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ORIGINAL PAPER

Degradation Kinetics of Anthocyanin of Traditional and Low-Sugar Blackberry Jam

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Abstract The objective of this study was to monitor the stability of anthocyanin and phenolic compounds contained in two formulations of blackberry jam (traditional and low-sugar) during storage. For that purpose, jams were prepared with varying amounts of hydrocolloids and investigated as to pH, total soluble solids, water activity, total acidity, total anthocyanins and total polyphenols. In order to accompany and assess the levels of phenolic compounds and colour (L^*, a^* and b^*) changes, the samples were stored for 180 days at two different temperatures (10 and 25 °C). The Arrhenius model was used to determine the relationship between the reaction rate (k) at the different storage temperatures, yielding activation energy values of 19 and 12 kcal/mol and Q_{10} values of 3.0 and 2.0 for traditional and low-sugar jams, respectively. The results show that by the end of the storage time investigated, the anthocyanin compounds had been partially degraded, with the greatest loss being observed in traditional jam stored at 25 °C. Colour stability was also lower in traditional jam as compared to the low-sugar product.

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Nomenclature

TSS	Total soluble solids (grammes citric acid per 100 g jam)
Aw	Water activity
ATT	Total acidity expressed as grammes of citric acid per 100 g jam
AT	Total anthocyanins (milligrammes per 100 g jam)
PFT	Total polyphenols (milligrammes per 100 g jam)
k_T	Reaction rate at temperature T (day^{-1})
k_{T-10}	Reaction rate at a temperature 10 °C lower than T (day^{-1})
Q_{10}	Quotient or general relationship between a reaction rate at a certain temperature and at a temperature 10 °C lower
Ea	Activation energy (kilocalories per mole)
VP	Shelf life (days)

CIELAB Parameters

L^*	Luminosity
a^*	Redness–greenness
b^*	Yellowness–blueness
ΔE	Total colour difference

Introduction

Blackberries are an important source of natural antioxidants, such as flavonoids, anthocyanins and phenolic compounds. Viewed from this perspective, products made from this fruit might be considered functional foods. The fruit is of significant nutritional value since it is a good source of vitamins A and B and minerals such as Fe^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, K^{+1}, Ca^{2+} and $(PO_4)^{3-}$. In addition, blackberries have been reported to have a number of functional properties, mostly associated with disease prevention (Jiao and Wang 2000). Blackberries are a great source of natural antioxidants, flavonoids, anthocyanins, for the most part cyanidin 3-glucoside and several phenolic compounds. The composition of blackberries also contains hydroxycinnamates, such as caffeic acid (Heinonen et al. 1998).

Due to their high levels of compounds with antioxidant properties, recent studies have increasingly linked the intake of fruits and vegetables to reduced risk for the development of certain chronic degenerative diseases. In view of the functional properties of anthocyanins, several studies are being conducted focusing on determining their exact content and on correlating the anthocyanin levels with antioxidant activity in an attempt to enhance the use of these natural pigments in the food processing and cosmetics industry (Delgado-Vargas et al. 2000).

According to Moraes et al. (2007), the blackberry exhibits high antioxidant activity compared to myrtle, which is a much studied fruit and commonly used as a basis for comparison. The authors also reported on an anti-inflammatory effect of blackberry extract—a fact not devoid of interest, as it is believed that cancer is somehow related to a chronic inflammatory process.

The blackberry is thus considered a functional fruit, that is, in addition to the basic nutritional characteristics, when consumed as a part of the regular diet, it produces a physiological/metabolic or beneficial effect on human health, with the advantage that it may be consumed freely without any medical supervision. The consumption of green leafy vegetables and fruits such as blackberries, combined with a healthy lifestyle, including a balanced diet and regular physical exercise, may prevent some diseases.

Anthocyanins in aqueous solutions exist in different basic structures in equilibrium, which, depending on the pH of the solution, may present different forms. An acidic pH is favourable to the coloured form of these pigments. Temperature is an important factor in the degradation of the colour of anthocyanins (Delgado-Vargas et al. 2000; Ou et al. 2002). During heating, degradation and polymerization generally cause discolouration of the pigments (Markakis 1982).

Studies on the composition of blackberry jam (da Mota 2006) and grape jam made from the Isabel (*Vittis labrusca*) and Refosco (*Vittis vinefera* L.) grapes (Falcão et al. 2007) investigated the level of anthocyanins and phenolic compounds during a preset storage time. The results of these studies show that there are losses of phenolic compounds and anthocyanins during the processing of jams and throughout their shelf life. Losses were greater during the first 40 days and then diminished with time.

