Kinetic and Thermodynamic Characteristics of Thermal Degradation of Anthocyanins from Strawberry and Blueberry Commercial Juices

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ABSTRACT

Thermal stabilities of anthocyanins in strawberry and blueberry commercial juices were studied over the temperatures 75, 85 and 95 ^{o}C. Results indicated that the thermal degradation of anthocyanins followed the first-order reaction kinetics. The temperature-dependent degradation was adequately modeled on the Arrhenius equation. During heating, anthocyanins in the strawberry juice degraded faster than in blueberry juice, with the activation energies of 74.16 kJ/mol and 65.75 kJ/mol, respectively. Cyanidin-3-glucoside (cyd-3-glu) was more susceptible to the thermal treatment than pelargonidin glycosides in strawberry juice. Delphinidin glycosides were more susceptible to the thermal treatment than cyanidin glycosides in blueberry juice. However, cyd-3-glu in strawberry juice was more sensitive to the thermal treatment than in blueberry juice. Obtained results for activation enthalpies indicated that the degradation process was endothermic and Gibbs free energy of activation indicated that they were not spontaneous.

Keywords: *Thermal degradation, anthocyanins, degradation kinetics, blueberry juice, strawberry juice*

Introduction

Anthocyanins are a group of naturally occurring phenolic compounds, which are responsible for the attractive colors of many flowers, fruits (particularly in berries), vegetables and related products derived from them (Wang and Xu, 2007). Except as colorants, anthocyanins have multiple biological roles, *e.g.*, antioxidant activity, anti-inflammatory action, inhibition of blood platelet aggregation and antimicrobial activity, treatment of diabetic retinopathy and prevention of cholesterol-inducted atherosclerosis (Clifford, 2000; Espin et al., 2000). Nevertheless, anthocyanins easily degrade during food processing and storage, being highly sensitive to factors such as light, pH, temperature, presence of oxygen and enzymes (Mercali, 2013).

Food processing generally includes heat treatments that effectively preserve foodstuffs and also provide desirable sensory properties. However, current knowledge indicates that heat processing, particularly under severe conditions, may affect anthocyanin levels in fruit products and vegetables (Hou et al., 2013; Jimenez et al., 2010). The thermal degradation of anthocyanins has been studied in grape juice (Dalisman et al., 2015), blackberries (Wang and Xu, 2007), blueberry juice (Kechinski et al., 2010), elderberry juices (Casati et al., 2015), and sour cherry juice (Szaloki-Darko et al., 2015). Reported results show that rate constants for anthocyanin degradation with respect to the temperature can always be assumed to follow a first-order reaction, and the Arrhenius model can be used to describe this dependence between temperature and anthocyanin degradation. The kinetics degradation of anthocyanins can also 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 that occur in foods and may provide valuable information concerning thermal degradation kinetics (Cassati et al., 2015).

The objective of the present study was to comparatively evaluate the effect of heating on the degradation kinetics of individual anthocyanins in strawberry and blueberry juices at temperatures ranging from 75 to 95°C.

Experimental

Chemical and reagents

Cyanidin-3-glucoside, pelargonidin-3-glucoside and delphinidin-3-glucoside were purchased from Merck (Darmstadt, Germany). Other anthocyanin-glycosides were purchased from Extrasynthese S.A.S (Ganay, France). Formic acid and acetonitrile (HPLC grade) were purchased from Merck (Darmstadt, Germany). Deionized water was used for the preparation of all solutions, and it was produced using MicroMed high purity water systems (TKA Wasseraufbereitungssystem GmbH).

Degradation studies of juice samples

Commercial strawberry and blueberry juices were purchased from local market. The thermal stability of strawberry and blueberry juices anthocyanins was studied at 75, 85 and 95°C. Juice aliquots (20 ml) were put into glass tubes which were well capped for avoiding evaporation of the samples. Tubes were put in preheated water bath at desired temperature. At predetermined time intervals, the samples were removed and rapidly cooled in the ice bath. Immediately, the anthocyanin content was analysed. All measurements were done in triplicate in each case.

