INFLUENCE OF MODERN STABILIZATION METHODS ON QUALITY VARIETAL WHITE WINES FROM UKRAINIAN BREEDING GRAPE

O. Tkachenko, Associate Professor, Doctor of Technical Sciences
T. Suhachenko, PhD, Associate Professor
O. Kananykhina, PhD, Associate Professor
1 Department of wine technology and sensory analysis
2 Departments of biochemistry, microbiology and nutrition physiology
Odesa National University of Technology
112 Kanatna str., Odesa, Ukraine, 65039

Abstract. Modern winemaking in Ukraine is being significantly transformed and is actively developing. Our state has now turned to the search for its own wines and grape varieties. For international recognition, it is important to develop your case of wines that will be able to show the diversity of wine regions from Southern Bessarabia and the Northern Black Sea Coast to Transcarpathia. There are more and more small winemakers who are experimenting with new varieties, such as Sukholimansky white, Citronny Magaracha, Zagrei, Johanniter, Zvalgate, Solaris, Aromatny, Telti Kuruk and various muscat varieties. The organoleptic profile of such wines should express the varietal characteristics of local grape varieties and the agro-climatic features of the terroir. At the same time, the modern technology of white table wines should be built on the principles of maximum preservation of varietal aroma and minimization of its oxidation during the technological process. The article reflects the results of theoretical studies of literary sources regarding the mechanisms of oxidative processes of various nature in the process of grape processing; the market of modern preparations for stabilizing wine materials is considered. According to the goal, the influence of the use of the enzyme preparation Viazim clarif one on the process of clarifying the wort was investigated. The effect of complex antioxidant pasting of wort with the stepwise application of "Tanal W4", "Polygreen" and "Granula" bentonite on aromatic compounds and the formation of the aromatic profile of the finished product was also studied. At the last stage of research, the organoleptic profile of white wine materials of the studied grape varieties was determined. It was established that the general trend of stabilization processes in modern winemaking is transferred to the wort stage. According to the results of practical tests, in the form of trial pastes of wort, it is proposed to use the enzyme preparation Viazim clarif one at the stage of extracting wort; the effect of complex antioxidant pasting of wort with stepwise application of "Tanal W4", "Polygreen" and "Granula" bentonite was studied. Practical recommendations have been developed for winemakers on the application of antioxidant wort pasting for domestic grape varieties Sukholimansky white and Citronny Magaracha, which are now gaining popularity in Ukraine.

Key words: stabilization, wort, white table wines, Sukholimansky white, Citronny Magaracha, winemaking of Ukraine.

Introduction. Formulation of the problem

The modern wine industry of our country is being significantly transformed and is actively developing. Currently, Ukraine has turned to the search for its own wines and grape varieties. Previously, the use of international varieties (for example, Chardonnay, Riesling, Aligote) was more widespread in production, and the varieties of domestic selection of the NSC "Institute of Viticulture and Winemaking named after V.E. Tairov", National Institute of Grapes and Wine "Margarach". Among producers, there are more and more small winemakers experimenting with new varieties, such as Sukholimansky white, Citronny Magaracha, Zagrei, Johanniter, Zvalgate, Solaris, Aromatny, Telti Kuruk and various muscat varieties [1,2]. The success of innovators is confirmed by participation in numerous exhibitions and competitions. Thus, in the II Ukrainian tasting competition "Odesa Bay 2020", out of 176 wines, 20% were from rare varieties [3].

It is important for Ukraine to develop its case of wines that will be able to show the diversity of wine regions from Southern Bessarabia and the Northern
Enzymatic oxidation of grape must and wine is catalyzed by monophenol-monoxygenase and grape peroxidase, which is located in the skin and adjacent layers of the pulp of the grape berry [14]. In an intact berry, the enzyme and substrate are located in different structural elements of the cell. When the berries are crushed, their integrity is violated, and in the presence of oxygen in the air, oxidative browning of the wort occurs. Oxidation products – quinones – involve organic acids and amino acids in the process of combined oxidation, as a result of these reactions, carbon dioxide and ammonia are formed [15].

