Romanian Biotechnological Letters *Vol. 16, No. 5, 2011*

ORIGINAL PAPER

Processing and storage impact on the antioxidant properties and color quality of some low sugar fruit jams

Received for publication, February 2, 2011
Accepted, September 15, 2011

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Abstract

The aim of the present study was to assess the effect of thermal processing and storage period on the antioxidant properties and color quality of strawberry, sweet and sour cherry low sugar jam. It was observed that thermal processing of fruits led to statistical significant alterations for all monitored parameters. Most important losses due to thermal processing were recorded for monomeric anthocyanins (92-93% from the value recorded in frozen fruits), followed by vitamin C content (54-78%), FRAP values (30-41%) and total phenolics content (25-43%). Additional, alterations of measured parameters occur during storage. Jams storage for a period of 3 months at 20°C led to a decrease in vitamin C content of 22-33% from the value recorded one day after processing and a loss of anthocyanins content, ranging from 22% in sour cherries jam to 33% in strawberry jam related to the value recorded one day after processing. The FRAP values showed not statistical significant alterations after 3 months of storage. Also, there was an increase in polymeric color in the range of 39-63% from the value recorded one day after processing while for the color density there were no statistically significant alterations. The practical implications of this work are that the derived knowledge could be very useful to optimize jam processing technology and storage conditions in order to improve the quality of these products.

Key words: FRAP, total phenolics, anthocyanins, vitamin C, polymeric color, low sugar jams

Introduction

Fruits generally possess a high level of antioxidant activity, which is linked to the levels of phenolic compounds in the fruit. Numerous studies have suggested that the phytochemical content and corresponding antioxidant activity of fruits contribute to their protective effect against chronic and degenerative diseases [1, 2]. The preservation of fruits by jam making is a major direction of the fruits processing but the antioxidant and sensorial characteristics of final products are strongly affected by thermal parameters, raw material quality, recipe manufacturing, storage conditions of final products, etc. [3, 4].

Processing methods varying in the number of processing steps and techniques, heating temperature, and processing period can significantly affect the phenolics content, vitamin C, antioxidant capacity and color quality of fruit products [5].

Low sugar jams were originally developed for diabetics and people with specific health problems. The food industry has been confronted with a new challenge in order to satisfy the consumers that is the development of low-calorie products with acceptable sensorial characteristics and competitive prices, by preferably employing the conventional processing equipment. Nowadays, consumers demand for low-calorie products has significantly risen in an attempt to alleviate the health problems, to reduce or stabilize the body weight, or because they are concerned about a healthy diet. The quality of the color may influence consumer acceptability. Anthocyanins content has a critical role in the color quality of many fresh and processed fruits. During processing and storage, degradation and polymerization usually lead to its discoloration. Color stability and bioactive compounds content of red fruits or red fruits products is influenced by many factors: temperature, time of processing, pH, oxygen, water activity, storage conditions [6, 7]. During heating, degradation and polymerization usually lead to anthocyanin discoloration [8, 9].

Previous reported results in literature motivated us to evaluate the influence of thermal processing and storage period on the antioxidant properties and color stability of low-calorie jam obtained from strawberries, sweet and sour cherries. This information is needed for consumers, who wish to incorporate higher levels of bioactive compounds into their diet, and processors who desire to retain, or possibly boost levels of bioactive compounds in their products. Also, this study is needed to improve the quality of products obtained by thermal processing of fruits rich in anthocyanins.

Materials and Methods

Samples. Three species of fruits: strawberries (*Fragaria ananassa*), sweet cherries (*Prunus avium* L.) and sour cherries (*Prunus cerasus* L.) harvested in 2009 at the fully ripe stage from their natural habitats in the Timis region from Romania were washed, drained and frozen using a home type freezer. Before freezing, sweet and sour cherries were destemmed and pitted. The fruits were stored in freezer at -18°C in closed plastic boxes for less than 1 month prior to processing. Prior to jam preparation, fruits were semi-thawed.

