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PHYSICAL AND CHEMICAL PROPERTIES OF MADZUN (grape molasses) PRODUCED FROM VRANEC GRAPE VARIETY BY TRADITIONAL AND INDUSTRIAL TECHNIQUES

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Abstract

Grape molasses is one of the most popular and traditional food in North Macedonia, mostly used in the past decades. Mainly it is produced by using a traditional protocol (technique) of preparing the molasses, commonly known as "Madzun". The present study summarizes data for characterization of some physical and chemical properties of grape molasses (Madzun) from Vranec grape variety. Comparative analyses have been conducted for samples produced using traditional (four samples) and industrial (one sample) techniques. The water-soluble dry mater contents of the samples were determined in the range from 61.67% to 75.17%. Total sugar contents of the grape molasses (Madzun) samples were determined in the range from: 47.27% to 72.42%. Furthermore, the content of sucrose in all samples was at low levels (<0.1%), which indicates that no sugar, additionally had been added in the production of grape molasses (Madzun). The total phenols expressed as gallic acid were identified in five samples and significant differences were observed between samples. Sensory analysis of the samples was carried out by a committee consisting of 7 members. All committee members were females with long-term experience in sensory evaluation of plant-based foods. The following parameters were evaluated: colour, smell, taste, sweetness, acidity, texture and aftertaste. Based on the sensory evaluation data, the highest score of 17.92 points (maximum referent declared value is 20 points) was obtained for V3 sample - the best grape molasses (Madzun) produced using traditional technique.

Keywords: *grape molasses, sugar, total phenols, total acids, hydroxymethyl furfural*

INTRODUCTION

Grape molasses is a traditional food that has been produced and used by the local population in North Macedonia for decades. Usually, grape molasses is produced by using traditional technique of preparation. Commercially, they are available in the markets with common name "Grape honey", as well as traditional name "Madzun". According to the national historical nonformal data the name "Madzun" comes from the Turkish word meaning boiled fruit with a certain density. Chronologically, grape production represents an important part of agricultural production and food processing. Thus, the grape molasses which is made with grapes, and many other food products are required to be manufactured in accordance with the standards and quality protocols. In North Macedonia, Madzun is produced mainly from the Vranec red wine variety, as well from the table varieties Cardinal, Muscat hamburg, Afus Ali (Dattier de Beyrouth), or similar. Grape molasses (Madzun) can be produced by using traditional and industrial techniques and have different flavour, structure and appearance in North Macedonia.

Fresh or processed grape (*Vitis vinifera* L.) is one of the widely consummated fruits all around the world due to its delicious taste and beneficial

effects on human health (Helvacıoğlu et al., 2018). Grape molasses is a popular processed product from grapefruits with dark-coloured, sweet and viscous liquid characteristics. Grape molasses is a concentrated and extended shelf-life form of grape juice, and it is formed with boiling without sugar or other food additives (Yoğurtçu & Kamış, 2006). Grape molasses is produced primarily from grapes by concentrating juices with a soluble dry matter content up to 70-80% (Cihat et al., 2016).

Grape molasses composition and structure vary according to grape variety and production process (Badem., 2018). Grape molasses represents a high calorie as well energy boosting food due to the high sugar content (up to 50%-80%). Madzun usually contains the sugar in the form of glucose and fructose; which increases their availability into the blood system (Karababa &Develi Isikli, 2005). The average energy value of grape molasses is 293 kcal·100 g^{-1} (Yoğurtçu & Kamişli, 2006).

The content of the phenolic compounds in the grape molasses (Madzun) is affected by many factors, such as properties of the varieties, cultivation conditions, the geographical location of the production area and the degree of ripeness of the grape (Kelebek at all, 2012). Titratable acidity is inversely proportional to pH. Thus, acidity may vary depending on the grape variety and producing regions. According to grape molasses notification (TMFAL 2007 and 2016), it is classified as sweet molasses if their pH range is from 5 to 6, and they are classified as sour molasses when their pH range is from 3.5 to 5.

