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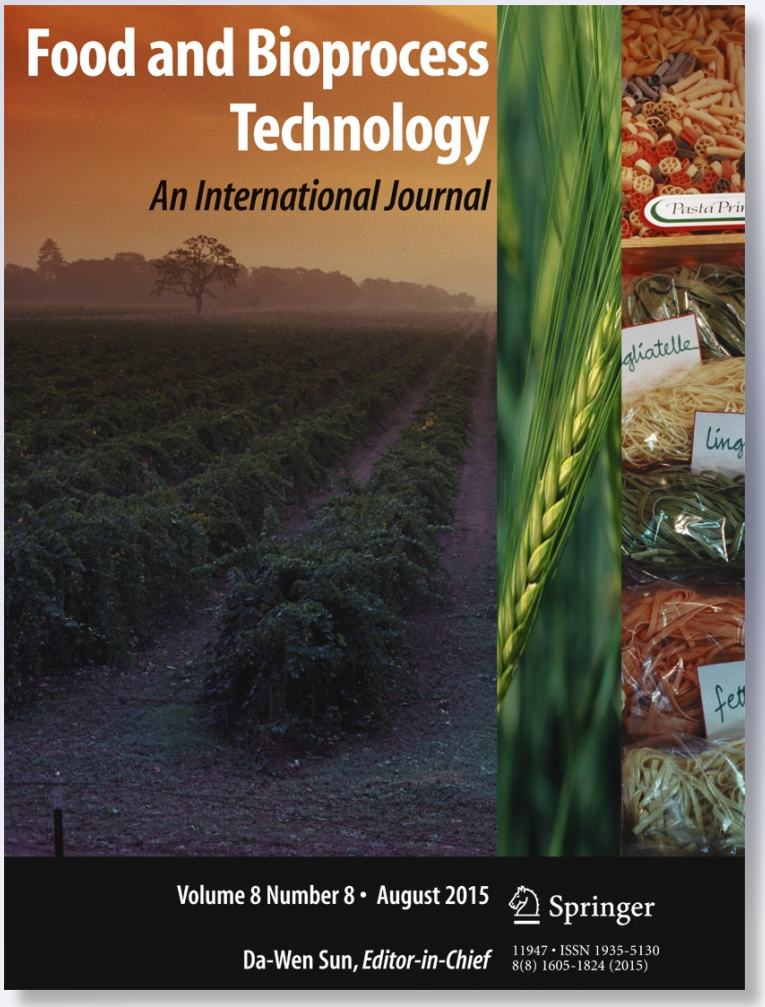

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ORIGINAL PAPER

Color and Bioactive Compounds Characteristics on Dehydrated Sweet Cherry Products

Lorena Franceschinis[1] · **Paula Sette**[1,3] · **Carolina Schebor**[2,3] · **Daniela Salvatori**[1,3]

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Abstract It is widely known that quality properties of fruits can be affected by drying processes. The approach was the quality improvement of dried cherry products through the application of combined technologies of drying and pretreatments. The objective of this work was to analyze the effect of blanching or sugar infusion prior to air-drying or freeze-drying on quality properties such as color, bioactive compounds, and antiradical power of two cherry products (discs and dices). Air-drying caused darkening, whereas freeze-drying provoked higher lightness of discs compared to fresh fruit ($p<0.05$). Cherry dices were lighter than the fresh fruit. A high retention of total anthocyanin (ACY) and phenolic content (TPC) was obtained in blanched freeze-dried discs (ACY=165±22 mg Cyd-3-glu/100 g d.w.; TPC=739±55 mg GAE/100 g d.w.). Sugar infusion pretreatment caused an important decrease in ACY (31–89 mg Cyd-3-glu/100 g d.w.) and TPC (222–271 mg GAE/100 g d.w.). When blanching was applied prior to air-drying, samples presented the highest antiradical power, similar to that observed in fresh fruit. In dices, the best quality attributes in terms of superficial color were found in control freeze-dried samples since they presented minor shifts in hue angle and a greater preservation of anthocyanin pigments (ACY=211±30 mg Cyd-3-glu/100 g d.w.). However, control air-dried dices presented the highest phenolic content (TPC=771±65 mg GAE/100 g d.w.). Regarding the possible application of the dry cherry products, discs could be directly consumed as snacks, while dices could be incorporated as ingredients in fruit bars, cookies, or muffins.

Keywords Sweet cherry · Air-drying · Freeze-drying · Blanching · Sugar infusion · Color · Bioactive compounds · Antiradical power

Introduction

The increased interest in cherry products has been motivated by numerous studies which highlight the health benefits associated with consumption of cherries and berries. Cherries are nutritionally dense food rich in anthocyanins, quercetin, hydroxycinnamates, potassium, fiber, vitamin C, carotenoids, and melatonin. These constituent nutrients and bioactive food components support the potential preventive health benefits of cherry intake in relation to cancer, cardiovascular disease, diabetes, inflammatory disease, and Alzheimer's disease (Kirakosyan et al. 2009; McCune et al. 2010). Among these compounds, anthocyanins, which are natural pigments belonging to the group of flavonoids, have received special attention. These pigments are of interest not only for their health-promoting properties but also because they are responsible for the orange, red, and blue colors in many fruits and vegetables, and they have a critical role in the color quality of many fresh and processed products. Sweet cherries (*Prunus avium* L.) contain substantial amounts of anthocyanins and polyphenols (Gao and Mazza 1995; Wang et al. 1999; Chaovanalikit and Wrolstad 2004), which are not uniformly distributed in fruit tissue. In the case of intensely red cherries, as Bing or Lapins cultivars, although anthocyanins and polyphenolics are present in both skin and flesh, they are mainly

✉ Daniela Salvatori
daniela.salvatori@probien.gob.ar

[1] PROBIEN (CONICET—Universidad Nacional del Comahue), Buenos Aires 1400, 8300 Neuquén, Argentina

[2] Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, 1428 Buenos Aires, Argentina

[3] Members of CONICET, Buenos Aires, Argentina

concentrated in the skin (Tomas-Barberan et al. 2001; Chaovanalikit and Wrolstad 2004). Therefore, the sample geometry used for processing will strongly affect the final bioactive content of the end-products.

Sweet cherries are mainly used for fresh market, but they are also processed into jams and jellies and canned, frozen, brined, candied, or dried products. In general, dehydration methods are beneficial as they allow using fruits bearing some imperfections as splitting, cracking, bird-pecking, or rain-damaged skin in otherwise unusable cherries (McLellan and Padilla-Zakour 2004). However, when the goal is to optimize the dry product quality, several other treatments may be used alone or in a combined technology to achieve industrially processed cherry products with characteristics more similar to original raw material. It is widely known that drying at high temperatures and long times may cause damage in the nutritive and sensorial characteristics, affecting flavor, color, and nutrients of the dried food (Lin et al. 1998; Kammski and Tomczak 2000; Di Scala and Crapiste 2008; Orak et al. 2012). Among the best food dehydration techniques, freeze-drying is known to produce the highest quality dehydrated products (Khalloufi and Ratti 2003; Muthukumaran et al. 2008; Orak et al. 2012), being more effective in preserving valuable food compounds than traditional methods of drying. Color change of a food product during drying is indicative of how severe the drying conditions are and is related to its pigment composition/concentration. Anthocyanin pigments are highly unstable and readily degrade during processing and storage of foodstuffs, which can have a dramatic impact on color quality and may also affect nutritional properties (Wrolstad et al. 2005).

