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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 an industrial scale [4].

According to the chemical nature anthocyanins are substituted glycosides of phenyl-2-benzopyrilium 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 flavylium cation, the blue quinoidal base, the colourless carbinol pseudo-base, and the colourless chalcone (fig. 1). At pH below 2, anthocyanins exist primarily in the form of the red flavylium cation. Hydration of the flavylium cation

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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

Composition of anthocyanins in berries [6]

Berries	Anthocyanins			
	Major amounts	**%**	**Minor amounts**	**%**
chokeberry	cyanidin-3-galactoside cyanidin-3-arabinoside	68.9 24.5	cyanidin-3-xyloside cyanidin 3-glucoside	3.8 2.8
elderberry	cyanidin-3-glucoside cyanidin -3 – sambubioside	83.1	cyanidin 3– sambubioside-5– glucoside cyanidin-3-rutinoside	15.1 1.8
blackberry	cyanidin-3-glucoside	90.4	cyanidin-3-xyloside cyanidin-3-rutinoside	8.3 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 flavylium cation. Morais et al. [15] reported that presence or absence of light exerted a negligible impact on the decomposition rate of grape anthocyanins.

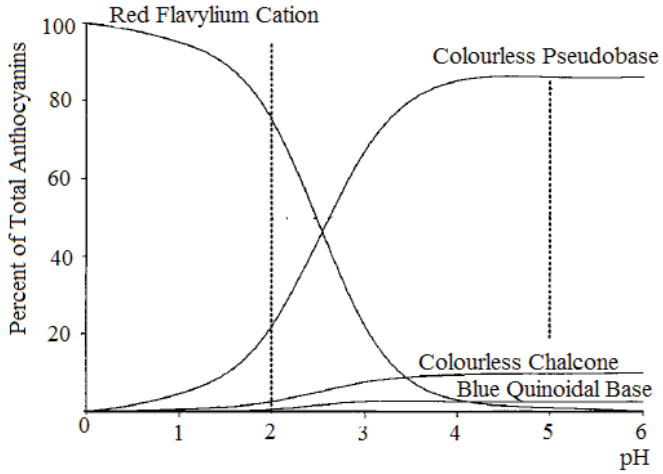

Fig. 1. The main equilibrium forms of anthocyanin existing in aqueous media [5]

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:

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

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*; ε 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:

$$\ln\frac{C}{C_o} = -kt,$$

$$t_{½} = \frac{\ln 2}{k},$$

where *C* is the anthocyanin concentration at time *t*; C_o 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:

$$k = k_o \exp\left(-\frac{E}{RT}\right),$$

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

where E_a is the activation energy; k_o 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.

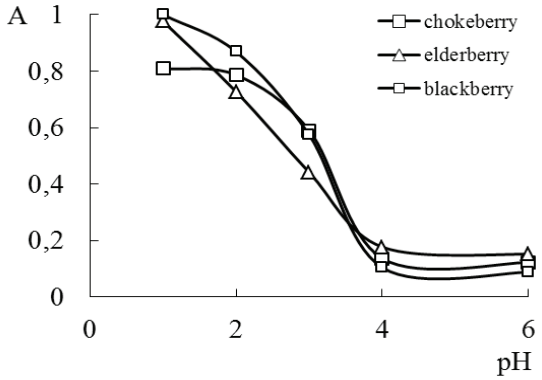

Fig. 2. Anthocyanins absorption in berry extracts at different pH (C_o=6 mg/L, t=20 °C, λ=515 nm)

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 (R^2) values were more than 0.9548 (table 2). In light the degradation constant at pH 2 was $2.2 \cdot 10^{-2}$ d^{-1} with a half-life time 32 days. In dark the degradation constant at pH 2 was $0.8 \cdot 10^{-2}$ 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.

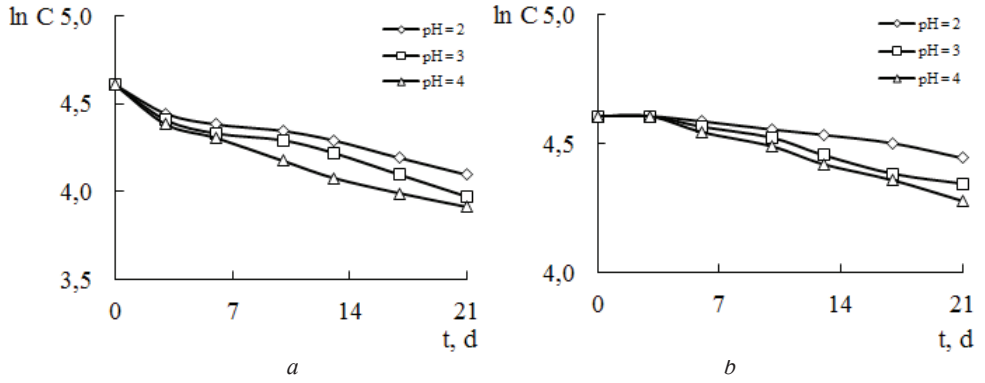

Fig. 3. Degradation kinetics of anthocyanins in chokeberry extracts during their stored: *a* – in light; *b* – in dark.

