



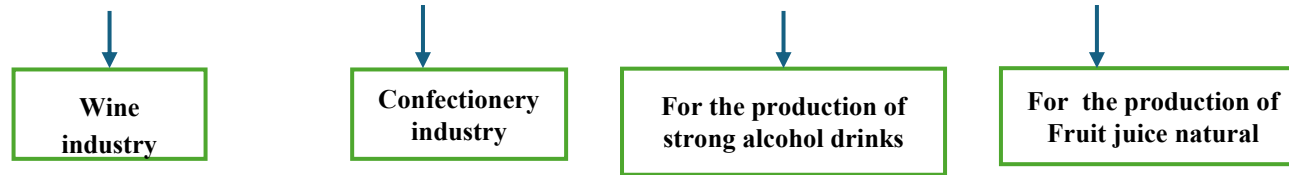
THE INFLUENCE OF PRODUCTION TECHNOLOGY ON THE CHEMICAL COMPOSITION OF MADZUN (grape molasses) FROM THE VRANEC GRAPE VARIETY

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INTRODUCTION

GRAPE MOLASSES – CONCENTRATED GRAPE JUICE



GRAPE MOLASSES AS FOOD

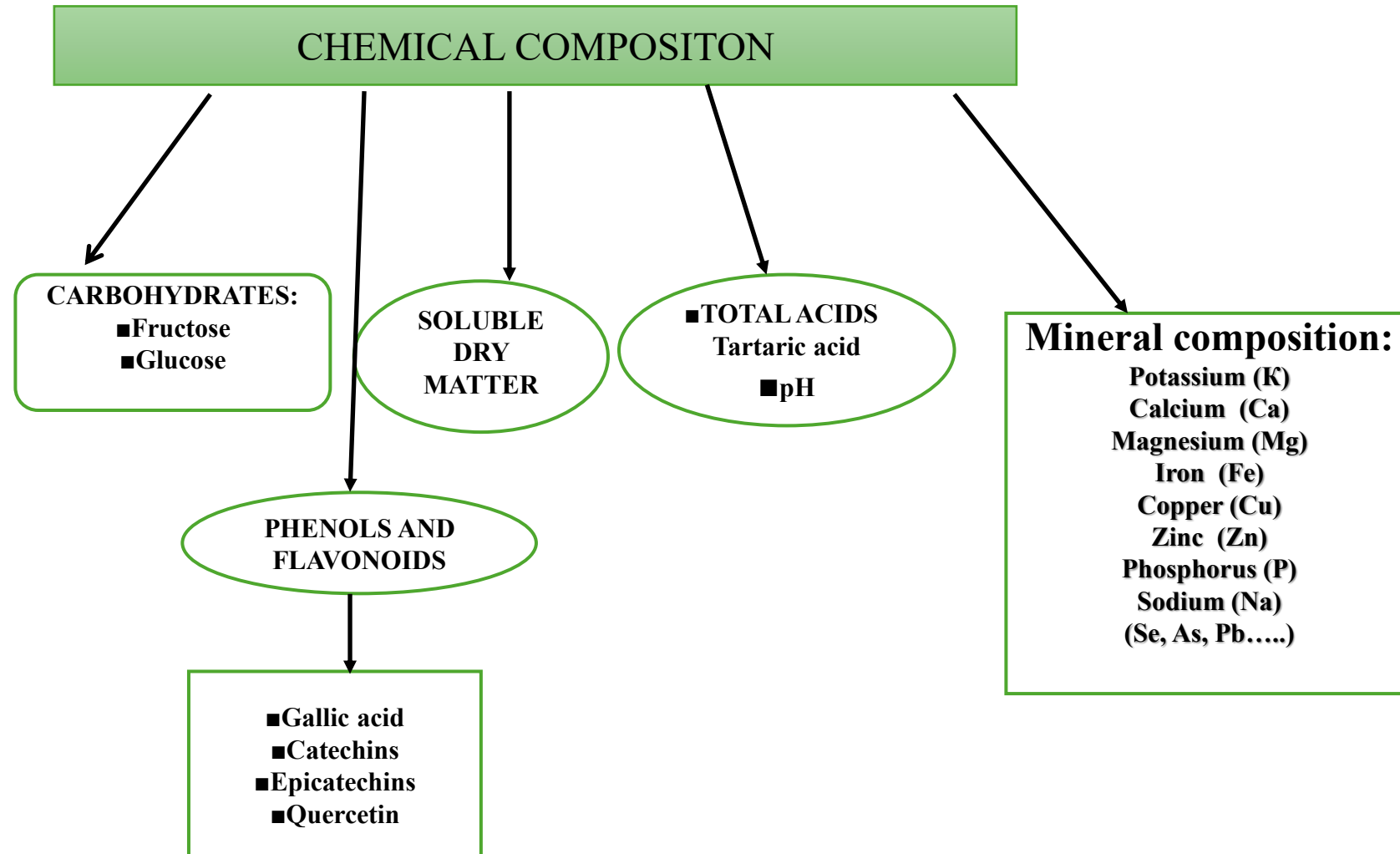
- ▶ GRAPE HONEY (гроздов мед)
- ▶ GRAPE MALT (гроздов слад)
- ▶ GRAPE SYRUP (гроздов сируп)
- ▶ MADZUN (Маџун) – traditional name
- ▶ GRAPELIXIR – CONCENTRATED GRAPE JUICE (Tikveš Winery)

