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Original article

Fruit snacks from raspberries: influence of drying parameters on colour degradation and bioactive potential

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Abstract Raspberries were dehydrated using air and freeze-drying with wet and dry sugar infusion pretreatments. Product quality factors such as colour, bioactive compounds, antioxidant capacity and sensorial characteristics were analysed. Special emphasis was placed on the analysis of anthocyanin degradation and its relationship with colour deterioration and with polymeric compounds development and browning. Freeze-dried raspberries presented a higher retention of bioactive compounds and a lower content of polymeric compounds than air-dried ones. Dried samples without pretreatment (control) showed the highest retention of total phenolic content (freeze-dried ≈82% and air-dried ≈37% retention), but the lowest sensory acceptability. Although sugar infusion pretreatments caused an important loss of bioactive compounds (9–18% of TPC retention), a higher sensorial acceptability was obtained. Pretreatments with bisulphite and acid allowed obtaining the best quality attributes in terms of anthocyanin and polyphenol content, antiradical activity and colour retention. Polyphenol intake through pretreated dried raspberries (115–299 mg gallic ac./100 g intake) would be higher in some cases than that of usually consumed foods as vegetables, cereals and several fresh fruits.

Keywords Air-drying, bioactive compounds, freeze-drying, osmotic dehydration, raspberries.

Introduction

Berry fruits are a rich source of bioactive compounds such as anthocyanins, flavonols and catechins. Numerous studies demonstrated that these phytochemicals exhibit a wide range of biological effects (Paredes-Lopez *et al.*, 2010; Vulić *et al.*, 2014). Raspberry is one of the most popular berries in the world, and its exploitation in diverse areas of food and health products is increasing in the last years (Vesna *et al.*, 2015). This fruit is very labile and has a short postharvest life due to its high respiration rate, loss of firmness and freshness, and susceptibility to darkness. For fresh consumption, raspberries tend to be available for only a short season and the main destination is the frozen market. Therefore, there is a need for alternative processing methods to generate new alternatives for obtaining shelf-stability while minimising changes in fruit quality attributes. Dehydration is a popular technique used to increase the shelf life of fruits and vegetables, as well as for reduction in packaging and transportation costs. However, quality of dried products could be affected, which could be detrimental to product characteristics in terms of texture, colour, nutritive value and sensory aspects (Ratti, 2001; Vesna *et al.*, 2015). Although conventional hot air-drying is one of the most economical drying techniques, water loss and heating usually cause stresses in the cellular structure, leading to changes in shape and volume decrease because of cell and intercellular spaces collapse (Michailidis & Krokida, 2015). It is also known that drying at high temperatures and long times may affect flavour, colour and nutrients of dried food (Franceschinis *et al.*, 2015). In contrast, during freeze-drying, the solid state of water and the low temperatures protect the primary structure and the shape of the products with minimal volume reduction. Besides, the low temperatures used ensure maximum retention of nutrients (Ratti, 2001).

Pretreatments of fruits may also influence the following drying process. Osmotic dehydration, used as a predrying step received attention in the field of fruit preservation in order to reduce energy consumption and improve the quality, mainly due to lower

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structural collapse and improved colour retention. In particular 'sugar infusion' treatments (SI) allow the modification of the food formulation, making it 'more suitable' to further processing (Torreggiani & Bertolo, 2001). Therefore, a judicious combination of this pretreatment with drying methods has been recommended (Sosa *et al*., 2012; Bruijn & Bórquez, 2014). During sugar infusion, not only solutes can be introduced into the fruit to control food water activity, but also those agents with antioxidant or other preservative properties.

The objective of this work was to analyse the effect of different drying methods (freeze- and air-drying) and sugar infusion pretreatments (wet and dry) on colour, bioactive compounds, antioxidant capacity and sensorial characteristics of raspberries. The use of several pretreatments was aimed at identifying the best conditions to minimise drying effects on product quality.

Materials and methods

Fruits

Frozen raspberries (*Rubus idaeus* L.) of the Autumn Bliss cultivar grown at the 'La Piedad' farm (Plottier, Neuquén province, Argentina) were used in this study. Fruit was totally hand-harvested from the end of November to April from a 3-ha plantation. After harvest, fruits were placed on plastic trays and visually classified according to maturity degree (defined by colour) into three groups. Only fruits of intermediate maturity and uniform size ($\approx 2.10^{-6}$ m^3) were selected and then randomly divided into nine lots of 100 g each. Fruits were then individually quick-frozen (IQF) in an air blast tunnel at −48 °C and air speed 1.5 ms^{-1}. After freezing, the raspberries were stored at −22 °C until use. The characterisation was carried out according to AOAC methods (1990): water content 85 ± 3%, water activity (a_w) 0.97 ± 0.02, total soluble solids 8.8 ± 0.8 °Brix, pH 3.13 ± 0.02, total acidity 0.267 ± 0.004% citric acid and ash 0.363 ± 0.012% (Sette *et al*., 2015).

Pretreatments

Fruits were subjected to sugar infusion pretreatments performed in glass vessels (8 × 16 cm) at 20°C ± 1 temperature controlled by a refrigeration air conditioning equipment. Different systems were prepared by immersing the frozen fruits into a mixture (dry or wet) of the humectant and the preservatives commonly used in the preparation of high- or intermediate-moisture fruits (Tapia de Daza *et al*., 1996). Sucrose was used in all cases as humectant. Potassium sorbate and sodium bisulphite are usually used as antimicrobial agents; sodium bisulphite also acts as inhibitor of enzymatic and nonenzymatic browning. Citric acid was added in some conditions to achieve different pH levels of the syrup system in order to study the pH effect on colour and red pigments. The final pH value of infused samples was 2.3 in wet infusions and 2.5 in dry infusions. Reagents were all food grade (Saporiti S.A., Argentina). The amount of sugars and chemical agents were determined according to the weight of the fruit (100 g) and the final levels required after equilibration of the components of the food system (a_w = 0.85). Sucrose concentration in the mixture was calculated using the Ross equation (Tapia de Daza *et al*., 1996) to attain the a_w equilibration value desired between raspberries and the formed syrup:

$$a_{w\,\text{equilibrium}} = (a_w^0)_{\text{raspberry}}(a_w^0)_{\text{sucrose}}, \quad (1)$$

where $(a_w^0)_{\text{raspberry}}$ is the water activity of the fresh fruit ($\approx$0.97) and $(a_w^0)_{\text{sucrose}}$ is the water activity of the sucrose solution, both at the same molality as in the water of the fruit. Value of $(a_w^0)_{\text{sucrose}}$ was obtained from the Norrish's equation:

$$(a_w^0)_{\text{sucrose}} = x_1 \exp(-Kx_2^2), \quad (2)$$

where x_1 and x_2 are molar fractions of water and sucrose and K is 6.47 for sucrose. The calculated values were as follows: x_1 = 0.898 and x_2 = 0.102.

Final water activity value achieved after infusion process was selected in order to have intermediate-humidity fruits of different acidity levels, as well as to study the impact of sugar concentration, sodium bisulphite and product pH on the analysed properties after further drying processes. Two different infusion treatments were performed: dry infusion (DI) and wet infusion (WI). In DI, fruits were mixed directly with the humectant and the additives. In WI, fruits were immersed in an aqueous solution of the humectants and additives. The fruit/sugar ratio was 1.27/1 for dry infusions and 0.36/1 for wet infusions. Systems were prepared as follows:

1 Dry infusion (DI): fruits and sucrose (the only additive).
2 Dry infusion with citric acid (DI-AC): fruits and a dry mix of additives (95.8% sugar and 4.2% citric acid).
3 Dry infusion with sodium bisulphite (DI-B): fruits and a dry mix of additives (sucrose and 250 ppm of sodium bisulphite).
4 Dry infusion with citric acid and sodium bisulphate (DI-BAC): fruits and a dry mix of additives (95.8% sugar, 4.2% citric acid and 250 ppm of sodium bisulphite).
5 Wet infusion (WI): fruits dipped in an aqueous solution of sucrose (61% w/w).
6 Wet infusion with citric acid (WI-AC): fruits immersed in an aqueous solution (59.4% sugar and 2.3% citric acid).
7 Wet infusion with sodium bisulphite (WI-B): fruits immersed in an aqueous solution (61% sugar and 250 ppm of sodium bisulphite).

8 Wet infusion with citric acid and sodium bisulphate (WI-BAC): fruits immersed in an aqueous solution (59.4% sugar, 2.3% citric acid, and 250 ppm of sodium bisulphite).
9 Reference samples: frozen fruits were used as reference samples.