A way of obtaining dried fruits of good quality is to use pre-drying treatments, such as osmotic dehydration, also termed as sugar infusion (SI) (Torreggiani and Bertolo 2001; Sosa et al. 2012; Yadav and Singh 2012). This concentration technique is carried out by immersing the fruits in concentrated solutions or dry mix of substances compatible with the material to be treated. It gives rise to three simultaneous mass flows that occur due to the water and solute activity gradients across the cell membranes: an important water flow out of the food into the solution, a minor one composed of those solutes able to cross the semipermeable membranes of the fruit out into the solution, and a third reverse flux of solutes transferred from the solution into the fruit. When SI is used as a pre-drying treatment, not only a partial depression of water activity takes place before the dehydration step but also it allows obtaining products with improved quality and more similar to the original fresh fruits (Raoult-Wack 1994; Torreggiani and Bertolo 2001). Previous studies have shown that infusion of sugars can stabilize color after drying of certain fruits like apple, banana, and also vegetables such as potato and carrot that otherwise would have experienced an extensive browning (Krokida et al. 2001; Mandala et al. 2005; Aktas et al. 2007; Sosa et al. 2012). However, during infusion some soluble pigments can also be transferred from the fruit to the osmotic solution with a significant loss of fruit color, especially in case of berries such as mulberries, tamarillo, Andes berry, blueberries, and cranberries (Grabowski et al. 2007; Osorio et al. 2007; Stojanovic and Silva 2007; Chottamom et al. 2012).

Although there have been several investigations on the effect of processing on pigments, color development, and antiradical activity in cherries (Šumic et al. 2013; Pirone et al. 2014; Wojdyło et al. 2014) and berries like raspberry, strawberry, bilberry, and *Arbutus unedo* L. fruit (Michalczyk et al. 2009; Orak et al. 2012), the available knowledge on changes after drying is still limited.

The objective of this work was then to analyze the effect of different pretreatments and dehydration methods on color, bioactive compounds, and antiradical power of products obtained from sweet cherries (Lapins var.). Two geometries were analyzed considering different possible applications of the cherry products.

Materials and Methods

Sample Preparation

Lapins cherry cultivar grown in Valentina Norte (Neuquén, Argentina) was used. Fruits were washed, peduncles were removed, and pitting was done with a manual cherry pitter. A group of cherries was cut into halves and another group was chopped in eighth pieces in order to obtain different dried product geometries: discs and dices, respectively. Then they were subjected to different pretreatments prior to drying process.

Pretreatments

The following pretreatments were applied:

1. *Dry sugar infusion (SI)*: the procedure was carried out by immersing cherry discs or dices into a dry mixture of sucrose and preservatives (in dry form) at room temperature. The amount of sugar and chemical agents were determined according to the weight of the fruit and the final levels required after equilibration of the components of the food system to decrease water activity till 0.87. Ross equation was employed to calculate the sucrose amount needed to reach the desired a_w (Alzamora et al. 1993):

$$a_{w\ \mathrm{equilibrium}} = \left(a_w{}^0\right)_{\mathrm{cherry}} \left(a_w{}^0\right)_{\mathrm{sucrose}} \quad (1)$$

where $(a_w{}^0)_{\mathrm{cherry}}$ is the water activity of the fresh fruit (≈0.97) and $(a_w{}^0)_{\mathrm{sucrose}}$ is the water activity of the sucrose solution, both at the same molality as in the water of the

fruit. Value of $(a_w{}^0)_{sucrose}$ was obtained from the Norrish's equation:

$$(a_w{}^o)_{sucrose} = x_1 \exp\left(-K{x_2}^2\right) \quad (2)$$

Where x_1 and x_2 are molar fractions of water and sucrose and K is 6.47 for sucrose (Chirife et al. 1980). The calculated values were x_1=0.912 and x_2=0.088.

The fruit/sugar ratio used in all systems was 0.7. Potassium sorbate (1000 mg/kg food with additives) and sodium bisulfite (150 mg/kg food with additives) were used as antimicrobial and anti-browning preservatives, respectively (Leistner 2000). Reagents were all food grade (Saporiti S.A., Argentina). Cherry discs and dices were separately prepared. A careful mixing of each system was performed twice a day in order to facilitate the dissolution of sugar and additives while pieces of fruit exuded the vacuolar content due to osmosis process, with the consequent formation of syrup. In each system, the a_w and the soluble solid content of the fruit and the syrup was monitored until a constant value was reached; the time to equilibrate the systems was 15 days. After equilibration, samples were taken out of the generated syrups, drained, and placed on tissue paper for the removal of the residual syrup from the surfaces.

Final water activity values achieved after infusion processes were selected in order to have dried fruits of a certain level of sweetness, as well as to study the impact of sugar concentration on the analyzed properties.

2. *Blanching (B)*: blanching was done by exposure of samples (discs only) to saturated steam at 100 °C for 90 s and then by cooling them in water at 4 °C for the same time.
3. *Control (C)*: cherry discs and dices without pretreatments were used as control.

Drying Process

Cherry samples with and without pretreatments were subjected to two different drying processes:

(a) *Freeze-drying (F)*: samples were quenched with liquid nitrogen just after cutting for control samples and after pretreatments for the rest of the samples. The freeze-drying process lasted 48 h and was carried out in a freeze drier Alpha 1-4 LD/2-4 LD-2 (Martin Christ, Gefriertrocknungsaniagen GmbH, Osterode, Germany). It was operated at −84 °C at a chamber pressure of 0.04 mbar.

(b) *Air drying (A)*: an air convection oven was used. Samples were dried for 24 h at 60±1 °C and ≅10 % relative humidity (RH). RH was controlled with a Hygro Palm hygrometer (Rotronic Instruments, West Sussex, UK).

Sample Analysis

Water Content, Soluble Solids Content, Total Acidity, pH, Water Activity, and Ashes

The chemical analysis was carried out by analyzing the following parameters according to AOAC methods (1990): water content (925.09), soluble solids content (932.12), total acidity (945.26), pH (945.27), and ash (940.26). Water activity (a_w) was measured at 25 °C with a psycrometer model Series 3 (Aqua-Lab, Decagon Devices Inc., Pullman, Washington, USA), calibrated with saturated saline aqueous solutions. The soluble solids content was analyzed by measuring the refraction index in an ABBE refractometer model DR A1 (Atago, Tokyo, Japan) at 25 °C. Total acidity was expressed as percent of citric acid (%, wet basis). A pH meter model EA 940 (ORION, Beverly, USA) was used for pH and total acidity measurements. Grinded fruit was used for all determinations. All measurements were made in triplicate and the average values were informed.

Color Analysis

The superficial color of cherries was determined by measuring tristimulus parameters (CIELAB color space) with a Minolta photocolorimeter (model CR 400) using illuminant C and 2° observer angle. The instrument was calibrated (standardized) each time with a white ceramic plate. Measurements were performed on skin and pulp in 40 discs for each condition. In the case of dices, 20 measurements were taken from a pull of samples randomly arranged in Petri dishes. The parameters L^*, a^*, b^* of CIELAB color space were recorded. L^* represents color lightness (0=black and 100=white). The a^* scale indicates the chromaticity axis from green (−) to red (+) while the b^* axis ranged from blue (−) to yellow (+). In order to analyze the red color evolution caused by treatments through Principal Components Analysis, these numerical values were converted into "global color change" (ΔE^*_{ab}), "chroma" (C^*_{ab}), and "hue angle" (h_{ab}) (Hutchings 1994).

