DEGRADATION KINETICS OF ANTHOCYANINS IN ACIDIC AQUEOUS EXTRACTS OF BERRIES

The effect of pH, light and temperature on degradation of anthocyanins in acidic aqueous extracts of chokeberries, elderberries and blackberries was studied. The degradation of anthocyanins in berry extracts under influence of pH, light and temperature followed the first-order reaction kinetics. Anthocyanins of chokeberry extracts had the highest values of rate constants of degradation. Anthocyanins of blackberry extracts had the highest values of half-life time.

The temperature dependences of the rate of anthocyanin degradation were described by the Arrhenius equation. Activation energies of anthocyanin degradation were 5.7, 10.1 and 15.0 kJ/mol at pH=2, respectively, for chokeberry, elderberry, and blackberry anthocyanins.

Keywords: chokeberry, elderberry, blackberry, anthocyanins, kinetics of degradation

INTRODUCTION

Anthocyanins are synthesized by many plants. They are responsible for pink, red, blue and purple colours of most berries, flowers, fruits, vegetables, leaves, and roots [1, 2]. In recent years there has been an increasing interest in anthocyanins not only as natural food colorants [1] but also as substances with certain therapeutic effects such as anti-inflammatory, anti-cardiovascular, anti-diabetic, and anti-cancer [3, 4]. Also anthocyanins are applied in prevention and treatment eyesight disorders [4].

Among all fruits and vegetables, especially berries of dark red or dark blue colours have a very high content of anthocyanins. For example, total anthocyanin content in the berries: chokeberry – 5060-10000 mg/kg, elderberry – 2000-15600 mg/kg, and blackberry – 1150 mg/kg [5]. This means the berries are suitable raw material for extraction of anthocyanins on an industrial scale [4].

According to the chemical nature anthocyanins are substituted glycosides of phenyl-2-benzopyrylium salts [1]. Different berries have also different amounts of various individual anthocyanins. Composition of anthocyanins in chokeberries, elderberries and blackberries is presented in table 1.

The main problem with the application of anthocyanins is their low stability to such important factors as pH [1, 7-12], light [1, 7, 9, 13-16] and temperature [1, 7, 9, 11-15, 17-26].

It was established that majority of anthocyanins are more stable in acidic solutions at low pH values than in alkaline solutions with high pH values [1]. This is due to the fact that anthocyanins are pH-dependent compounds in aqueous solution. Change of pH leads to change of their structures. Anthocyanins may form four major forms that exist in equilibrium: the red flavylum cation, the blue quinoidal base, the colourless carbinoxol pseudo-base, and the colourless chalcone (fig. 1). At pH below 2, anthocyanins exist primarily in the form of the red flavylum cation. Hydration of the flavylum cation
gives the colourless carbinol pseudo-base at pH values ranging from 3 to 6. Strong acidic conditions favoured the better stability of anthocyanins in red onion extracts during their storage at room temperature [12]. However it was noticed that some anthocyanins showed improved colour stability in region around pH = 5-6 [10] and pH = 8-9 [8], although the colour intensities were modest.

Table 1

| Berries   | Anthocyanins                              | Major amounts % | Minor amounts % |
|-----------|-------------------------------------------|-----------------|-----------------|
| chokeberry| cyanidin-3-galactoside cyanidin-3-arabinoside | 68.9            | 24.5            |
|           | cyanidin-3-glucoside                      | 3.8             | 2.8             |
| elderberry| cyanidin-3-glucoside cyanidin-3-sambubioside | 83.1            | 15.1            |
|           | cyanidin-3-glucoside-5-glucoside cyanidin-3-rutinoside | 1.8             |                 |
| blackberry| cyanidin-3-glucoside                      | 90.4            | 8.3             |
|           | cyanidin-3-xyloside cyanidin-3-rutinoside | 1.3             |                 |

Anthocyanins are generally unstable under light because it causes their photochemical degradation [13]. In this regard anthocyanins preserve their colour much better when they kept in dark. The difference was seen already after 24 hours when anthocyanins were stored in light and for comparison in dark at room temperature at pH 2.3 [7]. Furtado et al. [13] found that during the photochemical degradation of anthocyanins the formation of the same final products as for thermal degradation was observed, but the kinetic pathway of the photochemical reaction was different involving the excitation of the flavylum cation. Morais et al. [15] reported that presence or absence of light exerted a negligible impact on the decomposition rate of grape anthocyanins.

Fig. 1. The main equilibrium forms of anthocyanin existing in aqueous media [5]
Degradation kinetics of anthocyanins in acidic aqueous extracts of berries

Anthocyanins are easily degraded during thermal processing which can have negative impact on their colour, and may also change their properties. The precise mechanism of thermal anthocyanin degradation is still unclear [20, 23]. However, it has been reported about possible chalcone formation at the first step of the process [17], loss of glycosyl moieties and α-diketone formation [18], formation of end products including coumarin derivatives [26], benzoic acid derivatives [14] and trihydrobenzaldehyde [13].

