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Unveiling the Dynamics of "Vranac" Wine Anthocyanins Oxidation: Insights from Accelerated Chemical Testing

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ABSTRACT

To gain insights into the oxidative behavior of red wines, a comprehensive study was conducted. The rates of anthocyanins decrease were measured for "Vranac" red wine subjected to two different accelerated aging tests: chemical (with hydrogen peroxide) and thermal. The kinetics of malvidin-3-O-glucoside (M3G) and malvidin-3-O-acetylglucoside (M3AG) degradation in this red wine by hydrogen peroxide in aqueous solution at various temperatures were investigated. The trace amount of Cu(II) ions was used to catalyze the reaction, and it was monitored using an HPLC-DAD method through the application of the initial-rate method. The HPLC-DAD method was validated for determining M3G and its derivatives in red wines. The kinetic parameters of the reactions are reported, and rate equations are suggested. The activation energy values for the degradation of M3G and M3AG were calculated to be 57.70 and 57.74 kJ/mol, respectively. The thermodynamic functions of activation (ΔG^*, ΔH^*, *and* ΔS^*) have also been calculated.

Keywords: red wine, oxidation, HPLC-DAD, kinetic parameters, thermodynamic functions

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Introduction

Chemical reactions hinge significantly on the presence of oxygen. Oxidation occurs in red wines, spanning from the winemaking process, aging in barrels and finally in the bottle. These oxidation reactions significantly influence both the chemical and sensory characteristics of the wine, impacting factors such as color (Ugliano, 2013; Ferreira et al., 2014; Deshaies et al., 2020) and organoleptic characteristics (De Beer et al., 2016). At every stage of the winemaking process, the wine is exposed to specific oxygen levels. Given the close relationship between wine composition and its reactivity with oxygen, predicting the outcomes for a specific wine with a designated oxygen amount proves challenging. However, our research provides practical insights that can help in this prediction. Existing literature acknowledges three accelerated aging tests: the heat test, enzyme test, and chemical test (hydrogen peroxide test).

From a chemical perspective, polyphenols stand out as one of the wine constituents most susceptible to oxidation (Oliveira et al., 2011). Red wines undergo chemical oxidation reactions involving polyphenols, such as anthocyanins, proanthocyanidins, and flavan-3-ols (Waterhouse and Laurie, 2006; Kilmartin, 2009).

Reactive oxygen intermediates, including hydrogen peroxide (H_2O_2), hydroxyl radical (HO•), and superoxide anion, play a crucial role in the degradation of plant pigments (Waterhouse and Laurie, 2006; Oliveira et al., 2011). De et al. (1999) observed that the HO• radical serves as the primary reactive species, cleaving the benzene ring and facilitating substrate degradation into CO_2 and H_2O. Sondheimer and Kertesz (1952) and Ozkan (2002) also proposed that the HO• radical is responsible for the oxidation and subsequent degradation of anthocyanins.

Anthocyanins, originating from the Greek words "anthos" (flower) and "kianos" (blue), emerge as essential pigments within vascular plants. Renowned for their safety and effortless integration into aqueous solutions, these pigments are esteemed for their potential as natural water-soluble dyes (Smyk et al., 2008). Exhibiting vivid shades of orange, pink, red, violet, and blue, anthocyanins enrich the vibrant spectrum of colors found in flowers, fruits, and select vegetation. In the domain of red wine, they play a pivotal role in determining its hue, a key characteristic that significantly influences wine quality.

Tannins in wine, alongside anthocyanins, play a significant role in color development and stability. While anthocyanins contribute primarily to the red, purple, and blue hues in wine,

tannins enhance the wine's overall color intensity and longevity.

Various factors influence the stability of anthocyanins, encompassing pH, light, oxygen, enzymes, ascorbic acid, sugars, sulfur dioxide or sulfite salt, metal ions, and co-pigments. Temperature, a well-established factor affecting anthocyanin stability, has been extensively studied (Kechinski et al., 2010; Hillmann et al., 2011; Turturica et al., 2018; Yajing and Yuanping, 2019). Additionally, the impact of hydrogen peroxide on anthocyanin degradation in fruits is documented (Kechinski et al., 2010; Zorić et al., 2014; Gerard et al., 2019).

Notably, the combination of high temperature and oxygen emerges as particularly detrimental to the stability of these compounds (Cavalcanti et al., 2011). While existing literature lacks data on the effects of H_2O_2, Cu(II), and temperature on red wine anthocyanins, this study aims to fill this gap by investigating their degradation in Serbian red wine “Vranac”. The kinetics of anthocyanin degradation will be evaluated from a thermodynamic perspective, considering activation functions such as free energy (ΔG^*), enthalpy (ΔH^*), entropy (ΔS^*), and activation energy (Ea). These thermodynamic parameters offer valuable insights into the thermal degradation kinetics of these compounds in food systems.