Sweet Cherry Extract

Ethanolic extracts (80 %) of samples (fresh or dried sweet cherries) were prepared and used for the following measurements: percentage of polymeric color, browning index, total phenolic content, antiradical power, total sugar content, and reducing sugars. A UV/Vis spectrophotometer model 1700

(Metrolab Instruments, Buenos Aires, Argentina) was used for all spectrophotometric determinations above mentioned. Dried sweet cherries and edible flesh of fresh fruit were cut in small pieces and an appropriate amount of sample was weighed: 1 g for dried cherry or 4 g for fresh fruit, respectively. Distilled water (5 ml) was added to the sample and constantly mixed in a magnetic stirrer (1000 rpm) during 30 min; absolute ethanol (6 ml) was added and the system was homogenized during 10 min. The extract was then filtered under vacuum using a Büchner funnel. The pellet was extracted twice with the same procedure (6 ml of absolute ethanol during 10 min). The three extracts were combined and absolute ethanol was added to constitute a total volume of 25 ml.

Monomeric Anthocyanin Content (ACY) and Anthocyanin Degradation Index (ADI)

ACY was determined using the pH-differential method (Giusti and Wrolstad 2005). Extracts were obtained with ethanol 95 %–HCl 1.5 N (85:15). Monomeric anthocyanin content was expressed as Cyanidin-3-glucoside (MW=445.2 and a molar extinction coefficient ε=29,600 l cm^{-1} mol^{-1}). The results were expressed as milligrams of Cyd-3-glu in 100 g of dry matter content (d.w.). Anthocyanin degradation index (ADI) is indicative of the proportion of degraded anthocyanin in the sample. It was derived from the ratio between the total anthocyanin content (degraded and nondegraded) calculated by single pH method (absorbance measured at pH 1) and the monomeric anthocyanin content measured by pH differential method (Fuleki and Francis 1968).

Polymeric Color Percentage (%PC), Browning Index (BI), and $Abs_{420\ nm}$

The percent of polymeric color was expressed as a percentage of total color density (%PC=PC/CD×100). Color density (CD) and polymeric color (PC) parameters were determined using the bisulfite bleaching method, according to Giusti and Wrolstad (2005). Total color density is a measure of the total color strength of the sample solution. Polymeric color is an indicator of polymerized pigments, including phenol-anthocyanin complexes and brown compounds.

Browning was evaluated through two methods: the browning index (BI) reported by Giusti and Wrolstad (2005) and the absorbance measured at 420 nm (Abs_{420nm}) reported by Cernîsev (2010). Browning index corresponds to the absorbance at 420 nm of the bisulfite bleached samples and the $Abs_{420\ nm}$ corresponds to sweet cherry extract buffered at 4.5 (to minimize the influence of anthocyanin pigments on color) also measured at 420 nm.

Total Phenolic Content (TPC)

Total phenolic content was determined using the Folin–Ciocalteau reagent according to Singleton and Rossi (1965) with some modifications. In a test tube, 25 μl cherry extract was mixed with 1075 μl water and 100 μl Folin–Ciocalteau reagent; in the next 5 min, 600 μl 20 % sodium carbonate was added. After incubation during 30 min at 40 °C, the absorbance was measured at 765 nm. A calibration curve was done with gallic acid as standard. The results were expressed as gallic acid equivalents (GAE) in 100 g of dry matter content (mg GAE/100 g d.w.).

Antiradical Power (ARP)

The free radical scavenging ability of sweet cherry extracts was measured by using the bleaching method of the radical 1,1-diphenyl-2-picrylhydrazyl ($DPPH^{\bullet}$) (Brand-Williams et al. 1995) with some modifications. Three milliliters of $DPPH^{\bullet}$ solution in ethanol was placed into a cuvette and mixed with aliquots of sweet cherry extract. The absorbance decrease at 515 nm was monitored in 30 cycles in periods of 1 min. The initial radical absorbance was 1.00±0.01 AU at 515 nm when a solvent aliquot was added instead of the extract. The absorbance of the system at the steady state was estimated by mathematical fitting of kinetic curves performed with Origin 8.0 software. Percentages of radical consumption for different aliquots of cherry extracts (at least three) were measured in order to find an EC_{50} value that corresponds to the concentration that scavenged 50 % of the radicals. The antiradical power was defined as the inverse of EC_{50}.

Total Sugar Content (TS) and Reducing Sugars (RS)

The total sugar content was determined by an anthrone/sulfuric acid procedure (Southgate 1976). The reducing sugars were spectroscopically determined according to Nelson and Somogyi (1944). A curve with glucose as standard was used in both determinations for expressing results.

Statistical Analysis

The experimental design was a completely randomized design (CRD). For all determinations, except for superficial color, three replicates were determined. Calculations were corrected by the dry matter content and the results were expressed by mean and standard deviation of the mean (SD). Two-way analysis of variance (ANOVA) was performed on all variables according to the factors "Drying method" and "Pretreatment". Multiple comparisons were carried out by using the Tukey test and significance level was set at $p<0.05$. In case of significant interactions between factors, the Tukey test was run for the interaction. For non-significant interaction between factors,

Tukey test of main effects was performed; uppercase letters were used for expressing significant difference between means of "drying method" factor and lowercase letters were used for expressing significant difference between means of "pretreatment" factor. An analysis of principal component (PCA) was used to illustrate the relationship among variables and samples for the geometry of each product. All statistical analyses were carried out using the data analysis software system STATISTICA version 8.0 (StatSoft, Inc., Tulsa, OK, USA).

Results and Discussion

Sweet Cherry Physicochemical Properties

Physicochemical properties of fresh sweet cherry (Lapins var.) are described in Table 1. Total soluble solids and total acidity were coincident with data published by Raffo et al. (2009) for the same variety grown in North Patagonia, Argentina. The characterization of sweet cherries from Lapins cultivar was published by several authors around the world (Kappel et al. 1996; Drake and Elfving 2002; Jakobek et al. 2009; Usenik et al. 2008; Raffo et al. 2009; Serra et al. 2011). The results informed presented some differences, mainly in the bioactive compounds content such as anthocyanins and phenolics. However, it is widely known that bioactive compounds are regulated by environmental and post-harvest factors, including climatic conditions, fruit maturity, and storage (Serra et al. 2011). Furthermore, significant variations in the phenolic compound content among sweet cherry fruits grown on trees grafted on different vegetative rootstocks were reported by Jakobek (2009). The antioxidant activity of Lapins and other cultivars was studied by Serra et al. (2011). The high content of polyphenols, anthocyanins, and, in particular, catechin, epicatechin, neochlorogenic acid, chlorogenic acid, and quercetin explains the high antioxidant activity exhibited by Lapins cultivar, which was the most effective in inhibiting human LDL oxidation, and showed the highest antiproliferative effect on human colon and gastric cancer cell growth. Because of that, these authors affirmed that Lapins cultivar was among the varieties considered as promising functional foods for human health applications.

Table 1 Physicochemical properties of fresh sweet cherry (Lapins var.)

