Vacuum drying application to maqui (*Aristotelia chilensis* [Mol] Stuntz) berry: Weibull distribution for process modelling and quality parameters

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Abstract In this study, maqui berries were subjected to vacuum drying at 40–80 °C to assess and compare the effect on proximate composition, dietary fiber, phenolic and flavonoid compounds, antioxidant capacity and sugar content. The Weibull model was used for describing the vacuum drying process. The results indicated that the highest retention of total phenolic content (TPC) and total flavonoid content (TFC) was obtained after drying at 80 °C. Six phenolic compounds were identified and quantified by liquid chromatography. These were gallic acid, protocatechuic acid, ellagic acid, ferulic acid, myricetin and quercetin. In general, every phenolic compound showed a higher retention at temperatures above 60 °C. The antioxidant capacity of dried samples (ORAC assay) showed significant differences compared to the fresh fruit. Fructose and glucose were the two sugars present in the fruit. These results show that vacuum drying of maqui berries at 80 °C is an appropriate temperature for maintaining TPC, TFC, anthocyanins, sugars and dietary fiber with a shorter drying time compared to the other temperatures.

Keywords Vacuum drying · Antioxidants · Phenolic compounds · Dietary fiber

Introduction

Chile is one of the most important producers of exportable fresh berries and berry-derived products (Cerdeira et al. 2016). Berries are a set of fruits that are becoming increasingly popular in the human diet. “Maqui” (*Aristotelia chilensis*) is a less known berry, it highlights as a “superfruit” based on its composition that includes different chemical compounds such as phenolics, vitamins, organic acids, minerals and dietary fiber (Rodríguez et al. 2016; Brauch et al. 2016; González et al. 2015). Today, phenolic compounds have drawn considerable attention as potential protective factors against cancer and heart diseases due to their antioxidant potential. Likewise, many studies have reported that phenolic compounds possess other biological activities such as anti-inflammatory, anti-atherogenic, antidiabetic properties (Schreckinger et al. 2010; Miranda-Rottmann et al. 2002).

Maqui berry is a highly perishable fruit of short shelf life, reducing the availability as fresh fruit throughout the year (Fredes et al. 2014). Consequently, this fruit requires to be processed before consumption to maintain its functional, nutritional and sensory attributes. Severe processing conditions generally result in a high nutritional loss and lesser quality than that of fresh maqui. An optimal drying time and an adequate processing intensity must be considered when aiming to obtain desired food characteristics. Among the different drying methods employed in food processing, vacuum drying is characterized by applying a sub-atmospheric pressure that results in a higher quality product than that obtained by the conventional hot-air drying process at atmospheric pressure. Vacuum drying presents also advantages such as a higher drying rate and an oxygen deficient environment (Karam et al. 2016). For these reasons, this type of vacuum drying is used to process

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foods with temperature sensitive compounds, or compounds that are easily oxidized (Arévalo-Pinedo and Mur 2006). The effect of vacuum drying conditions on the drying process and the dried product quality have been evaluated by several authors (Arévalo-Pinedo and Mur 2006; Karaaslan et al. 2014; Orikasa et al. 2014; Akdaş and Başlar 2015). Commonly, control and optimization of food drying processes require the use of mathematical models. Among these, the Weibull model has been successfully used to describe the kinetics of chemical, enzymatic and microbiological degradation processes (Chen and Hoover 2004; Corzo et al. 2008) and is widely applied to fruit and vegetables to simulate the kinetics of mass transfer during the drying process. The Weibull model has been used achieving a good accuracy in the case of berries such as murta (Ah-Hen et al. 2013), blueberry (López et al. 2010) as well as grapes (Bai et al. 2013).

Many studies have assessed the potential of maqui berries as a source of natural antioxidants and the effects that convective drying temperature has on them (Fredes et al. 2014; Rodriguez et al. 2016; Brauch et al. 2016). Nevertheless, there are no studies reporting the effect of temperature on quality parameters during vacuum drying. Such evaluation is of great interest for industrial processes, when aiming to obtain wholesome foods that maintain their nutritional quality. Optimizing maqui's processing and promoting its consumption would provide the food industry with new products and ingredients.

