PROFILE OF SUGARS IN A GRAPE-WINE SYSTEM AS THE IDENTIFYING INDICATOR OF THE AUTHENTICITY OF WINE PRODUCTS

Nonna V. Gnilomedova, Nadezhda S. Anikina, and Viktoriya G. Gerzhikova

All-Russian National Research Institute of Viticulture and Wine-Making "Magarach",
Kirova Str. 31, Yalta 298600, Russian Federation

* e-mail: 231462@mail.ru

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Abstract: The current problem of winemaking is the confirmation of a method for producing table and liqueur wines to protect the economic interests of producers and protect the health of consumers. It is possible to determine the nature of the sugars contained in wine on the basis of regularities in the dynamics of the glucose-fructose index (GFI) and the proportion of disaccharides in the total sugar content in the process chain "raw materials – finished products". The study objects included: the grapes grown on the territory of the Crimean Peninsula, European, autochthonous technical varieties, as well as the varieties of a new selection; domestic and foreign wine materials and wines; model samples and wine falsifications. The content of disaccharides in terms of sucrose, glycerol, glucose and fructose was determined by high-performance liquid chromatography. As a result of the studies of the wines obtained by arrested fermentation, there are some trends in the reduction of GFI with a decrease in the level of endogenous sugars: for the wines with a sugar content of 230–270 g/l, the range of GFI is 0.75–0.94, with a mass concentration of sugars of 10–20 g/l – 0.05–0.14. In the case of a sugar concentration in wine of more than 120 g/l, it is necessary to study a sample for the glycerol content as a marker of fermentation depth in order to increase the reliability of conclusion. The values of the indicators characteristic of high-sugar grapes are typical for the wines obtained by sweetening with a grape must concentrate: GFI – not more than 1.0, the proportion of disaccharides is not more than 1.2%; falsifications are characterized by the profile of sugars atypical for grape products: GFI is higher than 1.02, the share of disaccharides is more than 2%.

Keywords: Glucose, fructose, sucrose, glycerol, high-performance liquid chromatography, concentrated grape must, falsification, banned supplements

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INTRODUCTION

The winemaking plants of the Crimea are able to produce the high-quality wines, both liqueur and table, obtained by arrested fermentation. The production of wines in this way is possible due to the significant accumulation of sugars in a grape berry, which is a consequence of favorable agroclimatic conditions for growing a grape plant, especially on the southern coast of Crimea. The content of sugars in a grape berry and the features of their qualitative composition depend on a number of factors: the species and variety of grapes, the climatic features of the region and the year of harvest, the stage of maturity at the time of harvesting [1–4]. In the future, the sugar content of grapes determines the trend of use of raw materials (the production of a must concentrate, the production of table or liqueur wines) and the features of technology for its processing. The predominance of fructose can cause slow fermentation and / or arrested fermentation [5], which is unacceptable in the production of dry wines. The difficulties of fermentation, in this case, are explained by the different degree of yeast glucophily. It is known that different yeast races, related to the species *Saccharomyces cerevisiae,* traditional for winemaking are characterized by a tendency to actively assimilate glucose, non-saccharomycetes *(Candida, Zygosaccharomyces* and others) are distinguished by high fructosophility [6–8]. Despite the fact that the activity of sugar consumption by yeast cells is a genetically determined sign, the peculiarities of fermentation also affect this process. Under the unfavorable conditions of fermentation (the non-correspondence of temperature conditions to the physiological optimum, the deficiency of nitrogenous substances and the presence of fermentation inhibitors), the fermenting capacity may not be fully realized [9, 10].

To correct the sugar content in wines, a must concentrate is used, including the rectified must produced from grapes (Federal Law No. 171-FZ of November 22, 1995 "On State Regulation of Production and Circulation of Ethyl Alcohol and Alcohol Products and Restriction on Alcohol Consumption", http://www.garant.ru/products/ipo/prime/doc/71335844/#ixzz4XPSWZJ7o). However, semi-dry, semisweet and sweet wines of high quality categories, such as wines with protected geographical indication (PGI) and wines with protected appellation of origin (PAO), can be produced only by incomplete alcoholic fermentation. The wines with the preserved natural (endogenous) sugars have more pronounced organoleptic characteristics and are appreciated much higher than those produced with the application of sugars (exogenous), but they are difficult to produce and require a high level of technological discipline.

The use of sugar-containing products with a non-grape basis is prohibited in the production of wines. Such sugar-containing substances include the glucose-fructose syrup (GFS) obtained by the enzymatic hydrolysis of starch-containing raw materials. A distinctive feature of GFS is the glucose content of more than 50%, as well as the presence of a disaccharide of maltose, which is a by-product of starch hydrolysis [11].

It is also unacceptable to sweeten wines with fruit juice concentrates, which are characterized by an individual profile of sugars in accordance with the characteristics of raw materials of various botanical species [12], in particular, a high content of sucrose is noted in apples [13].