15.000-20.000 L – TIKVEŠ WINERY

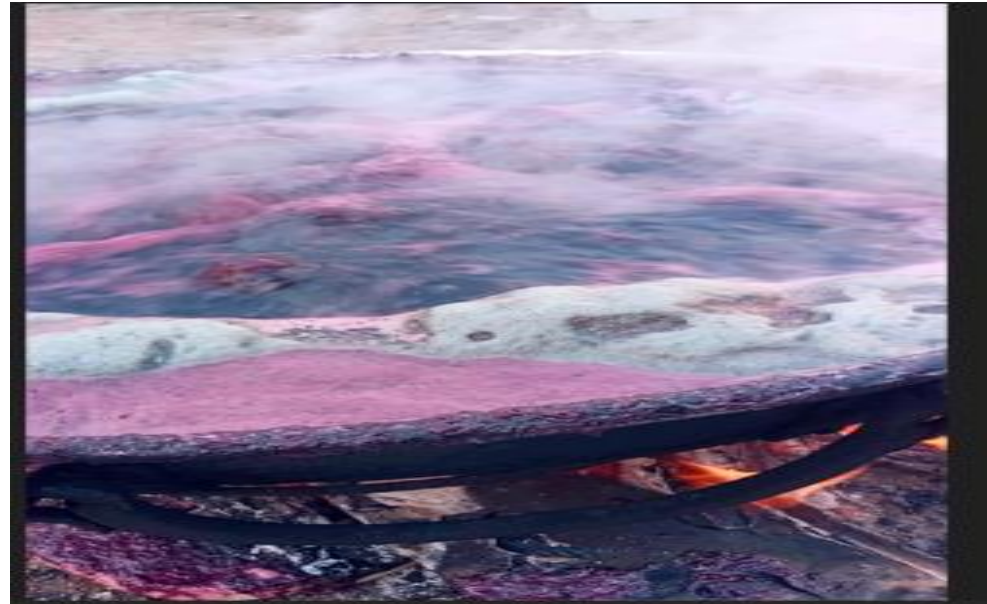
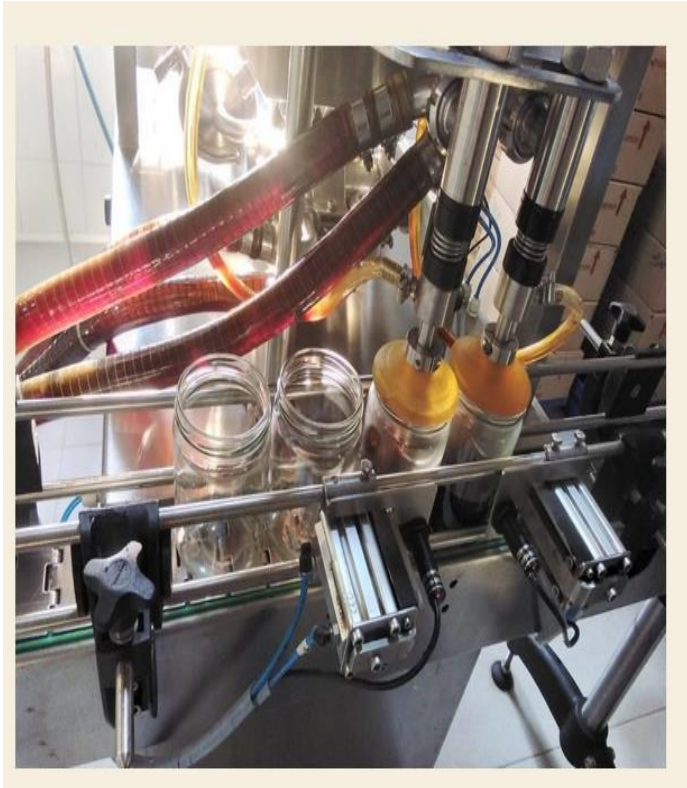
SMALL FAMILY PRODUCERS- 100 producers

Production per year -?





