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DEVELOPMENT OF IMPROVED TECHNOLOGY FOR THE PRODUCTION OF STRONG WINES OF MARSALA TYPE ON THE BASIS OF ENZYMATIC CATALYSIS

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In the assortment of wines produced in the Republic of Azerbaijan, strong wines occupy a significant place. To improve their technology, a number of technological modes and parameters aimed at improving the quality of finished products and the use of modern technology were proposed and tested.

As a result of the study, the effectiveness of the use of the mixed-action enzyme preparation Vinozim or Ultrazyme in the production of strong vintage wine of the Marsala type according to the blending scheme using the first must and press fractions was determined. It has been established that the use of this preparation in the process of fermentation of pomace provides a rational supply of phenolic substances for blends of marsala, and in the process of infusion of pomace of nitrogenous components and pentosis.

The fundamental possibility of obtaining high-quality wine materials for vintage marsala under the conditions of processing grapes of the variety Bayan-Shirei and Rkasiteli "in the red way" has been studied. Rational modes for obtaining blended wine materials for Marsala, based on the technology of fermentation or long-term infusion of pomace, have been developed. The effect of various enzyme preparations on the quality of wine materials for Marsala has been studied; a rational variant of blending and aging of wine materials for Marsala was experimentally substantiated.

It has been established that the rational option for obtaining vintage marsala is a blend of dry-fortified wine material and mistel, or dry-fortified wine material and vacuum must. Analysis of the dynamics of maturation of blended wine materials and data on changes in their chemical composition confirmed the choice of a rational scheme for their production and made it possible to establish the expediency of aging blends for marsala for 2.5 years. To improve the quality of ordinary marsala wine, a new technique for producing vacuum must was devised

Keywords: enzyme preparation, vacuum must, pomace fermentation, pomace infusion, pomace heat treatment, fluorucharization

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1. Introduction

Grapes with high nutritional value are widely distributed in most countries of the world, including Azerbaijan [1].

The intensive growth and development of the wine sector in the food industry makes it necessary to radically change some of the established traditions of winemaking and introduce modern technological regimes and parameters of industrial processing of grapes, treatment and aging of wine materials and wines. In this regard, the issues of further improving the technology of wine production and improving its quality is one of the important problems of world winemaking practice [2].

Consumers demand quality wines, in addition to safe and nutritious characteristics. As in other sectors in the food industry, wine producers have implemented various technological advancements based on biotechnological resources, such as dry yeast, ferments of acidic lactic acid bacteria, or enzymes. There are various ingredients or additives (potassium sorbate, sulfur dioxide, etc.) and technological admixtures that are allowed to be added during production; they vary depending on the type of wine, the technological function, or the legislation of the country. In this context, the use of commercial enzymes in the wine industry has a multitude of objectives, especially in the stages of processing (maceration, extraction), stabilization (clarification, filtration), and aging (ripening on the lees). The activity of enzymes naturally present in grapes and microflora plays an important role in winemaking processes. Unfortunately, the action of such endogenous enzymes is not enough to obtain regular results in the production of high-quality wines [3].

Food-grade industrial enzymes offer significant processing improvements. This leads to an overall economic effect. Industrial enzymes have quantitative advantages, such as increasing the yield of free juice and pressed juice. Qualitative advantages such as improved color extraction of red grape varieties, color stability, and extraction of phenols of red wines [4].

The problem of stabilizing ordinary grape wines is acute as there are frequent cases of violation of their presentation due to turbidity during the delivery and storage in the trading network. This also applies to the wine products from

Azerbaijan, where improving the quality of wines and ensuring the stability of wines is one of the key tasks facing industry specialists [5].

In the assortment of wines produced in the republic, strong wines occupy a significant place. To improve their technology, a number of technological modes and parameters aimed at improving the quality of finished products and the use of modern technology were proposed and tested [6].

The range of strong wines produced by various wineries is very narrow, and the organoleptic qualities of these wines do not always meet the requirements. Monitoring to study the quality of strong wines showed that the main disadvantages of this group of wines are insufficient completeness and aromaticity, quantities of phenolic and nitrogenous substances, pentose of other components of the extract [7].

The study of the effect of enzyme preparations of a new generation and polyenzyme compositions of higher activity on the juice yield of grapes, the dynamics of clarification of must and wines, the transformation of biopolymers is of scientific and practical interest.

A serious problem standing in the way of the introduction of modern technological techniques aimed at intensifying the processes of wine production is the preservation of product quality. A large share in the total volume of winemaking is occupied by special strong wines without aging. A characteristic feature of their preparation is the long-term contact of the must with the pomace, as well as the use of press fractions of the must – secondary raw materials obtained in the production of table and champagne wine materials [8].

Therefore, research into the development of an improved technology for the production of strong wines such as marsala based on enzymatic catalysis is relevant.

2. Literature review and problem statement

Enzymes play a decisive role in the ancient and complex process of winemaking. From a scientific and technical point of view, wine can be considered as a product of the enzymatic transformation of grape juice. Starting from the prefermentation stage, through fermentation, post-fermentation, and aging, enzymes are the main driving forces that catalyze various biotransformation reactions. These biocatalysts are obtained not only from the grapes themselves but also from yeast and other microbes (fungi and bacteria) that inhabit vineyards and wine cellars [9].

