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SO_2 - binding complex of grapes and factors of its formation

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Abstract. The studies of the factors of formation SO_2-binding complex of white and red grape cultivars from different soil and climatic regions of the Crimea were carried out. The formation of the SO_2-binding complex of grapes is associated with a combination of endogenous and exogenous factors. It was found that the most significant factors ($\alpha<0.05$) in the formation of SO_2-binding complex are the cultivar, soil-climatic region of growth, harvest year, and concentration of sugar. Revealed that in the case of white grape cultivars – the cultivar ($\alpha = 0.0002$) and the soil-climatic region of growth ($\alpha = 0.0003$) had a significant effect on the accumulation of aldehydes. In red grape cultivars the accumulation of SO_2-binding components (ketoacids and aldehydes) was determined by the grape cultivar ($\alpha<0.045$); α-ketoglutaric acid – soil-climatic region of growth ($\alpha = 0.014$). The relationship between the mass concentrations of aldehydes and sugars in red grape cultivars has been established.

1 Introduction

Recently, the number of organic vineyards around the world has significantly increased. Federal Law No. 280 (about organic products and amendments to certain legislative acts of the Russian Federation), which entered into force on January 1, 2020 in Russia opened the field of activity for the Russian production of organic products with the same basic principles as in the rest of the world which includes care for the environment, soil, ecosystems, human health, preservation of biodiversity and refusal to use agrochemicals [1].

Considering that winemaking is a significant part of the economic sector of the south of Russia, a scientifically based approach to the development of organic winemaking is an actual task. Limiting the use of preparation for winemaking, including sulfur dioxide (SO_2), remains a problematic issue in the production of organic wine.The SO_2 content in the must/wine protects it from oxidation and has an antimicrobial effect. SO_2 has the most effective properties when it is in a free form. It is known that the presence of certain

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substances can limit its functional properties [2] that increases total amount of added SO_2. Among these substances, the most stable compounds with SO_2 form ketoacids and acetaldehyde [3].

In International Organization of Viticulture and Winemaking (IOV) resolution considers a number of approaches to promote the production of quality wines with low SO_2 content. In this resolution also an important role is given to the grape cultivar. In our opinion, when choosing a grape sort for the production of wines with organic status, special attention should be paid to the SO_2-binding complex of the grape berry and the factors influencing its formation. It is known that ketoacids and acetaldehyde are formed as a result of glycolysis or cellular respiration during the oxidation of α-hydroxy acids, decarboxylation of oxaloacetic acid [4]. Considering the role played by ketoacids and acetaldehyde in plant physiology, it can be assumed that their content in different parts of the grape depends on the ambient temperature, insolation, and the intensity of photosynthesis [5].Previous studies have revealed differences in grape cultivar in terms of the content of pyruvic, α-ketoglutaric acids and acetaldehyde [6]. It was noted that the content of α-ketoglutaric acid in red grape must was higher than in white grapes. A distinctive feature of white grape cultivar was the high content of acetaldehyde and pyruvic acid [7]. This publication presents the results of researchments devoted to identifying the factors and regularities of the formation of an SO_2-binding complex of grapes from different soil and climatic regions of the Crimea.

2 Materials and Methods

The objects of research were white and red grape of the classic, Crimean autochthonous cultivars and cultivars bred at the All-Russian National Research Institute of Viticulture and Winemaking "Magarach" of the RAS, of 2009-2020 harvest from different regions of Crimea. Their characteristics presented in Table 1.

The features of the climatic conditions of different regions are following. The south coastal region of Crimea – higher sum of active temperatures. The mountain-valley seaside region – lower annual precipitation and fewer days with temperatures above 10 °C. The western piedmont-seaside region has a lower average annual air temperature [8].

Table 1. Climatic characteristics of soil-climatic regions of Crimea.

Region	Mean annual air temperature, °C	The sum of active temperatures above 10 °C	Annual precipitation, mm	Period with temperatures above 10 °C, days
South Coast of Crimea	13.5	3700-4200	750-900	210-217
Mountain-valley seaside	13.2	3635-3820	300-400	186-202
Western piedmont-seaside	12.3	3650-3680	380-450	197-209

The sampling of grapes was carried out during the period of industrial harvest. The average sample of grapes was taken from different sides of the bush and at different heights along the diagonal of the vineyard. The total sample volume was 3 kg. Only healthy bunches of grapes were used for research. To analyze the chemical composition, an average sample was taken from the total number of grapes by cutting the berries from different parts of the bunches. Table 2 shows the indicators of the carbohydrate-acid complex of the studied lots of grapes. The numerator arithmetic means value and standard deviation. The denominator means the range, the boundaries of which are the 10th and 90th percent of the sample used.