Cisse et al. (2009) investigated the impact of temperature (30 to 90 °C) on the degradation of anthocyanins in blood orange juice, two tropical highland blackberry juices and four roselle extracts. The data show that thermal degradation of the anthocyanins can be described in terms of first-order reaction kinetics. Values of activation energies were 66 and 37 kJ/mol for blood orange and blackberry, respectively, and 47–61 kJ/mol for roselle extracts.

Response surface methodology (RSM) was used to investigate the effects of ozone concentration (percent *w*/*w*) and treatment time (minutes) on the anthocyanin content and colour of fresh blackberry juice (Tiwari et al. 2009). Predicted models were found to be significant ($p<0.001$) with regression coefficients (R^2) of 0.89, 0.82, 0.95, 0.86 and 0.97 for L^*, a^*, b^*, ΔE and anthocyanin content, respectively.

The effect of storage time and temperature on degradation of bioactive compounds such as ascorbic acid, anthocyanins, total phenols, colour and total antioxidant capacity of strawberry jam were investigated by Patras et al. (2009). The results indicated that lightness (L^*) value decreased significantly ($p<0.05$) over 28 days of storage at 4 and 15 °C with lower values measured at higher temperatures. The results showed greater stability of nutritional parameters at 4 °C compared to 15 °C.

In a recent study, Watanabe et al. (2011) found that the stability of anthocyanin in strawberry jam affects not only the functions but also the colour of the jam. The authors concluded that impregnation of strawberries with a sucrose solution is effective in improving these properties. In the future, more detailed information about the behaviour of sucrose in the jam, such as inversion from sucrose to glucose and fructose, will be needed to enable more effective application of the impregnated jam. Impregnation should be available for the preservation of fruits and the various processed foods containing fruits.

The processing of blackberry fruits into jam may be a form to add value to excess production from regular crop cycles, generating income and jobs. However, there are some doubts as to the retention of phytochemicals contained in the fresh fruit during processing and throughout the shelf life of the product (Antunes et al. 2003).

For that reason, the objective of this study was to assess the stability of anthocyanins and colour during the shelf life of two formulations of blackberry jams (traditional and low-sugar).

Material and Methods

Material

Experiments were performed with frozen (−18 °C) blackberries of the commercial DeMarchi brand. In Brazil, there are a number of companies that specialize in producing tailor-made pulps for specific markets or according to the specifications of customers: jams, juices or ice creams. Thus, the study was conducted using raw materials that are representative of a real process within a typical jam making situation.

The jams were obtained by conventional processing in open vats (*T*=95 °C). Processing time was sufficient to reach the desired levels of soluble solids, that is, 64 °Brix for the traditional jam and 43 °Brix for the low-sugar jam. The jam production flow chart is presented in Fig. 1. In the process, a combination of pectin (*Cpkelco*), citric acid (up to reaching pH 3.0) and potassium sorbate (in the case of the low-sugar formulation*)* was added to the fruits. The formulation of low-sugar blackberry jam includes clarified and concentrated (70 °Brix) apple juice to increase soluble solids. The product, produced by Fischer S/A, has a typical, naturally golden colour, which derives from the degree of concentration of the fresh and pure apple juice, made without the addition of sugar, preservatives, pigments or any other additives. In this experiment, the raw material used was characterized, particularly in the light of the fact that in a country like Brazil, purity and quality of raw materials tend to vary excessively from one source of supply to another.