In all cases, 1000 ppm of potassium sorbate was added. The preparations were gently mixed twice daily and system a_w was controlled until equilibration was reached (fruit a_w = generated syrup a_w). The time to equilibrate the systems was 10 days. After that, the fruits were taken out of the generated syrup and drained on tissue paper to remove the residual syrup. Bioactive compounds and antioxidant capacity of both the osmosed raspberries and the different generated syrups were reported in a previous work (Sette *et al.*, 2015).

Drying process

Raspberry samples with and without pretreatments were subjected to two different drying processes. Drying time was set in each case in order to achieve a final a_w value of 0.33 corresponding to about 11–18 g water/100 g d.w.

1 *Freeze-drying (F)*: all samples were quenched with liquid nitrogen before the freeze-drying process, which lasted between 24 h (control samples) and 48 h (pretreated samples). It was carried out in a freeze drier Alpha 1-4 LD/2-4 LD-2 (Martin Christ, Gefriertrocknungsanlagen GmbH, Osterode, Germany). It was operated at −55 °C at a chamber pressure of 4 Pa.
2 *Air-drying (A)*: an air convection oven model Venticell 111-Standard (MMM Medcenter Einrichtungen GMBH, Munich, Germany) was used (air at 60 ± 1 °C, ≈10% relative humidity RH and speed = 1.5 m s^{-1}). RH was controlled with a Hygro Palm hygrometer (Rotronic Instruments, West Sussex, UK). The drying time required to achieve a_w = 0.33 was 22 h for control samples and 24 h for dry and wet infusions samples.

Sample analysis

Water content, soluble solids content, total acidity, pH and water activity

The chemical analysis was carried out by analysing the following parameters according to AOAC methods (1990): water content (925.09), soluble solids content (932.12), total acidity (945.26) and pH (945.27). 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. Total acidity was expressed as per cent 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.

Raspberry extracts

For all determinations, except for monomeric anthocyanin content, fruit extracts were obtained according to Cayupán *et al.* (2011) with some modifications. For extract preparation, 2.5 g of the samples obtained after air-drying or freeze-drying were homogenised in 7.5 mL methanol for 3 min using a blender and then filtered. The pellet was extracted twice again with 7.5 mL aliquots of methanol. The extracts were combined, and methanol was added to constitute a total volume of 25 mL. All spectrophotometric measurements from extracts were carried out using a UV–Vis spectrophotometer model 1700 (Metrolab Instruments, Buenos Aires, Argentina).

Total sugar content (TS)

The total sugar content was determined by an anthrone/sulphuric acid procedure (Southgate, 1976). A curve with glucose as standard was used for expressing results. Results were expressed as g of glucose per 100 g of dry matter (d.w.).

Total phenolic content (TPC)

Total phenolic content was determined using the Folin–Ciocalteu reagent according to Singleton & Rossi (1965) with some modifications. 150 μL of extract was mixed with 950 μL water, 100 μL Folin–Ciocalteu reagent and 600 μL 20% sodium carbonate in distilled water. 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 in milligrams per 100 g of dry matter (mg GAE/100 g d.w.).

Monomeric anthocyanin content (ACY) and anthocyanin degradation index (ADI)

For total anthocyanin determination, the extracts were obtained according to Nikkhah *et al.* (2007) with some modifications. For extract preparation, 3 g of the sample were homogenised in 35 mL of ethanol acidified with chloridric acid, shaken for 10 min using a magnetic stirrer and filtered. The pellet was extracted twice again with 10 mL and 5 mL of ethanol acidified with chloridric acid, respectively. The extracts were combined, and ethanol was added to constitute a total volume of 50 mL.

ACY was determined using the pH differential method (Giusti & Wrolstad, 2005). Monomeric anthocyanin content was expressed as Cyanidin-3-glucoside

(MW: 445.2 and a molar extinction coefficient = 29 600 L cm^{-1} mol^{-1}) per 100 g of dry matter. 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 & Francis, 1968).

Polymeric colour percentage (%PC), browning index (BI)
The per cent of polymeric colour was expressed as a % of total colour density (%PC = PC/CD × 100). Colour density (CD) and polymeric colour (PC) parameters were determined using the bisulphite bleaching method according to Giusti & Wrolstad (2005). Total colour density is a measure of the total colour strength of the sample solution; it was calculated as follows:

$$CD = [(Abs_{420\ nm} - Abs_{700\ nm}) + (Abs_{\lambda vis-max} - Abs_{700\ nm})]\text{Dilution Factor} \quad (3)$$

Polymeric colour, an indicator of polymerised pigments, including tannins and brown compounds was calculated using the same equation as for CD but applied to bleached samples, assuming that only monomeric anthocyanins get bleached.

Antioxidant capacity
The antioxidant activity of raspberries was determined through two different methods:

1 DPPH (free radical scavenging capacity). The bleaching method of the radical 1,1-diphenyl-2-picrylhydrazyl ($DPPH^{\bullet}$) (Brand-Williams *et al*., 1995) with some modifications was used. 3 mL of $DPPH^{\bullet}$ solution in methanol (0.002%) was placed into a cuvette and mixed with aliquots of raspberry 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 raspberry extract were measured in order to find EC_{50} value that corresponds to the concentration that scavenged 50% of the radicals. The antiradical power (ARP), defined as the inverse of EC_{50} expressed in dry matter, was used for comparison of different raspberry extracts.
2 FRAP (ferric ion reducing ability). The FRAP method (the ferric reducing-antioxidant power) described by Benzie & Strain (1996) was used. The change of absorbance at 595 nm was measured after 4, 30 and 60 min. At the same time, a calibration curve was obtained with known concentrations of Fe^{2+} between 100 and 2000 μM ($FeSO_4.7H_2O$). The change in absorbance was expressed in Fe^{2+} μmoles per 100 g sample of dry matter.

Colour analysis
The superficial colour of raspberries was determined by measuring tristimulus parameters (CIELAB colour space) with a photocolorimeter model CR 400 (Minolta, Tokyo, Japan) using illuminant C and 2° observer angle. The instrument was calibrated (standardised) each time with a white ceramic plate. Measurements were performed in ten raspberries for each condition with two readings in the equatorial zone. The parameters L*, a* and b* of CIELAB colour space were recorded. L* represents colour 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 (+). These numerical values were converted into 'global colour difference' (ΔE^*_{ab}) using the following equation:

$$\Delta E^*_{ab} = [(\Delta L^*_{ab})^2 + (\Delta a^*_{ab})^2 + (\Delta b^*_{ab})^2]^{1/2} \quad (4)$$

For ΔE^*_{ab} , differences were calculated taking into account L*, a* and b* values of fresh raspberries. The global colour difference indicates the magnitude of colour change after treatment.

Sensorial analysis
To evaluate the acceptability of raspberry products from the point of view of organoleptic parameters, sensory studies involving consumer's impression were performed. Samples dehydrated by air- and freeze-drying were individually analysed, and no comparison between drying methods was performed.

Dehydrated raspberries were assessed by eighty panellists, without experience in sensory evaluation of foods. For sensory testing, ≈3–4 dehydrated raspberries were placed on plates and served to the panellists. The order of presentation of each sample was randomized but balanced. Panellists were asked to indicate how much they liked or disliked each product on a 9-point hedonic scale (9 = like extremely; 1 = dislike extremely) according to texture, flavour, aroma and overall preference. Furthermore, acidity and colour were evaluated by the 'just right' scale. It is a 5-point scale with extremes from 'very high acidity' to 'very low acidity' and 'very dark' to 'very clear' to evaluate the colour. The sensory analysis was conducted in an appropriately designed and lighted room, and a mean score was estimated for each product.

Volumetric shrinkage (Sh)

The shrinkage caused by the different dehydration methods was evaluated through measurements of sample volume change. Volume was estimated gravimetrically by displacement of toluene in a pycnometer:

$$V = \frac{M_m + M_{p+t} - M_{p+t+m}}{\rho_t}, \quad (5)$$

where V = sample volume (mL); M_m = sample mass (g); M_{p+t} = mass of pycnometer with toluene (g); M_{p+t+m} = mass of pycnometer with toluene containing the sample (g); ρ_t = toluene density, corrected for temperature (g mL^{-1}).

Shrinkage was calculated according to the following equation:

$$\mathrm{Sh} = \left(\frac{V_0 - V}{V_0}\right)100, \quad (6)$$

where V_0 = initial average volume (taken from ten reference raspberries) and V = volume of each raspberry after treatment. Volume displacement was determined in quintupled.

Statistical analysis

A completely randomized design was used. For all determinations, except for superficial colour and shrinkage, three replicates were measured. The results were expressed by mean and standard deviation of the mean (SD). An analysis of variance was performed to establish the presence or absence of significant differences in parameters according to the factors 'additive', 'type of infusion' and 'drying method' (Montgomery, 1997). Multiple comparisons were carried out using the Tukey test, and significance level was set at $P < 0.05$. In the case of significant interactions between factors, the Tukey test was run for the interaction. For not significant interaction between factors, a Tukey test of main effects was performed. All of the measured variables used to characterise the raspberries under the different dehydration methods were descriptively compared with an analysis of principal components (PCA) (Chatfield & Collins, 1980). All statistical analyses were carried out using the data analysis software system STATISTICA version 8.0 (StatSoft, Inc., Tulsa, OK, USA).

