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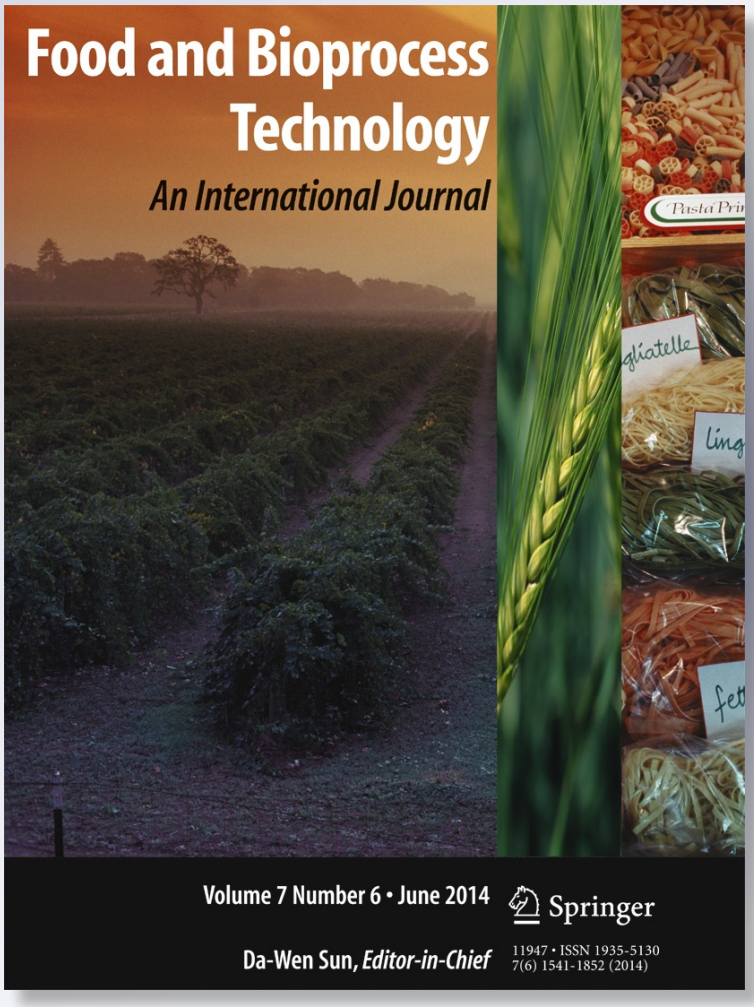

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ORIGINAL PAPER

Pretreatments Effect in Drying Behaviour and Colour of Mature and Immature 'Napolitana' Sweet Cherries

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Abstract The effect of different treatments on drying behaviour and colour of mature and immature cherries (Napolitana var.) has been studied. Drying was carried out at 70 °C with air at 4 m/s speed and 8 % relative humidity, and fruits were subjected to the following pretreatments: B (blanching), F (freezing), P (pitting), B+Dip1 (blanching and immersion in acid solution) and B+Dip1+Dip2 (blanching and immersion in saline acid solution) which affected the drying behaviour and the colour retention of fruits for both maturity degrees. Regarding skin colour in terms of chroma and hunter *a* parameters, the anthocyanin retention and the evaluation of anthocyanin degradation index, both B+dip1 and B+dip1+dip2 pretreatments led to better-quality dry products, mainly in mature cherries. Moreover, the incorporation of blanching in the combined pretreatments significantly reduced drying time. Lewis, Page and Logarithmic models were selected to represent in a simple way the thin-layer drying characteristics of pretreated cherries and to predict the process times required to reduce the moisture content to about 0.3–0.4 kg water/kg dm ($a_w \leq 0.6$). Logarithmic model provided the best fit to experimental data for each drying curve, based on the statistical tests used for evaluation.

Keywords Cherries · Drying · Colour · Anthocyanins · Maturity

Introduction

Cherry is a non-climacteric fruit that must be harvested at physiological maturity stage which is determined by the following indices: soluble solids content (SSC), acidity and colour. The choice of the harvest date will depend on cultivar and consumer preference. Appearance is a primary criterion in purchasing with colour contributing more to the assessment of quality than any other single appearance factor (Kays 1999; Cittadini 2007; Usenik et al. 2008). In general, full red cherries have higher consumer acceptance than full bright red cherries (Crisosto et al. 1997). Napolitana cherry is bright light red of small caliber, and it has an intermediate firmness when compared with other cultivars. Taste perception, related to a balance between SSC and acidity, is of 0.48 (≈26 % SSC and 54 % tritatable acidity) while the market demands values from 1.5 to 2.0 for the acceptance of fresh fruit (San Martino et al. 2008). Due to these characteristics, industrialisation is its only destination. Although dehydration constitutes a traditional conservation method used to extend the shelf life of fruits, it has been infrequently applied to this type of raw material, probably due to reactions that take place during the process, leading mainly to an important damage in colour. When fruits are harvested early, although they are unattractive in colour, more acidic, with lower sugar content and less aromatic, greater tissue firmness is obtained, reducing mechanical damage during handling and further processing (Romano et al. 2006). This aspect can be especially suitable to resist drastic preservation treatments which can include drying in combination with heat application or freezing.

In cherries, the pigments responsible for the attractive red colour are the anthocyanins, which are compounds relatively

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unstable to the variation of certain external factors, the acid environment being the factor where greatest stability is achieved (Rein 2005; Cavalcanti et al. 2011). In this type of food, the anthocyanins can exist in four structural forms, depending on pH: the blue quinonoidal base (pH near to 6.0), the red flavylium cation (pH≈1.0) and the colourless forms (pseudocarbinol and chalcone; pH≈4.5). As regards temperature, the chemical structures that exhibit a greater stability to pH increase also have greater thermal stability. By increasing the temperature, the equilibrium moves to the formation of chalcone, the inverse reaction being much slower that the direct reaction (García-Viguera et al. 1999; Fenema 2000).

It has been reported that cherries exhibit considerable colour changes at the earlier stages of the drying process, mainly those associated to browning reactions. The resulting loss of quality has adverse economic effects on domestic and international markets, and the available studies on the effect of operative variables of drying process on colour degradation have not evidenced positive results (Ohaco et al. 2001). The use of several pretreatment methods (chemical and non-chemical) can be proposed to preserve colour during drying. Blanching in hot water or steam has been widely used in the food industry for thermal inactivation of the enzymes responsible for enzymatic browning. Because thermal treatments are also responsible for undesirable changes in tissue texture, several other methods have been carried out to inhibit polyphenol oxidase (PPO) activity and avoid colour changes. The employment of organic acids (i.e. ascorbic, citric, oxalic) has been long applied in combination with calcium salts to prevent enzymatic browning and also maintain fruit firmness (Lamikanra 2002; Wang et al. 2007). Although ascorbic acid has been extensively used to protect fruits and juices against oxidation, it is thought to have several different roles in anthocyanin colour stability (Rein 2005). It enhances polymer pigment formation and whitens anthocyanin pigments. Besides, a direct condensation between acid ascorbic and anthocyanins has been postulated as a mechanism for anthocyanin degradation (Poei-Langston and Wrolstad 1981). On the other hand, the formation of hydrogen peroxide from ascorbic acid oxidation can also influence anthocyanins (Meschter 1953; Markakis 1982; Fenema 2000; Talcott et al. 2003). Instead, citric acid acts as a chelating agent and acidulant, both functionalities inhibiting PPO (Ahvenainen, 2000). Therefore, this acid can be used as an alternative to ascorbic acid not only to prevent enzymatic browning but also to improve anthocyanin stability.

Another problem in the drying of fruits such as cherries, grapes and plums is that they are covered with a thin layer of wax cuticle, which controls the rate of moisture diffusion through the samples. A common chemical pretreatment to break down the wax cuticular fruit surface and increase permeability consists of dipping the fruits into solutions of fatty acid esters such as ethyl or methyl oleate solutions for several seconds (Tarhan 2006; Doymaz and Ismail 2011; Orak et al. 2012). However, little information is available regarding the effect of other physical treatments such as blanching, pre-freezing or even mechanical pitting of the fruit, which may be used as an alternative to reduce skin resistance and facilitate moisture transfer during drying.

The optimal pretreatment for cherries should minimise drying time while retaining product quality of the dried product, mainly changes in colour. Therefore, the aim of this work was (1) to apply different treatments to cherry fruits in order to achieve greater colour retention during subsequent drying, obtaining a high-quality end product, as well as to reduce drying times, (2) to study the effect of different maturity degrees on drying rate and fruit colour evolution during drying and (3) to propose a simple model to estimate the process time.