Thermal stability of anthocyanins in ethanolic, aqueous extracts, juices, and concentrates has been studied using berries: cranberry [11], blackberry [21], elderberry [19, 24], cornelian cherry [25], and blackcurrant [22]. Reported results show that rate constants for anthocyanin degradation with respect to temperature always followed the first-order reaction.

In order to predict the changes in the quality of anthocyanins during their storage and processing, the accurate determination of kinetic parameters of their decomposition is a matter of great concern [11]. However, there are no kinetic data for the degradation of chokeberry, elderberry and blackberry anthocyanins from acidic aqueous extracts. Thus, the aim of this study is to determine the kinetic parameters of degradation for berry anthocyanins from acidified aqueous extracts during storage at different pH, temperatures and lighting. The kinetic parameters, namely, reaction order, rate constant and activation energy provide useful information on the changes of anthocyanins which occur during their storage and heating. Accurate knowledge of the degradation kinetics of berry anthocyanins in acidic aqueous extracts is essential for predicting of changes that may occur during their removal from berries and storage in various conditions.

MATERIALS AND METHODS

Chemicals

Chemical reagents of analytical grade without further purification that were used for preparing solutions for the analysis of anthocyanins (hydrochloric acid (37%), sodium acetate (trihydrate), potassium chloride) were obtained from the Kyiv Plant “RIAP” and Cherkassy State Chemical Plant (Ukraine).

Plant materials and preparation of extracts

Fully ripe chokeberry, elderberry and blackberry were harvested in Zhmerynka district of Vinnitsa region (Ukraine) in 2015. Berries were immediately frozen and kept at −20 °C until analysed.

Extraction was carried out by insisting of the berries in 0.1M HCl (as 1:2=w:v) for 24 hours at 20 °C in the dark. Then the berry extracts were separated from the berries by filtration through filter paper. Extracts of the berries were stored at 4 °C.

Methods

Degradation studies

Studies of degradation of anthocyanins in extracts with pH 2, 3 and 4 in light and in dark were performed respectively in transparent glass bottles and amber glass bottles. The transparent glass bottles with anthocyanin extracts were stored on the windowsill under influence sunlight, and the amber glass bottles with anthocyanin extracts were stored in a dark box at 20 °C.

The thermal degradation of anthocyanins was studied at 50, 75 and 100 °C. The bottles containing anthocyanin extracts were placed in a thermostatic water bath (WB type 357-Lubawa, Poland) and adjusted to the required temperature.
Anthocyanin analysis

Total monomeric anthocyanin concentration was determined by pH-differential method [27], using two buffer systems: potassium chloride buffer (pH 1 (0.025 M)), and sodium acetate buffer (pH 4.5 (0.4 M)). The absorbance of each extract was measured at 515 nm and 700 nm, using UV-VIS spectrophotometer (SF-56, Spectral, S.-Petersburg, Russia). Total monomeric anthocyanin concentrations were calculated as mg cyanidin-3-glucoside per litre extract according to the following equation:

\[
C = l \left[ \left( A_{515} - A_{700, \text{pH} 4.5} \right) - \left( A_{700} - A_{515, \text{pH} 1} \right) \right] \frac{M \cdot DF \cdot 1000}{l \cdot \varepsilon},
\]

where \(A_{515}\) and \(A_{700}\) is absorbance of an extract at pH 1 and at pH 4.5; \(M\) is molecular weight for cyanidin-3-glucoside (449.2 g/mol); \(DF\) is dilution factor as final volume per initial volume; \(l\) is path length in cm; \(\varepsilon\) is molar extinction coefficient (26900 L/(mol·cm) for cyanidin-3-glucoside); 1000 is conversion factor from g to mg. All absorbance measurements were made against distilled water.

Calculation of kinetic parameters of anthocyanin degradation

Knowledge of degradation kinetics of anthocyanins, including reaction order, rate constant and activation energy, allows predicting their quality loss during storage and thermal treatments. Therefore, kinetic studies are needed in order to minimize the undesired change and to optimize quality of anthocyanins in extracts, juices or concentrates.

The majority of studies of the degradation kinetics of anthocyanins from various sources is described using the first-order reaction model [23, 28, 29]. The first-order reaction rate constants \((k)\) and half-life time \((t_{1/2})\), i.e. the time needed for 50% degradation of anthocyanins, were calculated by the following equations:

\[
\ln \frac{C}{C_0} = -kt,
\]

\[
t_{1/2} = \frac{\ln 2}{k},
\]

where \(C\) is the anthocyanin concentration at time \(t\); \(C_0\) is the initial anthocyanin concentration; \(k\) is the first-order reaction rate constant; \(t\) is time.

