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Degradation kinetics and colour of anthocyanins in aqueous extracts of purple- and red-flesh potatoes (*Solanum tuberosum* L.)

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Abstract

The effect of pH and temperature on the stability and visual colour of aqueous anthocyanin (ACY) extracts from purple- and red-flesh potatoes was evaluated and compared to commercial ACY extracts from grape and purple carrot. Extracts from purple carrot and red-flesh potatoes showed higher stability than grape and purple-flesh potato extracts. Stability to pH ($\leqslant$3) and thermal degradation of extracts (pH 3) followed first-order kinetics. Changes in lightness and hue followed zero-order kinetics, while changes in chroma followed first-order kinetics. Degradation parameters such as $t_{1/2}$, *k*-, *D*-, *z*- and Q_{10}-values were determined. Extracts from red- and purple-flesh potatoes at pH 3 showed similar hues to FD&C Red #40 and red cabbage extracts, respectively. The visual colour of both potato ACY extracts was also affected by tinctorial strength. The use of purple- and red-flesh potatoes as a source of natural colorants shows potential use in the pH region around 3.

Keywords: Anthocyanins; Potatoes; Aqueous extracts; Stability; Colour; Kinetics

1. Introduction

Colour is an important attribute related to the visual appeal and the quality of food products (Bridle & Timberlake, 1997; Markakis, 1982). Due to increasing concerns about the safety of synthetic colorants, the use of natural sources of colorants has been considered (Francis, 1989; Jackman, Yada, & Tung, 1987). Anthocyanins, a group of phenolic compounds widely found in the plant kingdom, are responsible for the orange, red, violet and blue colours observed in nature (Mazza & Miniati, 1993). The colour and stability of aqueous ACY solutions is dependent on the changes in equilibrium of its 4 species due to pH or to protonation or hydration reactions during storage. At low pH, ACY are present as the flavylium cation, their most stable form (Jackman et al., 1987). This bright red-coloured form then transforms into blue quinonoidal bases or colourless carbinol pseudobases, and into yellow chalcone species thereafter (Brouillard, 1982). Besides the effect of pH, temperature and light are also known to influence the stability of ACY (Francis, 1989; Wrolstad, 2000). The stability of ACY is also affected by structural modifications with hydroxyl, methoxyl, glycosyl, and especially acyl groups (Mazza & Brouillard, 1987). In fact, acylated pigments are known to have higher stability than their non-acylated counterparts (Bridle & Timberlake, 1997).

In the US, the only ACY colorants clear from certification and approved for food use are fruit or vegetable juices, and should be prepared using only physical methods and avoiding chemical processes (Wrolstad, 2000). Although the use of ACY as natural colorants is favoured by their intrinsic antioxidant activity (Espín, Soler-Rivas, Wichers, & García-Viguera, 2000; Simon, 1997), their commercial use has been limited by their inherent instability, low tinctorial strength, organoleptic properties of the plant material, and economic and agronomic considerations such as availability, costs and yields (Cevallos-Casals & Cisneros-Zevallos, 2004; Jackman & Smith, 1992; Markakis, 1982; Mazza & Brouillard, 1987; Wrolstad, 2000).

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We have previously addressed the potential use of purple and red-flesh potatoes as novel sources of natural colorants and antioxidants (Reyes & Cisneros-Zevallos, 2003; Reyes, Miller, & Cisneros-Zevallos, 2004), but only few studies have focused on the stability of their aqueous ACY extracts under different storage conditions and the resulting changes in visual colour (Fossen, Cabrita, & Andersen, 1998; Rodríguez-Saona, Giusti, & Wrolstad, 1999). The objective of this paper was to study the effect of pH and temperature on the stability and colour of aqueous ACY extracts from purple- and red-flesh potatoes as compared to commercial ACY concentrates from grape and purple carrot. The main ACY constituents in purple- and red-flesh potatoes have been reported as 3,5-diglucosides derivatives from petunidin and pelargonidin, acylated with *p*-coumaric acid, respectively (Fossen & Andersen, 2000; Rodríguez-Saona, Giusti, & Wrolstad, 1998). Grapes show the presence of non-acylated 3-glucoside of malvidin and other anthocyanidins (Bridle & Timberlake, 1997); whereas, the presence of acylated cyanidin derivatives has been reported in purple carrot (Malien-Aubert, Dangles, & Amiot, 2001). In this study we determined first-order thermal degradation parameters, such as, *k*-values, activation energy (E_a), half-life values ($t_{1/2}$), *D*-values, *z*-values and Q_{10}-values; in addition, the changes in Hunter lightness (L^*), chroma (C^*) and hue (H°) parameters after storage were modelled. The effect of tinctorial strength on the visual colour of aqueous ACY extracts from purple- and red-flesh potatoes was also determined. The results from this study provide additional key information characterizing the stability and the changes in visual colour of aqueous ACY extracts from potatoes, to predict their stability during storage. These results strengthen the potential use of purple and red-flesh potatoes as natural colouring agents with added functional value for the food industry.

2. Materials and methods

2.1. Plant material and commercial colorants

Two purple-flesh (All Blue and CO94165-3P/P) and 2 red-flesh (NDC4069-4 and CO94183-1R/R) potato cultivars (cvs) (*Solanum tuberosum* L.) harvested in Springlake (Texas) were used to study the inactivation of peroxidase after steam blanching. The cvs with highest ACY content (CO94165-3P/P and NDC4069-4) were then used to study the changes in stability and visual colour of their ACY extracts during storage, as affected by pH and temperature. The effect of tinctorial strength (TS) on the visual colour of ACY extracts was evaluated for cvs CO94165-3P/P and CO94183-1R/R grown in Center (Colorado), due to their higher ACY content as compared to Texas-grown tubers (Reyes et al., 2004). The commercial ACY colorants used were Antho-Red grape concentrate and purple carrot concentrate, kindly provided by Warner Jenkinson (St. Louis, MO) and by Artemis International, Inc. (Fort Wayne, IN), respectively.

