VII. INTERNATIONAL AGRICULTURAL, BIOLOGICAL & LIFE SCIENCE CONFERENCE
September 7-10, 2025, Istanbul, Turkey

Some qualitative properties, minerals and heavy metals in juice and madzun (grape molasses) produced from Stanushina grape variety

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Introduction

Stanushina is an indigenous Macedonian grape variety (Korunoska et al. 2022). It is cultivated on an area of 233 ha (Strategy for Viticulture and Winemaking 2023/2033), with 80% of it in the Tikveš wine region, and a smaller part in other wine regions. Rose and red wines are produced from it, and due to its high yield of must, it is very suitable for the production of juice and madzun (grape molasses). Grape molasses is a traditional food that has been produced and used by the local population in North Macedonia for decades (Dimovska at al.,2024). Commercially are available in the markets with common name "Grape honey", as well as traditional name "Madzun" (Dimovska at all.2024). Grape molasses is produced primarily from grapes by concentrating juices with a soluble dry matter content up to 70-80% (Cihat et al., 2016). Glucose and fructose account for 50–80% of the sugars present in molasses (Simge Aktop at al., 2023). These are simple sugars, which easily pass into the blood through simple diffusion without the prior requirement for breaking down into simpler molecules, thereby enabling rapid energy production in the human body. The average energy value reported for molasses is 293 kcal per 100 g (Batu, 2006; Türkben et al., 2016). Grape molasses may be classified under different groups based on the production method. According to the most general classification, the following three categories exist—liquid molasses produced using traditional methods, liquid molasses produced using modern methods and white solid molasses (Batu, 2006). Standards, molasses with a pH value of 5.0–6.0 are considered sweet molasses, while molasses with a pH value of 3.5–5.0 are considered sour molasses (Batu, 2020; Tosun et al., 2014). Grape polyphenols reduce atherosclerosis and inflammation, regulate blood pressure, activate new proteins (Slavin and Lloyd, 2012). It is stated that regular consumption of grapes and products in the Mediterranean traditional diet may contribute to the reduction of chronic diseases such as cancer, cardiovascular diseases, stroke, nervous disorders and aging (Iriti and Faoro, 2009). The most commonly measured phenolic compounds in grape juice and molasses is gallic acids, its concentrations range usually within 295.82 mg/L (grape juice) and 9823.24 mg/L (grape molasses) (Özlem Aras Aşcı, Nilgün Göktürk Baydar, 2021). The mineral profile of grapes and grape products (grape juice, molasses) has been considered important not only from the nutritional aspect but also from a technological point of view. Some minerals may influence the production process, sometimes negatively via an oxo-reduction reaction and/or organoleptic alteration in the grape derivates (Olalla et al., 2004).

Results

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)

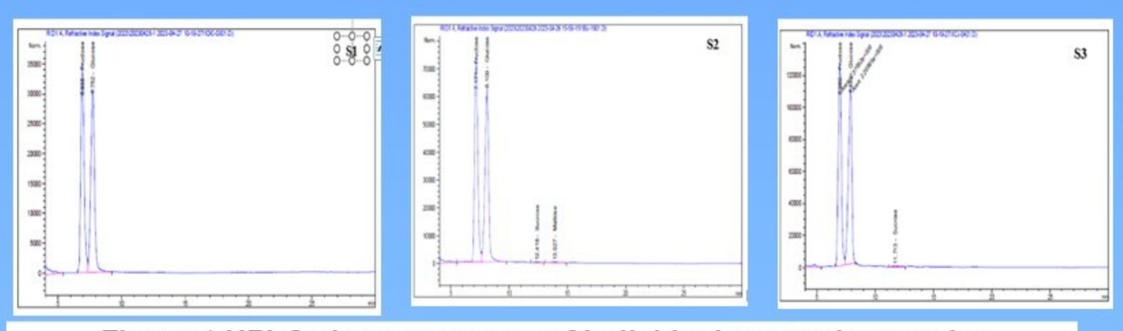
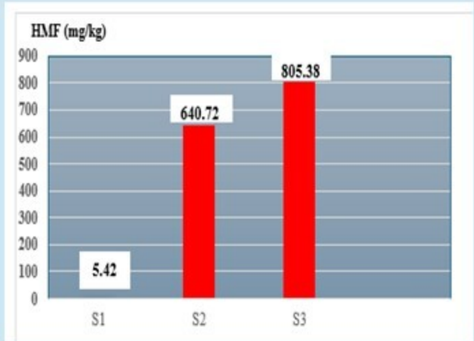


Figure 1 HPLC chromatograms of individual sugars in samples

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

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

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



Graph. 1 Content of hydroxymethyl furfural in the samples

Table 3 Content of macro elements in samples

Sample	Macro elements mg/kg		
	K	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 S1/S3	441	238.5	248.4

Table 4 Content of micro elements in samples

Sample	Micro elements mg/kg					
	Fe	Mn	Zn	B	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	0..35	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 S1/S3	13.52	3.33	12.72	37.2	0.56	198

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 value				**0.02**	**5**
	Hg	Pb	As	Cd	Co
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 value		**0.03**	**0.02**	**0.03**	**0.02**

Discussion

In the grape juice was determined 14.56% fructose and 13.48% glucose. In the madzun samples, the fructose content ranges from 30.99% (S2) to 35.17% (S3), and from 28.36% (S2) to 32.82% (S3) content of glucose. Fructose/Glucose (F/G) ratios were calculated and varied from 1.07 (S3) to 1.09 (S1, S2). In all samples, the sucrose content was below the detection threshold (<0.1) which confirms that no sugar (additionally) had been added. Total sugar contents varied from 28.04% in grape juice (S1) to 63.84% for madzun (average S2/S3). Özlem Aras Aşcı & Nilgün Göktürk Baydar (2021) determined that total sugar content varied from 14.77% in grape juice to 48.37% in molasses.