Marsala is an original strong wine. A distinctive feature is the specific tones of the “ship resin” in the aroma, softness in taste, tones of rye crust and red-hot nut. Marsala is a highly tonic drink. The homeland is the western part of the island of Sicily (Italy), in the area of the towns of Marsala [10].

Marsala differs from other strong wines in an increased amount of the above extract. The formation of the extract mainly involves glycerin, nitrogenous, phenolic substances, and products of melanoidin formation, the content of which is much higher than in other wines. This type of wine appeared as a result of attempts to make Portuguese wines widely known at that time – Madeira and port.

The use of specially selected strains of wine yeast and enzyme preparations is an effective way to improve the quality and stabilize special wines without aging to the turbidity of colloidal nature [11].

An effective technique to stabilize this category of wines, based on an understanding of the essence of the processes of formation of turbidity of a colloidal nature, is the use of highly specific enzymatic hydrolysis of biopolymers. There are various enzyme preparations in the market. There are a limited number of studies reporting the theoretical justification of the composition of preparations to increase the colloidal stability of wines, as well as the creation of polyenzyme compositions for this purpose [12].

The use of enzyme preparations is one of the promising areas in modern winemaking, facilitating the process of grape processing and contributing to the development of optimal technological modes for obtaining high-quality products. The quality of these wines is closely related to the use of enzymes in the winemaking process. Enzymes are involved in the pre-treatment, fermentation, filtration, flavoring, aging, and storage of fruit wines. This review systematically illustrates the role of pectinase, β-glucanase, β-glucosidase, glucose oxidase, lysozyme, protease, tannase, and urease in wine production and their current state of production. It also provides a theoretical basis for the better use of various enzymes in the production of wines [13].

The quality of wine, its structure and chemical composition depend on the characteristics of grapes as raw materials, the characteristics of alcoholic fermentation, and the oenological techniques used. Awareness of the important role of enzymes in winemaking contributes to the development of various new strategies for optimizing the production process. Numerous studies have confirmed the positive effect of the use of enzymes in the production of food and beverages, on improving the quality of the final product, optimizing the production technologies used [14].

The choice of preparations, the development of technological methods for their use to stabilize and improve the quality of wines of mass production and consumption are relevant [15].

The data showed the need to search for more rational technological schemes for the preparation and stabilization of wines such as Marsala. In this direction, the use of mixed-action enzyme preparations, the scientifically based selection of blending components, as well as the justification of the improved technology of wines such as Marsala [16] are especially promising.

3. The aim and objectives of the study

The aim of our study is to improve the technology for the production of strong vintage wines such as Marsala under the conditions of Azerbaijan based on the use of new generation enzyme preparations Vinozyme, Glucanax, Ultrazyme.

To accomplish the aim, the following tasks have been set:

– to investigate the effect of various enzyme preparations on the quality of wine materials for Marsala;

– to study the fundamental possibility of obtaining high-quality wine materials for vintage marsala under the conditions of processing grapes of the variety Bayan – Shirey and Rkasiteli “in the red way”;

– to develop rational modes for the production of blended wine materials for Marsala, based on the technology of fermentation or long-term infusion of pomace;

– to experimentally substantiate a rational variant of blending and aging of wine materials for Marsala.

4. The study materials and methods

4. 1. The study objects

As an object of research, the technology for the production of strong wine such as Marsala using a new generation of enzyme preparations was chosen. The modern technique of obtaining must leads to a significant enrichment of its high-molecular substances of colloidal nature, which greatly complicate clarification and obtaining more stable wines.

Experiments in the laboratory were carried out using Bayan-Shirei and Rkasiteli grapes, with a sugar content of 17–22 g/dm^3.

For processing, enzyme preparations of a new generation of the company "Novo-Nor-disk (Denmark), vinozime, glucanax ultrazyme were used. They provide not only a high yield of must but also hydrolysis of biopolymers, accompanied by a fairly good clarification without the use of pasting sorbents [17].

To study the effect of enzyme preparations on the yield of must, they were added to the pomace in the amount of 0.0125 % powder in dissolved form. After 45–60 minutes of fermentation, the pomace was infused for 14–16 hours or by heat treatment of the pomace at a temperature of 50–55 °C for 0.5–1 hour.

In the processing of grapes, a laboratory press (laboratory conditions), centrifugal crushers CDG-20, drippers VSN-20, and a screw press PD-20 were used in production [18].

Wine materials were prepared from the combined must of the first and press fractions, after a long infusion of the pomace, into which sulfur dioxide (100 mg/dm^3) and enzyme preparations in the form of a 10 % suspension in doses of 0.005–0.3 % vos were introduced. Wine materials were brought to the appropriate conditions with rectified alcohol. As a control, only wine materials were used, without obtaining enzymatic processing, infusion, and fermentation on the pomace.

The production sample of vacuum must (Moldovan) was characterized by the content of the components of the extract, color, concentration, and composition of sugars, amino acids, phenolic substances, aldehydes, the sum of phenolic and other compounds. An approximate "standard" of the composition of the vacuum must ready for blending was determined, after which experiments were carried out on the effect of temperature, oxygen, direct and alternating current treatment on the rate of chemical transformations of the must intended for the manufacture of vacuum must.

A rational mode for obtaining vacuum must was determined [19].