Grape molasses is very rich in minerals. Some minerals (such as calcium, iron, potassium, and magnesium) found in molasses contain enough to cover a significant portion of a person's daily needs. Molasses contains valuable iron minerals (with oxidation value +2) which can more easily be absorbed in the human digestive system (Batu, 2006).

MATERIALS AND METHODS

Grape molasses (Madzun) samples

In the present study, five grape molasses (Madzun) samples were characterized. One sample was produced with application of industrial methods (vacuum evaporation technology), while the other samples were produced with common traditional methods. All five samples were produced from Vranec grape variety. Vranec is a dominant wine grape variety in the assortment structure in North Macedonia. The traditional grape molasses (Madzun) samples (V2, V3, V4, V5) were collected from a local producer in Tikvesh wine region. The industrial grape molasses sample (V1) was purchased from a local supermarket. All the samples used in the study were produced in the year 2022. Prior to analysis, the samples were packed in glass jars.

Methods

The total sugar content of grape 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 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.

The soluble dry matter content of the grape 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 was 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-coloured complex. The intensity of the red colour was measured using a UV-Vis-NIR-5000 spectrophotometer (analytical wavelength of 550 nm was used).

Sensory analysis of the samples was carried out by a committee consisting of 7 members.

All members were women with experience in sensory evaluation of plant-based foods. There were 5 preparations for each member (V1, V2, V3, V4, V5), and each was packed in 100 g glass jars. The following sensory characteristics and maximum number of points were evaluated: colour (2), smell (2), flavour (4), sweetness (2) sourness (2), texture (4) and aftertaste (4). The maximum value of sensory evaluation points for each sample is 20 (referent maximum value). The procedure sensory evaluation was performed according to the protocols described in ISO 6564, ISO 8587 and ISO 11036.

RESULTS AND DISCUSSION

The basic chemical parameters that are important for the quality of grape molasses (Madzun) are: total sugar especially those that come from grapes (fructose, glucose), dry matter, the content of phenols, total acids and pH value.

The sugars represented in the form of glucose and fructose are the basic carbohydrates in the grape. The sucrose and maltose are present in other parts of the vine (leaf, shoot, perennial parts) in smaller amounts. The presence of sucrose in grape molasses (Madzun) indicates that it has been additionally added in order to increase the content of total sugars and dry matter. Glucose is less sweet than fructose.

Glucose and fructose are monosaccharides and energy sources and contain the same number of calories, i.e. 1 g = 4 calories (Tappy & Le, 2010). Glucose, usually is directly absorbed in the metabolism and generate energy fast, while fructose is firstly transformed (in the liver) to glucose and then is used to create highly energetic compounds (Lowette et al., 2015; Cihat et al., 2016). The average energy value of grape pekmez is 293 kcal 100 g^{-1} (Simsek &Artif,2002).

The results for the content of sugars (total and separately in the form of simple carbohydrates) and soluble dry matter are given in Table 1. Glucose content was determined in the range from 23.95% in sample V5 to 35.92% in sample V3. The fructose content ranged from 23.10% (V5) to 35.20% (V3). Fructose/Glucose (F/G) ratios were calculated and varied from 0.96 (V5) to 1.38 (V2). Among these samples, the highest fructose to glucose ratio (1.38) was found in V2 grape molasses produced by traditional method. In all samples, the sucrose content was below the detection threshold (<0.1), which confirms that no sugar (additionally) had been added. The sample V5 had the lowest content of total sugars of 47.27%, and sample V3 had the highest of 72.42%. The HPLC chromatograms of simple carbohydrates (sugar) forms in samples are represented in Figure1.

The soluble dry matter in grapes is primarily formed by sugar, including fructose, glucose and sucrose, and acids, such as tartaric acid, citric acid and malic acid (Cemeroğlu, 2010). In the analysed molasses samples, the soluble dry matter ranged from 61.67% (V5) to 75.17% (V2). In relation to minimal amount of dry matters (68%), the samples V1, V2, V3, V4 met the conditions prescribed in the Regulation (EU) No 1169/2011, except the sample V5.

