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Kinetic and Thermodynamic Parameters for Degradation of Anthocyanins from Red Currant and Sour Cherry Juices by Hydrogen Peroxide in the Presence of Cu(II)

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ABSTRACT

The kinetics of anthocyanins degradation in the red currant and sour cherry juices by hydrogen peroxide at pH 3.5 was investigated. The reaction was catalyzed by the trace of Cu (II), and it was followed spectrophotometrically at 520 nm by applying the initial-rate method. The reaction kinetic parameters are reported, and the rate equation is suggested. From the dependence of the rate constants on the temperature, the activation energy was calculated: 25.76 and 30.59 kJ mol^{-1} for the red currant and sour cherry juices, respectively. The thermodynamic functions of activation (ΔG^*, ΔH^* and ΔS^*) have been determined to understand red currant and sour cherry juice anthocyanins degradation.

Keywords: red currant, sour cherry, anthocyanins, kinetic parameters, thermodynamic functions

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Introduction

Anthocyanins are polyphenolic pigments, responsible for the red, blue, and purple color of numerous fruits. They are reported to have antioxidant properties and thus many health benefits (Harbourne et al., 2008). There are several reports focused on the effect of anthocyanins on cancer treatments (Nichenametle et al., 2006), human nutrition (Stintzing and Carle, 2004), and biological activity (Kong et al., 2003). Red currants and sour cherries are an excellent source of anthocyanins and, therefore, very interesting because they offer potential as an ingredient in functional beverages. Anthocyanins identified in red currants are cyanidin-3-*O*-sambubioside, cyanidin-3-*O*-rutinoside, cyanidin-3-*O*-(2"-*O*-xylosyl) rutinoside (Borges et al., 2010); cyanidin-3-rutinoside, cyanidin-3-sophoroside, and cyanidin-3-glucoside (Määttä et al., 2003). Also, the most abundant sour cherry anthocyanin is cyanidin-3-glucosyl-rutinoside (Damar and Eksi, 2012). After the harvest, red currant and sour cherry fruits easily lose its red color, resulting in reduced market value (Ruenroenglin et al., 2009). Several factors influence to anthocyanin stability, including pH, light, oxygen, enzymes, ascorbic acid, sugars, metal ions, and copigments (Kechinski et al., 2010).

Thermal degradation of anthocyanins has been studied for grape juice (Hillman et al., 2011), Chinese red radish (Liu et al., 2014), the raspberry pulp (Summen and Erge, 2014), and blood orange juice (Kirca and Cemeroglu, 2013). The kinetic degradation of anthocyanins can be evaluated from a thermodynamic perspective based on activation functions such as free energy (ΔG^*), enthalpy (ΔH^*), entropy (ΔS^*) and activation energy (E_a). These functions can be estimated for reactions occurring in foods and may provide valuable information concerning thermal degradation kinetics. Additionally, hydrogen peroxide (H_2O_2) has been used in foods and food packaging materials for various purposes in many European countries for over 30 years (Nikkhah et al., 2010). Degradation of anthocyanins by H_2O_2 has also been studied for litchi fruit (Ruenroengklin et al., 2009), sour cherry, pomegranate, and strawberry juices (Özkan et al., 2002). Copper, normally occurring in fruit and vegetables, plays a vital role in these oxidation reactions. No published data have been found in the literature on the effects of H_2O_2 in the presence of Cu(II) ions on the degradation of anthocyanins from the red currant and sour cherry juices. Therefore, the objective of the presented work was to investigate the effects of Cu(II)/H_2O_2 reagent on the stability of red currant and sour cherry juices. Different temperatures

were used to predict kinetic degradation and, at a temperature of 25^{o}C, the thermodynamic functions of activation were estimated.

Experimental

Material

The samples of sour cherry and red currant fruits used in the study were obtained from the Niška Banja (Serbia). Fruits were washed in cold tap water and homogenized in a high-speed blender. The homogenate was filtered and stored at -18^{o}C until use. All the analyses were performed in three replicates.

