บทความวิจัย

DEGRADATION KINETICS OF COLOR IN BUTTERFLY PEA (*Clitoria ternatea* L.) EXTRACT DRIED WITH SUGAR

Jintana Wiboonsirikul*

*Program of Food Science and Technology, Faculty of Agricultural Technology, Phetchaburi Rajabhat University, Phetchaburi, 76000, Thailand.

*E-mail: wiboonsirikul@yahoo.com

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ABSTRACT

The Butterfly pea extract dried with sugar is commonly well known as un-chan juice powder in Thailand. However, it is subjected to discoloration during storage in laminate pouch at ambient temperature. The objective of this study is aimed at investigation of degradation rate of the extract dried with sugar stored in 3 different packed conditions under accelerated test at the temperature range of 40-55 °C. The degradation of chroma value of the butterfly pea extract dried with sugar was found to follow a first order kinetics and its dependence on temperature was modeled by Arrhenius equation. The visual pigment degraded from azure to maya blue during storage in the conditions of normal atmosphere and partial vacuum for several weeks. The *L**a*b** and hue angle values of the extract dried with sugar increased with longer storage time. The butterfly pea extract dried with sugar was subjected to the slowest discoloration when it was kept in laminated aluminium pouch (PE/Al/PET) under normal atmospheric condition and the activation energy of the reaction was higher than that when it was kept under vacuum condition. The estimated half-life of the reaction was 55 days at 30 °C and the observed shelf-life of the extract dried with sugar kept at the same condition under ambient temperature (27-33°C) was 64 days.

Keywords: Butterfly pea, sugar, degradation kinetics

Introduction

Butterfly pea (*Clitoria ternatea* L.) known as un-chan is a blue and purple flower grown widely in Thailand and other countries in Southeast Asia. It is commonly used as a natural food coloring and extracted for juice, which is added with sugar during pasteurization. After water evaporation from the juice, the butterfly pea extract dried with sugar is turned into the crystallized particles and can keep in some types of laminated pouches at room temperature for several weeks. Major pigments of the butterfly pea flowers are anthocyanins, which are water soluble and stable in mild acid solution as well as gives out the blue color (Kungsuwan, Singh, Phetkao, & Utama-ang, 2014; Mohamad, Nasir, & Sarmidi, 2011). However, anthocyanins have still been limited use in food industries because of low stability during processing, formulation and storage. The anthocyanin stability is not only a function of the processing temperature but also is affected by the intrinsic properties of the products and the process such as pH, storage temperature, chemical structure, anthocyanin concentration in the presence of light, oxygen, enzymes, proteins, sugars, and metallic ions (Patras, Brunton, Donnel & Tiwari, 2010).

Nikkhah, Khayamy, Heidari, & Jamee (2007) report that increase in the sugar concentration has adverse affected on the stability of anthocyanin solution. When the sugar concentration is higher from 20% to 60%, the protective effect on anthocyanin is less. In addition, anthocyanin solution keeping in darkness has longer shelf-life than the one in a refrigerator. In addition, several researchers report that anthocyanins degrade faster at high temperature than at low one (Kirca, Özkan, & Cemeroglu, 2003).

Kinetic modeling is generally used to predict influence of processing and storage conditions on critical quality parameters. Knowledge of degradation kinetics including reaction order, rate constant, and activation energy is very important to predict food quality loss during storage. Anthocyanin degradation in both solutions and foods under isothermal heating are reported to obey first order kinetics (Mohamad, Nasir, & Sarmidi, 2011; Verbeyst, Van Crombruggen, Van der Plancken, Hendrickx, & Van Loey, 2011). Although the butterfly pea extract dried with sugar is dry, some of them in a packaging are subjected to degradation and consequently loss of good appearance quality for consumers. The objective of this study is to estimate stability of butterfly pea extract dried with sugar stored in different laminated pouches and conditions by using kinetic modeling and accelerated shelf-life testing.

