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Degradation kinetics of phenolic content and antioxidant activity of hardy kiwifruit (*Actinidia arguta*) puree at different storage temperatures

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ABSTRACT

The effect of storage temperature on the degradation of total phenolic content (TPC) and antioxidant activity in hardy kiwifruit (*Actinidia arguta*) puree was investigated at temperatures of 5, 15, 25, and 45 °C for 72 h. An increase in the storage temperature resulted in a decrease in the TPC and antioxidant activity of hardy kiwi puree over time. The degradation of total phenolic content and antioxidant activity followed a first-order kinetic model and the kinetic parameters such as k, $t_{1/2}$, Q_{10}, and Ea were calculated. The k and $t_{1/2}$ values decreased with increasing storage temperature and the Q_{10} values for TPC and antioxidant activity were 1.43 and 1.43, respectively. These results indicated strong dependence on temperature of phenolic content and antioxidant activity in hardy kiwi puree. The Ea for the degradation of TPC and antioxidant activity in hardy kiwi puree were 28.15 and 29.07 kJ/mol, respectively. Major phenolic compounds in hardy kiwi identified by UPLC-Q-TOF MS were epicatechin, procyanidin B type, procyanidin trimers, catechin, chlorogenic acid, and isoquercetin. These compounds were degraded with increase in storage temperature and time. This result is consistent with kinetic studies on phenolic content and antioxidant activity.

1. Introduction

Hardy kiwi (*Actinidia arguta*), also known as 'baby kiwi', has smooth, edible, thin, and predominantly green skin and a well balanced sour and sweet taste with very aromatic flavor (Maticha et al., 2003). Its fruit are smaller in size and contain higher levels of chlorophyll, lutein, and β-carotene than 'Hayward' kiwifruit (*Actinidia deliciosa*) which is the most commonly available cultivar (Nishiyama, Fukuda, & Oota, 2005). Hardy kiwis are a rich source of vitamin C and phenolics such as caffeic acid, esculetin, and quercetin (Lim et al., 2006), which resulted in their high antioxidant capacity (Latocha, Wołosiak, Worobiej, & Krupa, 2013; Nishiyama et al., 2004). Their phenolic compounds play a potentially significant role in human health by their anti-inflammatory and anti-oxidative effects (Lim et al., 2006). For this reason, kiwi fruits are sometimes called 'healthy fruits', and they are a promising fruit species with high commercial potential and increasing production worldwide (Ferguson & Ferguson, 2002; Okamoto & Goto, 2005; Williams et al., 2003). However, short shelf-life is main challenge due to rapid softening and skin wrinkling of vine-ripe fruit due to water loss and fruit decay (White, de Silva, Requefo-Tapia, & Harker, 2005). Hardy kiwifruit has a shorter storage life of 1–2 months (Strik & Hummer, 2006), than that of Hayward kiwifruit (4–6 months) when held at 0 °C (Cheah and Irving, 1997). This short storage life and fast loss of postharvest quality are detrimental to the nutritional and health-promotin value of the fruits during storage or distribution life.

Phenolic compounds are easily sensitive to degradation, by their unstable structure is under various environmental condition such as light, pH, oxygen, storage temperature, and time. Buchner, Krumbein, Rohn, and Kroh (2006) were demonstrated the heat sensitivity of phenol compounds and temperatures increase may lead to deterioration of phenolic compounds, resulting in readily the loss of antioxidant activity in foods (Kim & Padilla-Zakour, 2004). For these reasons, the monitoring and control of storage temperature is a very important factor in order to maintain their bioactive activity, which contribute to the phenolics and antioxidant activity. However, the influence of storage temperature on antioxidants and phenolic compounds of hardy kiwi has not been studied. The arrhenius equation has been widely applied to quantify the effect of temperature on the rate of several chemical and biochemical reaction. Accurate knowledge of the kinetic parameter is essential to predict the change in the nutritional quality that occur during storage. Therefore, data on the kinetics model can be useful in determining the processing system of hardy kiwi products.

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Accurate knowledge of kinetic parameters is essential to predict changes in the nutritional quality that occur during storage. Therefore, data on the kinetics model can be useful in determining the processing system of hardy kiwi products. The objective of this study was to investigate the degradation kinetics of phenolic contents and antioxidant activity in hardy kiwi puree as affected by the storage temperature and time.

2. Materials and methods

2.1. Plant materials and storage conditions

Commercially mature hardy kiwi were harvested in Gwangyang County (Jeonnam Province) in South Korea in 2015 and selected for uniform size (mean 2.0 ± 0.2 cm) and absence of visible defects. Samples were immediately stored at −80 °C in the dark until subsequent analysis. Analyses of the hardy kiwi showed an average pH, Brix, and pulp content were 3.35 ± 0.10, 11.53 ± 0.21°, and 39.3 ± 1.46%, respectively. The hardy kiwi were washed and approximately 100 g of the whole fruits was ground using a blender (HWF-630WG, Hanil Electric, Wonju, Korea) for 2 min at 20 °C (± 1 °C). The mean particle diameter of the puree was 157.02 ± 1.06 μm. The puree (20 g) was immediately packed into pouches (3.5 cm × 10 cm, low density polyethylene), and were then stored at various temperatures of 5, 15, 25, and 45 °C (± 0.5 °C) at intervals of 12 h up to 72 h in an incubator (JSBI- 150C, JSR, Seoul, Korea). The storage time was limited to 72 h to avoid microbial spoilage by molds. A sample right after grinding served as the storage of 0 h.