The dependence of the degradation of anthocyanins on temperature was determined by calculating the activation energy \((E_a)\) and temperature quotient \((Q_{10})\) values from the following equations:

\[
k = k_e \exp \left( -\frac{E_a}{RT} \right),
\]

\[
Q_{10} = \left( \frac{k_{T_2}}{k_{T_1}} \right)^{\frac{10}{T_2-T_1}},
\]

where \(E_a\) is the activation energy; \(k_e\) is the frequency factor; \(R\) is the universal gas constant; \(T\) is the absolute temperature.
RESULTS AND DISCUSSION

Total anthocyanin concentration
The concentrations of anthocyanins in initial extracts were calculated for chokeberry – 154; elderberry – 320; blackberry – 125 mg/L. In degradation studies the concentration of total anthocyanins in all berry extracts was 100 mg/L.

Absorption anthocyanins in extracts at different pH
Fig. 2 shows anthocyanins absorption in extracts of chokeberry, elderberry and blackberry. The values of absorption at different pH decreases sharply from pH 1 to 4 and are not changed at pH = 4-6. The obtained results are in good agreement with the fact that anthocyanins of berries intensively coloured in a strongly acidic medium.

Degradation kinetics of anthocyanins
Important factor which affects the stability of anthocyanins is value of pH. The studies showed that increasing pH had caused greater destruction to anthocyanins in aqueous berry extracts (fig. 3, table 2). Anthocyanins in chokeberry extracts were more stable at pH 2 than at pH 3 and 4. These results are in agreement with our study (fig. 2) and most studies regarding the stability of anthocyanins extracted from different plants [1, 9, 16]. Flavylium salts are stable only in highly acidic solutions and they loose the proton in higher pH and transform into quinoidal base, which is an unstable pigment, and immediately bond to water and form colourless compound called chromenol [9].

Light is another important factor, which can affect the stability of anthocyanins, because it accelerates destruction of anthocyanins. The effect of light at different pH on accelerating the destruction of anthocyanin in the chokeberry extracts has been presented in fig. 3. These results followed the first-order reaction kinetics; the coefficients of determination (R²) values were more than 0.9548 (table 2). In light the degradation constant at pH 2 was 2.2⋅10⁻² d⁻¹ with a half-life time 32 days. In dark the degradation constant at pH 2 was 0.8⋅10⁻² d⁻¹ with a half-life time 90 days. Storage of chokeberry extracts in the dark at 20 °C allowed to reduce the rate of anthocyanin degradation 2.8 times.
Our studies have been conducted in natural daylight. Increasing of intensity of the light source increases the photochemical degradation of anthocyanins. It was showed [16] the $t_{1/2}$ value of anthocyanins from alcoholic blackberry extract was 224.52 hours in dark (100 μlx) and was only 28.20 hours at high illuminance (3968.30 lx). In the study has also been reported that the degradation of blackberry anthocyanins from alcoholic extract followed second order reaction kinetics with respect to the illuminance of the light source. Our results and results of another studies have showed that storage of chokeberry extracts in dark is efficient to preserve the quality of anthocyanins.

**Table 2**

| System  | pH | $k \cdot 10^2$, d$^{-1}$ | $R^2$      | $t_{1/2}$, d |
|---------|----|-----------------|------------|-------------|
| in light| 2  | 2.2             | 0.9588     | 32          |
|         | 3  | 2.7             | 0.9588     | 29          |
|         | 4  | 3.1             | 0.9580     | 22          |
| in dark | 2  | 0.8             | 0.9548     | 90          |
|         | 3  | 1.2             | 0.9683     | 51          |
|         | 4  | 1.7             | 0.9808     | 42          |

Temperature also is another factor, which has an important role in destruction of anthocyanins. A lot of studies [1, 9, 23] have showed that anthocyanin degradation increases with increase in temperature. The results of our studies as the effect of three different temperatures of 50, 75, and 100 °C on degradation kinetics of berry anthocyanins at fixed pH 2, have presented in fig. 4 and table 3. The results of thermal degradation of berry anthocyanins are in agreement with the previous studies reporting first-order reaction kinetics for thermal degradation of anthocyanins [23, 28]. The coefficients of determination ($R^2$) values were more than 0.9284 (table 3).
Degradation kinetics of anthocyanins in acidic aqueous extracts of berries

Anthocyanins from chokeberry and elderberry extracts showed significantly lower stabilities than anthosyanins from blackberry extracts at 50 and 75 °C. Anthocyanins of all berry extracts had approximately the same rate of degradation at 100 °C (k=3.7·10^{-3} – 3.8·10^{-3} min^{-1}) and values of the half-life time are 3.0–3.1 h. Possibly, the different susceptibilities of anthocyanins to heating might be due to their varying anthocyanin compositions [6]. Thermal destruction of anthocyanins from elderberry concentrates at pH 1 and 95 °C was studied [30] and it was found that the value of half-life time is 3.0 h. The values of t_{1/2} for anthocyanins degradation were 8.8, 4.7 and 2.9 h from blackberry juice at 70, 80 and 90 °C, respectively [21].