HPLC analysis of anthocyanins

Quantification of individual anthocyanin compounds was determined using reversed phase HPLC method. The analysis was performed by HPLC-DAD (Agilent 1200 series, Agilent Technology, USA) system, equipped with four solvent delivery unit G1354A, UV-Vis detector G1315D and HP Chemstation chromatography workstation. Chromatographic analyses were performed on 150 mm x 4.6 mm i.d., Zorbax Eclipse XDB C18 column (Agilent Technologies, USA). The column was thermostated at 30°C. The flow rate was 0.8 ml/min and the injection volume was 5 µL. The mobile phase consisted of A: H_2O+5% HCOOH and B: 80% ACN+5% HCOOH+H_2O. The gradient procedure was: 0-10 min with 0% B, 10-28 min gradually increases 0-25% B, from 28 to 30 min 25% B, from 30 to 35 min gradually increases 25-

50% B, from 35 to 40 min gradually increases 50-80% B, and finally for the last 5 min gradually decreases 80-0% B. Individual cyanidin, delphinidin, peonidin, petunidin and pelargonidin glycosides were quantified as corresponding equivalents of the five anthocyanin glucosides using external calibration curves of authentic standards ranging from 5 to 125 μg/ml. Total anthocyanins were calculated as the sum of individual anthocyanin glycosides with results expressed as mg per 1L of juice.

Kinetic models

A first-order reaction model has been applied for the description of degradation of anthocyanins from various sources (Szaloki-Darko et al., 2015; Verbeyst et al., 2011; Zhao et al., 2012). The model is expressed as:

$$\ln\left(\frac{c_t}{c_o}\right) = -k \cdot t \qquad (1)$$

where c_0 is the initial anthocyanin content and c_t is the anthocyanin content after treatment time (min) at the given temperature, k is the rate constant (1/min), and the half-life $t_{1/2}$ is the time needed for 50% degradation of anthocyanin, which is calculated by the following equation:

$$t_{1/2} = \frac{\ln(0.5)}{k} = \frac{0.693}{k} \qquad (2)$$

Thermodynamic analysis

The activation energy was calculated using the Arrhenius equation, which was used to describe the temperature dependence of the first-order degradation rate constant. It is expressed as Eq. (3), and can be rearranged as a linear Eq. (4) (Liu et al., 2014):

$$k = k_0 \cdot e^{-E_a/RT} \qquad (3)$$

$$\ln k = \ln k_0 + \left(\frac{-E_a}{R}\right)\frac{1}{T} \qquad (4)$$

where: k_0-frequency factor (1/min); E_a-activation energy (kJ/mol); R-universal gas constant (8.314 J/mol·K) and T-absolute temperature (K).

The coefficient Q_{10} (temperature coefficient) is another way to characterize the effect of the temperature on the rate of a reaction, which represents the change in the degradation when the temperature increases by 10°C, is calculated as follows (Kechinski et al., 2010):

$$Q_{10} = \left(\frac{k_{T_2}}{k_{T_1}}\right)^{10/T_2 - T_1} \quad (5)$$

All of the activation parameters: activation enthalpy change, ΔH^* (kJ/mol), activation entropy change, ΔS^* (J/K·mol), and activation Gibbs free energy change, ΔG^* (kJ/mol), were used to investigate the thermodynamic changes in the transition state of the degradation reaction. ΔH^* and ΔS^* were calculated using the Eq. (6) and Eyring equation shown in Eq. (7), while the activation Gibbs free energy change was determined using Eq. (8) (Park and Kim, 2017):

$$\Delta H^* = E_a - RT \quad (6)$$

$$\frac{\ln k}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad (7)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (8)$$

The rate constant (k) was obtained using the Eq. (1), k_B is the Boltzman constant (1.3807 x 10^{-23} J/K) and h is the Planck constant (6.6261 x 10^{-34} J·s).

Results and Discussion

HPLC-DAD analysis of juices

Monomeric anthocyanins existing in red fruit juices were derivatives of cyanidin, delphinidin, pelargonidin, malvidin and peonidin. So, it is evident that juices produced with different red fruits, such as strawberry, raspberry, blueberry, black currant and grapes, differ in the quantity and the type of anthocyanins.