There are various approaches to identifying and determining the authenticity of juice and wine products, including a variety of analytical methods. The method of gas chromatography is used to determine the presence of syrup supplements in juices (GOST 32800-2014 Juice products. Detection of glucose and fructose syrups addition by capillary gas chromatography, http://standartgost.ru/g/%D0%93%D0%9E%D0%A1%D0%A2_32800-2014). A modern informative method for controlling the authenticity of wines is the mass spectrometry of stable oxygen and carbon isotopes [14–16], but the wide spread of this analytical study is limited to the significant cost of high-tech equipment.

To identify and determine the authenticity / identify the falsification of wines, the Magarach Institute developed a system of indicators that includes: the profile of organic acids, the content of glycerol, phenolic and aroma-forming substances and some other components. We proposed some criteria for verifying the authenticity of the grape origin of various products – physical and chemical characteristics, a phenolic content, an organic acid composition and the composition and content of sugars [17, 18]. The use of high-performance liquid chromatography and capillary electrophoresis allows to obtain the exact information about the state of soluble carbohydrates in any liquid product within a short period of time [19–21].

At the moment, the information on changes in these indicators, in particular, sugars, in literature during the process cycle in the "grapes-wine material-wine" chain, taking into account the sugar content of the raw materials and various categories of wine quality is not provided, which can reduce the reliability of conclusions in the identification of wine products.

The study aims at the profile of sugars at all stages of the process cycle in order to determine a method for producing different types of wines.

STUDY OBJECTS AND METHODS

The study objects included:

– the grapes of white (Aligote, Verdelho, Kok Pandas, Kokour White, Muscat White, Rkatsiteli, Sary Pandas, Sersial, Sauvignon Green, Tokay, Sabbath, Chardonnay) and red (Bastardo Magarachsky, Cabernet Sauvignon, Kefesia, Pinot Franc, Ekim Kara) European and autochthonous technical varieties of the species *Vitis vinifera*, as well as 2 varieties of a new selection (Golubok, the selection of Institute of Viticulture and Winemaking named after V.E. Tairov (the Ukraine)), a complex hybrid (Severny x the pollen mixture of the varieties Sorok Let Oktyabrya, Odesskiy Ranniy and No. 1-17-54 (Alicante Bouschet x Cabernet Sauvignon)); Bukovinka and the selection of the Magarach Institute, the hybrid of the varieties Pukhlyakovsky x Zeybel 13-666);

– the sweetening grape (a must concentrate of various manufacturers) and non-grape (glucose-fructose syrup) components;

– the table and liqueur wine materials and wines produced in the conditions of microvinification and at the plants of the Crimea;

– foreign-made wines (Azerbaijan, Germany, Italy, Portugal, France, Chile);

– the model samples that imitate table semi-dry, semi-sweet and sweet wines, as well as the liqueur wines obtained by adding various sugar-containing components to dry table and liqueur wine materials;

– the samples of the finished products provided by controlling authorities the falsification of which was established by us in accordance with a method for identifying the authenticity of grape wine materials and wines [17].

The samples were divided into groups in accordance with the mass concentration of sugars according to the normative documentation of the Russian Federation (http://standard.gost.ru/wps/portal):

– the table wines produced by arrested fermentation: No. 1 – semi-dry, No. 2 – semi-sweet, No. 3 – sweet (Table 1);

– the liqueur wines produced by arrested fermentation: № 1–7 – in accordance with the conditions encountered in various finished products (Table 2);

– the sweetened wines (the application of a grape must concentrate in dry wine material (Table 1, 4–6 and Table 2, No. 8–10) and the falsifications obtained by adding a non-grape component (Table 1, 7–9 and Table 2, No. 11–13) were combined according to the content of sugars into larger clusters due to lack of a reliable difference.

The informativeness of the glucose-fructose index was verified using the samples of elite liqueur wines (the Crimea), obtained by arrested fermentation that we referred to different groups in the content of sugars according to Table 2: 10 g/l – Madeira Dry (Group No. 1); 30–40 g/l – Madeira Massandra, Madeira Crymskaya (Group No. 2); 60 g/l – Port White and Magarach Red (Group No. 3); 95–110 g/l – Sevastopol Port White, Port White and Crymsky Port Red, Port White and South Coast Port Red (Group No. 4); 160–180 g/l – Surozh Dessert Kokour, Bastardo Magarachsky, South Coast Cahors (Group No. 6); 220–270 g/l – Magarach Muscat White, Red Stone Muscat White, Livadia Muscat White (Group No. 7). Group 5 includes the wines of a lower quality category that are not elite wine products.