4. 2. Research methods

In the course of the study, the methods of analysis adopted in oenochemistry and set forth in the relevant state standards and procedures [20] were used:

1. Ethyl alcohol – by an alcohol meter.
2. Sugar – by specific weight in the must, by the methods of Bertrand, Len and Einon in wines.
3. Titratable acidity – by the titration of 0.1 N with sodieum alkali solution, phenolrot indicator.
4. pH – by using a laboratory PH meter PH-340.
5. Extract – by a pycnometric method.

All determinations were made in at least five repetitions, the reliability of the results was proved by mathematical processing of the data.

Under the conditions of microwinemaking, in accordance with the matrix of a fractional factor experiment, experimental blended wine materials and mistels for Marsala were obtained.

4 schemes were studied:

a) dry-fortified wine materials obtained by fermentation of pomace;

b) the same materials obtained by heat treatment of pomace;

c) the same materials obtained by fermentation of unclarified must;

d) mistel with alcohol and infusion of pomace.

Various variants of the experiments provided for a change in the indicators: temperature and duration of the infusion process, the level of sulfitation, the type and dose of the enzyme preparation used.

Wine materials before and after blending were analyzed by conventional methods, in oenochemistry [21].

By tasting and data processing on a computer, the optimal modes of processes were determined.

A blend of wine materials selected by tasting was carried out; a blend and original wine materials were laid for vintage aging.

The procedure of setting up the experiment was as follows.

We prepared 2.0 liters (200 cm^3 for each mode) of must of the Rkatsiteli variety, in which the light absorption index was preliminarily determined at a wavelength of 440 nm. The must was treated under different operating modes: 1; 10; 30; 60 minutes, the current form of the must current for each mode: 0.2; 0.4; 0.6; 0.8 mA. For fluctuarization, the ASB-2-1 apparatus was used [22].

After processing, for an objective assessment of the intensity of the color of the must, depending on the processing modes, a rotometric method for determining light transmission at a wavelength of 440 nm was used.

5. Results of the study of an improved technology for the production of strong wines of the Marsala type based on enzymatic catalysis

5. 1. Investigation of the effect of various enzyme preparations on the quality of wine materials for Marsala

The must treated under the modes of 1 min and 1 h (maximum and minimum optical density) was evaporated on a Marsala sample based on the concentration of phenolic substances. The density was 663.5 mg/dm^3, nitrogenous substances (mainly amine nitrogen) 355.5 mg/dm^3, pentose 1.85 mg/dm^3. To ensure the required level of compounds entering complex reactions of redox transformations, traditional technological methods of pomace extraction (infusion, fermentation, heat treatment) must, as indicated, be combined with the use of enzyme preparations [22]. There is a known experience in the use of preparations of pectolytic, hemicellulous, cellulolytic type of action in the production of dessert sweet and semi-sweet wines, as well as wines such as port wine and madeira. However, many of these preparations have not yet been industrially mastered. At the same time, new promising preparations appeared, which it was advisable to check, along with the known ones, for the effectiveness of use in the production of blended wine materials for Marsala.

The effect of enzyme preparations on the accumulation of some components of the extract in wine materials is shown in Table 1.

Table 1

Effect of enzyme preparations on the accumulation of some components of the extract in wine materials

Variants, name of the preparation used	Mass concentration of components by pomace extraction options, mg/dm^3								
	Fermentation of pomace			Infusion of pomace			Heat treatment of pomace		
	Amine nitrogen	Phenolic substances	Pentoses	Amine nitrogen	Phenolic substances	Pentoses	Amine nitrogen	Phenolic substances	Pentoses
Preparation-free control	157.6	1437.1	1125	157.0	670.7	1700	178.5	557.7	1125
Pectinex USPL	174.7	1430.0	1100	No experiments were carried out			No experiments were carried out		
Pectinex BE	181.6	1501.5	1925						
PEC 1	164.4	1175.8	600	250.1	356.1	2100	174.7	988.2	435
PEC 2	152.5	1287.0	1375	No experiments were carried out			No experiments were carried out		
Vinozim	150.7	1351.4	2250	304.9	470.5	1570	147.5	643.6	1125
Ultrazyme	171.3	2216.5	650	255.5	243.1	2000	206.5	629.2	1225
Glucanex	147.3	986.7	1100	274.1	500.5	2250	143.9	657.5	1085

During the grape processing seasons of 2017–2018, a series of fortified wine materials for Marsala-type wine was obtained, provided for three main schemes for extracting pomace (fermentation, infusion, heat treatment) along with the use of enzyme preparations – Vinozyme, Ultrazyme, and Glucanax.

5. 2. Studying the fundamental possibility of obtaining high-quality wine materials for vintage Marsala under the conditions of grape processing

The general characteristics of wine materials for wine such as Marsala are given in Table 2.

For the most part, these wine materials had an acceptable tasting assessment and corresponded to the type of fortified wine materials in terms of the concentration of alcohol, sugar, volatile acids (Table 2).

The volume of titratable acids of wine materials for Marsala wine, analyzes were carried out in 5 parallel variants (%) and an average value of 4.052 was obtained. For comparison, according to the literature data, it is 4 %.

The results of statistical data processing are given in Table 3.