The results of HPLC-DAD analysis of the commercial strawberry and blueberry juices are shown in Table 1.

Table 1. Concentrations of anthocyanins in commercial juices (mg/L) determined by HPLC-DAD method and the percentage distribution of anthocyanins

Anthocyanins	Sample	Concentration (mg/L)	Total anthocyanins (%)
Cyanidin-3-glucoside (cyd-3-glu)	Strawberry juice	67.5±0.34	50.5
Pelargonidin-3-glucoside (pgd-3-glu)		62.4±0.42	46.7
Pelargonidin-3-rutinoside (pgd-3-rut)		2.84±0.42	2.8
Total anthocyanins (TA)		**133±0.29**	**100**
Delphinidin-3-galactoside (dpd-3-gal)	Blueberry juice	11.2±0.25	9.30
Delphinidin-3-glucoside (dpd-3-glu)		7.13±0.22	5.95
Delphinidin-3-arabinoside (dpd-3-ara)		53.9±0.87	44.9
Cyanidin-3-galactoside (cyd-3-gal)		10.3±0.37	8.6
Cyanidin-3-glucoside (cyd-3-glu)		9.45±0.18	7.88
Cyanidin-3-arabinoside (cyd-3-ara)		6.91±0.15	5.76
Petunidin-3-galactoside (ptd-3-gal)		10.9±0.24	9.15
Peonidin-3-galactoside (pnd-3-gal)		10.1±0.20	8.44
Total anthocyanins (TA)		**120±0.31**	**100**

The major anthocyanins in strawberry commercial juice were cyanidin-3-glucoside (50.5%), followed by pelargonidin-3-glucoside (46.7%), whereas the concentration of pelargonidin-3-rutinoside were relatively low (2.8%). Da Silva et al. (2007), Jakobek et al. (2007) and Stój et al. (2006) determined the existence of cyanidin 3-glucoside, pelargonidin 3-glucoside, and pelargonidin 3 rutinoside in strawberry juice, where the major anthocyanin was pelargonidin 3-glucoside.

Blueberry commercial juice contained a mixture of three delphinidin-3-glycosides (galactoside, glucoside and arabinoside), three cyanidin-3-glycosides (galactoside, glucoside and arabinoside), petunidin-3-galactoside and peonidin-3-galactoside, where the delphinidin-3-arabinoside being the most abundant (44.9%). These data are in accordance with those found in literature (Obon et al., 2011; Prior et al., 2001; Wu and Prior, 2005).

Thermal degradation kinetics of anthocyanins

Previous studies showed that thermal degradation of anthocyanins followed a first-order reaction. To verify the applicability of a first-order kinetic model, $\ln(c_t/c_0)$ is plotted against time (Figures 1 and 2).

It is clear from Figures 1 and 2 that the thermal degradation of strawberry and blueberry anthocyanins followed first order reaction kinetics.