The average concentrations of titratable acids, sugars and pH for red grapes must was 4.2 - 8.3 gL^{-1}, 206-243 gL^{-1} and 3.1-3.2 respectively. In white grapes must the concentration of titratable acids was 6.1–10.8 gL^{-1}, sugars –181-251 gL^{-1}, pH – 3.30-3.45.

Table 2. The carbohydrate-acid composition of grapes.

Grape cultivar	Concentration, gL^{-1}		pH
	sugars	titratable acids	
Bastardo magarachskiy	203±30 172-250	6.9±1.0 5.6-8.5	3.50±0.09 3.43-3.63
Cabernet Sauvignon	222±27 191-255	6.6±1.3 4.9-8.5	3.40±0.17 3.21-3.68
Merlot	224±29 186-158	6.7±1,0 5.6-8.1	3.31±0.08 3.24-3.43
Shiraz	243±28,6 215-279	7.3±1.8 5.1-8.6	3.35±0.19 3.12-3.52
Sangiovese	206±17 196-231	8.3±1.8 6.2-10.2	3.13±0.09 3.06-3.25
Kefesia	212±24 186-252	4.2±0.8 3.3-5.2	3.72±0.22 3.53-4.00
Ekim kara	206±24 167-234	4.2±0.8 3.2-5.4	3.63±0.25 3.29-3.90
Aligote	193±23 172-218	7.5±1.4 5.8-9.1	3.12±0.09 3.05-3.16
Chardonnay	187±36 160-223	10.8±4.2 5.0-13.9	3.14±0.20 2.98-3.41
Sauvignon vert	181±20 167-204	7.1±2.1 4.7-8.4	3.26±0.20 3.14-3.49
Muscat blanc	209±25 178-250	8.4±2.1 5.8-10.5	3.25±0.18 3.00-3.46
Kokur belyi	201±31 167-242	6.8±1.9 4.8-9.8	3.30±0.20 2.95-3.54
Sary Pandas	251±21 236-266	6.5±0.7 6.0-7.1	3.36±0.05 3.32-3.39
Tzitronnyi Magaracha	199±14 189-215	8.6±0.8 7.8-9.3	3.40±0.02 3.39-3.42
Rkatsiteli	234±27 194-258	6.1±0.5 5.4-6.6	3.45±0.10 3.37-3.54

2.1 Methods for the analysis of grapes and statistical data processing

To determine the chemical composition of grapes, the must was separated by pressing the berries manually, and then was centrifuged at 3000 rpm for 15 minutes. The determination of the concentration of sugars was carried out by the areometric method, titratable acids in terms of tartaric acid – by the titrimetric method, pH – by the potentiometric method [9, 10]. The content of α-ketoglutaric and pyruvic acids was determined by their ability to react with 2,4-dinitrophenylhydrazine, with the formation of bright orange or red colored substances, the color intensity of which was assessed by the colorimetric method [11].The concentration of aldehydes was determined by a titrimetric method based on the ability of aldehydes to bind with sodium hydrosulfite to form a complex non-volatile compound. Excess hydrosulfite is oxidized with iodine and then the aldehyde sulfite compound is decomposed with alkali. The released sulfur dioxide is titrated with 0.005M iodine solution [10].

Statistical data processing was carried out using the SPSS Statistica 17.0. In the illustrated materials and the text of the article, the arithmetic mean values of the indicators and their standard deviations are presented.The statistical significance of differences in grapes in terms of the content of ketoacids and aldehydes, due to the influence of various factors, was assessed by the Student's criterion at a significance level of $\alpha \leq 0.05$. The research sample was 143 grapes batches.

3 Results and discussion

It follows from Table 3 that Cabernet Sauvignon and Ekim cara were characterized by the lowest content of pyruvic acid – 15.2±10.8 and 16.4±1.6 mg L^{-1} respectively; Bastardo magarachsky and Sangiovese grape cultivars (cvs) – of α-ketoglutaric acid – 25.0±15.3 and 26.5±8.7 mg L^{-1} respectively. As for aldehydes, their lowest content was noted in the Syrah, Sangiovese and Ekim kara grape cultivars (the concentration of aldehydes averaged 14.6–15.9 mg L^{-1}. Among the studied white grape cultivars, the lowest concentration of aldehydes was found in the Sary Pandas, Kokur belyi and Sauvignon vert cultivars (on average 12.6–15.0 mg L^{-1}).

Table 3. Indicators of SO_2-binding complex of grapes.