Materials and Methods

Sample Preparation

Sweet cherries (*Prunus avium*) of Napolitana cultivar produced in the Andean Patagonian valleys of the El Bolsón region (Río Negro province, Argentina) were used in the present study. Taking into account the optimal maturity degree at harvest, two different pulls were selected from a local fruit farm: mature (optimal maturity) and immature. After harvest, fruits were maintained for 1 day at typical, industrially used storage conditions, that is, 1.5±0.5 °C and 90 % RH. Then, the fruits were washed; peduncles were removed and then subjected to different treatments prior to drying.

Pretreatments

Five pretreatments were considered in this study: Some of them involved dipping in chemical solutions and/or heating the fruit at high temperature in order to inactivate or inhibit browning reaction, as well as to stabilise the fruits' red colours. Others were physical treatments applied to the fruits to accelerate mass transfer during drying.

The pretreatments applied were:

1. Blanching: carried out by exposure to water vapour at 100 °C during 1.5 min and subsequent immersion in cool water at 4 °C for 2 min (B).
2. Combined treatment: blanching and subsequent fruit immersion at room temperature in a citric acid solution (10 %*w/v*) for 5 min (B+Dip 1)
3. Combined treatment: blanching and subsequent fruit immersion at room temperature in a citric acid solution (10 %*w/v*) and calcium lactate (2.5 %*w/v*) for 5 min (B+Dip1+Dip2).

4. Freezing: Cherries were placed into plastic bags and frozen at −18ºC for 4 days in a commercial freezer (Gafa, Argentina) (F)
5. Pitting: It was carefully done with a manual cherry pitter (P)
6. Control: Cherry fruits without pretreatments were used as control (C).

Drying Methods

Drying experiments were performed in a laboratory drier for thin-layer dehydration (Fig. 1). This dryer consists of a closed-loop system with recirculated forced air (70ºC, 4 m/s air speed and 8 % relative humidity). Previous studies revealed that degradation reactions, such as the conversion of sugars which can lead to toxic furfural and to the development of undesired brown compounds, as well as a greater degradation of fruit colour, occurred at temperatures above 70 °C (Ohaco et al. 2001; Pirone et al. 2004; Ochoa et al. 2006; Rufián-Henares et al. 2008; Mabellini et al. 2010; Pirone et al. 2010). This temperature would be the most suitable condition for drying with regard to the required drying time and quality retention.

The samples were dried in a perforated basket which had a flow cross-section of 490 cm^2. The air temperature was measured with a copper constantan thermocouple (sensitivity, ±1 °C), and air flow rate was regulated with a thermo-anemometer model 407117 Mini Vane CFM (Extech Instruments, Taipei, Taiwan) flowing transversal to the fruit layer (sensitivity, ±0.01 m/s). All variables were measured at the drying chamber inlet. Duplicated curves were obtained by weighing (balance sensitivity, ±0.0001 g) the samples periodically till 10–13 h drying. Samples (36±1 g of cherries) were removed every 0.5 h till 2 h treatment and, after that, every 1 h till the end of the process. The final moisture content (X) of dried cherries was ≈0.3–0.4 kg water/kg dm).

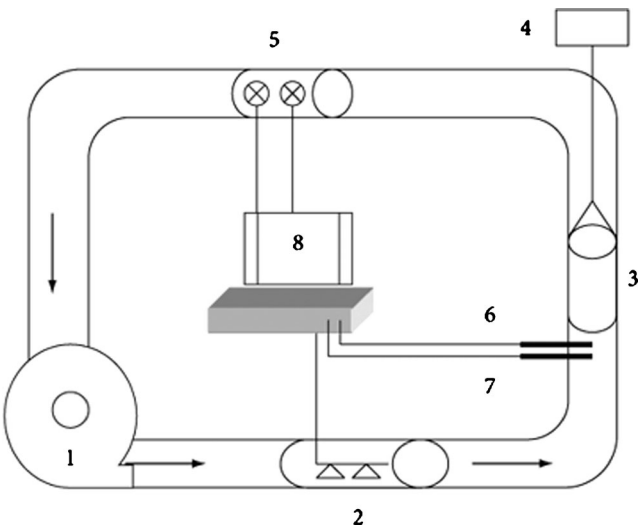

Fig. 1 Scheme of experimental drying equipment: (*1*) variable flow fan, (*2*) air humidifier, containing a saturated salt solution, (*3*) drying chamber, (*4*) balance, (*5*) electric heater controlled by a computer, (*6*) air dry bulb temperature recorder, (*7*) air moisture recorder and (*8*) computer

Sample analysis

Water content, water activity, pH, total acidity and soluble solid content of fresh fruit

The characterisation of raw fruit was carried out by analysing the following parameters according to AOAC (1990): moisture (930-40), water activity, pH (981-12), total acidity (942-15) and soluble solids content (932-12). For moisture determination, whole and pitted fruits were used and for water activity (a_w), pH, total acidity (TA) and SSC, a fruit puree was used. The a_w was measured at 25 °C with a psycrometer model Series 3 (Aqua-Lab, Decagon Devices Inc., Pullman, WA), calibrated with saturated salt aqueous solutions. Soluble solid content percentage in the liquid phase was analysed by measuring the refraction index in an ABBE refractometer model DR A1 (Atago, Tokyo, Japan) at 25 °C. TA was measured by adding 5 g of sample juice to 50 mL of distilled water and titrating with 0.1 N sodium hydroxide (NaOH) to an end point of pH 8.1. TA is expressed as percent of citric acid, which is the predominant acid in this species. The pH was measured with a pHmeter model EA 940 (ORION, Beverly, USA). All measurements were made in triplicate, and the average values were informed.

The cherries maturity index was evaluated by the ratio of total soluble solids and acidity as:

$$I_{maturity} = SSC\ (Brix)/TA\ (g\ citric\ acid/100\ g) \quad (1)$$

Pigment Evaluation

Total monomeric anthocyanin content (Acy) and anthocyanin degradation index (ADI) were evaluated after extraction and a subsequent spectrophotometric reading at the wavelength of maximum absorbance of red pigments. Visible spectra of samples were determined by scanning the absorbance between 420 and 550 nm. Quartz cuvettes of 1 cm path-length were used, and all measurements were carried out at room temperature (22 °C). Absorbance readings were made against distilled water as a blank.

1. Pigment extraction

   Extraction was performed by the method described by Abers and Wrolstad (1979). A certain weight of fruits (≅10 g) was pitted and mashed, mixed with 30 ml acetone and maintained overnight at 4 °C. Then the extract was filtered using Whatman N°1 paper (Whatman Inc., Clifton, NJ, USA). The filter cake was re-extracted with a

similar acetone volume, stored at 4 °C during 4 h and filtered. Filtrates were combined and mixed with 90 ml chloroform. The addition of chloroform results in phase separation between the aqueous portion (which contains the anthocyanin, phenolics, sugar, organic acids and other water-soluble compounds) and the bulk phase (which contains the immiscible organic solvents, lipids, carotenoids, chlorophyll pigments and other non-polar compounds). This method has the advantage of producing an extract with no lipophilic contaminants. The absence of a concentration step minimises the risk of acid-dependent pigment degradation. The lower phase of chloroform–acetone was discarded, and the upper aqueous phase where the anthocyanins are retained was collected and made up to 100 ml with distilled water.

2. Determination of Total Anthocyanins (Acy)

   Monomeric anthocyanin content of samples was performed by the pH-differential method described by Giusti and Wrolstad (2001). Aliquots of cherry extract were brought to pH 1.0 with buffer HCl–KCl 0.2 M and pH 4.5 with buffer HCl–sodium acetate 1 M and allowed to equilibrate for 1 h. At pH 1.0, anthocyanins exist in the highly coloured oxonium or flavilium form, and at pH 4.5, they are predominately in the colourless carbinol form. The absorbance of each equilibrated solution was then measured at 510 nm (λ_{max}) using a UV/Vis spectrophotometer model 1700 (Metrolab Instruments, Buenos Aires, Argentina). The method relies on the structural transformations of the anthocyanin chromophore as a function of pH, so that the difference in absorbance between the two buffer solutions will be proportional to monomeric anthocyanin content. Acy content was expressed as cyaniding-3-glucoside with molecular weight of 445.2 and a molar extinction coefficient ε of 29,600 $L\ cm^{-1}\ mol^{-1}$ (Giusti and Wrolstad 2001; Wrolstad et al. 2005). Resultant values were expressed in terms of milligrams of anthocyanin per 100 g of dry matter content.