The aims of this work were to determine the effect of maqui vacuum drying temperature on maqui's phenolic and antioxidant compounds and the quality of the final product; Additionally, to evaluate a suitable drying model for describing the drying process aiming to increase the base knowledge of this berry.

Materials and methods

All reagents were purchased from Merck (Merck KGaA, Darmstadt, Germany) and the standards from Sigma (Sigma Chemical Co., St Louis, MO, USA).

Vacuum drying and modelling

Maqui berries were collected in Mulchén, Bío-Bío Region in Chile (37°43'00"S, 72°14'00"O). Berries were kept refrigerated at 4–8 °C before the different drying processes were carried out (about 48 h). Vacuum drying was performed in a vacuum drying oven (Memmert VO 400, Schwabach, Germany) at five temperatures 40, 50, 60, 70 and 80 °C (± 0.2 °C) and at an absolute pressure of 150 mbar. Maqui berries were dried until reaching moisture equilibrium (constant weight). Then, the dried berries

were stored in vacuum-sealed bags at -20 °C until further analyses.

Moisture ratio (MR) was considered as a dependent variable [Eq. (1)], which relates moisture content of the sample in real time (X_{wt}), the initial moisture content (X_{wo}) and the equilibrium moisture content (X_{we}). The equilibrium moisture content was obtained at different temperatures from the study of desorption isotherms obtained at 60 °C (Quispe-Fuentes et al. 2016a). The equation used for modelling the isotherm was the Guggenheim, Anderson and de Boer (GAB) model that is usually applied to fruits and vegetables (Eq. (2), Ah-Hen et al. 2013). The model used to simulate the drying kinetics was an empirical equation proposed by Weibull [Eq. (3)] where α is a shape parameter and β is a scale parameter (Ah-Hen et al. 2013).

$$MR = \frac{X_{wt} - X_{we}}{X_{wo} - X_{we}} \quad (1)$$

$$X_{we} = \frac{X_m C k a_w}{(1 - k a_w)[1 + (C - 1)k a_w]} \quad (2)$$

$$MR = \exp\left(-\left(\frac{t}{\beta}\right)^\alpha\right) \quad (3)$$

where **C** and **k** are GAB Constants; X_m is Monolayer moisture content (g water/g d.m.); a_w is water activity.

Proximate composition analysis

Proximate Composition Analysis was determined following the AOAC methods (1990). Moisture content was determined by a vacuum oven (Gallenkamp, OVA-031-MA 1,9, Leicester, England) at 70 °C for 72 h (method n° 934.06), crude protein content was estimated by using the Kjeldahl method and multiplying the nitrogen content by 6.25 (method n° 960.52), lipid content was determined gravimetrically following the Soxhlet extraction (method n° 920.39) and ash was estimated by incineration in a muffle furnace (Felisa, FE-341, Jalisco, Mexico) at 550 °C (method n° 923.03). The total carbohydrate content was obtained by difference and finally, the crude fiber was determined by an acid/alkaline hydrolysis of insoluble residues (method n° 962.09). In addition, a water activity meter (AquaLab, 4TE, Pullman, USA) was used to determine water activity. All the analyses were performed in triplicate and expressed in g/100 g dry matter (d.m.)

Total dietary fiber (TDF)

Maqui berry samples were analyzed for soluble (SDF) and insoluble dietary fiber (IDF) following the AOAC (991.43) methodology and using a Total Dietary Fiber Assay Kit (TDF100A, Sigma, St Louis, MO, USA). Total dietary

fiber was calculated as the sum of soluble and insoluble dietary fiber, and expressed as g/100 g d.m.

Maqui extracts

Dried berries (1.0 g) were finely ground and then 70 mL 29% acetone was added. The extraction was carried out at 30 °C for 159 min in a temperature-controlled water bath with continuous agitation (Memmert WMB 22, Schwabach, Germany). These conditions were previously optimized (Quispe-Fuentes et al. 2017).