2.2. Chemicals

All chemicals used in this study were of the highest purity grade available. Folin & Ciocalteu's phenol reagent and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were obtained from Sigma-Aldrich (Sigma–Aldrich Corp., St. Louis, Mo., U.S.A.).

2.3. pH, brix level, and particle size distribution

The pH and Brix levels were measured using an Istek Model 735P pH meter (Istek, Seoul, Korea) and an Atago digital refractometer (Pal–1, Atago Co., Ltd., Tokyo, Japan), respectively, without further dilution. The pulp content was calculated by first separating the pulp by centrifuging at 5000 rpm for 1 h before determining the relation between the weight of the pulp and the initial weight of the sample (Qiu & Rao, 1988). The particle size in the hardy kiwi puree was determined using a Cilas 1090 Laser Particle Size Analyzer (Cilas Corporation, Orleans, France) according to the method described by Kim, Kim, Kerr, and Choi (2017).

2.4. Extraction procedure

Prior to analysis, the sample extracts were prepared as follows. All samples were first diluted with methanol-water (80:20, v/v) and blended at 10,000 rpm for 1 min using a D-500 homogenizer (Wiggen Hauser, Berlin, Germany). The homogenized samples were shaken overnight at 200 rpm at 20 °C (± 1 °C). The samples were centrifuged at 4500 rpm for 15 min at 4 °C and supernatants were analyzed for total phenolic content (TPC), antioxidant activity measured by DPPH radical scavenging activity, and individual phenolic compounds identified by ultra-performance liquid chromatography-quadrupole-time-of-flight mass spectrometry (UPLC-Q-TOF MS).

2.5. Determination of total phenolic content and DPPH radical scavenging activity

The total phenolic content was determined using the Folin–Ciocalteau reagent (Singleton & Rossi, 1965). 1 mL of Folin-Ciocalteau reagent was added to diluted supernatant (1:9 v/v in distilled water). After 5 min, 10 mL of 7% sodium carbonate was added, followed by distilled water to a final volume of 25 mL. The mixture was shaken and allowed to rest for 2 h in dark at ~18 °C. The absorbance of all mixtures was measured at 760 nm using a UV-Vis spectrophotometer (UV–1800, Shimadzu corporation, Kyoto, Japan). A standard curve was prepared using gallic acid, and the results expressed as mg gallic acid/100 g of fresh weight. The mean values were obtained from triplicate experiments.

The DPPH radical scavenging assay was conducted according to the method of Blois (1958) with slight modification. Briefly, 0.1 mL of supernatant was mixed with 0.9 mL of DPPH methanolic solution (1.5×10^{-4} M). The mixture was shaken vigorously and stored for 30 min in dark conditions at approximately 20 °C. The absorbance of the reaction mixture was then measured at 517 nm using a UV-Vis spectrophotometer (UV–1800, Shimadzu corporation, Kyoto, Japan). This activity was calculated as the percentage of DPPH radical scavenging ability using:

$$\%DPPH\ Activity = (A_{control} - A_{sample})/A_{control} \times 100 \quad (1)$$

where A_{sample} is the absorbance of the sample, and $A_{control}$ is the absorbance of the mix in which 100 μL distilled water was used instead of sample supernatant. The DPPH radical scavenging activity was expressed as mM of t-butylated hydroxyanisole equivalent (BHAE) per g of sample fresh weight. The mean values were obtained from triplicate experiments.

2.6. Degradation kinetics of total phenolic content and DPPH radical scavenging activity

The degradation kinetics for both total phenolic content and DPPH radical scavenging activity were calculated using the standard equation for a first-order reaction model:

$$ln\ C = ln\ C_0 - kt \quad (2)$$

where t is the storage time (min), k is the first-order rate constant (min^{-1}), C_0 and C are the TPC or DPPH radical scavenging activity at time zero and time t, respectively.

The temperature dependence of the reactions was modeled by the Arrhenius equation:

$$k = k_0 \cdot e^{-Ea/RT} \quad (3)$$

where Ea is the activation energy (kcal mol^{-1}), k is the rate constant; k_0 is the frequency factor; R is the universal gas constant ($8.314 \cdot 10^{-3}$ kJ mol^{-1} K^{-1}), and T is the absolute temperature (°K). The Ea value was calculated from the slope of the straight lines given by Eq. (3), using a linear regression procedure of the Sigma Plot (SigmaPlot 1.0 Windows version, SPSS Inc.).

The temperature quotient (Q_{10}) was also calculated, and taken as the increase in rate for every 10 °C increase in temperature:

$$Q_{10} = k^2/k^{1(10/T_2 - T_1)} \quad (4)$$

where k_2 is the rate constant of the degradation reactions at temperature T_2 and k_1 is the rate constant of the degradation reactions at temperature T_1. The half-life ($t_{1/2}$), the time required for TPC or DPPH radical scavenging activity to degrade to 50% of their original values, was calculated from the rate constant as follows:

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

where k is the rate constant (min^{-1}).

2.7. Analysis of phenolic compounds

The analysis of phenolic compounds was carried with UPLC-Q-TOF MS (Waters, Milford, MA, USA) equipped with an Acquity UPLC BEH