Results and discussion

Compositional changes

Water content of raspberries decreased from 85% (w/w) (reference fruit) to ≈51% (w/w) after infusion in all cases, with a final a_w of 0.85 (Sette *et al.*, 2015). After further drying stage, raspberries experimented different changes in water and sugar concentration, as well as in total acidity according to the type of applied pretreatment (Table 1). Although both dehydration processes were performed to achieve the same $a_w = 0.33$, differences in humidity could be ascribed to the different transport mechanisms involved in each dehydration method, highly dependent on the structural changes occurred in the cellular matrix. Moreover, it is known that sugar impregnation favours sugar crystallization in the outer layer of the fruit tissue during drying. The development of this concentrated solids surface layer (or crust) and the reduction of tissue porosity and shrinkage due to sugar infiltration and air-drying could be responsible for the higher humidity observed in air-dried samples with previous infusion when compared to freeze-dried ones. The combined treatment of sugar infusion and freeze-drying was not effective at preserving sample volume, mainly in wet infusions (Table 1).

The additives used in infusion formulation also affected the subsequent dehydration process. For both drying methods, a lower water content was reached in samples with sodium bisulphite incorporated as the only additive (WI-B, DI-B), with no significant differences when compared with samples infused without additives (WI, DI). However, higher water retention was observed in all samples with added acid. The product liquid phase is expected to get higher water content in products containing higher content of soluble compounds, which seems to be taking place in acidified samples. The effect of additives was more significant in freeze-dried samples, mainly in those subjected to wet infusions, probably because the generated porous structure allowed a higher interaction between the additives and the cellular matrix. When DI infusion pretreatment was applied, not significant differences were obtained between samples with different additives. Total sugar content (TS) of reference sample was 49.4 ± 0.5% (d.w.) and increased till ≈70% (d.w.) after dehydration (air or freeze-drying) and ≈100% (d.w.) when DI pretreatment was applied (Table 1). The total acidity increased not only in acidified but also in nonacidified fruits, being the reference sample acidity of 1.78 ± 0.04% (d.w.). Final acidity of control samples is due to concentration of the acids initially present in the tissue and to the fact that these samples did not experiment acid leaching throughout osmosis, which could be verified in pretreated samples without added citric acid, mainly those subjected to wet infusions (WI, WI-B).

Bioactive compounds and antioxidant capacity

Total polyphenol content (TPC) and monomeric anthocyanin content (ACY) were significantly reduced

Table 1 Initial water content before air-drying or freeze-drying (H_0), water content (H), total sugars (TS) and acidity (TA) of reference and dried raspberries obtained by freeze-drying or air-drying with and without pretreatments (d.w. = dry matter)

Drying method	Sample	H_0 (%, d.w.)	H (%, d.w.)	TS (%, d.w.)	TA (%, d.w.)	Sh (%)
	Reference	—	567 ± 14	49.4 ± 0.5	1.78 ± 0.04	—
Air-drying	C	567 ± 14^{c}	15.9 ± 0.5^{i}	67.8 ± 1.6^{a}	8.5 ± 0.2 ^{g}	81.2 ± 2.8 ^{g}
	WI	96 ± 4^{a}	11.2 ± 0.3^{bcd}	99 ± 1de	0.59 ± 0.07^{a}	56.4 ± 4.9 ^{cd}
	WI-AC	104 ± 3^{ab}	16.3 ± 0.6^{ij}	101.07 ± 0.59^{ef}	4.09 ± 0.08^{d}	60 ± 3^{cde}
	WI-B	94.3 ± 1.3^{a}	11.3 ± 0.9^{bcd}	97.29 ± 0.04^{b}	0.56 ± 0.02^{a}	59.9 ± 5.6^{cde}
	WI-BAC	103.6 ± 1.4^{ab}	14.4 ± 1.5^{gh}	101.7 ± 1.3^{f}	3.92 ± 0.13^{c}	65 ± 3^{ef}
	DI	106.7 ± 1.7^{ab}	12.7 ± 0.6^{defg}	97.9 ± 0.8^{bc}	1.45 ± 0.04^{b}	60 ± 4^{cde}
	DI-AC	111.5 ± 1.8^{b}	13.7 ± 0.3^{fgh}	102.2 ± 0.5^{f}	4.79 ± 0.04^{f}	71 ± 4^{f}
	DI-B	100 ± 12^{a}	14.1 ± 0.5^{fgh}	98.9 ± 0.9 ^{cd}	1.42 ± 0.02^{b}	66 ± 4^{ef}
	DI-BAC	114 ± 2^{b}	16.4 ± 0.4^{ij}	107.2 ± 0.7 ^{g}	4.42 ± 0.03^{e}	69 ± 3^{f}
Freeze-drying	C	567 ± 14^{c}	17.7 ± 0.3^{j}	69.3 ± 0.2^{a}	8.37 ± 0.15 ^{g}	11.4 ± 2.2^{a}
	WI	96 ± 4^{a}	6.9 ± 0.3^{a}	100.3 ± 0.4^{de}	0.62 ± 0.07^{a}	25 ± 4^{b}
	WI-AC	104 ± 3^{ab}	11.8 ± 0.5^{bcde}	101.1 ± 0.4^{ef}	4.09 ± 0.06^{d}	22 ± 3^{b}
	WI-B	94.3 ± 1.3^{a}	7.66 ± 0.03^{a}	97.4 ± 0.4^{b}	0.57 ± 0.02^{a}	29 ± 4^{b}
	WI-BAC	103.6 ± 1.4^{ab}	12.3 ± 0.4 ^{cdef}	102.9 ± 0.4^{f}	3.9 ± 0.2^{c}	24 ± 4^{b}
	DI	106.7 ± 1.7^{ab}	10.9 ± 0.2^{bc}	98.4 ± 0.4^{bc}	1.46 ± 0.05^{b}	63.8 ± 1.3^{def}
	DI-AC	111.5 ± 1.8^{b}	14.7 ± 0.3^{hi}	102.21 ± 0.06^{f}	4.79 ± 0.02^{f}	64 ± 3^{def}
	DI-B	100 ± 12^{a}	10.3 ± 0.3^{b}	99.4 ± 0.4^{cd}	1.42 ± 0.02^{b}	50 ± 4^{c}
	DI-BAC	114 ± 2^{b}	13.3 ± 0.2^{efgh}	107.2 ± 0.8 ^{g}	4.43 ± 0.05^{e}	60.8 ± 2.6^{cdef}
Interaction†	Infusion*additive	Drying*infusion *additive	Infusion*additive	Infusion*additive	Drying*infusion	*additive

Control: C; wet infusions: WI, WI-B, WI-AC and WI-BAC; dry infusions: DI, DI-B, DI-AC and DI-BAC; AC: citric acid, B: sodium bisulphite. Means within columns with a different lowercase superscript letter are significantly different ($P < 0.05$).

†Significant interactions obtained from factorial ANOVA; the Tukey test was run for the interaction.

($P < 0.05$) after drying (Table 2). Freeze-drying produced ≈18% loss of TPC and ≈10.7% loss of ACY when compared to the reference sample, while air-drying reduced substantially not only the amount of polyphenolic compounds (≈63% loss) but also of anthocyanins (55.5% loss) because of their sensitivity to degradation at high temperatures. Although freeze-drying decreases the heat damage and produces a dried product with reduced loss of bioactive compounds, polyphenolics are equally exposed to oxidative conditions, most likely due to the extended drying time. Mejia-Meza *et al.* (2010), when studying retention of polyphenol glycoside and aglycone compounds from dried raspberries by different drying techniques, also observed a tendency for freeze-drying to yield products with higher content of polyphenols. Pretreated samples exhibited a more profound loss, as during osmosis, water diffusion towards the hypertonic medium is accompanied by the migration of water-soluble substances as polyphenols and anthocyanins. Bioactive compounds loss to the osmotic solution has been demonstrated in different fruits subjected to osmotic dehydration (Osorio *et al.*, 2007; Chottamom *et al.*, 2012; Sette *et al.*, 2015). After SI stage (Table 3), higher retention of phenolics was obtained in dry infusions compared to wet infusions, and the addition of sodium bisulphite caused the highest losses. In the case of ACY, the decrease was much more evident after wet infusion treatments. After the second drying stage, in freeze-dried raspberries, TPC loss was lower in fruits with previous wet infusions compared to that obtained in fruits with previous dry infusions, while an opposite behaviour was observed in air-dried samples (Table 3). It is important to highlight that polyphenol decrease in WI samples took place almost entirely during pretreatment (82–85%), mainly in freeze-dried samples. When DI infusion was applied, although the main loss occurred during this first stage (≈80%), a certain % loss was also observed during the second drying stage (7–10%).