Experimental

Materials

For this study, samples of the red wine “Vranac”, produced in Serbia, were purchased in a local supermarket.

Chemicals

The reagents used, namely Cu(II) (chloride salt), hydrogen peroxide, acetonitrile, formic acid, and M3G, were all analytical grade (Merck, Darmstadt, Germany, and Sigma Chemical Co. St Louis, MO, USA). The solutions were prepared using deionized water from MicroMed's high-purity water system, TKA Wasseraufbereitungssysteme GmbH.

Preparation of standards

Preparing a stock solution of M3G (300 mg/L) involved dissolving the specified quantity in deionized water. The solution of Cu(II) ($1 \cdot 10^{-3}$ mol/L) was prepared by dissolving $CuCl_2 \cdot 2H_2O$

in deionized water. The hydrogen peroxide solution (0.979 mol/L) was prepared from a 30% commercial reagent just before it was used.

HPLC-DAD equipment and analysis

The oxidation kinetics for the anthocyanins was followed by measuring the concentration of anthocyanins at 520 nm on the Agilent 1200 chromatographic system equipped with a quaternary pump, an Agilent 1200 photodiode array detector with radiofrequency identification tracking technology for flow cells, a UV lamp, an automatic injection, and Chem-Station software. The column was thermostated at different temperatures (25 °C, 30 °C, 35 °C and 40 °C). After injection of 5 μL of the reaction mixture, the separation was performed on the Agilent-Eclipse XDBC-18 4.6x150 mm column. Two solvents were used for the gradient elution: A-(H_2O+5% HCOOH) and B-(80% ACN+5% HCOOH+H_2O). The elution program used was as follows: from 0 to 28 min, 0.0% B; from 28 to 35 min, 25% B; from 35 to 40 min, 50% B; from 40 to 45 min, 80% B, and finally for the last 10 min again 0% B (Mitić et al., 2012). The identification of the compounds was achieved using their retention times and UV-VIS spectra, analyzed with a Diode Array Detector (DAD). Quantification of M3G and M3AG was performed using calibration curves derived from standard M3G solutions.

The proposed method underwent validation in accordance with the guidelines established by the International Conference on Harmonization (ICH, 1996/2005) and the Commission Decision (2002/657/EC) guidelines. The method was validated by estimating linearity, precision, accuracy and sensibility. Linearity was evaluated by using the standard solution in the range of 2-150 mg/L M3G. Each concentration was analyzed in triplicate. The calibration curve was generated using peak areas of the reference M3G versus their concentration. The correlation coefficient of the calibration curve exceeded 0.999. The precision of the method was determined as repeatability and reproducibility in terms of per cent relative standard deviation (%RSD). The %RSD value for evaluated concentration (10, 50 and 100 mg/L) was lower than 2.20%. The limit of Detection (LOD) and Limit of Quantification (LOQ) were calculated at 0.528 mg/L and 1.584 mg/L, indicating the high sensibility of the method.

Accelerated aging test

The red wine "Vranac" was submitted to accelerated ageing tests experiments (Magalhaes et al., 2010; Deshaies et al., 2021), chemical (H_2O_2 and Cu (II) added) and heat treatment (at 25, 30, 35 and 40 ºC). The reaction was carried out in the following way. In a special four-compartment vessel, the solution of Cu(II) was placed in the first, the solution of H_2O_2 in the second, the red wine "Vranac" in the third, and the deionized water (total volume 2 mL) in the four compartments (adjusted to pH 3.5 with 1mol/L tartaric acid). The vessel was thermostated at 25±0.02 ºC (or 30±0.02 ºC, 35±0.02 ºC and 40±0.02 ºC). The content was mixed well and immediately injected into an Agilent 1200 chromatographic system. The change in concentration of anthocyanins was recorded at 520 nm as a function of time every 35 min (for M3G) and 40 min (for M3AG) for the first 175 min of the reaction. The kinetic analysis utilized the initial rates method. The zero-time concentration value was determined by preparing the red wine with deionized water (total volume 2 mL).

Results and Discussion

Kinetics of M3G and M3AG degradation

The catalytic effect of Cu(II) on the oxidation reaction of M3G and M3AG, by hydrogen peroxide was observed. The HPLC chromatograms for M3G (peak 1) and M3AG (peak 2), in the red wine "Vranac" from Serbia, recorded at 520 nm, are shown in Figure 1. The chromatogram in an aqueous solution (wine diluted with deionized water in a ratio of 1:1) is present in curve 1. The chromatogram of the mixture of wine-H_2O_2-water is shown in curve 2. After the wine was mixed with Cu(II)-H_2O_2, the concentration of anthocyanins strongly decreased. The reaction between anthocyanins and hydrogen peroxide occurs slightly at 25 ºC (curve 2), but the addition of Cu (II) ions particularly accelerates this reaction (curve 3).