Physicochemical properties of sweet cherry Lapins var.	Mean±SD
Water content (g water/100 g fresh fruit)	77.5±1.8
Water activity (a_w measured at 25 °C)	0.974±0.005
pH	3.54±0.07
Total acidity (g citric acid/100 g fresh fruit)	0.82±0.06
Total soluble solids (°Bx)	20±2
Ash (%)	0.499±0.009
Total sugar (g glucose/100 g fresh fruit)	13.3±0.4
Reducing sugars (g glucose/100 g fresh fruit)	11±2
Anthocyanins (mg Cyd-3-glu/100 g fresh fruit)	47±7
Total phenolics (mg GAE/100 g fresh fruit)	98±9

Figure 1 shows the content of reducing sugars (RS) and total sugars (TS) in dried cherry discs (Fig. 1a) and dices (Fig. 1b). The total sugar content was similar for air-dried or freeze-dried samples, while, as expected, a significant increase in sugar content (≈80–82 g of glucose/100 g d.w. for discs and ≈81–86 g of glucose/100 g d.w. for dices) was observed in samples with previous dry infusions when compared with the fresh sweet cherry (TS=66.4 g of glucose/100 g d.w.). In both geometries, SI pretreatment caused an important water content decrease after air drying when compared with their respective control samples. Water content of A-SI samples was 4.67±0.11 g water/100 g d.w. for dices and 6.12 ±0.14 g water/100 d.w. for discs, whereas in their respective control samples was 9.3±0.2 g water/100 g d.w. for dices and 10.0±0.3 g water/100 g d.w. for discs. However, when freeze drying was applied to samples with SI pretreatment (8.4± 0.2 g water/100 g d.w. for dices; 10.10±0.16 g water/100 g

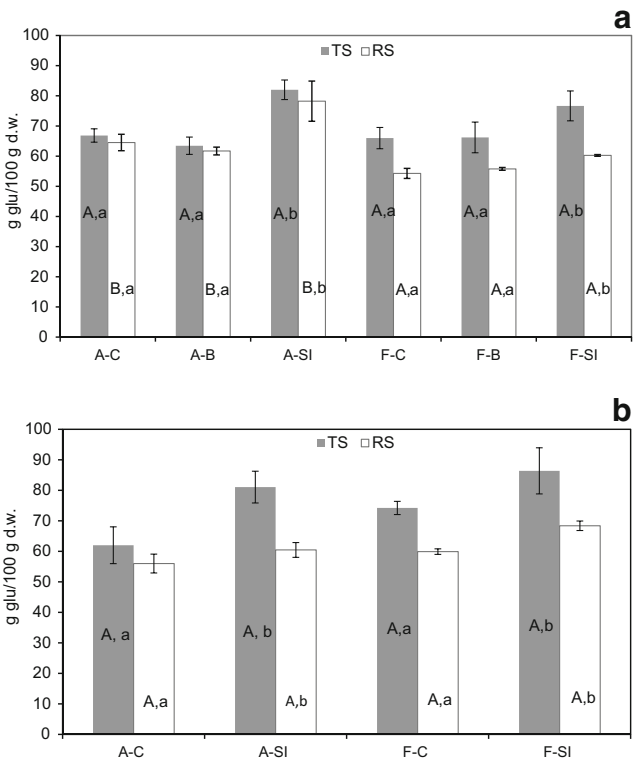

Fig. 1 Total sugar content (TS) and reducing sugar content (RS) of dried sweet cherry discs (**a**) and dices (**b**) obtained by freeze-drying (F) or air-drying (A) with and without the application of different pretreatments (C control, B blanching, SI sugar infusion). *Bars* represent standard error of the mean. Means with the same *superscript letter* were not significantly different ($p<0.05$). *Uppercase letters* and *lowercase letters* were used for main effect of factors "drying method" and "pretreatment", respectively

d.w. for discs), only a small decrease of water content compared with the correspondent control (10.5±0.4 g water/100 g d.w. for dices; 11.1±0.2 g water/100 g d.w. for discs) was obtained. Probably the structure collapse during desorption stage of freeze-drying process occurred due to glass transition temperature decrease by sugar uptake. A clear effect of the geometry was observed because sweet cherry dices presented lower water content than discs, in which the largest ratio area/volume favored drying. Despite these differences in water content, the values of water activity were not modified and presented a very homogeneous behavior in all samples, being 0.34±0.03 for dried sweet cherry discs and 0.33±0.04 for sweet cherry dices.

A high content of reducing sugars was present in all the dehydrated samples. The reducing sugar content of fresh fruit represented 80 % of the total sugar content (66.4±1.9 g glucose/100 g d.w.), in accordance with results reported by Usenik et al. (2008) who obtained a reducing sugar proportion of 88.8 % with respect to the total sugar content for the same cherry variety. The application of the SI pretreatment produced an increase in the content of reducing sugars for both geometries (Fig. 1). This increase could be due to sucrose hydrolysis during the long infusion time and the fruit acidity, resulting in the generation of reducing monosaccharides. Air-dried discs showed significantly higher RS content compared to freeze-dried ones, probably due to hydrolysis of sucrose, favored in this case by the high temperatures of the drying process. On the other hand, in sweet cherry dices, no significant differences in the RS content were observed when A-SI and F-SI samples were compared. It is possible that dices could have leached a higher amount of organic acids during sugar infusion, as they have a higher surface compared to discs. Therefore, the lower acidity present in cherry dices would account for the lower levels of sucrose hydrolysis during air drying.

Color Evaluation

Lapins cherry fruits have a dark red to a deep purple skin and are bright in appearance with a pulp of lighter red color. Considering the bicolor nature of cherry discs products, color parameters were measured on the skin side (Fig. 2a) and on the pulp side (Fig. 2b). Regarding the ANOVA analysis of data, interaction between the analyzed factors was significant for all variables, which implied that final color of samples could be ascribed to the combination of a specific pretreatment and the drying method applied. Air-drying caused darkening (L^* decrease) on both sides of control and blanched cherries. Samples without pretreatment (A-C) were affected by both enzymatic and non-enzymatic browning reactions during the process, whereas previous blanching protected A-B cherry discs against enzymatic browning, rendering L^* values higher than those for A-C samples. The browning development was more marked in the pulp side of the fruit. When sugar infusions were applied, samples exhibited a higher lightness. SI samples did not suffer darkening because of the addition of sodium bisulfite to infusion formulation, which is widely known to protect against both enzymatic and non-enzymatic browning reactions. On the other hand, pigments were transferred from the fruit to the osmotic syrups generated during infusions, contributing to fruits lightness increase. Moreover, sugar incorporation might have contributed to give a clearer appearance. In the case of freeze-dried samples, both the skin and the pulp presented higher lightness than that observed for