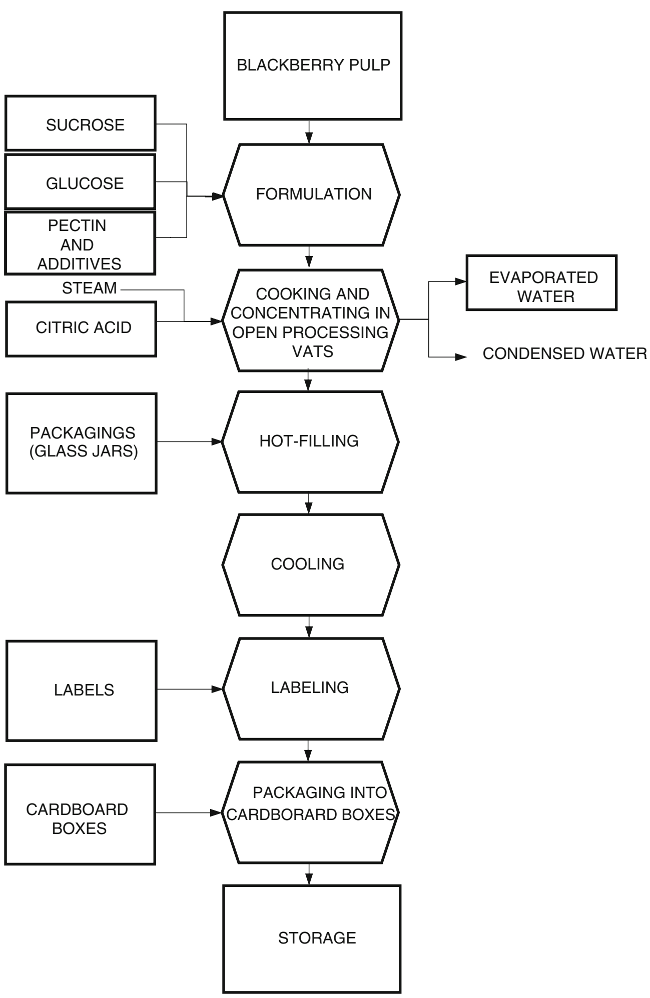

Fig. 1 Flow chart blackberry jam production

With the objective to compare the traditional and low-sugar blackberry jam produced for the purpose of this study with similar commercial products purchased at local retail outlets, each product type was subjected to sensory tests by the affection-related sensory ranking method. The sole purpose of the test was to establish a difference between the samples, or, in other words, verify whether the sensory characteristics of the products were similar to those of products commonly found in the market and also preference. A consumer panel of 30 potential buyers of this particular kind of product received four coded samples in a balanced complete block design, with three of the samples being commercial products and one an experimental test sample. The results were analysed by the Friedman method and consequently using the Newell and Mac Farlane table to get the critical difference between the total rank sums among the number of samples tested and the number of assessments obtained. If two samples differ from each other by a number greater than or equal to the table value, it is assumed that there is a significant difference between the two samples at the level of significance tested (Meilgaard et al. 1987).

It was concluded that the samples studied achieved intermediate preference ratings. It should be stressed that there is no product on the market identical to the product investigated in our study. All commercial samples contained added sweeteners to enhance the sweet flavour.

The final formulations are described in Table 1.

The samples were hot-filled into clear glass jars with a holding capacity of 267 ml, sealed with an ARJEK BR-1 63 metal lid (Rojek Ltda.) and subsequently stored in controlled temperature dark storage rooms at 10 °C (283.15 K)—for control and at 25 °C (298.15 K)—to simulate average retail storage temperature.

Methods

Total Soluble Solids

The total soluble solids (TSS) content was determined by refractometry, according to the method described by Carvalho et al. (1990), using a bench-top optical refractometer Abbe 10450 (AO Abbe Refractometer, USA). This analysis was performed in triplicate.

pH and Total Acidity

The pH was determined using a potentiometer Digimed DM 20.

Total acidity (ATT) was determined by the acidimetric method, as prescribed by AOAC Standard Test Method 942.15B (AOAC 2006). This analysis was performed in triplicate.

Table 1 Formulations of traditional and low-sugar blackberry jams

	Traditional	Low-sugar
Composition	Proportion (%)	Proportion (%)
Blackberry	60.0	55.0
Saccharose	30.0	5.0
Glucose	9.8	–
Pectin ATM 105	0.2	–
Apple juice[a]	–	39.0
Pectin LM 102	–	0.8
Calcium phosphate	–	0.07
Potassium sorbate	–	0.005

[a] Clarified apple juice concentrate—70 °Brix (*Fischer S/A*)

Water Activity

The jam samples were filled into the plastic sample cup in a manner as to completely cover the bottom of the cup before placing the cup in the reading chamber of the equipment. The water activity value (Aw) of each sample was determined in triplicate, at 25 °C, using an Aqualab CX-2 hygrometer (Decagon, EUA).

Colorimetry

Colour analysis was performed with a CR-400 colorimeter (Minolta, Japan) in accordance with the CIELAB system. Colour measurement was performed using the d/0 configuration and C illuminant.

The results were expressed in L^*, a^* and b^* values, where the L^* values (representing luminance or brightness) run from black (0) to white (100), while a^* parameter values vary from green (−60) to red (+60) and the b^* parameter values from blue to yellow, i.e., from −60 to +60, respectively.