3. Anthocyanin Degradation Index (ADI)

   ADI is defined as the ratio between the total anthocyanins (degraded and nondegraded) calculated by the single pH method (absorbance measured at pH 1) and the nondegraded anthocyanin content determined by pH differential. This index is indicative of the proportion of degraded anthocyanin in the sample and is useful even if the anthocyanins are unidentified or the extinction coefficients are unknown (Fuleki and Francis 1968).

Superficial Colour

The superficial colour was determined by measuring tristimulus parameters (HunterLab colour space) with a HunterLab Colour Difference meter Model D25L-2 (Hunter Associates Laboratory, Reston, VA, USA) in the reflection mode. The instrument was standardised each time with a white ceramic plate (L=92.8; a=−0.8and b=0.1). These numerical values were converted into "total colour difference" (ΔE_{ab}), "chroma" (C_{ab}) and "hue angle" (h_{ab}) colour functions using the following equations:

$$\Delta E_{ab} = \left[(\Delta L_{ab})^2 + (\Delta a)^2 + (\Delta b)^2\right]^{1/2} \quad (2)$$

(differences were calculated taking into account L, a and b values of raw cherries before treatments)

$$C_{ab} = \left(a^2 + b^2\right)^{1/2} \quad (3)$$

$$h_{ab} = \text{arctg}\,(b/a) \quad (4)$$

The total colour difference indicates the magnitude of colour change after treatment. Lightness separates colour into bright and dark. Hue is an angle in a colour wheel of 360° and can be distributed in the four quadrants of the *ab* plane. Values are defined as follows: red–purple, 0°, yellow, 90°, bluish-green, 180° and blue, 270°. Chroma represents the intensity or purity of the hue, with low values representing dull colours and high values representing vibrant colours.

Colour determinations were done on the cheek area of 12 fruits taken from the dryer after certain time intervals (0, 0.5, 1, 2, 3.5, 4.5 and 7 h). Two replicates of each fruit were measured.

Drying Models

Several models can be used to estimate convective drying characteristics of fruits. Some of them are empirical models proposed to simulate the drying curves, providing a direct relationship between average moisture content and drying time. They are quite simple models that neglect the fundamentals of the drying process, and their parameters have no physical meaning. Therefore, they may only describe the drying curves for the conditions of the experimental process. Among these models, the Lewis, Page and Logarithmic models have been extensively applied to predict drying kinetics of several products like fig, mulberry, strawberry, sour cherry, sweet cherry, grape, grape and pomegranate seeds, plum, apple, carrot pomace, finger millet, etc. (Doymaz and Pala 2002; Doymaz 2004, 2007, 2008; Mandala et al. 2005; Roberts et al. 2008; Jazini and Hatamipour 2010; Mabellini et al. 2010; Doymaz and Ismail 2011; Radhika et al. 2011;

Bchir et al. 2012; Kumar et al. 2012; Mujić et al. 2012; Srinivasakannan et al. 2012; Adabi et al. 2013), basically due to their simplicity. Therefore, for the purposes of this work, where processing times are only estimated at 70 ° C for different residual moisture contents of the fruits (not for drying kinetics determinations at different temperatures), these three models were selected to represent in a simple way the thin-layer drying behaviour of pretreated cherries. The equations corresponding to these models are:

Lewis model $$X^* = \exp(-kt) \quad (5)$$

Page model $$X^* = \exp(-kt^n) \quad (6)$$

Logarithmic model $$X^* = a\ \exp(-kt) + c \quad (7)$$

Where:

$X^*=(X-X_e)/(X_0-X_e)$ is the dimensionless moisture; X is the average water content of sample (dry basis) at any time, X_0 is the initial water content of sample (dry basis), X_e is the equilibrium water content (dry basis) with drying air, k is the drying rate constant (per hour), n, a and c are empirical parameters (dimensionless) and t is the drying time (hours). The X_e values used in this study were estimated by extrapolation of data reported by Vullioud et al. (2004). By fitting the air drying curves with the selected models, k, n, a and c values were obtained for each pretreatment.

Statistical Analysis

All statistical analyses were carried out using the STAT GRAPHICS PLUS package (StatPoint Technologies, Inc., Warrenton, USA). Results were expressed as mean±standard deviation of the mean (mean±SD). Two-way analysis of variance was carried out to establish the presence or absence of significant differences in parameters at the beginning and at the end of the drying process according to the factors "pretreatment" and "maturity stage." Since significant interactions between factors were observed in all variables, single effects were examined (i.e. effects of one factor holding the other fixed). Significance level was set at $p<0.05$, and multiple comparisons were performed using the least significant difference (LSD) test (Zar 1999).

The selected thin-layer drying models were fitted to drying curves, and the model parameters were determined by non-linear least-squares regression analysis. In order to evaluate the quality of fit obtained, in addition to the determination coefficient (r^2), other statistical parameters such as the reduced chi-square (χ^2) and the root mean square error (RMSE) were considered:

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(X^*_{exp,i}-X^*_{pre,i}\right)^2}{N-z} \quad (8)$$

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}\left(X^*_{exp,i}-X^*_{pre,i}\right)\right]^{1/2} \quad (9)$$

Results and Discussion

Fresh Fruit Characterisation

Table 1 shows that colour, SSC and acidity in fruits with an advanced stage of maturity were suitable for fresh produce marketing, while fruit harvested immature did not reach the necessary values for export market. Comparing the parameters used in postharvest, it was observed that SSC fresh cherry values ranged from 16.0 Brix (immature) to 22.5 Brix (mature) with the same acidity values (0.56 %), and surface colour turned from light yellowish pink in immature cherries to bright red in mature ones. The chromatic characteristics obtained for control samples (Table 2) revealed that differences in superficial colour for both ripeness stages can be mainly attributed to changes in Hunter L and b parameters. Immature cherries showed higher Hunter L and b and similar Hunter a values ($p<0.05$) than mature ones, which means that they are both less red fruits and lighter in colour. The small change in acidity and large increase in SSC during maturation/ripening as skin colour turned from light to dark was also observed for other sweet cherry cultivars (Crisosto et al. 2003). These results indicate that the increase in maturity index that cherries exhibited at the end of the maturation/ripening period is mainly related to an increase in SSC rather than in TA.

Table 1 Compositional measurement of sweet cherry fresh fruits

	Maturity degree	
	Mature	Immature
Moisture (% wet basis)	76.8±1.1a	79.7±1.1b
pH	4.05±0.07a	4.15±0.07a
TA (mg citric acid/100 g sample)	0.57±0.11a	0.55±0.11a
SSC (Brix)	22.5±1.3a	16.0±1.7b
$I_{maturity}$	40±2a	29.1±1.9b

Values expressed as mean±standard deviation of the mean. Single effects were analysed by LSD test. Means within rows followed by a different letter indicates significant differences at $p<0.05$

Table 2 Initial Hunter parameters of raw and pretreated cherries

Maturity degree	Pretreatments	L±SE[a]	a±SE[a]	b±SE[a]
Mature	C	32.8±0.9a	15.7±0.6a	7.5±0.5ab
	B	36.6±1.0b	3.2±0.3b	8.3±0.5b'c
	B+Dip 1	34.4±0.7a	2.8±0.4c	6.4±0.4a
	B+Dip 1+Dip 2	36.5±0.7b	2.4±0.4c	7.6±0.4b
	F	32.2±0.7a	10.6±0.5d	6.2±0.4a
	P	32.8±0.9a	15.7±0.6a	7.5±0.5ab
Immature	C	39.5±0.7c	14.6±0.7a	11.3±0.4d
	B	38.3±0.7b'c	3.9±0.7b	8.5±0.4b'c
	B+Dip1	38.2±0.6b'c	0.9±0.6e	9.6±0.4c
	B+Dip1+Dip2	37.1±0.6b	0.7±0.6e	9.3±0.4c
	F	39.5±0.7c	14.6±0.7a	11.3±0.4d
	P	39.5±0.7c	14.6±0.7a	11.3±0.4d

Single effects were analysed by LSD test. For each pretreatment, means within columns followed by the same letter were not significantly different at $p<0.05$

C without pretreatments, *B* blanched, *F* frozen, *P* pitted, *B+Dip1* blanched and immersed in citric acid solutions, *B+Dip1+Dip2* blanched and immersed in citric acid solutions with calcium lactate