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

Sample	Fructose (%)	Glucose (%)	F/G ratio	Sucrose (%)	Maltose (%)	Total sugar (%)	Soluble dry matter (%)
V1	29.43	29.91	0.98	<0.1	<0.15	59.34 ±2.56	73.13±3.15
V2	33.67	24.40	1.38	<0.1	0.31	59.38±2.57	75.17±3.24
V3	36.20	35.92	1.01	<0.1	0.30	72.42±3.13	73.90±3.19
V4	35.22	33.69	1.04	<0.1	0.18	69.09±2.99	70.80±3.05
V5	23.10	23.95	0.96	<0.1	0.22	47.27±2.04	61.67±2.66

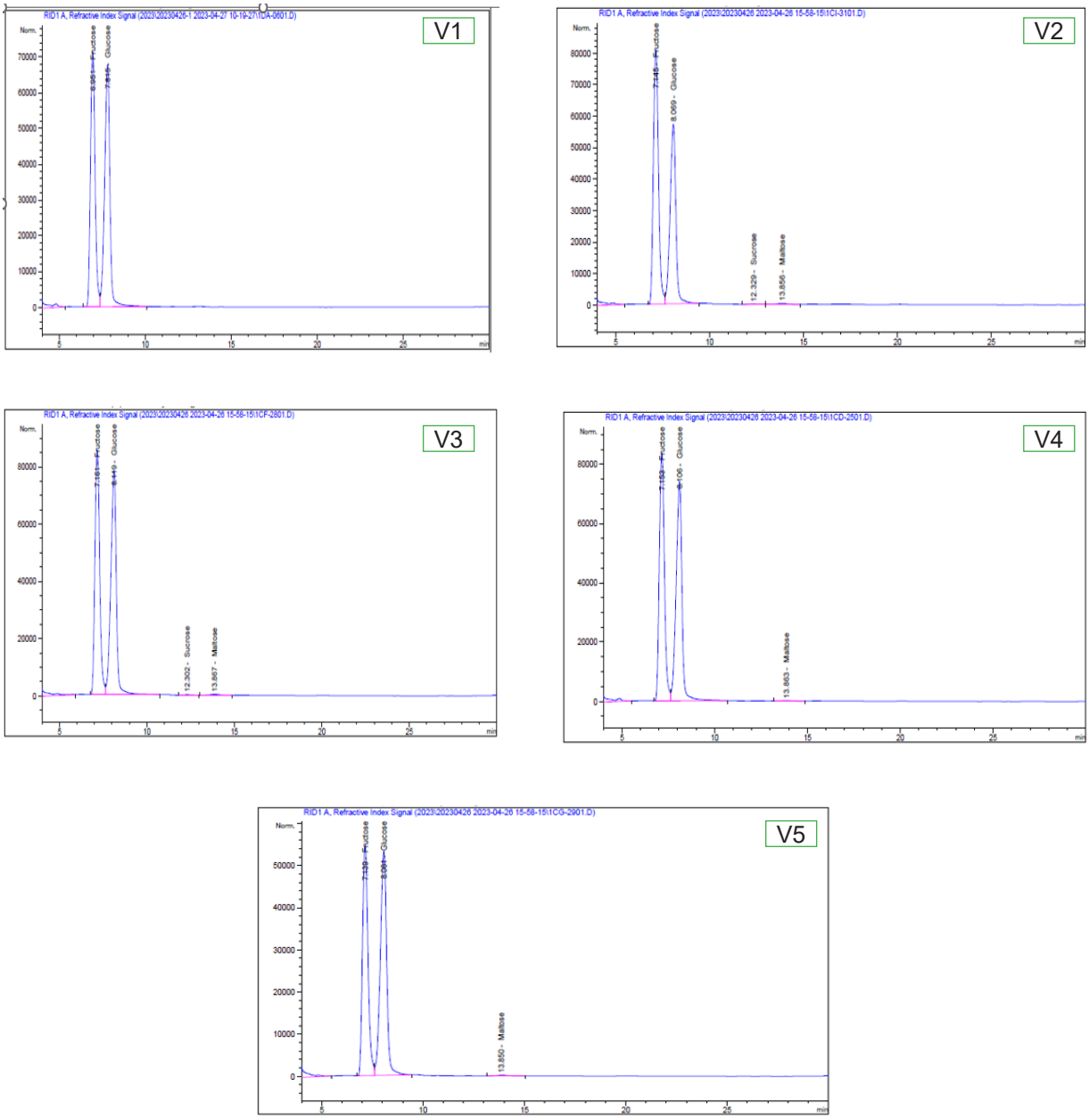

Figure 1. HPLC chromatograms of identified sugars in in the studied grape molasses samples V1(industrial vacuum technology), V2, V3, V4, V5 (traditional methods).

The results for the content of total phenols, total acids, pH and hydroxymethyl furfural in the analysed samples are presented in table 2. The grape molasses samples were rich in polyphenols and the polyphenol contents was variable. The highest content of total phenols of 1768 mg/L was determined in sample V1 (vacuum evaporation technology), while the lowest content of 807 mg/L was determined in sample V5 (traditional method). In our study, sample V1 (vacuum evaporation technology) had the highest content of total phenols (1767 mg/L), and sample V5 (traditional method) had the lowest content of total phenols (808 mg/L). In other grape molasses samples, the content of total phenols is 960 mg/L (V3), 1119 mg/L (V2) and 1471 mg/L (V4) respectively. The difference in the content of total phenols was due to the degree of ripeness of the grapes and the technology of grape molasses production (Aliyazicioğlu et.al., 2009).

The pH in grape molasses (Madzun) ranged from 3.12 (V5) to 4.05 (V3). The total acids (expressed as tartaric acid) were determined in all samples. The highest content was determined in the sample V5 (11.1 g/L) and the lowest content