2.2. Blanching of potatoes

After harvest, potatoes were stored at 2 °C until used for the experiments. Potatoes were then hand-washed in water, completely dried with paper towels and allowed to reach room temperature (~30 min). A Handy Steamer™ (Black & Decker, Inc., Shelton, CT) was used for blanching the potatoes. The steamer was filled with water and heated until boiling. Tubers were cut in half between the tuber ends and slices cut from each half using a kitchen vegetable slicer (thickness ~0.5 cm). Slices were placed on a plastic grid inside the steamer at a height ~7 cm. Analyses were performed in triplicates, using one tuber as a replicate. After each blanching time tested, samples were dipped in an ice-water bath to avoid heat accumulation, dried over paper towels and cut in small wedges. Samples were weighed according to each analysis and frozen at −20 °C until needed.

2.3. Quantification of peroxidase (POX) activity

Four-grams of recently blanched potatoes were weighed into plastic tubes, added PVPP (10% w/w) and frozen at −20 °C until analyzed. Samples were then homogenized at slow speed with 20 mL of 50 mM KH_2PO_4 buffer (pH 6.4) to a uniform consistency using an Ultra-Turrax T25 homogenizer (IKA Labortechnik; Staufen, Germany). Samples were kept in ice throughout the assay. The homogenate was filtered through 4-layers of cheesecloth and centrifuged at 31000*g* at 2 °C for 15 min. Enzyme extracts were transferred to clean test tubes, covered and assayed for POX activity. A 2.55 mL aliquot of the buffer and 0.1 mL of the enzyme extract were added to a 1-cm quartz cuvette. The spectrophotometer (Beckman DU 640) was blanked with this solution and absorbance measured at 420 nm. Immediately, 0.1 mL of 0.25% H_2O_2 and 0.25 mL of 0.1 M guaiacol were added to the cuvette, mixed, and the absorption at 420 nm was recorded for 3 min. The cuvette holder was kept at 25 °C using an Isotemp 1016S circulation bath (Fisher Scientific; Pittsburg, PA). One unit of enzyme activity was quantified as the increase in absorbance at 420 nm per minute. Results were expressed as % remaining POX activity for each blanching time to assess the effectiveness of blanching. Measuring residual POX activity would also assess the inactivation of other colour-degrading enzymes, since POX is known to be the most heat-stable enzyme (Williams, Lim, Chen, Pangborn, & Whitaker, 1986).

2.4. Preparation of aqueous ACY extracts

Frozen samples of blanched potato samples were homogenized with nanopure water (1:1 v/w) to a uniform consistency, filtered through 4-layers of cheesecloth and centrifuged using the same conditions described above. The clear supernatant was collected, and an aliquot of

Table 1
Preparation of buffers at different pH values

Buffer pH*	Volume of required solutions	Volume of acid or base [a]
1	25 mL of 0.2 M KCl	67 mL of 0.2 M HCl
2	25 mL of 0.2 M KCl	6.5 mL of 0.2 M HCl
3	50 mL of 0.1 M KHP	22.3 mL of 0.1 M HCl
4	50 mL of 0.1 M KHP	0.1 mL of 0.1 M HCl
5	50 mL of 0.1 M KHP	22.6 mL of 0.1 M NaOH
6	50 mL of 0.1 M KH_2PO_4	5.6 mL of 0.1 M NaOH
7	50 mL of 0.1 M KH_2PO_4	29.1 mL of 0.1 M NaOH
8	50 mL of 0.1 M KH_2PO_4	46.1 mL of 0.1 M NaOH
9	50 mL of 25 mM Borax	4.6 mL of 0.1 M HCl
10	50 mL of 25 mM Borax	18.3 mL of 0.1 M NaOH

[a] Final buffer volume completed to 100 mL with nanopure water.

the extract diluted in different pH buffers (Table 1; Robinson, 1986). The sample/buffer ratio used was such that the visible maximum absorption of the extract at pH 1 was about 0.7. This ratio was used to prepare the other pH solutions. In addition, sodium azide (0.1% g/v) was added to all the ACY solutions as a preservative. The final pH of the solutions was measured and adjusted by adding a few drops of NaOH (4–6 M) or HCl (1.5–4 M). Commercial colorant extracts were prepared in a similar way. All extracts were then allowed to equilibrate at room temperature in the buffer solutions for 1 h before taking any measurement (inserted to avoid confusion regarding sampling timing, see below). The aqueous ACY extracts were then transferred and capped into 8 mL clear glass vials (i.d. 1 cm).

2.4.1. Preparation of aqueous potato ACY extracts at different tinctorial strengths

Potato samples were homogenized with pH 1 buffer (1:1 v/w) and the pH adjusted to 3 using a few drops of 1.5 N HCl. Extracts were then centrifuged as described above and the supernatant collected in 8 mL clear glass vials (i.d. 1 cm). The visual colour of the extracts at different tinctorial strengths (TS) was evaluated with a spectrophotometer and a colorimeter. The TS of the extracts was calculated as the maximum absorbance in the visible range times the dilution factor (Wrolstad, 2000). Samples were analyzed in triplicates.

