An approach to the regulation of organoleptic parameters of sparkling wine by the introduction of expedition liqueur

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Abstract. The results of investigation of the influence of expedition liqueur on the formation and regulation of organoleptic indicators of ready-made sparkling rose wine are presented. A close correlation dependence between the change in the chemical composition of ready-made sparkling wine and its main tasting characteristics after dosage has been established. Sparkling wine is a multicomponent water-alcohol system, the quality of which depends on the chemical composition, as in the process of redox reactions sensory-active compounds are formed. At the first meeting with sparkling wine, the taster builds an associative row due to color tonality. The so-called "crunching" sound, reproduced by bursting bubbles on the surface of the sparkling wine poured into the glass, anticipates the standard of the color palette in terms of chromatic indicators. In the classical method of champanisation the final stage of formation of organoleptic parameters is the addition of expedition liqueur. In scientific literature there are studies aimed at studying the influence of dosage, but there is no summary of the positive result of the catalytic action of expedition liqueur on the opening and prolongation of organoleptic indicators. Differences in the degree of influence of the modified chemical composition and the reference one on the tasting evaluation of sparkling wine have been revealed. Based on the obtained data, a statistical study has been carried out, which has a high level of significance. Expedition liqueur can be recommended for formation and regulation of organoleptic indicators of a particular sparkling wine produced by any method of champanisation.

1 Introduction

The organoleptic performance of finished sparkling wine is mainly influenced by volatile compounds that are consumed by yeast during fermentation from amino acids found in grapes [1]. Wine yeasts during alcoholic fermentation need nitrogenous nutrition, which is provided by amino acids, the deamination of which releases ammonia, which is used by the yeast to synthesize other amino acids. During fermentation, most amino acids are assimilated intensively so that only imino acids remain in the must by the end of fermentation [2]. This allows the initiation of an enzymatic fermentation reaction due to the addition of expedition liqueur [3]. The passage of the Maillard reaction is confirmed by the detection of a number

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of substances, so-called "markers" in the finished sparkling wine. "Markers" show a copper tone in the pink sparkling wine, revealing a new flavor that was not detected before the addition of the expedition liqueur [3].

Sparkling wines are obtained after secondary fermentation of the base wine, which can be carried out in closed bottles or in hermetically sealed tanks. The essence of champenoise is the second fermentation, which takes place in the bottle and increases the internal pressure (up to 5-7 atmospheres). This is followed by aging on yeast lees for at least 9 months [4]. As sparkling wines remain in contact with the lees, flavors such as toasty, lactic, sweet and yeasty appear in the wine, which can be explained by yeast autolysis involving hydrolytic enzymes that release compounds of the cytoplasm (peptides, fatty acids, nucleotides, amino acids) and cell wall (mannoproteins) into the wine. Aging on yeast lees leads to significant changes in wine composition, while organoleptic parameters are modified [4]. The formation of organoleptic indicators is due to the main compounds that are formed during secondary fermentation, while the achievement of flavor-olfactive balance is carried out by organic acids, amino acids and volatile components that are formed during ageing on the lees. The complex and pleasing flavor of a wine is the result of a perfect balance between its soft (sugars, alcohols, polyalcohols) and hard (acids, tannins, minerals) components.

The chemical components that are presented in this study are involved in a large number of chemical interactions with the main components, revealing the refined, delicate and special style of the wine. For example, intermolecular copigmentation interactions between anthocyanins and caffeic acid exhibit both hyperchromic (increased maximum absorption coefficient) and bathochromic shifts towards bluish shades due to weak hydrophobic forces [5]. In addition, caffeic acid imparts moderate astringency and bitterness to wine. One of the major phenolic acid components that has tartness but does not clearly contribute to the bitter flavor is gallic acid. It, as a bitter-tasting component, regulates cellular proton secretion as a key mechanism of gastric acid secretion through activation of bitter taste-sensitive receptors. Isoleucine, leucine and valine are precursors of isobutyl, amyl and isoamyl alcohols [5], which are responsible for the fruity notes in wines. Glycine, along with ethanol, residual sugar and glycerol, contributes to the sweet flavor. Valine is usually obtained by amination of pyruvic acid and is a precursor to apple and banana flavors. Phenylalanine, a precursor of phenylethyl acid, gives the flavor of honey to wine. [5]

