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ANTIOXIDANT PROTECTION OF ACTIVE PRODUCTS FROM GRAPES

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Annotation

Enzymes entering into the system of oxidising protection of a work cycle of processing of white and red grades of grapes are studied. It is established that some technological operations predetermine strengthening of oxidizing stress. At processing of red grapes connected forms SO2 that reduces it's antioxidant properties increase. Sulfation a red mash in the quantity provided by the technological instruction obviously not enough for maintenance of antioxidant of protection.

Keywords: Enzymes, antioxidant protection, catalase, superoxide dismutase, peroxidase, oxidation, dismutation, sulfitation, oxygen.

In the technological chain of wine making, oxidative processes begin immediately after the harvest of grapes, which, in accordance with the recommendations [1], must be protected with sulfur dioxide (SO_2).

The study of the state of the antioxidant protection system during the processing of grapes and during the production of wine materials is of particular interest and will allow to regulate the degree of protection of the must and wine materials from oxidative stress, which is especially important when processing grapes for low-oxidized table wines.

A variety mixture of both white and red wine grape varieties, sulphited to 150 mg/dm^3, was subjected to analysis. Starting from the moment of acceptance of the grapes, up to the receipt of wine material, before and after each technological operation, the concentration of oxygen and the activity of the enzymes superoxide dismutase (SOD), peroxidase and catalase, which are part of the antioxidant protection system (AOZ), were determined.

SOD activities were determined by a method based on its ability to inhibit the reduction reaction of nitrotetrazolium blue; catalase activity was determined by reaction with ammonium molybdate and by a method based on the oxidation of pyrogallol in the presence of hydrogen peroxide to purpurogallin, peroxidase activity was determined. The results of analyzes during the processing of white grape varieties.

Table 1

Indicators	splitting up		stacker		press		infusion		fermentation	
	before	after	before	after	before	after	before	after	before	After
T°	12,7	13,7	15,2	14,3	14,0	14,12	17,8	18,2	15,5	14,4
O_2mg/dm ^{3}	10,1	16	9,0	19	22,0	15	30	35	21	14
SOD us.ed	0,14	0,69	1,27	1,11	0,41	1,00	0,14	0,62	0,53	0,45
Catalase m kmol/min/l	0,87	0,69	1,91	1,71	3,51	1,20	1,22	0,80	0,62	1,64
Gluthione peroxidase m kmol/min/l	60,2	65,6	51,5	55,8	53,4	48,9	49,1	58,3	70,2	52,8

The results of analyzes in the processing of red grape varieties.

Table 2

Indicators	splitting up		stacker		press		infusion		Fermentation	
	before	after	before	after	before	after	before	after	before	after
T°	24,3	24,4	24,3	25,2	24,4	24,6	26,3	25,5	25,6	25,3
O_2mg/dm ^{3}	14	14	12	20	5	3	10,3	24	20	33
SOD us.ed	2,93	4,60	4,84	2,98	2,81	5,74	4,76	1,90	1,95	1,78
Catalase m kmol/min/l	3,929	4,35	4,44	4,11	3,95	4,77	4,28	4,08	4,13	6,15
Gluthione peroxidase m kmol/min/l	40,6	22,3	21,1	25,0	41,8	19,3	22,4	25,0	24,2	13,3

The ionic forms bind oxygen most easily and mainly SO_{--3}. Sulfuric acid inhibits the action of oxidative enzymes and prevents the oxidation of polyphenols and other substances. SO_2 reacts directly with oxygen and protects polyphenols and other components from oxidation and the main function of SO_2 is to remove hydrogen peroxide formed during the oxidation of polyphenols. [2].

In samples where oxygen saturation is noted, the reaction of the active form of sulfurous acid with oxygen can be represented by reaction 2, where 2 moles of bisulfite react directly with one mole of oxygen, forming two moles of sulfate:

$$2HSO_3^- + O_2 \rightarrow 2H^+ + 2\,SO_4^{2-} \quad (1)$$

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During fermentation, runoff on HSS, SOD activity is negative, that is, these technological methods do not enhance oxidation.

