Food Research International 94 (2017) 29–35

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Estimation of kinetic parameters of anthocyanins and color degradation in vitamin C fortified cranberry juice during storage

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ARTICLE INFO

Article history:
Received 16 November 2016
Received in revised form 11 January 2017
Accepted 15 January 2017
Available online 21 January 2017

Keywords:
Cranberry juice
Anthocyanins
Color
Vitamin C
Kinetics
Parameter estimation

ABSTRACT

Color degradation in cranberry juice during storage is the most common consumer complaint. To enhance nutritional quality, juice is typically fortified with vitamin C. This study determined effect of gallic acid, a natural antioxidant, for the preservation of anthocyanins (ACYs) and color, and estimated kinetics of ACYs and color degradation. Juice, fortified with 40–80 mg/100 mL vitamin C and 0–320 mg/100 mL gallic acid, was pasteurized at 85 °C for 1 min and stored at 23 °C for 16 days. Total monomeric anthocyanins and red color intensity were evaluated spectrophotometrically and data were used to determine degradation rate constants (k values) and order of reaction (n) of ACYs and color. Due to high correlation, k and n could not be estimated simultaneously. To overcome this difficulty, both n and k were held at different constant values in separate analyses to allow accurate estimation of each. Parameters n and k were modeled empirically as functions of vitamin C, and of vitamin C and gallic acid, respectively. Reaction order n ranged from 1.2 to 4.4, and decreased with increasing vitamin C concentration. The final model offers an effective tool that could be used for predicting ACYs and color retention in cranberry juice during storage.

1. Introduction

Cranberries are abundant sources of phytochemicals, with potential health benefits such as anti-cancer and anti-inflammatory properties. Cranberries also exhibit antimicrobial activity, which helps prevent urinary tract infection (UTI) (Blumberg et al., 2013; Howell, 2007). UTI is a serious health issue for millions of women each year (Schappert & Rechtsteiner, 2011). Anthocyanins (ACYs) in cranberries are major compounds that create bright red characteristics in cranberry juice, and are well recognized for their antioxidant functionalities. Thirteen ACYs could be found in cranberry juice (Blumberg et al., 2013; Milbury, Vita, & Blumbergs, 2010), while only three of those are major ACYs, which are Peonidin-3-*O*-galactosides (~32%), Cyanidin-3-*O*-galactosides (23%), and Peonidin-3-*O*-arabinosides (18%). Preservation of the red color intensity of cranberry juice is critical for consumer acceptance of the product. Fortification of fruit juices with vitamin C is a common practice. Vitamin C is a well-known micronutrient, which is added to food products not only in order to extend shelf life, but also enhance nutritional levels. However, vitamin C is also known to promote ACY degradation (Remini et al., 2015; Starr & Francis, 1968) in pigment-rich juices thereby affecting the consumer acceptance of the products. Even though endogenous vitamin C in fruit juices seems not to exhibit significant impact on ACY degradation, fortifying vitamin C does damage ACY structures due to an increase of vitamin C concentration in food matrix (Choi, Kim, & Lee, 2002). It is believed that high amount of vitamin C could exhibit a pro-oxidant effect regarding Fenton's reaction, which increases formation of reactive oxygen species (ROS) by chelating with metal ions in food components. The ROS, especially $HO^{\bullet}$, could further degrade anthocyanin structures causing color loss (Paolini, Pozzetti, Pedulli, Marchesi, & Cantelli-Forti, 1999; Podmore et al., 1998; Rietjens et al., 2002).