It was suggested [9] that the rapid degradation of anthocyanin in higher temperatures could be due to hydrolysis of 3-glycoside structure, which has a protective effect in unstable anthocyanin. Another suggestion [9] is that the hydrolysis of the pyrillium ring takes place that results in production of chalcones.

In this paper, we have received low values of activation energy (5.7 – 15.0 kJ/mol) of anthocyanin degradation process in berry extracts at pH=2 and coefficients of determination (R²) values were high, between 0.9168 and 0.9960 (table 3). Comparing the result obtained from this study with other studies, the values of activation energy anthocyanin degradation process in chokeberry, elderberry and blackberry extracts are much lower than in cranberry aqueous extracts (47.39 kJ/mol [11]), blackberry juice (58.59 kJ/mol [21] and 91.2 kJ/mol [24]), elderberry juice (144.6 kJ/mol [19]), cornelian cherry concentrate (48.38 kJ/mol [25]). The calculated value of activation energy of anthocyanin degradation process in purple corn is 18.3 kJ/mol [31]. According to literature data [32]

![Degradation kinetics of anthocyanins in berry extracts during heating:](image)

- a – chokeberry;
- b – elderberry;
- c – blackberry (C₀=100 mg/L, pH=2).

![Graphs showing degradation kinetics.](image)
low values of activation energy signified a higher rate of degradation for anthocyanins whereas higher values of activation energy indicated a retarded rate of degradation.

### Table 3

| Extract   | t, °C | k·10^3, min^-1 | R^2  | t_1/2, h | E_a, kJ/mol | R^2  | Q_{10} |
|-----------|------|----------------|------|---------|-------------|------|--------|
|           | 50   | 2.8            | 0.9853 | 4.1 | 5.7 | 0.9168 | 1.1 |        |
|           | 75   | 3.5            | 0.9672 | 3.3 | 3.3 | 0.9672 | 1.0 |        |
|           | 100  | 3.7            | 0.9582 | 3.1 | 3.0 | 0.9582 | 1.1 |        |
| chokeberry | 50   | 2.3            | 0.9897 | 5.0 | 10.1 | 0.9581 | 1.2 |        |
|           | 75   | 3.3            | 0.9895 | 3.5 | 3.0 | 0.9895 | 1.1 |        |
|           | 100  | 3.8            | 0.9284 | 3.0 | 3.0 | 0.9284 | 1.1 |        |
| elderberry | 50   | 1.8            | 0.9753 | 6.4 | 15.0 | 0.9960 | 1.2 |        |
|           | 75   | 2.8            | 0.9793 | 4.1 | 15.0 | 0.9960 | 1.2 |        |
|           | 100  | 3.8            | 0.9763 | 3.0 | 15.0 | 0.9960 | 1.2 |        |

The Q_{10} values were obtained for the degradation of anthocyanins in berry extracts at 50-75 °C and 75-100 °C (Table 3). The low values of temperature coefficient (1.1–1.2 at 50–75 °C and 1.0–1.1 at 75–100 °C) were obtained at pH = 2. The same low temperature coefficient value (1.018 at 2–37 °C) was obtained in aqueous cranberry extracts at pH=3 indicating that low storage temperatures and acidic media are needed to inhibit degradation of anthocyanins [11].

## CONCLUSION

Knowledge of factors affecting anthocyanins stability can be used to minimize their degradation by the appropriate selection of storage conditions or production processing. The results show that stability of anthocyanins in aqueous extracts of chokeberries, elderberries and blackberries under influence pH, light and temperature followed first-order reaction kinetics. Activation energies of anthocyanin degradation process had low values (5.7, 10.1 and 15.0 kJ/mol at pH=2, respectively, for chokeberry, elderberry, and blackberry anthocyanins). In order to keep anthocyanins degradation rate as low as possible, aqueous extracts of chokeberries, elderberries and blackberries are recommended to store at low temperatures and pH in the dark.

## REFERENCES

1. Delgado-Vargas F., Paredes-López O. Natural Colourants for Food and Nutraceutical. – Boca Raton: CRC Press LLC, 2003. – 167 p.
2. Wu X., Beecher G.R., Holden J.M., Haytowitz D.B., Gebhardt S.E., Prior R.L. Concentrations of anthocyanins in common foods in the United States and estimation of normal consumption // J. Agric. Food Chem. – 2006. – Vol. 54. – P. 4069–4075. https://doi.org/10.1021/jf060300l CCC
3. Ghosh D., Konishi T. Anthocyanins and anthocyanin-rich extracts: role in diabetes and eye function // Asia Pac. J. Clin. Nutr. – 2007. – Vol. 16, N 2. – P. 200-208.
Degradation kinetics of anthocyanins in acidic aqueous extracts of berries