Crushing, pressing gives SOD activity, therefore, dismutation occurs. An increase in SOD activity determines the presence of the superoxide oxygen radical, which [3] intensifies the oxidation process and SOD protects against excessive oxidation.

Catalase is absent in both whites and reds during runoff, infusion is present during the fermentation of both musts, but runoff and infusion determined the activity of catalase, only in red must.

Peroxidase is significantly inactivated during fermentation and pressing. Drainage and infusion activate peroxidase in both wines. This is probably due to the presence of hard parts of the grape, in particular, the skin with enzymes deposited on its surface. A slight dismutation is present during the infusion of white wines, Academician Oparin explains this fact by the presence of an enzymatic process that takes place during the sludge of the must. Only crushing gives a difference in the activity of peroxidase, so in the case of white grapes it appears, and intensively falls for red grapes (see table 1). For draining and infusion, peroxidase and catalase activities are equally characteristic, which have a related effect. Peroxidases are peroxide oxidizers and catalyze according to the scheme: $AOOH + KH_2 \rightarrow K + AOH + H_2O$. (2)

Catalase is also a peroxidase, oxidizing one hydrogen peroxide molecule with another hydrogen peroxide molecule to form two water molecules and an oxygen molecule: $H_2O_2 + H_2O_2 \rightarrow 2H_2O + O_2$ (3)

If we judge the must oxidation by the number of active enzymes that make up the AOD system, then when processing both white and red grapes, during crushing, the must is most susceptible to oxidation, and only white must during infusion. What should be taken into account when choosing a technological scheme in the production of wines of various types.

And if we consider that SOD activity is the first sign of the presence of reactive oxygen species, then the most dangerous in the processing of white wines are such technological methods as pressing and infusion. In general, during the processing of white grapes, the following technological methods can serve as sources of "oxygen stress": crushing, where the increase in SOD activity was 0.55 units; pressing-0.59 us.u, sediment 0.48 us.u. When processing white grapes, catalase activity appears only during fermentation and its activity is 1.02 m kmol/min/l. Peroxidase oxidation is active during the infusion of white wort, when the increase in activity was 9.2 m kmol/min/l, then, when crushing 5.4 m kmol/min/l, it is somewhat less when draining and is completely absent during pressing and fermentation.

The behavior of enzymes of the AOP system during the processing of red grape varieties is somewhat different in that the activity of SOD is maximum at runoff 2.93 units , then during fermentation 2.02 units , crushing 1.67 units and 0.82 units during pressing and is absent only in the infusion of red must. That is, all operations in the processing of grapes, except for the infusion of the must, tend to oxidize the red must. If in white must the activity of catalase was noted only during the fermentation of white grape must, then the processing of red grapes activated it during fermentation at a maximum of 2.02 m kmol/min/l, then pressing 0.82 m kmol/min/l and during crushing 0.421 m kmol /min/l. Catalase activity, both in quantitative terms and in terms of technological methods where its activity is manifested, prevails in the processing of red grapes. That is, when processing red grapes, the danger of oxidation of one hydrogen peroxide molecule by another hydrogen peroxide molecule with the formation of two water molecules and an oxygen molecule is more significant than in white must.

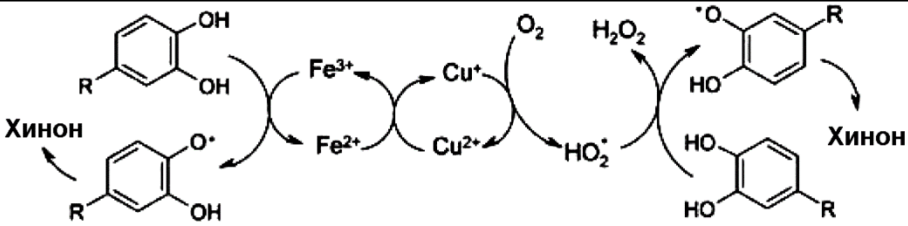
But peroxidase activity during the processing of red grapes appeared only in two cases: with a runoff of 3.9 m kmol/min/l and with an infusion of 2.6 m kmol/min/l**.** It can be concluded that during the processing of red grapes, the must is less susceptible to peroxidation.