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

Effect of pH on degradation kinetics of chokeberry anthocyanins in light and dark (C_0 = 100 mg/L, t = 20 °C)

System	pH	$k \cdot 10^2$, d^{-1}	R^2	$t_{½}$, 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).

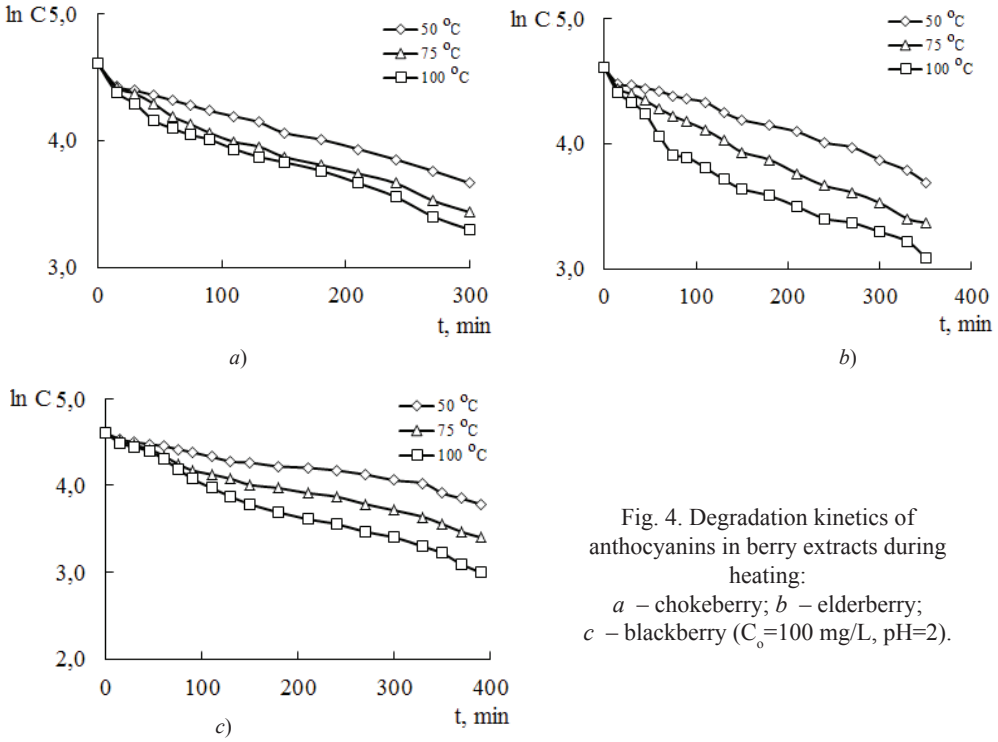

Fig. 4. Degradation kinetics of anthocyanins in berry extracts during heating:
a – chokeberry; *b* – elderberry;
c – blackberry (C_o=100 mg/L, pH=2).

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 ($k=3.7\cdot10^{-3}$ –$3.8\cdot10^{-3}$ 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 pyrilium 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 (R^2) 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]

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

Effect of temperature on degradation kinetics of berry anthocyanins (C_o=100 mg/L, pH=2)

Extract	t, °C	$k \cdot 10^3$, min^{-1}	R^2	$t_{½}$, h	E_a, kJ/mol	R^2	Q_{10}	
							50-75 °C	75-100 °C
chokeberry	50 75 100	2.8 3.5 3.7	0.9853 0.9672 0.9582	4.1 3.3 3.1	5.7	0.9168	1.1	1.0
elderberry	50 75 100	2.3 3.3 3.8	0.9897 0.9895 0.9284	5.0 3.5 3.0	10.1	0.9581	1.2	1.1
blackberry	50 75 100	1.8 2.8 3.8	0.9753 0.9793 0.9763	6.4 4.1 3.0	15.0	0.9960	1.2	1.1

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.

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КІНЕТИКА ДЕСТРУКЦІЇ АНТОЦІАНІВ№У КИСЛИХ ВОДНИХ ЕКСТРАКТАХ ЯГІД

Вивчено вплив pH, світла і температури на деструкцію антоціанів у кислих водних екстрактах ягід 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 – найвищі 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.

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КИНЕТИКА ДЕСТРУКЦИИ АНТОЦИАНОВ В КИСЛЫХ ВОДНЫХ ЭКСТРАКТАХ ЯГОД

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

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

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