4. Denev P., Cit M., Ambrozova G., Lojek A., Yanakieva I., Kratchanova M. Solid-phase extraction of berries' anthocyanins and evaluation of their antioxidative properties // Food Chem. – 2010. – Vol. 123. – P. 1055–1061. https://doi.org/10.1016/j.foodchem.2010.05.061

5. Clifford M.N. Anthocyanins – nature, occurrence and dietary burden // J. Sci. Food Agric. – 2000. – Vol. 80, N 7 – P. 1063–1072. https://doi.org/10.1002/(SICI)1097-0010(20000515)80:7<1063::AID-JSF605>3.0.CO;2-Q

6. Jakobek L., Seruga M., Medvidovic-Kosanovic M., Novak I. Anthocyanin contain and antioxidant activity of various red fruit juices // Deutsch Lebensmittel-Rundschau. – 2007. – Vol. 103, № 3. – P. 58-64.

7. Kearsley M.W., Rodriguez N. The stability and use of natural colors in foods: anthocyanin, β-carotene and ribofavin // J. Food Technol. – 1981. – Vol. 16. – P. 421-431. https://doi.org/10.1111/j.1365-2621.1981.tb01833.x

8. Cabrita L., Fossen T., Andersen É.M. Colour and stability of the six common anthocyanidin 3-glucosides in aqueous solutions // Food Chem. – 2000. – Vol. 68. – P. 101-107. https://doi.org/10.1016/S0308-8146(99)00170-3

9. Laleh G.H., Frydoonfar H., Heidary R., Jameel R., Zare S. The effect of light, temperature, pH and species on stability of anthocyanin pigments in four berberis species // Pakistan J. Nutr. – 2006. – Vol. 5, N 1. – P. 90-92. https://doi.org/10.3923/pjn.2006.90.92

10. Ozela E.F., Stringheita P.C., Chauca M.C. Stability of anthocyanin in spinach vine (Basella rubra) fruits // Cienc. Invest. Agraria. – 2007. – Vol. 34, N 2. – P. 115–120. https://doi.org/10.4067/S0718-16202007000200004

11. Molodovin B., David L., Chişhara C., Cimpoia C. Degradation Kinetics of Anthocyanins from European Cranberrybush (Viburnum opulus L.) Fruit extracts: effects of temperature, pH and storage solvent // Molecules. – 2012. – Vol. 17. – P. 11655–11666. https://doi.org/10.3390/molecules171011655

12. Oancea S., Drăghici O. pH and thermal stability of anthocyanin-based optimised extracts of Romanian red onion cultivars // Czech J. Food Sci. – 2013. – Vol. 31, N 3. – P. 283–291.

13. Furtado P., Figueiredo P., Chaves das Neves H., Pina F. Photochemical and thermal degradation of anthocyanidins // J. Photochem. Photobiol. A: Chem. – 1993. – Vol. 75, N 2. – P. 113–118. https://doi.org/10.1016/1010-6030(93)80191-b

14. Seeram N.P., Bourquin L.D., Nair M.G. Degradation products of cyanidin glycosides from tart cherries and their bioactivities // J. Agric. Food Chem. – 2001. – Vol. 49. – P. 4924–4929. https://doi.org/10.1021/jf0107508

15. Morais H., Ramos C., Forgács E. Influence of storage conditions on the stability of monomeric anthocyanins studied by reversed-phase high-performance liquid chromatography // J. Chromatogr. B. – 2002. – Vol. 770. – P. 297–301. https://doi.org/10.1016/S1570-0232(02)00055-7

16. Costerias-Lopez E., Castañeda-Orando A., Gonzalez-Olives L.G. Effect of light on stability of anthocyanins in ethanolic extracts of Rubus fruticosus // Food Nutr. Sci. – 2014. – Vol. 5. – P. 488-494. https://doi.org/10.4236/fns.2014.51007508

17. Markakis P., Livingston G. E., Fellers R. C. Quantitative aspects of strawberry pigment degradation // Food Res. – 1957. – Vol. 22. – P. 117–130. https://doi.org/10.1016/1357-2611(57)90019-3.x

18. Adams J.B. Thermal degradation of anthocyanins with particular reference to the 3-glycosides of cyanidin. I. In acidified aqueous solutions at 100 °C // J. Sci. Food Agric. – 1973. – Vol. 24. – P. 747–762. https://doi.org/10.1002/jsfa.2740240702

19. Casati C.B., Baeza R., Sanchez V., Catalano A., Lopez P., Zamora M.C. Thermal degradation kinetics of monomeric anthocyanins, colour changes and storage effect in elderberry juices // J. Berry Res. – 2005. – Vol. 5. – P. 29–39. https://doi.org/10.3233/JBR-150088

20. Reyes L.F., Cisneros-Zevallos L. Degradation kinetics and colour of anthocyanins in aqueous extracts of purple- and red-flesh potatoes (Solanum tuberosum L.) // Food Chem. – 2007. – Vol. 100. – P. 885–894. https://doi.org/10.1016/j.foodchem.2005.11.002