2.5. Thermal stability and visual colour attributes of aqueous ACY extracts

The thermal stability of the extracts was evaluated with a Hewlett Packard 8452A photodiode array spectrophotometer (Agilent Technologies; Palo Alto, CA) by measuring changes in absorption (ABS) at different wavelengths and comparing the colour retention (% ABS change) at maximum visible wavelength (λ_{max}) (Table 2). Measurements at 700 nm were taken to correct for turbidity. Browning index, a measurement of the changes in browning compounds, was determined as $(ABS_{420} - ABS_{700})/(ABS_{\lambda_{max}} - ABS_{700})$ (Jackman et al., 1987). Samples were analyzed in triplicates. In addition, the changes in visual colour were assessed with a Minolta CT-310 colorimeter (Konica Minolta Inc.; Mahwah, NJ) by measuring Hunter $L^*C^*H^\circ$ values (using Illuminant C). Although colour can be reported in different systems, lightness (L^*), chroma ($C* = \sqrt{a*^2 + b*^2}$), and hue ($H^\circ = \arctan b^*/a^*$) parameters were used since the most common $L^*a^*b^*$ coordinates do not express hue and chroma directly and are difficult to interpret independently (McGuire, 1992).

Table 2
Initial colour attributes of aqueous ACY extracts at pH 3

Extract	% Polymeric colour	Browning index	λ_{max} (nm)	Hunter $L^*C^*H^\circ$		
				L^*	C^*	H°
Purple-flesh potato	27	0.33	532	89	20	348°
Red-flesh potato	16	0.48	508	91	18	34°
Grape	22	0.35	526	90	18	359°
Purple carrot	16	0.39	526	75	47	10°

The effect of pH was evaluated during 4 weeks by storing the extracts at different pH conditions (pH 1–10), at room temperature (25 °C) and in the dark. The effect of temperature on the stability and visual colour of the extracts was evaluated in extracts at pH 3. Thermal degradation was evaluated at 25, 50, 80 and 98 °C after storing the extracts inside dark air-circulating ovens. Measurements were taken at time 0 h, 2 h, 12 h, 1 day, 2 days, 3 days, 1 week, 2 weeks and 4 weeks, for all the extracts, except for those stored at 98 °C that were sampled at 0, 30, 60, 90 and 120 min. The storage periods differed for each thermal treatment due to differences in ACY degradation rates. The polymeric colour of extracts at pH 3 was determined according to Wrolstad (1976). Briefly, 0.2 mL of 20% $K_2O_5S_2$ was added to 2.8 mL of the extract. As a control, 0.2 mL water was added to another 2.8 mL sample. Absorbance readings at 420 nm, λ_{max} and at 700 nm (to correct for turbidity) were recorded using a spectrophotometer. Colour density was calculated as $[(ABS_{420} - ABS_{700}) + (ABS_{\lambda_{max}} - ABS_{700})] \times DF$ (dilution factor) from the water-treated sample and polymeric colour was calculated as $[(ABS_{420} - ABS_{700}) + (ABS_{\lambda_{max}} - ABS_{700})] \times DF$ from the sulfite-bleached sample. The % polymeric colour was calculated as (polymeric colour/colour density) × 100.

First-order thermal degradation parameters of the different conditions tested were determined from the equation: $ABS/ABS_0 = e^{-kt}$. The temperature-dependence of k-values was determined from the Arrhenius equation: $k_T = K_0 e^{-E_a/RT}$, where E_a is the activation energy. Half-life values were calculated as $t_{1/2} = \ln(2)/k_T$, D-values were calculated as $D = \ln(10)/k_T$, z-values were calculated by plotting $\log D$ vs. T, and Q_{10}-values were calculated as $Q_{10} = 10^{10/Z}$. The changes in L^*, C^*, and H° values were modelled according to zero-order kinetics for the L^* and H° parameters (L^* or $H^\circ = kt$) and according to first-order degradation kinetics for the C^* parameter.

2.6. Graphs and statistical analysis

Summary statistics (mean and standard deviation) and graphs were obtained using Microsoft® Excel 2000 (Microsoft Corp., 1999). Linear and non-linear regressions were obtained using GraphPad Prism version 4.00 for Windows (GraphPad Software, San Diego, CA). Statistical analyses were performed with the GLM procedure from The SAS® System for Windows (version 8.1) (SAS Institute, Inc., 1999). Means were compared using Duncan's Multiple Range Test ($P < 0.05$).

3. Results and discussion

3.1. Blanching conditions prior to aqueous extraction

Purple- and red-flesh potatoes blanched for 3 min showed decreased POX activity by 98% for All Blue and CO94165-3P/P and 99% for NDC4069-4 and CO94183-1R/R. Aqueous extracts prepared from potatoes and blanched up to 1 min turned brown few minutes after extraction, while extracts blanched from 2 to 5 min did not show browning after 24 h of storage in the dark at 25 °C. Therefore, a blanching time of 3 min was used for all experiments.

3.2. Aqueous ACY extracts at different pH values

3.2.1. Effect of pH on initial visual colour

Although bright and attractive colours were initially observed, only the extracts at low pH (from 1 to 3) showed colour retention during the 4-week storage period at 25 °C (Fig. 1). The extracts from purple-flesh potato, red-flesh potato and grape concentrate showed red coloured solutions up to pH 3 ($H°$ from 348° to 49°). For pH values from 4 to 7, extracts were translucent (C^* from 6.9 to 3.1), and further increase in pH (from 8 to 10) yielded coloured extracts with greenish ($H°$ from 101° to 143°) or yellowish hues ($H°$ from 72° to 90°) (Fig. 1). On the other hand, purple carrot extracts were highly coloured throughout the pH range: bright reddish hues up to pH 4 ($H°$ from 4° to 14°), a shift towards bluish hues for pH values up to 8 ($H°$ from 353° to 293°), and reddish-brown hues for pH values of 9 and 10 ($H°$ from 18° to 40°) (Fig. 1). The colours observed in the alkaline region of the buffered extracts faded to yellow after 2–3 days.

