The study of Vermouth. Case: The relationship of taste and aroma parameters and their chemical composition

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Abstract. The problem of merchandise assessment of taste food products is the most important in terms of establishing their identity with the declared quality. This uniqueness underlies their fair selling proposition and pricing. This is especially true for flavored wines, which are valued by the target audience for their uniqueness and recognition: both in terms of trade name, brand, and place of origin, the totality of their flavour and aroma parameters. When making a purchase at a retail point of sale from buyers, there is no guideline about the presence of specific flavour and aroma parameters in flavored wines, except for the indication on the label of the trademark and the place of origin of the goods. This is often used by unscrupulous producers of this group of wines, endowing their products with false labels, giving them out under world-famous trademarks produced in regions with an undeniable business reputation. In terms of deliveries in the parallel import format, when retail chains do not have the possibility of direct deliveries from legitimate commodity producers, the purchase of a "pig in a poke" is more than likely, and the disappointment of the target consumer group is predetermined. The likely consequences of such uncertaintyty are quite obvious - the loss of legitimate commodity producers of their impeccable business reputation, the replacement of their trade offer with the proposals of competitors who are able to protect the authenticity of their trade offer due to the absence of restrictions on both supply and traceability of supply chains from third parties. The solution of the indicated problem is possible if the national bodies of commodity examination have effective methodological and hardware support for identifying the trade offer of the designated product group in terms of its authenticity and originality of origin. Previously, we described a methodical approach to solving a similar problem using organoleptic evaluation methods, in this publication we will describe the results of our analytical physicochemical studies of flavored wine samples, uniquely identified for the originality of trademarks and places of origin of goods [14]. The result of these studies was the statement about the statement about the possibility of establishing the typicality of flavored wines declared on the labels of the names of trademarks and places of origin of goods. These results, of course, can become the basis of a commodity examination in the customs assessment of flavored wines of world famous trademarks.

Keywords: flavoured wines, wine identification, organoleptic evaluation, chemical composition, gas-liquid chromatography, isobutanol, ethyl acetate

1 Introduction

Among the variety of flavoured foodstuffs, flavoured grape wines are in particular demand among consumers and are attributed not only to their excellent taste, but also to the mood-enhancing effects of their consumption. The wine offer is huge and varied: there is a drink for every taste and purse. For most wines, what is valuable is the stability of quality and the expected consumer flavour and aroma palette. Such wines have a global market and an international mix of consumers. These wines have a history, which winemakers strengthen in every possible way through their work. When the production of a famous wine passes from one owner to

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another, the parameters that remain unchanged are those that are valuable to a loyal audience, whose representatives, as a sign of their respect for a favourite type of wine, give it their blind preference in all conditions of consumption.

One of these types of wines are Vermouths - flavoured wines with a good pedigree based on wormwood. The name "vermouth" has been used since the Middle Ages. It comes from the German "wermut" - which means "wormwood". However, such drinks were prepared even in Antiquity, in particular, they were practised by Hippocrates [15, 18, 19].

It is a common story that vermouth was invented in Italy. The first enterprise to produce vermouth (as well as aperitif) was founded by Antonio Benedetto Carpano in the Italian city of Turin in 1786 [15]. Carpano made aperitifs for ladies, so the drink was sweet. This historical legacy has survived to our time - Turin type of vermouth even nowadays has a sweet flavour, it is served in Turin cafes (Piedmont region) as an aperitif especially for ladies even at night. In the middle of the 19th century, the production of sweet vermouths was industrialised under the name Martini [23]. The greatest influence on the development of this brand was the manager Luigi Rossi, who showed his talent in herbology (Herbology - the science of herbs). It was he who, experimenting with spicy herbs, spices and other aromatic ingredients, invented the classic recipe for Martini Rosso, thanks to which the Martini winery in Piedmont, Italy, surpassed its competitors and has been a leader in the vermouth market for almost two centuries [23].

Piedmont vermouth Martini deservedly retains the palm of superiority in the history of this drink. The elegant Martini Rosso vermouth is an outstanding representative of this product group, with a balanced, full, concentrated, complex flavour with a pleasant bitterness, a rich aroma and a characteristic dark amber colour, reflecting the peculiarity of its production with the addition of caramel colour.