WHAT WAS THE CHALLENGE ?



MATERIALS AND METHODS

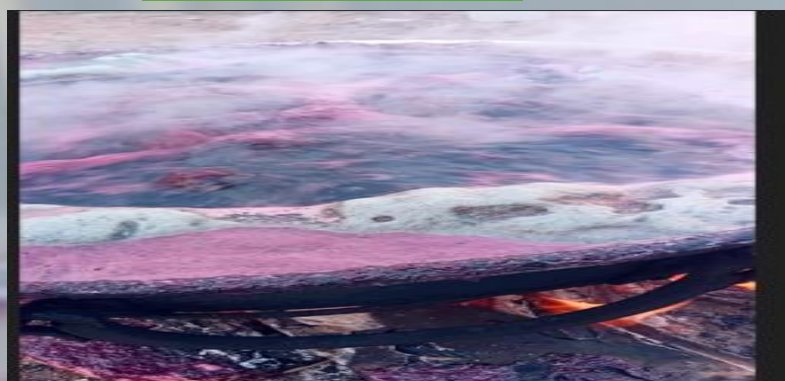
GRAPE MOLASSES FROM THE VRANEC GRAPE VARIETY

1 Sample
(Control)
vacuum
technology

T° max to 38°C

7 Samples
Traditional
method

By boiling grape juice
T° from 100°C to 110°C



VRANEC, SMEDEREVKA, CARDINAL, AFUZ-ALI AND STANUSHINA

WHAT WAS ANALYZED:

- ▶ **Carbohydrates:** Fructose, Glucose, Maltose, Sucrose
- ▶ **Soluble Dry Matter**
- ▶ **Total Phenols** – Gallic Acid
- ▶ **Total Acids** – Tartaric Acid
- ▶ **pH Value**
- ▶ **Mineral Composition: 32** chemical elements
- ▶ **Sensory Evaluation**

UNILAB - Laboratory,
Goce Delcev University, Stip

Antioxidant
Activity: (DPPH-
2,2-diphenyl-2-
picryl-hydrazil)

Laboratory for fruit,
grape and honey
quality- Faculty of
agriculture, Belgrade

HMF-hydroxymethyl furfural

Laboratory for Food Quality-Faculty
of Veterinary Medicine, Ss. Cyril and
Methodius, University, Skopje

RESULTS AND DISCUSSION

Table 1 Content of Total Sugars, Simple Forms of Carbohydrates and Soluble Dry Matter in Samples (%)

Sample	Fructose (%)	Glucose (%)	F/G Ratio (%)	Surcose (%)	Maltose (%)	Total Sugar (%)	Soluble Dry Matter (%)
V1 (control)	29.43	29.91	0.98	< 0.1	< 0.1	59.34±2.56	73.13±3.15
V2	39.64	35.18	1.13	0.11	0.48	75.41±3.26	79.30±3.42
V3	30.59	32.54	0.94	<0.1	< 0.1	63.13±2.73	64.05±2.76
V4	35.22	33.68	1.04	<0.1	0.18	69.09±2.99	70.80±3.05
V5	32.38	33.16	0.98	0.43	0.24	66.21±2.86	68.90±2.97
V6	36.20	35.92	1.01	<0.1	0.30	72.42±3.13	73.90±3.19
V7	23.10	23.95	0.96	<0.1	0.22	47.27±2.04	61.67±2.66
V8	33.67	25.40	1.32	<0.1	0.31	59.38±2.57	75.17±3.24
Min	23.10	23.95				47.27	61.67
Max	39.64	35.92				75.41	79.30
Average	32.53	31.27				64.03	70.86