3.2.2. Effect of pH on colour stability during storage

Changes in absorbance (% colour retention) allowed evaluating the stability of the coloured ACY extracts as affected by pH at 25 °C (Fig. 2). With pH increase, ACY

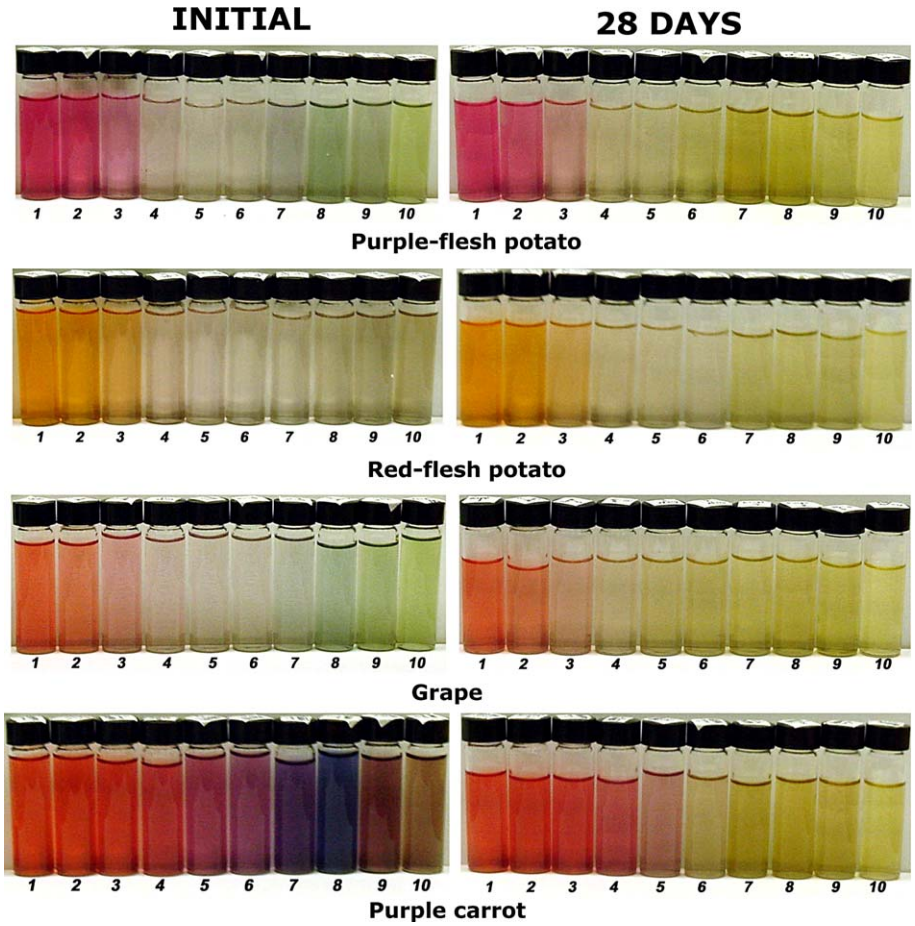

Fig. 1. Picture of aqueous anthocyanin extracts at different pH values 1 h after equilibration and after 28 days of storage at 25 °C in the dark.

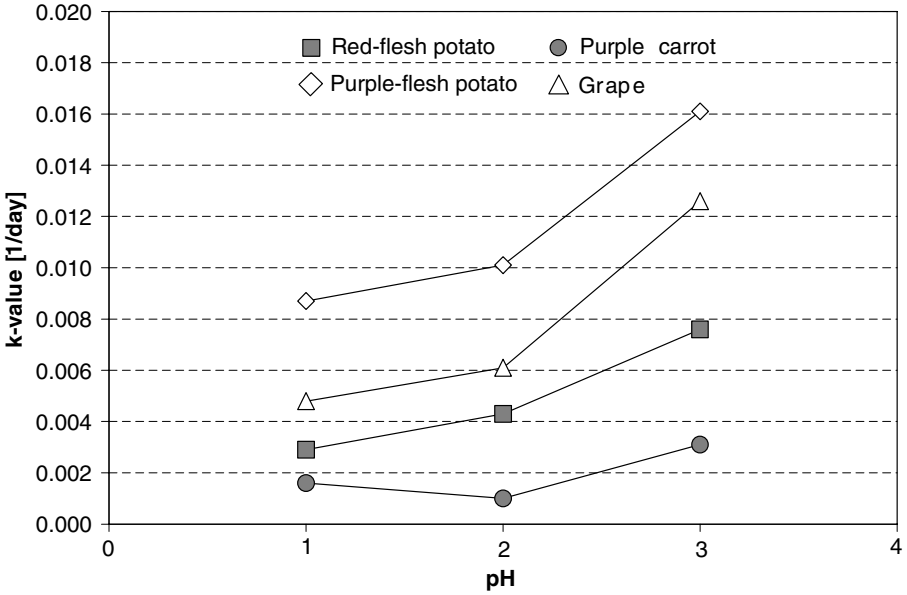

Fig. 2. Effect of pH on the colour stability of aqueous anthocyanin extracts after 28 days of storage at 25 °C in the dark.

stability decreased. At pH > 3, only purple carrot showed significant absorption at λ_{max} (~35–67% of that at pH 1), while the other extracts were very low (~4–13% of that at pH 1). After storage in the dark at 25 °C for 4 weeks, the colour retention for extracts at pH 3 was 68%, 86%, 68% and 92% for purple-flesh, red-flesh potato, grape and purple carrot extracts, respectively (data not shown). Changes in % colour retention due to pH followed first order kinetics ($R^2 > 0.8957$). The first order kinetics constant (k_{pH}) obtained, increased with pH in all extracts, confirming lower stability at higher pH. The k_{pH} values showed the following decreasing order for all pH values: purple-flesh potato > grape > red-flesh potato > purple carrot (Fig. 2). Based on our observations of pH stability, we further evaluated the thermal stability of aqueous extracts at pH 3 since most food products are in the pH range from 3 to 7 (Jackman & Smith, 1992).