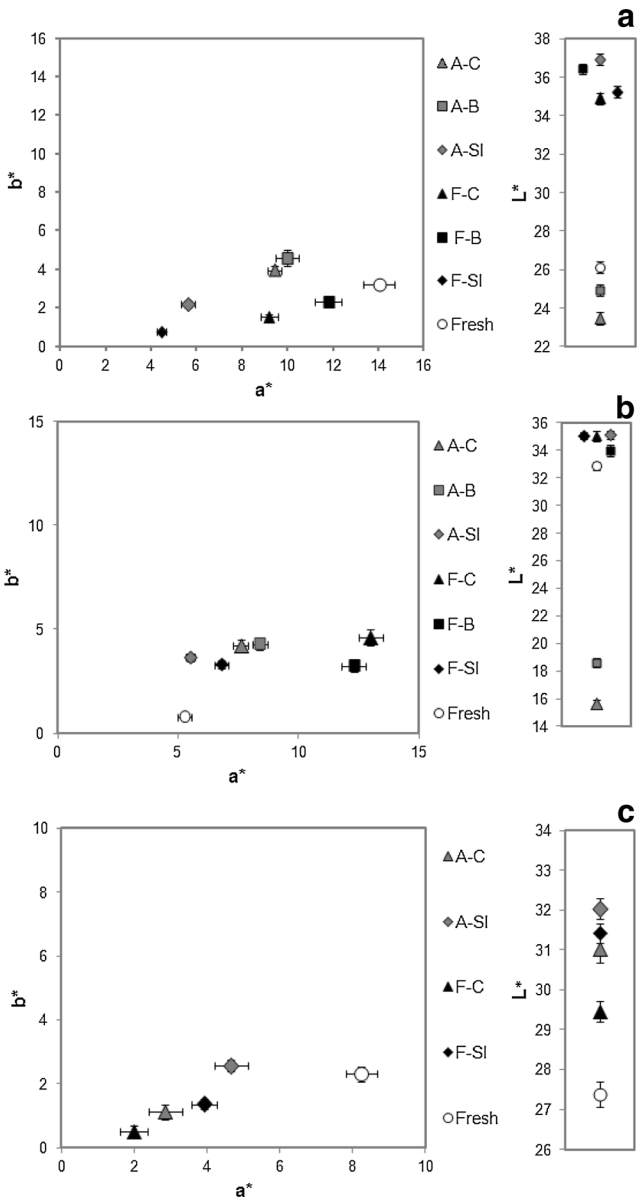

Fig. 2 CIELAB coordinates measured on **a** sweet cherry discs skin, **b** sweet cherry discs pulp, and **c** sweet cherry dices. Fresh fruit (fresh) and dried samples obtained by freeze-drying (F) or air-drying (A) with and without the application of different pretreatments (C control, B blanching, SI sugar infusion) are represented. *Bars* represent standard error of the mean

fresh fruit. Lower browning level seemed to occur upon freeze-drying compared to air-drying, as this process take place at low temperatures.

Regarding the chromatic coordinates measured on the skin of cherry discs, in general, a^* and b^* values were lower in comparison to those of fresh fruit. The main change occurred in the a^* variable, particularly for the SI-treated samples. Only in A-C and A-B cherries a small displacement to higher b^* values could be seen (Fig. 2a). On pulp side (Fig. 2b), all samples presented an increase of b^* values and only in F-C and F-B samples a significant increase of a^* was also observed.

Differences observed in chromatic properties of products are the result of browning development, mainly during drying stage, and also of the evolution of anthocyanins throughout both stages, pretreatment and subsequent drying. In general, freeze-drying allowed cherries to have a redder skin and pulp, except for samples with previous SI, which experimented on pulp similar changes than air-dried samples. In addition, freeze-dried samples presented a higher lightness than that of air-dried ones.

The evaluation of a pull of dices allowed getting a global behavior of tissue color, including the information of both the skin and the pulp in the same measurement (Fig. 2c). L^* values of all cherry dices were similar and slightly higher than that corresponding to the fresh fruit. Within each drying method, a significant but slight increase in L^* values was found in samples subjected to previous SI treatment in comparison with their respective control. A decrease of a^* values was observed in all cases, particularly in dried samples without pretreatments. The changes in the b^* variable were not very marked. Despite freeze-drying provoked the major changes in a^* and b^* values, the fruit surface true color changed towards redder hues, with slight differences in lightness and color saturation in comparison with air-dried dices.

These results demonstrate that the type of process and pretreatment had a clear impact on the color of cherries. In the case of discs, freeze-drying allowed cherries to have a redder skin and pulp, except for samples with previous SI, which experimented on pulp similar changes than air-dried samples. In addition, freeze-dried samples presented a higher lightness than that of air-dried ones. In the case of dices, slightly lighter and more desaturated samples were obtained when comparing with the fresh fruit. It is important to remark that the evolution of color in red fruits along drying will be not only the result of the concentration/degradation of red pigments throughout fruit dehydration but also of the development of dark, pigmented compounds, which tends to mask color.

Evaluation of Anthocyanin Degradation and Browning

In order to further investigate color, it is necessary to analyze the contribution of all pigments not only those naturally present in the fresh fruit but also the ones generated during processing. In this sense, the color of dried sweet cherry discs was described by the monomeric anthocyanin content (ACY), the anthocyanin degradation index (ADI), the percentage of polymeric color (%PC), the browning index (BI), and the $Abs_{420\ nm}$ (Table 2).

When comparing with fresh sweet cherry (ACY=236± 38 mg Cyd-3-glu/100 g d.w., ADI=1.20±0.01), relatively high ACY values were only obtained for F-C and F-B samples, showing a retention higher than 50 % and low ADI values. The remaining products presented low ACY values and higher anthocyanin degradation, in particular A-SI samples which showed the highest ADI values.

For fresh fruit, the ADI value was higher than 1, which is not supposed to contain degraded pigments. This could occur on one hand because some pigments have probably degraded during the pigment extraction step. The presence of oxygen during fruit grinding can accelerate the degradation of anthocyanins either by direct oxidative mechanism and/or through the action of oxidizing enzymes, such as polyphenoloxidase (Patras et al. 2010). On the other hand, anthocyanins have a small absorption at pH 4.5 which is reflected by the fact that the extinction coefficients are smaller than the corresponding value in pH 1.0 medium (Fuleki and Francis 1968). Other authors also reported ADI values higher than 1 in fresh cherries (var. Napolitana) (Pirone et al. 2014) and fresh strawberries, raspberries, and bilberries (Michalczyk et al. 2009). These authors also considered that ADI value is a better indicator of color than monomeric anthocyanin content. It must also be considered that anthocyanins can condense with other phenolic compounds to form colored polymeric pigments (Wrolstad et al. 2005), thus the percentage of polymeric color is also related to the degradation of anthocyanins and indicates the amount of color resulting from compounds derived from anthocyanins. The presence of epicatechin and catechin is relatively high in cherries, and the main phenolic compounds are anthocyanins and phenolic acids (Macheix et al. 1990). Then, polymeric pigments formed during processing may be generated by condensation of these pigments and flavan-3-ols and poliflavan-3-ols (Timberlake and Bridle 1976) and the formation of complexes between anthocyanins and phenolic acids (pyranoanthocyanins). Pyranoanthocyanins are orange pigments that have been detected during processing and aging of wines and sour cherry juice (Rentzsch et al. 2007) and strawberry and raspberry juices (Rein et al. 2005).

Browning development has to be considered as its products may affect the final color of the processed cherries. In this sense, BI and $Abs_{420\ nm}$ were analyzed (Table 2). Generally, enzymatic browning occurs during technological operations, like bruising, peeling, or crushing, and it is very specific of the early stage of technological processes, whereas non-enzymatic browning prevails in the later stages of food processing and further in storage and aging of fruit-derived foods

Table 2 Pigments of dried sweet cherry discs obtained by freeze-drying (F) or air-drying (A) with and without the application of different pretreatments (control, C; blanching, B; sugar infusion, SI)

Discs	Drying	Pret	ACY (mg Cyd-3-glu/100 g d.w.)	ADI	%PC	BI	$Abs_{420\ nm}$
A-C	A	C	$39\pm4^{a,b}$	1.93 ± 0.07^{a}	18 ± 1^{a}	0.13 ± 0.02^{a}	$0.24\pm0.03^{A,a,b}$
A-B	A	B	50 ± 16^{b}	1.7 ± 0.3^{a}	27 ± 4^{b}	$0.18\pm0.03^{a,b}$	$0.28\pm0.05^{A,b}$
A-SI	A	SI	6.2 ± 1.7^{a}	6.7 ± 1.7^{b}	46 ± 3^{c}	$0.18\pm0.02^{a,b}$	$0.238\pm0.017^{A,a}$
F-C	F	C	121 ± 8^{c}	1.46 ± 0.04^{a}	$20\pm3^{a,b}$	0.2414 ± 0.0004^{b}	$0.32\pm0.07^{A,a,b}$
F-B	F	B	165 ± 22^{d}	1.29 ± 0.06^{a}	17 ± 3^{a}	0.15 ± 0.03^{a}	$0.30\pm0.04^{A,b}$
F-SI	F	SI	$31\pm6^{a,b}$	2.1 ± 0.3^{a}	43 ± 1^{c}	0.137 ± 0.009^{a}	$0.215\pm0.018^{A,a}$
Drying × pretreatment[a]			Sig.	Sig.	Sig.	Sig.	N. Sig.