Studies carried out with other berries have shown similar results when studying the retention of bioactive compounds after air- and freeze-drying (Kwok *et al.*, 2004; Michalczyk *et al.*, 2009). The combination of long drying times, high temperatures and contact with oxygen during air-drying contributes to the higher loss of anthocyanins (Kalt *et al.*, 2000). However, Franceschinis *et al.* (2015) observed that cherry discs and dices obtained after the application of convective-drying at 60 °C exhibited higher TPC content than freeze-dried cherries. Que *et al.* (2008) observed a polyphenolic content 4.6 times higher in air-dried (at $T = 70$ °C) compared to freeze-dried pumpkin, and this TPC increase could be ascribed to the generation of phenolic compounds from precursors by nonenzymatic interconversion reactions that occur upon the application of high temperatures (60–70 °C) during drying.

Table 2 Total polyphenol content (TPC), monomeric anthocyanin content (ACY), antiradical power (ARP) and ferric ion reducing ability (FRAP) of raspberries without treatment (reference) and raspberries obtained after the application of air-drying or freeze-drying

Drying method	Sample	TPC (mg GAE/100 g d.w.)	ACY (mg Cyd-3-glu/100 g d.w.)	ARP ($1/EC_{50}$, 100 g d.w.)	FRAP (μmol Fe^{2+}/100 g d.w.)
	Reference*	1573 ± 13^{a}	542 ± 34^{a}	422 ± 22^{a}	$20\,611 \pm 478^{a}$
Air-drying	Control	582 ± 38^{c}	241 ± 12^{c}	84.8 ± 5.7^{c}	3498 ± 96^{b}
Freeze-drying	Control	1288 ± 21^{b}	484 ± 19^{b}	104 ± 2^{b}	3780 ± 28^{b}

Means within columns with a different lowercase letter superscript are significantly different ($P < 0.05$).
*Sette *et al.* (2015).

In pretreated raspberries (Fig. 1), the main differences in ACY content were due to infusion pretreatments, obtaining in general a higher retention of pigments in DI samples. Poor ACY retention was observed in raspberries subjected to WI and subsequent air-drying. TPC loss was significantly lower than ACY loss after air-drying stage as well as after freeze-drying (Table 3), and not significant correlation was obtained between these two parameters ($P < 0.05$, $r = 0.258$). This behaviour was attributed to the higher susceptibility of anthocyanins to high temperatures and the presence of oxygen during drying (Kalt *et al.*, 2000; Mejia-Meza *et al.*, 2010). On the other hand, Lohachoompol *et al.* (2004) observed that anthocyanins began to degrade at drying temperatures higher than 63 °C, enhanced by high sugar concentration. Sugars or their degradation products may sometimes accelerate anthocyanin degradation (Pirone *et al.*, 2014).

The antioxidant activity of dried raspberries is shown in Table 2 for the reference and the control samples, and in Fig. 2 for pretreated ones. The inclusion of different assays (FRAP and ARP) was considered important in order to provide comprehensive information on the total antioxidant activity of processed raspberries and to make precise estimates and comparisons from the different samples (Perez-Jimenez *et al.*, 2008). After air- and freeze-drying without pretreatment, a similar loss of antioxidant capacity (≈80%) was observed with both assays. However when analysing pretreated samples (Fig. 2), there were some differences according to the method applied. As expected, infusion pretreatments led to a large reduction of antioxidant activity in all dried raspberries as a consequence of the dilution effect of bioactive compounds with both ARP and FRAP methods. As it can be observed, all freeze-dried samples were grouped on the top in the diagram (Fig. 2a). Air-drying resulted in a higher loss of antioxidant capacity in all cases, and some differences between methods were detected when comparing the type of infusion. Higher differences between wet and dry infusions were detected when the ferric ion reducing capacity was studied (Fig. 2b) and all air-dried samples with previous DI were grouped on the bottom of this diagram, showing minimum antioxidant activity by this method, even though TPC loss was similar in comparison with samples with WI infusion. Despite it is difficult to compare antioxidant capacity results between two methods because the assays follow different mechanisms, some coincidences could be detected. On one hand, DI air-dried samples exhibited the lowest antioxidant capacity and on the other, the use of additives in the formulation of infusions improves the antioxidant properties and the TPC content in air-dried fruits. The addition of additives only had a significant effect ($P < 0.05$) on the ARP

Table 3 Loss percentage of total polyphenolic content (TPC) and monomeric anthocyanin content (ACY) in raspberries after the application of sugar infusion treatment (SI), the combined treatment of sugar infusion and air-drying, and sugar infusion and freeze-drying

Sample	SI*	SI + Air-drying	SI + Freeze-drying
% Loss of TPC			
WI	82.3 ± 0.4^{cA}	91.2 ± 0.9^{fC}	84.6 ± 0.9^{bB}
WI-AC	82.49 ± 0.12^{cA}	85.7 ± 0.3^{cdB}	82.6 ± 0.9^{aA}
WI-B	$85.13 \pm 0\text{-}36^{dB}$	91.2 ± 0.4^{eC}	84.2 ± 0.5^{bA}
WI-BAC	82.09 ± 0.42^{cA}	85.2 ± 1.3^{bcB}	82.09 ± 0.9^{aA}
DI	78.3 ± 0.5^{bA}	87.29 ± 1.06^{dB}	88.3 ± 0.3^{dC}
DI-AC	75.5 ± 0.6^{aA}	82.09 ± 1.24^{aB}	85.4 ± 0.5^{bC}
DI-B	81.9 ± 0.3^{cA}	86.57 ± 1.14^{cdB}	86.8 ± 0.7^{cB}
DI-BAC	75.7 ± 0.9^{aA}	83.6 ± 0.9^{abB}	87.2 ± 0.5^{cC}
% Loss of ACY			
WI	95.04 ± 0.43^{deA}	99.12 ± 0.27^{dB}	94.7 ± 0.2^{efA}
WI-AC	96.19 ± 0.13^{eB}	98.2 ± 0.2^{cdC}	94.07 ± 0.9^{dA}
WI-B	94.9 ± 0.9^{deA}	98.3 ± 0.2^{cdB}	95.18 ± 0.13^{fA}
WI-BAC	94.3 ± 0.6^{dA}	97.9 ± 0.4^{cB}	94.2 ± 0.6^{deA}
DI	87.2 ± 0.8^{aA}	95.9 ± 0.8^{bC}	90.79 ± 0.12^{aB}
DI-AC	88.8 ± 0.5^{cA}	95.6 ± 0.3^{bC}	92.6 ± 0.3^{cB}
DI-B	88.42 ± 0.12^{bcA}	94.8 ± 0.2^{abC}	91.4 ± 0.2^{abB}
DI-BAC	87.08 ± 0.52^{aA}	94.13 ± 0.65^{aC}	91.8 ± 0.2^{bB}

Wet infusions: WI, WI-B, WI-AC and WI-BAC; dry infusions: DI, DI-B, DI-AC and DI-BAC; AC: citric acid, B: sodium bisulphite. Means within rows with a different lowercase letter superscript are significantly different ($P < 0.05$). For each pretreatment, means within columns with a different uppercase letter superscript are significantly different ($P < 0.05$).
*Calculated from previous data (Sette *et al.*, 2015).

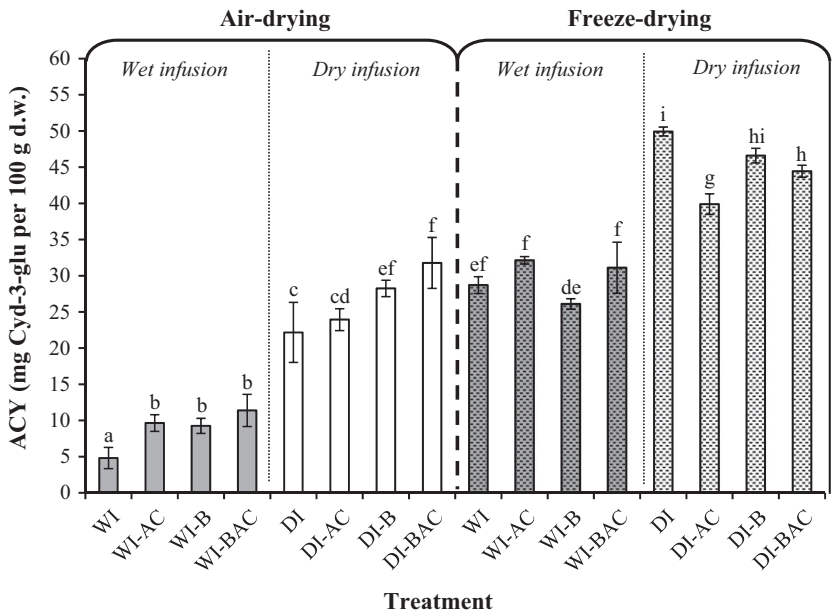

Figure 1 Monomeric anthocyanin content (ACY) of raspberries obtained after the application of air-drying or freeze-drying and pretreatments (Wet infusions: WI, WI-B, WI-AC and WI-BAC; dry infusions: DI, DI-B, DI-AC and DI-BAC) (d.w. = dry matter). Vertical bars represent standard deviation of the means. Means with a different lowercase letter are significantly different ($P < 0.05$). Lowercase letters were used for interaction between the three studied factors.