1 g sugar = 4 Kcal /energy
100 g = 64 g x 4 Kcal = 256 Kcal



Sample	Soluble Dry Matter (%)	
	Liquid Molasses Minimum 68%	Solid Molasses Minimum 80%
V1	√	
V2	√	
V3		
V4	√	
V5	√	
V6	√	
V7		
V8	√	

HPLC Chromatograms

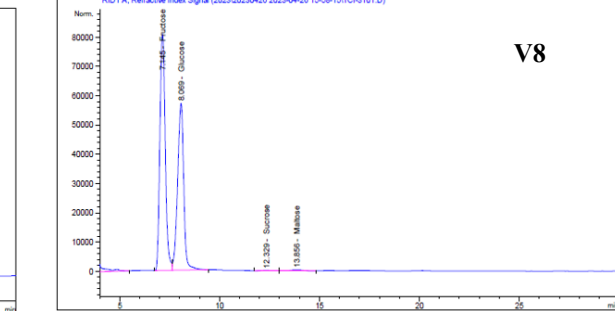
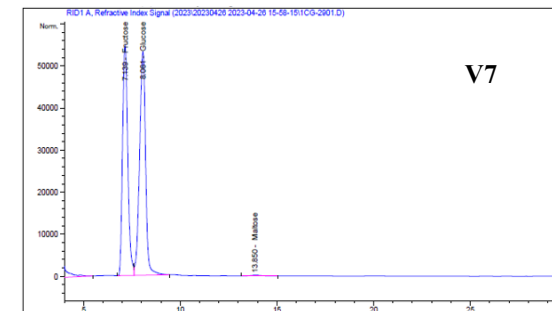
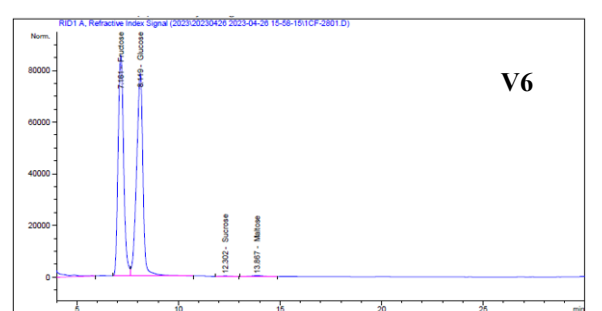
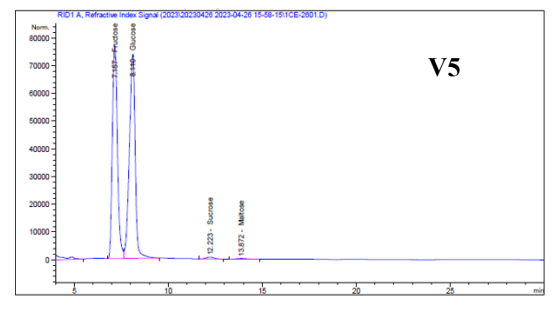
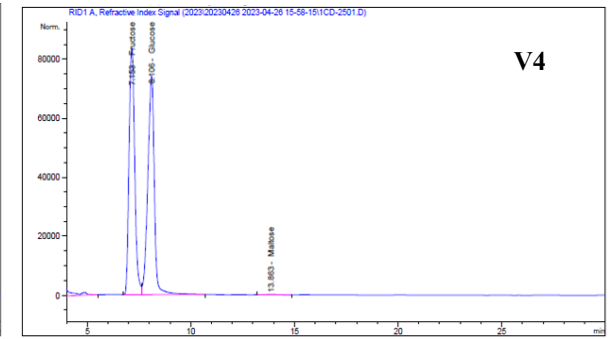
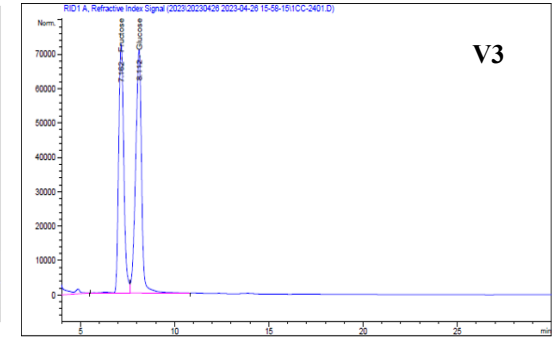
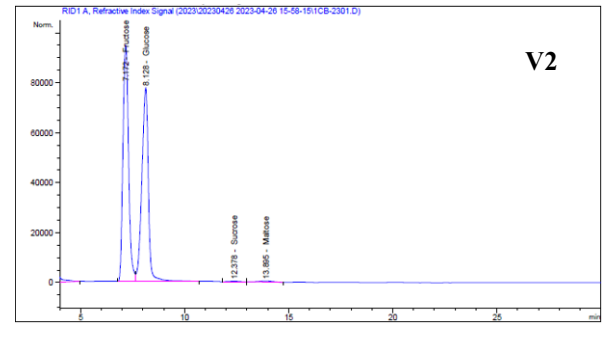
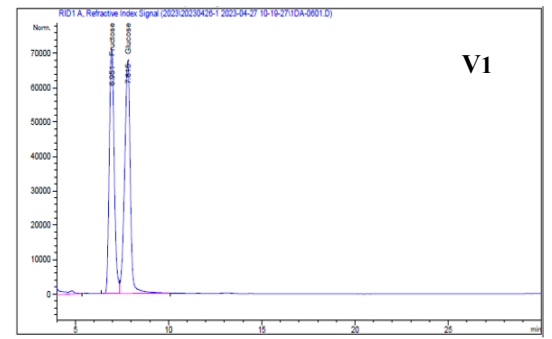


