Aroma profile of muscat wine from Citron Magaracha grapes grown in the Samara region

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Abstract. Aroma is one of the important organoleptic characteristics of wine. It determined by the volatile components of the grape berry, the components formed during fermentation and in the aging process. The aroma profile of muscat wine from Citron Magaracha grapes grown in the Samara region was first obtained using the method of liquid-liquid extraction and GC-MS analysis. The main aroma-forming components of the investigated wine are aliphatic and aromatic alcohols, terpene compounds, esters and acetals. Oxidized and esterified compounds are found among terpenes. Ethyl esters of C₁₄-C₁₈ fatty acids are present among the esters. A comparison is made of the main aroma components with profiles of typical representatives of muscat wines. A comparative analysis of the main aromatic components makes it possible to classify Citron Magaracha grapes grown in the Samara region as typical representatives of muscat grapes. Wine from grapes of this variety according to the complex of physicochemical parameters and the aroma profile can reasonably be attributed to muscat wines.

1. Introduction

Aroma is one of the important organoleptic characteristics of wine, which ultimately determine the quality of wine. Currently, about 800 volatile compounds of different families are known [1], which are part of the wine and affect the organoleptic perception of wine. The main contribution to the aroma of wine is made by aromatic, cyclic and alicyclic alcohols, aldehydes, ketones, carboxylic acids, esters and terpene compounds.

By origin, aromatizing compounds can be divided into three groups. The first group of aromatizing compounds is formed in the process of ripening of grapes and is present in the initial must. The presence of these compounds creates a primary aroma and is determined by the grape variety, climatic conditions of cultivation, soil characteristics, processing conditions and the use of enzyme preparations in pre-fermentation processing [2-4]. The second group of compounds is formed during fermentation process from carbohydrates, amino acids and lipids contained in the initial must. Their presence is affected by the fermentation conditions and the used yeast strain [5]. The third group of compounds is formed during the aging of wine as a result of redox and biochemical reactions between the components of the wine and the components of the oak barrel (if aging occurs in an oak barrel) [6].

Compounds of the first group, originally present in grape berry, make a significant contribution to the aroma of Muscat wines. This is due to the peculiarities of the technology of Muscat production, which involves unfinished fermentation, interrupted at the initial stage by the addition of rectified alcohol [7]. As a result, aromatic compounds present in grapes are largely preserved. The oxidizing processes that occur during aging can have a significant effect on the aroma of Muscat wines, giving a bouquet combining varietal fruit aromas and subtle tarry aging tones.

A distinctive feature of Muscat wines is the presence of a variety of terpene compounds: monoterpenes, cyclic terpenes, terpene esters, oxidized terpenes [8, 9].
One of the serious problems in the production of Muscat wines is that the grapes of many muscat varieties are susceptible to diseases (in particular, oidium). This leads to lower yields and, consequently, a shortage of raw materials for the production of Muscat wines. One solution to this problem is to use new grape varieties suitable for making Muscat wines and resistant to disease. To prove the compliance of the resulting wine with Muscat wines, it is necessary to study the profile of aromatic components and compare it with typical representatives of Muscat wines.

The purpose of our work was to study the profile of volatile aroma components in Muscat wine from Citron Magaracha grapes (Madeleine Anzhevin x Novoukrainsky early) grown in the Samara region using liquid-liquid extraction and gas chromatography in combination with mass spectrometry [10].

2. Materials and methods

2.1. Chemicals
Dichloromethane and n-pentane (GC grade) were purchased from Aldrich (Galachem company, Moscow), anhydrous sodium sulfate (reagent grade) was purchased from Vexton (St. Petersburg).

2.2. 2.2. Muscat Wine Sample from Citron Magaracha Grapes
Grapes (100 kg) were manually harvested at optimum maturity in Samara Region (52°52'41" N 49°7'6" E) in the third decade of September 2018. Processing was carried out in the laboratory of fermentation technology of Samara State Technical University. The grapes were processed on a destemmer, 75 mg/kg SO2 was added to the resulting pulp and infused at 20°C for 24 hours. The pulp was pressed in a Voran basket press, the must (61 L) was clarified at 0-2°C for 24 hours, then heated to 15°C and inoculated with Vitilevure 58w3 yeast (0.3 g/l must). Fermentation was performed at 15°C, controlling the content of sugars, and stopped when the residual sugar content was about 165 g/L by the addition of 95% food grade ethanol up to a total alcohol content 16% v/v. The resulting wine material was clarified and stored 6 months in an oak barrel.