3.3. Aqueous ACY extracts at pH 3

3.3.1. Temperature stability

Purple-flesh potato and grape extracts showed significantly lower stabilities than red-flesh potato and purple carrot extracts at 98 °C ($P < 0.05$) (Fig. 3). Similar trends were observed for extracts stored in the dark at 80, 50 and 25 °C (data not shown). In general, thermal degradation of the ACY extracts at pH 3 corresponded to first-order kinetics. The thermal degradation values (k_T) showed

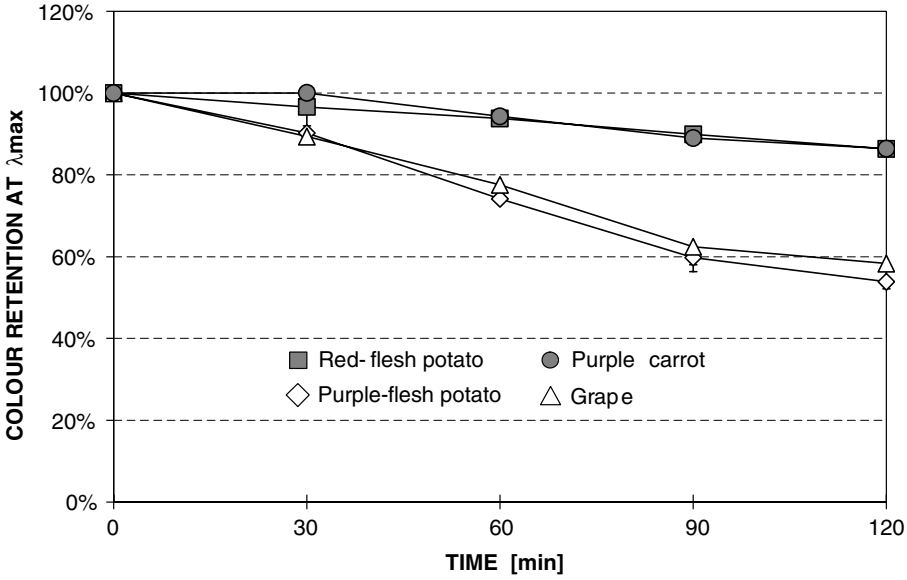

Fig. 3. Colour retention of aqueous anthocyanin extracts at pH 3 stored at 98 °C in the dark. Vertical lines represent the SD ($n = 3$).

the following descending order for each temperature: purple-flesh potato ≈ grape ≫ red-flesh potato ⩾ purple carrot. The k_T values obtained for each extract followed an Arrhenius relationship with temperature ($R^2 > 0.9744$; Table 3). According to this, the similar stability between purple-flesh potato and grape extracts is due to their similar E_a values. On the other hand, the higher stability of purple carrot extracts in relation to red-flesh potato extracts at lower temperatures compared to higher temperatures is due to the higher E_a value (81.34 kJ/mol) of purple carrot extracts (Table 3). Higher E_a and lower z-values are associated to increased temperature dependence of the ACY degradation rate. In general, the obtained E_a values (62.76–79.50 kJ/mol) are in similar range to those reported for ACY from cherry juice (Cemeroglu, Velioglu, & Isik, 1994). In the present study and in the work from Cemeroglu et al. (1994), all extracts showed increased E_a with corresponding higher K_0 values. However, in the present study, K_0 values were much lower (lower k values) indicating that the ACY extracts were more stable than cherry ACY. The obtained $t_{1/2}$ values for the temperature range 25–98 °C, confirm that purple-flesh potato and grape extracts were less stable compared to red-flesh potatoes and purple carrot extracts (Table 3). For example, at 25 °C purple carrot extracts showed a $t_{1/2}$ value 2–5 times higher compared to the other extracts.

Thermal degradation of ACY leads to colour loss and appearance of brown coloured compounds (Starr & Francis, 1968) but the precise mechanism is still unclear. However, possible events include chalcone formation as first step in the process (Markakis, Livingston, & Fellers, 1957), loss of glycosyl moieties and α-diketone formation (Adams, 1973). In addition, formation of end products including coumarin derivatives (Hrazdina, 1971; Jackman & Smith, 1992), benzoic acid derivatives (Seeram, Bourquin, & Nair, 2001) and trihydrobenzaldehyde (Furtado, Figueiredo, Chaves das Neves, & Pina, 1993) has been reported. In the present study, ACY degradation involves in part polymerization and brown pigment formation. For example, after 2 h at 98 °C, the % polymeric colour value was 50%, 26%, 35% and 18% for purple-flesh potato, red-flesh potato, grape and purple carrot extracts, respectively. Similarly, the browning index was 0.75, 0.55, 0.78 and 0.44 for purple-flesh potato, red-flesh potato, grape and purple carrot extracts, respectively. These results indicate that ACY polymerization and browning compound formation was more severe for purple potato and grape extracts compared to red potato and carrot extracts (Table 2).