Table 2 Content of Total Phenols, Total Acids, and pH Value in Samples

Sample	Total Phenols (mg/L)	Total Acids (g/L)	pH
V1 (control)	1767±6.11	7.52±0.03	3.65±0.01
V2	1020±2.0	5.10±0.11	3.63±0.01
V3	1247±7.37	5.44±0.05	4.18±0.01
V4	1472±2.00	5.41±0.01	3.65±0.02
V5	1112±4.62	7.85±0.07	3.17±0.03
V6	977±4.36	3.85±0.07	4.03±0.13
V7	808±2.08	11.2±0.00	3.12±0.01
V8	1119±2.09	6.33±0.04	3.70±0.17
Min	808	3.85	3.12
Max	1767	11.2	4.18
Average (V2/V8)	1108		

-40%

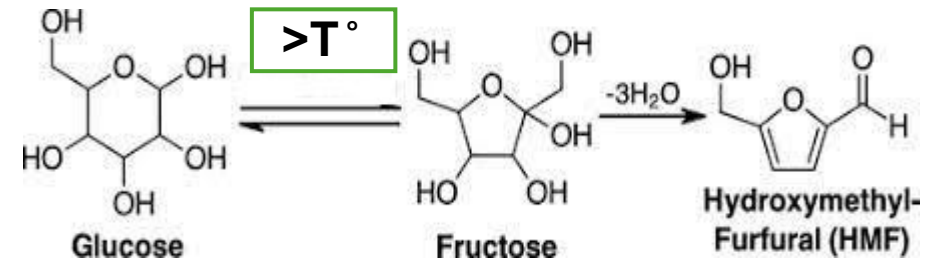
Optimal
5-6 g/L

HMF –HYDROXYMETHYL FURFURAL

Cyclic Aldehyde

- ▶ High T (°C) and Heating Time
- ▶ Storage Condition (Temperature and Light)
- ▶ High Concentration of Fe and Cu

**High Concentration of HMF is
ALLEREGEN**

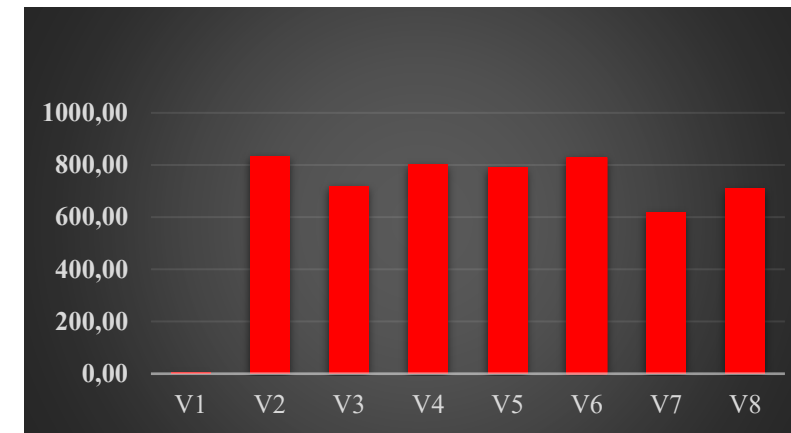


Time (min)	Temperature (°C)	^o Bx	pH value	HMF (mg/kg)
0	22.0	20.5	4.37	21.44
20	61.0	21.0	4.27	36.29
60	90.5	23.5	4.20	55.97
80	94.5	25.8	4.22	119.85
120	94.5	33.0	4.32	320.55
160	95.0	49.5	4.18	1543.85
190	95.0	68.0	4.34	3292.01