Table 2

General characteristics of wine materials for Marsala type wine

Variant of preparation of wine materials, used enzyme preparation	Alcohol, %, vol.	Sugar, g/dm^3	Acids, g/dm^3		pH	Reduced extract, g/dm^3	Chromaticity	Tasting evaluation, points
			Titratable	Volatile				
Fermentation of pomace								
Control without preparations	17.8	0.30	5.10	0.24	4.10	16.1	78.6	7.76
Vinozyme	16.9	0.15	4.10	0.27	3.55	14.9	78.7	7.68
Ultrazyme	17.1	0.12	4.13	0.36	3.80	15.8	78.1	7.70
Gluconex	17.3	0.33	4.15	0.30	3.80	14.3	80.9	7.78
Infusion of pomace								
Control without preparations	16.3	10.20	4.05	0.10	4.05	27.5	84.3	7.76
Vinozyme	14.0	10.60	4.20	0.10	3.85	24.4	85.5	7.76
Ultrazyme	16.0	10.90	4.10	0.10	3.70	21.5	84.9	7.80
Gluconex	16.2	10.90	4.10	0.10	3.80	20.3	84.4	7.85
Heat treatment of pomace								
Control without preparations	17.6	0.15	4.50	0.20	3.60	17.4	74.4	7.70
Vinozyme	17.4	0.19	4.15	0.25	3.90	17.7	76.4	7.50
Ultrazyme	17.6	0.29	5.10	0.18	3.60	23.4	68.9	7.72
Gluconex	17.4	0.16	4.80	0.15	3.75	17.8	77.8	7.80

Table 3

Results of statistical data processing

No.	The amount of minerals, %	$x_1 - \overline{x}$	$(x_1 - \overline{x})^2$
1	2	3	4
1	4.050	–0.002	0.000004
2	4.150	0.098	0.009604

Continued from Table 1

1	2	3	4
3	3.970	–0.082	0.066724
4	4.010	–0.042	0.001764
5	4.080	0.028	0.000784
n=5	$\sum x = 97.6$	–	$\sum (x_1 - \bar{x})^2 = 0.018860$
Variance of the population $D(x) = \dfrac{\sum (x_1 - x)}{n-1} = 0.0044715$			
Standard deviation $\sigma = \sqrt{D(x)} - 0.0687$			
Coefficient of variation $V = \dfrac{\sigma \cdot 100}{x} = 1.6954$			
Mean square error $M = \pm \dfrac{\sigma}{\sqrt{n}} = 0.0307$			
Percentage of error $M\% = \dfrac{m}{x} \cdot 100 = 0.7576$			
Next, we find the confidence error $E_x = \pm n \cdot m = 0.08$			
The average interval for this deviation indicator $\bar{x} + E_x = 4.13,\ \ \bar{x} - E_x = 3.97$			
Relative error $\Delta x = \dfrac{E}{x} \cdot 100 = 1.97$			

Thus, the relative error is 1.97 %. Consequently, the experimental error does not go beyond the calculated one. The rest of the indicators were determined in the same way.

5. 3. Development of rational modes for the production of blended wine materials for Marsala

The mass concentration in wine materials for Marsala of components that determine the quality and typicality is given in Table 4.

The maximum content of amino compounds falls on the variants of pomace infusion, in which both cellulolytic and hemicellulose preparations are used.

5. 4. Justification of a rational variant of blending and aging of wine materials for Marsala

The composition of the vacuum must, depending on its production technique, is given in Table 5.

Thus, based on the results of this series of studies, a new technique for obtaining vacuum must is proposed, which involves processing the initial must before evaporation with a fluctuating current (0.6 mA, 1 hour).

At the next stage of work using an experimental vacuum must, a series of blended wine materials were obtained (Table 6).

The composition of blends for Marsala using an experimental vacuum must is given in Table 6.

Table 4

Mass concentration of components in wine materials for Marsala, which determine the quality and typicality*

Variant of preparation of wine materials, used enzyme preparation	Nitrogenous substances, mg/dm^3		Phenolic substances, mg/dm^3			Carbohydrates, mg/dm^3			Aldehydes, mg/dm^3	Glycerin, mg/dm^3
	Amine nitrogen	Protein	General	Monomeric flavonoids	Leucoanthocyanins	Polysaccharides	Oligosaccharides	Pentoses		
Fermentation of pomace										
Control without preparations	167.0	1.0	421.8	123.5	153.9	780.5	670	1125	14.0	4.23
Vinozyme	167.5	6.0	386.1	73.5	54.1	505.0	845	1100	11.6	4.7
Ultrazyme	166.0	2.0	471.9	99.8	54.6	505.0	955	1100	12.1	4.32
Gluconex	164.5	1.0	572.5	106.5	75.9	655.0	895	1475	12.2	4.2
Infusion of pomace										
Control without preparations	206.0	3.0	164.5	22.8	25.3	1450	900	1900	21.6	The analysis was not carried out
Vinozyme	259.0	3.0	231.5	22.8	52.8	3600	750	1830	9.0	
Ultrazyme	265.5	3.2	257.4	10.5	44.0	1625	1225	1950	15.2	
Gluconex	255.5	5.0	243.1	22.8	30.2	1830	570	2000	10.6	
Heat treatment of pomace										
Control without preparations	178.5	6.8	557.7	84.7	100.9	740	710	1125	32.0	6.2
Vinozyme	203.0	3.0	600.6	90.3	178.9	500	750	1275	38.2	6.4
Ultrazyme	210.0	10.6	689.2	10.7	164.3	610	640	1200	88.4	6.7
Gluconex	206.5	0.6	629.2	95.2	176.8	552.5	318	1225	28.0	7.12

*Note: * – data are provided for wine materials obtained during the processing of grapes with a mass concentration of sugars of 16.2 g/100 cm^3*