Maqui extracts were filtered through Whatman no. 1 filter paper and the solid residue was separated for posterior use. Then the filtrates were concentrated in a rotary evaporator (Büchi RE 121, Flawill, Switzerland) at 37 °C and dissolved in 5 mL of methanol:formic acid (99:1). Extractions were performed in triplicate, and the dissolved extracts were used for the analyses of total phenolic content (TPC), total flavonoid content (TFC) and antioxidant capacity by ORAC and DPPH (2,2-diphenyl-2-picrylhydrazyl) assays.

Total phenolic, total flavonoid and total anthocyanin contents

Determination of total phenolic content (TPC) and total flavonoid content (TFC) were performed following Rodriguez et al. (2016). Absorbance was read at 725 nm (TPC) and 425 nm (TFC) by a spectrophotometer (Spectronic® 20 Genesys®, NY, USA). Results were expressed as mg gallic acid equivalent (GAE)/g d.m. for TPC and mg quercetin equivalent (QE)/g d.m. for TFC.

For the extraction of anthocyanins, 50–70 mg of dried maqui berries were extracted following Brauch et al. (2016). Total anthocyanin content (TAC) was measured by the pH differential method (Giusti and Wrolstad 2001) and expressed as mg delphinidin-3-glucoside equivalent/g d.m. for TAC.

Phenolic compound profiles

The free phenolic compound profile was identified and quantified directly by liquid chromatography (HPLC–DAD, Agilent Series 1200). The bound phenolic compound profile was obtained from the solid residue mentioned above. It was subjected to an alkaline hydrolysis for 4 h with 20 mL of NaOH (4 M) at room temperature. The mixture was acidified to pH 2 with concentrated HCl and extracted three times with ethyl acetate. The used chromatographic conditions were those reported by Rodriguez et al. (2016). The results of the main phenolic compounds were expressed as µg/g d.m.

Antioxidant capacity assays

The antioxidant capacity was measured by ORAC and DPPH (2,2-Diphenyl-1-picrylhydrazyl radical) assays. The ORAC assay was carried out by the synthetic antioxidant Trolox as a reference and a fluorescein disodium salt solution in a phosphate buffer (75 mM pH 7.4) following the method described by Uribe et al. (2016). For the determination of DPPH an aliquot of 3.9 mL of DPPH radical (50 µM) was added to a test tube with 0.05 mL of maqui berries extract. The reaction mixture was vortex-mixed for 30 s and left to stand at room temperature in the dark for 30 min (Uribe et al. 2016). For ORAC assay the fluorescence was read in a Multimode Plate Reader (Perkin-Elmer, Victor X3, Hamburg, Germany) at $\lambda_{\text{ex}} = 485$ nm and $\lambda_{\text{em}} = 535$ nm. For the DPPH assay the absorbance was read spectrophotometrically at 517 nm and to both assays the results were expressed as µmol Trolox equivalent (TE)/g d.m.

Determination of sugars

The extraction of sugars was performed following Quispe-Fuentes et al. (2016b). Two grams of finely milled sample was dissolved in 6 mL of methanol (80%, v/v), agitated for 30 min and centrifuged at 5000 rpm for 3 min. A 350 µL aliquot of the supernatant was passed through a reverse phase (RP) C18 cartridge (Sep-pak, Waters, Ireland) previously activated with MeOH/HCl (10%). The chromatographic measurements were carried out by a HPLC-RI (Perkin Elmer Flexar LC model with a refractive index (RI) detector), including a Flexar binary LC Pump, a Flexar LC autosampler and Flexar column oven. Separation of sugars was carried out using a Phenomenex Luna 5µ NH₂ (250 mm × 4.6 mm) with the temperature kept at 25 °C. Quantification of sugars was performed by HPLC with isocratic mobile phase of acetonitrile:water (82.5:17.5 v/v) and a flow rate of 1.0 mL/min. Identification of sugars was performed by comparing retention times to those of standards. The results were expressed as mg/g d.m.