Equipment

Spectrophotometric measurements were performed on UV-Vis spectrophotometer, model 8453 (Agilent, Germany) with a 1 cm match glass cell. For the pH measurements, Radiometer PHM 29Bb pH meter (MeterLab, USA) and a combined glass-calomel electrode, GK2311C, were used. All solutions were kept in a thermostatic water-bath, model MP-5A (Julabo, USA) at 25.0 ± 0.1 °C before the beginning of the reaction. High precision measuring for laboratory applications was performed using an analytical balance (±0.0001 g), model AB204-5 (Mettler Toledo, Switzerland). A stopwatch was used to record a reaction time.

Reagents and solutions

Analytical grade chemicals and deionized water (MicroMed high purity water system, TKA Wasseraufbereitungssysteme GmbH) were used for the preparation of all solutions. All the stock solutions were stored in polyethylene containers. All the polyethylene containers and the glassware used were cleaned in aqueous HCl (1:1) and then thoroughly rinsed with deionized water. 1.00 gL^{-1} Cu (II) (nitrate salt, Merck, KGaA, Darmstadt, Germany) was used as a stock solution. Cu (II) working solutions were made by suitable dilutions of the stock solution. A 1.0 molL^{-1} solution of hydrogen peroxide (Merck) was prepared by an appropriate dilution of 30% reagent in a volumetric flask of 50 mL with deionized water. A 0.1 molL^{-1} tartaric acid stock

solution was subsequently prepared by dissolving 1.50 g of $C_4H_6O_6$ (Merck) in water and diluting to 100 mL in a volumetric flask.

Recommended procedure

In a special four compartment vessel (Budarin's vessel), the solution of Cu (II) was placed in one compartment of a vessel, solution of H_2O_2 in the second, fruit juice in the third, and buffer solution (tartaric acid, pH = 3.5) and deionized water with the total volume 10 mL) in the fourth compartment. The vessel was thermostatted for 5 min at 25.0±0.1°C. Afterward the contents of all four separate compartments were mixed and then stirred during 60 s. The content was transferred to the spectrophotometric cell with a part length of 1 cm immediately after the stirring, and absorbance was recorded. The change in absorbance was recorded at 520 nm as a function of time every 2.5 min for the first 25 min of the reaction. The reaction rates at different concentrations of each of the reactants were obtained by measuring the slope of the linear kinetic curves to the absorbance plot (from Beer's law $A= \varepsilon \cdot l \cdot c$, $dA/dt = \varepsilon \cdot l \cdot (dc/dt)$, $dc/dt = (dA/dt)/\varepsilon \cdot l$, slope = dA/dt, rate =dc/dt).

Investigation on the effect of H_2O_2 concentration

Aliquots (0.10-0.75 mL) of H_2O_2 standard solution were pipetted into the one compartment of the four compartment vessel; 0.50 mL of the Cu (II) solution was placed in the second compartment; 0.5 mL of the red currant (0.2 mL of the sour cherry) fruit juice in the third and buffer solution (tartaric acid, pH = 3.5) and deionized water with the total volume 10 mL in the fourth compartment.

Investigation on the effect of Cu (II) concentration

Aliquots (0.12-0.50 mL) of Cu(II) standard solution were pipetted into the one compartment of the vessel; 0.5 mL (or 0.3 mL) of the H_2O_2 solution in the second; 0.5 mL of the red currant (0.2 mL of the sour cherry) fruit juice in the third and buffer solution (tartaric acid, pH = 3.5) and deionized water with the total volume 10 mL in the fourth compartment.

Investigation on the effect of anthocyanins concentration

Aliquots (0.25-0.75 mL) of the red currant juice and (0.1-0.30 mL) of the sour cherry juice were pipetted into one compartment of the four-compartment vessel; 0.50 mL for the red currant juice (0.30 mL for the sour cherry juice) of the H_2O_2 solution in the second; 0.5 mL of the standard of Cu(II) in the third, and tartaric acid (pH=3.5) and deionized water with the total volume 10 mL in the four compartment.