For the purpose of colour measurement, sample material was spread out onto a Petri plate in such a way as to not allow any voids. This method was suggested by the manufacturer of the equipment. Colour was measured at ten different points located at the lower part of the Petri plate (Konica Minolta 2007).

Monitoring of instrumental colour stability throughout shelf life was accomplished by assessing the colour using the same method described above. Instrumental colour of the samples stored at 10 °C (control) and 25 °C (commercial) was measured every 30 days in triplicate.

Total Polyphenols and Total Anthocyanins

The anthocyanin pigments were extracted from the jams by maceration with 70% acetone for 1 h. Next, the extracts were passed through Whatman no. 2 filter paper and subsequently subjected to analysis for the determination of total polyphenols and total anthocyanins, as prescribed by AOAC Standard Test Method 2005.02 (AOAC 2006).

The total polyphenols content was determined by the Folin-Ciocalteu method, as described by Kiralp and Toppare (2006); 1 mL extract was diluted in 13 mL deionized water and added with 1 mL Folin-Ciocalteu reagent and left o stand for 5 min, after which 10 mL of a 7% ($w\ v^{-1}$) saturated Na_2CO_3 solution was added. After 2 h, absorbance was read at 750 nm using a visible–UV absorption spectrophotometer. The level of total polyphenols was determined using a gallic acid calibration curve (0–500 mg L^{-1}). The results were expressed as milligrammes gallic acid equivalent per 100 g jam (fresh weight).

The total anthocyanin content was determined by the pH differential method. Absorbance was measured using visible–UV absorption spectrophotometer at wavelengths of 532 and 700 nm in buffer solutions pH 1.0 and 4.5. Total cyanin was calculated by Eq. 1 using the molar extinction coefficient of cyanidin 3-glucoside (26.900) and molecular weight 449.2 g mol^{-1}.

$$\text{Abs} = \left[\left(A = (A_{\text{lmax}} - A_{700})_{\text{pH1.0}} - (A_{\text{lmax}} - A_{700})_{\text{pH4.5}}\right],\right. \quad (1)$$

The results were expressed as milligrammes cyanidin 3-glucoside equivalent per 100 g jam (Giusti and Wrolstad 2001). This analysis was performed in triplicate.

Calculation of Kinetics Parameters

The total colour difference (ΔE) was calculated from the L^*, a^* and b^* values according to the following equation:

$$\Delta E = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{1/2} \quad (2)$$

where Δ is the difference between the values of each colour parameter of the initial sample (time zero) and the stored sample.

The data relative to the degradation of anthocyanins and total colour change (ΔE) of the samples were used to determine the reaction order of degradation and to calculate the respective reaction rates (k) at the different temperatures studied.

Table 2 Characterization of blackberry

SST (°Brix)	pH	ATT	AT	PFT
7.3±0.1	3.11±0.01	1.179±0.049	52.33±0.28	203.12±1.25

Table 3 Physical–chemical characteristics of traditional blackberry jam stored at the temperatures of 10 and 25 °C throughout shelf life

T (°C)	Time (days)	pH	ATT	(°Brix)	AT	PFT	Aw
	0	3.25bB±0.04	0.877cC±0.004	64.3aA±1.7	6.30aA±0.34	197.81aA±7.56	0.785bB±0.024
10	30	3.36a±0.01	0.879c±0.001	64.4a±1.6	5.38b±0.52	195.00a±1.04	0.816a±0.003
	60	3.24cb±0.01	0.887b±0.005	64.1a±0.1	5.28b±0.15	187.27ba±0.20	0.823a±0.001
	90	3.23cb±0.01	0.890b±0.005	64.3a±0.3	4.97cb±0.50	183.14b±13.05	0.823a±0.016
	120	3.22cb±0.01	0.900a±0.002	64.4a±0.1	4.60 cd±0.03	165.10c±1.37	0.819a±0.006
	150	3.21c±0.01	0.901a±0.001	64.3a±0.1	4.11ed±0.29	165.12c±0.21	0.813a±0.004
	180	3.23cb±0.0.1	0.903a±0.005	64.1a±0.2	3.99e±0.09	163.73c±1.80	0.815a±0.001
25	30	3.44A±0.0.1	0.876 C±0.001	64.6A±1.6	3.65B±0.01	190.15BA±6.21	0.810A±0.001
	60	3.24B±0.0.1	0.898B±0.008	64.7A±0.3	2.74 C±0.11	179.1BC±6.53	0.814A±0.006
	90	3.22B±0.0.1	0.898B±0.001	64.3A±0.1	1.20D±0.00	169.3 DC±3.03	0.821A±0.004
	120	3.23B±0.0.1	0.912A±0.001	64.2A±0.2	1.05D±0.00	159.72DE±0.37	0.818A±0.001
	150	3.22B±0.0.1	0.900B±0.006	64.2A±0.1	0.80D±0.01	148.57E±1.70	0.815A±0.003
	180	3.22B±0.0.1	0.899B±0.001	64.3A±0.1	0.72D±0.01	147.59E±1.01	0.815AA±0.001