in the sample V3 (3.85 g/L). Titratable acidity is inversely proportional to pH. According to Grape Pekmez Notification (2007), molasses is classified as sweet, if their pH ranges from 5 to 6, and sour when their pH ranges from 3.5 to 5. According to this Notification, the sample V5 classified as sour and other sample (V1, V2, V3, V4) were sweet grape molasses.

HMF is not naturality found compound in fruits. This compound is usually formed during the process by reducing the sugar in acids environment when they are heated (Maillard reaction). HMF content in grape molasses is restricted compound for preventing the application of excess heat in many products (Cihat et al., 2016). It is an important quality factor that reflects the severity of heat treatment (temperature and time) that were applied to the foods thickened with the application of the heat treatment (Cemeroğlu, 2010). According to quality molasses standard, the maximum allowed content of HMF in liquid molasses is 75 mg/kg (Regulation EU, No 1169/2011).

The HMF content of the analysed grape molasses (Madzun) varied from 5.1 mg/kg (V1-vacuum technology) to 827.84 mg/kg (V3-tradicional methods). This value in grape molasses samples derived from Vranec grape variety such as V2 (710.20 mg/kg), V4 (805.30 mg/kg) and V5 (620.30 mg/kg) were quite high. A study conducted on traditional methods found that HMF content was approximately 15 times higher in high temperature - produced molasses (110.38 mg/kg) compared to the grape molasses produced under vacuum (8.37 mg/kg) technology (Helvacıoğluet al., 2021). In the literature, the amounts of HMF in grape molasses sample range from 5.91 mg/kg to 762.22 mg/kg (Cihat et al., 2016), from 7.38 mg/kg to 166.05 mg/kg (Abdullah Badem, 2018) and from 29.56 mg/kg to 801.80 mg/kg (Koca et al., 2007).

Table 2. Content of total phenols, total acids, pH and HMF in the studied sample of grape molasses.

