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Kinetics of Color Loss of Djulis (*Chenopodium formosanum* Koidz.) Extracts during Storage in Different Concentrations of Alcohol and Temperature

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Abstract

The aim of this study was to investigate the effect of storage temperature on color loss (betacyanin degradation) of Djulis (*Chenopodium formosanum* Koidz.) extracts in various alcohol (10-60% EtOH) model systems. All samples were thermally processed and stored at 20-50°C for 21 days after pigment regeneration. Results showed that betacyanin degradation index (DI) was accelerated by ethanol and temperature. The rate of color loss during storage followed the first-order reaction kinetics. The higher ethanol concentration and temperature corresponded to the higher rate of color loss, which was in accordance with the trend of activation energy (E_a) of color degradation. For example, the E_a values of 0%, 10%, 20%, 40% and 60% EtOH samples were 81.04, 77.89, 71.75, 71.30 and 70.16 kJ mol^{-1}, respectively. Apparently, significant color loss of Djulis extracts occurred when ethanol concentration reached 20%.

Keywords: color loss; first-order reaction kinetics; activation energy

1. Introduction

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Djulis (*Chenopodium formosanum* Koidz.) is a native aboriginal cereal plant recently highlighted in Taiwan. In our previous work, betacyanin was found to be its major source of the red color and antioxidant capacity [1]. Usually, the absorbance at 530 nm (A_{530}) was indicated to be a good index for betacyanin pigment and closely related to the red color (Hunter a) performance. In addition, betacyanin pigment could be a good candidate for natural coloration in some alcohol beverages. However, betacyanin was not stable and susceptible to heat [2,3], oxygen [4], pH [5] and alcohol [6] during processing and storage [7] and lead to the loss of economic value. In red beet, the thermal degradation of betacyanin in alcohol system was found to follow the first order reaction kinetics [8]. But, in Djulis, the stability of color presence in ethanol was still in questions. Therefore, this study was aimed to investigate the color stability of Djulis extracts with various alcohol concentrations and different storage temperature in model system through kinetic analysis.

2. Materials and methods

2.1. Sample preparation

The pigment extracts was prepared by soaking 1 g of Djulis grains in 40 mL of distilled water in the dark at 4°C for 24 hr, and the filtrate were then freeze dried. Then 1 g of the freeze dried extract was dissolved in 100 ml of buffer solutions (pH 5.5) with HCl (1 M) and NaOH (2 M) after addition of ethanol contents (10, 20, 40 and 60% EtOH) in model systems. All samples were heated at 60°C for 30 min in a water bath. Samples were held at 4°C for 24 hr for the pigment regeneration and then stored at 20, 30, 40 and 50°C for 21 days.

2.2. *Color measurements*

A Nippon Denshoku Color meter (Model ZE-2000, Nippon Denshoku, Tokyo, Japan) was used to obtain Hunter a and color loss of the samples. A penetrable whiteboard (X, 93.15; Y, 95.18; Z, 112.17) was used as the standard plate. Hunter's a value was read to indicate the degree of redness.

2.3. Pigment retention percentage and betacyanin degradation index

Pigment determination was performed with a UV-Vis spectrophotometer (Model U-2001, HITACHI, Tokyo, Japan). The betacyanin content was estimated by using absorbance at 530 nm (A_{530}) and the A_{530} of original system is A_0, while the A_{530} of each sample at time was A. The pigment retention percentage (%) was calculated as $(A/A_0)\times100\%$. Degradation index (DI) was calculated from A_{405}/A_{530}.

2.4. Kinetics of color degradation

The changes in the color in alcohol solutions during storage were fitted into the following first order kinetics equation (eq.1):

$$ln(a/a_0)=-kt \qquad (eq.1)$$

for the calculation of k, where a and a_0 are Hunter a values at times t and 0, respectively. a/a_0 express the red color loss, and k is a rate constant for the color loss (day^{-1}). The dependence of the color loss upon temperature was determined by the Arrhenius equation (eq.2):

$$k = k_0\, exp^{-Ea/RT} \qquad (eq.2)$$

where; E_a is the activation energy of the reaction ($kJ\ mol^{-1}$), R is the universal gas constant ($8.3145\ J\ mol^{-1}\ K^{-1}$), T is the absolute temperature (K), and k_0 is the pre-exponential factor.