Results are expressed as mean±standard deviation of three measurements (n=3). Means compared by Tukey's minimum significant difference test at the 5% error level. Means within each column followed by the same lowercase letters are not significantly different at the 5% level for the temperature of 10 °C and means followed by the same uppercase letters do not significantly differ at the 5% level for the temperature of 25 °C

The order of reaction was determined from the best fit (best correlation coefficient) of the parameters evaluated vs. storage time.

The activation energy (Ea), together with the quotient or general relationship between a reaction rate at a certain temperature and at a temperature 10 °C lower (Q_{10}) (Teixeira Neto et al. 2010), was calculated at the end of VP using the following equations:

$$Q_{\Delta T} = \frac{k_{T_2}}{k_{T_1}} = Q_{10}^{\frac{\Delta T}{10}} = \frac{VP_{T_1}}{VP_{T_2}} \qquad (3)$$

where T_2=25 °C and T_1=10 °C

$$Q_{10} = \frac{k_T}{k_{T-10}} = \frac{VP_{T-10}}{VP_T} \qquad (4)$$

Where T (°C)

$$\mathrm{Ea} = 0.46 \times T^2 \times \log Q_{10} \qquad (5)$$

Where T (Kelvin)

Table 4 Physical–chemical characteristics of low-sugar blackberry jam stored at the temperatures of 10 and 25 °C throughout shelf life

T (°C)	Time (days)	pH	ATT	(°Brix)	AT	PFT	Aw
	0	3.91aA±0.05	1.066fE±0.007	42.8aA±0.5	23.24aA±1.03	201.30aA±5.43	0.930aA±0.003
10	30	3.83c±0.01	1.063g±0.003	42.8a±0.4	17.32b±0.35	193.35a±3.62	0.935a±0.004
	60	3.86bc±0.01	1.086e±0.011	42.3a±0.5	16.58c±0.41	189.16a±0.63	0.937a±0.002
	90	3.86bc±0.01	1.087d±0.0015	42.4a±0.1	11.20d±0.08	174.16b±2.23	0.932a±.0001
	120	3.87b±0.01	1.094c±0.003	42.1a±0.1	10.24e±0.04	164.06b±5.63	0.932a±0.001
	150	3.85bc±0.01	1.095b±0.004	42.2a±0.1	10.06e±0.02	164.01b±0.01	0.932a±0.001
	180	3.88ba±0.01	1.098a±0.001	42.1a±0.2	9.94e±0.13	163.07b±0.47	0.933a±0.001
25	30	3.87B±0.01	1.068D±0.009	42.6A±0.4	10.51B±1.16	193.34A±2.08	0.936A±0.001
	60	3.87B±0.01	1.091C±0.007	42.2A±0.2	5.52C±0.05	165.54B±10.34	0.938A±0.005
	90	3.88BA±0.01	1.091C±0.006	41.5A±0.3	3.45D±0.55	158.17B±22.96	0.933A±0.001
	120	3.86B±0.01	1.093B±0.001	42.2A±0.1	2.04E±0.50	151.79B±0.34	0.931A±l0.001
	150	3.86B±0.01	1.093B±0.002	42.2A±0.1	1.91E±0.21	151.8B±1.51	0.931A±0.001
	180	3.87B±0.01	1.098A±0.001	42.3A±0.2	1.83E±0.03	151.88B±0.48	0.931A±0.001

Results are expressed as mean±standard deviation of three measurements (n=3). Means compared by Tukey's minimum significant difference test at the 5% error level. Means within each column followed by the same lowercase letters are not significantly different at the 5% level for the temperature of 10 °C and means followed by the same uppercase letters do not significantly differ at the 5% level for the temperature of 25 °C