Analysis of kinetics and thermodynamics

Order of reaction*:* The degradation process for anthocyanins can be described by the general rate equation:

$$-\frac{dc}{dt} = kc^n \quad (1)$$

Where *-dc/dt* represents the rate of anthocyanins degradation, *k* the rate constant, *c* the anthocyanin concentration at each time, and *n* the reaction order.

For n = 1 and after integrating:

$$-\frac{dc}{dt} = kc;\ -\frac{dc}{c} = k \cdot dt$$

$$\ln(c_o/c_t) = kt \quad (2)$$

Eq. (2) is obtained where c_0 is the initial anthocyanins concentration (t = 0) and c_t the concentration of anthocyanins at each time.

Thermodynamic analysis: The temperature and degradation constant are related according to the Arrhenius equation:

$$k = A \cdot e^{-E_a/RT} \quad (3)$$

where *k* represents the rate constant for the degradation process, *A* the Arrhenius constant, E_a the apparent energy of activation, *R* the universal gas constant, and *T* the absolute temperature. Taking natural logarithms

$$\ln k = \ln A - \frac{E_a}{RT} \quad (4)$$

Eq. (4) is obtained. When the natural logarithm of the degradation constant compared with the inverse of the absolute temperature is plotted according to the Eq. (4), the E_a value from the slope and the *lnA* value from the ordinate intercept are obtained. Thus, the thermodynamic parameters, change in enthalpy (ΔH^*), entropy (ΔS^*), and free energy of activation (ΔG^*), are obtained using the following equations:

$$\Delta H^* = E_a - RT \quad (5)$$

$$\Delta S^* = 19.14[\log k - \log T - 10.3178 + \Delta H^*/19.14T] \quad (6)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (7)$$

where *k*, represents degradation rate constant and *T*, absolute temperature.

Results and Discussion

Absorption spectra and kinetics of anthocyanin degradation

The juice samples were diluted with deionized water to give an absorbance reading between 0.6 and 0.8 units. These absorbance values were achieved by diluting 0.1 mL of sour cherry and 0.25 mL of red currant juice with 4.9 and 4.5 mL of deionized water, respectively. The absorption spectra were scanned from 300 to 700 nm. The absorption maximum was recorded at 520 nm (Figure 1A). All absorbance readings were made against deionized water as a blank.