[a] Standard errors of the means

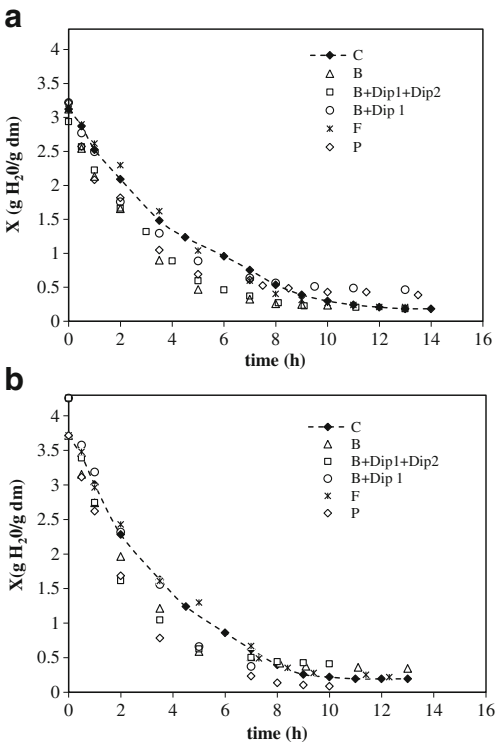

Fig. 2 Experimental drying curves obtained in mature (**a**) and immature (**b**) cherries subjected to different treatments prior to convective drying process. *C*: without pretreatments, *B*: blanched, *F*: frozen, *P*: pitted, *B+Dip1*: blanched and immersed in acid solution, *B+Dip1+Dip2*: blanched and immersed in saline acid solution

Drying Curves and Fitting to the Proposed Model

The values of water activity found after drying in all conditions were below the minimum necessary values for microorganism development ($a_w \leq 0.6$) (Fontana, 2008), confirming the efficiency of the drying process in the preservation of the cherries. Dehydrated cherries obtained had the chewy texture, the colour and the moisture content characteristic of products like raisins.

The time required to reduce the moisture content to any given level depended on the pretreatment applied, in mature cherries (Fig. 2a) as well as in immature (Fig. 2b). A constant drying rate period was not detected in any of the experiments, and falling-rate period was seen to occur. This shows that diffusion is the dominant physical mechanism governing moisture movement in the samples, which is consistent with the drying behaviour reported in the literature for several fruits and vegetables, such as apples, carrots, potatoes, strawberries, green peas, mango, tomatoes, grapes, apricots, mulberries, raisings, cherries, etc. (Raouzeos and Saravacos 1986; Vagenas and Marinos-Kouris 1991; Alvarez et al. 1995; Nieto et al. 1998, 2001; Simal et al. 1998; Doymaz and Pala 2002; Contreras et al. 2008; Mabellini et al. 2010).

Pitting, freezing and blanching normally have a disrupting effect on fruit tissue, which increases permeability to water along with other ingredients. Freezing usually involves cell membrane breakage and cell wall collapse (Delgado and Rubiolo 2005; Chassagne-Berces et al. 2010; Bchir et al. 2012). However, mature cherries subjected to previous freezing did not show any significant different trend from untreated samples. In spite that this pretreatment could have altered internal tissue of cherries after thawing, it was not enough to break down the waxy cuticle fruit surface and influence drying rate. As expected, the blanching used in B, B+Dip1 and B+Dip1+Dip2 treatments increased the amount of moisture removed from cherries, and the time to achieve specific moisture content was reduced, with a significant change in drying rate observed at a water content of $\approx X=0.5$ kg water/kg dm. Cherries previously pitted exhibited a behaviour similar to blanched fruits in the early stage of process (till ≈4 h) and then drying rate decreased drastically to reach and maintain at a moisture content $X=0.4$ kg water/kg dm. The change in drying behaviour of pretreated samples can be attributed to the fast drying rates exhibited at the beginning of the process, which often causes shrinkage and migration of solutes to the surface. This phenomenon, known as "case-hardening," makes the product more compact, with a crust on the surface, and is particularly common in foods that contain dissolved sugars and other solutes in high concentration (Ratti 1994; Potter and Hotchkiss 1995; Rahman and Perera 2007). Drying of cherries pretreated with blanching (alone or combined with

dips) and unpretreated cherries were completed approximately in 7 and 10 h, respectively, to reach X=0.3 kg water/kg dm. Pitted cherries could not reach the desired moisture value even after 12 h treatment, these samples having extensively collapsed the drying rate-controlling mechanism.

For immature cherries, the effect of the different pretreatments combinations in reducing the mass transfer resistance was rather similar, although samples previously pitted presented higher drying rate, reducing significantly drying time. Probably, the lower sugar content of fresh fruit would considerably contribute to diminish case-hardening in these samples.

Experimental drying curves were fitted to the selected models (Eqs. 5–7), and the drying constants were obtained for each pretreatment applied to mature and immature cherries (Table 3). In this table, the corresponding statistics obtained in each case are listed. In all cases, the determination coefficients were greater than 0.987, and in most conditions, the values obtained were greater than 0.99, corresponding to very low (Vega-Gálvez et al. 2009) and very similar values of χ^2 and RMSE, indicating a very good prediction of the proposed models.

Regarding the estimation of process duration, the models allowed to predict the drying times of all treated and non treated mature (MC) and immature (IC) samples with low percent mean errors (Lewis model, −5.2 % for IC and 7.5 % in MC; Page model, −3.9 % for IC and −3.8 % in MC and Logarithmic model, −0.54 % for IC and −0.53 % for MC, respectively), which can also be considered satisfactory. However, in some conditions, the Lewis and Page models did not adequately predict drying behaviour of cherries over the whole drying process. As an example, the experimental drying curves and the simulation provided by the three models have been represented versus drying time in Fig. 3 for the experiments carried out with mature cherries without pretreatment and subjected to previous B+Dip1 and P (Fig. 3a–c) and with immature ones subjected to control, blanching and B+Dip1+Dip2 pretreatments (Fig. 3d–f). As it can be observed, the simulation obtained by using the Logarithmic model was much better than those of the Lewis and Page models, mainly at very low water contents of the sample, where these models were not able to predict accurately the experimental curves.

When the experimental data (X^* vs. t) were plotted together with predicted data and the residuals plots were analysed for all the conditions, the accuracy of the Logarithmic model to represent the drying behaviour could be verified. Regarding these results and the statistical parameters obtained, it can be concluded that the Logarithmic model has shown a better fit to the experimental data when compared with the other models. Therefore, it can be used to satisfactorily describe drying behaviour of untreated and pretreated cherries for both maturity degrees.

Colour Evolution Throughout Drying

The colorimeter average L, a and b values of cherries just before the drying process are presented in Table 2. Cherries in both states of maturity and subjected to pretreatments showed significant differences in superficial colour, except in the case of pitted samples. The Hunter L for ripe cherries increased with the pretreatments that included a blanching process due to dilution of pigment colour and swelling of the fruit by the application of a thermal treatment and a subsequent immersion in water. This led to a greater lightness of the product. For immature fruits (higher initial L and less initial pigments content), blanching affected this parameter slightly. The Hunter a values diminished in an abrupt way with pretreatments in all cases, mainly in samples previously blanched, even in acidified cherries, which increased acidity after dipping from 0.51 to 1.03 in mature samples and from 0.55 to 0.66–0.7 in immature ones. The b values also decreased in immature cherries but remained constant in mature ones.

After pretreatments, a decrease in cherry lightness along drying was observed (Fig. 4a and b). After 2 h of drying, the most significant change occurred in fruits previously pitted and frozen in both mature and immature cherries, whereas no significant differences (p<0.05) were observed among the rest of pretreatments at this drying stage. Change in lightness (ΔL) expressed as differences with the parameter of fresh fruit for non-pretreated samples (control) was 5.2 % in mature cherries and 14.7 % in immature ones. For freezing and pitting conditions, ΔL values were ≈12–15 % in mature cherries and 22–25 % in immature ones. The lowest values were obtained in mature samples subjected to pretreatments with previous blanching (≤2.7 %). At the end of the drying process, lightness diminished in all cases. Immature cherries presented, in general, a higher Hunter L than mature ones, except for control and frozen cherries, which did not present significant differences (p<0.05). The values obtained in immature samples subjected to a previous blanching process were slightly higher than those obtained for the rest of pretreated samples. On the other hand, immature cherries experienced a higher ΔL than mature ones, when compared with the corresponding fresh fruits.