The experience of Turin sweet vermouth, almost a century after the first Martini Rosso vermouth, was embodied in Piedmontese Asti by Giuseppe Perlino, who named his drink Vermouth di Torino Rosso Perlino (1930) [25]. This vermouth has a dark amber colour, its aroma is saturated with tones of fragrant spices and herbs with pronounced hints of peppermint, wormwood and cinnamon, effectively accentuated by balsamic notes and nuances of vanilla. The taste of this vermouth is balanced, enveloping the palate, with a smooth texture, slightly tart, combining hints of dried fruits, orange zest and tobacco, leaving a rich sweet and fragrant aftertaste.

Both of these vermouths from Piedmont are dark in colour and sweet in flavour. Both are made from white grape varieties, filling the light canvas of the original colour of the grape wine with the colours of the dyes used for their production ingredients. For the fullness of artistic creativity, the two renowned Piedmont vermouth producers have also created light coloured drinks without darkening the light colour of the white grape berry wine: Martini Bianco Vermouth and Perlino di Torino Bianco Vermouth. Vermouth Martini Bianco has a pale yellow colour with straw hues, an intense, harmonious, balanced in sweetness and bitterness taste and an aroma full of vanilla tones [12, 15]. Vermouth Perlino di Torino Bianco has a similar story: its elegant light straw colour intrigues with a sweet fruity taste with fine tartness and refined bitterness in the long aftertaste, the aroma is harmonious, intense with notes of white fruits, fragrant herbs, vanilla and spices.

In the mid-18th century, vermouth was also produced in the French town of Chambéry, which, together with Turin, was part of the Duchy of Savoy until its division in the 19th century. For this reason, France can also be considered the fatherland for Vermouth [15]. In France, its name evolved into the French "Vermouth" and its own French dry (not sweet) type appeared. The French winemaker Joseph Noyilly began producing Noilly Prat dry white Vermouth in the early 19th century in the town of Marseillan in the South Pyrenees region [24].

To prepare white Noilly Prat Original Dry vermouth they use herbs and spices that grow in different regions of the world: chamomile, coriander in Morocco, bitter oranges in Tunisia, etc [5]. In the composition of white Noilly Prat Extra Dry vermouth chamomile and coriander from Morocco, bitter oranges from Tunisia, iris root from Italy are used. For preparation of red semi-dry vermouth Noilly Prat Rouge with more intense flavour sweet orange from Spain, cinnamon from Sri Lanka, cinnamon bark from Ecuador, cloves from Madagascar and cocoa beans from Venezuela are used, and for red semi-sweet vermouth Noilly Prat Ambré coriander and roses from Morocco, cardamom from India, cinnamon from Sri Lanka are used [3, 17, 24].

Because of their distinct sweet flavour, all of the sweet vermouths described are used as an ingredient for sophisticated cocktails, and the white ones with green olive berry, adored by female consumers in all countries of the world. In the 20th century, vermouths become an essential ingredient in classic cocktails for the international consumer such as: Martini, Manhattan, Negroni. White dry vermouths such as Noilly Prat Original Dry are ideal as an aperitif, for example with seafood.

Historically, Italy is considered to be the ancestor of sweet red vermouth and France of dry white vermouth. Even in the names of cocktail ingredients, international guides label vermouths Italian Vermouth and French Vermouth [22], honouring their place of origin and informing consumers about their style.

Since the end of the 19th century, vermouth has been an essential ingredient in many classic cocktails such as Martinis, Manhattans, and Negronis. Also from the beginning of the 20th century, you can find recipes for dishes that use dry vermouth as an alternative to white wine.

In Italy, the main vermouth producers are: Martini, Cinzano, Carpano, Barbero, Ricadonna, Gancia and others; in France - Noilly Prat, Lillet, Bussot, Dollin and others. Vermouths are also produced in Spain (Vermouth Yzaguirre), USA (Tribuno Sweet Vermouth, Tribuno Dry Vermouth, Kedem Kosher Sweet Vermouth, Galo etc), Argentina (Lacuesta Vermouth Blanco), as well as in the Czech Republic, Bulgaria, Romania, Hungary,

Moldova, Russia, Ukraine, other countries. Germany, Holland. In Russia, white, pink and red vermouths are produced, each of them of two types: strong (18 % of ethyl alcohol) and dessert (100-160 g sugar/dm^3) [1, 2, 4, 22, 26, 27].

2 Methodology

The object of the study was samples of vermouths of world-famous brands purchased in a retail chain (Kemerovo city, Kemerovo region, Russia). The subject of the study was organoleptic and analytical parameters of purchased vermouth samples.

Organoleptic evaluation of samples of aromatic wines (vermouths of red and white types) was carried out according to the requirements of GOST 32051-2013 [7]. Before tasting the samples were cooled to the temperature: red - to 12°C, red - to 15°C [8].