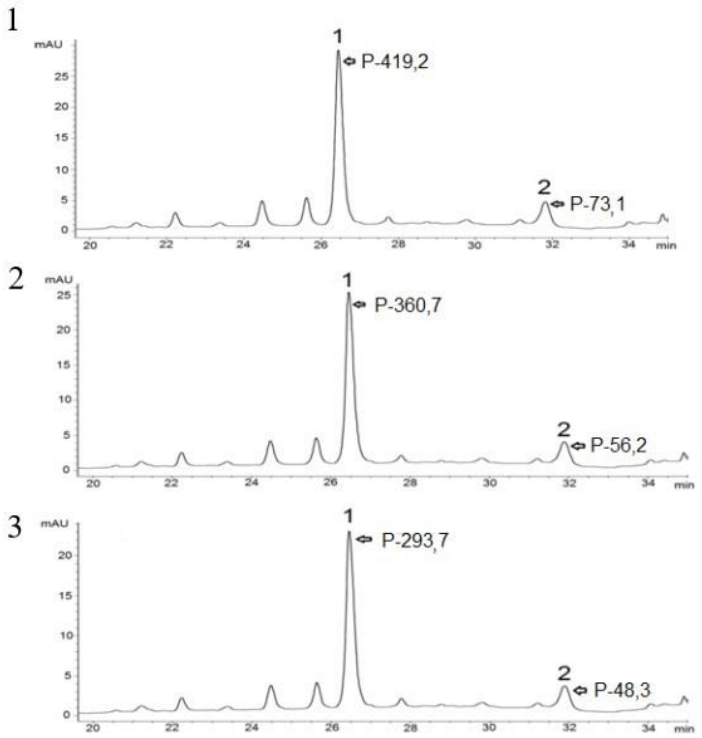
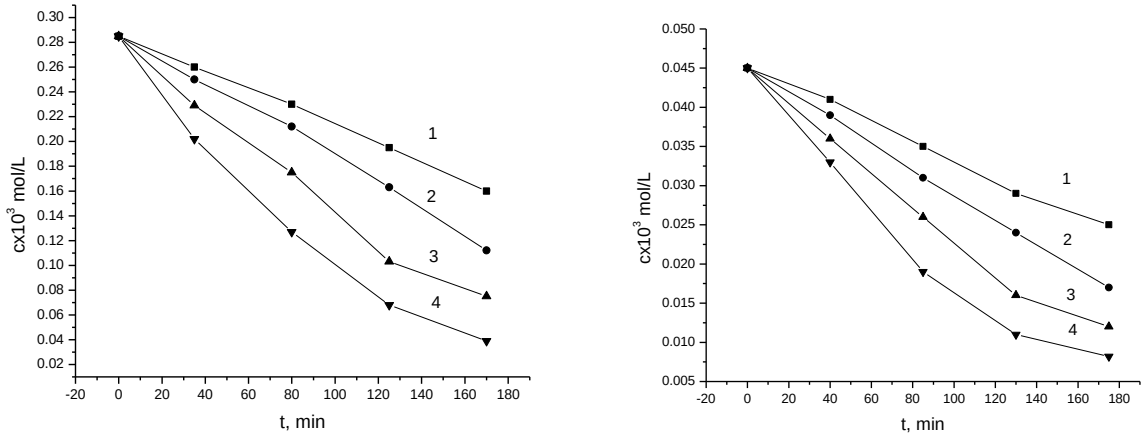


Figure 1. HPLC chromatogram of red wine anthocyanin after 35 min of incubation. Peak 1- M3G (retention time- 26.55 min), peak 2- M3AG (retention time- 31.90 min); (1) wine + water; (2) wine + H_2O_2 + water; (3) wine + H_2O_2 + Cu(II) + water.



a) b)

Figure 2. Concentration as a function of reaction times for different temperatures: 1 - 25 ^oC; 2 - 30 ^oC; 3 - 35 ^oC; 4 - 40 ^oC; for M3G (a) and M3AG (b). c(H_2O_2) =$14.69 \cdot 10^{-3}$ mol/L; c(Cu(II))=$0.185 \cdot 10^{-4}$ mol/L; pH=3.5

Figure 2 shows the relationships between the concentration of M3G and M3AG and time at different temperatures. Anthocyanins' concentration decreases with time. It is possible to follow the reaction rate by the HPLC-DAD method as the change of the pick areas values with time because of the linear dependence of pick area on time during the first 130 min (of reaction at 25º C and 30 ºC) or first 180 min (of reaction at 35 ºC and 40 ºC). The initial rate method was used to determine partial orders (Mottola and Perez-Bendito, 1996). The initial reaction rates were established by measuring the slopes of the initial tangents on the anthocyanin concentration-time curves, represented by dc/dt.