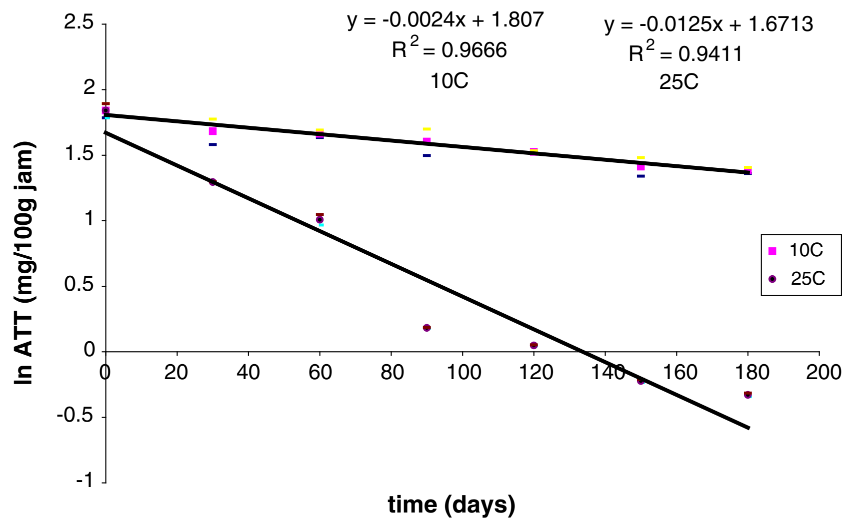

Fig. 2 Degradation of total anthocyanins in traditional jam stored at the temperatures of 10 and 25 °C

Statistics Analysis

In statistical analysis, software SAS (1993) was used with an analysis of variance (ANOVA) and means test (Tukey) at $p<0.05$.

Results and Discussion

The total anthocyanin levels in blackberry in this study (Table 2) were lower than those found by da Mota (2006), who reported levels ranging from 133 to 98 mg/100 g pulp for seven different cultivars of this fruit. This is probably due to the fact our study was performed on commercial samples, that is, sample material composed of fruits of different cultivars and at different ripening stages. The same author states that the pulp of blackberry should be considered a source of anthocyanin compounds, since the levels found in blackberry are much higher than those present *in natura* fruits of other red fruits, such as strawberry (30 to 60 mg/100 g), pitanga roxa (*Eugenia uniflora*) or Surinam or Cayenne cherry (16.23 mg/100 g), or acerola (3.79 to 59.74 mg/100 g). On the other hand, Falcão et al. (2007) found values for the anthocyanin content in grape extract between 25.8 and 70.9 mg/100 g.

The results contained in Tables 3 and 4 show that the values of pH, total titrable acidity and TSS of both jam formulations had remained practically unchanged after 180 days storage. A slight change in the water activity of the traditional jam could be noticed, which did not occur in the low-sugar jam.

It was observed that the levels of total anthocyanins and total polyphenols diminished with time during 180 days storage, with the decline being more pronounced in the

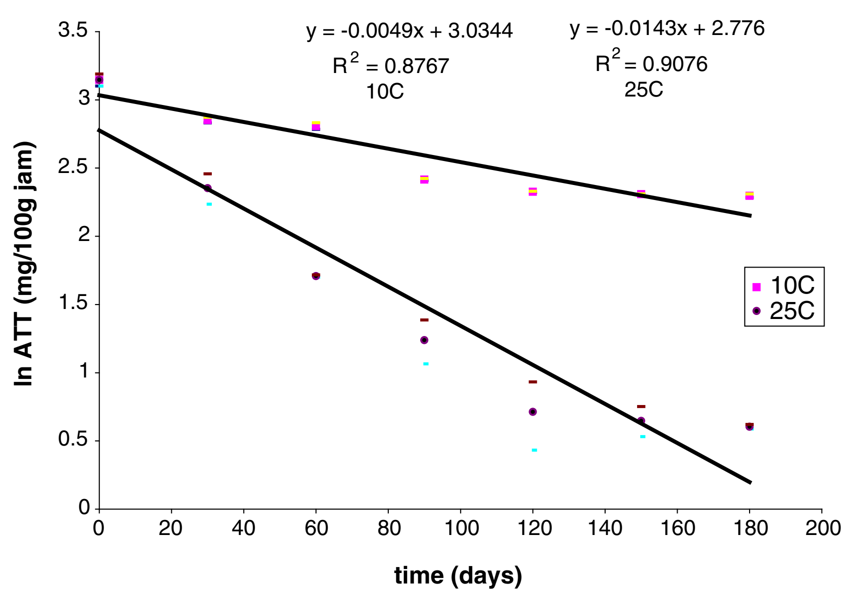

Fig. 3 Degradation of total anthocyanins in low-sugar jam stored at the temperatures of 10 and 25 °C

Table 5 Degradation kinetics parameters of anthocyanins in traditional and low-sugar blackberry jam

Jam	*k* (10 °C)	*k* (25 °C)	Q_{10}	Ea (kcal/mol)
Traditional	−0.0024	−0.0125	3.0	19,490.33
Low-sugar	−0.0049	−0.0143	2.0	12,297.03

jams stored at 25 °C. The reduction was about 80% in traditional jam and 19% in low-sugar jam. This is explained by the fact that anthocyanins are sensitive to heat, and in the case of the traditional jam, it need to be cooked for a longer period of time during manufacture in order to reach the required soluble solids content.