The evaluation was carried out on a 10-point scale. Transparency, colour, aroma, flavour and bouquet of wine samples were assessed blindly (closed) in tasting glasses. Tones were recorded, as well as the presence of halftones, special shades, extraneous odours (artefacts).

The tasters were selected from among sommeliers with special training and professional experience and who had been instructed in the specific features of organoleptic analysis of flavoured wines.

The mass fraction of volatile substances was measured by gas chromatographic method as the most universal and effective method for separation of mixtures of substances with subsequent identification and quantification of the content of individual components [9].

The array of experimental data, was subjected to statistical analysis [11, 20]. The interval scale of variables reflects the formula (1).

$$Y = a \times X + b \quad (1)$$

The methods of parametric statistics assumed that a random vector of variables forms some multivariate distribution and is transformed into a normal distribution. The methods of correlation and regression analysis were applied in statistical analysis, which assumes that there can be a functional relationship between variables (random variables), manifested in the fact that one of them is measured as a function of the other (argument).

The correlation analysis took into account that between the analysed variables there can hypothetically exist a stochastic relationship, which is manifested in the presence of factors of parametric nature (historically established technology of viticulture and winemaking). The correlation coefficient (r) was used as a measure of dependence between the analysed variables, which was calculated according to formula 2.

$$Correl(X,Y) = \frac{\sum_{i=1}^{n}(x_i-\bar{x})\times(y_i-\bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i-\bar{x})^2\times(y_i-\bar{y})^2}} \quad (2)$$

Correlation dependencies were calculated between the sum of scores of the analysed wine samples for flavour and aroma indicators and the mass concentration of volatile substances in them. The values of the correlation coefficient can range from -1 (inversely proportional dependence) to +1 (directly proportional dependence). If the mutual dependence between the analysed variables could not be revealed, the correlation coefficient is 0 (variables are not correlated). The closer the value of this coefficient is to 1, the stronger is the revealed mutual dependence. Correlation analysis allowed us to establish the strength and direction of stochastic relationship between the analysed variables.

For the purpose of application value, the mean result of the analysed feature of one parameter for one series of experiments was different from the mean result of another series, then the method of comparison of mean was applied.

The deviation of the general population of experimental data from the mean value was determined by the standard deviation method according to formula 3. The standard deviation is calculated using the "n-1" method. The standard deviation from the mean shows a measure of how far the population data points are scattered from their mean. Function 3 assumes that the arguments are only a sample of the population.

$$\delta = \pm\sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{X})^2}{(n-1)}} \quad (3)$$

where $\bar{X}$ - is the mean value and n is the sample size.

$\bar{X}$ - the average value of a variable is calculated as the arithmetic mean, which is calculated by adding a sample of variable values and then dividing the resulting sum by their number.

To realise the objectives of the applied value, for each parameter analysed, the Median function was measured, reflecting the value of the variables, which is the middle of a set of numbers, that is, the half at which exactly half of the values of the variables have values greater than the median and half of these values have values less than the median.

In order to establish the nature of the relationship between the two sets of data variables, we calculated the covariance function using formula 4.

$$Cov(X,Y) = \frac{\sum_{i=1}^{n}(x_i-\bar{x})\times(y_i-\bar{y})}{n} \quad (4)$$

where $\bar{x}$ и $\bar{y}$ - are the mean values of the array of the 1st variable and the array of the 2nd variable; n - sample size.

Covariance is a function reflecting the mean value of the products of deviations for each pair of points of two sample arrays of variables. This function was used in our study to statistically test whether a higher level of organoleptic evaluation corresponds to a higher level of values of the mass concentration of the analysed volatile substances.

The measure of interdependence of two interrelated arrays of variables was also characterised by the coefficient of determination, which was determined by formula 5.

$$R^2 = r(x,y)^2 \quad (5)$$

For the linear relationship adopted in the analysis, the coefficient of determination is equal to the square of the correlation coefficient. The value of the coefficient of determination means a functional measure of interdependence between the analysed arrays of variables (sums of the score for taste and aroma of the

analysed vermouth samples and the mass concentration of essential volatile substances in them).

3 Results

The experimental data obtained in the study are summarised in Tables 1 and 2.

