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Changes in the color, chemical stability and antioxidant capacity of thermally treated anthocyanin aqueous solution over storage

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ABSTRACT

Many anthocyanin-containing foods are thermally processed to ensure their safety, and stored for some time before being consumed. However, the combination of thermal processing and subsequent storage has a significant impact on anthocyanins. This study aimed to investigate the color, chemical stability, and antioxidant capacity of thermally treated anthocyanin aqueous solutions during storage at 4, 25, 45, and 65 °C, respectively. Anthocyanin aqueous solutions were thermally treated before storage. Results showed that the degradation rate of anthocyanins in aqueous solutions was much faster than those in real food. The color of the anthocyanin aqueous solutions changed dramatically during storage. The anthocyanin aqueous solutions stored at 4 °C showed the best chemical stability. Interestingly, the antioxidant capacity of the anthocyanin aqueous solutions stored at lower temperatures remained the same; however, the antioxidant capacity of those thermally treated at 120 or 140 °C and stored at 45 or 65 °C significantly decreased.

1. Introduction

Color plays an important role in every food item we eat or drink, and it is often taken by consumers as a quality indicator and as well as for esthetic reason. One class of colorants is anthocyanins which are usually derived from natural sources, such as fruits, vegetables, legumes, and cereals (Bridle & Timberlake, 1997). Anthocyanins, belonging to the flavonoid group, are water-soluble compounds providing red, purple, and blue hues (Castañeda-Ovando, Pacheco-Hernández, Páez-Hernández, Rodríguez, & Galán-Vidal, 2009). They are also good antioxidants being able to prevent neuronal and cardiovascular illnesses, cancer, and diabetes (Konczak & Zhang, 2004).

Thermal processing is one of the most common processes in the food industry, which helps to keep foods safe, prolong their shelf-life and enhance their functional properties. According to its heating intensity and temperature employed, thermal processing may be classified as pasteurization (63–100 °C), sterilization (100–130 °C), and ultra-high-temperature (UHT) treatment (130–160 °C). However, thermal processing can result in some undesired outcomes, such as loss of color and degradation of nutrients. Anthocyanins were reported to readily degrade during thermal processing and the color of the food containing them was simultaneously affected (Patras, Brunton, O'Donnell, & Tiwari, 2010; van Boekel et al., 2010). Besides storage temperature and duration were found to play a critical role in the loss of anthocyanins and color throughout storage (van Boekel et al., 2010). Thermally treated foods, such as juices and jams, often undergo long term storage before being consumed. The color, chemical stability, and nutritional properties of anthocyanins in such thermally treated foods may therefore change greatly during the storage. Fracassetti et al. (2013) reported an overall reduction of anthocyanin content in freeze-dried wild blueberry powder at the storage temperatures of 25, 42, 60, and 80 °C over 49 days of storage. A loss of anthocyanin content was also observed in blueberry juice and blueberry fruits stored at 4 and −18 °C (Reque et al., 2013). Similarly, losses of anthocyanins in strawberry jams stored at room temperature were reported by Amaro et al. (2013). They also observed that the color of strawberry jams turned from red to brownish after storage. From these studies, it is clear that the stability of anthocyanins is not merely affected by thermal processing but also influenced by storage.

Studies on changes in the stability, color, and nutritional properties of thermally treated anthocyanins during storage are of great importance in order to better understand the degradation

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mechanisms of anthocyanins. However, to date, no studies have reported the impact of thermal processing and subsequent storage on the color, chemical stability, and antioxidant capacity of anthocyanins, especially in an aqueous system instead of real food matrix. Real foods generally contain sugar, salt, fat, protein, etc., which may positively or negatively affect anthocyanins. Therefore, the studies of anthocyanins in real foods or model food systems are hard to relieve the real change of anthocyanins, which has also been addressed in our previous study that anthocyanins (cyanidin-3-glucoside and cyanidin-3-rutinoside) in an aqueous system degraded much faster than those in real foods or model food systems (Sui & Zhou, 2014). The present study was aimed to investigate the color, chemical stability, and antioxidant capacity of anthocyanin aqueous solution that was thermally treated at 90, 100, 120, and 140 °C for both 30 s and 2 min, respectively, over 21 days of storage at 4, 25, 45, and 65 °C. Results of the study will be of value to understanding and predicting changes in the color, chemical stability, and antioxidant capacity of thermally treated anthocyanin-containing liquid foods throughout storage.

2. Materials and methods

2.1. Materials

Anthocyanin-rich black rice extract powder was purchased from Shaanxi Taiji Huaqing Technology Co., Ltd., China. Anthocyanins standards including cyanidin-3-glucoside and cyanidin-3-rutinoside were purchased from Polyphenols Laboratories (Sandnes, Norway). Trifluoroacetic acid (TFA, analytical grade), 2,2-diphenyl-1-picrylhydrazyl (DPPH), formic acid, and 6-hydroxy-2,5,7,8-tetramethylchloroman-2-carboxylic acid (Trolox) were purchased from Sigma–Aldrich (Sigma–Aldrich, St Louis, MO, USA). All the other chemicals are analytical grade.