2.5. Statistical analysis

Mixed model factorial experiments were used in this study. Statistical analysis was conducted using SAS statistical software Version 9.1 (SAS Institute Inc, 2003). The data were subjected to analysis of variance (ANOVA). Mean separations were conducted using Duncan's multiple range tests. All experiments were carried out in triplicate.

3. Results and discussion

3.1. Pigment and color qualities of Djulis betacyanin extracts in alcohol model system

The pigment retention of Djulis extracts in different alcohol model systems progressively decreased and the color loss increased after heating and storage at 20, 30, 40 and 50°C (data not shown). The higher rate of color loss corresponded to increase in alcohol concentration. Degradation index (DI) of all samples was greater at the higher alcohol concentrations and storage temperature. At 60% ethanol treatment, the DI increased more drastically for all the other treatments and control (Fig. 1). This is in accordance with the report by Lin and Tsai [9], who indicated that betacyanin is unstable at high concentrations of alcohol.

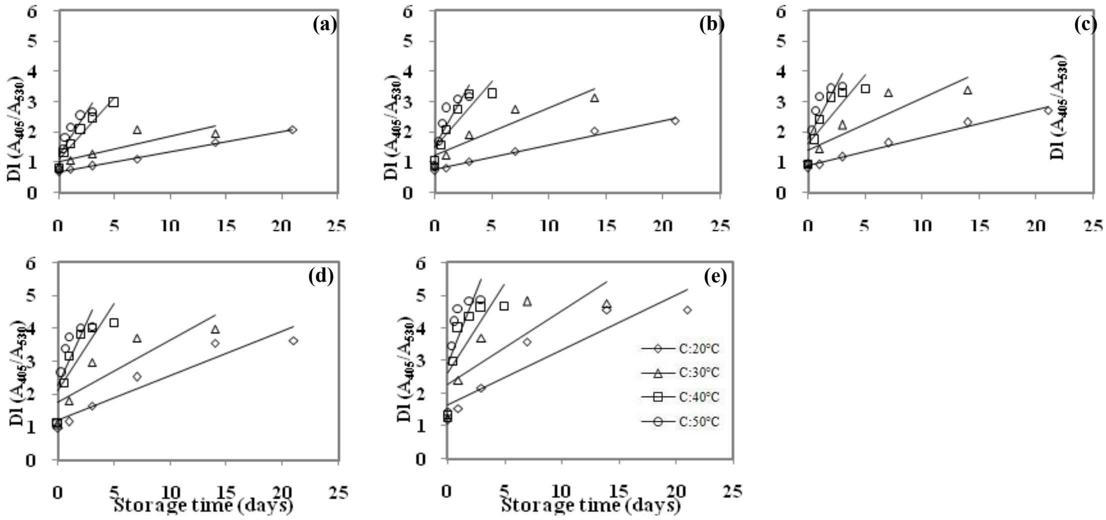

Fig. 1. Betacyanin degradation index of Djulis extracts in various alcohol model systems at 0% (a), 10% (b), 20% (c), 40% (d) and 60% (e) ethanol concentrations during storage at 20-50°C.

3.2. Kinetics study of Djulis betacyanin extracts in alcohol model system

The color degradation of betacyanin from Djulis extract confirmed by F-value indicated that Hunter a value was more significant ($p<0.0001$) than that other parameters in betacyanin degradation and color loss (data not shown). The kinetic curves of semi-logarithmic plotting of the red color loss (Hunter's a/a_0) versus time (day^{-1}) were performed at various storage temperatures and at various ethanol concentrations. The color degradation of all samples followed the first-order reaction kinetics as shown in Figure 2. The rate of color loss increased as the temperature increased. For example, the rate constants (*k*) of samples in 0, 10, 20, 40 and

60% EtOH samples at 20°C storage were 0.051, 0.082, 0.097, 0.175 and 0.320 day^{-1}, respectively. They are increased to 1.058, 1.384, 1.197, 2.359 and 4.235 day^{-1}, respectively, when the storage temperature was to 50°C (Table 1). The results of rate constant determination indicated that the temperature was an important factor affecting the stability of betacyanin in alcohol solutions. These findings are in accordance with previous studies in betanin solutions, red beet [8], and purple pitaya juice [10].