The reaction rate dependence on the H_2O_2 concentration was studied in the range of 4.90-24.49 mmol/L (Figure 3). As the concentration of H_2O_2 increased, the reaction rate accelerated. This figure shows that the degradation of M3G and M3AG in red wine "Vranac", follows the first-order reaction with respect to H_2O_2 concentrations because the curve is linear. For further work, a concentration of H_2O_2 of 14.69 mmol/L was selected as the optimal value.

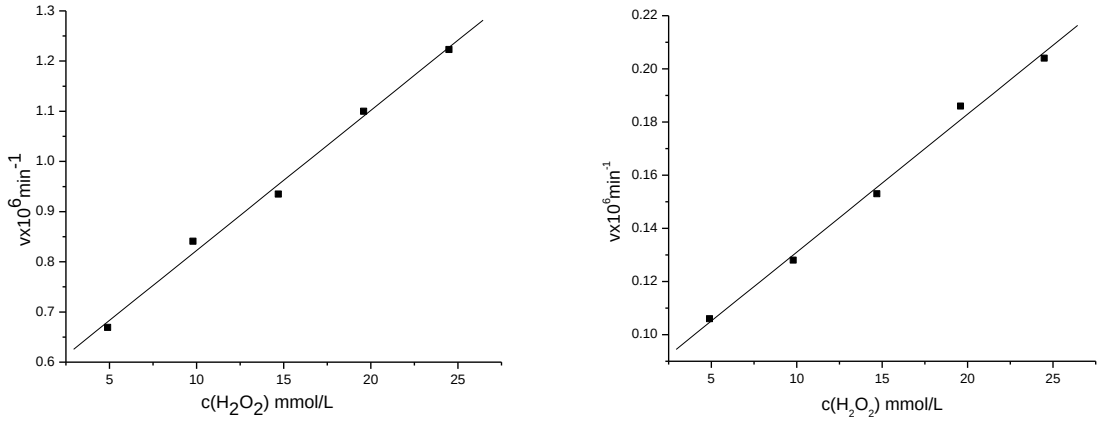


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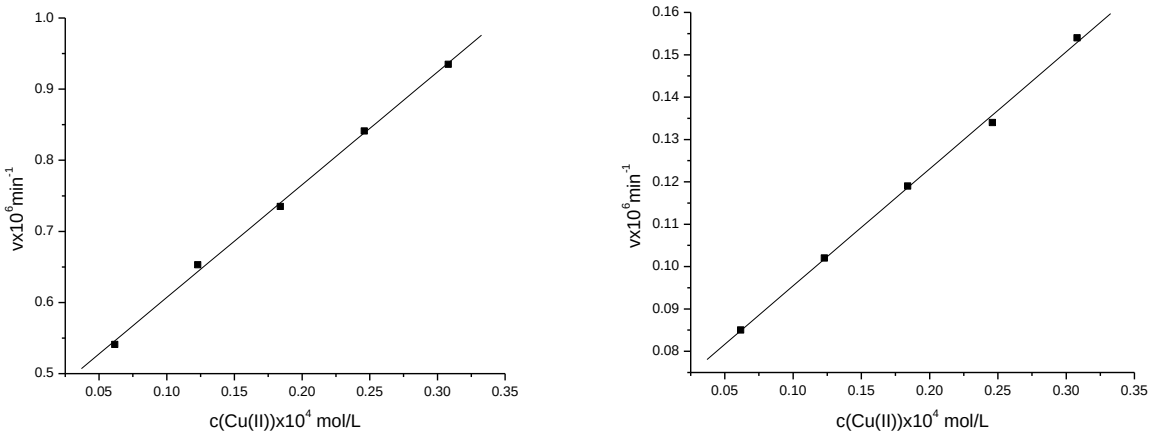
Figure 3. The reaction rate's dependence on the concentration of H_2O_2 for M3G (a) and M3AG (b). c(M3G)=2.85·10^{-4} mol/L; c(M3AG)=4.49·10^{-5} mol/L; c(Cu(II))=3.08·10^{-5} mol/L, pH=3.5, t =25 ºC.

Keeping the H_2O_2 and anthocyanins concentration constants, the Cu(II) dependence on the system was studied in the range of 0.62-3.10·10^{-5} mol/L (Figure 4). It was observed that Cu(II) ions had catalytic activity in this reaction. The reaction rate increased with increasing the concentration of Cu(II). The linear relationship indicated that the degradation of anthocyanins in