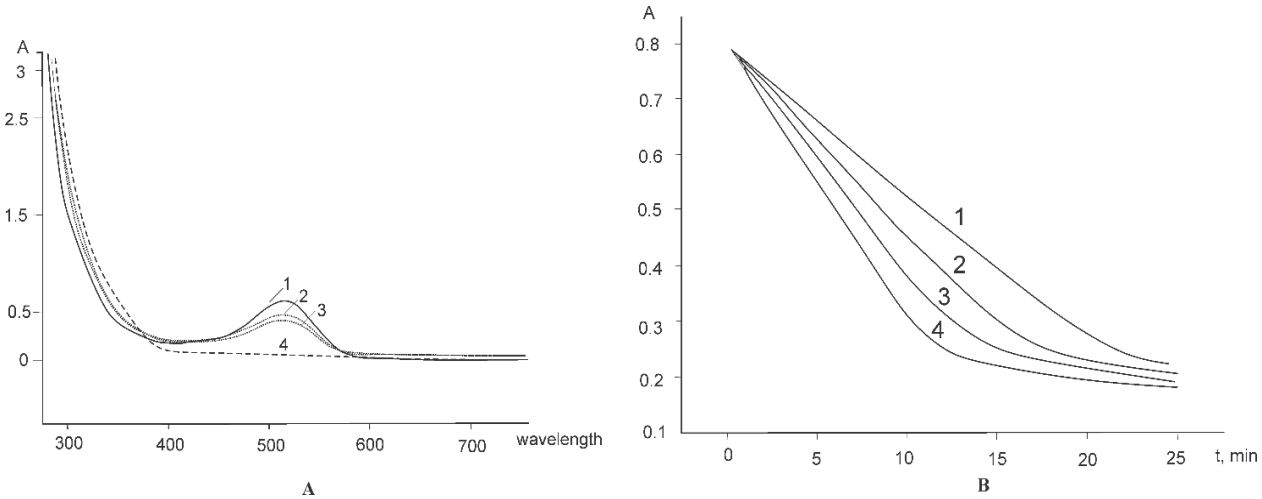

Figure 1. A) Absorption spectra of: 1) aqueous solution of sour cherry juice; 2) sour cherry juice-H_2O_2; 3) sour cherry juice- H_2O_2-Cu(II); 4) sour cherry juice- H_2O_2-Cu(II) 24 h after mixing; **B**) Relationship between the absorbance of reaction mixture and time at: 1) 25; 2) 30; 3) 35; 4) 40°C recorded at 5 min intervals, V (sour cherry juice) = 0.2 ml; c(H_2O_2) = 0.059 mol·L^{-1}, $c_{Cu(II)}$ = $1.85 \cdot 10^{-4}$ mol·L^{-1}; pH=3.5

In order to confirm that decrease of absorption at 520 nm comes from the anthocyanins' degradation, absorption spectra for different mixtures of reaction components were recorded 3 min after mixing the reagents. The spectrum of anthocyanins in aqueous solution (juice diluted with deionized water) is presented in Figure 1A, curve 1. The spectra of a mixture consisting of aqueous solution juice-H_2O_2 and mixture made of aqueous solution juice-H_2O_2-Cu (II) are presented in Figure 1A, curve 2 and 3, respectively. The reaction between anthocyanins and hydrogen peroxide occurs very slightly, but the addition of Cu (II) ions particularly accelerates this reaction as a result of the strong catalytic action of this metal ion. For mixture juice-H_2O_2-Cu (II), the absorbance band at 520 nm significantly decreased (Figure 1a, curve 4) after degradation during 24 h. Meanwhile, the baseline gradually ascended from 400 to 300 nm, similarly to the previous report (Song et al., 2011).

Figure 1B shows the relationships between the absorbance of the reaction mixture (which is directly proportional to the concentration of anthocyanins) and time at different temperatures. Anthocyanin concentration decreases with time. It is possible to follow the reaction rate spectrophotometrically as the change of the solution absorbance values with time, because of the linear dependence of absorbance on time during the first 20 min of reaction at 25^0C. The initial-rate method was used to determine partial orders (Perez-Bendito and Silva, 1988). The initial

rates of the reaction were determined by measuring the slope of the initial tangents to the absorbance-time curves, dA/dt.

The reaction rate dependence on the H_2O_2 concentration was studied in the range 0.019-0.147 $molL^{-1}$ (Figure 2). The reaction rate increased by increasing the concentration of H_2O_2. This figure shows that the degradation of anthocyanins in sour cherry and red currant juices follows the first-order reaction with respect to H_2O_2 concentrations because the curve is linear. For further work, a concentration of 0.098 and 0.059 $mol \cdot L^{-1}$ was selected for the red currant and sour cherry juices, respectively.