Statistical analysis

For drying kinetics modelling, the goodness of the fit between the predictive and experimental data was evaluated based on statistical analyses including sum squared error [SSE, Eq. (4)]; Chi square [χ^2 , Eq. (5)] and coefficient of determination [r^2 , Eq. (6)] to estimate parameters in linear models. A model is commonly considered acceptable if r^2 values are over 0.85, and if SSE and χ^2 values are close to zero (Lomauro et al. 1985).

The quality parameter analysis of the results was carried out by an analysis of variance (ANOVA) by the program

Statgraphics® Centurion, where the difference between the averages was analyzed with the least significant difference test (LSD) with a significance level of $\alpha = 0.05$ and a confidence interval of 95%. In addition, the multiple range test (MRT) included the existence of homogeneous groups within each of the parameters.

$$SSE = \frac{1}{N} \sum_{i=1}^N (MR_{exp,i} - MR_{calc,i})^2 \quad (4)$$

$$\chi^2 = \frac{\sum_{i=1}^N (MR_{exp,i} - MR_{calc,i})^2}{N - m} \quad (5)$$

$$r^2 = \frac{\sum_{i=1}^N (MR_{calc,i} - MR_{exp,i})^2}{\sum_{i=1}^N (MR_{exp,i} - MR_{exp,i})^2} \quad (6)$$

where MR_{exp} is the experimental moisture ratio, MR_{calc} is the calculated moisture ratio and N is the number of data, m is the number of constants.

Results and discussion

Vacuum drying modelling

The results of the water desorption isotherm at 60 °C are shown in Fig. 1a, where the equilibrium moisture content increases with water activity or relative humidity at a constant temperature. In the figure the range corresponding to $a_w < 0.70$, a linear increase of equilibrium moisture content was observed (multilayer sorption region) while $a_w > 0.70$ the equilibrium moisture content increased steady (capillary condensation region). This model was selected because it is considered the most versatile sorption model available in the literature (Al-Muhtaseb et al. 2002). The GAB parameters at 60 °C correspond to a previous work of the same authors (Fig. 1a), were $C = 18.71$; $k = 1.04$; and $X_m = 0.0308$ g water/g d.m. and the values of equilibrium moisture content (X_{we}) were obtained at each drying temperature (Table 1). The monolayer moisture content (X_m) is an important parameter giving a physicochemical meaning representing the monolayer moisture content which can interact thermodynamically with other components of the product. There are very few researches on maqui berry isotherms. However, when comparing against other berries, the X_m values reported for murta berries (Ah-Hen et al. 2013) and strawberries (De Bruijn et al. 2015) were somewhat higher than the X_m value for maqui berries, which could indicate that there is a lower amount of water strongly bound to specific sites on the maqui berry surface than in other berries. In addition, C and k are interaction energy constants between the first and further molecules at the individual sorption sites (Al-Muhtaseb et al. 2002). In maqui berries the k value was

Fig. 1 a Experimental and calculated desorption isotherm curve at 60 °C by GAB (Quispe-Fuentes et al. 2016a, b); b vacuum drying process at different temperatures and data modelling by Weibull

near one, which shows multilayer behavior properties that are close to liquid water (De Bruijn et al. 2015).

The experimental vacuum drying curves for all working temperatures (40–80 °C) are shown in Fig. 1b. These curves are typical for fruit dryings such as vacuum-dried black currant (Stéger-Máté et al. 2011) and vacuum-dried murta berries (Ah-Hen et al. 2013) where there is a steady drying time decrease at higher temperatures. The water vapor pressure within food increases in parallel to a temperature increase which may be responsible for water transfer to outwards (Karaaslan et al. 2014). The Weibull model showed an adequate fit of drying curve with $r^2 > 0.90$, $SSE < 0.0034$ and $\chi^2 < 0.0037$ in all the drying temperature range (Table 1), therefore the prediction using this model shows MR values as the experimental values (Fig. 1b) which proved the suitability application of the Weibull model in describing the vacuum drying characteristics of maqui berries. Similar results have been reported by Ah-Hen et al. (2013) for murta berries. Table 1 shows the Weibull parameters at five temperatures. The scale parameter (β) which is related to the reciprocal of the process rate constant and represents a kinetic reaction constant, a decrease was noticed by a temperature increase (temperature dependent). On the other hand, the shape