values, showing those samples without additives incorporated (DI and WI) a reduced ability to scavenge free radicals. This could be explained on one hand because of the presence of a higher proportion of polymerised anthocyanins. The fact that polymeric polyphenols are more potent antioxidants than simple monomeric phenolics (Moure *et al*., 2001) might explain the higher antiradical activity of fruits in these conditions. On the other hand, in the case of sulphited fruits, the colourless complex formed with anthocyanin molecule involves the C-4 position. The hydroxyl group (proton donor) may be acting as stabilizers of free radicals, increasing antioxidant properties. Figure 2a shows that most of sulphited samples are located all together at the top of the graph. The relatively similar antioxidant activity obtained by ARP assay in most samples, even in those with different TPC content, could indicate that other nonphenolic antioxidants are present and contribute to the $DPPH^{\bullet}$ antiradical activity.

To conclude from a nutritional standpoint, if we consider the consumption of a glass of red wine, which provides around 115–198 mg of polyphenols (Scalbert *et al*., 2005; Ignat *et al*., 2011), 100 g serving of dehydrated raspberries obtained in the present study would supply, in some cases (freeze-dried: WI-AC and WI-BAC, air-dried: DI-AC), over 50% of polyphenols provided by a glass of wine (Table 4). Furthermore, if we consider other usually consumed foods as polyphenols source, the intake through dried raspberries would even be higher than vegetables, cereals and several fresh fruits, indicating the benefits of consumption of freeze-dried raspberries pretreated with wet infusions. However, considering anthocyanins content (ACY), the intake of raspberries pretreated with dry infusions would be more beneficial. Consumption of dried raspberries without pretreatment (control), containing even higher levels of bioactive compounds, may be an ideal way to increase the intake with a smaller portion.

Colour evaluation

Superficial colour

Colour of raspberries is mainly influenced by the concentration and distribution of anthocyanins. The global colour changes of the different dehydrated fruits compared to the fresh sample are shown in Table 5. The lowest ΔE^*_{ab} values were observed for the control samples both air- and freeze-drying, while the pretreated samples with sodium bisulphite exhibited the highest ΔE^*_{ab} values. Regarding pretreated samples, the WI-B sample presented a significantly higher ΔE^*_{ab} value in each dehydration process (air- and freeze-drying). This different behaviour of the samples with sodium bisulphite was also observed when analysing the a*, b* and L* variables (Fig. 3). Freeze-dried raspberries were grouped together and near the reference, showing the highest values of a*, except WI-B

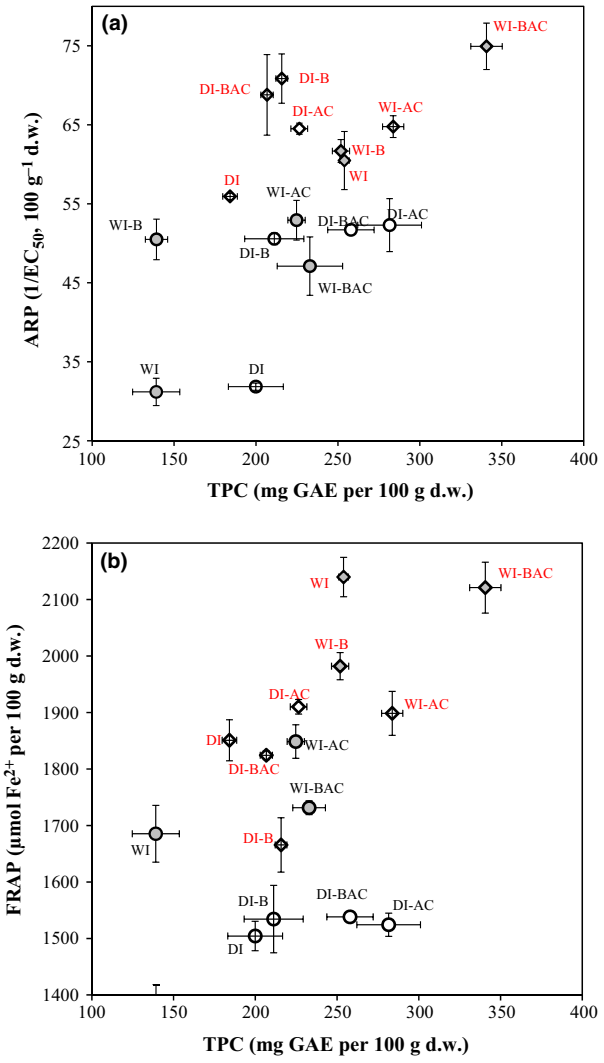

Figure 2 Antiradical power (ARP) versus total phenolic content (TPC) (a), and ferric ion reducing ability (FRAP) versus total phenolic content (TPC) (b) of raspberries obtained after the application of air-drying (circles) or freeze-drying (diamonds) and pretreatments (Wet infusions: WI, WI-B, WI-AC and WI-BAC; dry infusions: DI, DI-B, DI-AC and DI-BAC) (d.w. = dry matter). Bars represent standard deviation of the means. Interaction between the three studied factors was significant for the three variables. [Colour figure can be viewed at wileyonlinelibrary.com].

freeze-dried sample that exhibited a higher increase in b* and a decrease in a*, turning the sample to a yellowish tonality (Fig. 3a). This particular behaviour could be attributed to the interaction of anthocyanins with sodium bisulphite to form colourless sulphonic adducts (Francis & Markakis, 1989; Berké *et al.*, 1998; Wrolstad *et al.*, 2005). This effect was not observed in freeze-dried DI-B samples, probably because after DI raspberries contained higher ACY than after WI (Sette *et al.*, 2015). On the other hand, the reaction can be reversed in acid medium (Wrolstad *et al.*, 2005), and this effect, magnified by acid concentration during dehydration, could explain the higher a* values observed in freeze-dried WI-BAC when compared to WI-B. In the case of acidified samples, the acidity level (pH = 2.65–2.73) achieved in fruits after infusion and further freeze-drying, at which the red flavylium cation dominates, could also be beneficial for colour stabilization.

When air-drying process was applied, lower values of a* and b* were observed, particularly for DI samples. This fact is in agreement with the lower ACY content compared to freeze-dried samples.

Regarding lightness (Fig. 3b), drying promoted an increase in L* values (L* = 24 ± 2 for the reference sample). As anthocyanins are highly concentrated in the dried material, it would be expected to observe a darker appearance after drying. However, it is essential to consider not only pigment amount but also differences in internal structure. After freeze-drying, water contained in intra- and intercellular spaces is replaced with air. Therefore, the dull and pale appearance observed in freeze-dried matrices could be due to diffusion of the light throughout a material with interfaces having different refractive index (Saarela *et al.*, 2008), and this effect is more pronounced in fruits with defined hue as the raspberry fruit. This behaviour has also been observed in other fruits such as strawberry, tomato and kiwi (Lana *et al.*, 2006; Agudelo-Laverde, 2012). In control air-dried samples, the lightness increase was slightly lower than that observed after freeze-drying. In this case, a collapsed dense material was generated (Table 1) suggesting a higher concentration of pigment per tissue volume. The higher lightness of air-dried control samples could be related to the high loss of pigments (55%) not compensated by density increase or by pigment concentration as a consequence of water loss. When pretreatments were applied, a brighter and clearer appearance was provoked not only by pigment loss but also by sugar uptake.

Evaluation of anthocyanin degradation and browning

To investigate in-depth colour changes, it is necessary to analyse the contribution of all pigments, not only those naturally present in the fresh fruit but also the ones generated during processing. Therefore, dried raspberries colour was also analysed through anthocyanin degradation index (ADI) and polymeric colour (PC) parameters (Table 6). ADI values were higher than 1 in all samples, including the reference one (1.21 ± 0.02), which is not supposed to contain degraded pigments. This has been ascribed to degradation by oxidative mechanisms during pigment extraction step and also to the small absorption of anthocyanins at pH 4.5 (Fuleki & Francis, 1968).