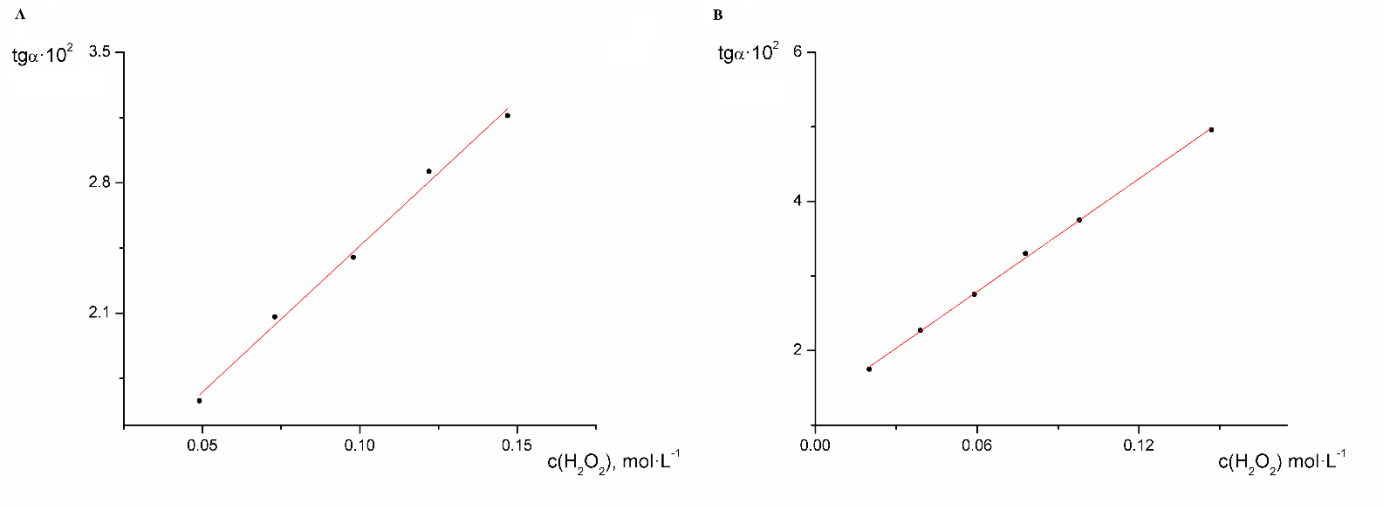

Figure 2. Dependence of the reaction rate on the H_2O_2 concentration. Concentration in measured solution: $c_{Cu(II)} = 1.23 \cdot 10^{-4}$ $mol \cdot L^{-1}$; pH=3.5; t = 25.0±0.1 ^{0}C. A) V (red currant juice) = 0.5 ml; B) V (sour cherry juice) = 0.2ml

Keeping all the other experimental parameters constant, Cu (II) dependence on the system was studied in the range $0.31 \cdot 10^{-4}$-$1.23 \cdot 10^{-4}$ $mol \cdot L^{-1}$. It was observed that Cu (II) ions had catalytic activity. The reaction is first order with respect to Cu (II) concentration (Figure 3).

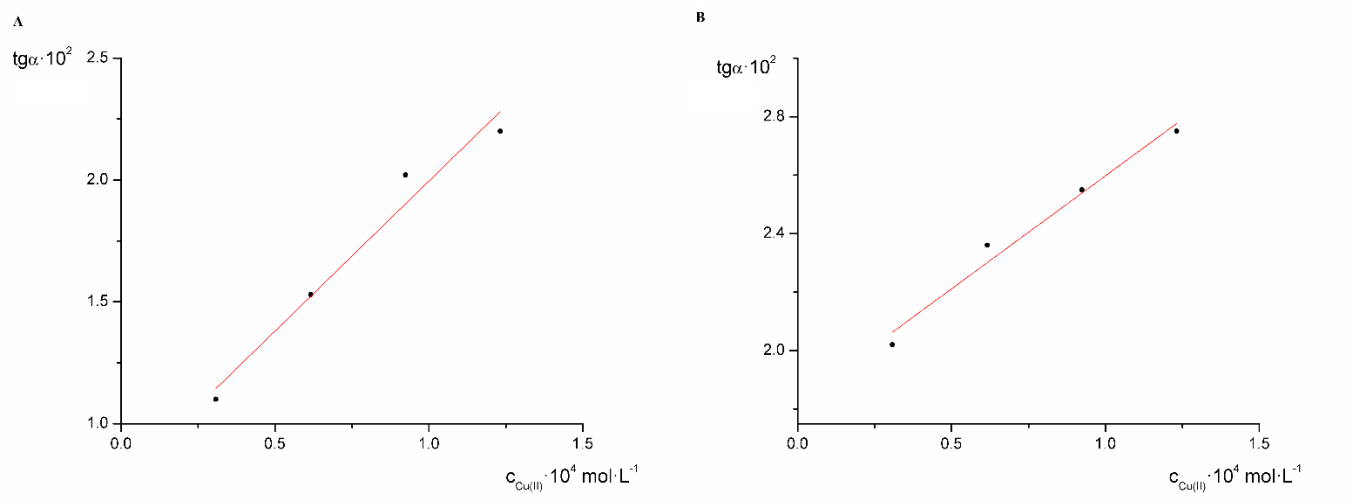

Figure 3. Dependence of the reaction rate on the Cu (II) concentration. Concentration in measured solution: pH = 3.5; t=25.0±0.1°C. A) V (red currant juice) = 0.5 ml, $c(H_2O_2)$ = 0.098 $mol \cdot L^{-1}$; B) V (sour cherry juice) = 0.2 ml, $c(H_2O_2)$ = 0.059 $mol \cdot L^{-1}$