The chromatic indicators of the wines line up as a color gradient that is set from north to south. The color of pink wine is neutral and transitional from the female style to the male style. Pink is the most difficult color to study as it is evaluated by the proportionate contribution of three pigments: red, yellow and blue. The gradient of pink color starts from weak shades (sandy) and ends with juicy shades (pomegranate, apricot and crimson) [6]. Color-tonality regulates not only the gradient, but also the "coloring of music" determined by a number of sounds - gamma, which forms the harmony [7]. Due to musical-color synesthesia, the taster builds an associative series at the first meeting with sparkling wine.

Anthocyanins in wine are mainly responsible for color, undergoing redox processes at all stages of production, affecting the final color of the wine [8]. The bathochromic effect of anthocyanins having an ortho-diphenol group (cyanidin, delphinidin and petunidin) is known, as they can chelate metal cations such as: Al³⁺, Fe³⁺, Cu²⁺, Mg²⁺[9]. The chemical composition of rose wines is unknown. Wirth J. quantifying polyphenols [10] proved that proportionally rose wines differ from red wines which were made from the same grape variety. Rose wines are dominated by hydroxycinnamic acids in their composition. Anthocyanins and phenolic compounds in higher concentrations at low pH are responsible for the intense shades of pink color [10].

In the classical technology of sparkling wine production, wine and expedition liqueur are produced from the same wine material, and since the technology of production of expedition
liqueur involves sugar dosing and sulphitation, the dosing is characterized by a high concentration of compounds of phenolic nature [11].

The phenomenon that arises at the gas-liquid interface in sparkling wine, as a result of cavitation desorption of carbon dioxide, determines mainly its quality [12]. When sparkling wine is poured into a flute, dissolved carbon dioxide leaves the vessel in two ways: diffusion through the free surface of the solution, due to zero-order kinetics and bubble formation. Before the gas molecules join together to form nucleated bubbles, they need to overcome the path through the solution, the molecules of which are strongly bound due to van der Waals forces (dipole attraction) [12]. The nucleation of bubbles is restrained by an energy barrier and the supersaturation is weak to overcome it alone. Therefore, in low supersaturated carbon dioxide solutions, including sparkling wines, bubbles nucleate when the pre-existing gas cavities are large enough to overcome the energy barrier to nucleation [13]. The cavities must be large because the curvature of the gas-liquid interface leads to an overpressure inside the gas pocket that is inversely proportional to its radius. The smaller the bubble, the greater the overpressure inside it. Carbon dioxide cannot diffuse into bubbles smaller than the critical size [14].

A bubble is formed when dissolved carbon dioxide molecules migrate into one of the smallest gas pockets. It eventually grows to macroscopic size, but initially remains tethered to the nucleation site by capillary forces [15]. Finally, the increasing buoyancy of the bubble causes it to detach and a new bubble can form in its place. The process is repeated until there is no dissolved carbon dioxide left for bubble formation [15].

The aim of this research is to conceptually analyses the beneficial effects of expedition liqueur on finished sparkling wine and to establish a correlation dependence that links the chemical composition of sparkling wine with its organoleptic performance.

2 Materials and methods

The work was based on the results of our previously conducted studies aimed at investigating the effect of expedition liqueur on the variation of finished sparkling rose wine in general. The research used averaged data that meet the quantification of the association between organoleptic parameters and expedition liqueur, which were established by statistical analysis and then approximated and interpreted by analytical dependencies.

Finished sparkling wines, regardless of the production method, have an identical chemical composition, which is within the quality standards used to classify this type of product [12]. The generalized chemical composition of wines, which was carried out by capillary electrophoresis, contains groups of compounds: organic acids, amino acids, volatile components, etc. (Figures 1-3) [14]. Sparkling wines are characterized by low concentrations of acetaldehyde, lactic and acetic acids considering their olfactory threshold. It has been shown that the chemical composition and quality of sparkling wine is independent of the method of champanisation. B. Cisilotto studied sparkling wines from the same base wine made by different methods and concluded that the method of champanisation does not significantly affect the quality of the finished sparkling wine [15]. Therefore, expedition liqueur can be applied to sparkling wine made by both the classical method of champanisation and the Charm method.
Fig. 1. Quantitative composition of organic acids