Table 5

The composition of the vacuum must depending on its production technique

Samples of vacuum must	Current form	Duration of processing	Current density, m A	Mass concentration of components in vacuum must										Optical density, at 440 nm %		
				Sugar, g/100 cm^3	Titratable acids, g/dm^3	Reduced extract, g/dm^3	Protein, mg/dm^3	The amount of phenolic substances	Monomeric flavonoids, mg/dm^3	Leucoanthocyanins, mg/dm^3	Aldehydes, mg/dm^3	Pentoses, mg/dm^3	Total nitrogen mg/dm^3	Original must	Must processing	Vacuum must
Industrial batch of vacuum must (Italy)	–	–	–	91.3	39.0	56.4	2650	2574.0	70	330.0	135	10.0	2520	–	–	29.1
Vacuum must without treatment (control)	–	–	–	84.5	45.0	25.7	580	2030.6	63	429.0	200	6.5	2240	–	–	54.8
Vacuum must, treated	–	1 min	0.2	84.0	57.0	34.9	128	2288.0	70	400.4	40	9.5	2975	29	29	42.0
fluctuating current	–	1 hour	0.6	83.3	45.0	30.3	117	2330.9	70	352.0	100	8.5	2905	21	23	40.0

Table 6

The composition of blends for Marsala using an experimental vacuum must

Component	Acids, g/dm^3		pH	Reduced extract, g/dm^3	Chromaticity, Y, %	Amine nitrogen, mg/dm^3	Amine nitrogen, mg/dm^3			Carbohydrates, mg/dm^3			Carbohydrates, mg/dm^3
	Titratable	Volatile					Sum	Monomer. flavonoids	Leucoanthocyanins	Polysaccharides	Oligosaccharides	Pentoses	
Blend: fermentation of pomace with Vinozyme x mistal x vacuum must	5.1	0.22	3.8	20.8	72.7	239.0	768.4	145	82	775	1050	1560	3.7
Blend: fermentation of pomace with Vinozyme x mistal without preparations x vacuum must	4.9	0.18	4.1	18.5	78.6	205.0	643.2	128	76	830	950	1100	3.6
Blending: pomace fermentation (control) x vacuum must	8.9	0.24	4.1	21.7	72.3	194.0	676.0	136	186	1190	1230	2125	4.3
Blend: fermentation of pomace Ultrazyme x vacuum must	8.0	0.36	3.85	21.3	74.0	202.0	728.0	106	87	925	1530	2100	4.32
Blend: pomace fermentation, Glucanex vacuum-must	8.5	0.2	3.85	20.0	76.1	196.0	827.0	113	109	1070	1470	2450	4.2
Moldavian Marsala (standard)	7.95	0.2	4.3	16.0	24.4	343.0	665.5	17.5	94.6	1550	1050	1850	5.47

On the basis of the experimental results obtained, the technological scheme for the production of Marsala-type wine has been improved (Fig. 1).