Methods

1. Preparation of butterfly pea extract dried with sugar and accelerated storage conditions

Butterfly pea flowers were obtained from a local market of Phetchaburi province, washed thoroughly and removed superficial water with paper sheet. Ten grams of flowers were added to 150 g of boiling water. The mixture was maintained to boil for 5 min. After filtration with sheet clot, the deep blue extract was collected and again boiled before addition of 300 g of table sugar. The mixture was stirred under heat until the sugar was crystallized. After sifting through 4-mm sieve, the butterfly pea extract dried with sugar was divided into 3 portions of 100 g each and then packed into the following 3 types of packing conditions. Pouch A was composed of laminated pouch with a clear side of oriented polypropylene (OPP) and the other opaque side with metallized cast polypropylene (OPP-MCPP). Pouch B was composed of opaque laminated film with polyester aluminium and polyethylene (PE/Al/PET) for both sides. After placing the extract dried with sugar into the pouch A and pouch B, they were sealed under atmospheric condition using a hand sealer (PFS-200, China). Pouch C was the same compositions as pouch B but sealed under vacuum condition using a vacuum sealer (DZ-260, China) after placing the extract dried with sugar into the pouch. All pouches were stored in an environment maintained at 85±3% relative humidity and 40, 45, 50, and 55 ^{o}C. One of the pouches from every condition was randomly taken out of the control environment for every 2-7 days and was evaluated for color using colorimeter (Colorflex, Reston, VA) in terms of Hunter L^* (lightness), a^* (greenness, $-a^*$ to redness, $+a^*$), and b^* (blueness, $-b^*$ to yellowness, $+b^*$). The instrument was calibrated with standard white and black tiles. All experiments were conducted in triplicates and for each sample, ten Hunter L^*, a^*, b^* values were recorded by rotating the glass cuvette between 0 and 360^{o}. The chroma value and hue angle were obtained from the equation (1) and (2), respectively. The average of 10 readings of each Hunter color value was taken for the kinetic analysis.

$$\text{Chroma value} = (a^{*2} + b^{*2})^{1/2} \quad (1)$$

$$\text{Hue angle} = \tan^{-1}(b^*/a^*) \quad (2)$$

2. **Kinetic calculations**

Degradation of visual color has been found to follow first order reaction kinetics according to the model as follows (Fernando Reyes & Cisneros-Zevallos, 2007; Patras, Brunton, Ó Donnel, & Tiwari, 2010):

$$ln\,(C/C_0) = -kt \quad (3)$$

where C is the evaluated chroma values at any time t, C_0 is the evaluated chroma value at time zero, k is the temperature dependent rate constant (day^{-1}), and t is the storage time (day).

Dependence of degradation rate constant (k) on temperature is quantified by Arrhenius equation (4):

$$k = k_0\, exp(-E_a/RT) \quad (4)$$

where k is the rate constant at temperature T, k_0 is the frequency factor (day^{-1}), E_a is the activation energy (KJ/mol), R is the universal gas constant (8.314 J/mol.K), and T is the absolute temperature (K). Half life ($t_{1/2}$, days) was calculated by the equation (5).

$$t_{1/2} = ln0.5/k \quad (5)$$

3. **Statistical analysis**

A completely randomized design was used to schedule the experiments and collect data of color values. The effect of storage conditions were determined by analysis of variance (ANOVA) and graph using Microsoft Excel® 2013. The kinetic data were analyzed by linear regression analysis between each color value and time to obtain the suitable equations and coefficient of determination (R^2).

Results and Discussion

Butterfly pea flowers are dark purple. The major blue pigment of butterfly pea extract dried with sugar was resulted from anthocyanins as shown in Fig. 1(a), which were subjected to degrade during storage (Kungsuwan, Singh, Phetkao, & Utama-ang, 2014; Mohamad, Nasir, & Sarmidi, 2011) and resulted in light blue as shown in Fig. 1(b).

(a) (b)

Figure 1 Appearance of the butterfly pea extract dried with sugar packed in pouch A (a) before storage and (b) after storage for several weeks at ambient temperature.

1. Effect of storage conditions on visual color degradation

Degradation of the butterfly pea extract dried with sugar occurred as discoloration of the blue pigment from azure to maya blue as shown in Fig. 1(a)-(b). The *L**, -*a**, -*b**, and hue angle values increased but the chroma value decreased with longer storage time as shown in Table 1. During degradation of the pigment among the visual color parameters of *L**, *a**, *b**, chroma, and hue angle values, the color degradation rate was controlled by the chroma value with highest rate constant of the first order kinetic equation and R^2 at the same storage temperature. This result was in agreement with the other report (Mohamad, Nasir, & Sarmidi, 2011). In addition, color degradation of the butterfly pea extract dried with sugar indicated decrease in anthocyanin contents and the longer the storage time, the more the anthocyanin contents decreased (Fernando Reyes & Cisneros-Zevallos, 2007; Wesche-Ebeling, Argaíz-Jamet, Hernández-Porras, López-Malo, 1996).

Table 1 *L**, *a**, *b**, chroma value, and hue angle of the butterfly pea extract dried with sugar before and after storage for several weeks.