Table 4 Total polyphenol content of common consumed food (fresh fruits and vegetables, cereals, beverages, seeds and nuts) and dried raspberries (w.b. = wet basis)

Dietary sources		TPC (mg gallic ac./100 g w.b.)	Dried raspberries	TPC (mg gallic ac./100 g w.b.)
Fruits	Apples[†]	77 ± 9	Air-dried	
	Bananas[†]	104 ± 14	C	502 ± 6
	Oranges[†]	148 ± 17	WI	115 ± 4
	Pears[†]	72 ± 4	WI-AC	188 ± 4
	Strawberries[†]	239 ± 89	WI-B	125 ± 5
	Sweet cherries[¶]	98 ± 9	WI-BAC	210 ± 5
	Blueberries[‡]	393 ± 1	DI	169 ± 8
Vegetables	Tomatoes[†]	60 ± 13	DI-AC	246 ± 7
	Carrots[†]	35 ± 7	DI-B	170 ± 9
	Red pepper[†]	137 ± 26	DI-BAC	221 ± 8
	Onions[†]	109 ± 2	*Freeze-dried*	
	Spinach[‖]	106 ± 1	C	2452 ± 26
Cereals	Oats[†]	93 ± 13	WI	236 ± 3
	Noodles[†]	126 ± 16	WI-AC	250 ± 6
	Wheat flour[†]	99 ± 14	WI-B	233 ± 5
	White bread[†]	68 ± 19	WI-BAC	299 ± 8
	Rice[†]	42 ± 10	DI	164 ± 4
Commercial juices	Apple*	33.9 ± 4.3	DI-AC	193 ± 4
	Orange*	75.5 ± 1.8	DI-B	193 ± 3
Beverages	Black tea*	72 ± 15	DI-BAC	179 ± 3
	Instant coffee*	133 ± 9		
	Beer*	31 ± 1		
Chocolates	Dark chocolate[§]	1617 ± 161		
	Milk chocolate[§]	515 ± 79		
	White chocolate[§]	222 ± 60		
Nuts and seeds	Walnuts[§]	3529 ± 1137		
	Sunflower seeds[§]	1358 ± 81		
	Hazelnuts[§]	±127		

Control: C; wet infusions: WI, WI-B, WI-AC and WI-BAC; dry infusions: DI, DI-B, DI-AC and DI-BAC; AC: citric acid, B: sodium bisulphite.
*Ignat *et al.* (2011).
[†]Zujko & Witkowska (2011).
[‡]Giovanelli *et al.* (2013).
[§]Zujko & Witkowska (2014).
[¶]Franceschinis *et al.* (2015).
[‖]Lutz *et al.* (2015).

Other authors also reported ADI values higher than 1 in berries and cherries (Michalczyk *et al.*, 2009; Pirone *et al.*, 2014; Franceschinis *et al.*, 2015). In control air-dried samples, ADI values increased 48% when compared to the reference fruit, while control freeze-dried ones only experimented 2.8% increase, in accordance with the highest ACY content registered in these samples (Fig. 1). Similar results were reported by Michalczyk *et al.* (2009), who considered that ADI value is a better indicator of colour than monomeric anthocyanin content.

Table 5 Global colour change (ΔE^*_{ab}) of dried raspberries obtained by freeze-drying or air-drying with and without pretreatments

Drying method	Sample	ΔE^*_{ab}
Air-drying	C	14 ± 2^{a}
	WI	16.3 ± 0.9^{b}
	WI-AC	16.3 ± 1.8^{b}
	WI-B	18.52 ± 1.06^{de}
	WI-BAC	14.5 ± 1.2^{a}
	DI	16.9 ± 1.2^{bcd}
	DI-AC	16.2 ± 1.2^{b}
	DI-B	16.8 ± 0.8^{bc}
	DI-BAC	16.4 ± 0.6^{b}
Freeze-drying	C	18 ± 2^{bcd}
	WI	21.2 ± 1.6^{f}
	WI-AC	21.04 ± 1.92^{f}
	WI-B	26.8 ± 2.8^{h}
	WI-BAC	24.6 ± 2.8^{g}
	DI	18.2 ± 1.9^{cde}
	DI-AC	19.8 ± 1.5^{ef}
	DI-B	24.6 ± 2.2^{g}
	DI-BAC	23.12 ± 2.03^{g}
Interaction[†]	Drying*infusion*additive	

Control: C; wet infusions: WI, WI-B, WI-AC and WI-BAC; dry infusions: DI, DI-B, DI-AC and DI-BAC; AC: citric acid, B: sodium bisulphite. Means within rows with a different lowercase superscript letter are significantly different ($P < 0.05$).
[†]Significant interactions obtained from factorial ANOVA analysis; the Tukey test was run for the interaction.

Differences between drying methods are mainly due to the high temperatures during air-drying process, having a high influence on pigment degradation. This degradation implies a lower content of monomeric anthocyanins and a higher presence of polymeric compounds. Moreover, the development of brown pigments produced by enzymatic and nonenzymatic browning during air-drying must be considered as they contribute to an absorbance increase at pH = 1 and therefore to ADI increase. Maillard reactions under acidic and heat conditions often lead to the formation of intermediate products like furfural and 5-hydroxymethyl-furfural (Perez-Locas & Yaylayan, 2010) and considering the low pH of processed raspberries (between 2.7 and 3.4), these compounds could be formed during dehydration. As freeze-drying does not imply the use of high temperatures or gradual a_w changes during drying, browning and anthocyanin degradation reactions are minimised. It must also be considered that anthocyanins can condense with other phenolic compounds to form coloured polymeric pigments (Wrolstad *et al.*, 2005), thus the polymeric colour (PC) is also related to anthocyanin degradation

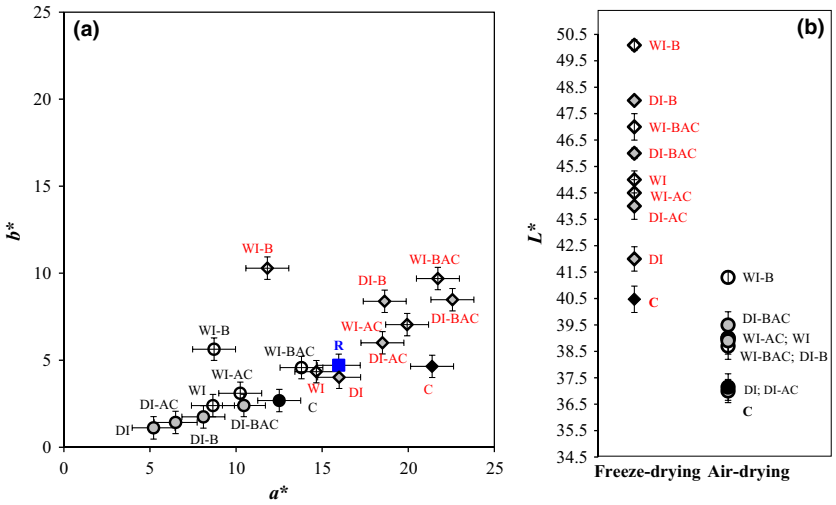

Figure 3 CIELAB coordinates b* versus a* (a) and lightness (L*) (b) of raspberries without treatment (R) and raspberries obtained after the application of air-drying (circles) or freeze-drying (diamonds) and pretreatments (Wet infusions: WI, WI-B, WI-AC and WI-BAC; dry infusions: DI, DI-B, DI-AC and DI-BAC). Bars represent standard deviation of the means. Interaction between the three studied factors was significant for the variables L* and a*. [Colour figure can be viewed at wileyonlinelibrary.com].

and indicates the amount of colour resulting from compounds derived from anthocyanins (Table 6). The behaviour of control samples with respect to PC was similar to that observed in ADI. With regard to pretreated raspberries, consistently with ADI, air-dried samples also had the highest PC content, especially those involving citric acid as an additive, with and without sodium bisulphite incorporated. It is important to note that fruits during osmotic dehydration generated a certain polymerisation degree (Sette *et al.*, 2015), and these initial differences between DI and WI samples might explain the differences observed after further dehydration. The low PC values observed in control air-dried sample could be related to lower levels of anthocyanin polymerisation due to the low sugar content (Table 1), in agreement to the lower ADI values.

Differences between treatments in ADI and ACY values could not be visually detected in the images of Figs 4 and 5. Except for WI-B freeze-dried sample, dried fruits did not exhibit important colour differences compared to control samples despite the great anthocyanin loss, which would indicate a marked stabilization of red pigments, probably because of the copigmentation phenomenon. This phenomenon is due to molecular associations between pigments and other (usually noncoloured) organic molecules that cause the pigments to exhibit more intense colour than would be expected from their concentration. The anthocyanin–copigment complex formation protects the flavylium group against hydration, so that the colour change of the chromophore is not dependent on pH (Mazza &

Table 6 Anthocyanin degradation index (ADI) and polymeric colour (PC) of raspberries without treatment (reference) and dried raspberries obtained by freeze-drying or air-drying with and without pretreatments.