In general, the stability of the extracts to temperature was similar to that observed in the pH studies. The difference in stability observed among the ACY extracts could be related to the chemical structure of the ACY present in the extracts (Von Elbe & Schwartz, 1996) including, the types of aglycones (Keith & Powers, 1965), types of sugar moieties (Attoe & von Elbe, 1981), the complexity of sugar residues (Dyrby, Westergaard, & Stepelfeldt, 2001), presence of acylating structures (Bridle & Timberlake, 1997) or even the presence of other phenolic compounds in the extracts (Del Pozo-Insfran, Brenes, & Talcote, 2004).

3.3.2. Changes in visual colour attributes

There were noticeable changes in $L^*C^*H^\circ$ parameters for all extracts, confirming the degradation of visual colour attributes in the ACY extracts. However, these changes were less evident in the extracts with higher stability (red-flesh potato and purple carrot extracts). Extracts at pH 3

Table 3
Thermal degradation parameters of aqueous anthocyanin extracts at pH 3

Extracts	Temperature (°C)	k_T (1/h)[a]	D-value[b]	$t_{1/2}$[b]	z-Value (°C)	Q_{10}	Arrhenius equation	
							E_a (kJ/mol)[a]	K_0 (1/h)
Purple-flesh potato	25	0.0007 (0.9976)	137 d	41 d	28.4	2.25	72.49 (0.9744)	4.12E + 09
	50	0.0118 (0.9258)	8.6 d	2.5 d				
	80	0.0463 (0.9634)	2.1 d	15 h				
	98	0.3259 (0.9836)	7.1 h	2.1 h				
Red-flesh potato	25	0.0003 (0.9995)	297 d	89 d	31.5	2.08	66.7 (0.9962)	1.73E + 08
	50	0.0034 (0.9426)	28 d	8.4 d				
	80	0.0206 (0.9461)	4.7 d	34 h				
	98	0.0725 (0.9953)	32 h	9.6 h				
Grape	25	0.0006 (0.9842)	157 d	47 d	28.0	2.28	75.03 (0.9910)	7.98E + 09
	50	0.0057 (0.9436)	17 d	5.0 d				
	80	0.0453 (0.9472)	2.1 d	15 h				
	98	0.2853 (0.9842)	8.1 h	2.4 h				
Purple carrot	25	0.0001 (0.9921)	717 d	216 d	26.0	2.44	81.34 (0.9950)	2.76E + 10
	50	0.0025 (0.9904)	38 d	11 d				
	80	0.0212 (0.9999)	4.5 d	33 h				
	98	0.1004 (0.9820)	23 h	6.9 h				

[a] Coefficient of determination (R^2) shown in parenthesis.
[b] Time units: h = hours; d = days.

and exposed to 98 °C showed that values of L^* and H° increased, and C^* decreased with time (Fig. 4). Similar trends were observed at other temperatures. The L^* and H° parameters increased through time following a zero-order reaction model, whereas the C^* parameter decreased following first-order kinetics. The increase in L^* values would be related to the formation of translucent extracts due to the colour fading, while the changes in H°, would