A comparison between the results of this study and those reported by da Mota (2006) as to the characterization of blackberry jam (50 °Brix) shows that the values for total anthocyanins were lower in the present study. This is probably due to the shorter heating time reported by that author to achieve the required soluble solids level. Furthermore, the initial anthocyanin content of the cited study was higher.

da Mota (2006) obtained a mean anthocyanin degradation rate of 43% for blackberry jam stored at room temperature (20±2 °C) for 40 and 90 days. In the present study, the anthocyanin degradation rate over 90 days of storage at 10 °C was 21% for the traditional product and 52% for the low-sugar version.

Table 6 Colour parameters of traditional blackberry jam stored at the temperatures of 10 and 25 °C throughout shelf life

Temperature (°C)	Time (days)	*L**	*a**	*b**
	0	19.55cD±0.07	2.64eC±0.05	0.85cD±0.16
10	30	24.12a±0.16	11.50a±016	3.73a±0.08
	60	22.89b±0.68	10.02bc±1.28	3.03b±0.54
	90	23.05b±0.21	10.68ba±0.32	3.51ba±0.03
	120	22.73b±0.42	10.34bc±0.33	3.53ba±0.05
	150	22.48b±0.03	9.57dc±2.82	3.44ba±0.04
	180	22.48b±0.20	8.78d±4.35	3.13b±0.19
25	30	24.00A±0.30	10.55A±0.21	3.55A±0.13
	60	24.58A±0.94	9.97A±0.84	4.00A±0.50
	90	22.00B±0.41	8.81B±0.06	2.90B±0.04
	120	21.14C±0.12	8.12B±0.07	2.45CB±0.04
	150	21.24C±0.04	8.12B±0.03	2.35C±0.04
	180	21.20C±0.02	8.09B±0.03	2.17C±0.11

Results are expressed as mean±standard deviation of three measurements (n=3). Means compared by Tukey's minimum significant difference test at the 5% error level. Means within each column followed by the same lowercase letters are not significantly different at the 5% level for the temperature of 10 °C and means followed by the same uppercase letters do not significantly differ at the 5% level for the temperature of 25 °C

Table 7 Colour parameters of low-sugar blackberry jam stored at the temperatures of 10 and 25 °C throughout shelf life

Temperature (°C)	Time (days)	*L**	*a**	*b**
	0	22.45cbA±0.12	8.74bA±0.36	2.29cB±0.10
10	30	21.95a±0.20	8.88b±0.14	2.63bc±0.08
	60	22.89b±0.68	10.48a±0.21	2.98ba±0.12
	90	21.99cd±0.54	8.13b±0.17	2.62bc±0.13
	120	21.47d±0.70	8.21b±0.01	3.29a±0.04
	150	21.53d±0.04	8.23b±0.02	3.29a±0.03
	180	21.47d±0.01	8.20b±0.01	3.24a±0.01
25	30	21.64DC±0.13	6.62B±0.07	2.49B±0.08
	60	22.20BA±0.40	5.90CB±0.57	2.37B±0.23
	90	22.48A±0.21	6.03CB±0.35	3.08A±0.32
	120	21.80BDC±5.10	5.61 C ±0.40	3.29A±0.04
	150	21.50D±0.05	5.62 C±0.01	3.29A±0.03
	180	21.45D±0.01	5.63 C ±0.02	2.27A±0.01

Results expressed as mean±standard deviation of 3 measurements (n=3). Means compared by Tukey's minimum significant difference test at the 5% error level. Means within each column followed by the same lowercase letters are not significantly different at the 5% level for the temperature of 10 °C and means followed by the same uppercase letters do not significantly differ at the 5% level for the temperature of 25 °C.

As for the degradation kinetics of anthocyanins as a function of storage time, the best-fit order for the data, as shown in Figs. 2 and 3, was the first order, both for traditional jam as for the low-sugar jam. First-order reactions are, by far, the most common and best studied in foods. Among the most important of these are the destruction of pigments and vitamins during processing and storage.