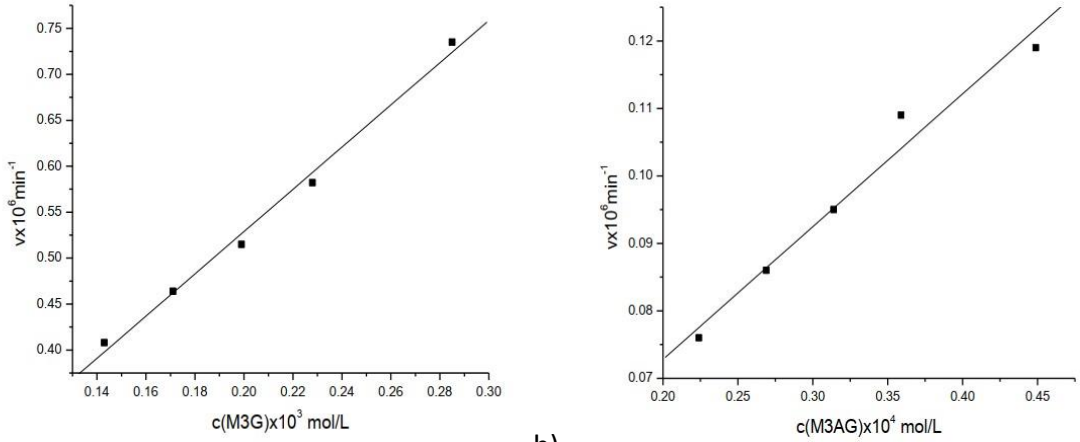
the red wine followed first-order reaction kinetics with respect to Cu(II) concentrations. For further work, a concentration of Cu(II) of $1.85 \cdot 10^{-5}$ mol/L was selected as the optimal value.



a) b)

Figure 4. The reaction rate's dependence on the concentration of Cu (II) for M3G (a) and M3AG (b). c(M3G)=$2.85 \cdot 10^{-4}$ mol/L; c(M3AG)=$4.49 \cdot 10^{-5}$ mol/L; c(H_2O_2) =$14.69 \cdot 10^{-3}$ mol/L, pH =3.5, t =25 ^oC.

The influence of the concentration of M3G and M3AG on the reaction rate was studied in the range 0.142-0.285 mmol/L M3G and 0.224-0.449 mmol/L M3AG, respectively under the following working conditions: c(H_2O_2)= 14.69 mmol/L, c(Cu(II))= $1.85 \cdot 10^{-5}$ mol/L, pH=3.5 and t=25 ^oC. Linear dependence confirmed that the degradation of M3G and M3AG in red wine "Vranac" followed the first-order reaction (Figure 5).



a) b)

Figure 5. Dependence of the reaction rate on the concentration M3G (a) and M3AG (b). c(H_2O_2)=14.69 mmol/L, (Cu(II))=1.85·10^{-5} mol/L, pH =3.5, t =25 ºC.

Based on the present kinetic investigation, the kinetic equations for degradation of M3G and M3AG in the red wine "Vranac" by H_2O_2 in the presence of Cu (II) as a catalyst were formulated:

$$-\frac{dc}{dt} = k_1 \cdot c_{H_2O_2} \cdot c_{Cu(II)} \cdot c_{M3G}$$

$$-\frac{dc}{dt} = k_2 \cdot c_{H_2O_2} \cdot c_{Cu(II)} \cdot c_{M3AG}$$

where k_1 and k_2 are rate constants. Based on these equations, the rate constants for the reactions were calculated and presented in Table 1. As expected, the k values increased with temperature, indicating that greater degradation occurs at higher processing temperatures.

Table 1. Rate constant k of the degradation of anthocyanins *vs* temperature.

t, ºC	k_1 (M3G)·10^{-4}/mol^{2}dm^{-6}min^{-1}	k_1 (M3AG)·10^{-4}/mol^{2}dm^{-6}min^{-1}
25	0.951	0.976·10^4
30	1.315	1.369·10^4
35	1.884	1.895·10^4
40	2.547	2.649·10^4

Mechanism of anthocyanins degradation by H_2O_2

As red wine oxidation induces color changes, measurements were done to compare natural and forced oxidation. The primary contributors to the red color are anthocyanins (Tanaka et al., 2008), and their degradation due to oxidation could explain the differences in absorbance measurements. Absorbance at 520 nm, as shown in Figure 7 (curve 1), corresponds to the flavylium ring of anthocyanin. The malvidin-3-glucoside, the main anthocyanin present in wine, is not readily oxidized (Waterhouse and Laurie, 2006). In the presence of H_2O_2 or Cu(II)/H_2O_2 reagent, it is possible that brown oxidized polyphenols were formed, which could increase the absorbance to 420 nm. As shown in Figure 7 (curve 3), an accelerated degradation of the wine anthocyanin was observed in the presence of Cu(II)/H_2O_2. Therefore, it can be concluded that Cu(II) acts as a catalyst in the anthocyanin's hydrogen peroxide oxidation reaction.