Organic acids, mg/kg

- ascorbic acid
- chlorogenic acid
- nicotinic acid
- orotic acid
- caffeic acid
- gallic acid

Fig. 2. Quantitative composition of amino acids

Amino acids

- Arginine
- Tyrosine
- α-phenylalanine
- Leucine
- Methionine
- Valine
- proline
- Threonine
- Cerin
- α-alanine
- glycine

Fig. 3. Volatile components of sparkling wine

Volatile components

- Acetoin
- Furfurol
- 2.3-butylen glycol
- 2.3-butylen glycol
- Ethylcaproate
- Ethyl lactate
- Ethylcaprilat
- ethylcaprinat
- ethylaurate
The correlation between several independent variables and one dependent variable was analysed by means of multiple regression using StatSoft statistical software. The statistical methodology of conducting multiple regression analysis allows the determination of the factors of the principal components, through the projection of the forecast variables and the observed variables into a new space. In a first step, in order to reduce the number of variables that will be part of the mathematical prediction algorithms, the main selection criteria were taken into account such as: a high level of positive or negative correlation between the chemical composition of sparkling wine and organoleptic parameters. In order to reduce the number of model variables, a partial least squares regression analysis was carried out, in which those chemical compounds that showed a reliable correlation with a 90% confidence level with organoleptic parameters were retained.

3 Results and discussions

Expedition liqueur is a sugar-containing product. Prepared from bottling wine material after completion of secondary fermentation with the addition of high purity white sugar (without betaine alkaloid) and citric acid.

3.1 Chemical composition

Expedition liqueur is used to impart sweetness to sparkling wine, therefore it is used to make wines by vintage. The most valuable chemical compound is proline, as it is not consumed by yeast during fermentation and is found in wines in the highest concentration. Proline in the free state is present at a level of up to 800 mg/dm3 on average, but it is not identified (less than 0.1 mg/dm3) when dosing expedition liqueur due to the increased concentration of reduced sugars, which as a result of an equilibrium shift actively enter the reaction of saccharoamine condensation of carbohydrates and proteins. The related components, acetoin and furfuroil, on the contrary have a significant increase in concentration, in addition to this the introduction of dosage generally affects the change in the composition of volatile aromatic components in sparkling wine [15]. Also esters and higher alcohols had an increased concentration after the application of expedition liqueur, indicating the passage of the Maillard glucose-proline reaction [15].

3.2 Foaming and sparkling properties

When expedition liqueur is dosed, there is a reduction in foaming ability and an increase in bubble formation. Sparkling wines, in which expedition liqueur is not supposed to be added, having a low content of residual sugars, are characterized by a sharp aroma, aggressive "play" and spicy tingling on the tongue. It has been proved that foam formation and persistence depend on the chemical composition of sparkling wine [16]. Proteins and amino acids have the greatest influence, as they are related to the physical parameters of the foam [16]. Wine proteins are destroyed after the introduction of expedition liqueur. Sparkling wines contain the greatest amount of surface active substances in their composition, it is these compounds that increase the life of bubbles at the gas-liquid interface and therefore contribute to the formation of "pearl necklace". By adding expedition liqueur, foam stabilization is achieved due to the tensioactive components transient from the dosage to the sparkling wine, which give texture to the bubble [16].
### 3.3 Chromatic indicators

The pink color of wines is attractive from a marketing point of view and has been the subject of many studies, particularly those aimed at studying the psychology of color [16]. The color increases the emotional perception of wine in consumers. Assessing sensory characteristics in the literature there are proven facts of the influence of wine color on the assessment of other organoleptic indicators due to the visual "anchor". The phenomenon of expectation arises, which is related to aroma, in terms of psychology, the human brain expects certain aromas based on the observed color [17]. Visual evaluation initiates an impact on the olfactory senses and therefore subjectively determines the overall evaluation of the wine. In a study by S. Peres [17], it was hypothesised that the color of rosé wines is emotionally linked to the formation of expectation of certain aromas and flavors.