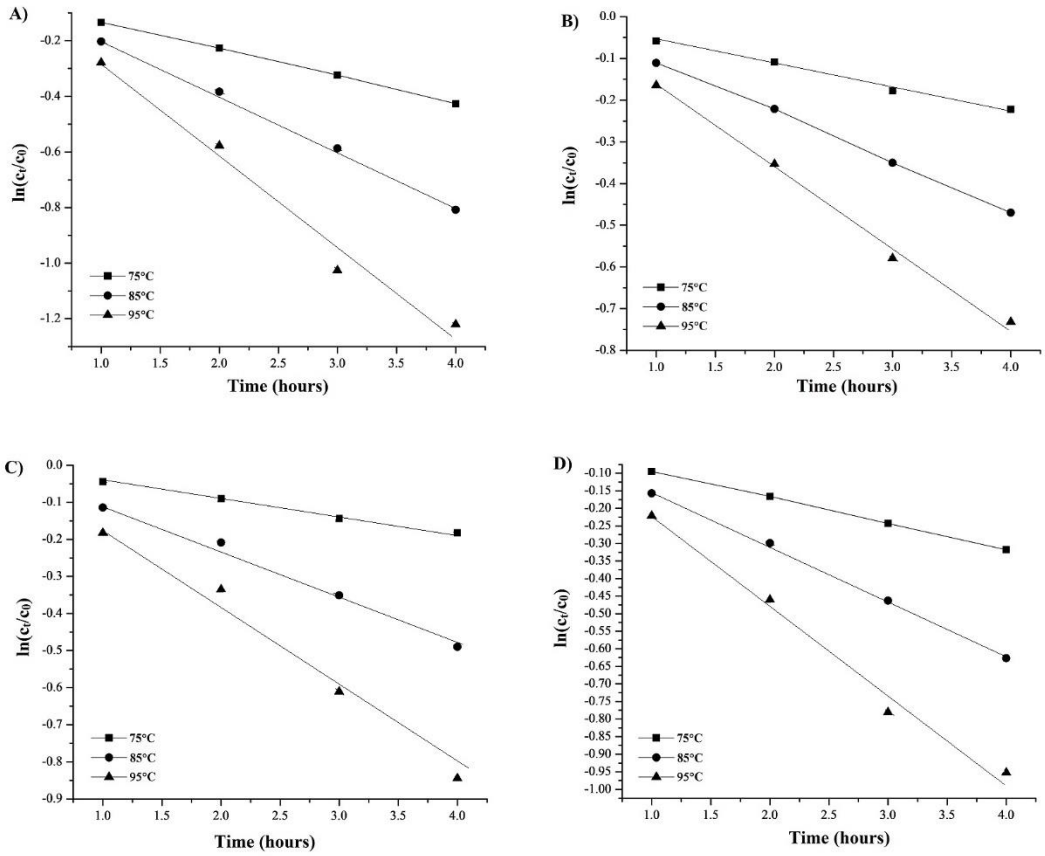

Figure 1. Degradation of anthocyanins in strawberry juice during heating: **A**) cyd-3-glu, **B**) pgd-3-glu, **C**) pgd-3-rut, **D**) total anthocyanins.