2.2. Purification procedure of anthocyanins

Impurities in the anthocyanin-rich black rice extract powder were removed using solid phase extraction (SPE) technique according to our previous work (Sui, Dong, & Zhou, 2014). In brief, the anthocyanin-rich black rice extract powder was mixed with deionized (DI) water to make a concentrated anthocyanin aqueous solution. Afterwards, the solution was loaded on a pre-conditioned Sep-Pak C_{18} cartridge (WAT023635, Waters, USA) connected with a vacuum manifold (WAT200677, Waters, USA). A purification procedure was started with passing 20 mL of acidified DI water (0.5% v/v, TFA) followed by 20 mL of ethyl acetate through the cartridge. Purified anthocyanin-rich fraction was collected in methanol via washing the cartridge using 40 mL of acidified methanol (0.5% v/v, TFA). The methanol was removed from the fraction in a rotary evaporator at 40 °C. The working anthocyanin aqueous solution was then prepared by suspending the purified anthocyanin-rich fraction in DI water and stored at −20 °C until use. The purity of the anthocyanin fraction was checked at 280 nm using high-performance liquid chromatography with photodiode-array detection (HPLC–DAD).

2.3. Thermal treatment of anthocyanin aqueous solution

Thermal treatment was conducted in a microwave reactor (Biotage, Sweden). Anthocyanin aqueous solution was heated for 30 s and 2 min at four designated temperatures including 90, 100, 120, and 140 °C, respectively. The thermally treated anthocyanin aqueous solutions were consequently transferred into incubators for accelerated shelf-life testing for up to 21 days.

2.4. Accelerated shelf-life testing

Control (i.e., non-thermally treated) and thermally treated anthocyanin aqueous solution were stored in dark at 4, 25, 45, and 65 °C in four separate incubators, respectively, for up to 21 days. During the storage, samples were withdrawn from anthocyanin aqueous solutions for measuring their color, anthocyanin concentration, and antioxidant capacity once every 3 days.

2.5. Quantification of anthocyanins using HPLC–DAD

Anthocyanins were quantified with a focus on two specific anthocyanins: cyanidin-3-glucoside and cyanidin-3-rutinoside. Not only that the percentage of the two anthocyanins accounted for more than 90% of total anthocyanins in solutions, but also that cyanidin-3-glucoside is regarded as one of the most predominant anthocyanins in nature and cyanidin-3-rutinoside has been found to be the most thermally stable anthocyanin (Rubinskiene, Jasutiene, Venskutonis, & Viskelis, 2005; Stintzing & Carle, 2004). Therefore, they serve as important markers for the study. A C_{18} reversed-phase column (250 × 4.6 mm, Sunfire, Waters, Wexford, Ireland) was applied to separate anthocyanins. The total flow rate was set to 1 mL/min and the column oven temperature was kept at 25 °C. One mL of sample was subjected to passing through a 0.45 μm Whatman Nylon filter (Whatman, NJ, USA). 50 μL of the filtered sample was auto-injected into a Shimadzu HPLC–DAD system (Shimadzu, Tokyo, Japan). A binary gradient elution (mobile phase A: 5% formic acid in DI water; mobile phase B: 100% acetonitrile) process was started with 0% B for 5 min, ramping up to 10% B at 20 min, 13% at 40 min, 20% at 44 min, 25% at 50 min and 100% at 55 min. Detection was performed at 520 nm. The two individual anthocyanins were quantified using cyanidin-3-glucoside and cyanidin-3-rutinoside standard curves which were prepared using a series of standard solution between 0.0001 and 0.1 mg/mL.

2.6. Color measurement and modeling

The color measurement was conducted in a transparent rectangular cell (size: 50 × 38 mm; optical path: 10 mm) using a bench-top colorimeter CM-5 (Konica Minolta Sensing Inc., Tokyo, Japan). Since the most commonly used CIE $L^*a^*b^*$ coordinates are difficult to interpret color changes, the $L^*C^*H^\circ$ system, which was recommended by the International Commission on Illumination (CIE) as an optimized version of CIE $L^*a^*b^*$ method in 1976 (Loughrey, 2001; Wrolstad, Durst, & Lee, 2005), was adopted in measuring the color in this study. The coordinates of $L^*C^*H^\circ$ were calculated from L^*, a^*, and b^* values based on the following equations: $C^* = \sqrt{\left(a^{*2} + b^{*2}\right)}$ and $H^\circ = \tan^{-1} b^*/a^*$, where L^* represents the lightness measuring brightness with 100 and 0 equaling to absolute white and absolute black, respectively. Chroma (C^*) measures intensity or saturation. H° indicates hue angle which is expressed on a 360° grid, with 0° and 180° corresponding to $+a^*$ axis (red) and $-a^*$ (green), respectively, and 90° and 270° for the $+b^*$ axis (yellow) and $-b^*$ (blue), respectively. To understand color changes, total color difference (TCD) was computed using the formula $\mathrm{TCD} = \sqrt{\Delta L^{*2} + \Delta b^{*2} + \Delta a^{*2}}$ (Shin & Bhowmik, 1995), and modeled using a first order model (Eq. (1)) which has been commonly applied to model color changes in food systems (Ávila & Silva, 1999; Li, Taylor, Ferruzzi, & Mauer, 2013).

$$\frac{T - T_f}{T_0 - T_f} = \exp\left(-kt\right) \tag{1}$$

where T is TCD at time t, T_f is the final value of TCD, T_0 is the initial value of TCD on day 0, k is reaction rate constant, and t represents