The influence of the temperature on the reaction of the degradation of anthocyanins in sour cherry and red currant juices with H_2O_2 and Cu(II) as catalyst (at optimal conditions: pH = 3.5; $c_{Cu(II)}$ = $1.23 \cdot 10^{-4}$ $mol \cdot L^{-1}$; $c(H_2O_2)$ = 0.059 $mol \cdot L^{-1}$ and 0.098 $mol \cdot L^{-1}$, respectively) was studied.

The effect of the temperature on the reaction rate was followed in the range 298-313 K. The reaction rate was increased with increasing temperature. The degradation of anthocyanins in sour cherry and red currant juices by Cu (II)/H_2O_2 reagent followed Arrhenius equation (tartaric acid buffer, pH = 3.5; t = 25.0±0.1°C). Previous studies showed that thermal degradation of anthocyanins followed the first-order reaction (Garzon and Wrolstad, 2002; Wang and Xu, 2007; Mercali et al., 2013). The optimum reaction temperature of 298 K was selected. At the higher temperature (313 K), the reaction became too fast and not suitable for following during the 2.5-20 min after mixing. The reaction rate dependence on the anthocyanins concentration was investigated under selected and constant reaction concentrations: $c_{Cu(II)}$ = 1.23 $mol \cdot L^{-1}$, $c(H_2O_2)$ = 0.098 $mol \cdot L^{-1}$ and pH=3.5. Linear dependence confirmed that the degradation of anthocyanins in red currant and sour cherry juices followed the first-order reaction.

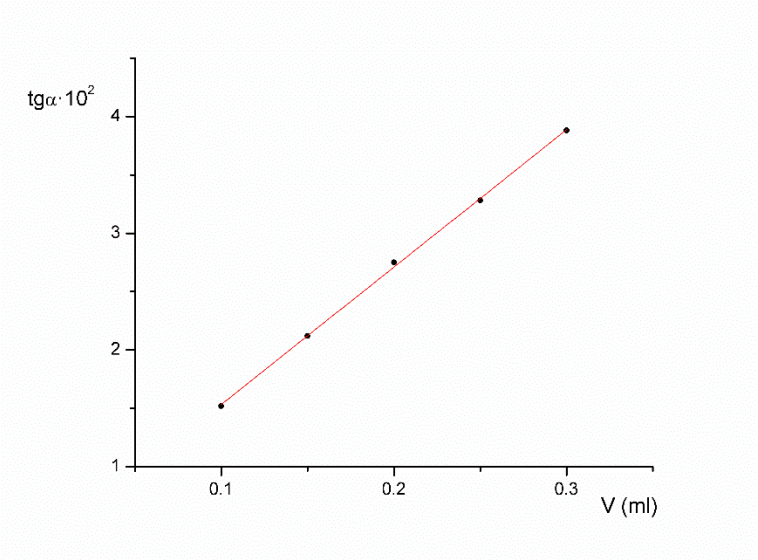

Figure 4. Reaction rate dependence on the concentration of anthocyanins. Concentration of the reactants in the solution: V (red currant juice) = 0.5 mL, c(H_2O_2) = 0.098 mol·L^{-1}, $c_{Cu(II)}$ = 1.23 mol·L^{-1}; pH = 3.5; t=25.0±0.1°C.

Based on the present kinetic investigation, the kinetic equation for degradation of anthocyanins in sour cherry and red currant juices by H_2O_2 in the presence of Cu (II) as catalyst was formulated:

$$-\frac{dc}{dt} = k \cdot c_{H_2O_2} \cdot c_{Cu(II)} \cdot c_{Anthocyanins} \quad (8)$$

where *k* is rate constant.