Jam preparation. For low sugar jam preparation the following materials were used: fruits (1000 g), sucrose (470 g), low methoxyl pectin LM 40 (Danisco Ingredients, Denmark) (10 g) and citric acid (4 g). Citric acid was used for adjusting pH values for proper pectin gelatinisation (pH necessary for LM gelatinisation was 2.8-3.3). Fruit blended with larger part of sucrose and citric acid were mixed and thermal processed at 80°C. Pectin was mixed with part of sucrose and added at the final stage of the jam processing. Fruit jams were cooked until the final product contained 45°Brix. Time of thermal processing was ~ 20 min at 80°C. When the processed mass reached 45°Brix the jams were filled into hot glass jars, capped and pasteurized at 80°C for 10 min. They were allowed to cool at room temperature and stored in the dark until analysis. Jams were analyzed after a day of processing and after 1 and 3 months of storage at 20°C.

Sample analysis. For bioactive compounds determination and evaluation of antioxidant activity, three replicates of extracts were prepared according to Kalt *et al.* (2000) [10]. In the case of anthocyanins and antioxidant activity evaluation 95% (v/v) ethanol acidified with HCl (0.1%, v/v) was used for extraction. For extraction of total phenolics compounds and vitamin C 95% (v/v) ethanol was used.

Total phenolics content was spectrophotometrically measured using the Folin-Ciocalteu reagent [11]. The samples were incubated for 2 h in the dark at 20°C prior to measuring the absorbance at 750 nm. Quantification of total phenolic content was based on a gallic acid standard curve and the results were expressed as mM of gallic acid equivalents (GAE) per 100 g dry substances (ds).

Total monomeric anthocyanins content of fruits extracts were determined by the pH-differential method [12]. Samples were diluted to the appropriate concentration with 0.025 M potassium chloride buffer (pH=1.0) and 0.4 M sodium acetate buffer (pH=4.5). The absorbance was measured with the UV-VIS spectrophotometer using 1 cm path length disposable cells at 520 nm and 700 nm after 15 min of incubation at 20°C. The content of total anthocyanins was expressed as mg of cyandin-3-glucoside equivalents per 100 g ds.

Color analysis. Color density, polymeric color and percentage of polymeric color were determined using the bisulfite bleaching method [12].

Vitamin C (VC) was measured by titration with a 2,6-dichlorophenolindophenol sodium salt solution and chloroform was used for intensely colored extracts [13].

Total antioxidant activity was evaluated by FRAP (*ferric reducing antioxidant power*) assay according to Benzie and Strain (1996) [14]. The FRAP method consists in the reduction of Fe^{+3} ions to Fe^{+2}, which forms a blue-colored complex with 2,4,6-tripirydylo-s-triazine (TPTZ). This reduction was monitored by absorption change measured at 595 nm. The color intensity depends on the antioxidant concentration. Results were expressed as mmol of Fe^{2+} equivalents per 100 g ds.

Calculations. Data obtained for total phenolics, vitamin C, anthocyanins and FRAP values of analyzed jams, were converted to original weight of the fruits using the following calculation, according with the protocol described by Brownmiller *et al.* (2008) [4]:

$$\text{Csample} \times R = C_{\text{fruits}}$$

where: C_{sample} - concentration of jam sample; R - ratio of the mass of product produced to the mass of the original fruit; C_{fruit} - concentration based on original weight of the fruits. This conversion allowed for concentration and dilution effects to be accounted for and all products to be compared on an equivalent basis.

Statistical analysis. All data was reported as means ± standard deviation of three (n = 3) replicates. The data of the present work were subjected to analysis of variance (ANOVA) in order to compare the mean values of the investigated parameters at different statistical levels of significance: 0.1, 0.05, 0.01 and 0.001. Computations Tukey post-hoc means comparisons and Levene's test for equal variance was also included. Statistical analysis of data was performed using the computer software Origin version 7.0.

Results and discussions

To provide a clear view on the changes incurred among the four stages of experiment (frozen fruits - jam after a day of processing - jam in storage after a month - jam in storage after three months), the results of total phenolics content, vitamin C, monomeric anthocianyns content and total antioxidant capacity were processed by ANOVA test.

Based on information obtained through statistical processing can be pointed a response to alterations in monitored parameters due to thermal processing relative to the initial material, frozen fruits, as control [C] - Table 1. Figure 1 provides information on the depreciation degree of the investigated parameters as response to storage period relative to fruit jam after a day of processing as control [C]. Table 2 shows the losses recorded for antioxidant activity, monomeric anthocyanins content, total phenolics and vitamin C content over 1 and 3 months of storage at 20°C.