21. Wang W.-D., Sh.-Y. Xu. Degradation kinetics of anthocyanins in blackberry juice and concentrate // J. Food Eng. – 2007. – Vol. 82, N 3. – P. 271–275. https://doi.org/10.1016/j.jfoodeng.2007.01.018

22. Harbourne N., Jacquier J.Ch., Morgan D.J., Lyng J.G. Determination of the degradation kinetics of anthocyanins in a model juice system using isothermal and non-isothermal methods // Food Chem. – 2008. – Vol. 111. – P. 204–208. https://doi.org/10.1016/j.foodchem.2008.03.023

23. Patras A., Brunton N.P., O’Donnell C., Tivari B.K. Effect of thermal processing on anthocyanin stability in foods; mechanisms and kinetics of degradation // Trends Food Sci. Technol. – 2010. – Vol. 21. – P. 3-11. https://doi.org/10.1016/j.tifs.2009.07.004
24. Zozio S., Pallet D., Dornier M. Evaluation of anthocyanin stability during storage of a coloured drink made from extracts of the Andean blackberry (Rubus glaucus Benth.), açai (Euterpe oleracea Mart.) and black carrot (Daucus carota L.) // Fruits. – 2011. – Vol. 66. – P. 203–215. https://doi.org/10.1051/fruits/2011030

25. Yalçınöz Ş.K., Ercelebi E.A. Anthocyanin degradation and colour kinetics of cornelian cherry concentrate // Br. J. Appl. Sci. Technol. – 2015. – Vol. 10, N 12. – P.1-12. https://doi.org/10.1111/j.1365-2621.2011.02780.x

26. Hrazdina G. Reactions of anthocyanidin-3,5-diglucosides: Formation of 3,5-di-(O-β-D-glucosyl)-7-hydroxy coumarin // Phytochem. – 1971. – Vol. 10. – P. 1125–1130. https://doi.org/10.1016/S0031-9422(00)89950-1.

27. Lee J., Durst R.W., Wrolstad R.E. Determination of total monomeric anthocyanin pigment content of fruit juices, beverages, natural colorants, and wines by the pH differential method: collaborative study // J. AOAC Int. – 2005. – Vol. 88, N 5. – P. 1269 –1278.

28. Hou Zh., Qin P., Zhang Y., Cui S., Ren G. Identification of anthocyanins isolated from black rice (Oryza sativa L.) and their degradation kinetics // Food Res. Int. – 2013. – Vol. 50. – P. 691–697. https://doi.org/10.1007/s10068-010-0055-5

29. Kirca A., Özkın M. & Cemeroğlu B. Stability of black carrot anthocyanins in various fruit juices and nectars // Food Chem. – 2006. – Vol. 97. – P. 598–605. https://doi.org/10.1016/j.foodchem.2005.05.036

30. Sadilova E., Stintzing F.C., Carle R. Thermal degradation of acylated and nonacylated anthocyanins // J. Food Sci. – 2006. – Vol. 71. – P.504–512. https://doi.org/10.1111/j.1750-3841.2006.00148.x

31. Yang Z., Han Y., Gu Z., Fan G., Chen Z. Thermal degradation kinetics of aqueous anthocyanins and visual color of purple corn (Zea mays L.) cob. // Innovative Food Sci. Emerging Technol. – 2008. – Vol. 9. – P. 341–347. https://doi.org/10.1016/j.ifset.2007.09.001

32. Ahmed J., Shivhare U. S., Raghavan G.S.V. Rheological characteristics and kinetics of colour degradation of green chilli puree // J. Food Eng. – 2000. – Vol. 44. – P. 239–244. https://doi.org/10.1016/S0260-8774(00)00034-0

Стаття надійшла до редакції 15.12.2016

Л. М. Солдаткіна1, В. О. Новотна1, І. Шаламон2
1Одеський національний університет імені І. І. Мечникова, кафедра фізичної та колоїдної хімії, Дворянська 2, 65082, м. Одеса, Україна, email: soldatkina@onu.edu.ua
2Пряшівський університет, кафедра екології, вулиця 17 листопада 15, 08001, Пряшів, Словаччина

КІНЕТИКА ДЕСТРУКЦІЇ АНТОЦІАНІВ У КИСЛИХ ВОДНИХ ЕКСТРАКТАХ ЯГІД

Вивчено вплив pH, світла і температури на деструкцію антоціанів у кислих водних екстрaktuях ягод аронії, бузини і ожини. Показано, що процес деструкції антоціанів ягід під впливом pH, світла і температури описується рівнянням кінетики першого порядку. Знайдено, що для антоціанів ягід аронії спостерігаються найвищі значення констант швидкості деструкції, а для антоціанів ягід ожини – найвищу значення часу напіврозпаду. Температурні залежності швидкості деструкції антоціанів ягід описані за допомогою рівняння Арреніуса. Розраховані енергії активації процесу деструкції антоціанів при pH=2, які дорівнюють відповідно для антоціанів аронії, бузини і ожини 5,7, 10,1 і 15,0 кДж/моль.