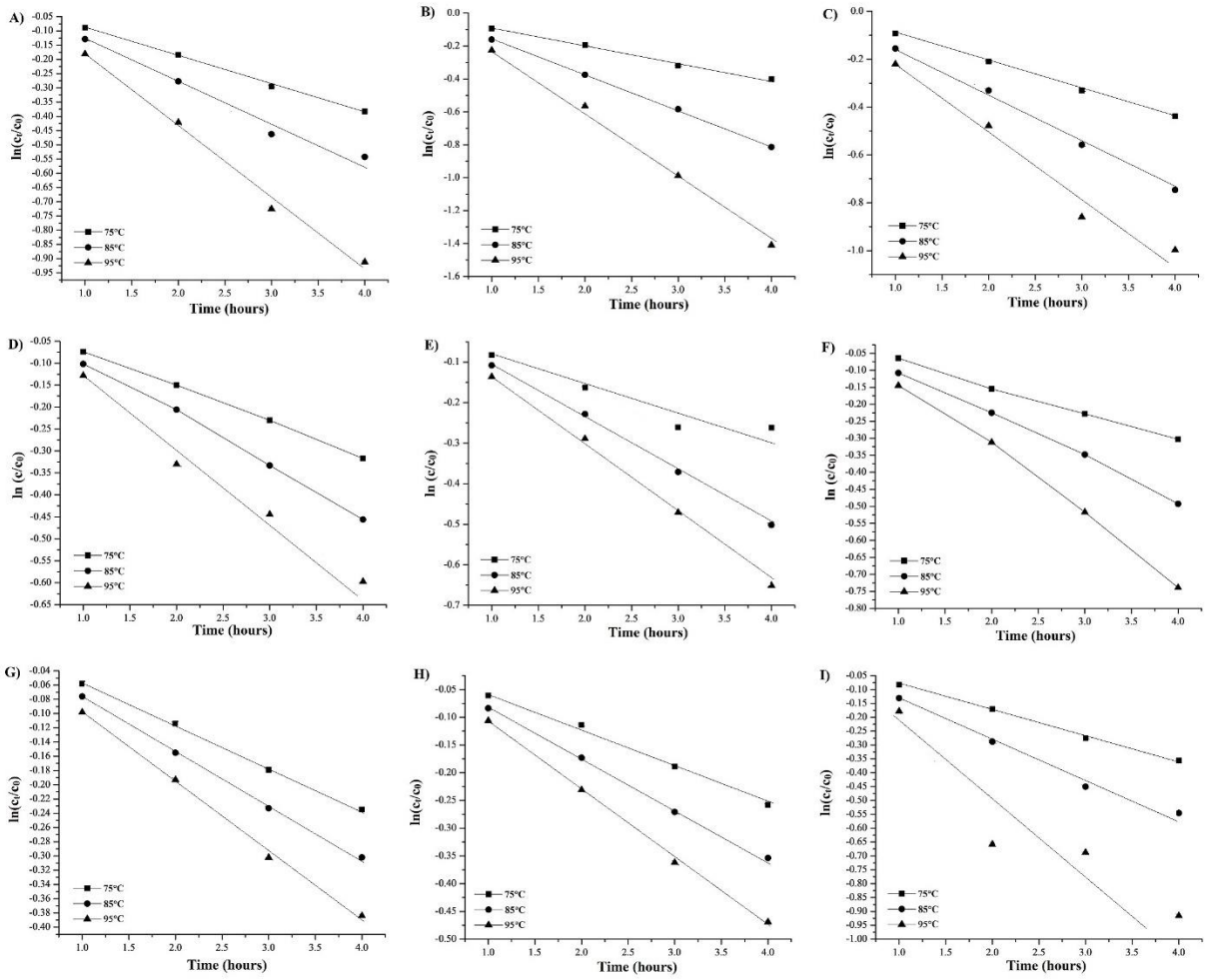

Figure 2. Degradation of anthocyanins in blueberry juice during heating: **A**) dpd-3-gal, **B**) dpd-3-glu, **C**) dpd-3-ara, **D**) cyd-3-gal, **E**) cyd-3-glu, **F**) cyd-3-ara, **G**) ptd-3-gal, **H**) pnd-3-gal, **I**) total anthocyanins.

The kinetic parameters of individual anthocyanins and total anthocyanins in juices are shown in Table 2. It is clear that the degradation of strawberry and blueberry anthocyanins increased with increasing heating temperature and time.

For the cyd-3-glu as a predominant anthocyanin in strawberry juice, the degradation rate constant (k) increased from 1.58 to $6.22 \cdot 10^{-3}$ 1/min with the temperature increase from 75 to 95°C. For the pgd-3-rut, the degradation rate also showed similar trend, with k increasing from 0.84 to $3.57 \cdot 10^{-3}$ 1/min as a result of temperature increase. Increasing the temperature for 20°C (from 75 to 95°C), k is increased by

approximately 3.8 to 4.3 fold. For dpd-3-ara as a predominant anthocyanin in blueberry juice, for the same temperature increase (20°C), the degradation rate constant (k) increased from 1.88 to $6.35 \cdot 10^{-3}$ 1/min. In this case, increasing the temperature for 20 °C (from 75 to 95 °C), k increased by approximately 1.7 to 3.4 fold.

Table 2. Effect of heating temperature on the degradation of strawberry and blueberry juices anthocyanins