Department of Food Engineering, Ege University Bornova,
İzmir, 2020

Table 3 Content of HMF in Samples (mg/kg)

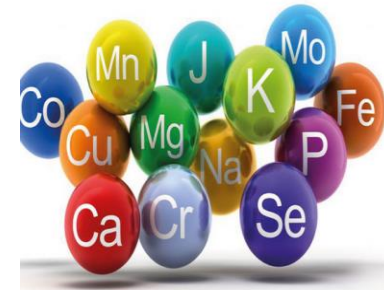
Sample	HMF	Index
V1 (control)	5.1±12	100
V2	835.41±66.83	163
V3	720.60±57.64	140
V4	805.30±64.42	157
V5	790.30±63.22	154
V6	827.84±66.22	161
V7	620.30±49.62	121
V8	710.20±56.81	138
Min	5.12	
Max	835.41	
Average V2/V8	758.56	147



Sample	EU regulative	
	75 mg/kg liquid molasses	100 mg/kg Solid molasses
V1	√	
V2	√	
V3		
V4	√	
V5	√	
V6	√	
V7		
V8	√	

Mineral Composition (32 elements)

Element	Unit	V1	V2	V3	V4	V5	V6	V7	V8
Li	mg/kg	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001
Be	mg/kg	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001
B	mg/kg	24,6	39,7	33,5	28,2	27,4	33,2	20,7	30,9
Na	mg/kg	1984	192	9115	208	1375	2346	123	972
Mg	mg/kg	235,3	287,3	159,0	176,9	156,7	158,3	137,4	253,2
Al	mg/kg	95,0	14,8	109,9	10,3	8,4	229,1	29,9	28,3
K	mg/kg	1490	1003	1370	1119	1000	1480	1118	380
Ca	mg/kg	85,7	113,8	100,6	78,7	100,6	150,4	90,2	192,7
V	mg/kg	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001
Cr	mg/kg	0,880	0,205	0,497	0,348	0,223	0,271	0,233	0,478
Mo	mg/kg	1,22	3,42	2,30	1,84	1,42	1,15	0,85	1,30
Fe	mg/kg	12,56	9,42	26,68	10,52	16,0	7,98	21,84	13,93
Co	mg/kg	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001
Ni	mg/kg	0,1859	<0,0001	0,1682	<0,0001	<0,0001	0,3723	<0,0001	<0,0001
Cu	mg/kg	0,42	1,45	0,88	1,13	1,02	0,94	2,98	1,39
Zn	mg/kg	2,39	17,43	18,40	7,87	14,20	18,37	11,02	30,97
Sn	mg/kg	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001
Sb	mg/kg	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001
Ba	mg/kg	0,37	0,52	0,49	0,32	0,30	0,40	0,32	0,31
Hg	mg/kg	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001
Tl	mg/kg	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001
Pb	mg/kg	0,0325	<0,0001	0,0146	0,0211	<0,0001	<0,0001	<0,0001	0,0466
Bi	mg/kg	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001
Ga	mg/kg	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001
Ge	mg/kg	<0,0001	0,00084	<0,0001	0,0053	0,0016	0,022	<0,0001	<0,0001
As	mg/kg	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001
Se	mg/kg	<0,0001	<0,0001	<0,0001	0,0015	<0,0001	<0,0001	<0,0001	<0,0001
Sr	mg/kg	2,0757	2,6874	1,2221	1,0279	1,0505	1,7924	1,1299	1,6473
Mo	mg/kg	<0,0001	0,005	0,007	0,014	0,006	0,005	0,017	0,015
Pd	mg/kg	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001
Ag	mg/kg	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001
Cd	mg/kg	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001	<0,0001



Macro Elements
K, Ca, Mg



Electrolyte – regulates the fluids in the body
Cardiovascular system – heart diseases and strokes



Protection against bone osteoporosis



It supports the function of over 300 enzymes in the human body

COENZYME

Micro Elements
Fe, Mn, Zn, B, Ba, Na



Structure of red blood cells – proteins hemoglobin



To maintain the proper balance of water and minerals



A constituent component of insulin and stimulates its secretion, as well as other enzymes

Heavy Metals:
Cr, Ni, Cu, Hg, Pb, As, Cd, Co

Toxic, they cause chronic degenerative changes, especially in the nervous system, liver, and kidneys, and in some cases, they are also carcinogenic.



