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INFLUENCE OF DIFFERENT SWEETENERS ON THE TOTAL ANTHOCYANIN CONTENT OF HOMEMADE FOREST FRUIT JAM

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ABSTRACT. Anthocyanins, natural water-soluble pigments, responsible for the red, purple and blue colors in many fruits, are valued for their nutritional properties in fruit-based food products such as jams. However, their stability during storage is influenced by various factors among which the type of sweetener used to obtain these jams plays an important role. The present study aims to evaluate the impact of different sweeteners – sucrose, fructose, xylitol and aspartame – on anthocyanins' degradation in homemade forest fruit jams during storage. Results indicate that xylitol offers the highest anthocyanins retention, the rate constant of the degradation process of the investigated pigments being k = 0.0124 days^{-1}. Sucrose and fructose demonstrated a similar protective effect presenting comparable values of the degradation process of anthocyanins in their presence ($k_{sucrose}$ = 0.0184 days^{-1} and $k_{fructose}$ = 0.0196 days^{-1}). The use of aspartame, a non-caloric sweetener, was associated with significantly higher degradation rate of anthocyanins over time. Overall, the choice of sweetener plays the critical role in preserving anthocyanins content in the homemade forest fruit jam with important implications for product quality, shelf-life and nutritional value.

Keywords: *forest fruits, sweeteners, anthocyanins, antioxidant activity.*

INTRODUCTION

Forest fruits, such as blueberries, raspberries, blackberries, blackcurrants and strawberries, are highly valued for their rich content of anthocyanins and other antioxidant compounds which contribute to their vibrant colour and well

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documented health benefits, making them valuable for their functional potential in health promoting foods. Jams made from forest fruits are a popular way to preserve these seasonal products but the heat treatment and formulation involved in jam production can lead to significant degradation of their bioactive compounds. Various factors, including pH, temperature, light and the type of sweetener can influence the preservation of anthocyanins and other antioxidant compounds [1].

Anthocyanins, a subgroup of flavonoids, are potent natural antioxidants associated with a range of biological activities including anti-inflammatory, cardioprotective and neuroprotective effects [2]. These compounds are particularly sensitive to processing and storage conditions, making their stability a critical factor in the development of functional food products such as jams.

Sweeteners are among the most influential formulation variables in jam production, not only affecting taste and texture but also potentially altering the chemical composition of the food matrix containing antioxidant compounds. While sucrose (table sugar) is widely used as the standard sweetener in jam making, increasing consumer demand for healthier, low calorie alternatives has led to the use of artificial or natural sugar substitutes, such as aspartame, polyols or other monosaccharides like fructose or tagatose. These sweeteners differ in chemical structure, sweetness intensity, metabolic impact and interaction with other components of the food matrix and can influence the stability of anthocyanins and the overall antioxidant potential of the final product during processing or storage. For example, fructose is known to participate in Maillard reaction that can degrade antioxidants [3] whereas sugar alcohols like xylitol may offer a more stable environment. Artificial sweeteners, such as aspartame, despite their low caloric profile, may also impact the thermal and chemical stability of phenolic compounds.

The present study aimed to evaluate the influence of four commonly used sweeteners (sucrose, aspartame, fructose and xylitol) on the stability of anthocyanins and antioxidant activity of forest fruit jam during storage. By evaluating changes of total anthocyanins content and antioxidant capacity of the investigated jam, this research seeks to provide a better understanding of how sweeteners choice can affect the nutritional and functional properties of fruit preserves, providing relevant information both for industrial food formulations and consumers who are constantly looking for healthier and functional food options.

RESULTS AND DISCUSSION

Anthocyanins are water soluble flavonoid pigments responsible for the red, purple and blue hues in various forest fruits [4]. Their stability is crucial for maintaining the colour and the nutritional quality of fruit-based products, such as jams. Understanding their degradation pathways and kinetics during processing and storage is essential for optimizing the preservation methods of these highly-consumed fruit derived food products. Storage conditions, including temperature, duration and composition of the food matrix significantly affect the stability of these high valued bioactive compounds present in fruits [5].

The composition of jams typically includes a blend of fruits, sweetener (sucrose or alternatives) and, depending on natural pectin fruit level, a gelling agent. As the sweetener is the main additive in these fruit derived products, the stability of anthocyanins in forest fruit jams is significantly influenced by the type and concentration of this ingredient. Anthocyanins' degradation kinetics in various food products, such as beverages and jams, typically follows a first order kinetic model, the rate of degradation being proportional to the anthocyanin concentration [6].