White wines obtained without infusing the pulp are characterized by an insignificant content of flavonoids, but contain a significant amount of hydroxycinnamate derivatives. Hydroxycinnamate derivatives are substances of a non-flavonoid nature and are found in grapes, must and wine in significant quantities. They are the dominant group of phenolic substances in the must from white grape varieties, which was obtained using technological methods that exclude the oxidation of the must and infusion of the pulp [4].

Enzymatic oxidation of must and wine takes place with the participation of grape berry oxidases, derivatives of hydroxycinnamates, reduced glutathione and flavanoid forms of phenolic compounds. Chemical oxidation occurs in wine materials and wines with the participation of phenolic compounds, which are oxidizing agents, metal ions as catalysts, sulfur dioxide as inhibitors, and sulfur-containing amino acids. Oxidation of phenolic substances occurs in several stages and is associated with the formation of highly reactive intermediate products of a free radical nature [16].

Chemical reactions leading to oxidation of wine materials are numerous and occur in the field of both volatile and non-volatile components [5].

Ascorbic acid (mass concentration of 10–125mg/kg of grapes), which is an oxygen activator, can also act as an initiator of redox reactions [16].

Intermediate products of its oxidation are monoammonium, diamin, anion-radical, ascorbate-radical; the final one is dehydroascorbic acid, which is prone to hydration, rearrangement and degradation in an acidic environment. Ascorbic acid in the presence of Cu²⁺ catalyzes the process of oxidative browning of white table wine materials, which is associated with the formation of the natural dye xanthylum, the structure of which is formed by a dimer of epicatechin or catechin and glyoxylic acid, which plays a bridging role [4].

Manifestation of pro-oxidant properties of ascorbic acid in wine materials is inhibited by sulfur dioxide. The antioxidant effect of ascorbic acid is that, being a stronger reducing agent than catechins, it reduces their corresponding quinones and semiquinones [15]. In addition, ascorbic acid is able to restore the oxidized forms of terpene alcohols,
contributing to the preservation of the varietal aroma of table wines. Non-enzymatic oxidation of phenolic compounds, associated with the performance of pro-oxidant or antioxidant functions, occurs with the formation of semiquinones.

The chemical composition of white table wines has been studied in detail thanks to the capabilities of modern analytical technology.

In terms of our research, we are interested in the groups of chemical compounds that most actively influence the formation and transformation during the technological process of the main qualitative characteristics of wine – color, aroma and taste.

The composition of the aroma-forming complex of white table wines largely depends on the grape variety, as well as on the soil, climate, and agricultural techniques. The main groups of compounds that determine the aroma of white wines are terpenes, C13-norisoprenoids and thiols (mercaptans) [14].

The grape variety determines the group of compounds responsible for the aroma. Muscat grape varieties, which according to the OIV international classification belong to the aromatic group, deserve special attention. More than 60 monoterpenic compounds have been found in Muscat grape varieties and wines made from them, the most common of which are geraniol, linalool, and nerol [4]. More than 90% of terpenes are present in grapes in the form of glycosides. Oxidation of this group of compounds can occur at the first stage of grape processing – crushing. In the case of insufficient protection from oxygen, the concentration of terpene alcohols will decrease and the aromas characteristic of them may reach threshold values or be completely lost by the end of alcoholic fermentation [6]. Thus, linalool is converted into a less aromatic compound [4].

The aromatic profile of Sukholimansky white grape wines is determined by the presence of C13-norisoprenoids, mainly in the form of precursors, which are products of oxidative degradation of carotenoids belonging to the group of terpenes with 40 carbon atoms. Among this group, β-damascenone is particularly interesting, which is characterized by a complex aroma of exotic fruits and baked apple and is also present in muscat varieties [15].

Research by domestic and foreign scientists has established that the quality of white wines during their production and storage is largely determined by the oxidative transformation of phenolic compounds, aroma-forming substances. Acetaldehyde, sotolone and 2-aminoacetophenone play an important role in the perception of wine as oxidized to varying degrees [5].

From the moment the grapes was crushed, enzymatic oxidation processes actively take place in the wort, at the stage of clarifying the wort, these processes continue at a slower rate. With the beginning of fermentation, they disappear due to the inactivation of oxidases [7]. After alcoholic fermentation of grape must, new redox systems appear: ethanol – acetaldehyde; reduced glutathione – oxidized glutathione; ascorbic acid disappears due to irreversible degradation of its oxidized form [8]. Some of the phenolic substances are absorbed on the yeast cell walls, their quantitative content and degree of oxidation change [4].