Table 1 Equilibrium moisture content (X_{we}) calculated by GAB equation and Weibull parameters determined for vacuum drying curves at different temperatures

	Temperatures (°C)				
	40	50	60	70	80
X_{we}^*	0.0935	0.0913	0.0843	0.0549	0.0586
Weibull parameters					
α	0.83 ± 0.02^b	0.74 ± 0.00^a	0.72 ± 0.03^a	0.84 ± 0.08^b	0.88 ± 0.06^b
β	198.96 ± 8.35^d	158.55 ± 31.84^c	96.40 ± 5.47^b	54.56 ± 9.81^a	39.03 ± 8.65^a
Statistical test					
r^2	0.9724	0.9733	0.9115	0.9457	0.9460
SSE	0.0017	0.0025	0.0034	0.0013	0.0010
X^2	0.0018	0.0028	0.0037	0.0014	0.0011

α is dimensionless; β expressed in minutes; (*) g water g⁻¹ d.m. Different letters in same row indicate that values are significantly different ($p < 0.05$)

parameter (α) is food specific and showed a slight temperature dependence. Nonetheless, some authors use a different nomenclature of these parameters. Hence, it is important not to be confused with the position of each parameter in the equation and the meaning of each one of them (Eq. 3).

Proximate composition analyses

Table 2 shows the proximate composition analysis of vacuum dried maqui berries at five temperatures and of the fresh fruit. The fresh maqui berries had a moisture content of 65.2 g/100 g sample, close to the value reported by González et al. (2015). In vacuum dried berries, the batch was removed from the dryer when it reached a moisture

content of about 10% (wet basis), being lower than those reported for a convective drying of maqui berries (Rodríguez et al. 2016). An important parameter to estimate the shelf-life of a food is the water activity, where a high-water activity can decrease the shelf life of a product due to the possibility of adverse biochemical changes and microbial growth, therefore, the water activity in dried fruits should range from 0.600 to 0.800 to eliminate these unfavorable changes but, it is even better when it is below 0.600 (Samoticha et al. 2016). In this case, the water activity of vacuum-dried berries was found to be lower than 0.500 indicating a microbiologically stable product. Table 2 provides the effect of vacuum drying on crude protein, fat, ash and fiber contents. In general, the crude protein content was not affected by this process, perhaps

Table 2 Proximate composition, fiber content and water activity of vacuum dried maqui

Parameters	Fresh	Temperatures (°C)				
		40	50	60	70	80
Moisture ⁽¹⁾	65.19 ± 0.12^a	9.91 ± 0.63^b	9.52 ± 0.82^b	7.66 ± 1.38^c	5.64 ± 0.38^d	5.65 ± 0.46^d
Crude protein	7.78 ± 0.77^a	6.71 ± 0.07^{bc}	6.65 ± 0.08^{bc}	7.23 ± 0.05^{ab}	7.55 ± 0.25^a	6.59 ± 0.12^c
Fat	5.99 ± 0.19^a	6.33 ± 0.09^a	7.14 ± 0.35^b	7.41 ± 0.29^{bc}	7.90 ± 0.50^c	6.14 ± 0.29^a
Ash	2.98 ± 0.11^b	3.33 ± 0.28^c	2.34 ± 0.16^a	2.41 ± 0.10^a	3.35 ± 0.18^c	3.54 ± 0.08^c
Total carbohydrates ⁽²⁾	83.22 ± 0.47^a	83.81 ± 0.78^a	83.86 ± 1.21^a	83.71 ± 1.03^a	81.19 ± 1.08^b	83.72 ± 0.54^a
Total dietary fiber	–	51.36 ± 1.02^a	55.82 ± 0.43^{bc}	57.21 ± 0.23^{cd}	60.27 ± 2.14^d	53.61 ± 2.35^{ab}
Available carbohydrate ⁽³⁾	–	32.45 ± 1.48^a	28.04 ± 1.32^{bc}	26.50 ± 1.24^c	20.92 ± 1.32^d	30.11 ± 2.09^{ab}
Crude fiber	35.59 ± 4.15^a	27.55 ± 2.24^d	28.78 ± 1.18^{cd}	31.40 ± 0.88^{bc}	33.85 ± 0.40^{ab}	30.82 ± 0.76^{bcd}
Water activity (dimensionless)	0.961 ± 0.004^a	0.482 ± 0.008^b	0.435 ± 0.005^{bc}	0.461 ± 0.017^b	0.431 ± 0.007^{bc}	0.387 ± 0.058^c