In the first drying stages (0.5 h), the Hunter a diminished abruptly in all cases (Fig. 5). In the control, pitted and frozen ripe cherries (Fig. 5a), the reduction was ≈ 65–69 %, with the appearance of brown shades characteristic of enzymatic browning that pigments suffer due to the high temperatures of the process. After that, the a values remained approximately constant until the final stage of dehydration. In contrast to this behaviour, Hunter a values of samples pretreated with blanching and dips slightly increased with time at the early stages, but a significant decrease in comparison with the value obtained in fresh cherries (78–87 % from 0.5 h) was produced. In all cases, a significant recovery of the values after 2 h of

Table 3 Model parameters estimated from Eqs. 5–7 and statistics used to evaluate the goodness of fit for each experimental condition

Lewis model									
Maturity degree	Treatment			k (h^{-1})	SE_k			r^2	χ^2	RMSE
Mature	C			0.223	0.003			0.998	0.0004	0.019
	B			0.330	0.012			0.995	0.0009	0.029
	B+Dip1+Dip2			0.289	0.007			0.996	0.0006	0.025
	B+Dip1			0.282	0.018			0.994	0.003	0.054
	F			0.206	0.009			0.994	0.002	0.047
	P			0.288	0.018			0.987	0.004	0.063
Immature	C			0.265	0.006			0.997	0.0007	0.027
	B			0.300	0.018			0.990	0.0013	0.025
	B+Dip1+Dip2			0.41	0.03			0.991	0.002	0.044
	B+Dip1			0.330	0.012			0.993	0.0009	0.029
	F			0.242	0.008			0.995	0.0011	0.032
	P			0.396	0.012			0.998	0.0005	0.022
Page model										
Maturity degree	Treatment			k (h^{-1})	SE_k	n	SE_n	r^2	χ^2	RMSE
Mature	C			0.192	0.008	1.05	0.02	0.998	0.0002	0.013
	B			0.37	0.02	0.93	0.04	0.995	0.0006	0.023
	B+Dip1+Dip2			0.284	0.016	1.02	0.04	0.996	0.0004	0.019
	B+Dip1			0.32	0.03	0.80	0.05	0.989	0.0013	0.032
	F			0.149	0.011	1.22	0.04	0.997	0.0004	0.019
	P			0.41	0.03	0.71	0.04	0.988	0.0013	0.033
Immature	C			0.213	0.009	1.11	0.02	0.999	0.0002	0.011
	B			0.34	0.03	0.91	0.06	0.988	0.0015	0.034
	B+Dip1+Dip2			0.49	0.04	0.79	0.06	0.988	0.0014	0.033
	B+Dip1			0.29	0.02	1.07	0.07	0.993	0.0073	0.072
	F			0.198	0.016	1.12	0.05	0.995	0.0004	0.019
	P			0.371	0.013	1.09	0.03	0.999	0.0002	0.012
Logarithmic model										
Maturity degree	Treatment	a	SE_a	k (h^{-1})	SE_k	c	SE_c	r^2	χ^2	RMSE
Mature	C	1.031	0.014	0.202	0.008	−0.023	0.015	0.998	0.0002	0.013
	B	0.96	0.02	0.38	0.03	0.040	0.017	0.996	0.0005	0.019
	B+Dip_1+Dip_2	0.990	0.017	0.313	0.016	0.024	0.014	0.997	0.0004	0.017
	B+Dip_1	0.877	0.010	0.345	0.012	0.127	0.007	0.999	0.0002	0.012
	F	1.09	0.04	0.20	0.02	−0.05	0.04	0.992	0.0010	0.027
	P	0.86	0.02	0.40	0.03	0.119	0.015	0.992	0.0008	0.024
Immature	C	1.069	0.016	0.226	0.010	−0.055	0.018	0.999	0.0002	0.010
	B	0.94	0.02	0.38	0.02	0.071	0.014	0.995	0.0005	0.019
	B+Dip_1+Dip_2	0.914	0.012	0.54	0.02	0.092	0.007	0.998	0.0002	0.011
	B+Dip_1	1.09	0.07	0.26	0.04	−0.10	0.08	0.994	0.0007	0.021
	F	1.05	0.03	0.23	0.02	−0.03	0.03	0.994	0.0007	0.020
	P	1.019	0.018	0.41	0.02	−0.001	0.014	0.997	0.0003	0.015

C without pretreatments, *B* blanched, *F* frozen, *P* pitted, *B+ Dip1* blanched and immersed in citric acid solutions, *B+ Dip1+ Dip2* blanched and immersed in citric acid solutions with calcium lactate

process was observed. After 7 h of drying, control, pitted and frozen samples reached between 61 and 67 % of the initial value measured when fresh, whereas cherries with previous blanching and dips exhibited a smaller change in this parameter (≈48–51 %). During heat exposure, part of phenolases (enzymes that act on anthocyanins due to their phenolic structure) would be inactivated. At the same time, a concentration of the acids present would allow a greater pigment expression along the course of dehydration of the fruits. In cherries pretreated with immersion in an acid environment, a greater

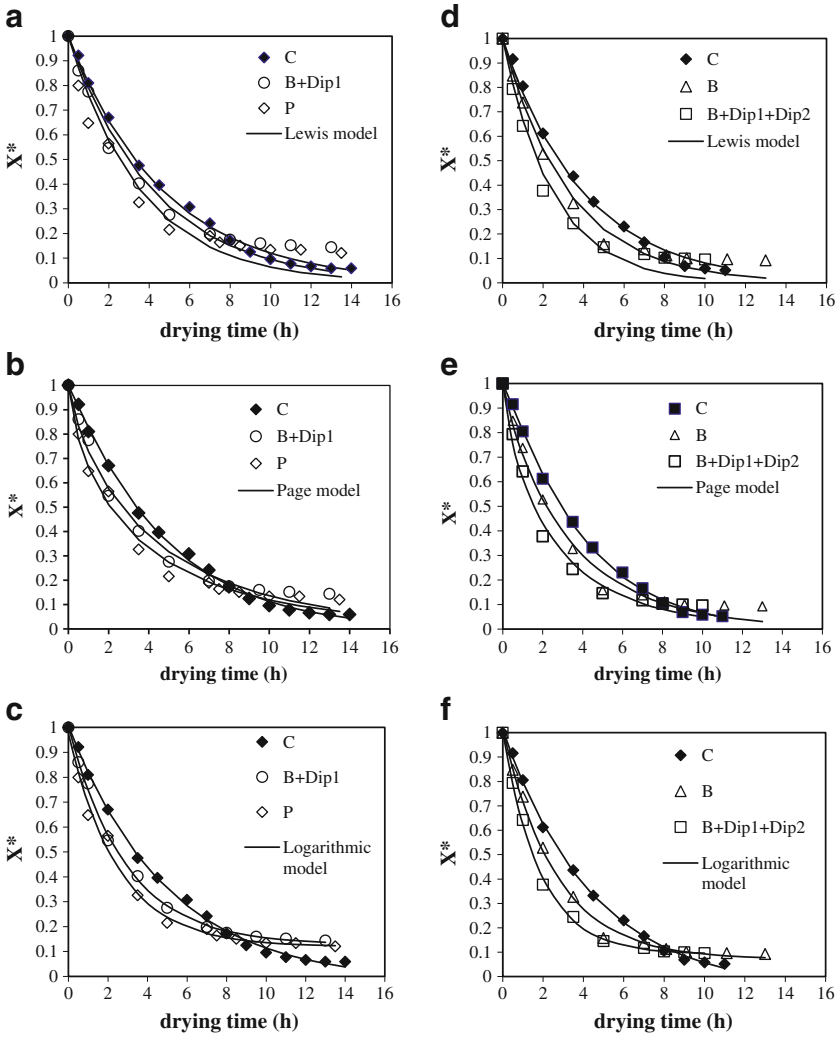

Fig. 3 Comparison of experimental and predicted drying curves of cherries: experimental data (*symbols*) and prediction given by Eqs. 5–7 (*continuous lines*). **a**–**c**: mature cherry (examples of pretreatment: C, P and B+Dip1); **d**–**f**: immature cherry (examples of pretreatment: C, B and B+Dip1+Dip2). *C*: without pretreatments, *B*: blanched, *P*: pitted, *B+Dip1*: blanched and immersed in acid solution, *B+Dip1+Dip2*: blanched and immersed in saline acid solution

protection of the anthocyanin pigments during drying would explain the highest rate of increase of Hunter *a* in the early hours of these curves (Fig. 5a). Even though pretreated immature cherries (Fig. 5b) presented a greater variation in the Hunter *a* parameter in the first drying stages, similar values to those obtained in mature cherries were reached at the end of the process, independently of the pretreatment used. However, although *b* values remained rather constant throughout drying for both maturity stages (Fig. 6a and b), at the end of the process, *b* values of mature cherries were lower than those obtained in immature ones.