Sample	Compounds			
	Total phenols (mg/L)	Total acids (g/L)	pH	HMF (hydroxymethyl furfural) (mg/kg)
V1	1767±6.11	7.52±0.03	3.65±0.01	5.1±12
V2	1119±2.08	6.34±0.04	3.69±0.13	710.20±56.81
V3	960±27.43	3.85±0.05	4.05±0.10	827.84±66.22
V4	1471±1.15	5.41±0.01	3.65±0.02	805.30±64.42
V5	808±2.08	11.1±0.06	3.12±0.02	620.30±49.62

Chemical analysis and organoleptic evaluation (tasting) are an important indicator for determining the quality of the grape molasses (Madzun). The complexity of molasses flavour reflects the quality of the grape molasses (Boluk et al.,2023).

The sensory evaluation protocol of the grape molasses samples, includes the following parameters: colour, smell, taste-flavour, sweetness, sourness, texture and aftertaste. The sum of the calculated values gives the total evaluation value of grape molasses.

Values of the sensory parameters of the studies samples of grape molasses are presented in Figure 2, and total points are presented in Figure 3.

In this study, V1 and V3 were positively appreciated by tasters, with higher "complexity" scores compared to the other molasses samples (V2, V4 and V5). Aftertaste, also called flavour length, is often described as short, medium, or long. Usually on the premise of a pleasant aftertaste, the longer it lasts, the better the quality of grape molasses. Regarding the overall tasting score, samples V1 and V3 stand out from the other samples, i.e. the highest rated with 17.92 points (V3) and 17.86 points (V1).

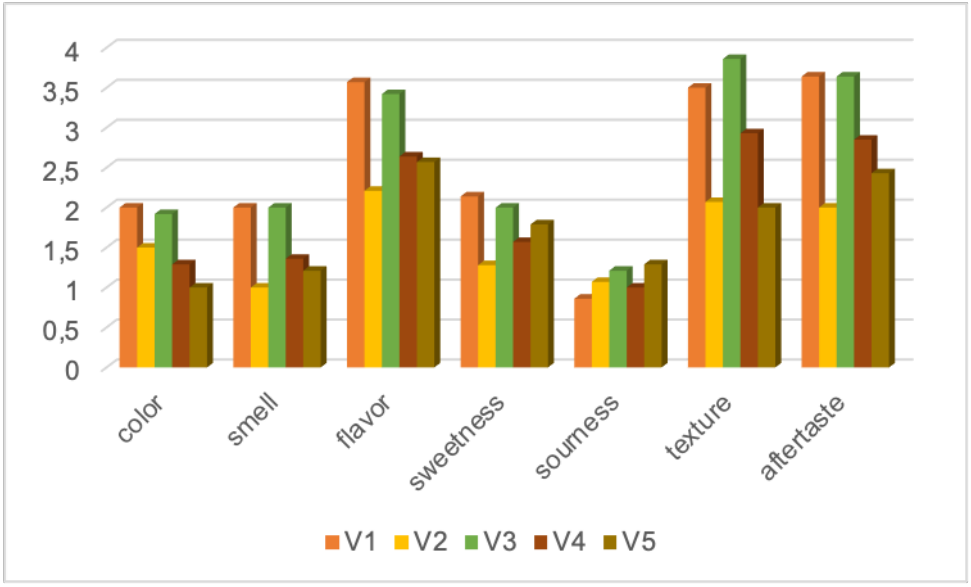

Figure 2. Values of the sensory parameters of the studied sample of grape molasses.