Ключові слова: аронія, бузина, ожина, антоціани, кінетика деструкції.
Л. М. Солдаткина1, В. А. Новотная1, И. Шаламон2
1Одесский национальный университет имени И. И. Мечникова, кафедра физической и коллоидной химии, Дворянская 2, 65082, г. Одесса, Украина, email: soldatkina@onu.edu.ua
2Пряшевский университет, кафедра экологии, улица 17 ноября 15, 08001, Пряшев, Словакия

КИНЕТИКА ДЕСТРУКЦИИ АНТОЦИАНОВ В КИСЛЫХ ВОДНЫХ ЭКСТРАКАХ ЯГОД

Изучено влияние рН, света и температуры на деструкцию антоцианов в кислых водных экстрактах ягод аронии, бузины и ежевики. Показано, что процесс деструкции антоцианов под влиянием рН, света и температуры описывается уравнением кинетики первого порядка. Найдено, что для антоцианов ягод аронии характерны самые высокие значения константы скорости деструкции, а для антоцианов ягод ежевики — самые высокие значения времени полураспада. Температурные зависимости скорости деструкции антоцианов были описанны с помощью уравнения Аппенеуса. Рассчитаны энергии активации процесса деструкции антоцианов при рН=2, которые равны соответственно для антоцианов ягод аронии, бузны и ежевики 5.7, 10.1 и 15.0 кДж/моль.

Ключевые слова: арония, бузина, ежевика, антоцианы, кинетика деструкции.

REFERENCES

1. Delgado-Vargas F., Paredes-Lópes O. Natural Colourants for Food and Nutraceutical. Boca Raton: CRC Press LLC, 2003, 167 p.
2. Wu X., Beecher G. R., Holden J. M., Haytowitz D. B., Gebhardt S. E., Prior R. L. Concentrations of Anthocyanins in Common Foods in the United States and Estimation of Normal Consumption. J. Agric. Food Chem., 2006, vol. 54, pp. 4069–4075. https://doi.org/10.1021/jf0603000
3. Ghosh D., Konishi T. Anthocyanins and anthocyanin-rich extracts: role in diabetes and eye function. Asia Pac. J. Clin. Nutr., 2007, vol.16, no 2, pp. 200-208.
4. Denev P., Ciz M., Ambrozova G., Lojek A., Yanakieva I., Kratchanova M. Solid-phase extraction of berries’ anthocyanins and evaluation of their antioxidative properties. Food Chem., 2010, vol. 123, pp. 1055–1061. http://doi:10.1016/j.foodchem.2010.05.061
5. Clifford M.N. Anthocyanins — nature, occurrence and dietary burden. J. Sci. Food Agric., 2000, vol. 80, no 7 pp. 1063-1072. https://doi.org/10.1002/(SICI)1097-0010(200000515)80:7<1063::AID-JSFA605>3.0.CO;2-Q
6. Jakobek L., Šeruga M., Medvidovic-Kosanovic M., Novak I. Anthocyanin contain and antioxidant activity of various red fruit juices. Deutsch Lebensmittel-Rundschau, 2007, vol. 103, no. 3, pp. 58-64.
7. Kearsley M.W., Rodriguez N. The stability and use of natural colors in foods: anthocyanin, β-carotene and riboflavin. J. Food Technol., 1981, vol.16, pp. 421–431. https://doi.org/10.1111/j.1365-2621.1981.tb01833.x
8. Cabrita L., Fossen T., & Andersen É. M. Colour and stability of the six common anthocyanin 3-glucosides in aqueous solutions. Food Chem., 2000, vol. 68, pp. 101-107. https://doi.org/10.1016/S0308-8146(99)00170-3
9. Laleh G.H., Frydoonfar H., Heidary R., Jameei R., Zare S. The effect of light, temperature, pH and species on stability of anthocyanin pigments in four berberis species. Pakistan J. Nutr., 2006, vol. 5, no 1, pp. 90–92. https://doi.org/10.3923/pjn.2006.90.92
10. Ozela E.F., Stringheta P.C., Chauca M.C. Stability of anthocyanin in spinach vine (Basella rubra) fruits. Cienc. Invest. Agraria, 2007, vol. 34, no 2, pp. 115–120. https://doi.org/10.4067/S0718-16202007000200004
11. Moldovan B., David L., Chisbora C., Cimpoiu C. Degradation kinetics of anthocyanins from European cranberry (Viburnum opulus L.) fruit extracts. Effects of temperature, pH and storage solvent. Molecules, 2012, vol. 17, pp. 11655–11666. https://doi.org/10.3390/molecules171011655
12. Oancea S., Drăghici O. pH and thermal stability of anthocyanin-based optimised extracts of Romanian red onion cultivars. Czech J. Food Sci., 2013, vol. 31, no 3, pp. 283–291.
13. Furtado P., Figueiredo P., Chaves das Neves H., Pina F. Photochemical and thermal degradation of anthocyanidins. J. Photochem. Photobiol. A: Chem., 1993, vol. 75, no 2, pp. 113–118. https://doi.org/10.1016/1016-6030(93)00191-b
14. Seeram N.P., Bourquin L.D., Nair M.G. Degradation products of cyanidin glycosides from tart cherries and their bioactivities. J. Agric. Food Chem., 2001, vol. 49, pp. 4924–4929. https://doi.org/10.1021/jf0107508