Currently, there are a sufficient number of new methods that allow regulating the oxygen content in wine, including the use of new generation equipment, antioxidants, inert gases, aging on yeast sediment, the appearance of new types of clogging that counteract the negative impact of oxygen [14].

In addition to sulfur dioxide and ascorbic acid, preventive drugs present on the modern market include tannins, bentonites, and drugs of complex action [8].

Various preparations of tannins are widely used in winemaking to increase the effectiveness of pasting, improve the taste structure of wines, and reduce the risks of oxidation due to the suppression of the action of oxidases.

Depending on the chemical composition, tannins are divided into hydrolyzed, condensed and mixed types. Hydrolyzed tannins are esters of gallic or ellagic acids, condensed (enotannins) consist of monomers, oligomers and polymers of flavanols, mainly catechin, epicatechin, epicatechin gallate and epigallocatechin. Tannins differ in the content of hydroxyl groups, which determines their reactive activity [9].

Raw materials for the production of tannins are the bark of the quebracho tree, oak, acacia, hazelnuts, seeds and skin of grapes, etc. Such a variety of raw materials, as well as the climatic conditions of its cultivation and other factors determine the different chemical composition and properties of tannins [10].

Preparations of complex action may contain components of both plant and animal origin, as well as other mineral components [7].

Preparations of a complex formula based on polyvinylpolypyrrolidone (PVPP), bentonite and vegetable proteins are recommended for use to fight against the manifestations of oxidation processes present in wine as a whole: protection of wort, which has a tendency to oxidation (counteracts atypical aging of white wines); elimination of brown color in oxidized white wines; noticeable decrease in the degree of pinking [4].

Preparations based on PVPP and sodium bentonite improve the sensory profile of wine obtained from damaged, poor-quality raw materials or as a result of pressing in a non-gentle mode.

Innovative auxiliaries include drugs that consist of plant polymers, do not contain GMOs, allergenic substances, components of animal and synthetic origin, which do not affect human health and the finished product. They are an alternative to the use of PVPP and potassium caseinate. Thanks to the efficiency and speed of action, it is possible to fight against the changes caused by oxidation, both in must and in wine, while preserving all the qualities inherent in the...
original product. Enzymes of pectolytic action are an extremely effective means for splitting pectins [16]. In modern winemaking, the use of pectolytic enzyme preparations is the most effective way of separating colloidal fractions, sedimentation of solid particles and clarification of grape must, in cases where the grape berry's own enzyme system is not able to separate pectin bonds on its own.

Thus, the modern technology of white table wines should be built on the principles of maximum preservation of varietal aroma and minimization of its oxidation during the technological process. The organoleptic profile of white wine implies the presence of aroma-forming compounds characteristic of the variety, regardless of the age of the wine.

The purpose of the work is to improve the technological scheme for the production of white table wines from local grape varieties by introducing the process of antioxidant pasting of the wort.

The objectives of the research were:
1) Investigate the effect of the use of the Viazim clarif one enzyme preparation on the wort clarification process.
2) To investigate the effect of complex antioxidant pasting of wort with the step-by-step application of "Tanal W4", "Polygreen" and bentonite "Granula" aromatic compounds and the formation of the aromatic profile of the finished product.
3) To determine the organoleptic profile of white wine materials of the studied grape varieties.

Research materials and methods

The objects of the study are wort and wine materials of Sukholimansky white, Citronny Magaracha, Chardonnay and Riesling Rhine 2018-2020 harvest years in the conditions of VKF "Borodino-A" LLC, a full-cycle production enterprise, Ukraine, Odesa region, Tarutynsky district.

Preparations for treatment:
"Viazim clarif one" is an enzyme preparation from Aspergillus niger with a high concentration of pectinases (polygalacturonase, pectinmethylesterase, pectinlyase) for effective and quick clarification. The absence of cinnamoylsterase in the composition of the drug prevents the appearance of volatile phenols. Manufacturer ‒ Martin Vialatte, France.