2.3. Standard chemical parameters
Density, ethanol, extract, total acidity, pH, volatile acidity, reducing sugar, total SO2 and total phenolic compounds were analyzed [11].

2.4. Isolation of volatile components
The isolation of volatile components was carried out by liquid-liquid extraction. A sample of Muscat wine (200 ml) was extracted continuously with 25 ml of n-pentane - dichloromethane (60/40 v/v) for 12 hours with stirring on a magnetic stirrer. The solvent was separated by centrifugation (3000 rpm, 15 min), dried with anhydrous sodium sulfate and extract was then concentrated with a Vigreux column (50 cm) to a volume of 1 ml and then under stream of nitrogen to a volume of 0.2 ml.

2.5. GC-MS analysis
An Agilent model 7890A gas chromatograph coupled to a mass-selective detector model 5975C was used. An amount of 1 μl of the extract was injected in splitless on a HP5ms column (30 mx 0.25 mm; 0.25 μm film thickness) in an alkali-free regime. Oven temperature program was: 70°C (5 min) - 1°C/min - 95°C (10 min) - 2°C/min - 190°C (40 min). Injector and transfer line temperature were 250°C and 280°C, respectively. Mass detector conditions were: electronic impact mode (EI) at 70 eV; source temperature 178°C; scanning rate 1 scan/s; mass acquisition range 45-450 amu. Helium was used as the carrier gas at a flow rate of 0.7 ml/min.

Peak identifications were based on a comparison of their mass fragmentation with those reported by the commercial libraries such as Wiley 275, NIST 08 and NIST 11.

3. Results and discussion
Standart chemical parameters of muscat wine produced from grapes Citron Magaracha are shown in Table 1.
Table 1. Standard chemical parameters of Muscat wine produced from grapes Citron Magaracha

| Parameter                              | Value   |
|----------------------------------------|---------|
| Density (20°C), g/sm³                  | 1.025   |
| Ethanol, %v/v                          | 16.0    |
| Titratable acidity, as tartaric acid, g/L | 6.6     |
| pH                                     | 3.3     |
| Volatile acidity, as acetic acid, g/L  | 0.4     |
| Reducing sugar, g/L                    | 145     |
| Total phenolic compounds, mg/L         | 390     |
| Total sulphur dioxide, mg/L            | 64.0    |

The profile of aroma components determined by the GC-MS method in Muscat wine produced from Citron Magaracha grapes are given in Figure 1. Among the 63 compounds detected, there were 13 alcohols and diols, 23 esters, 11 terpene compounds, including oxidized and esterified, 5 acetals, 3 hydrocarbons and 6 compounds of other classes.

![Figure 1. Total ion chromatogram of the aroma components of Muscat wine made from Citron Magaracha grapes. The time scale is graduated in minutes. Peak identification (Table 2)](image-url)

The terpene compounds extracted from the skin of grapes are present in the original must and determine the floral and fruit aromas of the resulting wine. Some of these compounds are transformed during fermentation, undergoing oxidation and esterification (trans-linalool oxide, rosen oxide, nerol oxide, linalool propionate). Aromatic and aliphatic alcohols, diols and part of the esters are formed during fermentation. It is interesting to note that, along with esters traditional for muscat varieties, esters of higher molecular weight carboxylic acids (tetradecanoic, palmitic, hexadeceno-9-enoic, and stearic acids) were found in the aroma profile.

A number of compounds involved in the formation of muscatel aroma from Citron Magaracha grapes are formed during aging in an oak barrel. These are cyclic (cis-5-hydroxy-2-methyl-1,3-dioxane, trans-4-
hydroxymethyl-2-methyl-1,3-dioxolane and cis-4-hydroxymethyl-2-methyl-1,3-dioxolane) and alicyclic (triethylorthoformate, 4-methyl-3,5-dioxadecane) acetals. The presence of ethyl vanillate indicates the transformation of lignin substances extracted from oak barrel.