Color values	Pouch A		Pouch B		Pouch C	
	before	after	before	after	before	after
*L**	*52.02*	*54.58*	*53.53*	*54.48*	*53.53*	*60.11*
*a**	*-4.92*	*-0.89*	*-4.86*	*-2.0*	*-4.86*	*-2.85*
*b**	*-17.49*	*-12.75*	*-19.36*	*-15.99*	*-19.36*	*-12.90*
Chroma	*18.17*	*12.78*	*19.96*	*16.11*	*19.96*	*13.21*
Hue angle	*254.28*	*266.02*	*255.88*	*262.89*	*255.88*	*257.53*

The degradation data were analyzed using the equation (3) and linear regression to determine the rate constant for the degradation reaction. Destruction of color in the butterfly pea extract dried with sugar during storage is shown in Fig. 2a-2c. The chroma value decreased continuously with longer storage time. The reaction followed the first-order kinetics and the rate constant (*k*) of the reaction are shown in Table 2. The higher the rate constant, the higher the degradation rate is (Van Boekel, 2009). Decrease in chroma values as a function of storage temperature and time was in agreement with the reports of the other researchers (Pratras, Brunton, Tiwari, & Butler, 2011; Wesche-Ebeling, Argaíz-Jamet, Hernández-porras & López-Malo, 1996)

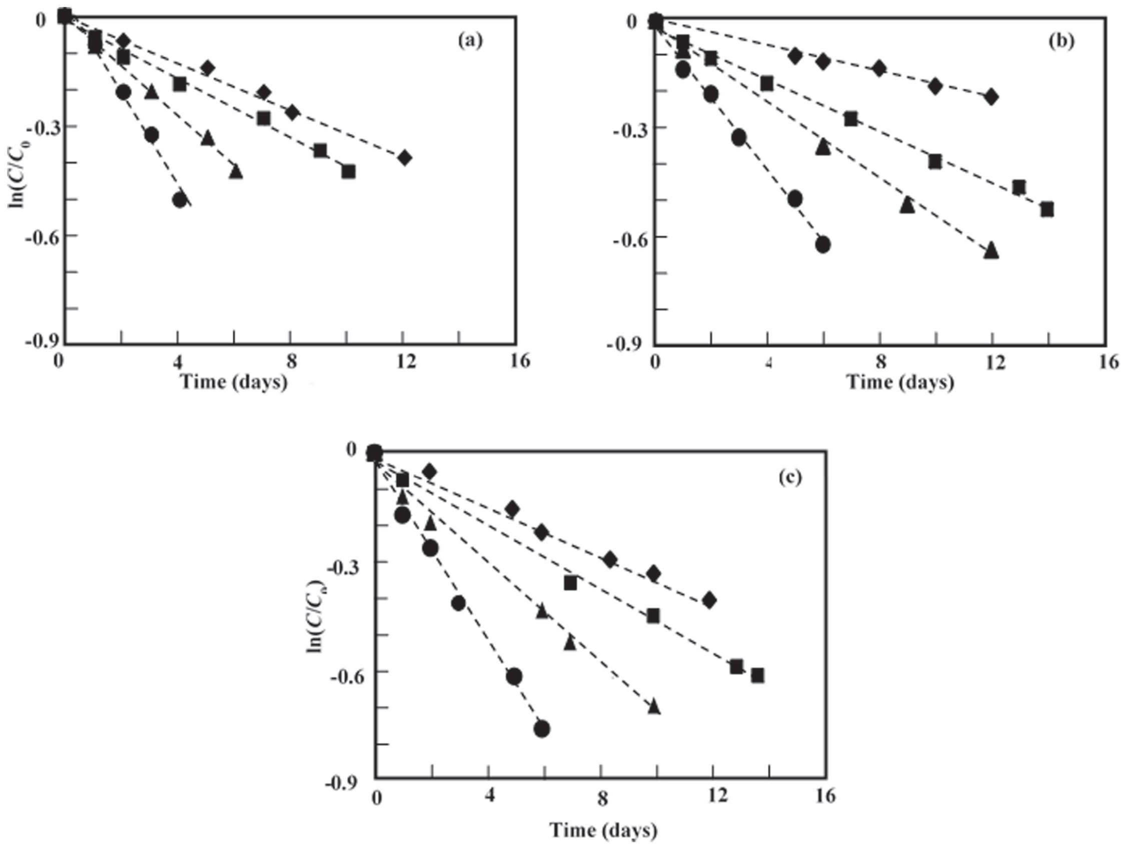

Figure 2 The first-order kinetic plots of changes in chroma values
of the crystallized butterfly pea extract dried with sugar
at various packing conditions of (a) pouch A, (b) pouch B, and (c) pouch C
at the storage temperatures of (◆) 40°C, (■) 45°C, (▲) 50°C, and (●) 55°C.

According to Figure 2, the degradation rates of chroma values at the same temperature under vacuum condition of pouch C were higher than those under normal atmospheric condition of pouch A and pouch B and the degradation rates of both pouches were close together. This reason may be explained that some outer oxygen could more diffuse into the pouch A through the clear plastic side than into the pouch B due to higher oxygen permeability of the OPP film than the laminated aluminium film and participated in oxidation reaction (Siracusa, 2012).