Mean values $\pm$ SD and all the data are expressed as g/100 g d.m. Different letters in the same row indicate that values are significantly different ($p < 0.05$)

⁽¹⁾g 100 – 1 g sample

⁽²⁾Total carbohydrates (TC) by difference: TC = 100 – (Moisture + Crude protein + Fat + Ash)

⁽³⁾Available carbohydrate by difference between TC and TDF

due to the protective action that certain sugars confer, which would preserve the protein native structure upon a loss of water. In addition, the tendency of proteins to form stable glassy matrices would also confer protection against drying (Sharma and Kalonia 2004). As to fat content, a significant increase ($p < 0.05$) at 50–70 °C was observed. Brauch et al. (2016) also observed an increase in the fat content when maqui berries were dehydrated. Regarding the ash content a significant decrease at 50 and 60 °C was observed.

Fiber contents

Table 2 shows the crude fiber content and the total dietary fiber. Knowing the Total Dietary Fiber (TDF), the carbohydrate available content can be estimated. A decrease in crude fiber was observed in dried samples, that might be due to a thermal degradation resulting in a disruption of the polysaccharides network of the cell wall (Miranda et al. 2010).

The TDF is composed of soluble (SDF) and insoluble (IDF) portions. The SDF and IDF content in maqui berries was found in the range from 1.7 to 4.3 g/100 g and from 47.1 to 56.4 g/100 g, respectively. The maqui berries present cell wall polysaccharides that may be valuable healthy compounds since they belong to the class of dietary fiber. The IDF corresponds to polysaccharides as hemicelluloses and cellulose and the SDF corresponds to pectin and some soluble hemicellulose. In maqui berries the portion IDF corresponds to about 90% as to the fraction of TDF. This result can be associated to the skin and seeds because maqui berry is characterized for containing 3–4 seeds. A slight decrease at 40 °C was observed in TDF probably due to a long drying time. These results are higher than those reported by Singh et al. (2016) of different fruits and vegetables. They also obtained higher insoluble dietary fiber content than soluble dietary fiber. Dietary fiber is known to have many health benefits and an intake of 25–30 g/day for an individual is recommended (Singh et al. (2016)).

Total phenolic, total flavonoid, total anthocyanin contents and antioxidant capacity

Maqui berries are characterized for the presence of three main groups of compounds: phenolic acids, flavonoids and anthocyanins. The total phenolic content (TPC) and total flavonoid content (TFC) are shown in Table 3 and the degradation level of these compounds by a vacuum drying process was evaluated. The results of TPC were close to those obtained by Fredes et al. (2014) (10.7–20.5 mg GAE/g fresh weight) and González et al. (2015) (21–28 mg GAE/g dry weight) for the same berry. The vacuum drying