The absence in the aroma profile of carboxylic acids and some terpenediols (3,7-dimethylocta-1-ene-3,7-diol, 3,7-dimethylocta-1,7-diene-3,6-diol) can explain the high affinity of these compounds to the aqueous phase and their poor extraction with organic solvents.

Comparison of the aroma profile of Muscat wine produced from Citron Magaracha grapes with typical representatives of Muscat wines is presented in Table 2.

Table 2. Comparison of volatile components of Muscat wine produced from Citron Magaracha grapes with those of typical Muscat wines

| Component | CM | Mpg | M | MIV | MB | Odor |
|-----------|----|-----|---|-----|----|------|
| **Alcohols and diols:** |    |     |   |     |    |      |
| propan-1-ol | + (1) | + | - | - | + | fusel, fruit |
| butan-1-ol | + (2) | - | - | - | + | fusel, herb |
| iso-butan-1-ol | + (3) | + | + | + | + | essential, wine |
| pentan-1-ol | + (4) | - | - | - | - | fruit, balsamic |
| 2-methylbutan-1-ol | - | + | + | + | - | malt |
| 3-methylbutan-1-ol | + (23) | + | + | + | + | fusel, essential, fruit |
| hexan-1-ol | + (9) | + | + | + | + | floral |
| hex-2-en-1-ol | - | - | - | - | + | green, herbal |
| benzylic alcohol | + (34) | + | - | + | + | fruit, jasmine |
| 2-phenylethanol | + (29) | + | + | + | + | rose, fruit |
| butan-2,3-diol | + (5) | - | + | + | + | ripe fruit, buttery |
| 3-ethoxypropan-1-ol | + (7) | - | - | - | + | overripe pear |
| 3,3-dimethylbutan-2-ol | + (17) | - | - | - | - | - |
| propan-1,2-diol | + (19) | - | - | - | - | - |
| 2-ethoxyethanol | + (25) | - | - | - | - | - |
| heptan-1-ol | - | - | - | - | + | oily |
| **Ester:** |    |     |   |     |    |      |
| ethyl acetate | + (10) | + | + | + | - | fruit, pineapple |
| ethyl lactate | - | + | - | - | + | butter, cream, raspberry |
| ethylbutanoate | - | - | + | + | + | fruit |
| iso-amylacetate | - | + | + | + | + | pear, banana |
| ethylhexanoate | + (21) | + | + | + | + | apple, banana, wine |
| ethyleptanoate | + (47) | - | - | + | - | fruit, wine, brandy |
| ethyloctanoate | + (38) | + | + | + | + | floral, fruit, brandy |
| ethylnonanoate | + (48) | - | + | + | - | - |
| ethyldecanoate | + (44) | + | + | + | + | floral, soap |
| ethyldodecanoate | + (51) | - | + | + | - | green tea, pineapple |
| ethyltetradecanoate | + (59) | - | + | + | - | - |
| ethylhexadec-9-enoate | + (61) | - | - | - | - | - |
| ethylpalmitate | + (62) | - | - | - | - | - |
| ethylstearate | + (63) | - | + | - | + | - |
| hexylacetate | + (22) | + | + | + | + | apple, pear, flower |
| ethyl β-methylbenzenepropanoate | + (12) | - | - | - | - | - |
| methyl 3-methoxypropanoate | + (16) | - | - | - | - | - |
| butyl 3-methylbut-3-enylfumarate | + (20) | - | - | - | - | - |
| Compound                                    | Value | Flavours                                      | Notes                          |
|---------------------------------------------|-------|----------------------------------------------|--------------------------------|
| ethylbenzoate                               | + (33) | fruit, flower                                |                                |
| diethylsuccinate                            | + (35) | fruit, apple, ylang                          |                                |
| monoethylfumarate                           | + (41) |                                              |                                |
| di(3-methylpentyl)succinate                 | + (42) |                                              |                                |
| ethylvalinate                               | + (50) | vanilla, honey                               |                                |
| ethyl 2-methylpentylsuccinate               | + (52) |                                              |                                |
| iso-butylpentadecanoate                     | + (55) |                                              |                                |
| triethylcitrate                             | + (57) |                                              |                                |
| 2-phenylethylacetate                        | -     | rose                                         |                                |
| Terpenes:                                   |       |                                              |                                |
| trans-linalooloxide                         | + (26) | flower, green                                |                                |
| cis-linalooloxide                           |       |                                              |                                |
| linalool                                    | + (27) | citrus, floral                               |                                |
| hotrienol                                   | + (28) | fennel, ginger                               |                                |
| rozenoxide                                  | + (31) | flower, lychee, rose                         |                                |
| nerol oxide                                 | + (32) | oil, flower                                  |                                |
| α-terpineol                                 | + (36) | flower, lilac, anise                         |                                |
| citronellol                                 | -     | rose                                         |                                |
| nerol                                       | -     | floral, herbal                               | citrus, geranium, orange       |
| geraniol                                    | + (40) |                                              |                                |
| 3,7-dimethyloct-1-7-diene-3,7-diol           | -     |                                              |                                |
| 3,7-dimethyloct-1-7-diene-3,6-diol           | -     |                                              |                                |
| α-terpinolen                                | + (24) | pine                                         |                                |
| 3,3,6-trimethylheptan-1,5-diene-4-ol         | + (46) |                                              |                                |
| linalool propionat                          | + (37) |                                              |                                |
| 2-methyl-6-methyleneocta-2,7-diene-4-ol      | + (53) |                                              |                                |
| Acetals:                                    |       |                                              |                                |
| cis-5-hydroxy-2-methyl-1,3-dioxane          | + (11) |                                              |                                |
| trans-4-hydroxymethyl-2-methyl-1,3-dioxolan | + (13) |                                              |                                |
| cis-4-hydroxymethyl-2-methyl-1,3-dioxolane  | + (15) |                                              |                                |
| triethylortoformiate                        | + (14) |                                              |                                |
| 4-methyl-3,5-dioxadecane                    | + (18) |                                              |                                |
| Hydrocarbons:                               |       |                                              |                                |
| 2,4-dimethylheptane                         | + (49) |                                              |                                |
| 3,3-dimethylhexane                          | + (54) |                                              |                                |
| pentacose-3-en                              | + (60) |                                              |                                |
| Other:                                      |       |                                              |                                |
| furfural                                    | + (6)  | fusel, fried bread                           |                                |
| furan-2,5-dion                              | + (8)  |                                              |                                |
| pyrazine-2-carboxylic acid                  | + (30) |                                              |                                |
| 2,6-dimethylmorpholine                      | + (39) |                                              |                                |
| diethyl-2-hydroxypentadecioato              | + (43) |                                              |                                |
| malic acid                                  | + (45) |                                              |                                |