	Temperature (°C)	$k \cdot 10^3$ (1/min)	$t_{1/2}$ (h)		Temperature (°C)	$k \cdot 10^3$ (1/min)	$t_{1/2}$ (h)
Strawberry juice							
	75	1.58±0.02	7.04		75	0.92±0.01	12.6
cyd-3-glu	85	3.2±0.1	3.61	pgd-3-glu	85	1.98±0.01	5.83
	95	6.22±0.02	1.86		95	3.45±0.02	3.35
	75	0.84±0.01	13.8		75	1.23±0.01	9.39
pgd-3-rut	85	1.97±0.01	5.86	**TA**	85	2.55±0.02	4.53
	95	3.57±0.02	3.23		95	4.66±0.02	2.48
Blueberry juice							
	75	1.72±0.02	6.72		75	2.02±0.01	5.72
dpd-3-gal	85	2.78±0.01	4.15	dpd-3-glu	85	3.35±0.02	3.44
	95	5.43±0.03	2.13		95	5.32±0.03	2.17
	75	1.88±0.01	6.14		75	1.29±0.01	8.95
dpd-3-ara	85	3.52±0.02	3.26	cyd-3-gal	85	1.92±0.02	6.02
	95	6.35±0.02	1.82		95	2.63±0.04	4.39
	75	1.36±0.01	8.49		75	1.48±0.02	7.80
cyd-3-glu	85	1.99±0.01	5.80	cyd-3-ara	85	2.19±0.03	5.27
	95	3.1±0.1	3.72		95	2.79±0.02	4.14
	75	1.01±0.01	11.4		75	1.06±0.01	10.9
ptd-3-gal	85	1.31±0.02	8.82	pnd-3-gal	85	1.55±0.01	7.45
	95	1.69±0.02	5.42		95	2.13±0.03	5.42
	75	1.61±0.01	7.22				
TA	85	2.67±0.02	4.32				
	95	4.25±0.02	2.72				

The $t_{1/2}$ values of anthocyanins are expressed in Eq. 2 and presented in Table 2. The $t_{1/2}$ values varied from 13.8 to 1.86 h and 11.4 to 1.82 h for strawberry and blueberry juices, respectively. The half-life at 95°C of cyd-3-glu (in strawberry juice) and dpd-3-ara (in blueberry juice) was 1.86 and 1.82 h, respectively. The half-life values of anthocyanin degradation in blackberry juice at 60-90°C were from 16.7 to 2.9 h (Wang and Xu, 2007) and in plum juice at 50-120°C were from 6.27 to 0.40 h (Turturica et al., 2018).

Cemeroglu et al. (1994) reported that $t_{1/2}$ value of anthocyanin degradation at 80°C in sour cherry juice and concentrate was 8.1 and 2.8 h, respectively. These results for $t_{1/2}$ values of anthocyanin degradation were considerably higher, compared to the juices analyzed in the present study. Sugar and ascorbic acid present in juices can also increase or decrease the anthocyanin degradation depending on their concentration (Gerard et al., 2019; Svensson, 2010). Different food matrix and chemical structure of anthocyanin-conjugated sugar (the type and place of glycosylation, the presence of hydroxyl groups) probably affect its thermal stability (Dai et al., 2009).

The activation energy E_a was calculated based on a linear regression of ln k and 1/T using Eq. (4). Table 3 presents activation energy values for both juices during heating process. The compared activation energy values for total anthocyanins were: 74.16 kJ/mol and 65.75 kJ/mol, for strawberry and blueberry juice, respectively. High activation energy implies that the degradation of anthocyanins in strawberry juice are more susceptible to temperature elevations that those in blueberry juice. The high activation energy value indicates strong temperature dependence which means that the reaction runs very slowly at low temperature, but relatively fast at high temperatures.

Table 3. The activation energy E_a and temperature coefficient Q_{10} obtained for anthocyanin degradation during heating

	E_a (kJ/mol)	R^2	Q_{10} 75-85°C	Q_{10} 85-95°C
Strawberry juice				
cyd-3-glu	75.99	0.9935	2.02	1.94
pgd-3-glu	73.27	0.9856	2.15	1.42
TA	74.16	0.9912	2.07	1.83
Blueberry juice				
dpd-3-ara	71.50	0.9954	1.62	1.95
dpd-3-gal	63.68	0.9932	1.87	1.80
TA	65.75	0.9948	1.67	1.59

The obtained results are similar to the previously reported E_a for grape juice (64.89 kJ/mol) at 70-90°C (Dalisman et al., 2015), Bordo grape anthocyanins (72.74 kJ/mol) at 70-90°C (Hillman et al., 2011), Cornelian cherry juices (58.09 kJ/mol) at 2-75°C (Moldovan and David, 2020) and blackberry anthocyanins

(58.95 kJ/mol) at 60-90°C (Wang and Xu, 2007). Morever, Kechinski et al. (2010) reported a higher value (80.4 kJ/mol) for the degradation blueberry anthocyanins at 40-80°C.