Table 1. Mass concentration of sugars in table wines and their falsifications

Group No.	Number of samples	Mass concentration of sugars, g/l
Wines produced by arrested fermentation		
1	n = 17	5–17
2	n = 34	18–40
3	n = 41	more than 45
Wines with the addition of a grape must concentrate to dry wine material		
4	n = 27	5–17
5	n = 15	18–40
6	n = 5	more than 45
Falsification		
7	n = 7	5–17
8	n = 8	18–40
9	n = 5	more than 45

Table 2. Mass concentration of sugars in liqueur wines and their falsifications

Group No.	Number of samples	Mass concentration of sugars, g/l
Wines produced by arrested fermentation		
1	n = 13	10–20
2	n = 36	30–40
3	n = 22	50–60
4	n = 31	70–120
5	n = 8	130–140
6	n = 31	160–180
7	n = 16	230–270
Wines with the addition of a grape must concentrate to dry fortified wine material		
8	n = 10	10–60
9	n = 15	70–120
10	n = 7	160–270
Falsification		
11	n = 11	10–60
12	n = 8	70–120
13	n = 6	160–270

The total sample size was 74 batches of the grapes grown on the territory of the Crimean Peninsula, 94 samples of sweetening grape (a must concentrate of various manufacturers) and non-grape (glucose-fructose syrup) components, 400 samples of wine materials and wines (including model and falsified samples). The studies were carried out within the period of 2010–2016 based at the department of wine chemistry and biochemistry of All-Union Scientific Research Institute of Winemaking and Viticulture Magarach.

When studying grapes, the average sample of the berries previously separated from the stems, weighing 20–50 grams was selected and ground in a homogenizer. The obtained homogeneous mass was filtered through a glass filter to separate gross impurities. The indicators were determined in must after centrifugation (the speed of the centrifuge rotor is 7000 rpm, the separation time is 10 minutes).

The table and liqueur wine materials were produced according to classical schemes. The wine materials produced under microvinification conditions were fermented using pure yeast cultures from the "Collection of microorganisms of winemaking of "Magarach". In the experimental samples of wine materials, the content of sugars was varied within the range of 0–230 g/l, in accordance with the normative documentation for table and liqueur wines [http://standard.gost.ru/wps/portal].

The flow sheet of table wines involved the following procedures [22]:

I – from white grapes: destemming → grape crushing → sulfitation → pressing the crushed grapes → clarification of must → the crushed grapes fermentation culture must → racking → clarifying the wine material.

II – from red grapes: destemming → grape crushing → sulfitation → the fermentation of pure yeast culture crushed grapes to the fermentation of 2/3 of sugars → pressing the crushed grapes → afterfermentation → racking → clarifying the wine material.

The flowsheet of liqueur wines suggested:

– destemming → grape crushing → sulphation → the crushed grapes fermentation culture crushed grapes → pressing the crushed grapes → afterfermentation to obtain the required sugar content → fortification → racking → clarifying the wine material.

The moment of fermentation arrest depended in all cases on the type of wine and the maintenance of the required standards for the content of sugars in the finished products.

The sweetening ingredients were: the permitted supplement – a grape must concentrate, the banned supplements – glucose-fructose syrup.

Varying the sweetening methods was provided by adding glucose-fructose syrup and a grape must concentrate to dry wine material (table wines) or dry wine material with the addition of alcohol (liqueur wines).

The mass concentration of organic acids, sugars and glycerol was determined when separating one sample by high-performance liquid chromatography (a Shimadzu LC Prominence chromatograph, Japan). The determination was made according to the preliminary calibration of the device for the standard solutions of pure substances using a refractometric (glucose, fructose, disaccharide, glycerol) and spectrophotometric (citric, tartaric, malic acid) system detector, taking into account the time of each individual substance efflux. The operating wavelength for the determination of organic acids was 210 nm. The sample was separated using a Supelcogel C610H column filled with a sulfonated polystyrene/divinylbenzene sorbent (the column size is 300 × 7.8, the sorbent particle size 9.0 μm, Supelco®, Sigma-Aldrich), in an isocratic mode (an 0.1% aqueous solution of orthophosphoric acid, the rate is 0.5 ml/min). Before the analysis of samples or to obtain calibration dependences, the refractometric detector of the system was additionally calibrated for the standard solutions of substances, and the obtained analytical characteristics were noted. The final calculation of the mass concentration of glucose and fructose was performed taking into account the refraction data for the respective groups of substances (tartaric and malic acids) that have the same efflux time as the listed carbohydrates, by the mathematical recalculation of the data previously obtained using a UV detector. In the case of the presence of suspensions or insoluble particles in the visual estimation of the sample, they were preliminarily separated using a centrifuge (the speed of the rotor is at least 6–7 thousand rpm, the duration is 5–7 minutes). The relative error of the method (δ) did not exceed 10% with the confidence probability P = 0.95.

The content of sugars was calculated as the sum of the mass concentration of disaccharides (sucrose and maltose in terms of sucrose), glucose and fructose.

The glucose-fructose index (GFI) is a quotient of the glucose and fructose content in the sample, herewith, the error of the final result did not exceed 0.01.

The mass concentration of phenolics was determined using the colorimetric method with the Folin-Ciocalteu reagent [23].

RESULTS AND DISCUSSION

The profile of sugars was studied at various stages of processing grapes and producing wine products: in fresh and concentrated must, in wine materials and the finished products.