Monomeric anthocyanin content (ACY), anthocyanin degradation index (ADI), percentage of polymeric color (%PC), browning index (BI), and Abs_{420nm}

[a] Interaction factor: Sig. (significant); N.Sig. (not significant). Means with the same letter superscript were not significantly different ($p<0.05$). Uppercase letters and lowercase letters were used for main effect of factors: "drying method" and "pretreatment", respectively

(Es-Safi et al. 2003). The development of Maillard reaction in acidic conditions leads to the formation of intermediate products like furfural and HMF (5-hydroxymethyl-furfural) (Perez-Locas and Yaylayan 2010), and considering the low pH of the sweet cherry, these compounds could be formed during air-drying conditions. It is important to note that the presence of furfural can accelerate and/or induce the polymerization of flavanols and anthocyanins (Es-Safi et al. 2000).

Upon sugar infusion, the loss of anthocyanin pigments to the osmotic syrup was about 70 and 97 % for F-SI and A-SI, respectively. According to %PC data, ≈50 % of total color density of infused samples corresponds to polymeric pigments (Table 2). In fresh sweet cherry, polymeric color represented 14.7 % of the total color density, mainly due to the formation of complexes between these pigments and other polyphenols, and including brown compounds produced enzymatically by the decompartmentalization conducted during grinding of the sample (which should be minimized by the extraction method). The IB (0.11±0.02) and $Abs_{420\ nm}$ (0.17) of fresh fruit would only quantify the enzymatically produced browning because brown compounds produced by Maillard reaction would be absent. The highest %PC values were obtained in discs with SI pretreatment, while the lowest values were observed in F-B samples, which also retained the highest monomeric anthocyanin percentage. It is well known that intermolecular copigmentation phenomenon is a way of enhancing anthocyanin stability because the anthocyanin-copigment complex formation protects the flavylium group against hydration, so that the color change of the chromophore is not dependent on pH (Mazza and Miniati 1993).

Regarding the sweet cherry pH (3.5) and the content of anthocyanins, phenolic acids, and especially flavonols which are considered among the most efficient copigments (Asen et al. 1972), the necessary conditions for this association are present in this fruit. Copigmentation is verified by a hyperchromic phenomenon in the wavelength at which the maximum absorbance is observed, and certain copigments lead to a bathochromic shift to higher λ values (Mazza and Miniati 1993). When comparing the spectra corresponding to cherry discs with that of fresh fruit (data not shown), the largest bathochromic shift ($\Delta\lambda_{max}$=6 nm) was effectively found in F-B samples. Boulton (2001) affirmed that copigmentation occurs at a minimum anthocyanin concentration of 18.5 mg/l; only F-B and F-C discs ($\Delta\lambda_{max}$=4 nm) exhibited concentrations above that limit (30 and 20 mg/l, respectively). On the other hand, A-SI samples showed a hypsochromic shift ($\Delta\lambda_{max}$=−7 nm). Rentzsch et al. (2007) when analyzing unfermented sour cherry juice informed the presence of an anthocyanin derivative (pyranoanthocyanin) detected by a hypsochromically shifted maximum of absorption from 520 up to 510 nm. Probably, the pyranoanthocyanin formation would be favored by sugar infusion conditions since discs were immersed in the syrup during 15 days, being a suitable medium for condensation reactions of anthocyanins and phenolic acids.

Regarding the evaluation of browning in cherry discs, the color differences detected between air-dried and freeze-dried samples, essentially given by the L^* decrease and b^* increase normally associated with browning during convective drying, was not reflected in the measured BI values (Table 2) since no significant differences were observed among freeze-dried and air-dried samples. Blanching was applied in order to inactivate (at least partly) the enzymes responsible for enzymatic browning. On the other hand, sodium bisulfite was added in sugar infusion formulation in order to prevent oxidation reactions, as well as enzymatic and non-enzymatic reactions; it also acts as bleaching agent. However, the obtained values of BI demonstrate that in general no effect of pretreatments was observed. Another parameter frequently used to evaluate browning is the $Abs_{420\ nm}$. However, in berry extracts, anthocyanin-degradation compounds could also contribute to $Abs_{420\ nm}$; although they do not exhibit maximum

absorbance at that wavelength, they may weakly contribute to the optical density since they do not show color changes with pH change. Table 2 shows a clear effect of pretreatments. On the one hand, blanching was not enough to reduce browning since no significant differences were observed between control and blanched samples. It has been reported from optical microscopy studies that blanching of fruit tissues also results in breakage of membranes and damage in cell walls (González-Fesler et al. 2008; Gómez et al. 2010), which would increase enzyme-substrate contact with the consequent increase in tissue browning. However, it was possible to reduce browning by SI application since A-SI and F-SI samples showed minor absorbance. It is interesting to remark that the higher values of $Abs_{420\ nm}$ registered in F-C and F-B samples would reflect the effect of co-pigmentation phenomenon previously mentioned because the absence of high temperatures and of gradual a_w changes during freeze-drying processes should imply minimum browning reactions. For dices, the parameters are shown in Table 3. Retention of anthocyanin pigments in freeze-dried dices was significantly higher than that observed in air-dried ones. The SI samples showed lower pigment content when compared to their respective control ($p<0.05$) and A-SI dices exhibited the highest ADI and %PC values. In this kind of geometry, the effect of pretreatment on browning was verified in both parameters Abs_{420nm} and BI. A-C dices showed significantly higher BI values in comparison with the rest of the experimental conditions. Again, the effect of the copigmentation phenomenon for control samples was observed: A-C ($\Delta\lambda_{max}=7$ nm) and F-C ($\Delta\lambda_{max}=5$ nm). In both cases, the high Abs_{420nm} values would reflect, at least partially, the red pigments of the sample (Table 3).