SO_2 performs its antioxidant function mainly in reaction with hydrogen peroxide. The main antioxidant effect of sulfur dioxide in wine is due to the bisulfite ion, which reacts with H_2O_2, resulting in sulfuric acid, thus limiting further oxidation of phenolic molecules or ethanol. Undissociated sulfurous acid H_2SO_3 ionic ($HSO^1{}_3$ and $SO^2{}_3$) and associated forms have these properties to a small extent. In an aqueous system, SO_2 forms sulfurous acid, which dissociates in such a way that the bisulfite form (HSO_3^-) predominates in wine, as shown in the reaction:

$$H_2O + SO_2 \quad HSO_3^- + H^+ \overset{\leftarrow}{\rightarrow} SO_3^{2-} + 2H^+ \quad (4)$$

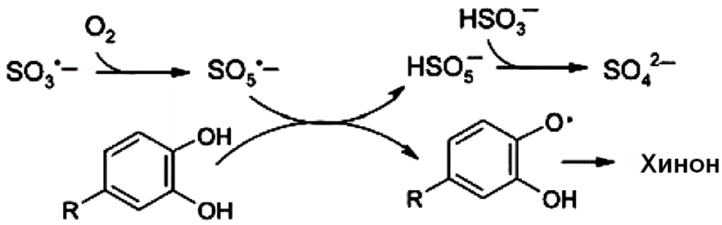
The antiseptic effect of SO_2 in red wort is much less than in white wort, since most of the SO_2 is spent on binding to coloring substances. Dose increase SO_2 reduces color stability by up to 50%. To protect colorants from oxidation, it is necessary to introduce free SO_2 at the level of 20-30 mg/l.

According to the results of the analyzes (Table 2), it follows that red wines are not sufficiently protected from oxidative stress, which can be explained by the binding of SO_3, decreasing its antimicrobial activity. Part of the oxygen dissolved in wine is used to oxidize it into sulfuric acid and is catalyzed. Not, which are always present in wine in the form of iron ions. Sulfurous acid inhibits the action of oxidases. It is customary to add SO_2 to red wine in a smaller amount (how much) since tannins and catechins contained in sufficient quantities have natural antimicrobial properties and, secondly, SO_2 reacts with wine anthocyanides and discolors them. It seems that for this reason, in wine, especially in red, the interaction of SO_2 with oxygen is effectively blocked by polyphenols. At the same time, wine aldehydes (acetic, etc.), reacting with anthocyanins, prevent excessive oxidation. Oxidation of catechins by catalysis of Fe (III) to give hydroperoxide (hydroperoxyl) radicals and quinone is shown in Scheme 5



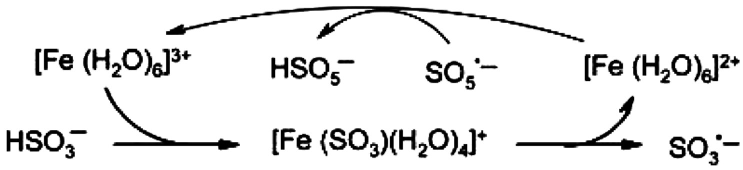
(5)

Removal of catechins using peroxmonosulfate radicals leads to the suppression of SO $_2$ autoxidation according to scheme 6.