The content of sugars (the sum of glucose, fructose and disaccharides) in grapes characterizes technical maturity and determines the way of its processing: the production of table or liqueur wines. The ratio of glucose and fructose (the glucose-fructose index) is one of the criteria for identifying the grape origin of sweeteners, and also determines the choice of yeast and fermentation conditions for obtaining wine products with the specified conditions.

To form a unified system for establishing the authenticity of wines, we carried out a study of the variation of GFI in grape must. 74 batches of the grapes grown on the Crimean Peninsula and collected at a sugar content of 160–330 g/l were analyzed.

As can be seen from the variety of the actual data presented in Fig. 1, with the equal sugar content in grape must, the values of GFI can be different, while the same GFI values can correspond to different levels of sugar accumulation. The variability of the index in the must of various batches of grapes is explained by a multitude of simultaneously and multidirectionally affecting factors, including the stage of physiological maturity [1–4]. The statistical processing of the results of the study (mode – 0.93, median – 0.97, a standard deviation – 0.03, dispersion – 0.001) shows that the GFI values are within the range of 0.89–1.04, which corresponds to the world data obtained for grapes growing in other wine-growing regions of the world [1–3].

We compared the index in the grapes of some varieties at a sugar content range of 200–230 g/l, which provides obtaining conditioned table and liqueur wines. The obtained results demonstrate that for each variety, as sugar is accumulated in grapes, there is a tendency to a decrease in the GFI values by 0.015–0.06 (within the studied sample), Fig. 2 presents the examples of actual values. According to the values of this index, we conditionally divided the studied grape varieties into three groups: the first group – the lowest GFI (0.94) – Aligote, Sauvignon Green; the second group – the intermediate GFI (0.97–0.99) – Muscat White, Rkatsiteli, Kokour White, Cabernet Sauvignon, Bastardo Magarachsky; the third group – the highest GFI (1.02–1.04) – the varieties of grapes of a new selection Golubok and Bukovinka.

Different values of GFI at the same level of sugars can be explained by the fact that in the Crimea conditions the grape varieties prone to high sugar accumulation (the second group) have a long vegetative period and the prolonged synthesis of carbohydrates, while glucose is not expended on the process of cell respiration. The grapes of the varieties with a shorter maturation period (the first group) stop the anabolic process earlier, the high sugar accumulation in this case is due to the evaporation of moisture through the skin of a berry; the stopped carbohydrate anabolism causes an active glucose intake, which reduces the glucose/fructose ratio (GFR) [24].

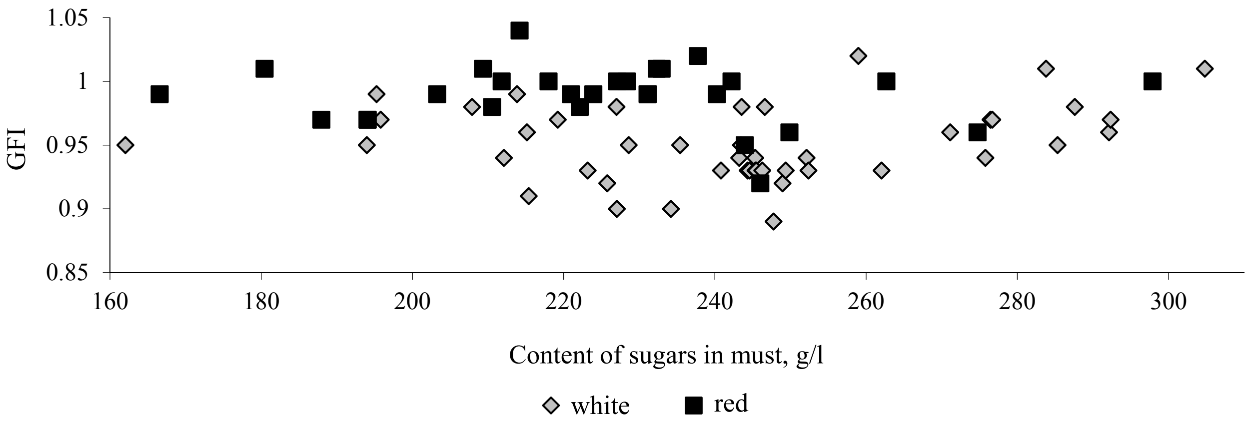

Fig. 1. Glucose-fructose index (GFI) in the must of grapes of white and red varieties (the list of varieties is provided in the methodical part).