Mechanism of reaction

In an aqueous solution, H_2O_2 can quickly decompose to form very active products: the perhydroxyl anion (HOO^-), hydroxyl ($^{\bullet}OH$) and perhydroxyl ($^{\bullet}OOH$) radicals (De et al., 1999). These reactive oxygen species might affect anthocyanin degradation (Matta et al., 2008). The catalytic activity of Cu (II) in the decomposition of H_2O_2 has been extensively investigated due to their implication in many chemical and biological processes. The mixture Cu (II)/H_2O_2 is a Fenton-like reagent, analogues to the iron/Fenton reagent, Fe (II)/H_2O_2. The mixture Cu (II)/H_2O_2 is a strong oxidant, and it may react with various organic substances. In acidic medium, at pH 1.0 and pH 3.8 the spectra show a characteristic absorption of the cation form (AH^+) of the

flavylium structure, with a strong peak absorption at λ_{max}=520 nm. Anthocyanins are decomposed in acidic medium by H_2O_2, as shown by the following reaction scheme (Song et al., 2011; Lopes et al., 2007; Alecu et al., 2008):

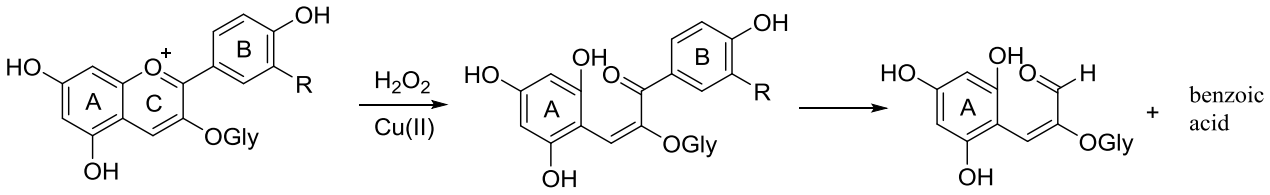

Figure 5. Hypothetical scheme for the degradation reaction of Cy-3-glycosides.

The opening of the C-ring for Cy-3-glycosides (AH^+) formed a neutral chalcone (C). This compound is further oxidized to compound D, which is in fast equilibrium with its tautomeric quinone forms (Nikkhah et al., 2010).

However, this reaction proceeds slowly without catalytic amounts of Cu(II). In the presence of the catalyst Cu(II) the process occurs at several stages:

$$Cu(II) + H_2O_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} [Cu(II)H_2O_2]$$

This is reversible formation of an intermediate product (Stewart, 1964). The second stage is the formation of an activated complex (Salem et al., 2000):

$$[Cu(II)H_2O_2] + Athocyanin \underset{k_4}{\overset{k_3}{\rightleftarrows}} [AnthocyaninCu(II)H_2O_2]$$

Finally, the activated complex decomposes into the products and the catalyst:

$$[AnthocyaninCu(II)H_2O_2] \overset{k_5}{\rightarrow} \Sigma\, Products + Cu(I)$$

The kinetics indicated that a Cu (II)-anthocyanine peroxo complex is involved in the rate-determining step. The complex $[AnthocyaninCu(II)H_2O_2]$ undergoes intramolecular electrontransfer, generating Cu(I) species that can react with hydrogen peroxide:

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

The rate of catalyzed reaction is (at constant pH):

$$v = k_5[AnthocyaninCu(II)H_2O_2] \quad (9)$$

In the stationary state the concentration of the activated complex can be determined from the relation:

$$[\text{AnthocyaninCu(II)}H_2O_2] = \frac{k_1 k_3 [\text{Cu(II)}][\text{Anthocyanin}]}{(k_4+k_5)(k_2/k_1+[H_2O_2])}$$

Substituting this into Eq. (9), an expression for the observed reaction rate is obtained:

$$v = \frac{dx}{dt} = K_I \frac{[H_2O_2][\text{Anthocyanin}]}{K_{II}+[H_2O_2]} c_{Cu} \quad (10)$$

when $[H_2O_2] << K_{II,}$

$$v = \frac{dx}{dt} = \frac{K_I}{K_{II}} C_{Cu}[H_2O_2][\text{Anthocyanin}] \quad (11)$$

where: C_{Cu}- total concentration of copper, K_I, K_{II}- new constants.