Table 4 Macro Minerals in Samples (mg/kg)

Sample	K	Ca	Mg
V1/C	1490	85.7	235.3
V2	1003	113.8	287.3
V3	1370	100.6	159.0
V4	1119	78.7	176.9
V5	1000	100.6	156.7
V6	1480	150.4	158.3
V7	1118	90.2	137.4
V8	380	192.7	253.2

Table 5 Micro Minerals in Samples (mg/kg)

Sample	Fe	Mn	Zn	B	Ba	Na
V1/C	12.56	1.22	2.39	24.6	0.37	1984
V2	9.42	3.42	17.43	39.7	0.52	192
V3	21.68	2.30	18.4	33.5	0.49	9115
V4	10.52	1.84	7.87	28.2	0.32	208
V5	16.0	1.42	14.20	27.4	0.30	1375
V6	7.98	1.15	18.37	33.2	0.40	2346
V7	21.84	0.85	11.02	20.7	0.32	123
V8	13.93	1.30	30.97	30.9	0.31	972
Limit value	15					

Table 6 Heavy Metals in Samples (mg/kg)

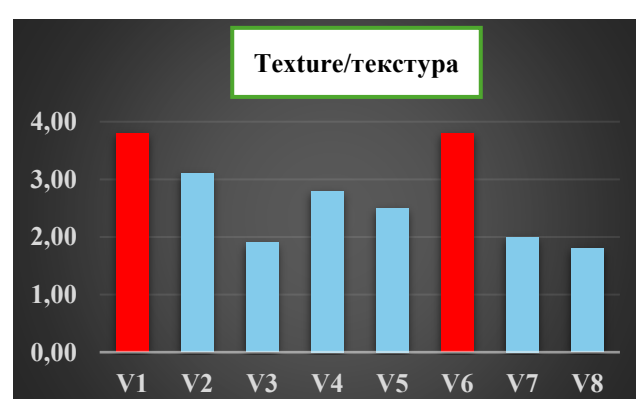
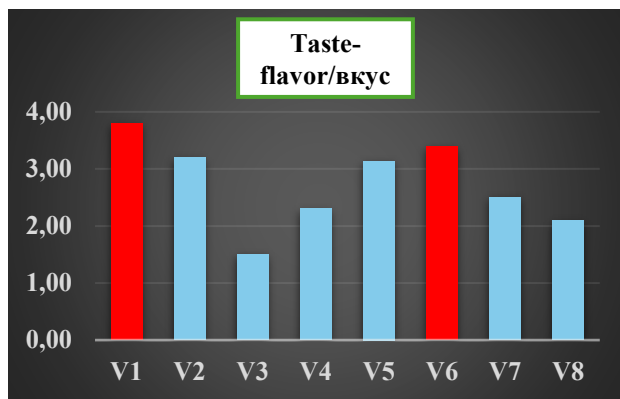
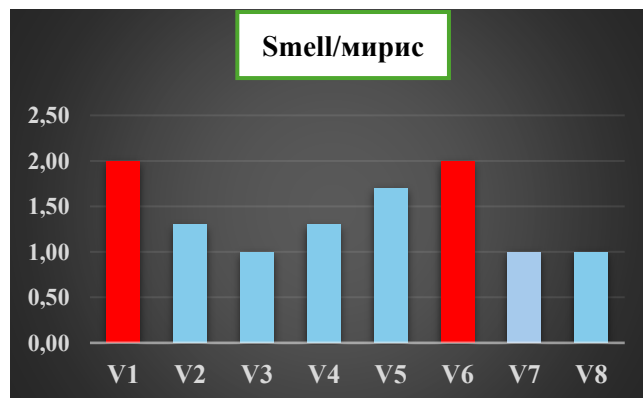
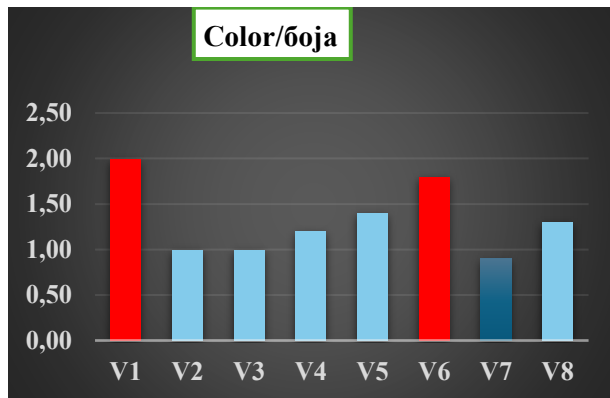
Sample	Al	Li	Cr	Ni	Cu
V1/C	95.0	<0.0001	2.0757	<0.0001	0.42
V2	14.8	<0.0001	2.6874	0.1859	1.45
V3	109.9	<0.0001	1.2221	0.1682	0.88
V4	10.3	<0.0001	1.0279	<0.0001	1.13
V5	8.4	<0.0001	1.0505	<0.0001	1.02
V6	229.1	<0.0001	1.7924	0.1723	0.94
V7	29.9	<0.0001	1.1299	<0.0001	2.98
V8	28.3	<0.0001	1.6473	<0.0001	1.39
Limit value				0.02	5