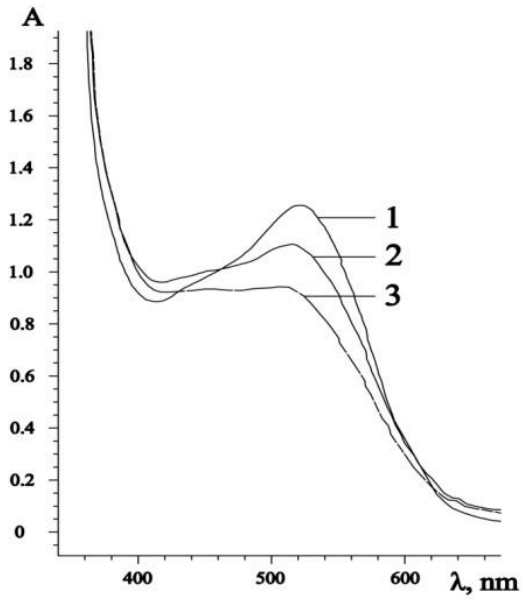


Figure 6. Absorbance measurements (350–650 nm) for three different wine mixtures: 1) aqueous solution of wine; 2) aqueous solution of wine + H_2O_2; 3) aqueous solution of wine + H_2O_2 + Cu(II) -20 min after preparing the mixture.

Hydrogen peroxide is an oxygen species and the simplest peroxide, and this relatively reactive species may influence the biogeochemistry of various transition metals and their complex can act effectively as a reductant or as an oxidant. However, in the presence of certain metals, the presence of H_2O_2 could potentially result in the generation of the highly reactive and

harmful hydroxyl radical (HO•). Many kinetic studies on the reaction of both Cu(I) and Cu(II) with H_2O_2 have been reported (Perez-Bendito, 2004; Pham et al., 2012; Pham et al., 2013).

Gray (1996) suggested that the reaction between Cu(II) and H_2O_2 produced Cu(I) and $O_2^{\bullet-}$ (Eguations I-IV). Thus, free radical pathway has been promoted by several investigations both in the absence and presence of organic ligands with production of Cu(I) subsequently resulting in formation of $HO^{\bullet}$ via a "Fenton-like" reaction between Cu(I) and H_2O_2.

$$H_2O_2 \leftrightarrow H^+ + HOO^- \quad \text{I}$$

$$Cu(II) + HOO^- \rightarrow Cu(I) + HO_2^{\bullet} \quad \text{II}$$

$$HO_2^{\bullet} \leftrightarrow H^+ + O_2^{\bullet-} \quad \text{III}$$

$$Cu(I) + H_2O_2 \rightarrow Cu(II) + HO^{\bullet} + OH^- \quad \text{IV}$$

Anthocyanins, as thermolabile compounds in wine, are the primary targets of chemical changes caused by the presence of hydroxyl radicals. The de-glycosylation and cleavage of anthocyanins will lead to the release of the A and B rings of anthocyanins (Redus et al., 1999). It can be explained by the oxidation of malvidin 3-O-diglucoside in the presence of hydrogen peroxide under acidic conditions, which leads to the formation of ortho-benzoyloxyphenylacetic acid esters through Baeyer–Villiger oxidation type (Harazdina, 1970; Harazdina and Franzese, 1974). New compounds produced from malvidin 3-O-glucoside according to Baeyer–Villiger oxidation are 2,4,6-trihydroxybenzaldehyde (Piffaut et al., 1994), syringic acid or anthocyanone A (8-β-D-glucopyranosyl-2,4-dihydroxy-6-oxo-cyclohexa-2,4-dienyl acetic acid) (Lopes et al., 2007). Hypothetical scheme for the formation of new compounds from malvidin O-glucoside through a Baeyer−Villiger-type oxidation is presented in Figure 7 (Lopes et al., 2007).