In order to evaluate the influence of different sweeteners on the variation of total anthocyanin content of homemade forest fruits jam, the total anthocyanin content of an alcoholic extract obtained from jams stored at room temperature was spectrophotometrically monitored at 520 nm for 56 days.

The obtained data were successfully fitted to a first order kinetic model (Figure 1), enabling us to calculate the degradation kinetic parameters, rate constants and half-lives, of the anthocyanins in the investigated jams.

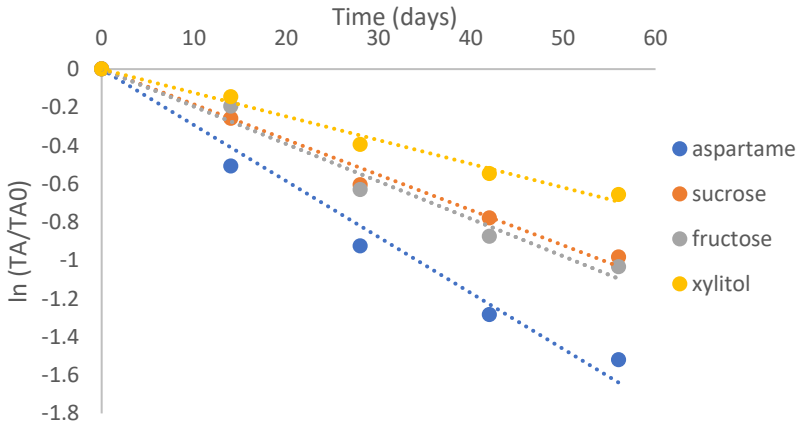

Figure 1. Degradation plots of anthocyanins from forest fruit jam in the presence of various sweeteners

Anthocyanins present in the forest fruit jam prepared with xylitol presented the highest stability over time. After 56 days of storage, the xylitol sweetened forest fruit jam lost 48% of its total anthocyanin content. The rate constant of the degradation of anthocyanins in the presence of this sweetener was ~1.5 fold lower than that obtained for sucrose (Table 1), recommending xylitol as a suitable sweetener in functional and low-calorie food products. Our results were in accordance with those obtained in previous studies concerning anthocyanins stability in blackberry jam [7], which demonstrated that anthocyanins degrade more slowly in the presence of xylitol compared to other sweeteners. Unlike reducing sugars, such as fructose, xylitol does not participate in Maillard reaction, which can degrade phenolics and reduce antioxidant levels and does not generate pro-oxidative intermediates during storage. Its non-reducing nature and chemical stability make it a favourable alternative to sucrose or fructose in the production of functional, low-sugar jams.

Using aspartame as sweetener for the forest fruit jam resulted in an accelerate anthocyanins degradation, the loss of total anthocyanin content being of 78% after 56 days (Table 1), demonstrating that aspartame was not able to preserve the colour intensity of the jam as well as carbohydrates and polyols. Aspartame tends to accelerate anthocyanin degradation, especially in acidic environments, being unstable in low pH overtime, especially below pH = 4, the typically pH of the forest fruit jams [8], acidic pH where anthocyanins are more stable. During heat processing, applied by jam preparation, aspartame degrades into aspartic acid, phenylalanine and methanol, which will further affect anthocyanins' stability [9]. Unlike sucrose or xylitol, aspartame does not reduce water activity [10] or significantly interact with anthocyanins, via hydrogen bonding, to protect their structure.

Compared to sucrose (non-reducing sugar) or xylitol (a sugar alcohol), fructose led to a faster degradation process of the anthocyanins in forest fruits jam (Table 1). Being a reducing sugar, fructose participates in Maillard reaction especially during thermal processing, Maillard intermediates degrading anthocyanins [11,12]. Unlike polyols, such as xylitol, fructose lacks the molecular structure to stack for co-pigmentation reactions of anthocyanins, process that also enhance the stability of these health promoting compounds [13].

Anthocyanins' degradation involves several pathways including hydrolysis, oxidation and condensation. Numerous degradation studies have identified the formation of various degradation products such as phenolic acids, which can contribute to changes in antioxidant properties of the anthocyanins containing food products during processing and storage [14, 15].

Table 1. Kinetic parameters of anthocyanins' degradation in the presence of various sweeteners

Sweetener	k (days^{-1})*	$t_{1/2}$ (days)	$t_{1/2}$ / $t_{1/2\ sucrose}$
Sucrose	0.0184 (0.9834)	37.66	1
Fructose	0.0196 (0.9745)	35.35	0.94
Xylitol	0.0124 (0.9828)	55.88	1.48
Aspartame	0.0293 (0.9745)	23.65	0.63

* Numbers in parentheses are the correlation coefficients.