Bioactive Compounds of Dried Sweet Cherries

The antiradical power (ARP) versus the total polyphenol content (TPC) of fresh and dried cherries (discs and dices) is shown in Fig. 3. In general, high phenolic contents were observed at high antiradical power values. It can be seen that all the SI samples were grouped on the left in the diagram and below the fresh fruit, showing not only the loss of bioactive compounds but also the decrease of the antiradical power. This is because during the osmotic dehydration, water diffusion towards the hypertonic medium is accompanied by the migration of water-soluble substances contained in the vacuole as organic acids, flavonoids, anthocyanins, etc. This dilution effect of certain phenolic compounds may explain the observed decrease of the antiradical power of these samples. These results are consistent with studies by Osorio et al. (2007) on Andes berry (*Rubus glaucus* Benth.) fruits, who observed ≈43 % loss of monomeric anthocyanins and 100 % loss of antioxidant capacity after three cycles of osmotic dehydration. In contrast, control and blanched air-dried discs showed an enhancement of their antiradical power with respect to the remaining studied cherries (Fig. 3). Blanching pretreatment led to samples with higher TPC and ARP values in comparison to the other two pretreatments. This fact could be due to the inactivation of polyphenoloxidase during blanching, allowing the preservation of a certain proportion

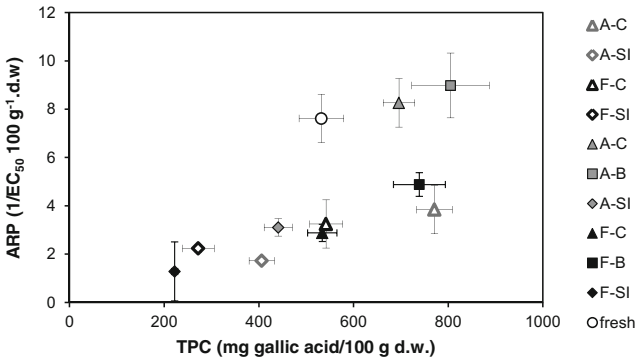

Fig. 3 Antiradical power (ARP) against total phenolic content (TPC) of fresh sweet cherry and different dried sweet cherries: discs (*filled symbols*) and dices (*unfilled symbols*) obtained by freeze-drying (F) or air-drying (A) with and without the application of different pretreatments (C control, B blanching, SI sugar infusion). *Bars* represent standard error of the mean

Table 3 Pigments of dried sweet cherry dices obtained by freeze-drying (F) or air-drying (A) with and without the application of different pretreatments (control, C; sugar infusion, SI)

Dices	Drying	Pret.	ACY (mg Cyd-3-glu/100 g d.w.)	ADI	%PC	BI	$Abs_{420\ nm}$
A-C	A	C	$125\pm6^{A,a}$	1.37 ± 0.03^{a}	$29\pm4^{A,a}$	0.167 ± 0.005^{b}	$0.25\pm0.06^{A,b}$
A-SI	A	SI	$22\pm4^{A,b}$	2.4 ± 0.2^{b}	$34\pm3^{A,b}$	0.11 ± 0.03^{a}	$0.11\pm0,02^{A,a}$
F-C	F	C	$211\pm30^{B,a}$	1.26 ± 0.03^{a}	$16\pm3^{B,a}$	0.084 ± 0.007^{a}	$0.22\pm0.04^{A,b}$
F-SI	F	SI	$89\pm8^{B,b}$	1.36 ± 0.03^{a}	$25\pm2^{B,b}$	0.11 ± 0.02^{a}	$0.16\pm0.02^{A,a}$
Drying × pretreatment[a]			N.Sig.	Sig.	N.Sig.	Sig.	N.Sig.

Monomeric anthocyanin content (ACY), anthocyanin degradation index (ADI), percentage of polymeric color (%PC), browning index (BI), and $Abs_{420\ nm}$

[a] Interaction factor: Sig. (significant); N.Sig (not significant). Means with the same letter superscript were not significantly different ($p<0.05$). Uppercase letters and lowercase letters were used for main effect of factors: "drying method" and "pretreatment", respectively

of polyphenols. It is important to note that the A-B cherries showed even a higher TPC value than that of the fresh fruit, and this could be related to the release of phenolic compounds bound to the fruit epidermis upon exposure to steam. It is known that blanching not only acts inactivating oxidative enzymes in the processed fruits but also improving permeability of the pigmented cells of the pericarp (Brambilla et al. 2008). Other authors also showed that blanching berries (before milling) improved the stability and recovery of bioactive phenolic compounds (Rossi et al. 2003). When comparing the dehydration methods, the discs obtained by the application of convective drying exhibited higher TPC and ARP values than freeze-dried cherries ($p<0.05$). The increase in antioxidant activity could be due to the increase of polyphenols due to their formation from precursors by non-enzymatic interconversion reactions that occur upon the application of temperature during drying (Que et al. 2008). On the other hand, the increase in antioxidant capacity may be due to the generation and accumulation of Maillard-type antioxidants. It has been reported that the compounds derived from the Maillard reaction have different degrees of antioxidant activity depending on their origin (Kim et al. 1986; Wijewickreme et al. 1999; Yilmaz and Toledo 2005). In this regard, the convective drying conditions (T=70 °C and time to reduce a_w to 0.3≈48 h) used in this study were adequate to generate Maillard products, and this was reflected in the values of $Abs_{420\ nm}$ measured in these samples. Additionally, the combination of dry infusion pretreatment and freeze-drying (F-SI) resulted in less retention of bioactive compounds and less captation capacity of free radicals (Fig. 5). Que et al. (2008) studied the influence of processing on the phenolic content and the antioxidant activity in pumpkin; they observed a polyphenolic content 4.6 times higher in air-dried compared to freeze-dried pumpkin, demonstrating that the generation of phenolic compounds occurs during drying at 70 °C. In the case of cherry dices, the air-drying method yielded samples with higher phenolic content, while the application of dry infusion caused once again a significant decrease of TPC. F-C dices retained the fresh fruit polyphenols, while A-C ones showed a significant increase of these compounds. In general, discs and dices having the same "pretreatment-dehydration method" behaved similarly in terms of bioactive compounds retention and antiradical power, except for the A-C case. This could be related to the effect of an excessive heat treatment for cherry dices. Considering that the air-drying conditions (temperature-time) were the same for both geometries, it is possible that in the case of dices, Maillard compounds had a polymerization degree (Table 3) that could have caused a decrease on the antiradical power. These results are consistent with a study about the antioxidant capacity of Maillard reaction products (MRP) which showed that systems heated at higher temperatures (120 °C) for 1 h exhibited a reduced antioxidant capacity compared with the same system heated at 100 °C due to the degradation of antioxidants MRP formed in the early stages of the reaction (Yilmaz and Toledo 2005). It was also observed that freeze-dried control cherries (discs and dices), despite maintaining the phenolic content of fresh fruit, showed an ARP decrease. It has been shown that upon freeze-drying as well as ionizing radiation and ultrasound treatments, peroxyl radicals may be formed (Nazareno et al. 2011). This could explain that although the bioactive compounds are in the same amount as in fresh fruit, some of them could be stabilizing free radicals produced during the freeze-drying process.

Principal Component Analysis (PCA)

PCA analysis was applied to detect patterns between the variables and the samples analyzed. In the case of dried sweet cherry discs (Fig. 4), PCA resumed the information of 23 variables measured in two new, uncorrelated variables termed "principal components" (PC1 and PC2). For this geometry, PC1 explained 49.2 % of the total of variance and PC2 explained 32.2 %; therefore, the PCA analysis explained 81.4 % of the total variability of this system. For dried sweet cherry dices (Fig. 5), PCA resumed the information of 17 variables, being 94 % of the total variability explained, with 66.4 % from PC1 and 27.6 % from PC2. Several observations can be made from the sample score plot for PC1 versus PC2 (Figs. 4 and 5). Ellipsoidal figures obtained from cluster analysis enclose samples presenting similar behavior with respect to the variables represented in each PCA plot. In the case of sweet cherry discs (Fig. 4), different relationships between color coordinates and variables could be appreciated depending on the zone evaluated for color determination (skin or pulp). For example, a^* of pulp side presented a strong correlation with ACY content, whereas a^* of skin, and also C^*_{ab} of pulp and skin, showed correlation with TPC content. On the other hand, increases in b^* and hue angle were related with ARP parameter. This behavior would confirm the presence of Maillard compounds in A-C and A-B samples. Cherry discs that experienced higher ΔE^*_{ab} on the skin (A-SI and F-SI) were also those that showed higher ADI and %PC. On the other hand, control and blanched samples subjected to air-drying (A-C and A-B) exhibited higher ΔE^*_{ab} on the pulp, mainly given by the hue shifts toward yellow tones, a color saturation increase, and a lightness decrease. In both skin and pulp sides, all the variables related to total global change represent color transformation due to anthocyanin degradation and brown pigment formation, so that ΔE^*_{ab} parameter would indicate, to some extent, the browning phenomenon. For instance, Agudelo-Laverde et al. (2011) also have used the "global color change" function for browning determination in freeze-dried melon and pear. In the present study, when analyzing BI and $Abs_{420\ nm}$ parameters measured to evaluate browning after drying, it was found that these variables explained unsatisfactorily this phenomenon. In fact, the contribution of BI variable