"Tanal W4" is a pure hydrolyzed tannin with a low degree of purity and was specially developed for use in the food industry. It has a high degree of purity and was specially developed for use in the food industry. A 100% natural product, which is obtained from renewable plant raw materials, using special production equipment, the work of which is strictly controlled. "Tanal W4" has the best antioxidant properties of all halotannins, complementing the action of SO₂ and reducing the dose of its use. Protects the wort from the unwanted influence of oxygen, sunlight and the appearance of the so-called "worldly flavor" (signs of oxidation) in the wine; has an antioxidase effect, suppressing the natural enzymatic activities of grapes, as well as lactase (derived from Botrytis) and polyphenoloxidase.

"Polygreen" is a complex preparation containing a mixture of vegetable proteins, PVPP, bentonite and cellulose, designed for clarification and treatment against oxidation of must, white and rosé wines. Manufacturer ‒ Martin Vialatte, France.

"Granula" bentonite is a granulated activated calcium bentonite with a high deproteinization capacity. The granular form of this bentonite simplifies its use and limits the dustiness of the product. Manufacturer ‒ Martin Vialatte, France.

The scheme of the experiment is presented in Fig. 1.

As a control experiment, grapes were processed using the generally accepted technology "by the white method" [7].

To obtain control samples of wine materials, grapes were used, which were harvested by hand in a state of technical maturity.

After receiving the grapes for primary processing, they were initially sorted, selecting damaged and affected berries and bunches using a sorting table.

The sorted grapes were sent for processing with preliminary separation of the ridges and further crushing.

The resulting pulp was sulfited to a sulfuric anhydride content of 50 mg/l. The muscle was pressed using a periodic press. Pressed wort was directed to illumination at a temperature of 12°C for 24 hours, without the addition of additional drugs, and decanted. Fermentation of the wort was carried out using a pure yeast culture at a temperature of 18°C in stainless steel tanks. Next, decanting and stabilization (sticking, cold treatment, filtration) of wine materials were carried out.

The selection of dosages and combinations of drugs was carried out based on the results of trial processing of wort.


The influence of agrotechnical cultivation methods on the sensory characteristics and physic-chemical parameters of experimental samples of grapes and wine was studied using the method of one-way analysis of variance, the method of principal components (Analysis of Variance, ANOVA; two-way ANOVA; Principal Component Analysis, PCA) in the MS software environment Excell 2010 Statistica Statsoftver 7.0.
**CONTROL**

**MAIN STAGES OF THE TECHNOLOGICAL PROCESS**

- harvest, transportation and grape sorting

**EXPERIMENT**

- enzyme preparation "Viazim clarif one"

**without the introduction of the drug**

- crushing with ridge separation

**pressing**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>harvest, transportation and grape sorting</td>
<td></td>
</tr>
<tr>
<td>crushing with ridge separation</td>
<td>enzyme preparation &quot;Viazim clarif one&quot;</td>
</tr>
<tr>
<td>pressing</td>
<td></td>
</tr>
<tr>
<td>temperature 12 °C 24 hours</td>
<td>clarification of the wort</td>
</tr>
<tr>
<td>clarification of the wort</td>
<td></td>
</tr>
<tr>
<td>wort decantation</td>
<td></td>
</tr>
<tr>
<td>fermentation</td>
<td></td>
</tr>
<tr>
<td>pouring wine materials</td>
<td></td>
</tr>
<tr>
<td>stabilization</td>
<td></td>
</tr>
<tr>
<td>storage</td>
<td></td>
</tr>
</tbody>
</table>

**Fig 1. Scheme of the experiment**

### Results of the research and their discussion

According to the scheme of the experiment (Fig. 1), at the first stage, the effect of the enzyme preparation "Viazim clarif one" was studied. The drug was introduced at the pressing stage according to the recommended technological instructions for it. Under the action of pectolytic enzymes, insoluble protopectin underwent depolymerization and de-esterification. As a result of the use of the enzyme preparation, the relief of pressing was recorded; increasing the yield of wort and the speed of filtration. The effect of the drug was analyzed by conducting an organoleptic analysis and by turbidity indicators using a nephelometer (Table 1).

The next stage after the enzyme preparation was antioxidative pasting of the wort, which consisted in the sequential introduction of preparations: Tanal W4, g/10 l (1), POLYGREEN, g/10 l (2), Bentonite GRANULA, g/10 l (3) (Table 1).