15. Morais H., Ramos C., Forjás E. Influence of storage conditions on the stability of monomeric anthocyanins studied by reversed-phase high-performance liquid chromatography. J. Chromatogr. B, 2002, vol. 770, pp. 297–301. https://doi.org/10.1016/S1570-0232(02)00055-7

16. Contreras-Lopez E., Castañeda-Ovando A., González-Olivares L.G. Effect of light on stability of anthocyanins in ethanolic extracts of Rubus fruticosus. Food Nutr. Sci., 2014, vol. 5, pp. 488-494. https://doi.org/10.4236/fns.2014.56058

17. Markakis P., Livingston G.E., Fellers R.C. Quantitative aspects of strawberry pigment degradation. Food Res., 1957, vol. 22, pp. 117–130. https://doi.org/10.1016/j.jsfa.2740240702

18. Casati C.B., Baeza R., Sanchez V., Catalano A., López P., Zamora M.C. Thermal degradation kinetics of monomeric anthocyanins, colour changes and storage effect in elderberry juices. J. Berry Res., 2005, vol. 5, pp. 29–39. https://doi.org/10.3233/jBR-150088.

19. Reyes L.F., Cisneros-Zevallos L. Degradation kinetics and colour of anthocyanins in aqueous extracts of purple- and red-flesh potatoes (Solanum tuberosum L.) // Food Chem., 2007, vol. 100, pp. 885–894. http://doi: 10.1016/j.foodchem.2005.11.002

20. Wang W.-D., Sh.-Y. Xu. Degradation kinetics of anthocyanins in blackberry juice and concentrate. J. Food Eng., 2007, vol. 82, no 3, pp. 271–275. https://doi.org/10.1016/j.jfoodeng.2007.01.018

21. Harbourne N., jacquier j.Ch., Morgan D.j., Lyng j.G. Determination of the degradation kinetics of anthocyanins in a model juice system using isothermal and non-isothermal methods. Food Chem., 2008, vol. 111, pp. 204–208. https://doi.org/10.1016/j.foodchem.2008.03.023

22. Patras A., Brunton N.P., O’Donnell C., Tiwari B.K. Effect of thermal processing on anthocyanin stability in foods; mechanisms and kinetics of degradation. Trends in Food Sci. Technol., 2010, vol. 21, pp. 3–11. https://doi.org/10.1016/j.tifs.2009.07.004

23. zozio S., Pallet D., Dornier M. Evaluation of anthocyanin stability during storage of a coloured drink made from extracts of the Andean blackberry (Rubus glaucus Benth.), açai (Euterpe oleracea Mart.) and black carrot (Daucus carota L.). Fruits, 2011, vol. 66, pp. 203–215. https://doi.org/10.1051/fruits/2011030

24. Yalçinöz Ş.K., Erçelebi E.A. Anthocyanin degradation and colour kinetics of cornelian cherry concentrate. Br. J. Appl. Sci. Technol., 2015, vol. 10, no 12, pp. 1-12. https://doi.org/10.1111/j.1365-2621.2011.02780.x

25. Kirca A., Özkan M., Cemeroğlu B. Stability of black carrot anthocyanins in various fruit juices and nectars. Food Chem., 2006, vol. 97, pp. 598–605. https://doi.org/10.1016/j.foodchem.2005.05.036

26. Sadilova E., Stintzing F. C., Carle, R. Thermal degradation of acylated and nonacylated anthocyanins. J. Food Sci., 2006, vol. 71, pp. 504–512. https://doi.org/10.1111/j.1750-3841.2006.00148.x

27. Yang Z., Han Y., Gu Z., Fan G., Chen Z. Thermal degradation kinetics of aqueous anthocyanins and visual color of purple corn (Zea mays L.) cob. Innovative Food Sci. Emerging Technol., 2008, vol. 9, pp. 341–347. https://doi.org/10.1016/j.ifset.2007.09.001

28. Ahmed J., Shivhare U.S., Raghavan G.S.V. Rheological characteristics and kinetics of colour degradation of green chilli puree. J. Food Eng., 2000, vol. 44, pp. 239–244. https://doi.org/10.1016/S0260-8774(00)00034-0