According to Hunter *a* and *b* variations, there were also significant changes ($p<0.05$) in hue angle and chroma values after pretreatments (h_{ab0}, C_{ab0}) as well as after drying (h_{abf}, C_{abf}) (Table 4). Immediately after pretreatments, mature cherries always showed lower hue angle, chroma and *L* than immature ones, which means they are redder and darker cherries. After pretreatments, including blanching, hue values significantly increased for both maturity degrees with no significant differences between treatments for mature cherries. For instance, average *h* values of control mature cherry was 26° and increased to 70° after blanching and acid-dipping (B+Dip1), indicating the fruit surface true colour changed towards the orange shade. Average value for control immature cherry was 39° and after the same treatments before drying increased to≈78°; therefore, the sample achieved a more yellowish shade than that observed in mature cherries. Average chroma value for mature control decreased from 18 to 7–11 in those samples treated with blanching and subsequent dips. Values of immature samples decreased from 19 to 9–10. This would imply that, regardless of the combination used in the pretreatment, the heat application led to lower colour saturation and therefore to a less vivid colour. These results demonstrate that heat application had a clear impact on the colour of fresh cherries. Probably, even after having applied a further acid dipping, blanching could not only have produced thermal pigments degradation, but it could also have acted on them, shifting the chemical balance to the colourless resonance structures of anthocyanins, that is, to the formation of pseudocarbinol base and chalcone.

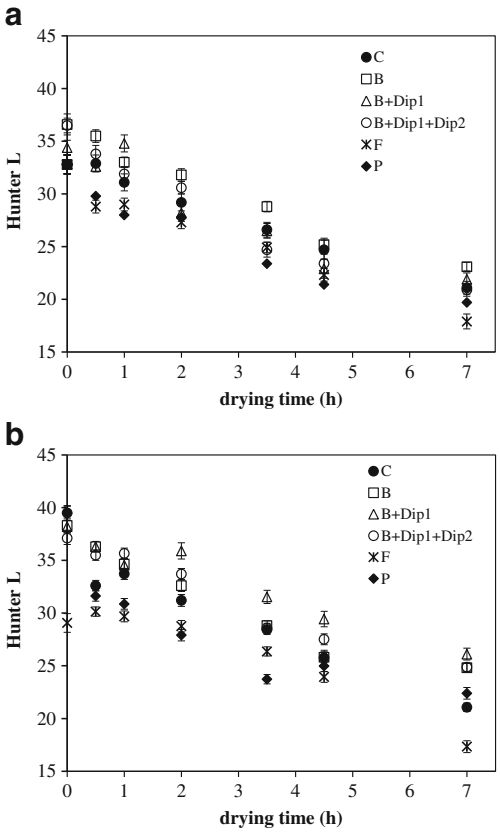

Fig. 4 Evolution of Hunter *L* parameter along the drying process in mature (**a**) and immature cherries (**b**) with or without pretreatment. *Vertical bars* represent standard errors of the means. *C*: without pretreatments, *B*: blanched, *F*: frozen, *P*: pitted, *B+Dip1*: blanched and immersed in acid solutions, *B+Dip1+Dip2*: blanched and immersed in saline acid solution

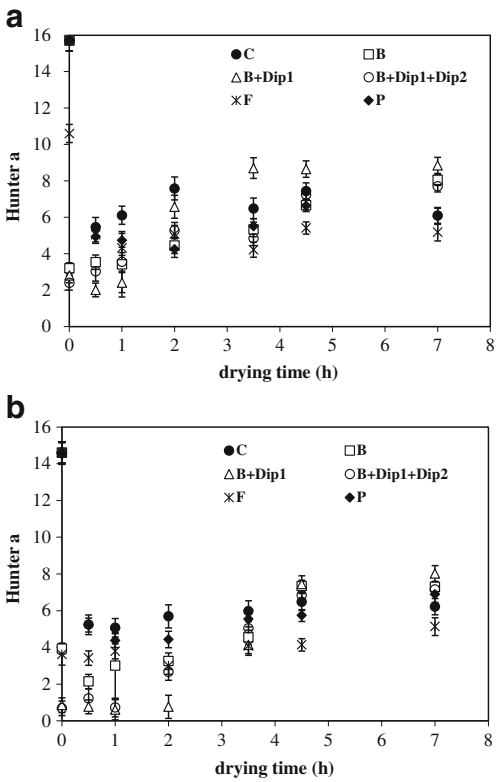

Fig. 5 Hunter *a* parameter evolution during drying of mature (**a**) and immature (**b**) cherries with or without pretreatment. *Vertical bars* represent standard errors of the means. *C*: without pretreatments, *B*: blanched, *F*: frozen, *P*: pitted, *B+Dip1*: blanched and immersed in acid solution, *B+Dip1+Dip2*: blanched and immersed in saline acid solution

At the end of the drying process, hue values of control, pitted and frozen mature samples increased when compared with the corresponding non-dried samples. However, hue values of dried samples with previous blanching and/or acid dipping were lower than those of non-dried cherries for the same kind of pretreatment, mainly for B+Dip1 condition. Despite that these variations occurred after pretreatments and throughout drying, overall hue angle of dried cherries at the end of the drying process was rather similar regardless of pretreatments, with colours between red and orange (h_{ab}≈ 31–45°). Although immature cherries showed higher initial hue values, they behaved in a similar way throughout drying. Overall, dried immature cherries exhibited a slightly higher hue angle when compared with mature ones, indicating a slight yellowing, mainly in samples previously blanched (h_{ab}=52–53°). The recovery observed in hue angle after the drying of cherries with heat pretreatment confirmed that only a fraction of anthocyanins was degraded by heat action. Besides, the addition of calcium lactate seemed to slightly affect colour parameters (<*a*, <*L* and >hue angle).

Control, pitted and frozen cherries showed chroma values significantly smaller than those exhibited by the samples before drying, for both maturity degrees. On the contrary, the values increased in samples with previous blanching and dipping, mainly in mature cherries, this being directly related to the water loss rate. In blanched samples, the faster drying rate observed at the first process stages favoured the concentration of components (acids, pigments, etc.) giving rise to an increase in colour saturation, without significant differences between treatments with blanching (B) and blanching and acid dipping (B+Dip1+Dip2).

Differences in hue angle and chroma of final products could be attributed to differences in anthocyanin and phenols composition but also to brown pigment development and to the interaction of anthocyanins with other compounds at the relatively low pH of the fruits (copigmentation) (Goncalves et al. 2007; Contreras et al. 2008). Copigmentation is optimal within the range pH 3–5 (Brouillard et al. 1991) and can take place through several interactions. The main effect of copigmentation is a bathochromic shift of the wavelength and an increase of the absorbance of the band in the visible spectrum, which produces a higher colour intensity (hyperchromic effect) (Rein 2005). The pH value of fresh cherries (Napolitana var.) is ≈4.1–4.2 and did not change along drying. The combination of a high drying temperature and natural conditions of acidity in cherries without

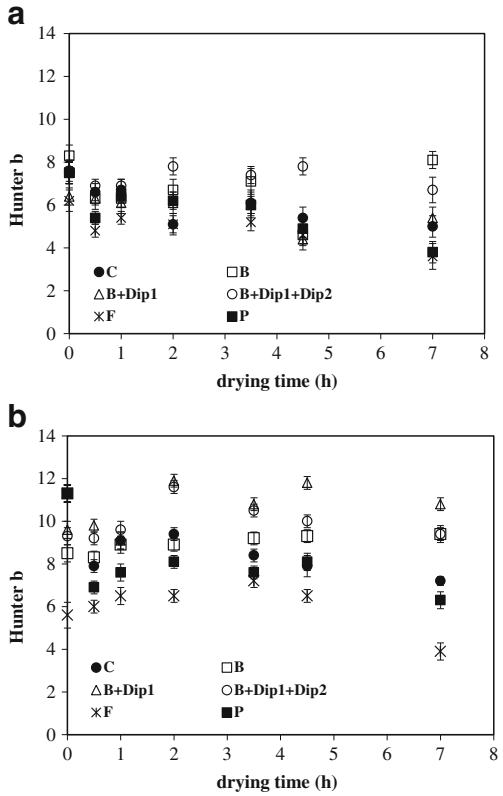

Fig. 6 Hunter *b* parameter evolution during drying of mature (**a**) and immature (**b**) cherries with or without pretreatment. *Vertical bars* represent standard errors of the means. *C*: without pretreatments, *B*: blanched, *F*: frozen, *P*: pitted, *B+Dip1*: blanched and immersed in acid solution, *B+Dip1+Dip2*: blanched and immersed in saline acid solution