Table 2 Effects of packing conditions and storage temperatures on the rate constant (*k*) and activation energy (*E*a) on color degradation of crystallized butterfly pea extract dried with sugar.

Packing conditions	Storage temperature (°C)	k x10^2 (day^{-1})	$t_{1/2}$ *(days)*	R^2	*E_a (KJ/mol)
Pouch A	40	3.253	21.44±2.239	0.9939	78.46±2.235^b
	45	4.035	17.31±1.944	0.9928	
	50	6.864	10.18±1.238	0.9866	
	55	12.65	5.508±0.5603	0.9831	
Pouch B	40	1.763	39.57±3.815	0.9907	95.61±4.571^c
	45	3.554	19.61±1.875	0.9941	
	50	5.292	13.25±1.983	0.9957	
	55	9.964	6.992±0.6751	0.9947	
Pouch C	40	3.495	20.14±3.346	0.9936	71.97±3.027^a
	45	4.373	16.14±3.031	0.9844	
	50	6.781	10.36±1.708	0.9831	
	55	12.34	5.669±0.7666	0.9802	

*Values followed by different letters are significantly different at $p < 0.05$.

2. Temperature dependence

Effect of temperatures on the rate constants was fitted to an Arrhenius-type equation according to Equation (4). The dependence of color degradation of the crystallized butterfly pea extract dried with sugar on storage temperatures at different packing conditions was presented in Fig. 3. Estimated activation energy (E_a) for the degradation of color in the crystallized butterfly pea extract dried with sugar stored in the pouch B was higher than in the pouch A and C, which indicated the color degradation in the pouch B was less sensitive to storage temperature or the color of the extract dried with sugar was more difficult to degrade than that in the other pouches. As the intensity of blue color is related to the anthocyanin contents, the darker blue at a specific pH, the higher the anthocyanin contents were (Mohamad, Nasir, & Sarmidi, 2011; Patras, Brunton, Tiwari, & Butler, 2011).

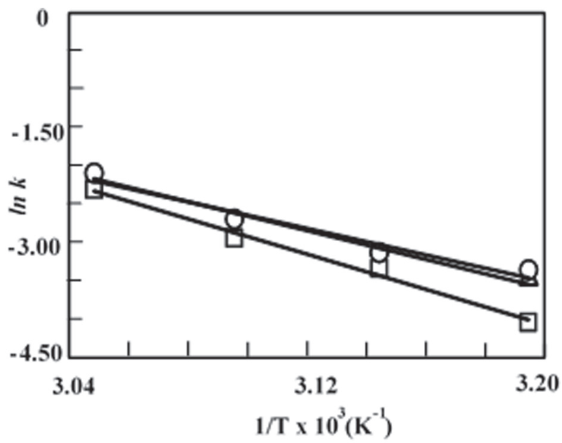

Figure 1 The Arrhenius plots for color degradation in crystallized butterfly pea extract dried with sugar in storage conditions of (△) pouch A, (○) pouch B, and (□) pouch C.

It should be noted that storage of the butterfly pea extract dried with sugar under vacuum condition caused faster color degradation than that under other packing conditions. The reason may be attributed to the particles of the butterfly pea extract dried with sugar under vacuum was subjected to caking phenomenon started from bridging, agglomeration, and finally compaction. Reduction of the interparticle spaces resulted in clumped particles (Aguilera, del Valle, & Karel,1995). The caking phenomena may be responsible for faster color degradation (Barbosa-Cánovas, Ortega-Rivas, Juliano, & Yan, 2005; Shirkole, & Sutar, 2018).

The packing condition of the pouch B was selected to conduct the stability of the crystallized butterfly pea extract dried with sugar under storage at ambient temperature (27-33°C). In order to validate the rate constant at 30°C, the predicted rate constant was obtained from the Arrhenius plots according to Fig. 3 using extrapolation method, which was 0.0107 day^{-1} and the half-life ($t_{1/2}$) calculated from the equation (5) was 55 days. The observed shelf-life of the crystallized butterfly pea extract dried with sugar stored at ambient temperature was 64 days.

Conclusions

Estimation of color degradation using change in chroma values of the crystallized butterfly pea extract dried with sugar stored in different laminated pouches and conditions followed well the first order kinetics with the coefficients of determination (R^2) of 0.98 or higher for all accelerated temperatures from 40 to 55°C. The crystallized butterfly pea extract dried with sugar stored in the pouch C (PE/Al/PET) degraded faster than in pouch A and pouch B with the activation energies of 71.97, 78.46, and 95.61 KJ/mol, respectively. Thus, the appropriate storage condition for the butterfly extract dried with sugar should be at as low temperature as possible and under atmospheric condition not under vacuum condition. The results from this kinetic study under different conditions may use for suggestion of the suitable packaging and condition to store other herb extracts to extend their shelf-life to be as long as possible.

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