The results of trial gluing of test samples are presented in Table 1.

According to the results of organoleptic analysis and turbidity indicators, the optimal concentrations of drugs and their appropriate combination were chosen: enzyme preparation "Viazim clarif one" 5.0 mg/100 dm³, Tanal W4, 1 g/10 l, POLYGREEN 5 g/10 l, Bentonite GRANULA, 2 g/10 l. The results of the organoleptic analysis of the best samples of Sukholimansky white and Citronny Magaracha wine materials in the form of profilograms are presented in Fig. 2.

### Table 1 – Results of determination of turbidity (turbidity units) after trial pasting of the wort of the studied grape varieties*

<table>
<thead>
<tr>
<th>№</th>
<th>Name of the grape variety</th>
<th>Enzyme-free drug</th>
<th>Enzyme preparation &quot;Viazim clarif one&quot;, mg/100 dm³</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
<td>5.0</td>
</tr>
<tr>
<td>1</td>
<td>Citron Magaracha</td>
<td>65</td>
<td>55</td>
<td>51</td>
</tr>
<tr>
<td>2</td>
<td>Sukholimansky white</td>
<td>65</td>
<td>53</td>
<td>52</td>
</tr>
</tbody>
</table>

*Mathematical data processing was carried out using the Dispersion one-factor method. NSR (smallest significant difference), if the difference according to the test options is less than or equal to the calculated number of NSR, then it is mathematically proved by 95% (0.5 is the accuracy of the experiment).
In the course of the sensory research, the intensity of aromas of the studied wine materials from Sukholimansky white and Citron Magaracha grapes was determined (Fig. 2). As can be seen from Fig. 2a in the wine material obtained with the use of antioxidant pasting, the indicators of "fruitiness", "florality" and "harmony of taste" are significantly higher than in the control sample. Such characteristics are probably related to the origin of the varieties. In general, the use of antioxidant pasting contributes to the manifestation of the varietal characteristics of the grapes used. Similar results were observed during the study of wine materials from the Citronny Magaracha variety (Fig. 2b): the indicators responsible for the varietal descriptors are more intensively manifested when using the preparations Tanal W4, Polygreen, Bentonite Granula.

Among the vineyards owned by VKF "Borodino-A" LLC, there are also plantings of international varieties such as Chardonnay and Riesling, so it is advisable to apply the proposed scheme in the production of wines from these varieties.

The results of the study of the organoleptic profile of the obtained wines are presented in Fig. 3.

As can be seen from fig. 3, the aromatic flavor of the wines produced at the VKF "Borodino-A" LLC enterprise correlates with the existing generally accepted ones, but has its own distinctive features. So, Chardonnay wines are dominated by fruity aromatic components, while Riesling wines are dominated by floral components, the presence of which is due to aromatic substances: terpenes, C_{13}-norisoprenoids [18]. These features can be related both to the proposed agrotechnological techniques and to the agroclimatic features of the terroir of Ukrainian Bessarabia. This area is characterized by a warm arid climate, the soil is formed by deluvial sediments, which are favorable for growing grapes.

As a result of the tests, an improved technological scheme for the processing of white grape varieties into table wines was proposed, which is presented in Fig. 4.

The developed scheme was implemented at the production of LLC VKF "Borodino-A" in the production of wines from white grape varieties Sukholimansky white, Citronny Magaracha, Chardonnay, Riesling Rhine during 2018–2020.
The results of the conducted research demonstrate that the developed technological scheme, which includes the process of antioxidant pasting of wort, can be applied in the production of varietal wines from grapes of both domestic selection and international varieties. The use of a combination of the proposed preparations allows not only to prevent negative oxidation processes, but also has a beneficial effect on the preservation of existing and the formation of new aromatic components that reflect the varietal characteristics of the grape varieties used and the terroir.

**Approbation of the results.** VKF "Borodino-A" LLC, a full-cycle production enterprise, Ukraine, Odessa region, Tarutyn district, tourist complex "Frumushyka Nova".

