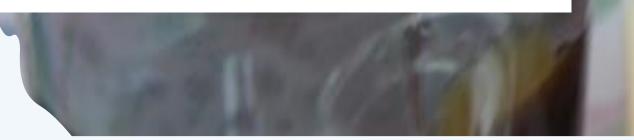
Table 4 Content of microminerals in samples

Sample	Micro minerals mg/kg						
	Fe	Mn	Zn	В	Ba	Na	
S1	15.18	4.90	17.47	36.4	0.84	170	
S2	14.12	2.42	13.34	39.9	0.49	299	
S3	11.26	2.67	7.34	35.2	035	126	
Min	11.26	2.42	7.34	35.2	0.35	126	
Max	15.18	4.90	17.47	39.9	0.87	299	
Average	13.52	3.33	12.72	37.2	0.56	198	
S1/S3							

Table 3 Content of macro minerals

in samples					
Sample	Macro mineral mg/kg				
	Κ	Ca	Mg		
S1	386	375	297.1		
S2	398	228.7	205.5		
S3	640	111.7	242.5		
Min	386	375	205.5		
Max	640	228.7	297.1		
Average	441	238.5	248.4		
S1/S3					

Graph. 1 Content of hydroxymethyl furfural in the samples



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÷‡•	Table 5 Content of heavy metals in sample							
	Sample	Heavy metal mg/kg						
	Al		Li	Cr	Ni	Cu		
	S1	53.6	< 0.0001	0.460	0.343	2.64		
	S2	133.7	< 0.0001	0.215	< 0.0001	1.53		
	S3	147.8	< 0.0001	0.366	< 0.0001	0.44		
	Min	53.6		0.215	< 0.0001	0.44		
	Max	147.8		0.460	0.343	2.64		
	Limit				0.02	5		
	value							
		Hg	Pb	As	Cd	Со		
	S1	< 0.0001	0.0395	< 0.0001	0.0021	< 0.0001		
	S2	< 0.0001	0.0775	< 0.0001	0.0185	< 0.0001		
	S3	< 0.0001	0.0350	< 0.0001	< 0.0001	< 0.0001		
	Min		0.0350					
	Max		0.0775					
	Limit		0.03	0.02	0.03	0.02		
	value							

### CONCLUSION

The soluble dry matter content of the grape juice and molasses (madzun) samples was determined according to the Official Method SOP 345 (Institute for Standardization of the Republic of Macedonia, 2010).

The content of total phenols (TPC) was determined using Folin-Ciocalteu method by spectrophotometer (model Paro 300 Merck Germany). The content of total phenols was expressed as mg equivalents of gallic acid per g of dry matter (mg GAE/g).

Titratable acidity was determined by titration with 0.1 N NaOH to the titration point of pH 8.3, monitored with a pH meter and expressed as tartaric acids content (g/L). The pH were measured by pH meter (model Mettler Toledo Seven Compact pH/ion S220, Switzerland).

Hydroxymethyl furfural (HMF) was determined according to the official method 890.23 (AOAC 2005), based on the colorimetric reaction between barbituric acid, p-toluidine and HMF, which forms a red-colored complex. The intensity of the red color was measured using a UV-Vis-NIR-5000 spectrophotometer (analytical wavelength of 550 nm was used).

The mineral composition (32 elements) in samples was carried by inductively coupled plasma with mass spectrometry (ICP-MS, model 7500cx Agilent Technologies, USA).

As a conclusion, this paper shows that grape juice and grape molasses (madzun) are represent a potentially important source of the carbohydrates, minerals and phenolics.

In all samples, the sucrose content is below the detection threshold (<0.1), which confirms that no sugar (additionally) has been added.

In the grape molasses samples (S2 and S3), the high HMF content is due to the high temperature (>100°C) during the production process

. The mineral composition (macro and micro elements) and the content of heavy metals depend primarily on the growing conditions (soil, fertilizers, protection), and very little on the production technology.