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Buffering colour fluctuation of purple sweet potato anthocyanins to acidity variation by surfactants

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ABSTRACT

Anthocyanins are intriguing natural pigments with beneficial bioactivities and their colour is extremely susceptible to acidity variation. Minimisation of colour fluctuation is essential to maintain quality consistency in food industry. A new strategy employing surfactants to mimic encapsulation was attempted with typical anionic, cationic and nonionic surfactants and proved effective although the traditional copigmentation method was inactive. The exceptional colour fluctuation buffering effect of anionic surfactants especially sodium dodecyl sulphate (SDS) was revealed and then carefully analysed by colorimetric and spectroscopic methods. The outstanding activity of SDS presumably resulted from effective shielding of anthocyanins from external acidity through strong interaction with the positively charged flavylium cations owing to its anionic nature. These results suggest SDS is a valuable additive for buffering colour fluctuation of anthocyanins. The strategy of surfactant will be useful for buffering colour fluctuation of natural colourants.

1. Introduction

Anthocyanins are complicated secondary metabolites which are widely distributed in fruits and vegetables including purple sweet potatoes, berries and red cabbages (Harborne & Grayer, 1988). Purple sweet potato is regarded as an excellent source for anthocyanins owing to its high content of anthocyanins and large quantity (Oki et al., 2002). Extensive studies have demonstrated numerous beneficial effects of anthocyanins including antioxidant properties, anti-mutant activity, anti-tumour activity, blood glucose decreasing activity (Di Carlo, Mascolo, Izzo, & Capasso, 1999; Furuta, Suda, Nishiba, & Yamakawa, 1998; Matsui et al., 2002; Tsuda, Horio, & Osawa, 1998; Wang, Cao, & Prior, 1997; Wang et al., 1999; Yoshimoto et al., 1999). Direct absorption of anthocyanins into the blood was observed (Matsumoto et al., 2001; Miyazawa, Nakagawa, Kudo, Muraishi, & Someya, 1999; Tsuda, Horio, & Osawa, 1999). Suppression of rat colon carcinogenesis by oral intake of anthocyanins from purple sweet potato and red cabbage was also observed (Hagiwara et al., 2002). The association of a lower risk of coronary heart disease with a moderate consumption of anthocyanins was revealed by epidemiological investigations (Muth, Laurent, & Jasper, 2000; Renaud & de Logeril, 1992).

Owing to their beneficial health effects, there are growing interests in anthocyanins. Despite great application potential of anthocyanins in food, pharmaceutical and cosmetic industries, the application is severely affected by their instability. It is well documented that anthocyanins are highly susceptible to pH, temperature, light, oxygen, metallic ions (Castañeda-Ovando, Pacheco-Hernández, Páez-Hernández, Rodríguez, & Galán-Vidal, 2009; Cavalcanti, Santos, & Meireles, 2011). Intensive efforts have been directed to increase chemical stability of anthocyanins. It was discovered that encapsulation effectively improved stability of light- and heat-labile anthocyanins (Delgado-Vargas, Jimenez, & Paredes-Lopez, 2000). Intermolecular copigmentation of isoflavonoids from red clover enhanced overall stability of anthocyanin 3,5-diglucosides in muscadine grape juice and wine (Talcott, Peele, & Brenes, 2005). The addition of caffeic acid significantly increased the stability of anthocyanins in Cabernet Sauvignon grape extracts through copigmentation interaction (Gris, Ferreira, Falcão, & Bordignon-Luiz, 2007).

Besides their beneficial health effects, anthocyanins have characteristic natural colour. Maintaining their colour steadiness is essential to have stable sensory quality of products which is required in industrial application. It is well known that the colour of anthocyanins is even more vulnerable than their chemical stability to many factors especially pH variation (Bicard, Fougerousse, & Brouillard, 1999). Depending on their acidity,

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anthocyanins are intensely coloured in red, violet or blue. The colour of anthocyanins change dramatically from red to purple and blue as pH changes from 2 to 4 and 6. Therefore, it is necessary to buffer colour fluctuation of anthocyanins to expand their scope of application in acidic to near neutral systems except for strong acidic circumstance. Although significant improvements in chemical stability of anthocyanins have been achieved, there are few studies on buffering their colour fluctuation.

This study is focusing on evaluation of colour fluctuation buffering of purple sweet potato anthocyanins to pH variation. The effect of copigmentation that is frequently applied in improving chemical stability of anthocyanins was tested. Especially a new strategy was attempted employing surfactants to mimic encapsulation which is proved to be effective in promoting their chemical stability. The prominent colour fluctuation buffering effect of certain surfactants was found and carefully studied by colorimetric and spectroscopic methods. To the best of our knowledge, it is the first time to report colour fluctuation buffering of anthocyanins by surfactants.