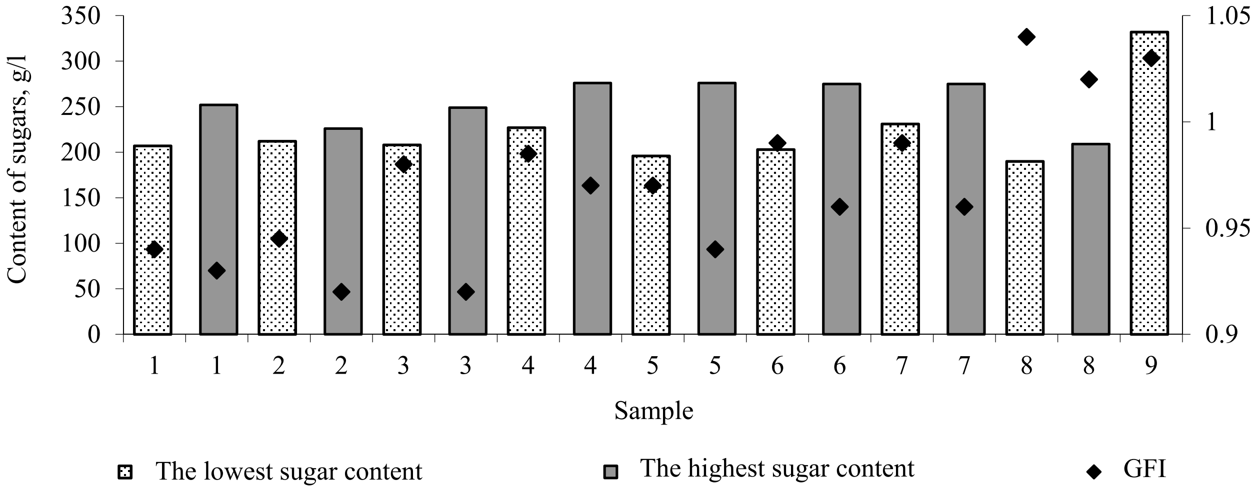

Fig. 2. Glucose-fructose index (GFI) in the must of various grape varieties depending on sugar accumulation (in the studied sample). Grape variety: (1) Aligote, (2) Sauvignon Green, (3) Rkatsiteli, (4) Kokour White, (5) Muscat White, (6) Cabernet Sauvignon, (7) Bastardo Magarachski, (8) Golubok, (9) Bukovinka.

A characteristic feature of a grape berry is the insignificant accumulation of the disaccharides presented by sucrose, in comparison with glucose and fructose [12]. The study of the profile of sugars showed that the content of disaccharides in the must of grapes of the first and second group does not exceed 1.7 g/l, making up no more than 0.7% of the total sugar content; in the third group, the content of these carbohydrates is significantly higher and can reach 14 g/l (4 %). This is due to the fact that the varieties of a new selection with the genes of the species *Vitis labrusca* have a distinctive feature of this species of grapes, prone to the higher accumulation of sucrose and glucose than the European varieties that belong to the species *Vitis vinifera*. The results are consistent with the data presented in the world literature on the biochemical features of grapes [cit. by 1].

The level of GFI in the grapes used for processing must be taken into account when choosing a yeast race for fermentation. It has been shown that yeasts differ significantly in the activity of fructose consumption [25] and in the case of a high proportion of fructose in grapes, as can be seen in the case of the grape varieties Sauvignon Green and Aligote, difficulties may arise due to the complete fermentation of sugars. This problem is typical for wine-making regions with a hot climate, where GFI in some cases is reduced to 0.77 at the time of harvesting [26].

When processing grapes for the production of a must concentrate, it is economically justified to use raw materials with the maximum content of sugars. In addition, technological costs are reduced due to the exclusion or reduction of the acid loss of fresh must, which is due to a low content of titratable acids in high-sugar grapes. However, a must concentrate is more expensive than the sugar-containing products widely represented in the market and used in the food industry, which prompts unfair wine producers to use them in the production of the wines that are falsified wine products.

One of the distinguishing features of the origin of concentrated juices, as already noted, may be the profile of sugars. In our previous studies, it was shown that when concentrating must, the values of GFI characteristic of this batch of grapes remain unchanged [27]. This allows us to use this indicator as a reliable criterion that confirms the grape origin of must before and after concentration.

The study of grape and non-grape products showed (Table 3) that in a grape must concentrate that belongs to the species *Vitis vinifera*, the glucose-fructose index does not exceed 1.0, the proportion of disaccharides is not more than 0.6%, which is close to the values typical for mature grapes with a high sugar content, which is used to obtain this product. Glucose-fructose syrups and the falsifications of a grape must concentrate differ from an authentic grape product in GFI that exceeds 1.04 and a higher proportion of disaccharides – more than 2%. In the case of the production of a must concentrate from grapes of the species *Vitis labrusca* or its hybrids, there is an increase in the limits established for *Vitis vinifera*.

The next stage of our studies was the study of the peculiarities of the profile of sugars in wine materials and the finished products obtained by arrested fermentation or sweetening to provide the specified standards for the content of sugars. The obtained results demonstrate that the values of GFI in the table and liqueur wines obtained by arrested fermentation, by mixing dry wine materials with a grape must concentrate or sugar-containing non-grape products differ significantly (Fig. 3 and 4).

For the table and liqueur wines obtained by arrested fermentation, there is a direct positive relationship between the sugar content and the index value. The correlation coefficient for the whole sample of wines ($n = 249$) is $r = 0.87$ (at $p = 0.95$).