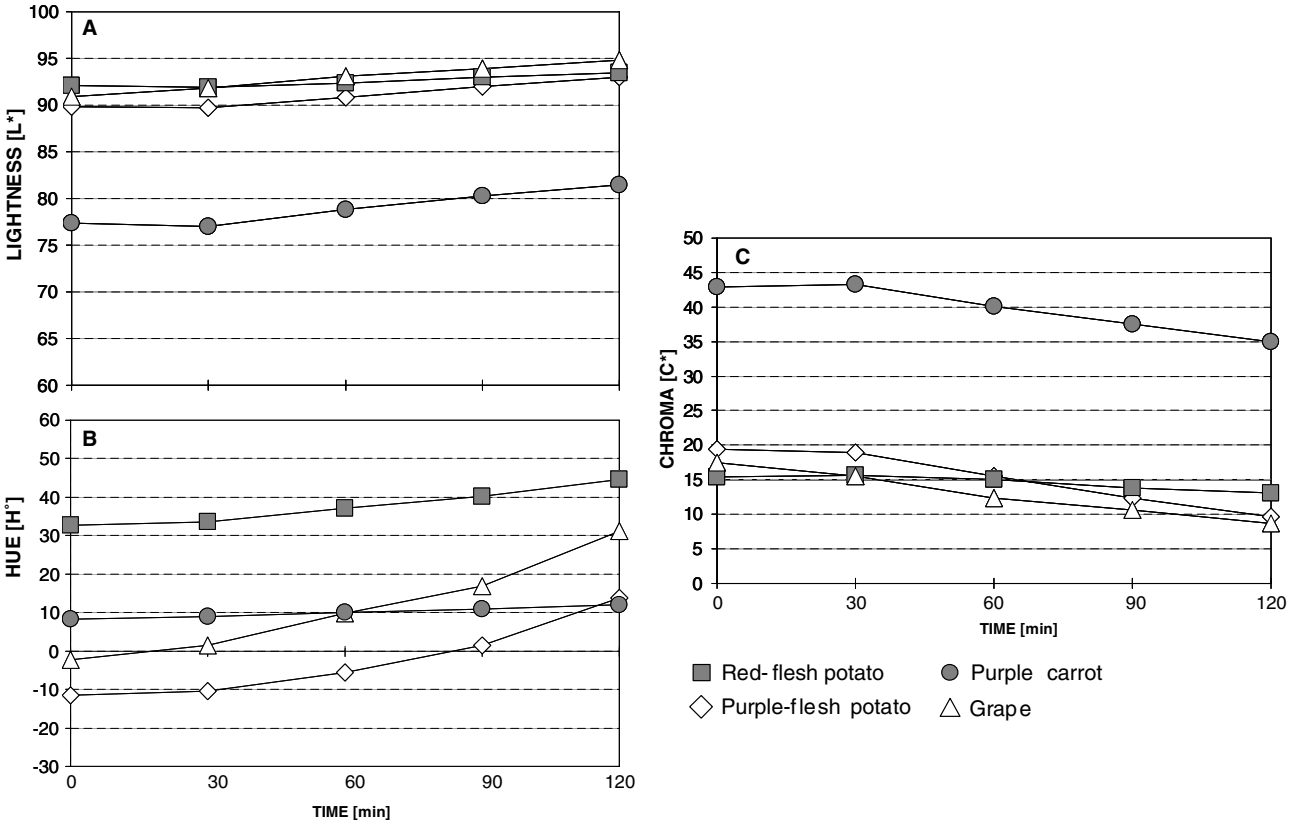

Fig. 4. Hunter lightness (A), hue (B) and chroma (C) parameters of aqueous anthocyanin extracts at pH 3 stored at 98 °C in the dark. Negative H° values were calculated as $H^\circ - 360^\circ$.

Table 4
Thermal degradation parameters for the chroma parameter of aqueous anthocyanin extracts at pH 3

Extracts	Temperature (°C)	k_{C^*} (1/h)[a]	D-value[b]	$t_{1/2}$[b]	z-value (°C)	Q_{10}	Arrhenius equation	
							E_a (kJ/mol)[a]	K_0 (1/h)
Purple-flesh potato	25	0.0008 (0.9872)	127 d	38 d	27.16	2.33	76.37 (0.9845)	2.19E + 10
	50	0.0145 (0.8608)	6.6 d	2.0 d				
	80	0.0756 (0.9777)	1.3 d	9.2 h				
	98	0.4396 (0.9977)	5.2 h	1.6 h				
Red-flesh potato	25	0.0002 (0.9486)	452 d	136 d	27.10	2.34	74.24 (0.9571)	2.96E + 09
	50	0.0058 (0.9722)	17 d	5.0 d				
	80	0.0174 (0.9480)	5.5 d	40 h				
	98	0.1244 (0.9886)	18.5 h	5.6 h				
Grape	25	0.0007 (0.9768)	136 d	41 d	27.51	2.31	76.61 (0.9958)	1.78E + 10
	50	0.0070 (0.7559)	14 d	4.1 d				
	80	0.0652 (0.9400)	1.5 d	11 h				
	98	0.3498 (0.9911)	6.6 h	2.0 h				
Purple carrot	25	0.0001 (0.9885)	1175 d	354 d	23.06	2.71	88.79 (0.9744)	4.14E + 11
	50	0.0036 (0.9985)	27 d	8.1 d				
	80	0.0193 (0.9997)	5.0 d	36 h				
	98	0.1412 (0.9993)	16 h	4.9 h				

[a] Coefficient of determination (R^2) shown in parenthesis.
[b] Time units: h = hours; d = days.

be associated to the formation of yellow chalcone species ($H°$ towards 90°). On the other hand, the decrease in C^* values would be related to the degradation of monomeric ACY. The kinetic rate constants for L^* (k_{L^*}), C^* (k_{C^*}) and $H°$ ($k_{H°}$) followed an Arrhenius relationship with temperature (Tables 4 and 5). The obtained k_{L^*} values were similar among the extracts for each temperature. The obtained k_{C^*} values were similar between purple-flesh

Table 5
Thermal degradation parameters for the lightness and hue parameter of aqueous anthocyanin extracts at pH 3

Extracts	Temperature (°C)	Lightness			Hue		
		k_{L^*} (1/h)[a]	Arrhenius equation		k_{H^0} (1/h)[a]	Arrhenius equation	
			E_a (kJ/mol)[a]	K_0 (1/h)		E_a (kJ/mol)[a]	K_0 (1/h)
Purple-flesh potato	25	0.0039 (0.9150)	72.76 (0.9499)	2.35E + 10	0.0238 (0.9981)	75.51 (0.9446)	7.04E + 11
	50	0.0592 (0.8975)			1.093 (0.9925)		
	80	0.1799 (0.8143)			4.191 (0.9703)		
	98	2.176 (0.9992)			12.50 (0.8986)		
Red-flesh potato	25	0.0022 (0.9997)	72.32 (0.9680)	1.13E + 10	0.0093 (0.9887)	78.46 (0.9734)	7.55E + 11
	50	0.0321 (0.9725)			0.3007 (0.9991)		
	80	0.1208 (0.9546)			1.536 (0.9995)		
	98	1.070 (0.9891)			6.042 (0.9565)		
Grape	25	0.0039 (0.9643)	73.44 (0.9713)	2.90E + 10	0.0276 (0.9990)	76.24 (0.9728)	8.68E + 11
	50	0.0462 (0.8214)			0.7602 (0.9918)		
	80	0.2115 (0.8727)			3.226 (0.9898)		
	98	2.006 (0.9961)			16.42 (0.9542)		
Purple carrot	25	0.0020 (0.9990)	82.63 (0.9780)	3.63E + 12	0.0012 (0.9999)	91.20 (0.9898)	1.50E + 13
	50	0.0566 (0.9959)			0.0432 (0.9969)		
	80	0.3144 (0.9934)			0.4479 (0.9966)		
	98	2.972 (0.9912)			1.920 (0.9983)		

[a] Coefficient of determination (R^2) shown in parenthesis.