**Conclusion**

As a result of theoretical studies of literary sources, the mechanisms of oxidative processes of various nature in the process of grape processing were studied; the market of modern preparations for stabilizing wine materials is considered. It was established that the general trend of stabilization processes in modern winemaking is transferred to the wort stage. To determine the optimal dosages and combinations of drugs, it is necessary to carry out trial pastings and organoleptic analysis. Based on the results of trial pasting of wort, the influence of the use of the Viazim clarifier enzyme preparation on the wort extraction process was proposed and practically verified. For the first time, the effect of complex antioxidant coating of must with the step-by-step application of "Tanal W4", "Polygreen" and "Granula" bentonite was investigated for wine materials from rare local grape varieties – Sukholimansky white and Citronny Magarachka. Practical recommendations have been developed for winemakers on the use of antioxidant fining of must grape varieties that are now gaining popularity in Ukraine.

**Fig. 4. Technological scheme of the production of white table wines**

The scheme of the conducted research demonstrates that the developed technological scheme, which includes the process of antioxidant pasting of wort, can be applied in the production of varietal wines from grapes of both domestic selection and international varieties. The use of a combination of the proposed preparations allows not only to prevent negative oxidation processes, but also has a beneficial effect on the preservation of existing and the formation of new aromatic components that reflect the varietal characteristics of the grape varieties used and the terroir.

**References:**

ВПЛИВ СУЧАСНИХ ПРИЙОМІВ СТАБІЛІЗАЦІЇ НА ЯКІСТЬ БІЛИХ СОРОТОВИХ ВИН ІЗ ВИНОГРАДУ УКРАЇНСЬКОЇ СЕЛЕКЦІЇ

О.Б. Ткаченко1, доктор технічних наук, професор, E-mail: obtkachenko@gmail.com
Т.С. Сугаченко2, кандидат технічних наук, доцент, E-mail: tanya.lozovskaia@ukr.net
О.М. Кананихіна2, кандидат технічних наук, доцент, E-mail: k_eln@ukr.net

1 Кафедра технології вина та сенсорного аналізу
2 Кафедра біохімії, мікробіології та фізіології харчування
Одеський національний технологічний університет бул. Канатна, 112, м. Одеса, Україна, 65039

Анотація. Сучасне виноробство України істотно трансформується і активно розвивається. Наша держава в даний час звернулася до пошуку своїх вин і сортів винограду. Для міжнародного визнання важливо розробити свой кейс вин, які зможуть показати багатогранність винних регіонів від Південної Бессарабії і Північного Причорномор'я до Закарпаття. Серед виробників з'являється все більше малих виноробів, які експериментують з новими сортами, такими як Сухолиманський білий, Цитронний Магарача, Тельті Курук та різними мускатними сортами. Органолептичний профіль таких вин має виражати сортові характеристики винограду місцевих сортів і агрокліматичні особливості теруару. В той же час сучасна технологія білих столових вин має бути побудована на принципах максимального збереження сортового аромату та мінімізації його окиснення в ході технологічного процесу. У статті відображено результати теоретичних досліджень літературних джерел щодо механізмів окисних процесів різного характеру в процесі переробки винограду; розглянуто ринок сучасних препаратів для стабілізації виноматеріалів. Відповідно до поставленої мети досліджували вплив використання ферментного препарату «Viazim clarif one» на процес освітлення сусла. Також вивчали вплив комплексного антиоксидантного обклеювання сусла з поетапним внесенням бентоніту «Tanal W4», «Polygreen» та «Granula» на вміст ароматичних сполук та формування ароматичного профілю готового продукту. На останньому етапі досліджень визначено органолептичній профіль білих виноматеріалів досліджуваних сортів винограду. Встановлено, що загальна тенденція процесів стабілізації в сучасному виноробстві переноситься на стадію сусл. За результатами практичних випробувань, у вигляді пробних обклеювань сусл, запропоновано використання ферментного препарату «Viazim clarif one» на стадії вилучення сусл; викно вплив комплексного антиоксидантного обклеювання сусл з поетапним застосуванням препаратів «Tanal W4», «Polygreen» та бентоніту «Гранула». Розроблено практичні рекомендації для виноробів про застосування антиоксидантного обклеювання сусл для сортів винограду вітчизняної селекції, які зраз зацікавляють популярності в Україні.

Ключові слова: стабілізація, сусло, білі столові виноматеріали, Сухолиманський білий, Цитронний Магарача, виноробство України.