From a semantic approach, the color of wines can be described in terms of intensity, tint or with certain terms, and analysis by spectrophotometric method allows an objective assessment of the measure of color. A study aimed at investigating the effect of expedition liquor on the values of color parameters proved its direct significant effect on this indicator [18]. In addition to spectrophotometric analysis, there is an instrumental method of color evaluation for practical applications.

When evaluating the pink color of sparkling wines, the use of sulphiting agents must be taken into account. Sparkling rose wines to which the sulphited expedition liquor was added were characterized by chromatic indicators ranging from soft pink to copper. It is known that pink wines with an orange tint are characterized by a high content of hydroxycinnamic acid and low levels of glutathione [18]. Sparkling pink wines to which unsulphured expedition liquor was added were characterised by a clear gradient of the color palette: from the color of "the thigh of a frightened nymph" to the color of "Akaju". In this case, the color tonality varied according to the "golden ratio" [18].

### 3.4 Statistical analysis

The correlation study based on the constructed model for the attributes "foamy and sparkling properties", "chromatic indicators" and the dependent variable, which includes the averaged total quantitative chemical composition of the analytes of sparkling wine, revealed a significant influence of the factor, since the given level of significance is greater than p=0.0076.

The corresponding correlation (Fig.4), constructed on the basis of multiple regression, allows visualising the relation between the explanatory and dependent variables.
Scatter plots showed no obvious outliers, and many of the plots also clearly show a linear dependence between predictor and response. The observations were categorized into four groups that corresponded to the organoleptic attributes analyzed. The attributes "flavor" and "aroma" were excluded from the analysis, as tasting evaluation is an interpretation of sensory impression. A correlation matrix was constructed for each group to test the assumption of linear dependence and to take into account possible strong correlations between variables when building the regression model. Multiple regression was conducted stepwise so that the variables that contribute most to the regression were included in the model. Once the model was constructed, an adequacy test was conducted. Despite the significance of all variables in the regression model (p-level less than 0.05), the coefficient of determination is significantly lower for the 'shade of color' group of observations. The coefficient of determination shows what proportion of the variance in the response is explained by the influence of the predictors in the constructed model. Fisher's F-statistic is used to test the hypothesis of null values of regression coefficients and is rejected at a small significance level. In our case, the value of $F = 9.3648$ at a significance level of $p=0.0076$, hence the hypothesis of no linear relationship is rejected. Analysis of residuals confirmed the adequacy of the model.

This statistical analysis allowed us to identify the main organoleptic indicators that undergo changes depending on the chemical composition of sparkling wine. For simplicity of the analysis, the chemical components of sparkling wine were separated into an average total quantitative composition, which includes the content of volatile compounds, amino acids, aromatic compounds, higher alcohols, etc. Having obtained statistically significant results on the influence of the modified chemical composition of sparkling wine, on chromatic, frothy and sparkling indices, it can be stated that it is possible to regulate organoleptic properties of the finished product by means of expedition liqueur.
4 Conclusions

The organoleptic performance of sparkling wine does not depend on a specific compound, but on the profile and interactions of the many active compounds present, which have evolved from their precursors during aging after fermentation and modification of volatiles through chemical changes. Organic acids, amino acids and volatile compounds are the most obvious factors affecting the organoleptic of sparkling wine, but these classes of compounds are accompanied by a diverse set of organic molecules that can combine to create a striking variety of background components of flavor, nuance and aroma.

Finished sparkling wines, regardless of the method of production, have an identical chemical composition that falls within the quality standards used to classify this type of product.

By means of multiple regression, a clear dependence between the chemical composition of sparkling wine and certain organoleptic indicators was revealed. The regression revealed many correlations allowing to determine the main organoleptic indicators that undergo changes depending on the chemical composition of sparkling wine.

The use of expedition liqueur gives an opportunity to correct the frothy and sparkling, chromatic, olfactory and flavor characteristics of the finished sparkling wine, as the dosage informs the sparkling wine not only sweetness, but also enriches the chemical composition. Based on current research, it can be stated that sparkling wines produced by the Charm method have an impoverished chemical composition compared to wines produced by the Chapmanoise method. Dosage can be recommended to enrich the chemical composition of sparkling wines produced by any method. Dosage of expedition liqueur is considered as one of the approaches to correct certain characteristics and in addition allows prolonging organoleptic indicators of the finished sparkling wine, which makes the product more attractive to the consumer.

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