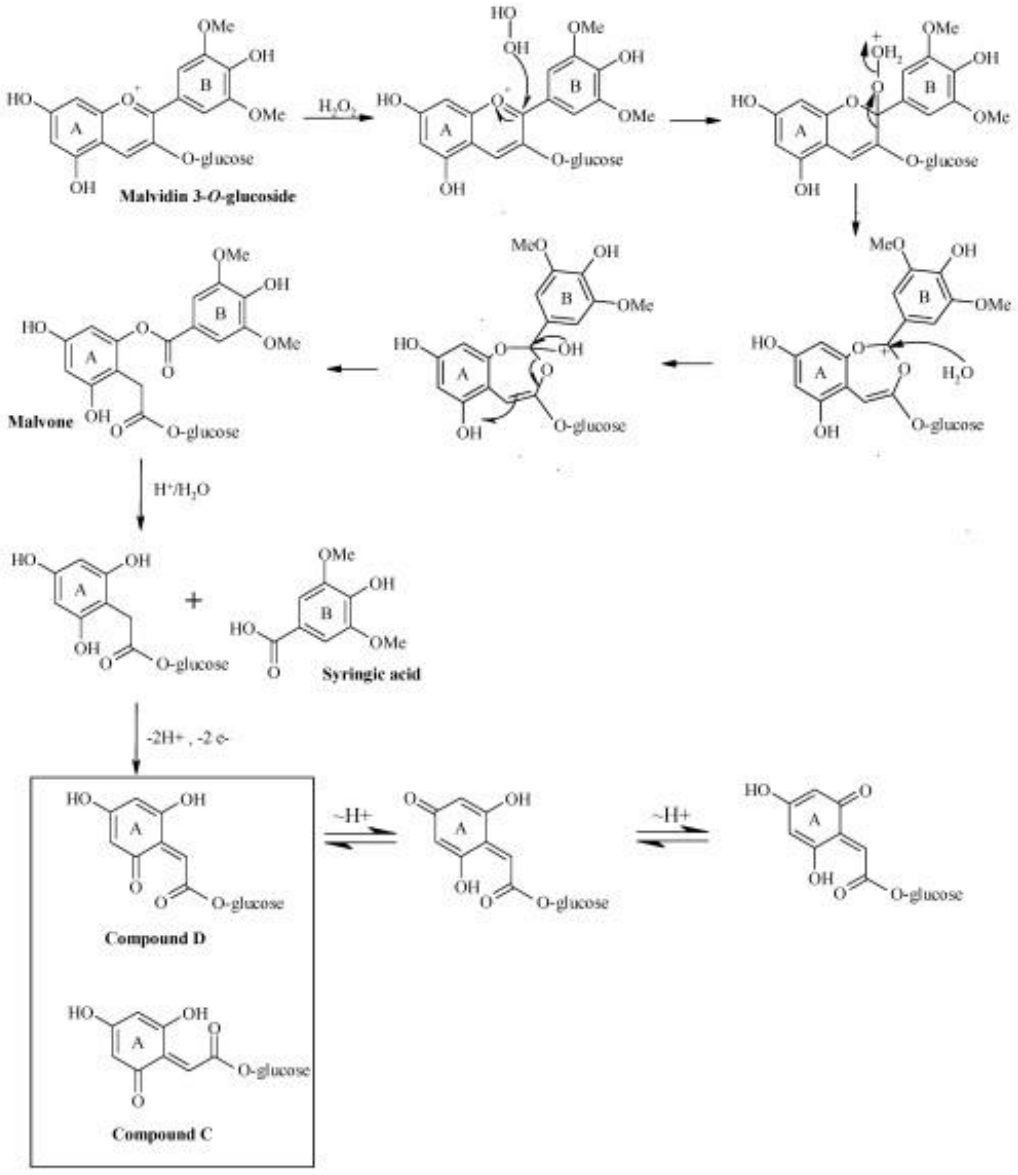


Figure 7. Hypothetical scheme for the formation of compounds C and D (anthocyanone A) from malvidin-O-glucoside through a Baeyer-Villiger-type oxidation (Lopes et al., 2007).

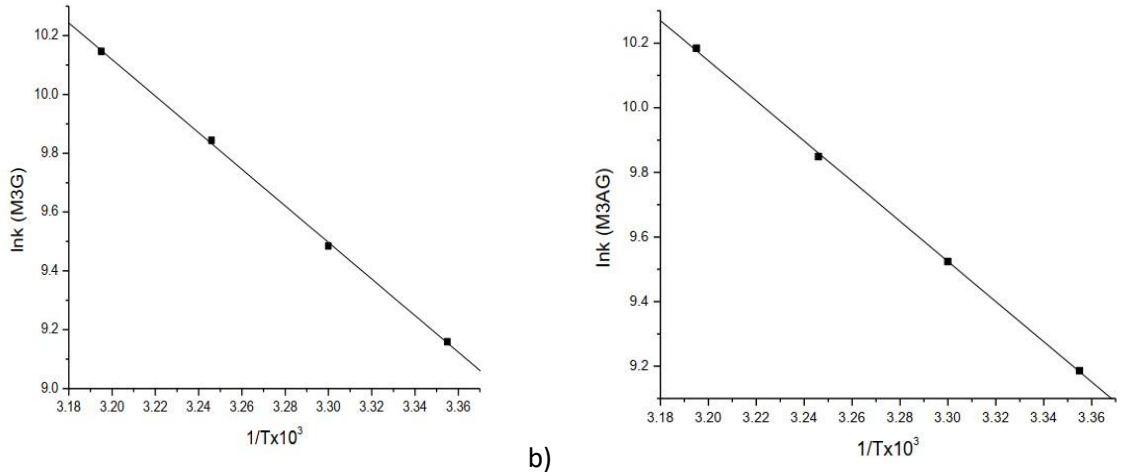
Thermodynamic analysis

Estimating thermodynamic parameters could provide additional and useful information for degradation kinetics. Table 2 presents the activation energy (Ea), activation enthalpy (ˆH*), activation entropy (ˆS*), and free energy of activation (ˆG*).