Changes in vitamin C content

Based on data presented in Table 1 we can see that thermal processing of fruits led to extremely significant alterations ($p<0.001$) in vitamin C content in agreement with other previous results [15]. Thus, thermal processing of fruits caused a loss of 78% of the vitamin C content recorded for frozen fruits in the case of strawberry, 70% for sour cherry and 54% for sweet cherry - Table 1. From the Figure 1a could be observed that storage time induce non-significant alterations ($p>0.1$) after 1 month for jam obtained from all species of fruits, only after 3 months of storage it revealed statistical significant differences: significant ($P<0.05$) for sour cherry jam and highly significant ($p<0.01$) for strawberry and sweet cherry jam.

Jam storage for 3 months at room temperature led to a decrease in vitamin C content of 22-33% of the value recorded one day after processing – Table 2.

Strawberry is the only species out of the three investigated that exhibits the highest loss of vitamin C (78%) when subjected to the process of jam making. In addition, after 3 months of storage, the highest loss of vitamin C content was also recorded for the strawberry jam (32.69%). Based on these data we can say that strawberry jam shows the lowest tolerance to storage.

Table 1. Alterations of measured parameters as a result of fruits thermal processing

Samples	frozen fruits [C]	jam after a day of processing
Vitamin C (mg·100^{-1} g ds)		
strawberry	314.43±28.41 *(F=3.71)*	69.9±5.43***
sweet cherry	78.11±6.28 *(F=2.13)*	35.65±3.12***
sour cherry	172.93±14.61 *(F=2.13)*	51.12±4.29***
Total phenolics (mM GAE·100^{-1} g ds)		
strawberry	17.79±1.56 *(F=2.00)*	10.24±0.81**
sweet cherry	19.37±1.64 *(F=1.14)*	13.32±1.06**
sour cherry	21.58±1.79 *(F=0.33)*	16.15±1.45*
Total anthocyanins (mg·100^{-1}g ds)		
strawberry	233.44±20.24 *(F=3.96)*	15.80±1.35***
sweet cherry	303.61±28.27 *(F=3.97)*	21.4±1.82***
sour cherry	547.46±40.11 *(F=3.95)*	42.55±3.12***
Antioxidant activity (mM Fe^{2+}·100^{-1} g ds)		
strawberry	60.22±5.17 *(F=1.77)*	35.29±2.85**
sweet cherry	45.47±3.85 *(F=0.97)*	30.17±2.61**
sour cherry	72.99±6.47 *(F=0.84)*	50.60±4.52**

Data are shown as means, relative to control (C) response recorded in the frozen fruits. Statistical differences are indicated as P<0.05=* (significant), P<0.01=** (highly significant) and P<0.001=*** (extremely significant).
F – Fischer's variance ratio (F should be higher for the predictions to be significant).

Table 2. The losses of measured parameters as a result of fruit jam storage at 20°C

Losses (%)	jam in storage after a month			jam in storage after 3 months		
	Strawberry	Sweet cherry	Sour cherry	Strawberry	Sweet cherry	Sour cherry
vitamin C	13.97	14.91	7.82	32.69	28.68	22.18
total phenolics	11.23	9.61	8.98	25.39	21.92	18.2
monomeric anthocyanins	10.78	14.36	9.56	33.11	27.59	21.57
FRAP	6.83	5.83	4.41	19.1	14.72	10.63