Gallic acid is a natural phenolic compound that has been extensively studied for its antioxidant activities and it potentially offers protection against color degradation (Navruz, Turkyilmaz, & Ozkan, 2016; Roidoung, Dolan, & Siddiq, 2016). In addition, gallic acid is a potent reducing agent that can neutralize ROS to become less active in damaging ACY structures (Daglia, Di Lorenzo, Nabavi, Talas, & Nabavi, 2014; Yen, Duh, & Tsai, 2002), and hence could solve discoloration problem in pigment-rich juices fortified by vitamin C fortification. Potentiality of using gallic acid in food application has been reported (Roidoung et al., 2016, Srinivas, King, Howard, & Monrad, 2010; Verhagen, Scott, & Giza, 2002). Gallic acid is relatively inexpensive ($26–29/kg food grade gallic acid). Instead of astringent taste, gallic acid introduces long-lasting non-

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http://dx.doi.org/10.1016/j.foodres.2017.01.013
0963-9969/

caloric sweetness, the mildly sour taste is developed at concentrations > 850 mg/100 mL. To assess the efficacy of gallic acid in cranberry juice, kinetic studies are necessary, which are required for shelf-life prediction. An *nth*-order kinetic model is widely used to determine degradation rate constant of reactions (Remini et al., 2015; Wibowo et al., 2015; Ozkan, Yemenicioglu, & Cemeroglu, 2005; Wang & Xu, 2007). The *nth*-order degradation kinetic model Eq. (1) consists of three parameters: degradation rate constant (k, $[\text{conc}]^{1-n}\,\text{day}^{-1}$), initial concentration (C_0, conc), and reaction order (n, dimensionless). Concentration at any time t is given by $C(t)$. The n value is typically fixed at $n = 0$ for color change, or 1 for nutritional degradation reactions, including degradation of ACYs (Ozkan et al., 2005; Wang & Xu, 2007).

$$\frac{dC}{dt} = -kC^n \tag{1}$$

Some studies determined the most suitable n by varying n from 0, 0.5, 1, and 2 and chose the n that gave the lowest RMSE between predicted and experimental values (Remini et al., 2015; Wibowo et al., 2015).

Parameter estimation is an effective method to estimate n, k, and C_0. Unlike curve-fitting or optimization, parameter estimation considers parameter errors, scaled sensitivity coefficients, the sensitivity matrix, and confidence intervals (CIs), which inform whether parameters are accurate, identifiable, correlated, or are significantly different from zero and can be removed from model (Dolan & Mishra, 2013). Parameter estimation results in food science research have often not included error and significance of parameters (van Boekel, 2008; van Boekel, 1996), which limits applications of the results. In addition, due to the complication of a non-linear method, non-linear equations are generally transformed to linear models and resulting transformation impacts error structure, which could result in different parameter estimates (Chowdhury & Das Saha, 2011). Therefore, in recent years, non-linear methods have gained interest in food quality research (Wibowo et al., 2015). The objectives of this study were: (1) to estimate the kinetic parameters of a primary model using non-linear inverse methods, and (2) to develop secondary models for predicting color and ACYs in cranberry juice during storage, at various concentrations of vitamin C and gallic acid.

2. Materials and methods

2.1. Juice sample preparation

Cranberry juice concentrate (Dynamic health Laboratories Inc., Brooklyn, NY) was diluted with HPLC water at a ratio 1:14 mL (DF 15) to obtain 3.8 °Brix, which is typical of the commercial cranberry juice. The diluted juice was centrifuged at 7600*g* for 10 min and the supernatant was filtered through Whatman® No.1 filter paper. The juice (100 mL) was fortified with 40, 60, and 80 mg of L-ascorbic acid (CAS no. 50-81-7, Sigma Aldrich, St. Louis, MO, USA). Gallic acid (CAS no. 149917, Sigma Aldrich) was added at 0, 80, 160, and 320 mg/100 mL. Vitamin C and gallic acid were mixed well in juice using a magnetic stirrer.

2.2. Juice pasteurization and storage

Eight milliliters prepared juice were pipetted into each glass tube, and capped before pasteurization at 85 ± 2 °C for 1 min. Pasteurization was performed in a thermostatic water bath equipped with a shaker. Temperature of the juice during pasteurizing was monitored using a hand-held thermometer (Digi-Sense Dual J-T-E-K, Model 91100-40, Cole-Palmer®, Vernon Hills, IL, USA). Pasteurization time started when the thermocouple inside an assigned tube reached 85 °C. After one minute at 85 °C, the juice was then hot-filled into a 5-mL polypropylene vial, screw-capped and cooled in ice bath for 2 h. The pasteurized cranberry juice was kept in the dark at room temperature (23 ± 2 °C) for 16 days. Red color intensity and total monomeric ACY content were measured on day 1 and every 2 days from days 2 to 16. Samples were prepared in 4 replications.