In sweet table wines (Group No. 3), the GFI values are on average 0.47 within the range of 0.16–0.73 (Fig. 3). For semi-sweet wines (Group No. 2), the average value of the indicator decreases to 0.18, the range is 0.08–0.31. Semi-dry wines (Group No. 1) differ by the minimum value of the index – 0.08, with the range of values of 0.02–0.21.

Table 3. Profile of sugars in various sweetening components

Study object	number of samples, pcs.	GFI		Percentage of disaccharides,%	
		average	range	average	range
Grape must concentrate	72	0.95	0.88–0.99	0.3	0.1–0.6
Sugar-containing non-grape components	22	1.12	1.04–1.19	3	2–4

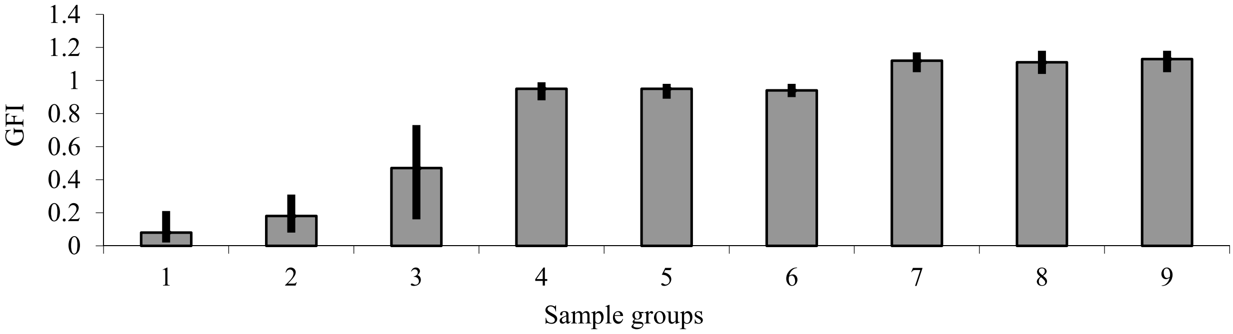

Fig. 3. Glucose-fructose index value in table wines and falsifications (the list of sample groups is provided in the methodological part, Table 1).

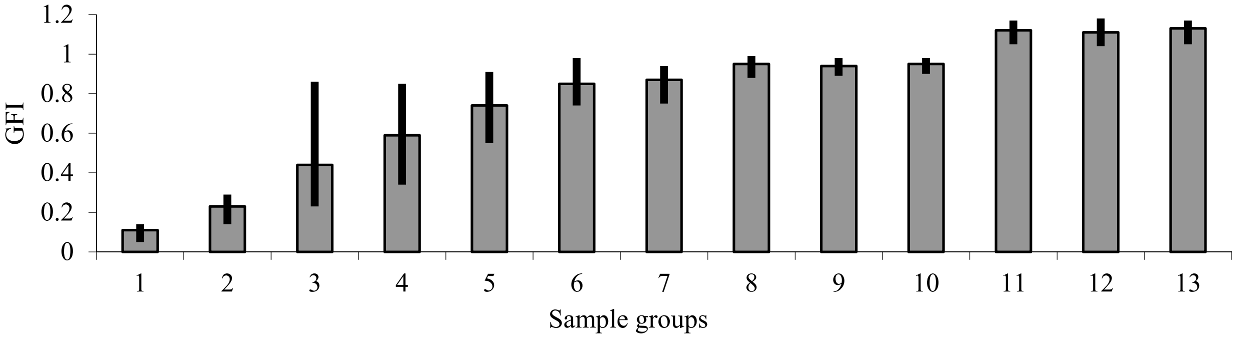

Fig. 4. Value of the glucose-fructose index (GFI) in liqueur wines and falsifications (the list of samples groups is provided in the methodological part, Table 2).

The allowed technological method for sweetening wine materials by adding a grape must concentrate (Group No. 4–6) gives the expected result – regardless of the sugar content, the value of the indicator was 0.95, within the range of 0.89–0.99, characteristic for GFI of grape must (Table 3). Using the example of the authentic samples obtained under microvinification conditions, it has been found that GFI of wine corresponded to GFI of a must concentrate, the difference did not exceed the error limit of the method. The models of table wines, obtained with the use of the forbidden sugar-containing components (Group No. 7–9), were characterized by a sugar profile unusual for grapes. Regardless of the mass concentration of sugars, the average index value was 1.12 with a range of 1.04–1.18. The minimum value significantly differs from the maximum, characteristic for the wine produced with the application of a grape product -1.0 ($F = 319$, at $F_{crt} = 4.3$).

The study of liqueur wines (Fig. 4) confirms the regularities established for table wines. In the case of the wines obtained by arrested fermentation (Group No. 1–7), GFI decreases as the fermentation of sugars increases by 85–90%: with a sugar content of 230–270 g/l, the range is 0.75–0.94 (on average 0.87), with a residual sugar content of 10–20 g/l, the range is 0.05–0.14 (on average up to 0.11). The highest variations of the index – from 0.23 to 0.83 – have been noted for the wines with a sugar content of 50–120 g/l. The glucose-fructose index in the samples produced with the application of grape (Group No. 8–10) and of non-grape products (Group No. 11–13) is 0.94–0.95 and 1.11–1.13, respectively.