Drying method	Sample	ADI	PC
Air-drying	Reference	1.21 ± 0.02	0.89 ± 0.08
	C	1.79 ± 0.09^{cde}	0.707 ± 0.005^{cde}
	WI	2.37 ± 0.13 ^{fg}	1.14 ± 0.08 ^{g}
	WI-AC	2.8 ± 0.2^{hi}	1.62 ± 0.02^{j}
	WI-B	2.6 ± 0.2^{gh}	1.35 ± 0,03^{hi}
	WI-BAC	2.9 ± 0.2^{i}	1.45 ± 0.03^{ij}
	DI	2.2 ± 0.2^{e}	1.27 ± 0.03^{gh}
	DI-AC	2.06 ± 0.17^{ef}	1.92 ± 0.06 ^{l}
	DI-B	1.88 ± 0.05^{de}	1.44 ± 0.04^{ij}
	DI-BAC	1.99 ± 0.12^{e}	1.8 ± 0.2^{k}
Freeze-drying	C	1.24 ± 0.03^{a}	0.85 ± 0.07^{ef}
	WI	1.64 ± 0.12^{bcd}	0.84 ± 0.04^{ef}
	WI-AC	1.67 ± 0.16^{cde}	0.73 ± 0.04^{cde}
	WI-B	1.59 ± 0.04^{bc}	0.62 ± 0.05^{abc}
	WI-BAC	1.59 ± 0.08^{bc}	0.72 ± 0.03^{bcde}
	DI	1.55 ± 0.07^{bc}	0.68 ± 0.07^{bcde}
	DI-AC	1.53 ± 0.06^{bc}	0.55 ± 0.04^{a}
	DI-B	1.42 ± 0.02^{ab}	0.59 ± 0.04^{ab}
	DI-BAC	1.52 ± 0.03^{bc}	0.79 ± 0.03^{def}
	Interaction†	Drying*infusion* additive	Drying*infusion* additive

Control: C; wet infusions: WI, WI-B, WI-AC and WI-BAC; dry infusions: DI, DI-B, DI-AC and DI-BAC; AC: citric acid, B: sodium bisulphite. Means within columns with a different lowercase superscript letter are significantly different ($P < 0.05$).

†Significant interactions obtained from factorial ANOVA; the Tukey test was run for the interaction.

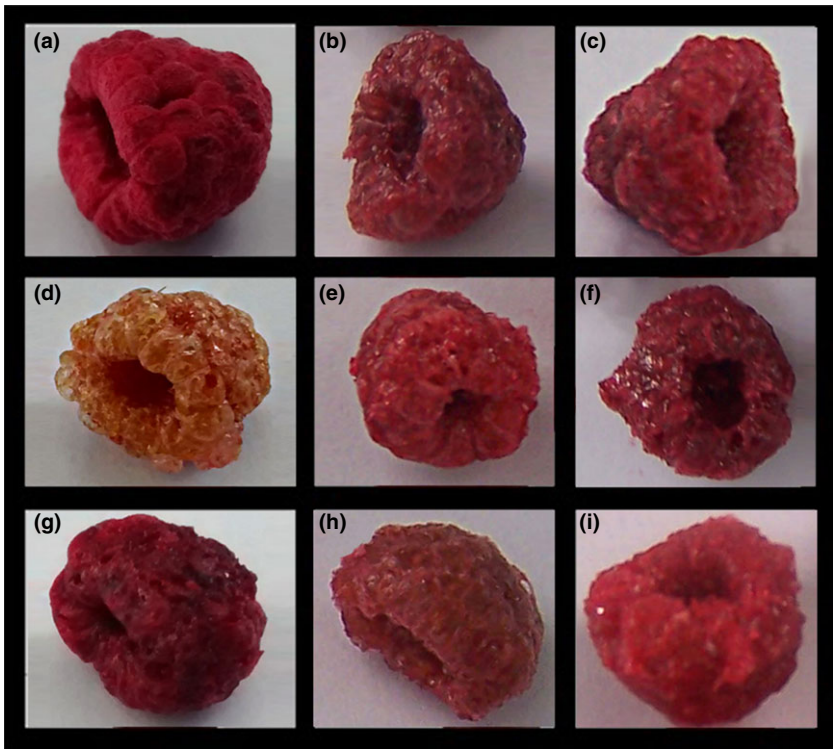

Figure 4 Images obtained after the application of sugar infusion treatments and freeze-drying. Control (a). Wet infusions: WI (b), WI-AC (c), WI-B (d) and WI-BAC (e). Dry infusions: DI (f), DI-AC (g), DI-B (h) and DI-BAC (i). [Colour figure can be viewed at wileyonlinelibrary.com].

Miniati, 1993). Moreover, not only the absorption of this cation on a suitable substrate (copigment) can stabilize anthocyanins by intermolecular copigmentation, but also anthocyanins can form strong bonds with groups of organic acids (in this case citric acid) favouring intramolecular copigmentation (Sari *et al.*, 2012). Therefore, the interaction between the remaining anthocyanins and the acids, naturally present or incorporated during pretreatment, probable prevailed over thermal destruction of red pigments or development of brown pigments during air-drying. The copigmentation processes appears to be crucial to stabilize coloured forms of the anthocyanins and allowed explaining colour expression in dried raspberries in spite of the severe experimental conditions during processing.

Analysis of principal component (PCA)

PCA was applied to detect patterns between the variables and the samples analysed. PCA resumed the information of thirteen variables measured on sixteen different dehydration processes in two new, uncorrelated variables termed 'principal components' (PC1 and PC2). PC1 explained 55% of the total variance of the data set while PC2 explained 20%. Several observations may be made from the sample score plot for PC1 vs. PC2 (Fig. 6). On one hand, samples subjected to air-drying are located on the left side of the graph, while those subjected to freeze-drying are located on the right side. Additionally, samples without additives (DI and WI) or with only bisulphite (DI-B and WI-B) are in the top half, and samples with the addition of citric acid (DI-AC, WI-AC, DI-BAC and WI-BAC) were grouped into the lower half of the graph. The figure also shows that Sh, ADI and PC are in the opposite direction to the variables TPC, ACY, ARP and FRAP, thus suggesting that samples with lower concentration of polymeric pigments, lower anthocyanins degradation and lower shrinkage also presented higher content of bioactive compounds (>ARP, >ACY, >TPC, >FRAP). Not surprisingly, the colorimetric variable a* is grouped on right lower quadrant along with the freeze-dried samples having citric acid in their infusions. This could be due to the higher amount of monomeric and copigmented anthocyanins, which conducted to an intensification of the red colour. On the other hand, the colorimetric variables L* and b* are grouped together with freeze-dried samples without additives or with only bisulphite.

Regarding principal component analysis a new variable called 'quality' can be drawn with similar direction to that of ARP, ACY, TPC and a* variables. The

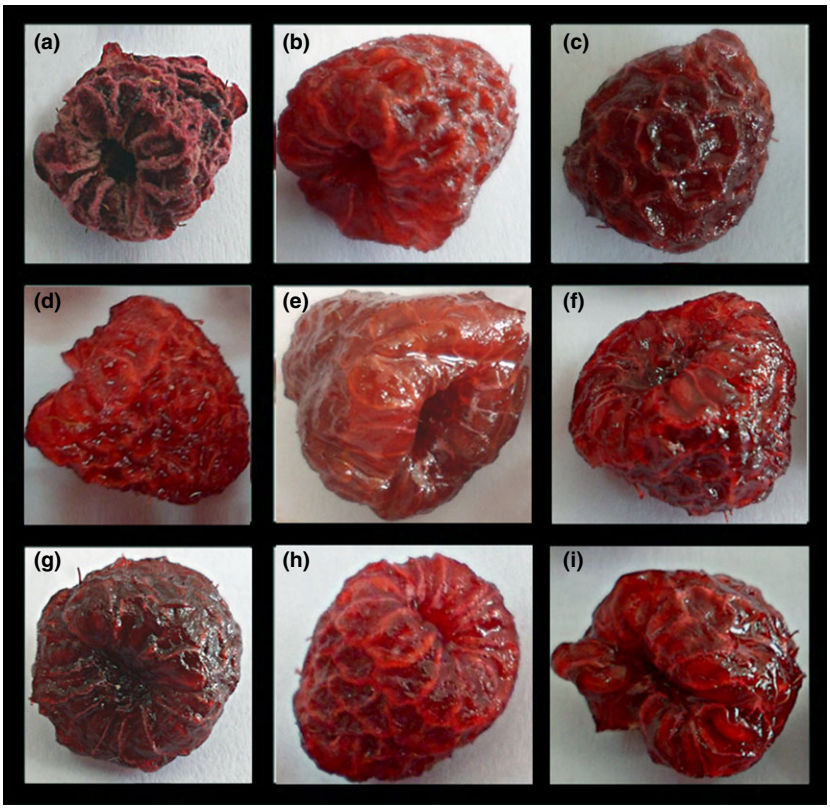

Figure 5 Images obtained after the application of sugar infusion treatments and air-drying. Control (a). Wet infusions: WI (b), WI-AC (c), WI-B (d) and WI-BAC (e). Dry infusions: DI (f), DI-AC (g), DI-B (h) and DI-BAC (i). [Colour figure can be viewed at wileyonlinelibrary.com].

best attributes of quality are related to colour conservation (>a* and >ACY retention), a higher polyphenol content, and therefore higher antiradical activity. According to this, freeze-dried raspberries exhibited better attributes than air-dried samples and pretreated raspberries with citric acid appeared to be products with higher quality, specially DI-BAC and WI-BAC samples. In air-dried samples, it was also observed that the highest quality in terms of colour and bioactive compounds would be in acidified samples, mainly with dry infusion pretreatments (DI-BAC and DI-AC). Also freeze-dried samples without additives could be selected (DI).