2.3. Quality analysis

2.3.1. Red color intensity

Two milliliters of each sample were pipetted into a cuvette. A dual beam Genesys 10S UV–vis spectrophotometer (Thermo Scientific, Waltham, MA)was used to measure absorbance values (AU) at 520 nm (AU_{520}), which is the maximum absorbance of red color from monomeric ACYs (Vegara, Marti, Mena, Saura, & Valero, 2013).

2.3.2. Total monomeric anthocyanin content

Monomeric anthocyanins are the structures that give bright red color to cranberry juice (Pappas & Schaich, 2009). The total monomeric ACY content was determined by the pH differential method of (Lee, Durst, & Wrolstad, 2005). Cranberry juice (1 mL) was diluted separately with 1 mL each of pH 1.0 (potassium chloride, 0.025 M) and pH 4.5 (sodium acetate, 0.4 M) buffers. The absorbance values of the solution were determined spectrophotometrically at both 520 and 700 nm (Genesys10S UV–vis spectrophotometer, Thermo Scientific, Waltham, MA). ACY content was calculated by following equation:

$$\text{Anthocyanin content}(\text{mg/L}) = \frac{A \times MW \times DF \times 10^3}{\varepsilon \times l}$$

where

$A = (A_{520} - A_{700})_{\text{pH 1.0}} - (A_{520} - A_{700})_{\text{pH 4.5}}$;
MW (molecular weight) of *peonidin-3-galactoside* = 463.41 g/mol;
DF = dilution factor;
L = pathlength in cm;
ε = molar extinction coefficient (48,340 $L \times mol^{-1} \times cm^{-1}$);
10^3 = factor for conversion from g to mg.

2.4. Mathematical modeling

2.4.1. Estimation the kinetic parameters

All 4 replicates of ACYs and color measurements during storage were used to estimate parameters k, C_0, and n in an *nth*-order kinetic model Eq. (1) by the ordinary least squares inverse method in MATLAB. Parameter C_0 is initial red color intensity (AU), or initial ACY content (mg/L), at time = day 1. The k is degradation rate constant ($\text{conc}^{(1-n)}\,\text{day}^{-1}$). The n is reaction order, dimensionless. Table 1 shows all parameters that were estimated for all 12 treatments of both color and ACYs. Significance of parameters was determined by noting if confidence intervals (CIs) did not contain zero, which is equivalent to $p < 0.05$. The correlation matrix was used to determine correlation between parameters. Relative error indicated accuracy of estimates. The ease of estimating parameters was evaluated via the size of scaled sensitivity coefficients (SSC) (Dolan & Mishra, 2013). The best model was determined by corrected Akaike Information Criteria (AIC_c). AIC_c (Eq. (2)) is calculated based on the change of *SS* in regard to an increase/decrease in number of estimated parameters. Although adding a parameter would always decrease *SS*, however, if the decrease is insufficient to justify the addition

Table 1
Experimental design for parameter estimation of both color and anthocyanins at different concentration of vitamin C and gallic acid (12 treatments each for color and anthocyanins), 4 replications per treatment.

	Vitamin C (40 mg)	Vitamin C (60 mg)	Vitamin C (80 mg)
Gallic acid (0 mg)	$(k, C_0, n)_1$	$(k, C_0, n)_5$	$(k, C_0, n)_9$
Gallic acid (80 mg)	$(k, C_0, n)_2$	$(k, C_0, n)_6$	$(k, C_0, n)_{10}$
Gallic acid (160 mg)	$(k, C_0, n)_3$	$(k, C_0, n)_7$	$(k, C_0, n)_{11}$
Gallic acid (320 mg)	$(k, C_0, n)_4$	$(k, C_0, n)_8$	$(k, C_0, n)_{12}$