Table 1: Analysed parameters of white type vermouths

Flavoured wines (vermouth) of the white type	Sum of flavour and aroma scores, points	Concentration in samples of analysed substances, mg/dm^3	
		ethyl acetate	isobutanol
Martini Bianco	6,4	34,5	20,1
Martini Extra dry	4,5	79,3	19,7
Cinzano Bianco	5,8	25,2	25,2
Cinzano Extra dry	6,6	62,3	23,3
Perlino Bianco di Torino	5,6	40,3	19,9
Cesare da Sesto	5,7	58,7	19,6
Salvatore Bianco	5,4	36,7	23,7
average value	5,6	48,1	19,8
Deviation from the average	±0,69	±19,1	±2,3

As can be seen from the data in Table 1, the sum of scores for the most important parameters of flavoured wines is rather high (5.6 out of 10 maximum scores for all organoleptic parameters), with a standard deviation from the mean of ±0.75. Thus, the variability of this indicator is 13.4%. The median of the analysed indicators is 5.7 points. On the basis of these results it is possible to consider the presented sample of aromatic wine samples (white vermouths of global commodity brands) as representative, adequately representing the analysed group of aromatised wines (white vermouths).

As previously indicated by researchers of flavoured wines [13], the formation of flavour and aroma parameters of vermouths is most influenced by two chemical compounds: ethyl acetate (middle ester) and isobutanol (higher alcohol). The data presented in Table 1 on the measurement of these two highly volatile substances in the analysed samples of flavoured wines (in particular, white type vermouths) showed that the concentration of ethyl acetate in the analysed samples is 25.2 ÷ 79.3 mg/dm^3 with a mean value equal to 48.1±19.1 mg/dm^3 , with a median of 40.3 mg/dm^3 . The concentration of isobutanol in analysed samples of white vermouth is 19.6 ÷ 23.7 mg/dm^3 with a mean value of 19.8±2.3 mg/dm^3 , with a median of 20.1 mg/dm^3 .

Mathematical processing of the above data showed that there is a certain correlation (relationship) and covariance (interdependence) between the values of the total score of taste and aroma indicators of the analysed aromatic wines (white type vermouths) and the highly volatile compounds listed in Table 1: between the flavour evaluation and ethyl acetate concentration the correlation coefficient is (r^2 = -0.41), which means an inverse relationship between these two indicators, while a similar relationship between the analysed organoleptic indicators and the concentration in white type vermouths of isobutanol the mentioned correlation has a direct character, but weak in the value of this coefficient (r^2 = 0.27). The coefficient of determination between the analysed indicators was 16.72 units for ethyl acetate and 7.50 units for isobutanol. It means that ethyl acetate participation in the formation of flavour parameters of white vermouths is estimated at 16.72 %, and isobutanol - at 7.5 %. The covariance (interdependence) of these three analysed parameters (flavour, ethyl acetate and isobutanol concentration in wines) is (-4.61) and (0.38), respectively. The values of covariance coefficients are not equal to 0, so the interdependence between them is revealed, and in the first case (ethyl acetate) it has an inverse character, i.e. with increasing concentration of this ester the total evaluation of flavour parameters of white vermouths decreases.

Table 2. Analysed parameters of red type vermouths

Flavoured wines (vermouth) of the red type	Sum of flavour and aroma scores, points	Concentration in samples of analysed substances, mg/dm^3	
		ethyl acetate	isobutanol
Martini Rosso	6,7	53,2	20,4
Martini Rosato	6,0	40,7	22,3
Cinzano Rose	6,4	55,1	26,8
Cinzano Rosso	7.0	59,2	23,6
Perlino Rosso di Torino	6,0	46,9	17,1
Sperone Rosso	6,8	116,0	26,1
Salvatore Rojo	5,2	58,9	29,0
average value	6,3	54,6	23,6
Deviation from the average	±0,6	±25,0	±4,1

As can be seen from the data in Table 2, the sum of scores for the most important parameters of flavoured wines (red type vermouths) is also high (6.3 out of 10 maximum scores for all organoleptic parameters), with a standard deviation from the mean of ±0.6. Thus, the variability of this indicator is 9.5%. The median of the analysed indicators is 6.2 points, which also exceeds the same indicator for white vermouths by 8.8%. This fact demonstrates that Russian tasters appreciated the flavour and aroma parameters of red vermouths higher, which, as noted earlier, have more intense flavour and aroma parameters. As in the case of white vermouths, the analysed sample of red vermouths is also representative, adequately representing the analysed group of flavoured wines (red vermouths).