Table 2. Kinetic parameters for degradation of anthocyanins of red wine "Vranac"

	M3G	M3AG
Ea, kJ/mol	57.70	57.74
ΔH^*, kJ/mol	55.22	55.26
ΔS^*, J/Kmol	16.60	16.94
ΔG^*, kJ/mol	60.17	60.31

The activation energy (*Ea*) describes the energy required to reach the transition state of a reaction. The activation energy is usually evaluated from experimental data using the Arrhenius model. Figure 8 presents the Arrhenius plot developed from the kinetic constant rates of anthocyanins obtained in this study.



a) b)

Figure 8. The Arrhenius plots for degradation of M3G (a) and M3AG (b) in red wine "Vranac" c(H_2O_2) =14.69 mmol/L, c(Cu(II)) = $1.85 \cdot 10^{-5}$ mol/L, pH= 3.5.

The calculated value of *Ea* was 57.78 and 57.74 kJ/mol for M3G and M3AG. This means that there are no statistical differences ($p<0.05$) between the *Ea* values obtained for the two monomeric anthocyanins. Earlier research has demonstrated similar activation energy (*Ea*) values for the degradation of anthocyanins in food items, with studies on black carrots revealing *Ea* values spanning from 68.8 to 95.1 kJ/mol (Kirca et al., 2007); thermal treatment (40–80 ºC) of blueberry juice presented anthocyanin degradation with activation energy value of 80.4 kJ/mol (Kechinski et al., 2010); anthocyanins thermal degradation at 60-90 ºC from wild strawberry showed *Ea* value 21.6 kJ/mol (Özşen and Erge, 2012), 68 kJ/mol for acerola pulp (Silva *et al.*,

2016). The activation energy of the degradation of anthocyanins in grape juice was determined as 64.89 kJ/mol at 70–90 °C (Danisman et al., 2015). Muche et al. (2018) reported that each anthocyanin compound had a different degradation rate and temperature sensitivity. These authors determined activation energy of 49.63 kJ/mol and 29.75 kJ/mol for M3G and peonidin-3-glucoside (Pn3G) in Rudy grape juice in a temperature range of 5-35 ^{o}C. Also, Oliveira et al. (2015) reported an activation energy value of 60.7 kJ/mol for M3G in red Port wine after oxygen addition.

The activation enthalpy (ΔH^*) signifies the minimum energy necessary for the reactant to initiate the reaction, correlating with the strength of the chemical bonds involved in its formation and breakage. The positive value of ΔH^* indicated that the reaction of anthocyanin degradation is an endothermic reaction, proving our previous results that the degradation rate increased with temperatures. ΔH^* for M3G and M3AG degradation with Fenton-like reagent (Cu (II)/H_2O_2) in this study was 55.22 and 55.26 kJ/mol.

The Gibbs free energy (ΔG^*) is defined as the difference between the energies of reactants and activated state and usually serves as a measure of process spontaneity. Both ΔH^* and ΔG^*, values obtained in the current study are like the values represented by Kechinski et al. (2010) for blueberry juice (77.8 and 91.3 kJ/mol for ΔH^* and ΔG^*, respectively); Moldovan et al. (2019) for wild blackthorn fruit extracts (51.51 and 55.82 kJ/mol) and Yajing and Yuanping (2019) for rose anthocyanin extracts (141.53 and 100.93 kJ/mol).

Entropy (ΔS^*) values imply the change of disorder of molecules in the reaction system and it is usually related to the number of molecules with appropriate energy that can react. ΔS^* values determined in this study were positive, 16.60 and 16.94 J/mol K. The positive ΔS^* values of wine anthocyanins indicated that the entropy increased when reaching the transition state (Celli et al., 2016). The relatively low value of ΔS^* implies the low significance of this function (Al-Zubaidy and Khalil 2007). Additionally, the ΔS^* values were relatively smaller than those reported by Yajing and Yuanping (2019) at 118.31 J/molK. In contrary to our results, the negative ΔS^* values were reported for anthocyanins thermal degradation in blueberry juice (Kechinski et al., 2010) and for wild blackthorn fruit extracts (Moldovan et al., 2019).

Conclusion

In this study, the degradation kinetics of M3G and M3AG in "Vranac" red wine were investigated using the Cu(II)/H_2O_2 reagent over a temperature range of 25 to 40 °C. Temperature, H_2O_2 concentration, Cu(II) concentration, and anthocyanin levels were found to notably influence the reaction rate. The degradation rate constants varied with temperature according to the Arrhenius relationship. The positive activation enthalpies for the degradation processes suggested an endothermic nature, while the Gibbs free energy of activation indicated a nonspontaneous character. These findings imply that controlled oxygen levels can stabilize the wine and promote the development of unique aromas during aging. Winemakers should carefully manage their exposure to ensure optimal outcomes without compromising the wine's quality.

Acknowledgement

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Conflict-of-Interest Statement

The author did not declare any conflict of interest.

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