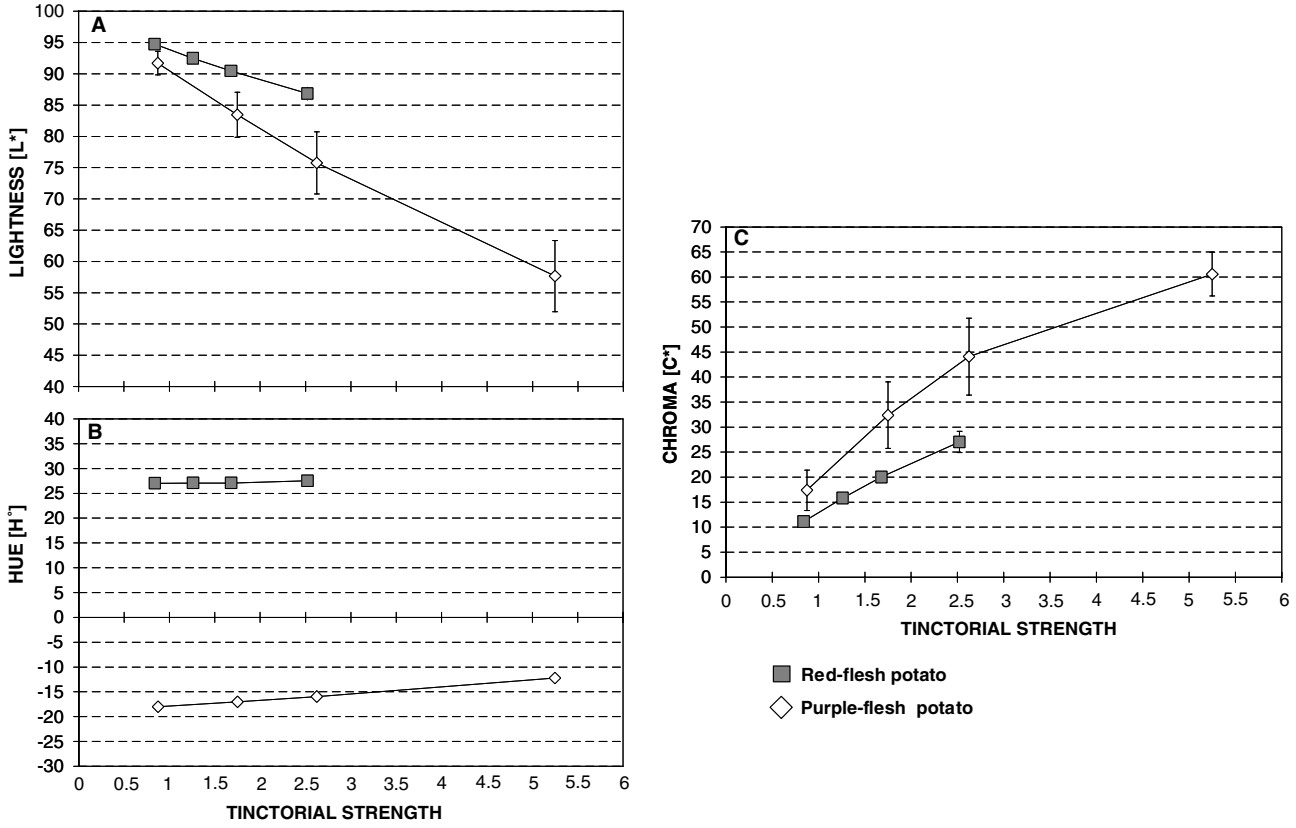

Fig. 5. Effect of tinctorial strength on the Hunter lightness (A), hue (B) and chroma (C) parameters of aqueous potato anthocyanin extracts at pH 3.

potato and grape extracts, while those of red-flesh potato were similar to purple carrot extracts for each temperature. On the other hand, the obtained k_{H° values showed the following descending order for each temperature: purple-flesh potato ≈ grape > red-flesh potato ⩾ purple carrot. The obtained $t_{1/2}$ values for C^* in the temperature range 25–98 °C, confirmed that purple-fleshed potato and grape extracts were less stable compared to red-fleshed potatoes and purple carrot extracts (Table 4). For example, at 25 °C purple carrot extracts showed a $t_{1/2}$ value for C^* 1.6–8.3 times higher compared to the other extracts.

3.3.3. Effect of tinctorial strength

When aqueous extracts at pH 3 were prepared at different tinctorial strengths, L^* decreased and both C^* and H° increased with colorant concentration (Fig. 5). Purple-flesh potato extracts showed bluish hues (~345°) similar to those of red cabbage (Malien-Aubert et al., 2001), whereas red-flesh potato extracts showed reddish hues (~27°) similar to those from red radish and FD&C Red #40 (Rodríguez-Saona et al., 1998).

4. Conclusions

The results from the present study provide detailed information regarding the changes in kinetic stability and colour of aqueous ACY extracts from purple- and red-flesh potatoes as affected by pH and temperature during storage. Higher stability was achieved by storing extracts at low pH and temperature conditions. The stability of ACY extracts to pH (⩽3) and the thermal degradation of ACY (at pH 3) followed first order kinetics. Commercial purple carrot extracts showed the highest stability followed by red-flesh potato extracts, whereas purple-flesh potato and commercial grape were the least stable extracts. Red-flesh potato ACY extracts showed similar hues to FD&C Red #40, and purple-flesh potato extracts had similar hues to red cabbage. Visual colour of the potato extracts was markedly influenced by tinctorial strength. This study supports the potential use of coloured potatoes as a source of natural colorants for the food industry by predicting the degradation changes of aqueous ACY extracts from potatoes under different storage temperatures and periods.

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