Changes in total phenolics content

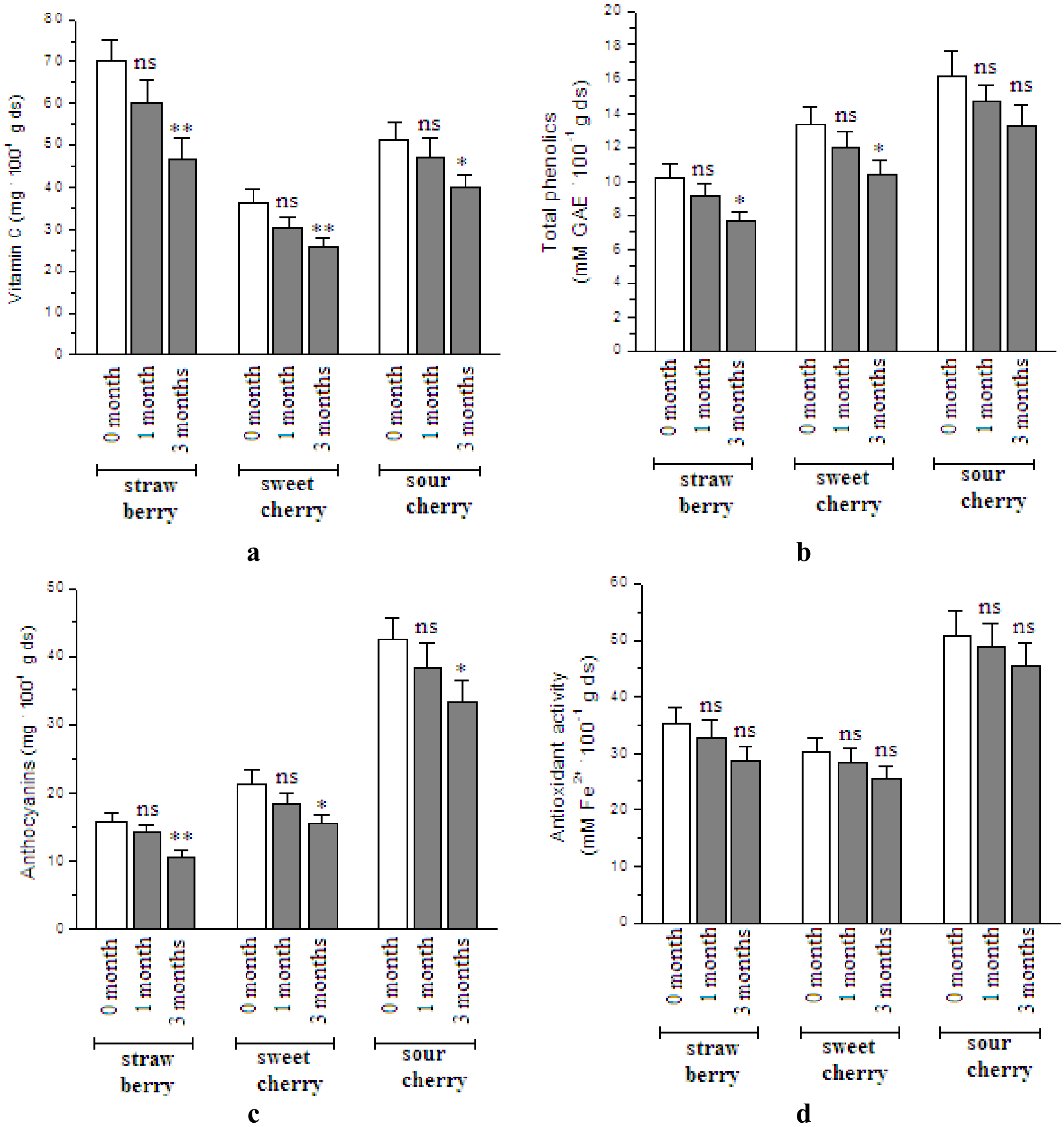
From data presented in Table 1 it is observed that thermal processing of fruits induce alterations of phenolic compounds content, point out by statistical processing. During jam processing 25-42% of total polyphenols content related to frozen fruit was lost. These depreciations of the total phenolics content are highly significant (p<0.01) for strawberry and cherries and significant (p<0.05) for sour cherries.

On storage, significant statistical differences were noticed after a period of 3 months – Figure 1b. Thus, during storage time, polyphenols content decreased after one month with 9-

11% relative to the value recorded one day after processing, reaching 18-25% after 3 months – Table 2.

The biggest loss of polyphenolic compounds due to thermal processing was recorded in the case of strawberry jam and was lowest for sour cherry jam.

At the end of the experiment, after 3 months of storage, the same trend is observed, which suggests that total phenolics compounds in sour cherries have a better stability compared to strawberries during thermal processing and storage.



Data are shown as means, relative to control (C) response recorded in the jam after preparation (0 month). Statistical differences are indicated as ns = non-significant (P>0.1), P<0.05=* (significant), P<0.01=** (highly significant).