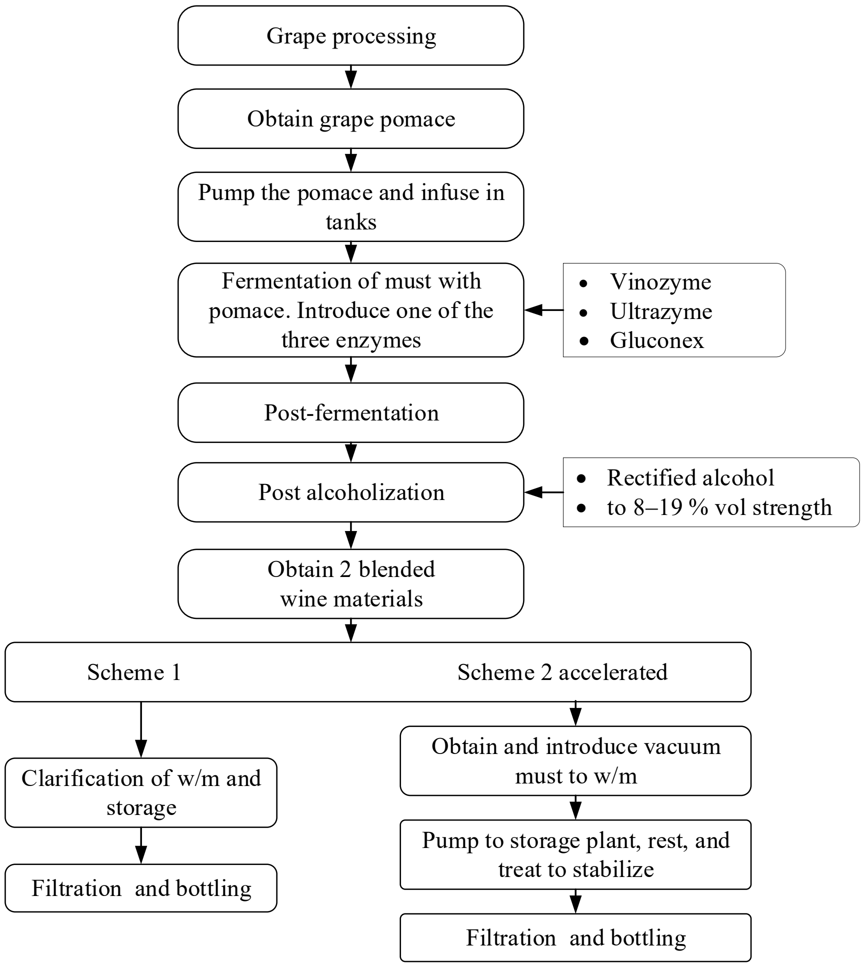

Fig. 1. Improved technological scheme for the production of Marsala wines

The grapes are processed and separated from the ridges in the production line and the resulting pomace is pumped using a pomace pump into the apparatus for infusion and fermentation of the must. Then the enzyme preparation Vinozyme, Glucanex, or Ultrazyme is injected at a dose of 0.00125 units/g, then the pomace is pumped on a dripper, where the gravity fractions are separated from the flowing pomace, sent for pressing. All fractions of the must obtained are sent for post-fermentation, after which additional alcoholization and clarification of the resulting wine material are carried out. Then it is pumped into a blending tank in the case of using an accelerated scheme – the production and introduction of vacuum must, then the mixture is transferred to an aging workshop or accelerated oxygen treatment for maturation. Next, rest and clarification are carried out, and processing in order to stabilize, after which the resulting wine is filtered and bottled.

6. Discussion of results of the technology for the production of strong wines such as marsala based on enzymatic

As a result of our study, the effectiveness of the use of the mixed-action enzyme preparation Vinozyme or Ultrazyme in the production of strong vintage wine of the Marsala type according to the blending scheme using the first must and press fractions was determined. It has been established that the use of this preparation in the process of fermentation of pomace provides the best supply of phenolic substances for marsala blends, and in the process of infusion of pomace, nitrogenous components, and pentoses.

Studies have shown (Table 1) that, depending on the pomace extraction scheme and the type of preparation used, fortified wine materials can be obtained, significantly differentiated in the content of amino acids, phenolic substances, and pentoses. At the same time, the highest concentrations of amine nitrogen and pentoses are characteristic of variants with an incomplete fermentation process (infusion of pomace at normal temperature, followed by alcoholization at an early stage of fermentation). The maximum concentrations of phenolic substances were found in the variants of fermentation of pomace dry. These variants, which are characterized by the course of most of the extraction processes under conditions of excess CO_2 and trace amounts of oxygen, are characterized by "moderate oxidation" of phenolic substances, which, however, are marked by enzyme preparations. The presence of cellulolytic preparations is apparently accompanied by accelerated oxidation and condensation of phenolic substances [23], as a result of which the level of phenolic substances in wine materials obtained with glucanex turned out to be minimal. The most promising is the preparation of mixed-type action – Vinozyme and PEC 1 (Table 1), in the presence of which the mass concentration of phenolic substances in the wine material exceeds the control by more than 50 %. In variants with pomace infusion, along with a high accumulation of amino acids and pentoses, a low content of phenolic substances was noted. Heat treatment of pomace, although it intensifies the extraction processes, is accompanied by a simultaneous increase in the intensity of oxidative processes, as a result of which the average values of the concentration of the studied components were obtained for all variants of the experiments. Thus, it follows from the data obtained that it is apparently difficult to ensure the simultaneous high accumulation of all three groups of compounds by one of the methods of pomace extraction. More promising are the options for fermentation of pomace (for the accumulation of phenolic substances) and infusion of pomace (for the accumulation of amine nitrogen and pentoses). For these options, the use of preparations of a mixed type of action, with the predominant activity of xylanases – Glucanex, Vinozyme – appears rational. However, it is possible to definitively justify the choice of a particular preparation only by the totality of technological experiments. Nevertheless, it is obvious that enzyme preparations can significantly increase the efficiency of pomace extraction processes [24].

The specific scheme of extraction of pomace is decisive in the values of the indicators of the reduced extract and color. Thus, the infusion of the pomace is distinguished by the maximum values of the reduced extract and the brightness of the color (Y, %), which confirms the "soft" modes of extraction and oxidation of the components of the extract. The values of the indicator Y % in the variants with heat treatment, as well as the indicators of the above extract, indicate more intensive oxidation inherent in these variants. For indicators included in the general characteristics of wine materials, the influence of enzyme preparations is not noticeable. It can only be noted that wine materials with Vinozyme had, as a rule, a higher tasting rating [25]. Much more contrasting is the use of those and other enzyme preparations against the background of the analysis of the components that determine the quality and typicality of fortified wine materials (Table 4). The maximum content of amino compounds falls on the variants of pomace infusion, in which both cellulolytic and hemicellulose preparations are used. Under the conditions of processing of raw materials with a moderate mass concentration of sugars (16.2 g/100 cm^3), the total mass concentration of phenolic substances turned out to be slightly higher in variants with heat treatment of pomace. However, even in this case, the fermentation of the pomace with Glucanex provided a level of these compounds close to the maximum. In addition, this variant of enzymatic processing of pomace is characterized by a higher concentration of monomeric flavonoids, which is more significant in assessing the "reserve" of phenolic substances that can be consumed in oxidative processes.

Infusion of pomace is characterized by a maximum concentration of carbohydrates – poly- and oligosaccharides, as well as pentoses. Since the presence of carbohydrates of varying degrees of polymerization in wines is associated with such an organoleptic sign as the "fullness" or "oiliness" of the product. The data obtained (Table 4), taking into account the necessary long-term aging of wine materials, can be interpreted from a positive point of view, stands out here among other preparations also with Glucanex.