pretreatment may increase PPO activity and cause browning from the beginning of the drying process, due to enzymatic browning reactions. In the case of pretreated samples, the acidity achieved in fruits after dips increased over 60 % with a corresponding decrease of 0.6 units of pH, which may be beneficial for colour stabilisation of dried fruits where the red flavylium cation dominates. Moreover, it is not only the absorption of this cation on a suitable substrate (copigment) that can stabilise anthocyanins by intermolecular copigmentation, but also anthocyanins can form strong bonds with groups of organic acids (in this case citric) favouring intramolecular copigmentation (Rein 2005; Sari et al. 2012). If a thermal treatment prior to dipping is added, the PPO enzyme may be inactivated, at least partially, during drying. All these factors must be considered in the expression of surface colour, which can be appreciated in the images included in Fig. 7. Red shades are better preserved in mature dried fruits, with a more homogeneous distribution of dark red colour in samples with a previous pretreatment of heat and acid dip. In contrast, this pretreatment was less effective in the preservation of skin colour of immature cherries, which presented yellowish brown colour with reddish areas. These results are in accordance with the global change colour of cherries showed in Table 4. The major changes of colour occurred immediately after pretreatments without significant changes along drying (curves not shown). At the end of the drying process control, pitted and frozen cherries showed the greater variation in ΔE_{ab} values, and the major changes were evidenced mainly in immature cherries.

Table 4 Hue angle (h_{ab}), chroma (C_{ab}) and global change colour (ΔE_{ab}) values of cherries with and without pretreatments before drying (h_{ab0}, C_{ab0}, ΔE_{ab0}) and after drying (h_{abf}, C_{abf}, ΔE_{abf})

Maturity degree	Pretreatment	C_{ab0}±SE[a]	C_{abf}±SE[a]	h_{ab0}±SE[a]	h_{abf}±SE[a]	ΔE_{ab0}±SE[a]	ΔE_{abf}±SE[a]
Mature	C	17.7±0.5a·A	7.9±0.5b·B	26±2bA	39±2bB	0.0±0.0aA	15.4±0.6bB
	F	12.5±0.5b·A	6.4±0.6a·B	31±2bA	34±3abAB	6.9±0.1dA	18.7±0.7cB
	P	17.7±0.5a·A	7.2±0.5b·C	26±2bA	32±2aAB	0.0±0.01aA	17.2±0.6bB
	B	10.9±0.5c·B	11.5±0.4c·B	64±4aA	45.0±1.7cB	13.0±0.5bA	12.6±0.4aA
	B+Dip1	7.1±0.4d·C	10.4±0.5d·A	70±3aA	31±2aB	13.8±0.2bcA	13.2±0.6aA
	B+Dip1+Dip2	8.1±0.4d·C	10.3±0.4d·A	74±3aA	40.5±1.7bcB	14.4±0.3cA	13.3±0.4aA
Immature	C	18.9±0.5a·A	9.3±0.3b·B	39±3cB	49.5±1.3bC	0.0±0.0aA	19.7±0.4aB
	F	18.9±0.5a·A	6.5±0.4a·B	39±3cB	37.1±1.8aB	16.1±0.4bA	23.7±0.4dB
	P	18.9±0.5a·A	9.4±0.4b·B	39±3cBC	41.9±1.8aC	0.0±0.0aA	18.8±0.4aB
	B	8.9±0.5b·A	11.9±0.3c·B	73±3aC	52.0±1.3bD	14.1±0.4dA	16.6±0.4cB
	B+Dip1	9.9 ±0.5b·A	13.6±0.4d·B	78±3abC	53.6±1.8bD	17.3±0.3cA	14.2±0.4bB
	B+Dip1+Dip2	9.4±0.5b·A	11.9±0.3c·B	80±3bC	53.0±1.3D	16.9±0.3cA	15.3±0.4bB

Single effects were analysed by LSD test. For each ripeness degree, means within columns with a different lowercase letter are significantly different at $p<0.05$. For each pretreatment, means between columns followed by same uppercase letter indicates differences between initial and final drying stages ($t=0$, $t=t_f$) at $p<0.05$

C without pretreatments, *B* blanched, *F* frozen, *P* pitted, *B+Dip1* blanched and immersed in citric acid solutions, *B+Dip1+Dip2* blanched and immersed in citric acid solutions with calcium lactate

[a] Standard errors of the means

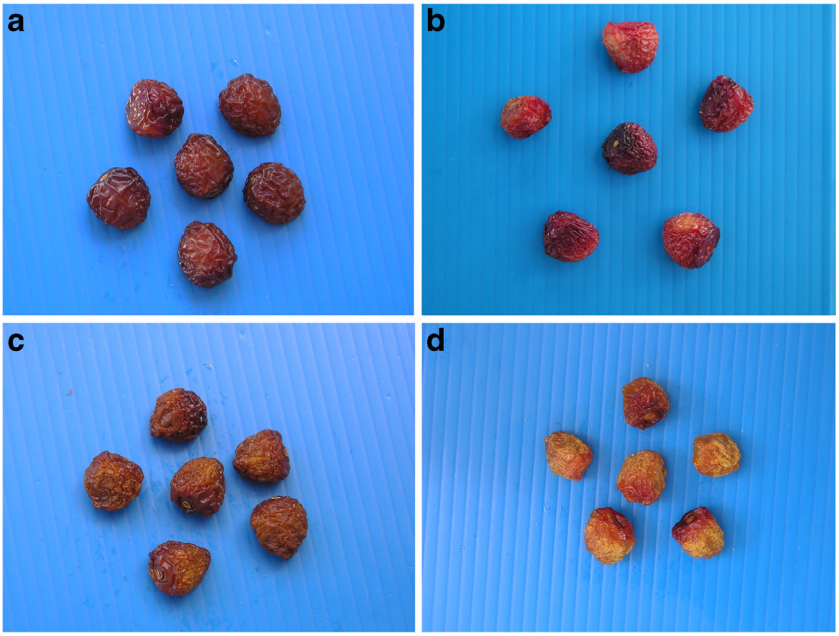

Fig. 7 Images taken from mature (**a**–**b**) and immature (**c**–**d**) cherries after 7 h convective drying. Control (*C*): **a**, **c**. Fruits subjected to B+Dip1+Dip2 condition: **b**, **d**. *C*: without pretreatments, *B+Dip1+Dip2*: blanched and immersed in saline acid solution

Calcium has been extensively used in low concentration as a firming agent to improve post-processing quality characteristics and extend shelf life of fruit products (Poovaiah 1986; Luna-Guzmán and Barret 2000; Martin-Diana et al. 2007). Resistance to softening resulting from calcium addition has been attributed to the stabilisation of membrane systems and the formation of Ca-pectates by cross-linking free carboxyl groups on adjacent polygalacturonate chains present in the middle lamella, contributing to cell–cell adhesion and cohesion (Jackman and Stanley 1995). Although different calcium salts and different techniques for treating fruits and vegetables with calcium have been studied in a wide variety of commodities, no information is available on the effect of calcium salts on pigments and colour in processed cherries or berries. Some authors (Rein 2005; Badui 2006) affirmed that anthocyanins can change colour when forming complexes, chelates or salts with sodium, potassium, calcium, magnesium, tin, iron or aluminium ions. Regarding our results, the use of acidic solutions of calcium lactate following blanching had a slight effect on superficial colour of dried cherries. It can be concluded that the use of calcium in dipping solutions would be more convenient than the use of those without calcium as a way of reinforcing fruit tissue after blanching and also diminishing damage during further drying.