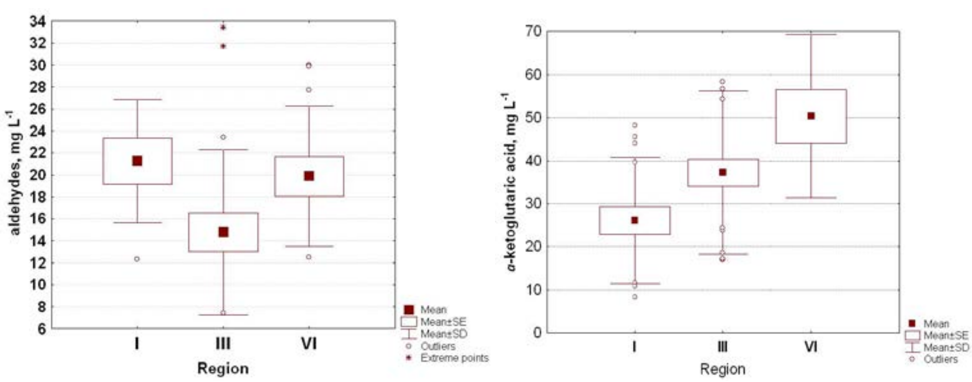
Grape cultivar	Concentration, mg L^{-1}		
	aldehydes	piruvic acid	α-ketoglutaric acid
Bastardo magarachskiy	23.7±8.5 14.8-32.6	18.2±8.9 10.7-28.2	25.0±15.3 10.9-45.5
Cabernet Sauvignon	17.7±9.9 8.8-36.1	15.2±10.8 1.7-26.2	29.5±13.2 13.6-43.1
Merlot	20.4±9.3 11.2-33.4	34.0±28.7 14.05-86.1	49.3±20.5 34.3-71.8
Shiraz	14.6±1.9 12.0-16.7	38.2±41.5 12.4-100.1	56.3±17.5 30.9-68.2
Sangiovese	14.9±3.4 11.2-18.04	18.2±2.7 15.8-22.1	26.5±8.7 17.3-38.2
Kefesia	17.8±8.0 10.7-35.2	23.3±12.0 12.7-43.2	46.7±27.7 27.4-95.5
Ekim kara	15.9±9.3 7.4-37.8	16.4±1.6 14.7-17.8	43.2±21.3 18.6-56.8
Aligote	18.1±6.1 12.5-27.5	18.3±11.3 4.9-35.2	20.6±14.2 6.1-53.6
Chardonnay	21.5±9.6 7.7-29.9	4.7±4.0 1.9-7.5	19.7±4.6 14.7-23.6
Sauvignon vert	13.2±5.5 7.4-18.3	8.8±3.1 6.6-11.0	17.5±4.5 14.4-23.0
Muscat blanc	19.9±4.8 12.3-24.2	10.0±1.8 8.8-12.1	17.9±4.4 13.2-22.0
Kokur belyi	15.0±6.8 8.8-29.0	19.1±10.3 7.1-30.4	28.0±6,5 21.4-37.9
Sary Pandas	12.6±2.3 10.9-14.2	34.7±3.6 30.5-38.4	21.4±0.4 21.1-21.6
Tzitronnyi Magaracha	18.0±1.5 16.4-19.4	10.9±11.8 1.9-24.2	27.1±15.5 13.7-44.1
Rkatsiteli	20.6±10.1 12.3-33.4	12.4±5.1 8.8-16.0	24.5±8.6 18.4-20.6

Statistical processing of experimental data on the SO_2-binding complex of grapes revealed the factors influencing its formation and establish their significance.

The study of the influence of the technical maturity of grapes on its SO_2-binding complex showed (in red grape varieties) the presence of a relationship between the content of aldehydes and sugars ($R^2 = 0.79$, at $\alpha<0.00001$), described by the equation of the second degree. The change in the content of pyruvic acid, in the process of accumulation of sugars, had a similar tendency. The lowest concentration of aldehydes and pyruvic acid in red grapes was observed at a sugar concentration in the range of 190-220 g L^{-1}. In the range of sugar content in grapes from 166 to 298 g L^{-1}, a tendency towards a decrease in the content of α-ketoglutaric acid was observed. The revealed relationship reflects the lability of ketoacids and aldehydes, mainly acetaldehyde, their participation in biochemical processes during the ripening of grapes. In white grape cultivars, the concentration of acetaldehyde was 12.6-21.5 mg L^{-1}, in red cultivars – 14.6-23.7 mg L^{-1}. In white grape cultivars, the relationship between the content of SO_2-binding components and the concentration of sugars in the berry was not revealed.

The obtained results show that the concentration of SO_2-binding components (aldehydes and ketoacids) in red grape cultivars ($\alpha < 0.045$) and aldehydes in white grape ($\alpha=0.0002$) is largely determined by the grape cultivar.