CONCLUSIONS

The present study reports the influence of different caloric and non-caloric sweeteners (sucrose, fructose, xylitol and aspartame) on the variation of total anthocyanin content of homemade forest fruit jam during storage for 56 days at room temperature. In all cases, the degradation process of anthocyanins follows mainly a first order kinetics (but other paths might also interfere). Among the tested sweeteners significant differences were observed in the rate of anthocyanin degradation, confirming the sensitivity of these pigments to the jam matrix components. The most deleterious effect on anthocyanin stability was noticed for aspartame ($t_{1/2}$ = 23.65 days), while xylitol presented the best stabilizing effect on these dyes ($t_{1/2}$ = 55.88 days). Overall, the results indicate that the choice of sweetener plays a critical role in the long-term anthocyanin retention in fruit-based products. For low-caloric jam formulations aiming to maximize color and nutritional properties stability, xylitol can be used as an effective sweetener while aspartame should be used cautiously in anthocyanin rich food products.

EXPERIMENTAL SECTION

Chemicals and reagents

All chemicals and reagents were purchased from Merck (Darmstadt, Germany), not needing purification.

Preparation of jams

A mixture of frozen forest fruits (blueberries, strawberries, black currants, raspberry and blackberries) was purchased from a local supermarket and stored at -18°C until used for jam preparation.

In order to obtain the fruit purees necessary for making jams, 900 g of frozen berries were crushed for 2 minutes in a 2L blender at 3.500 rpm. The obtained mixture was further boiled for approximately 30 minutes together with the sweetener and the gelling agent (pectin with added citric acid to correct the acidity). Four sweeteners were used to obtain various jam formulations given in Table 2:

Table 2. Formulations of the forest fruit jams

Formulation	**1**	**2**	**3**	**4**
Fruit puree (g)	200	200	200	200
Sucrose (g)	100	-	-	-
Fructose (g)	-	75	-	-
Aspartame (g)	-	-	0.5	-
Xylitol (g)	-	-	-	100
Pectin (g)	4	4	4	4

The amount of added sweetener was chosen in such a way as to maintain the same intensity of the sweet taste of the obtained jam in all cases (regardless of the sweetener used in the preparation of the jam).

Sample storage conditions

Jams were stored in sealed glass jars at ambient temperature (22±2 °C) and protected from direct light. Over a 56-days period, samples were collected at designated time intervals (day 0, 14, 28, 42 and 56) to monitor anthocyanins degradation.

Extraction of anthocyanins from forest fruit jams

At each time point, 5 g of each jam formulation were mixed with 20 ml ethanol and stirred for 1 hour at room temperature. The obtained extract resulted after vacuum filtration of the mixture was further used to evaluate the total anthocyanin content of the investigated jams.

Evaluation of total anthocyanin content

Determination of the total anthocyanin content was conducted according to the pH-differential method of Giusti and Wrolstad [4]. Briefly, 0.5 mL of extract were mixed with 3.5 mL of buffer solution (pH = 1 potassium chloride/HCl and pH = 4.5 sodium acetate/acetic acid). After 15 minutes, the samples were spectrophotometrically analyzed and absorbances were read

in triplicate, against a buffer blank, at 520 and 700 nm, using a Perkin Elmer Lambda 25 UV-Vis spectrophotometer. The total anthocyanin content was calculated and expressed as mg cyanidin-3-O-glucoside/L of extract.

Changes in anthocyanin concentration over time were use to determine the kinetic parameters of the degradation process of these pigments during storage.

Kinetic analysis

Anthocyanins' degradation was modeled as a first order kinetic process. The natural logarithm of the relative anthocyanin concentration, at each time point, was plotted against storage time in days. The rate constant k (days^{-1}) was calculated from the slope of the linear regression, according to eq. 1. A minimum correlation coefficient of 0.95 was considered acceptable for confirming the first order kinetics.

$$\ln[TA/TA_0] = -kt \qquad \text{(eq. 1)}$$

The degradation half-life $t_{1/2}$ in days was calculated using eq. 2:

$$t_{1/2} = -\ln 0.5/k \qquad \text{(eq. 2)}$$

where: $t_{1/2}$ = half-life (days); k = reaction rate constant (days^{-1}).

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