As in the case of white-type vermouths, researchers of flavoured wines [13] indicate that the formation of flavour and aroma parameters of red-type vermouths is most influenced by the same two chemical compounds: ethyl acetate and isobutanol. The data presented in Table 2 on the measurement of these two chemicals in the analysed samples of red type vermouths showed that the concentration of ethyl acetate in the analysed samples is

46.9 ÷ 116.0 mg/dm^3 , which exceeds similar values for white type vermouths (25.2 ÷ 79.3 mg/dm^3) with a median value of 54.6±25.0 mg/dm^3 , it is also higher than for white type vermouths (48.1±19.1 mg/dm^3) with a median of 55.1 mg/dm^3 , which also exceeds similar values for white type vermouths (40.3 mg/dm^3).

Concentration of isobutanol in the analysed samples of white type vermouth is 17,1 ÷ 26,8 mg/dm^3 , which corresponds with a small error to the values of the analysed indicator for white type vermouth (19,6 ÷ 23,7 mg/dm^3) with the average value of this indicator 23,6±4,1, which also does not reliably differ from the values of the similar indicator for white vermouths (19,8±2,3 mg/dm^3), with the median value equal to 23,6 mg/dm^3 , which exceeds the similar value for white vermouths (20,1 mg/dm).[3]

Mathematical processing of the data presented in Table 2 showed that there is also a certain correlation and covariation between the values of the total score of taste and aroma indicators of the analysed aromatic wines (red vermouths) and the volatile compounds mentioned in this table: between the total taste and aroma score and ethyl acetate concentration the correlation coefficient $r^2 = 0.46$ units, which differs from the value of this coefficient for white vermouth ($r^2 = -0.41$) not only in absolute value, but also in sign. This means a direct relationship between these two indicators, while for white vermouths such a relationship was inverse. The relationship between the analysed organoleptic indicators and the concentration of isobutanol in red vermouths is estimated by the inverse type correlation coefficient ($r^2 = -0.25$), which also has an opposite character in comparison with white vermouths ($r^2 = 0.27$). At the same time, in red vermouths, as well as in white vermouths, the analysed correlation has a weak character (according to the value of this coefficient).

The coefficient of determination between the analysed indicators of red vermouths was 21.2 units for ethyl acetate, which is higher than the value of the same indicator for white vermouths (16.72 units), and for isobutanol the value of the coefficient of determination is 6.31 units, which is lower than the value of this indicator for white vermouths (7.50 units). Determination means that the participation of ethyl acetate in the formation of flavour parameters of red vermouths is estimated at 21.2 %, and isobutanol - at 6.31 %.

The covariance (interdependence) of these three analysed parameters (flavour, concentration of ethyl acetate and isobutanol in red vermouths) is 6.16 (in white vermouths it is negative and equal to -4.61) and 0.55 (in white vermouths it has a value of 0.38), respectively. Values of covariance coefficients in red vermouths, as well as in white vermouths are not equal to 0, so the interdependence between them is revealed, and in the first case (ethyl acetate) it has a direct character, i.e. with the increase in the concentration of this ester the total evaluation of flavour parameters of white vermouths increases, and for the second key substance - the reverse character.

4 Conclusions

The conducted research allowed to establish the nature of influence of two key volatile natural compounds - ethyl acetate and isobutanol - on flavour parameters of flavoured wines on the example of white and red vermouths. This influence is ambiguous both on the strength of participation of these substances in the formation of the main parameter of flavoured wines, and on the direction of this influence.

In particular, it was found that the level of influence of middle ester on the formation of flavour parameters of vermouths significantly exceeds the similar level of participation of isobutanol. It was noted that in the case of red vermouths this influence is positive, while for white vermouths this influence is negative, i.e. when the concentration of the said ester in the finished white vermouth increases, the total evaluation of flavouring properties of these wines decreases.

The nature of participation of the higher alcohol isobutanol in the formation of flavour parameters of white and red vermouths is contradictory: for white vermouths its influence is positive, while for red vermouths, on the contrary, it is negative.

The median concentration values of the mentioned volatile compounds for original vermouths of white and red types were revealed: ethyl acetate - 40.3 and 55.1 mg/dm^3 , respectively; isobutanol - 20.1 and 23.6 mg/dm^3 , respectively. The concentration values of ethyl acetate middle ester in original vermouths differ significantly for flavoured wines of Russian origin [10], in which values of 4.45 mg/dm^3 ÷ 24.3 mg/dm^3 , i.e. 2 ÷ 10 times lower, were registered. Taking into account the revealed influence of this ester on the flavour evaluation of flavoured wines, such a difference leads to dramatic consequences for consumers of these wines.

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