The accumulation of aldehydes in white grape cultivars ($\alpha=0.0003$) and α-ketoglutaric acid ($\alpha = 0.014$) in red cultivars is determined by the growing region (Fig. 1). The lowest concentration of aldehydes (7.4–33.4 mg L^{-1}) was observed in white grape cultivars from the mountain-valley seaside region. We believe this may be due to the cultivars composition of the studied batch of grapes from this region, which is represented mainly by the Crimean autochthonous cvs of Sary Pandas and Kokur belyi. As for red grape cvs, it was noted that the lowest content of α-ketoglutaric acid was distinguished by the grapes from the South Coast of Crimea. Its content was 8.4 to 63.9 mg L^{-1}, which, on average, is 1.5 times lower than in grapes from other regions.



Regions: I – South Coast of Crimea; III – Mountain-valley seaside; VI – Western piedmont-seaside

Fig. 1. The SO_2-binding complex of grapes from different soil and climatic regions.

Climatic conditions – temperature, humidity, and the number of sunny days – have a significant effect on the accumulation of ketoacids and aldehydes [12]. Assessing the influence of the harvest year on the formation of the SO_2-binding complex of grapes, we note the following. The concentration of aldehydes in white and red grape cultivars of the 2019 harvest significantly ($\alpha<0.001$) exceeded that in the grapes of 2020 harvest (Fig. 2). On average, the content of aldehydes in grapes in 2019 is from 7.4 to 33.4 mg L^{-1}. The content of aldehydes in the must of red and white grapes was at the same level, which, respectively, is 1.8 and 2.3 times higher than in grapes in 2020. Conditions of 2020 contributed to the accumulation of pyruvic acid in white grape cultivars (the concentration was 7.35 ± 24.0 mg L^{-1}), which is 1.5 times higher than the value of the indicator in the 2019 grape harvest on average.

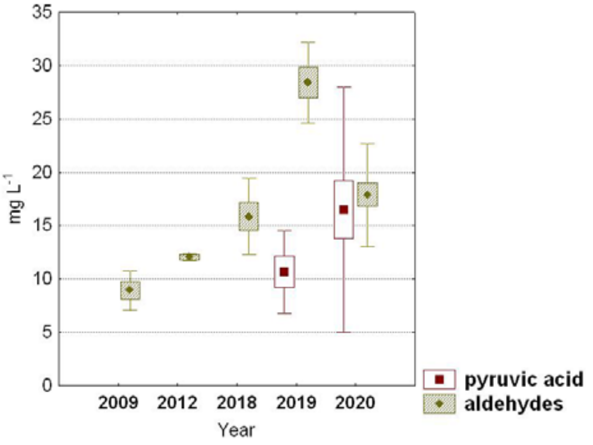


Fig. 2. Influence of the harvest year on the content of SO_2-binding compounds in white grape cultivars

Assessing the influence of the harvest year on the formation of the SO_2-binding complex of grapes, we note the following. The concentration of aldehydes in white and red grape cultivars of the 2019 harvest significantly ($\alpha<0.001$) exceeded that in the grapes of 2020 harvest (Fig. 2). On average, the content of aldehydes in grapes of 2019 harvest has been from 7.4 to 33.4 mg L^{-1}. The content of aldehydes in the must of red and white grapes was at the same level, which, respectively, of 1.8 and 2.3 times higher than in grapes in 2020. It was found that the conditions of 2020 contributed to the accumulation of pyruvic acid in white grape cultivars (the concentration was 7.35 ± 24.0 mg L^{-1}), what on average of 1.5 times higher than in the grape of 2019 harvest.

4 Conclusion

The studies revealed and assessed the significance of the factors influencing ($\alpha<0.05$) on the formation of the SO_2-binding complex of grapes – cultivar, region, harvest year, sugar concentration. It was found that the cultivar ($\alpha = 0.0002$) and the soil-climatic region ($\alpha = 0.0003$) were significant factors in the accumulation of aldehydes in white grape cultivars. In the case of red grape cultivars, ($\alpha<0.045$), the accumulation of ketoacids and aldehydes depends on the cultivar, α-ketoglutaric acid ($\alpha = 0.014$) – on the growing region. The relationship between the concentrations of aldehydes and sugars has been established. This dependence in the case of red grape varieties is described by an equation of the second degree. A similar trend was observed in the case of pyruvic acid. As for white grape cultivars, at this stage of research, the relationship between the content of SO_2-binding components and the concentration of sugars has not been established.

The presented results are the basis for continuing research in the direction of justifying grape cultivars for the production of organic wine products.

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