The intensification of oxidative processes in the variants with heat treatment of pomace was accompanied by an increased accumulation of aldehydes in the wine materials of this series. In other embodiments, the concentration of these compounds was low. As for glycerin, the mass concentration of this component in wine materials was found in the range of 4.2 to 8.12 g/dm^3. Heat treatment, which contributes to the effective extraction and hydrolysis of triglycerides of the wax coating of the berry, was distinguished by higher concentrations of this product, which affects the fullness of wines.

Data in Table 4 confirm the need to differentiate the technology for the production of wine materials for Marsala into at least two groups, due to the impossibility of ensuring the maximum accumulation of all the required components within one pomace extraction scheme. However, it is difficult to derive from these data an unambiguous conclusion of a specific technological sequence for the production of wine materials, without the involvement of additional data characterizing, first of all, volatile components and the aroma of the products obtained.

Gas chromatographic analysis showed [25] that the most significant factor regulating the concentration of higher alcohols and esters in wine materials is the method of extracting the pomace, the second most important is the use of enzyme preparations. Fermentation of the pomace while dry leads to the accumulation of 909–1193 mg/dm^3 in wine materials of aliphatic alcohols, 2-phenylethanol, and butylene glycol, while the infusion of the pomace by subsequent short-term fermentation by alcohol of the must is only 8–36 mg/dm^3. Similarly, high concentrations of isoamyl acetate and ethyl esters of organic, fatty acids, and aromatic alcohols (138–167 mg/d^3) were found in the pomace fermentation variants, whereas only 5.5–6.03 mg/dm^3 were found in the pomace infusion. Obviously, in the case of using a blending scheme in the production of Marsala, the decisive role in the content of the components in the blends that are the "background" for the manifestation of the aroma of terpene glycosides will be played by option with the fermentation of pomace. Therefore, it is interesting to note that the experimental scheme of pomace fermentation using Vinozyme and Ultrazyme is characterized by a smaller accumulation of higher alcohols, and above all isoamyl, undesirable with the position of aromatic effects [26].

For a number of compounds of the group of fatty acid esters, for which a number of followers have confirmed a positive effect on aroma (ethyl capronate, ethyl caprynate, ethyl laurate), the option with enzymatic treatment also seems preferable.

Based on the results of the completed cycle of studies, a technological scheme (Fig. 1) for the production of basic blended wine materials for the vintage type of Marsala was devised. The scheme provides for the processing of Rkatsiteli grapes with a mass concentration of sugars of at least I6 g/I00 cm^3, by crushing, separating, and sulfitating the pomace (50–I00 mg/dm^3 sulfur dioxide). The enzyme preparation Vinozyme (0.01 % with standard activity) is injected into the resulting pomace, after which its further processing proceeds in two directions. The first of them involves the fermentation of the pomace while dry, followed by the separation of wine material and additional alcohol up to 8–19 % by volume. The second is the infusion of the pomace for 36 hours (without heating), followed by the separation of the liquid phase and its immediate alcoholization to 19–20 % of the volume fraction of alcohol. Such a technological scheme makes it possible, as noted, to obtain two main blended wine materials, characterized together by a high accumulation of nitrogenous phenolic substances, pentoses, and oligosaccharides, glycerol. The blended material obtained by fermentation of the pomace with the introduction of the preparation Vinozyme is also close to the chosen standard (Moldovan Marsala) in terms of titratable and volatile acidity, pH. It has a reduced color (in terms of Y, %) and a lower content of aldehydes, which indicates the incompleteness of oxidation processes. The possibility of implementing these processes during the aging of wine materials is confirmed by increased values of the given extract, phenolic substances, including monomeric flavonoids and leucoanthocyanins, more in the experimental sample of oligosaccharides and glycerol. At the same time, the control variant with pomace fermentation is characterized by a significantly higher mass concentration of higher alcohols and a lower mass concentration – pentoses, oligosaccharides, phenolic substances. In general, its tasting score turned out to be significantly lower than the prototype. In variants with the infusion of pomace, a reduced mass concentration of glycerol, phenolic substances, and in general the components of the above extract was recorded. On the contrary, these options, especially with enzymatic treatment, indicate the possibility of compensating for a certain lack of amine nitrogen, pentoses, which takes place in samples with pomace fermentation, by blending.

The composition of blends, providing a combination of options for heat treatment and infusion of pomace, is given in Table 6 (a sample from a series of blends, the most typical for this group of experiments, is given). A distinctive feature of these blends is an increased mass concentration of glycerol and a slightly higher titratable acidity. The reason for the higher accumulation of glycerol in heat-treated variants has already been discussed. As for the difference in the mass concentration of organic acids, it is caused, apparently, by a more significant consumption of acids by yeast in the variants of fermentation of the pomace while dry.

According to the main indicators of the composition, which are of interest from the point of view of the formation of wines such as Marsala, blends using the method of heat treatment of pomace are inferior to a series of samples «fermentation of pomace» and «infusion of pomace». This is obviously explained by the reduced concentration of phenolic and nitrogenous substances in wine materials with heat treatment of pomace, which ultimately affects the composition of blends. Early oxidation of phenolic substances, characteristic of the heat treatment of pomace, is also reflected in the mass concentration of monomeric flavonoids, the supply of which in blends can ultimately be assessed as insufficient.