* wine from Citron Magaracha grapes
* wine from Muscat “a petit grains” grapes [2]
* wine from Muscat grapes [12]
* wine from Malvastia moscat grapes [13]
* wine from Muscat Bornova grapes [14]
Data analysis (Table 2) shows that the aroma compounds composition of wine from Citron Magaracha grapes, along with typical C4-C6 alcohols, contains a number of alcohols with functional substituents (3-ethoxypropan-1-ol, 3,3-dimethylbutan-2-ol, 2-ethoxyethanol, propane-1,2-diol). The ester profile is in good agreement with the profile of typical representatives of Muscat wines. In addition, it is supplemented with esters of higher C14-C18 acids, aromatic acids, succinic, fumaric and citric acids. The profile of terpene compounds also agrees well with the profile of typical Muscats. The absence of typical representatives of terpenes such as nerol and citronellol can be explained by the oxidation of these compounds during fermentation and aging to form nerol oxide (1) and rosen oxide (2). A distinctive feature of Muscat wine from the Citron Magaracha grapes is the presence in the aroma components of a number of cyclic and alicyclic acetals, several hydrocarbons and furan compounds.

4. Conclusion
In the present work, the aroma profile of Muscat wine from Citron Magaracha grapes grown in the Samara region is described for the first time. The main treasure in the aroma of this wine is made by aliphatic and aromatic alcohols, esters, terpene compounds and acetals. A comparative analysis showed the similarity of the profiles of aroma compounds of the class of alcohols, esters and terpenes of wine from Citron Magaracha grapes and typical representatives of muscat wines. Thus, wine from Citron Magaracha grapes grown in the Samara region, according to the set of chemical parameters and the aroma profile, can be reasonably attributed to Muscat wines.

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