Sample	Hg	Pb	As	Cd	Co
V1/C	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
V2	<0.0001	0.0325	<0.0001	<0.0001	<0.0001
V3	<0.0001	0.0146	<0.0001	<0.0001	<0.0001
V4	<0.0001	0.0211	<0.0001	<0.0001	<0.0001
V5	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
V6	<0.0001	0.0466	<0.0001	<0.0001	<0.0001
V7	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
V8	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Limit value		0.03	0.02	0.03	0.02

ANTIOXIDANT ACTIVITY - Trolox equivalent antioxidant capacity

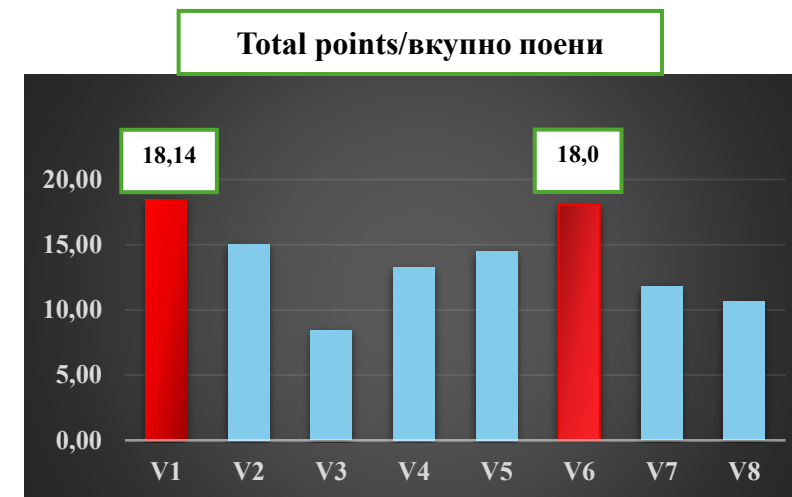
Sample	Mg TE/100 g	SD
V1 (control)	312	2.79
V2	129.25	0.00
V3	206.99	14.26
V4	88.23	6.67
V5	126.23	0.95
V6	265.29	34.28
V7	80.08	1.42
V8	157.61	9.13

SENSORY EVALUATION



Element	Max points
Color/боја	2
Smell/мирис	2
Taste-flavor/вкус	4
Sweetness/сладост	2
Sourness/киселост	2
Texture/текстура	4
Aftertaste/ после вкус	4
Total/вкупно	20

Sensory Analysis Methods :
ISO 6545, ISO 8587, ISO 11036



CONCLUSION

Traditional Methods (100-110°C)

High concentration of HMF

Significantly reduced total phenols

Decrease in antioxidant activity

Vacuum Technology (T to 38°C)

HMF is not formed

The content of total phenols does not change

Higher antioxidant activity

The mineral composition (macro- and micro- minerals) and the content of heavy metals depend primarily on the growing conditions (soil, fertilizers, protective agents), and very little on the production technology or the variety.

The recommendations are:

Storage Condition:

- ▶ Temperature to 25°C and
- ▶ dark condition

Storage time –non more than 12 mounts



THANK YOU FOR YOUR ATTENTION!

*Grape Molasses is History,
Tradition, a Source of Energy,
Delight and Pleasure*

