OXIDATIVE-REDUCING PROCESSES IN WINEMAKING

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Oxidative-reducing processes are indispensable for the production, maturation and aging of wines. Some of them lead to the ennobling of wines, their stabilization, while others to the alteration, degradation of wines, to numerous defects in wines. Their consecutive, parallel, spontaneous realization, the dependence of many factors characteristic of the concrete variety of *Vitis vinifera*, on the pedo-climatic, agrotechnical, technological conditions in wine production determine their complexity and interaction with many wine parameters, as well as difficulties in studying their time impact on the main pillars of wine - structure, appearance, aromas / bouquet, taste, stability. Knowing the mechanisms of their production, the influencing factors, the particularities, allows the implementation of the precision vinification, reduction of technological, additive and subtractive interventions, quantities of adjuvants and the production of organic wines. Lately they industry focus on the realization of the equipment, meant to monitor and adjust the redox potential of wines during their production and storage. The processing of the grapes themselves involves redox processes, especially in the case of damaged and contaminated grapes, when the contact of oxygen in the air with the grape juice is facilitated. The substances, which form redox couples in grapes, must and wine, are numerous - polyphenols / quinones, GSH / GSSG, endiol diketones, acetoin / diacetyl, anthocyanins / reduced anthocyanins, dioximaleic acid / dioxitartaric acid, etc., and their influence on the product depends on their share in the general transformations during the life of the wine and become responsible for their self-life. In oxidative-reducing chemical transformations, an essential role belongs to the pairs of transition metals Fe^{3+}/Fe^{2+}, Cu^{2+}/Cu^{+}, naturally present in wines, but also in many enzymes (until their inactivation by ethanol and elimination by technological processes). The presence of phenolic substances in grapes, must and wine largely determines the physicochemical properties and quality of the finished product. In grains their oxidative transformations are catalysed by oxidase enzymes, present in healthy grapes. Monophenols are converted to ortho-diphenols by oxidation in the presence of tyrosinase (monophenoloxidase), while di- and triphenols are oxidized to quinones in the presence of polyphenol oxidase (PFO). This ferment is quite specific in relation to ortho-diphenols, which are oxidized to ortho-quinones, compounds highly reactive. They form brown polymers in the must, which affect the color of white wines. Grapes affected by Botrytis cinerea contain a much more active yeast produced by gray rot, which oxidizes a much wider spectrum of substances in must and wine. All of these oxidative enzymes contain active sites of Cu ions. Oxidations are favored by high temperatures, high pH, oxygen content. At the stage of processing white grapes is crucial inactivation of these enzymes, which is achieved by administering in grapes or must the antioxidants, SO_2 and ascorbic acid. Monitoring redox processes during alcoholic fermentation by oxygen management is essential for the resulting quality of dry wines. Oxidations in the wine production process lead to a decrease in varietal aromas. At the same time, the reducing conditions are responsible for possible undesirable aromas of disulfides and hydrogen sulfide. In particular, ensuring the reduced environment in bottled white wines affects the quality of white wines, in which, after several months, atypical, reduced aromas can be attested. Ensuring strongly reducing bottling conditions by applying inert gases and sealing, contributes, in the long run, to achieving reactions with the participation of varietal thiols. The quality of wines can be disastrously affected by the phenomenon of redox photoactivation of wine bottled in transparent

vessels, exposed for a certain period (a few hours being sufficient) to natural or artificial light. As a result, the redox state is modified, which causes the modeling of the organoleptic properties of wines and causes the olfactory defect called "light taste" (sunlight flavour, light-struck gout). It is accompanied by the smell of boiled cabbage, onions, damp wool, rubber. A major role in this adverse phenomenon belongs to riboflavin (B2), the photoreduction of which involves the photooxidative degradation of sulphur amino acids (methionine) and the formation of volatile methanethiol (MeSH, with a perception threshold of 0.3-3 ug/L), responsible for the smell of cabbage, hydrogen sulfide), dimethylsulfide (DMS), dimethyldisulfide (DMDS), thiol esters and mercaptans in wines. At the same time, the redox balance of wines is disturbed by the simultaneous formation of peroxides, glyoxylates, acrolein. In the production of red wines, the redox processes are no less important, although the impact is less significant. During alcoholic fermentation, the presence of oxygen contributes to the activity of yeast cells by stimulating the production of sterols. At the same time, at this stage, oxygen influences the colour of the must, contributing to its stability, including the formation of tannin-anthocyanin compounds. In the post-fermentation phases, redox processes with the participation of oxygen can have both a positive impact (maturation) and a negative impact (uncontrolled oxidations). Redox phenomena are decisive for the production of certain types of wines (Heres, Marsala, Madeira, Portwein, etc.) and their production must be carried out under the control of the oenologist.

Keywords: Polyphenols/quinones, anthocyanins, transition metals, photooxidative degradation, glyoxylates, acrolein, maturation, uncontrolled oxidations.

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