Patras et al. (2009) also observed that anthocyanins followed first-order kinetic where the rate constant increased with an increase in temperature, when investigated on strawberry jam. The reactions rate constant (k) increased from 0.95×10^{-2} to 1.71×10^{-2} at 4 and 15 °C for anthocyanins.

The Q_{10} and Ea values for traditional and low-sugar jam were calculated using Eqs. 3, 4 and 5 and the data for anthocyanin degradation.

Table 5 shows that the temperature influenced the degradation of anthocyanin to a greater extent in the traditional jam, since its Q_{10} value (3.0) is greater than the Q_{10} value (2.0) of low-sugar jam. This means that an increase of 10 °C in storage temperature brings about a

Table 8 Kinetics parameters of total colour change (Δ*E*) in the traditional and low-sugar jams throughout shelf life

Jam	*k* (10 °C)	*k* (25 °C)	Q_{10}	Ea (kcal/mol)
Traditional	0.0169	0.0282	2.0	12,297.03
Low-sugar	0.0033	0.0094	1.0	176.52

threefold increase in the anthocyanin degradation rate for the traditional sample and a twofold increase in for low-sugar sample.

The results shown in Tables 2, 3 and 4 show that the total polyphenol levels decrease with storage time. This reduction was slightly greater in traditional jam (2.8%) than in the low-sugar product (0.8%). It was further observed that, over time, polyphenol levels decreased more significantly at the temperature of 25 °C.

As for colour, certain differences in the L^*, a^* and b^* parameters were noted during the 180 days of storage investigated, both in the traditional jam (Table 6) and the low-sugar product (Table 7).

There was a reduction in the values of the L^* parameter (darkening) and the a^* parameter (loss of red colour) for both samples (traditional and low-sugar). With regard to the b^* parameter value, the traditional jam exhibited a decreased (loss of yellow colour), whereas the b^* value of the low-sugar jam increased (increase of yellow colour). The colour changes were more pronounced in the samples stored at the temperature of 25 °C.

Similar results were reported by Wicklund et al. (2005), when studying changes in the L^*, a^* and b^* values of jams made from five varieties of strawberry, stored at 4 and 20 °C. The authors suggest that strawberry jams should be stored at a temperature of 4 °C to minimize changes in colour.

Garcia-Alonso et al. (2003) also observed that colour degradation during storage (8, 21 and 30 °C) of desserts formulated with concentrated juice of grapes, blackberries, raspberries and cherries. The authors concluded that the colour parameters and the concentration of different antioxidant compounds are affected by the storage conditions, particularly in samples stored at 30 °C.

As for the degradation kinetics of the L^*, a^*, b^* and ΔE parameters, the order that best fits the data is the zero order, both for the traditional jam as for the low-sugar version.

Similar results were reported by Saxena et al. (2010), when studying the kinetics of colour and carotenoid degradation in jackfruit bulb slices during hot air drying at 50, 60 and 70 °C. Zero-order reaction kinetics was found adequate to describe changes in total colour difference (ΔE) and non-enzimatic browning. The process activations energies (Ea) for ΔE and total carotenoids were 6.50 and 13.3 kcal/mol. Higher Ea for total carotenoids content indicated greater temperature sensibility as compared with colour parameters.

Table 8 shows that the temperature influenced the colour changes to a greater extent in traditional jam, with the Q_{10} value of this sample (2.0) being twice that of the light jam (1.0). In the traditional product, an increase of 10 °C in the storage temperature doubled the rate of colour change, whereas the low-sugar sample did practically not undergo changes in colour as a result of the same increase in storage temperature.

Conclusions

- The processing of blackberries into low-sugar jam brought about a smaller reduction in the anthocyanin content as compared to the traditional formulation.
- A reduction in the amounts of anthocyanin compounds occurred in both types of jam during storage, with the loss being greater in the traditional jam stored at a temperature of 25 °C.
- The storage temperature affected to a greater degree the loss of anthocyanins in the traditional jam. Each 10 °C increase in temperature caused a threefold increase in the rate of this reaction during storage.
- The storage temperature influenced to a greater extent the change in instrumental colour in the traditional jam. Each 10 °C increase in temperature cause a twofold increase in the rate of this reaction during storage.
- The low-sugar product can still be considered a source of anthocyanin compounds even after six months of storage at an average temperature of 10 °C. However, additional studies should be conducted to investigate the effect of processing and storage conditions on the antioxidant activity of anthocyanins.

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