Thus, the analysis of the composition of various blends before laying on aging leads to a conclusion. It includes the rationality of using the scheme «dry strength wine material obtained by fermentation of pomace with the introduction of Vinozyme + sweet wine material, obtained by prolonged infusion of pomace with the introduction of the same preparation.» The final conclusion about the possibility of this or that blending scheme can be made after analyzing the dynamics of the composition of the blends during their aging. In addition, the issue of introducing vacuum must into the blend was of particular interest.

It has been established that of all the studied techniques for the production of blended wine materials for Marsala, from the standpoint of their rational composition, two schemes are the most promising: fermentation and infusion of pomace in the presence of Vinozyme. With all the advantages of these schemes, a certain «deficit» of the content of amine nitrogen components and phenolic substances was recorded in the obtained blends, which can adversely affect the quality of the finished product after aging the blends. In this situation, it was advisable to investigate the possibility of introducing vacuum must into the blends, which allows for a certain adjustment of their composition.

A detailed description of the industrial batch of vacuum must (manufactured in Italy) is given in Table 5. Compared to this sample, the laboratory batch of vacuum must was characterized by a significantly lower reduced extract, a lower mass concentration of phenolic substances, total nitrogen, and a higher concentration of aldehydes. In order to rationalize the composition of the vacuum must, experiments were carried out on the treatment of the initial samples of grape must with a fluctuating current, followed by its evaporation on a vacuum-rotary evaporator. In the process of processing the must with a fluctuating current, regardless of its density, an increase in the light transmission value (440 nm) was first recorded in the must, and then (after 10 minutes of processing or more) its sharp decrease. This fact testifies to the occurrence of redox processes in the must under the influence of a fluctuating current, in which carbohydrates, nitrogenous and phenolic compounds are probably involved. Table 5 shows the result of these processes: the composition of the control vacuum must (without current treatment) and two prototypes with minimum and maximum treatment. It can be seen that the prototypes differ from the control one by a significantly higher content of the components of the above extract – organic acids, phenolic substances, pentoses, and total nitrogen, as well as a darker brown color. The concentration of protein and aldehydes turned out to be lower in experimental versions. The tendency to a certain decrease in the amplitude of oxidative processes during evaporation of samples exposed to fluctuating so far indicates a «softer» oxidation inherent in this method of must processing. At the same time, in most of the composition indicators, the experimental vacuum must, especially the second sample, is close to the high-quality Italian vacuum must.

Analysis of blends in Table 6 included:

a) wine materials obtained by fermentation of pomace with its enzymatic processing;

b) mistels obtained after enzymatic treatment and infusion of pomace;

c) vacuum must makes it possible to conclude that in this scheme the use of vacuum must is not significantly reflected in the composition of blends.

Compared with similar samples without the introduction of vacuum must, the increase in titratable acids will not exceed 0.4 g/d^3, phenolic substances – 25–26 mg/dm^3, amine nitrogen – 3–4 mg/dm^3; pentoses – 100 mg/dm^3. Obviously, such a sequence of using vacuum must in blends does not provide a significant adjustment in their composition. Blends look somewhat different, consisting of two components – dry-fermented wine materials and vacuum must. Due to the higher percentage of the second component (up to 10 % of the total volume of blended material), in these variants, a significant increase in the limited accumulation of compounds, mainly phenolic substances and carbohydrates, was achieved. Especially promising is the blending of dry-fermented wine material (using Vinozyme) with vacuum must. In the obtained sample, the mass concentration of titratable acids, phenolic substances, carbohydrates in poly-, oligo- and monomeric forms was recorded, exceeding that in the «reference» sample of Marsala. And it approaches the blend of «fermented wine material – wine material after infusion of the pomace», with the double use of Vinozyme. Thus, a blend of dry wine material with vacuum must in the production of Marsala can be considered as promising, however, due to the significant volume share of the second component, its implementation may be limited to the production of products with an accelerated maturation cycle.

7. Conclusions

1. The mass concentration of components according to the variants of pomace extraction has been established, which makes it possible to assess the effect of various enzyme preparations on the quality of wine materials for Marsala. A series of fortified wine materials for wine of the Marsala type was obtained, provided for three main schemes for extracting pomace (fermentation, infusion, heat treatment) along with the use of enzyme preparations – Vinozyme, Ultrazyme, and Glucanax.

2. The fundamental possibility of obtaining high-quality wine materials for vintage marsala under the conditions of

processing grapes of the variety Bayan – Shirey and Rkasiteli according to the "red method" has been established.

3. Rational regimes for obtaining blended wine materials for Marsala, based on the technology of fermentation or long-term infusion of pomace, have been developed. The following initial blended wine materials for the preparation of marsala are substantiated: the main wine material is dry-strong, obtained by fermentation of Vinozyme or Ultrazyme, or pomace in the presence of the preparation Glucanex; mistel obtained by infusion of pomace in the presence of one of these preparations; vacuum-must. It has been established that the rational variant of obtaining vintage marsala is a blend of dry-fortified wine material and mistel, or dry-fortified wine material and vacuum must.

4. A rational variant of blending and aging of wine materials for Marsala has been experimentally substantiated. Analysis of the dynamics of maturation of blended wine materials and data on changes in their chemical composition confirmed the choice of a rational scheme for their production and made it possible to establish the expediency of aging blends for marsala for 2.5 years. To improve the quality of ordinary wine such as marsala, a new technique for obtaining vacuum must has been developed, which provides for the treatment of the original must before evaporation with a fluctuating current (0.6 mA, 1 hour).

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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Data availability

All data are available in the main text of the manuscript.

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