2. Materials and methods

2.1. Materials and chemicals

Purple sweet potato anthocyanins (PSPA) was purchased from Anhui Sunshine Biotech (China). Potassium chloride, anhydrous sodium acetate, sulfur trioxide pyridine complex, sodium hydroxide, hesperidin, *p*-coumaric acid, rutin trihydrate, ferulic acid, caffeic acid, hydrogen chloride, sodium dodecyl sulphate, sodium dodecylbenzenesulfonate, hexadecyltrimethyl ammonium bromide, 1-propanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decyl alcohol, 1-undecanol, 1-tetradecanol, 1-hexadecanol, 1-octadecanol, 1-docosanol, dichloromethane, ethylacetate, span-60 and tween-80 were purchased from Aladdin-Reagent (China) and used as obtained. The alkyl sulphates with different carbon chain length of three, five, six, seven, eight, nine, ten, eleven, fourteen, sixteen, eighteen and twenty-two were prepared according to the method described by Coevering (van de Coevering et al., 2005).

2.2. Visual screening of colour fluctuation buffering activity of different agents for anthocyanins

0.01 g PSPA was dissolved in 240 mL distilled water and the pH value was adjusted to 2.00 with HCl. Then the PSPA solution was titrated to 250 mL with distilled water in a volumetric flask. Aqueous NaOH solutions with variable concentrations (1 M, 0.1 M and 0.01 M) were also prepared for pH adjustment during tests. An aliquot of 20 mL PSPA solution was sampled in a beaker, and the colour change of the solution was monitored by taking photos at fixed position and fixed angle as pH value of the solution was gradually increased from 2.0 to 7.5 by the addition of the NaOH solutions. All these photos were used as blank control for the corresponding pH value.

The colour buffering activity of the copigments (ferulic acid, caffeic acid, rutin trihydrate, *p*-coumaric acid, hesperidin) were tested as follows. To 20 mL PSPA solution was added the copigment in a molar ratio of 100 times to that of the anthocyanin contained in the solution which was determined according to the literature procedure (Lee, Durst, & Wrolstad, 2005). As described above, the colour change of the solution with pH increasing was monitored by taking photos. With pH value increasing, the copigments which obviously delayed the colour changing compared with the corresponding blank control were selected out as the active ones.

The colour buffering activity of the surfactants (hexadecyl trimethyl ammonium bromide, sodium dodecylbenzenesulfonate and alkyl sulphates with different carbon chain lengths, Span-60 and Tween-80) were tested as follows. The specified amount of surfactants was added in 20 mL solution and the photos were taken with the pH value changing in the same method described before. To 20 mL PSPA solution was added 0.5 wt.% of the surfactant in the solution. The surfactants which obviously delayed the colour changing compared with the corresponding blank control were sought out as the active ones.

2.3. Analysis of colour fluctuation buffering effect of SDS for anthocyanins by colorimeter

The colour variation of anthocyanins solution with SDS at different pH was measured by CM-600D colorimeter (Konica Minolta). The previously prepared PSPA solution (0.04 g/L, pH = 2.0) was used as blank. During the test, 50 mL of the PSPA solution with addition of variable amount of SDS was applied and the pH value of the solution was adjusted with aqueous NaOH solution at an interval of 0.5 within a range of 1.5–7.5. At each pH value, the colour of the solution was measured by the colorimeter. All the measurements were carried out in triplicate. The composite colour of food was precisely described by four parameters: L^*, a^*, b^*, ΔE^*.

2.4. Analysis of the colour fluctuation buffering effect of SDS for anthocyanins by UV–Vis irradiation

The PSPA solution (0.04 g/L) at about pH 1.50 was added a specified amount of surfactants. The pH value of the solution was adjusted with aqueous NaOH solution at an interval of 0.5 within pH range of 2.0–8.0. At each pH value, 10 mL of the solution was sampled and scanned by UV–Vis spectrophotometer (SP-756, Shanghai Spectrum Inc.) between 300 nm and 700 nm. A series of UV–Vis absorption spectra of the samples at different pH values were obtained. Absorbance at 528 nm (A_{528}) was applied to estimate intensity of the anthocyanin's characteristic red colour ($c(AH^+)$). The retention of flavylium cation was calculated as follows:

$$\%\ \text{Retention of flavylium cation} = (A_n/A_0) \times 100\%$$

A_0: absorption at 528 nm with pH below 1.5; A_n: absorption at 528 nm after pH was adjusted.

3. Results and discussion

3.1. Visual screening of colour fluctuation buffering activity of different agents

In spite of the importance of eliminating colour fluctuation of anthocyanins to realise quality consistency of products, colour fluctuation buffering has not been seriously treated because it is a more subtle issue than their chemical stability. We reasoned that the methods which improved chemical stability also could buffer colour fluctuation since the anthocyanin molecules were shielded from exposure to either oxidative or acidic external environment. The most effective ways to stabilise anthocyanins are encapsulation, copigmentation and metal complexation. Considering that introduction of metal ions sometimes would be a concern in food processing, we left out metal complexation this time. Although encapsulation is very effective in chemical stabilisation of anthocyanins, the characteristic colour of anthocyanins would be blanketed by encapsulation. However, surfactants can be employed to mimic encapsulation at molecular level through micellation. As a result, copigmentation and surfactant micellation were evaluated in colour fluctuation buffering of anthocyanins.