Pigments Evaluation

As expected, the monomeric anthocyanins concentration, expressed as cyanidin 3-glucoside, was much higher in fresh mature cherries (11.4 mg/100 g d.b.) than in immature ones (1.3 mg/100 g d.b.). Anthocyanin pigment retention (Acy/Acy_0) after drying for both maturity stages (Table 5) showed that drying induced a drastic reduction in the anthocyanin levels in all cases, suggesting that colour attributes of fresh fruit have changed. Mature dried cherries without pretreatments (control) exhibited the most profound decrease with respect to fresh fruit, and a similar value of pigments retention ($p<0.05$) was observed after the drying of samples previously frozen or blanched. However, a greater retention was obtained when acid immersions were included, mainly in cherries

Table 5 Anthocyanin pigment retention (Acy/Acy_0) and Anthocyanin Degradation Index (ADI) of dried cherries with and without pretreatments

Maturity degree	Pretreatments	Acy/Acy_0±SD[a]	ADI±SD [a]
	Fresh	–	1.49±0.03a[a]b
	C	0.06±0.01a	1.64±0.19b[b]c
	B	0.10±0.02a	1.70±0.17c
	B+Dip 1	0.46±0.04b	1.24±0.04d
Mature	B+Dip 1+Dip 2	0.80±0.04c	1.23±0.03d
	F	0.06±0.01a	1.64±0.19b[b]c
	P	0.17±0.04b	1.31±0.03b[b]d
	Fresh	–	2.5±0.5a
	C	0.06±0.01a	4.7±0.7b
	B	0.36±0.12ab	1.27±0.15c
	B+Dip1	0.59±0.12b	1.5±0.16c[c]d
Immature	B+Dip1+Dip2	0.30±0.12ab	1.5±0.3c[c]d
	F	0.06±0.01a	4.7±0.7b
	P	0.09±0.02a	2.3±0.01a[a]d

Single effects were analysed by LSD test. For each pretreatment, means within columns followed by the same letter were not significantly different at $p<0.05$

C without pretreatments, *B* blanched, *F* frozen, *P* pitted, *B+Dip1* blanched and immersed in citric acid solutions, *B+Dip1+Dip2* blanched and immersed in citric acid solutions with calcium lactate

[a] Standard deviation of the means

subjected to B+Dip1+Dip2 pretreatments where calcium lactate is added to the acid medium. A study carried out on the evolution of anthocyanins during the drying of mature cherries (Fig. 8) showed that 74 % of anthocyanins in control samples was lost at the early stages of the process and then remained without variations with a final value of 1.6 mg/100 g d.b.) after 9.5 h. Anthocyanins found in cherries after B+Dip1+Dip2 pretreatment significantly increased (38 mg/100 g d.b.), and although the pigment loss during drying was similar (78 %), the anthocyanin content of final dried product was higher (7.8 mg/100 g d.b.). It should be emphasised that the pH differential method is a measure of the monomeric anthocyanin pigments at the wavelength of maximum absorbance. In these samples, copigmentation reaction of anthocyanins with the acids incorporated during pretreatment and by means of heat improved cherry colours during drying, which was manifested by an increase in absorbance at the same wavelength at pH 1. These results suggest that this mechanism of colour stabilisation has prevailed over thermal degradation of pigments during drying. In dried samples without pretreatment (control), heating experimented by samples during the process accelerated the degradation of anthocyanins, thus resulting in a decrease in colour intensity and the formation of polymeric colour. On the other hand, the higher stability exhibited by mature cherries could also have been due to the higher content of fresh fruit pigments, which express themselves better in an acid medium, where they exist mainly in the highly coloured oxonium or flavilium form. Anthocyanin content of immature cherries was 1.34 mg/100 g (d.b) when fresh and decreased to 0.4 mg/100 (d.b) after 9.5 h of drying. However, the retention occurring in unripe samples previously blanched or subjected to B+Dip1 was higher than that observed in ripe fruits.

In studying anthocyanin degradation of cranberry juice, Fuleki and Francis (1968) utilised the ADI. Samples containing degraded pigment or other brownish-coloured compounds should give ADI higher than 1. The values obtained for cherry fruits after drying (Table 5) appeared to be higher than 1 for all

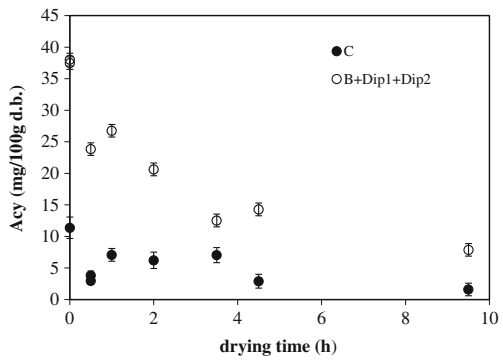

Fig. 8 Monomeric anthocyanin content (Acy) of mature cherries during drying. *B+Dip1+Dip2*: with previous blanching and subsequent immersion in saline acid solution; *C*: without pretreatment. *Vertical bars* represent standard errors of the means

samples, mainly in immature ones. This indicates that results determined by single pH method, where absorbance was measured only at pH 1, are different from those by the pH differential method, even for fresh fruit products, where presence of brown polymeric pigments should be insignificant. In the case of immature fruits, fresh and control cherries presented a higher degradation of pigments when compared with mature ones, due to the different sugar concentration. The higher levels of sugars present in mature cherries favoured the stability of anthocyanin, due to their water–activity-lowering capacity, which affects the water mobility in the system and thus the potential for anthocyanin degradation (De Ancos et al. 1999). Several authors have pointed out that water activity of systems, as well as anthocyanin concentration on its own, influences colour stability (Katsaboxakis et al. 1998; Garzón and Wrosltad 2001; Nikkhah et al. 2007). On the contrary, when the concentration is low enough to have little effect on water activity, sugars or their degradation products may sometimes accelerate anthocyanin degradation, as it seemed to occur in immature samples along drying. For example, furfural produced from sugars readily condenses with anthocyanins to form brown compounds through a highly temperature-dependent mechanism (van Gorsel et al. 1992; Fenema 2000). When immature samples were blanched prior to drying process, the ADI values drastically diminished since enzymatic browning may have been controlled by inactivating the enzymes by heat, reducing the formation of melanoidins. When B+Dip1 or B+Dip1+Dip2 pretreatments were applied, no significant differences were observed. In mature cherries, the higher stability of pigments in acid medium allowed the formation of degradation products to be slightly reduced when compared with only blanched samples. As a result, ADI values were in the range 1.2–1.5, with no significant differences between ripe and unripe cherries.

Anthocyanin concentration in 100 g of product (wet basis) changed from 2.84 to 1.11 mg after drying but increased to 7.64 mg when B+Dip1+Dip2 treatment was applied before drying, meaning that, from a nutritional standpoint, consuming 100 g of these dried cherries would be more advantageous than eating 100 g of fresh product.

Correlations Between Anthocyanin Content and Colour

The chromatic coordinates, chroma and hue angle were correlated with anthocyanin retention. When lumping the data for all mature samples, Hunter *a* values had a high positive correlation with Acy/Acy_0 ($p<0.05$, $r=0.71$) and with chroma ($p<0.05$, $r=0.80$), that is, an increase in pigment concentration causes both redness and a better saturation of colour. Furthermore, the highest values of chroma corresponded to the samples having the highest lighteness ($p<0.05$, 0.82), but there is less correlation with pigment retention ($p<0.05$, $r=0.47$). This behaviour can be mainly ascribed to the effect of heat treatment in samples

previously blanched. The same pattern was observed in immature cherries. However, hue angle seems to give poor information about spatial distribution of colour in cherries for both ripeness degrees and showed little correlation to changes in anthocyanin content, indicating that factors other than pigment concentration increase are involved in hue changes. In dried cherries, hue angle appeared to be more related to lightness than to anthocyanin content, showing a relatively high positive correlation with L values ($p<0.05$, $r=0.61$–0.65). Hence, samples that became more luminous were also less red.

Conclusions

Combined treatments were effective in relation to colour retention during the drying of both ripe and immature cherries. On the one hand, the thermal treatment permitted the protection of the anthocyanic compounds from the action of polyphenoloxidase. On the other hand, the acid environment allowed the anthocyanin resonance structures to move to the formation of flavylium cation, the only molecular structure present and with greater stability than the other resonance forms.

The observed changes in surface colour in terms of h_{ab} were not in accordance with anthocyanin pigment behaviour throughout the different stages of the proposed technology, probably due to brown pigment development from non-enzymatic browning reaction during drying and also to copigmentation phenomenon that enhanced and stabilised colour.

Regarding skin colour in terms of chroma and Hunter a, the pigment retention and the evaluation of anthocyanin degradation index, both B+dip1 and B+dip1+dip2 pretreatments led to better-quality products, mainly in mature cherries. Moreover, the incorporation of blanching in the combined pretreatment significantly reduced drying time. The raisin-like cherries obtained can be consumed whole as a snack, and, in the case of pitted fruits, these raisins can be used as an ingredient in foods such as cereal mix, bakery and confectionary products, desserts or candies (i.e. chocolate-covered fruits).

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