Table 3 presents the values of Q_{10} for the temperatures used in this study. The higher value is obtained for the cyd-3-glu and pgd-3-glu in strawberry juice within the range 75-85°C, indicating that in this range the degradation kinetics was strongly affected by the temperature. Similar behavior can be observed for the dpd-3-ara and dpd-3-gal in blueberry juice within the range 85-95°C, but to a minor extent. In the range of 85-95°C for pgd-3-glu in strawberry juice and in the range of 75-85°C for dpd-3-ara in blueberry juice Q_{10} values were lower indicating that within those 2 ranges the degradation kinetics are barely affected by the temperature change. According to Kechinski et al. (2010) the relatively low values of Q_{10} suggest the significance of molecular association that could decrease the rate of anthocyanin degradation. Al-Zubaidy and Khalil (2007) also mentioned that this effect can be confirmed by determining the activation energies and other related thermodynamic functions of this degradation process.

Estimation of thermodynamic parameters may also provide valuable information regarding thermal degradation kinetics of anthocyanins. The equilibrium state between an activated complex and reactant is called the transition state. When an activated complex passes the transition state, products are formed (Park and Kim, 2017). Calculated thermodynamic parameters: Gibbs free activation energy ΔG^*, the activation enthalpy ΔH^* and the activation entropy ΔS^*, at all temperatures evaluated during heating are presented in Table 4.

Table 4. Activation thermodynamic parameters obtained for anthocyanin degradation during heating

	Temperature (°C)	ΔH^* (kJ/mol)	ΔS^* (J/mol·K)	ΔG^* (kJ/mol)
Strawberry juice				
cyd-3-glu	75	73.1	-89.7	104.3
	85	73	-90.2	105.3
	95	72.9	-90.6	106.3
pgd-3-glu	75	70.4	-102.1	105.9
	85	70.3	-101.8	106.7
	95	70.2	-102.9	108.1

TA	75	71.3	-97.1	105.1
	85	71.2	-97.2	106
	95	71.1	-99.6	107.8
		Blueberry juice		
dpd-3-ara	75	68.6	-108.9	106.5
	85	68.5	-109.4	108.8
.	95	68.4	-109.7	108.8
dpd-3-gal	75	60.8	-124.4	104.1
	85	60.7	-125.7	105.7
	95	60.6	-125.2	106.7
TA	75	62.9	-119.1	104.4
	85	62.8	-120.3	105.8
	95	62.7	-121.6	107.5

According to the obtained results, the positive values of the activation enthalpies indicated the process was endothermic and that external source energy was required to raise the energy level of anthocyanins contributing to degradation yield to their state transition. Negative values of activation entropy may arise as a result of association mechanism; degrees of freedom were lost due to this activation complex formation, which meant that reacting species joined themselves from state transition during degradation process (Borsato et al., 2014). The Gibbs free energy of that activation was used to determine the spontaneity of the degradation process for all temperature tested. Positive value of ΔG^* indicated that the degradation process was not spontaneous. The obtained results are similar to the previously reported thermodynamic parameters for anthocyanins in acerola pulp (ΔH^* 71.91 to 71.79 kJ/mol; ΔS^*, -82.23 to -82.63 J/mol·K; ΔG^*, 100.53 to 101.78 kJ/mol) at 75-90°C and for blood orange, blackberry and roselle anthocyanins (ΔH^*, 34.24 to 63.11 kJ/mol; ΔS^*, -149 to - 233 J/mol·K;) at 35-90°C (Cisse et al., 2009).

Conclusion

The present study analyzed the thermal degradation of individual and total anthocyanins determined by HPLC-DAD method in strawberry and blueberry commercial juices. The results show that the degradation of strawberry and blueberry anthocyanins follows a first-order reaction kinetics and that the variation in the degradation rate constants according to the temperature obey the Arrhenius relationship.

The strawberry and blueberry anthocyanins, during heating, degraded more quickly with temperature increasing. Obtained results for activation enthalpies indicated that the thermal degradation processes were endothermic, and Gibbs free energy of activation indicated that they were nonspontaneous.

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Conflict-of-Interest Statement

None.

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