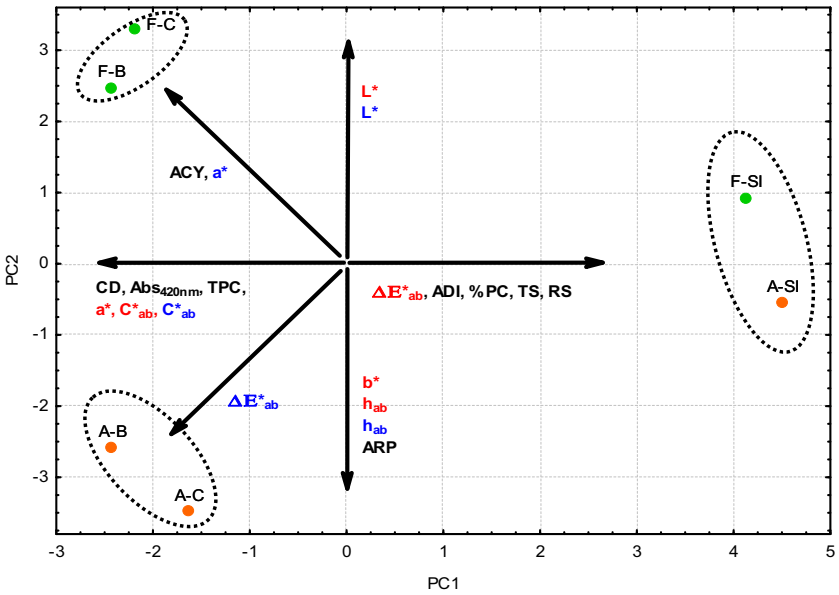

Fig. 4 Principal component analysis (PCA) plot for dried sweet cherry discs obtained by freeze-drying (F) or air-drying (A) with and without the application of different pretreatments (C control, B blanching, SI sugar infusion). Color coordinates in *red* correspond to skin side, color coordinates in *blue* correspond to pulp side

to principal components was not significant. In the case of $Abs_{420\ nm}$, high correlations with a^* (0.91) and C^*_{ab} (0.93) from pulp, CD (0.87), and ACY (0.84) were obtained. Therefore, these results confirm the influence of high anthocyanin content on the $Abs_{420\ nm}$ values, observed in those cases where the phenomenon of copigmentation probably occurred (F-C and F-B discs).

From the standpoint of product quality, it can be stated that sugar infusion pretreatment did not allow the preservation of quality attributes. In contrast, blanching prior to air-drying led to bioactive compound preservation when comparing to their respective control since they exhibited higher retention of anthocyanin and total phenolic content (see also Table 2 and Fig. 3). However, similar color attributes were observed in blanched and control cherries (Fig. 2a, b). All freeze-dried samples were located in the upper half of the PCA diagram, which is associated with a greater lightness and a reddish tonality on both sample sides, pulp and skin (Fig. 2a, b), because of a greater preservation of anthocyanin pigments. On the contrary, air-dried samples presented an opposite behavior as they appeared in the lower half of the graph (Fig. 4). Despite using high temperatures was detrimental of the color and the preservation of anthocyanin pigments, sweet cherry discs obtained by air-drying showed a higher capacity of trapping free radicals (see also Fig. 3).

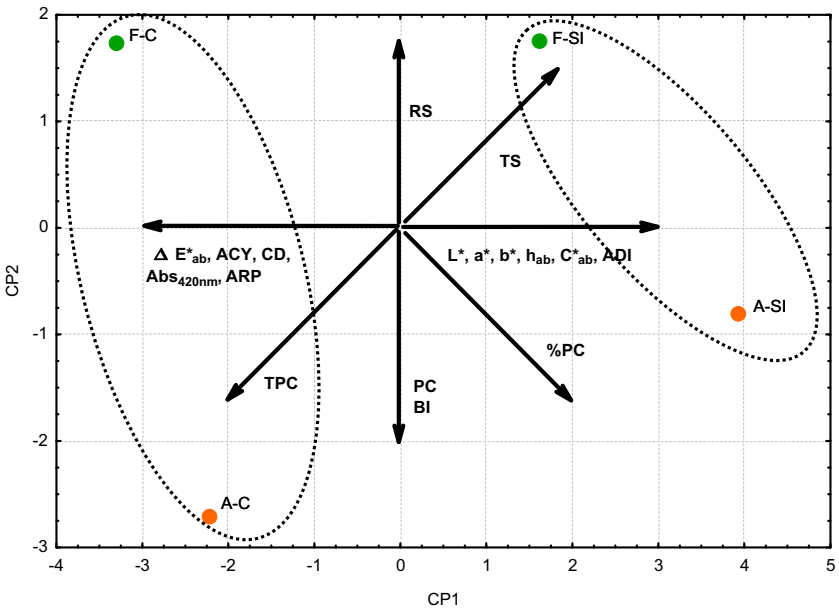

Fig. 5 Principal component analysis (PCA) plot for dried sweet cherry dices obtained by freeze-drying (F) or air-drying (A) with and without the application of different pretreatments (C control, SI sugar infusion)

In sweet cherry dices (Fig. 5), global color change appeared in the opposite direction of the other color coordinates. Samples with higher antiradical power also exhibited higher anthocyanin content. Also, TPC content presented opposite direction to TS content, which supports that IS pretreatment was not effective in the preservation of bioactive compounds. Control samples, which appeared on the left side of the graph, showed not only a higher ACY and TPC content but also higher ARP. The highest anthocyanin degradation was observed in samples with SI pretreatment, in agreement with b^* increase and higher h_{ab} values. As it was expected, in this product geometry, air-dried samples exhibited higher %PC values which corresponded to more brownish (>BI) samples (see also Table 3). The effect of high temperatures on polyphenol content could be verified since A-C samples presented the highest TPC values (see also Fig. 3).

Conclusions

In this work, different geometries of dehydrated cherry products were obtained in order to employ them in different applications. Discs could be consumed as is, like fruit snacks, due to their adequate size and shape. The most suitable combined technology to obtain sweet cherry discs products was the application of blanching and air-drying due to their high content of phenolic compounds and antiradical power.

In the case of dices, these products could be considered as ingredients to be incorporated in fruit bars, a cereal mix, cookies, or muffins. Although freeze-dried dices without pretreatment presented the best quality attributes in terms of superficial color and anthocyanin pigment retention, the use of air-drying without pretreatment could also be recommended because it allowed obtaining samples with similar antiradical activity but a higher phenolic content than the freeze-dried samples.

Although sugar infusion pretreatment caused a significant phenolic loss, the application of this pretreatment might be interesting to generate fruit snacks for kids that usually prefer sweets and replace the consumption of unhealthy snacks with a fruit option.

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