The noticeable fluctuations of GFI in both the table and liqueur wines obtained by arrested fermentation can be explained by the different sugar content of the raw materials used for processing, by the considerable variability of industrial yeast races in the ability to assimilate fructose and by various fermentation conditions [10, 25, 26].

The established relationships between GFI and the amount of the fermented carbohydrates are confirmed when studying the high-quality liqueur wines produced at the leading wine-making plants of the Crimea. By reducing GFI and the content of sugars, they can be arranged as follows: Magarach Muscat White, Red Stone Muscat White, Livadia Muscat White → Surozh Dessert Kokour, Bastardo Magarachsky, South Coast Cahors → Sevastopol Port White, Crymsky Port White (Red), South Coast Port White (Red) → Magarach Port White → Madeira Massandra, Madeira Crymskaya → Madeira Dry.

Table 4. Physico-chemical indicators of authentic and falsified table and liqueur wines

Variant*	Content, % vol.	Mass concentration, g/l									Estimate indicators	
	Ethanol	Sugars	Citric acid	Tartaric acid	Malic acid	Glucose	Fructose	Disaccharides	Phenolics	Glycerol	GFI	Percentage of disaccharides, %
Dry table wine material (the sugar content is less than 4 g/l)												
Complete fermentation	14.2	0.6	0.2	2.0	1.7	0.3	0.1	0.2	0.27	6.8	–	–
Semi-sweet table wine (the sugar content is 35 g/l)												
1	12.4	32.3	0.2	2.0	1.8	6.0	26.0	0.3	0.25	5.2	0.23	0.9
2	14.0	34.4	0.3	2.1	1.9	16.5	17.6	0.4	0.30	6.6	0.94	1.2
3	14.1	36.6	0.2	1.9	1.2	18.2	17.5	0.9	0.26	6.6	1.04	2.5
Liqueur wine (the sugar content is 60 g/l)												
1	17.2	60.5	0.3	1.5	2.0	22.1	37.9	0.5	0.50	5.7	0.58	0.8
2	17.8	60.4	0.3	2.0	1.7	28.6	31.3	0.5	0.56	5.8	0.91	0.8
3	17.9	63.5	0.3	1.9	1.5	33.1	28.6	1.8	0.25	5.8	1.16	2.8
Liqueur wine (the sugar content is 160 g/l)												
1	15.9	161.0	0.3	1.5	1.9	78.0	82.2	0.8	0.62	3.1	0.95	0.5
2	16.5	157.9	0.3	2.5	2.0	74.9	81.6	1.4	0.34	5.6	0.92	0.9
3	16.3	159.0	0.2	2.1	1.6	83.0	70.4	5.6	0.24	5.3	1.18	2.8

Note. * 1 – fermentation arrest; 2 – the dry wine material sweetened with a grape must concentrate; 3 – the dry wine material sweetened with GFS.

When determining the authenticity of wines with a sugar content of 120–270 g/l, in some cases the range of GFI of wine overlaps with that of a must concentrate, which does not allow us to identify with a high degree of confidence a method for obtaining a particular sample.

We carried out the studies of wines of this range of sugars according to the additional physicochemical parameters (Table 4), proposed earlier for establishing the authenticity of wines: organic acids, phenolics and glycerol [17, 28–30]. In each group, the samples developed with the preservation of endogenous sugars (Variant 1) and their application in the form of a grape must concentrate (Variant 2) and GFS (Variant 3) were considered.

The results allow us to conclude that the application of a grape must concentrate leads to a logical increase in the content of tartaric acid as a natural component of a grape berry by 0.1–1.0 g, and GFS – to a decrease in its mass concentration by 0.1–0.2 g/l due to the dilution of a sample with a sweetening component. The content of malic and citric acids changes to a lesser degree. Similar trends have been noted with regard to the mass concentration of phenolics – sweetening with a grape must concentrate increases the content of this component from 0.26 g/l to 0.3–0.56 g/l, depending on the applied volume that provides the required standards; sweetening with GFS does not significantly affect the content of the specified substances. The change in the concentration of organic acids and phenolic compounds is noted with respect to the control wine material before sweetening, however, the content of these components is within the limits established for grape wines [17].

It was noted during the experiment that the mass concentration of glycerol is within the range of 5.2–6.8 g/l for all the variants, with the exception of the liqueur wine with a sugar content of 160 g/l obtained by arrested fermentation. In the latter case, the concentration of this substance is much lower – 3.1 g/l, which corresponds to the literature data on the accumulation of fermentation products in wines [28].

The high value of this indicator, typical for the wines obtained by complete fermentation, is not compatible with an index of more than 0.85, characteristic of the wines with a small amount of fermented sugars, and indicates sweetening. This approach allows us to confirm the authenticity of high quality wine technology (PGI, PAO), in the production of which the applied sugar-containing components should not be used.