In this study, the soluble dray matter content was found to be 29.42% (S1-juice) to 84.98% (S2-molasses). The S2 and S3 samples are solid molasses, according to content of soluble dry matter (>80%), and accordance Regulation (EU) No 1169/2011.

Phenolic compounds are a great importance because of the effects on the color, flavor, bitterness, and astringency in grape and grape products (Burin VM, Falcão LD, Gonzaga LV, Fett R, Rosier JP, Bordignon-Luiz MT. 2010).

In this study, total phenols contents in grape juice (S1) were significantly higher than the molasses samples (S2, S3). It varied from 875mg/L (C3), 1114 mg/L (S2) to 1212 mg/L (S1). The difference in the content of total phenols was due to the degree of ripeness of the grapes and the technology of grape juice and molasses production.

The pH was found to range 3.45 (S1) to 4.43 (S2). The total acids (expressed as tartaric acid) were determined in all samples. The highest content was determined in the sample S3 (9.50 g/L) and the lowest content in the sample S2 (3.92 g/L).

According to grape pekmez Notification (2007), the sample juice (S1) and samples madzun (S2, S3) classified in group - sweet grape products.

HMF is not naturality found compound in fruits. According to quality molasses (pekmez) standard, the maximum allowed formation of HMF in liquid molasses is 75 mg/kg, whereas in solid molasses, 100 mg/kg is allowed (Regulation EU, No 1169/2011).

The HMF content of the samples analyzed varied from 5.25 mg/L (S1), 640.72 mg/L (S2) to 805.38 mg/L (S3). This value in madzun samples derived from Stanushina grape variety were higher than in sample grape juice. The high content of HMF in madzun samples is a result of the boiling process in open vessels at high temperature.

In terms of the average values of macro element, the higher amount was found for K, with value of 441 mg/kg, followed by Mg (248.4 mg/kg) and Ca (238.5 mg/kg).

The micro elements Ba and Mn was identified in juice and madzun samples was found lower amounts than other minerals (Fe, Zn, B, Na).

The content of micro element Fe found in grape juice and molasses were determined to range from 11.26 mg/kg (S3) to 15.18 mg/kg (S1).

Food products contaminated with various types of heavy metals threaten human health. In this study, the trace elements ranked by the mean concentration as follows: Cu> Cr> Ni> Pb> Cd> Co> As> Hg >, Li. Generally, for producing grape juice and madzun, after grape washing and crushing, the obtained grape juice is heated and some clarifying agents such as bentonite, gelatin, or white soil is added to the juice in order to remove the suspended solids.

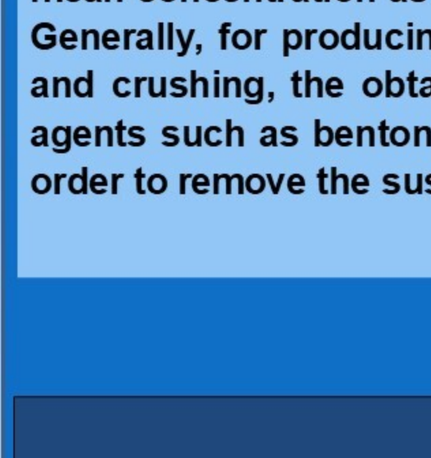
Conclusions

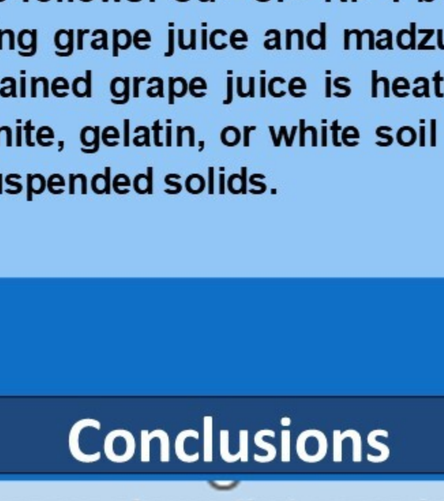
►As a conclusion, this paper shows that grape juice and grape molasses (madzun) are represent a potentially important source of the carbohydrates, minerals and phenolics.

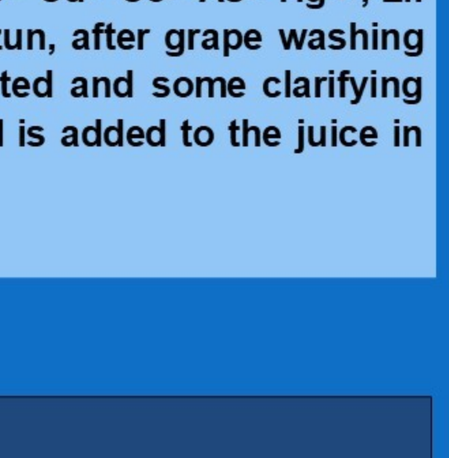
►In all samples, the sucrose content is below the detection threshold (<0.1), which confirms that no sugar (additionally) has been added.

►In the grape molasses samples (S2 and S3), the high HMF content is due to the high temperature (>100⁰C) 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.







Acknowledgement

►LABORATORY FOR PLANT AND ENVIRONMENT PROTECTION (Faculty of Agriculture - "GOCE DELČEV" University – Štip, R. N. Macedonia)
►LABORATORY OF FOOD (Faculty of Veterinary Medicine, Institute for Veterinary, Ss. Cyril and Methodius, University –Skopje, R.N. Macedonia)