Figure 1. The changes of measured parameters (**a** – vitamin C content; **b** - total phenolic content, **c**- anthocyanins content, **d** - FRAP values) as a result of fruit jam storage at 20°C

Changes in total anthocyanins content

From Table 1 could be observed the massive decrease of anthocyanins content due to thermal processing which is revealed by obtained significant statistical differences (extremely significant, P<0.001). Thus, in agreement of other studies [16, 17, 18] jam processing caused a 90-93% decrease in anthocyanins content from the three species of fruits.

Anthocyanins pigments are labile compounds, their stability is highly variable depending on their structure and the composition of the matrix in which they exist [4, 6, 7].

Anthocyanins losses are probably due to complex formation with other compounds during jam processing. The nature of the transformation products is not known but there is clear evidence of the involvement of sugars and ascorbic acid (or their thermal degradation products), metal ions and hydrogen peroxide derived from ascorbic acid [2].

Loss of anthocyanins and/or formation of brown compounds in jam during storage have been attributed to many factors such as pH and acidity, phenolic compounds, sugars and sugar degradation products, oxygen, ascorbic acid, fruit maturity and thawing time. Other factors may have a significant role in the expression of color in fruit jams by copigmentation or some other physico-chemical processes [6, 19]. The losses of monomeric anthocyanins were most likely due to the formation of anthocyanins polymers during the jam processing steps and storage period of these [6, 17].

Nevertheless, after jam processing the total anthocyanins content in all analyzed jams was reduced to 6.5 to 8% of its initial content. Levels of monomeric anthocyanins continued to decline during storage, losing 22-33% from the value recorded one day after processing at the end of 3 months of storage – Table 2.

Jam storage for 1 month doesn't induce significant statistical differences regarding anthocyanins content (p>0.01), and after 3 months of storage anthocyanins content decreasing becomes significant (p<0.05) for cherry and sour cherry jam and highly significant (p<0.01) for strawberry jam – Figure 1c.

Changes in the antioxidant activity

The decrease of the vitamin C, total phenolics compounds and total anthocyanins content led to a decreasing of antioxidant capacity as a response of thermal processing of fruits. According to data showed in the Table 1 could be observed that these depreciations of the FRAP values are highly significant (p<0.01) for all investigated samples. Despite marked losses of anthocyanins during thermal processing, the antioxidant capacity is affected to a lesser extent. Thus, fruit processing into jam caused loss of 30-41% of the antioxidant capacity recorded for frozen fruit. The most significant loss recorded for FRAP value due to thermal processing has been recorded for strawberries and the lowest was recorded for the sour cherries.

During storage period, due to losses of investigated bioactive compounds, occur depreciations of the FRAP values. Even if jam storage leads to decreasing of FRAP values, these are not statistical significant even after a three months period – Figure 1d. Decrease recorded in antioxidant activity after one month of storage was between 4-7%, and after three months reached values of 11-19% of the value recorded after a day of processing – Table 2.

Changes in color quality

The effect of jam storage for 1 and 3 months at 20°C on jams color was quantified by measuring color density, polymeric color, and percentage of polymeric color. The percentage of polymeric color is the ratio between polymeric color and color density being used to determine the percentage of the color that is contributed by polymerized material [19].

Changes in the color parameters as response of storage period relative to fruit jam after a day of processing as control [C] were presented in the Table 3.

In terms of color quality alteration, it is important to mention that while all the previous changes were noticed in anthocyanins concentration, only minor changes were found when analyzing the color intensity of these products stored at room temperature. After a month of storage, the color intensity decreases with 4-7.5% of the value recorded after a day of processing, reaching 7-11% after three months of storage at room temperature.

From the Table 3 could be observed that 3 months of jam storage at 20°C induce non-significant alterations in color density of investigated jams (p>0.1). Progressive increase of polymeric color and corresponding loss of monomeric anthocyanins during of storage were most likely due to extensively polymerization phenomena, similar to what was mentioned above for wines or juices [6, 17, 20]. Thus, after one month the increase in percentage of polymeric color was situated in the range 12-17% of the values obtained one day after processing (non-significant, P>0.1) and after three months it reached 39-63% (highly significant, P<0.01). Most relevant increases of polymeric color percent were obtained for strawberries jam. Thereby, no significant differences were noticed between values registered for percent of polymeric color of sweet and sour cherries jam.

Based on the results obtained by statistical processing of data is pointed out that even highly significant increases (P<0.01) of polymeric color percentage did not induce statistically significant alterations in the density of color, proving the stability of the jam color during the 3 months storage.