The equation (11) is in good agreement which those obtained by the experimental data (equation 8).

Thermodynamic analysis

Based on equation (8), the rate constants, as the average value of three measurements at indicated temperature, were calculated (Table 1).

Table 1. Rate constants at four temperatures

T, K	$k \cdot 10^2$, $mol^2\,dm^{-6}\,min^{-1}$	
	Red currant juice	Sour cherry juice
298	2.18	2.72
303	2.64	3.44
308	3.10	4.18
313	3.59	4.91

The temperature-dependence degradation rate constant is represented by the Arrhenius equation. Graphic dependence of the rate constant as a function of reciprocal value of absolute temperature gives a linear relationship at the studied temperature range ($r^2 > 0.9$), which allowed the calculation of the activation energy values, which was 30.59 $kJ \cdot mol^{-1}$ for sour cherry and 25.76 $kJ \cdot mol^{-1}$ for red currant juices (Table 2).

Table 2. Thermodynamic parameters for degradation of anthocyanins in red currant and sour cherry juices

Juice	E_a (kJ·mol^{-1})	ΔH^* (kJ·mol^{-1})	ΔS^* (J·K^{-1}·mol^{-1})	ΔG^* (kJ·mol^{-1})
Red currant	25.76	23.29	121.92	59.61
Sour cherry	30.59	28.12	115.48	62.53

Kirca et al. (2007) found an increase in the activation energy with increasing concentration, while research carried out by Toralles et al. (2008) indicates lack of relation dependency between the activation energy and concentration in the substance degradation. Also, different anthocyanins had different degradation kinetics in juices (Hellstrom et al., 2013). The sour cherry and red currant juices contained only cyanidin-glycosides. In any case, the effect of the sugar moiety was irrelevant compared to the effect induced by the type of core anthocyanidin in these anthocyanins. However, juice matrix had a major impact on the stability of anthocyanins. Hellstrom et al. (2013) suggested that the cyanidin 3-galactoside and cyanidin 3-arabinoside degraded 3-4 times faster in crowberry juice than in chokeberry juice. Generally, co-pigmentation of anthocyanins with other compounds is very important in the color stabilization in plants (Castaneda-Ovando et al., 2009).

Examination of thermodynamic parameters may also provide valuable information regarding degradation kinetics of anthocyanins by Cu/H_2O_2 reagent. Thermodynamic parameters (ΔG^*, ΔH^* and ΔS^*) are presented in Table 2. ΔG^* represents the difference between the activated state and reactants (Al-Zubaidi and Khalil, 2007) The positive values of ΔG^* indicate that the formation of the activated complex is a nonspontaneous reaction. ΔH^* is related to the strength of the bonds, which are broken and made in the formation of the transition state (Vikram et al., 2005). ΔH^* values evaluated in this study are 23.29 and 28.12 kJ·mol^{-1} for the red currant and sour cherry juices, respectively. The positive sign of ΔH^* represents an endothermic state between the activated complex and reactants. ΔS^* is a measure of the disorder change of molecules in the system. The negative entropy values found in this study suggest that the transition state has lower structural freedom than the reactants (Mercali et al., 2013).

Conclusion

The present study analyzed the degradation kinetics of anthocyanins in sour cherry and red currant juice by Cu (II)/H_2O_2 reagent at a temperature ranging from 25 to 40^oC. The temperature, concentration of H_2O_2, Cu (II), and anthocyanins have a significant influence on the degradation of cyanidin-3-glycosides in red currant juice. Variation of degradation rate constants with temperature obeyed the Arrhenius relationship. Compared to sour cherry juice anthocyanins, red currant juice anthocyanins were much more susceptible to Cu (II)/H_2O_2 reagent, based on the higher values of the degradation rate constants.

Conflict-of-Interest Statement

Declarations of interest: none

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