Sensorial analysis

A sensorial analysis with consumers was conducted on a group of selected dehydrated raspberries: control (C) and pretreated by DI, DI-AC and DI-BAC, with both air-drying and freeze-drying. The selection of these samples was based on the consideration of quality parameters showing that raspberries with dry infusion presented the best characteristics. Sensorial attributes (global preference, colour, acidity, texture, flavour and appearance) of raspberries are shown in Table 7. Regarding the global preference results of air-dried raspberries, it was observed that control samples had a significantly lower global preference value ($P < 0.05$), corresponding to the category 'neither like nor dislike' (Table 7). Although no significant differences were recorded in all pretreated and air-dried samples, DI air-dried raspberries had a slightly higher global preference, corresponding to the category 'I like' from the nine-point scale. With respect to freeze-dried raspberries, DI sample showed significantly higher values than the remaining samples. From sensory evaluation of colour, air-dried samples showed no significant differences between samples, but significant differences ($P < 0.05$) were obtained between control and pretreated raspberries in freeze-dried samples. Possibly, the brightness of freeze-dried samples caused by the presence of sugars influenced the consumer appreciation on surface colour. In the case of acidity attribute, similar results were obtained for both types of drying method, and DI sample appeared to be the lowest acid raspberry, in agreement with TA results (Table 1).

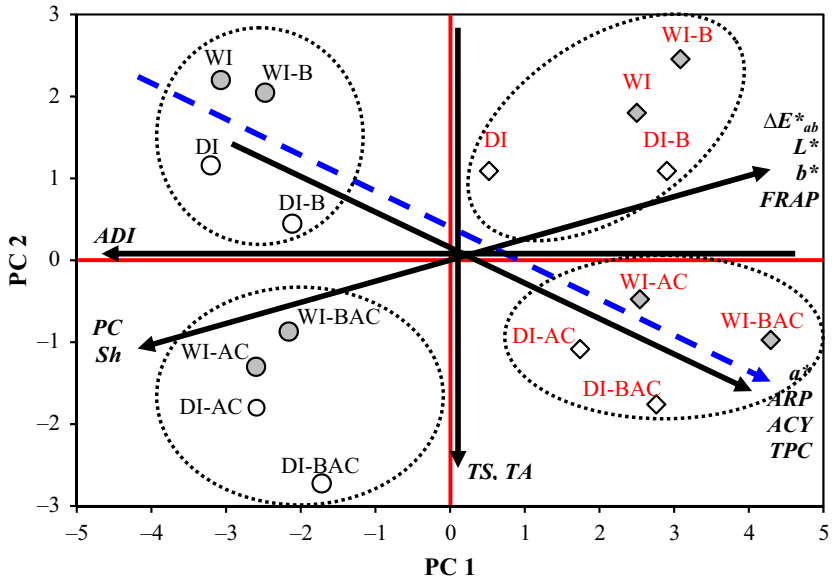

Figure 6 PCA two-dimensional scatter plot based on the first two principal components (PC1 and PC2) generated for the studied dehydration processes and based on data of the analysed variables. Dry infusions: DI, DI-AC, DI-B and DI-BAC. Wet infusions: WI, WI-AC, WI-B and WI-BAC. Air-drying (circles) and freeze-drying (diamonds). [····] Grouping of samples according to cluster of Euclidean distance. [- - - -] Direction of 'quality' variable. [Colour figure can be viewed at wileyonlinelibrary.com].

Table 7 Acceptability for sensorial attributes: overall preference, colour, acidity, texture, flavour and appearance of raspberries obtained after the application of air-drying (a) and freeze-drying (b) with and without pretreatments

Sample	Global preference	Colour	Acidity	Texture	Flavour	Appearance
(a)						
C	4.8 ± 1.8^{a}	2.9 ± 0.9^{a}	3.62 ± 1.08^{b}	4.8 ± 1.7^{a}	5.12 ± 2.13^{a}	5.2 ± 1.7^{a}
DI	7.4 ± 1.6^{b}	3.3 ± 0.7^{a}	2.2 ± 0.8^{a}	6.6 ± 1.7^{b}	7.4 ± 1.5^{b}	6.5 ± 1.9^{b}
DI-AC	7 ± 2^{b}	3.3 ± 0.6^{a}	3.4 ± 0.7^{b}	6.9 ± 1.6^{b}	7.2 ± 1.6^{b}	7.2 ± 1.7^{b}
DI-BAC	6.9 ± 1.4^{b}	3.2 ± 0.7^{a}	3.3 ± 0.9^{b}	6.3 ± 1.7^{b}	6.6 ± 1.7^{b}	6.9 ± 1.5^{b}
(b)						
C	5.03 ± 1.98^{a}	2.8 ± 0.9^{a}	3.05 ± 0.94^{b}	5.13 ± 2.08^{a}	5.39 ± 2.06^{a}	5.6 ± 1.1^{a}
DI	6.5 ± 1.9^{b}	3.6 ± 0.6^{b}	2.02 ± 0.15^{a}	5.72 ± 2.13^{a}	7.12 ± 1.98^{b}	5.5 ± 2.4^{a}
DI-AC	5.6 ± 1.7^{a}	3.5 ± 0.6^{b}	0.95 ± 0.16^{b}	5.3 ± 1.9^{a}	6.4 ± 1.8^{b}	5.32 ± 2.04^{a}
DI-BAC	6 ± 2^{a}	3.4 ± 0.7^{b}	1.01 ± 0.17^{b}	5.2 ± 1.9^{a}	6.2 ± 1.9^{b}	5.3 ± 1.1^{a}

Control: C; dry infusions: DI, DI-B, DI-AC and DI-BAC; AC: citric acid, B: sodium bisulphite. Not significant interaction between factors was obtained; a Tukey test of main effects was performed. Means within columns with a different lowercase letter superscript are significantly different ($P < 0.05$).

In air-dried raspberries (Table 7), control air-dried sample presented significantly lower values ($P < 0.05$) of appearance, texture and flavour, indicating the lowest acceptability in these attributes. However, on freeze-dried raspberries, significant differences ($P < 0.05$) were only obtained on flavour attribute, showing the control sample the lowest value.

From the obtained results, control samples were differentiated because they presented the less acceptability in most of the sensorial attributes. On the other hand, the highest acceptability was obtained for DI condition with both air-drying and freeze-drying.

Conclusions

Dehydrated raspberries without pretreatments showed the highest retention of bioactive compounds. However, they obtained the lowest sensory acceptability in global preference, texture and flavour compared to pretreated samples. Therefore, the application of infusion treatments could be a promising alternative to develop products with high consumers' acceptance. Samples with the combined pretreatment of acid and bisulphite allowed optimising dehydrated raspberries quality from the point of view of colour and bioactive

compounds, especially with further freeze-drying. However, regarding sensorial analysis, the acceptability of these samples was not as high as that observed for dehydrated fruit without additives, suggesting that concentrations of the additives could be adjusted to preserve quality properties with adequate sensory characteristics.

The results are useful to select the most appropriate processing technology for obtaining high-quality processed raspberries for direct consumption or for incorporation in a composite food. Possible applications could include, for example, the use as an ingredient in a cereal mix and cookies or the direct consumption as snacks. In this case, the suitable fruits were those with DI treatments, which presented a higher sensorial acceptability by consumers. It is worthy to remark that, in spite of the high sugar content of pretreated raspberries, the incorporation of these dried fruits to diet in both children and adults will increase healthy bioactive compounds consume and also could decrease the intake of traditional candies and other snacks of high-caloric level such as potato chips or cookies.

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Conflict of interest

The authors declare no conflict of interest.

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