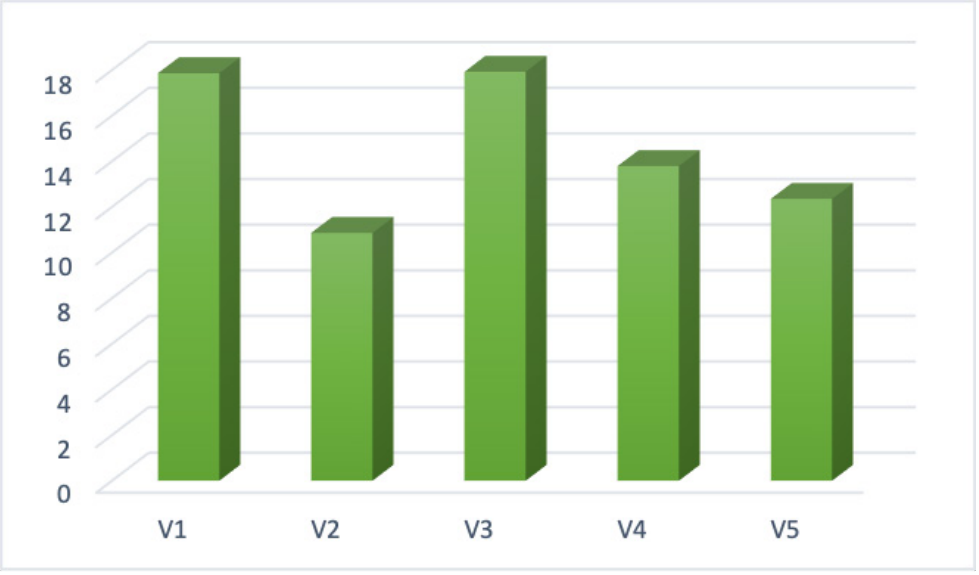

Figure .3 Total points from sensory evaluation of the studied sample of grape molasses.

CONCLUSION

The current study represented the first attempt at national level to characterized the chemical properties of grape molasses sample from Vranec grape variety. Furthermore, the quality of the molasses was characterized with sensory evaluation of the samples as well. Two types of producing technology were compared in order to determine the impact of the producing technology on the quality of the grape molasses from Vranec grape variety.

The chemometric evidence of the samples was determined through chemical characteristics such as: soluble dry matter, sugar, total phenolic, total acids and HMF.

It can be concluded that the use of traditional methods for production of grape molasses, significantly effects on the quality of the molasses resulting with decreased quality. This is related to the higher content of HMF compound which is harmful to human health.

For the production of high-quality molasses, standardization should be applied by using modern technology. Our recommendation is that traditional production should be adapted according to vacuum technology.

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ФИЗИЧКИ И ХЕМИСКИ СВОЈСТВА НА МАЏУН (меласа од грозје) ОД СОРТАТА ГРОЗЈЕ ВРАНЕЦ ПРОИЗВЕДЕН НА ТРАДИЦИОНАЛЕН И ИНДУСТРИСКИ НАЧИН

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Резиме

Меласата од грозје е една од популарните и традиционална храна во Република Северна Македонија во последните 10 години. Најмногу се произведува на традиционален начин под името „маџун". Во оваа студија беа анализирани некои физички и хемиски својства на меласа од грозје (маџун) од сортата Вранец, произведена со традиционален (четири примероци) и индустриски (еден примерок) начин (вакум технологија). Содржината на сувата материја растворлива во вода во анализираните примероци се движи во границите од 61.67 % (V5) до 75.17 % (V2). Содржината на вкупните шеќери е во границите од 47.27 % (V5) до 72.42 % (V3), а на сахароза во сите примероци беше на ниско ниво (<0,1 %), што укажува дека не бил додаван гликозен сируп пред и во текот на производниот процес. Во однос на содржината на вкупните феноли (гална киселина) беа забележани значителни разлики помеѓу примероците, а се должи на технологијата и должината на производниот процес. Сензорна анализа на примероците беше спроведена од страна на комисија составена од 7 члена. Сите членови се жени со искуство во сензорна евалуација на храна од растително потекло. Беа оценети следните параметри: боја, мирис, вкус, сладост, киселост, текстура и после вкус. Максималниот број на поени е 20 (ISO 6564, ISO 8587 и ISO 11036). Врз основа на резултатите од сензорната анализа, со највисока оценка од 17,92 поени е примерокот V3 - произведен на традиционален начин.

Клучни зборови: *меласа од грозје (маџун), шеќер, вкупни феноли, вкупни киселини, хидроксиметил фурфурал.*