Activation energy (E_a), the slop of the semi-logarithmic plot of the rate constant versus the inverse of temperature (K) is the activation energy for color loss. The result showed that red color has the highest in the control sample (0% EtOH) at 81.04 kJ mol^{-1} and the lowest value at 70.16 kJ mol^{-1} in 60% EtOH sample as shown in Table 1. No significantly different of E_a in the samples treated with 20 to 60% EtOH (70.16-71.75 kJ mol^{-1}). These E_a values are corresponded to the E_a of betacyanin pigment in Djulis, which varied from 38.72-65.22 kJ/mol (9.25-15.58 kcal/mol) at pH 3-7 [1], and the lowest E_a was found in the water/ethanol system for the thermal degradation of betanin [8].

Table 1. Rate constants (k) and activation energies (E_a) for the color loss of Djulis extracts in different ethanol concentrations during storage at 20-50 ℃ .

EtOH (%)	Temperature (°C)	Rate constant (day^{-1})	Activation energy (E_a, kJ mol^{-1})	r^2
0%	20	0.051±0.001	81.04^a	0.9883
	30	0.106±0.002		
	40	0.403±0.001		
	50	1.058±0.001		
10%	20	0.082±0.006	77.89^b	0.9695
	30	0.179±0.001		
	40	0.830±0.001		
	50	1.384±0.008		
20%	20	0.097±0.001	71.75^c	0.9343
	30	0.179±0.001		
	40	0.938±0.001		
	50	1.197±0.004		
40%	20	0.175±0.001	71.30^c	0.9708
	30	0.422±0.000		
	40	1.603±0.001		
	50	2.359±0.017		
60%	20	0.320±0.002	70.16^c	0.9843
	30	0.826±0.001		
	40	2.896±0.206		
	50	4.235±0.130		

$^{a-c}$: values with different letters superscripts within column are significantly different (P<0.05).

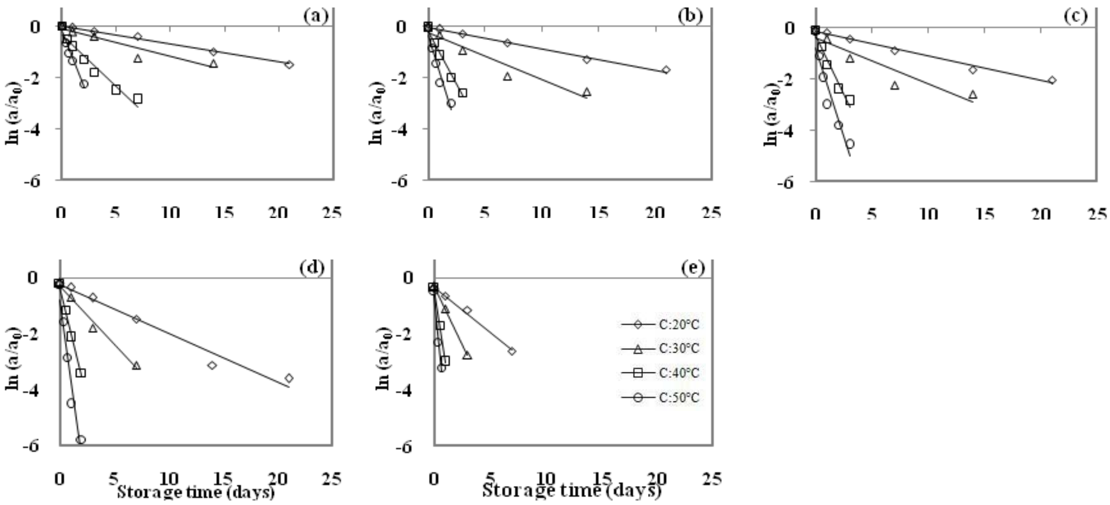

Fig. 2. First-order kinetics plots for the color loss of Djulis extract in various alcohol model systems at 0% (a), 10% (b), 20% (c), 40% (d) and 60% (e) ethanol concentrations during storage at 20-50°C.

In conclusion, color loss and betacyanin degradation of Djulis extracts was accelerated by ethanol and temperature. People should avoid soaking of betacyanin Djulis material more than 20% in potable alcohol. This study provides an adequate process for Djulis wine making, which can also be valuable references to further investigation and application to wine industry.

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