Table 3. The influence of storage period at 20°C on the jam color

Jam samples	**color density**		
	jam after a day of processing [C]	**jam in storage after 1 month**	**jam in storage after 3 months**
strawberry	3.811±0.320 (*F=0.29*)	3.524±0.360^{ns}	3.389±0.320^{ns}
sweet cherry	4.703±0.390 (*F=0.29*)	4.447±0.410^{ns}	4.311±0.390^{ns}
sour cherry	5.503±0.470 (*F=0.02*)	5.278±0.480^{ns}	5.102±0.450^{ns}
Jam samples	**polymeric color**		
	jam after preparation	**jam in storage after 1 month**	**jam in storage after 3 months**
strawberry	0.48±0.05 (*F=0.82*)	0.52±0.035^{ns}	0.7±0.06**
sweet cherry	0.53±0.04 (*F=0.40*)	0.57±0.037^{ns}	0.69±0.05**
sour cherry	0.55±0.06 (*F=5.38*)	0.59±0.04^{ns}	0.71±0.08*
Jam samples	**percentage of polymeric color (%)**		
	jam after preparation	**jam in storage after 1 month**	**jam in storage after 3 months**
strawberry	12.60±1.15 (*F=0.76*)	14.76±1.35^{ns}	20.66±1.82**
sweet cherry	11.27±1.08 (*F=0.08*)	12.82±1.14^{ns}	16.01±1.45**
sour cherry	9.99±0.88 (*F=0.44*)	11.18±1.02^{ns}	13.92±1.24**

Data are shown as means, relative to control (C) response recorded in the after a day of processing (0 month). Statistical differences are indicated as ns = non-significant (P>0.1), P<0.05=* (significant) and P<0.01=** (highly significant). F – Fischer's variance ratio.

Although total phenolics and vitamin C are the major potential candidates as a selection criterion for antioxidant properties of fruits jams, antioxidant activity is not limited to these [2, 15, 16]. Previous results obtained by Tsai *et al.* (2004) [21], Brownmiller *et al.*, (2008) [4] proved that polymeric anthocyanins show antioxidant activity, which compensates for the loss of a part of antioxidant capacity due to monomeric anthocyanins degradation.

Also, it has been proven that some degradation products of anthocyanins have the antioxidant capacity [22].

The obtained data revealed that, after 3 months of storage at 20°C, antioxidant capacity of fruit jam recorded lower depreciation compared with the content of investigated bioactive compounds. This is confirmed by the fact that a storage period of 3 months does not induce statistically significant changes in FRAP values, while for the other measured parameters such as total phenolics, monomeric anthocyanins, vitamin C were noticed changes with statistical significance.

Conclusions

It could be concluded from the results of the present investigation that thermal processing of fruits led to statistical significant alterations for all measured parameters. The storage of fruit jam at 20°C for one month has not determined significant alterations, while three months of storage led to significant and highly significant alterations. Thermal processing of frozen fruits (strawberries, sweet cherries and sour cherries) into jam form resulted in significant losses of antioxidant capacity (30-41%), phenolics compounds (25-43%), vitamin C content (54-78%). Monomeric anthocyanins were extensively degraded (approximate 90%) during thermal processing. Strawberry is the only species out of the three investigated that exhibits the highest losses of bioactive compounds when subjected to the process of jam making. Losses of monomeric anthocyanins during storage were accompanied by increasing in percentage of polymeric color, indicating that monomeric anthocyanins were extensively polymerized during storage. The color density showed a similar trend over time for all investigated jams. It is remarkable that the rate of color loss is much slower than the rate of anthocyanins degradation. In terms of the investigated properties, the lowest tolerance to storage conditions was showed by the strawberry jam and the better tolerance by the cherry jam. This may have implications on the nutritional value of the jam. Taking into account all these factors, and in spite of the fact that some losses occur, our data suggest that the investigated low sugar jams may still represent an excellent source of compounds with antioxidant potential.

Acknowledgements

This study was supported by S.C. ETCO EUROPE TRADE COMPANY from SEBIS (ARAD), research project no. 637/21.01.2009, Theme: "*Studies regarding the impact of technological treatments on the antioxidant characteristics of products derived from berries*, Project Manager: Ph.D Assoc. Prof. Mariana-Atena Poiana

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