In all the experimental variants with sweetening, the values of GFI correspond to the ranges established for sugar-containing grape and non-grape components (Table 3), and are 0.91–0.94 and 1.04–1.18, respectively.

The significant indicator that allows us to prove the falsification of wine products is also the share of disaccharides in the total content of sugars. In variants 3, the value of this indicator is 2.5–2.8%, which exceeds the range characteristic of the authentic wines that contain grape sugars – 0.5–0.9% (Variant 1 – fermentation arrest) and 0.8–1.2% (Variant 2 – sweetening with a grape must concentrate). This allows us to include the profile of sugars in the system of indicators to authenticate wines.

The analysis of the imported wine products showed (Table 5) that the values of GFI in the studied sample do not always coincide with the ranges established by us for domestic wines. In samples of semisweet wines No. 2 and 3, the value of GFI (0.83 and 0.84) is higher than that for similar domestic wines and approaches to the wines that contain exogenous grape sugars. Sample No. 6 differs from the general trend in a high value of GFI, but at the same time it is characterized by a high sugar content, which is not typical for domestic table wines. The deviation from the range has also been noted for liqueur samples No. 7 (0.88) and No. 16 (0.59), which may also be due to the peculiarities of the biochemical characteristics of grapes at the time of harvesting and wine technology specific for a particular region. This can be explained by the fact that when obtaining wines there is a variety of technological and biotechnological techniques that can be legislated for separate wine regions, which does not apply to other countries, including Russia. In all cases, the GFI value did not exceed 1.0, which indicates the absence of falsifications in this sample. This is consistent with the foreign literature data [31], as well as the results obtained by LA. Valgina, who showed that the range of the glucose/fructose ratio, characteristic for the imported table wines is 0.7–0.8 [http://mgutm.ru/files/graduates-and-doctors/avtoreferat_valgina_la.pdf]. The proportion of disaccharides in all the analyzed samples did not exceed 0.5%, which is also characteristic of authentic wines. A further study of the wine products of different regions of the world is planned to compare their physicochemical parameters with the ranges established for domestic wines, with the presence of endo- or exogenous sugars.

CONCLUSIONS

The dynamics of the profile of sugars in the "grape-wine" system has been studied for the first time:
– the ratio of different sugars in grapes is determined by the variety-specificity and level of sugar accumulation;
– when concentrating grape must, the glucose-fructose index and the proportion of disaccharides remain unchanged;
– during fermentation, GFI and the content of disaccharides decrease, their values depend on the amount of the fermented sugars;
– GFI and the proportion of disaccharides in the wines that contain exogenous sugars correspond to the values of the parameters of the applied sugar-containing component;
– sweetening the wine material with a sugar-containing non-grape product determines the profile of sugars uncharacteristic for grape wines.

Identifying indicators and the ranges of their variation for authentic wines with various contents of sugars – GFI and the share of disaccharides have been established; to increase the reliability it is necessary to determine the content of glycerol as a marker of fermentation depth.

The revealed regularities make it possible to identify the table and liqueur wines obtained by arrested fermentation, mixing with a grape must concentrate, as well as the inadmissible modification of their composition by introducing sugar-containing non-grape components.

Table 5. Value of the glucose-fructose index (GFI) in imported wines

№	Sample	Country of origin	Sugar content, g/l	GFI	
				Range set for domestic wines	Value in the sample
Table wines					
1	Brackenheim Riesling Kabinett	Germany	23.7	0.08–0.31	0.1
2	Casa Verde Cabernet Sauvignon/Merlot Semi-Sweet	Chile	36	0.08–0.31	0.83
3	Winemaker Sauvignon-Blanc Chardonnay Semi-Sweet White	Chile	37		0.84
4	Chateau d'Yquem Sauternes AOC 1-er Grand Cru Superieur	France	52	0.16–0.73	0.15
5	Eiswein Riesling Blue Nun	Germany	169		0.59
6	Vin Santo del Chianti Classico	Italy	210		0.72
Liqueur wines					
7	Blandys Alvada Rich	Portugal	58	0.23–0.86	0.88
8	Calem Old Friends White Porto	Portugal	63		0.42
9	Calem White and Dry Porto	Portugal	65		0.45
10	Graham's 10 Year Old Tawny Porto	Portugal	113	0.34–0.85	0.68
11	Calem Special Reserve Porto	Portugal	113		0.64
12	Calem Old Friends Ruby Porto	Portugal	115		0.64
13	Alabashli	Azerbaijan	120		0.85
14	Calem Friends White Porto	Portugal	126	0.55–0.91	0.88
15	Agstafa	Azerbaijan	129		0.90
16	Calem Old Friends Ruby Porto	Portugal	148	0.74–0.98	0.59
17	Calem Lagrima Porto	Portugal	164		0.91
18	Macvin du Jura Blanc	France	178		1.00

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ORCID IDs
Nonna V. Gnilomedova http://orcid.org/0000-0003-1784-2370
Nadezhda S. Anikina http://orcid.org/0000-0001-5682-3426

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