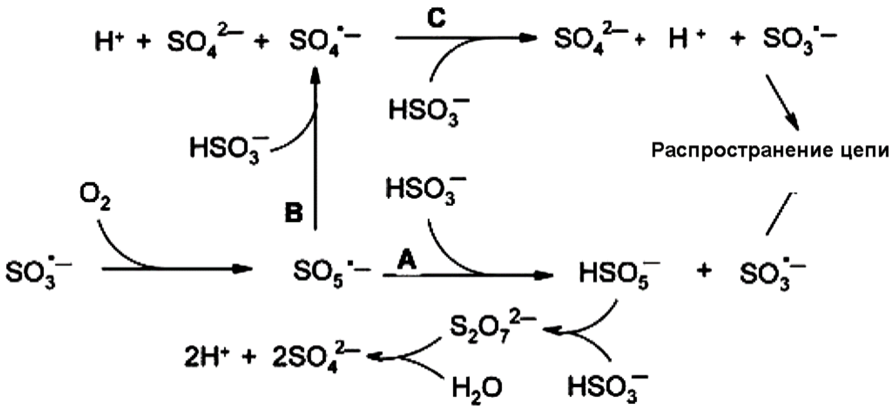
(6)

In acidic conditions of grape must, bisulfite forms metal-sulfite complexes, according to scheme 7



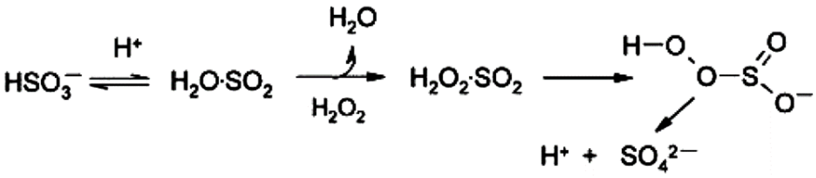
(7)

The sulfite radical reacts rapidly with oxygen according to scheme 8, forming the peroxmonosulfate radical ($SO_5^{\bullet-}$) [4].



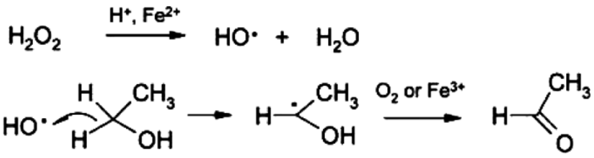
(8)

The reaction of hydrogen peroxide with SO $_2$ is presented as a nucleophilic displacement of water from the bisulfite ion. Scheme (9) in a possible mechanism reaction of hydrated SO $_2$ with hydrogen peroxide:



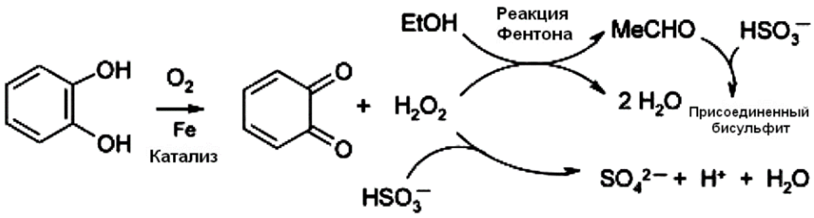
(9)

Oxygen is converted to hydrogen peroxide, which in the presence of iron forms a hydroxyl radical according to the Fenton reaction, scheme 10).



(10)

Obviously , SO $_2$ removes hydrogen peroxide, thus preventing its destructive action, as shown in scheme 11



(11)

However, the oxidation product of the sulfite radical ($SO_3^{\bullet -}$), the peroxmonosulfate radical ($SO_5^{\bullet -}$), is a very strong oxidizing agent . In the presence of oxygen, SO $_2$ also promotes oxidation, which is prevented by the action of polyphenols, which scavenge radicals.

Therefore, the processing of red grapes appears to increase bound forms of SO_2, thus reducing its antioxidant effects.

- SO $_2$ removes hydrogen peroxide, and polyphenols block its interaction with oxygen, and only then the antioxidant effect is realized.

-Sulfation of red must in the amount provided for by the technological instruction is clearly not enough to provide antioxidant protection.

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