in the range at 40–70 °C caused a decrease of TPC near 21–30%. This same trend was observed on other berries and fruits such as vacuum dried black currant at 40–60 °C (Stéger-Maté et al. 2011), vacuum dried mandarin orange between 45 and 75 °C (Akdaş and Başlar 2015) and vacuum dried pomegranate at 55–75 °C (Karaaslan et al. 2014). The TFC shows a similar value to the one reported by Genskowsky et al. (2016) (12.19 ± 0.02 g RE/kg d.m.) expressed in rutin equivalents (RE), for maqui berries harvested in Bío-Bío Region, Chile. The same TPC tendency was observed in TFC at 40–70 °C range. However, an increase on TPC and TFC at 80 °C was observed. This exception may be due to the heat energy during drying that has the ability to break down the molecular structures of the covalent complex and release some antioxidant compounds, such as flavonoids, carotenes, tannins, flavoproteins, and polyphenol polymers (Orikasa et al. 2014). Yan and Kerr (2013) explained that high temperatures could cause the degradation of lignin and other polysaccharides complexes leading to a further phenolic acid release. Besides, drying time was less than 200 min at 80 °C, with a higher drying rate favoring the retention of phenol compounds. Rodríguez et al. (2016) reported the highest degradation of phenolic compounds at 80 °C when maqui berries were subjected to convective drying. This study also showed a positive effect at the same temperature. Then, the vacuum drying can be more adequate than convective drying to maintain these antioxidant compounds, possibly due to an oxygen absence and a shorter drying time at such a temperature. Table 3 shows also that TAC in fresh berries was 8.01 ± 0.71 mg delphinidin-3-glucoside equivalent/g d.m. which agrees with values reported by Fredes et al. (2012) for maqui berries in a mid-ripe stage (purple, dark red). In addition, higher values of TAC have been reported by Brauch et al. (2016), Rodríguez et al. (2016) and Genskowsky et al. (2016) for the same fruit. This can indicate that anthocyanin content or biosynthesis of these compounds in maqui fruit is tightly associated to the fruit development stages, genetic variation (genotypes), environmental factors (soil conditions, growth temperature, among others) (Fredes et al. 2012). The observed differences may be due to the extraction methodology and the solvents employed (Genskowsky et al. 2016). The TAC was increased in vacuum dried maqui berries compared to the fresh ones, excepting at 70 °C. Considering that drying mainly causes damage to cell walls and membranes and that anthocyanins could be localized in the fleshy part of maqui berries then, these compounds could be protected against drying and therefore, there would be an effect of a better anthocyanin extraction (González et al. 2015). The same positive effect was observed at 80 °C for TPC and TFC. González et al. (2015) highlighted the maintenance of phenolic contents on dried maqui berries (sun and shade

Table 3 Effect of vacuum dried maqui on polyphenols, anthocyanins and antioxidant capacity at different temperatures

	Fresh	Temperatures (°C)				
		40	50	60	70	80
TPC ¹	32.93 ± 1.85 ^a	23.16 ± 1.61 ^b	23.62 ± 0.99 ^{bc}	24.6 ± 1.54 ^{bc}	26.12 ± 1.81 ^c	36.49 ± 0.38 ^d
TFC ²	19.54 ± 0.99 ^a	16.82 ± 1.17 ^{ab}	11.93 ± 0.72 ^c	17.33 ± 0.49 ^b	12.11 ± 0.74 ^c	21.09 ± 0.89 ^d
TAC ³	8.01 ± 0.71 ^b	10.2 ± 0.46 ^c	10.8 ± 0.44 ^{cd}	10.9 ± 0.06 ^{cd}	6.79 ± 0.14 ^a	11.57 ± 0.80 ^d
ORAC ⁴	616.06 ± 3.12 ^a	408.70 ± 2.40 ^d	424.74 ± 10.83 ^d	454.02 ± 12.05 ^e	366.7 ± 14.2 ^c	326.00 ± 18.79 ^b
DPPH ⁵	240.29 ± 6.23 ^a	195.6 ± 7.06 ^c	184.45 ± 5.93 ^c	184.63 ± 0.55 ^c	183.09 ± 9.01 ^c	220.26 ± 7.17 ^b

Different letters in the same row indicate a significant statistical different ($p < 0.05$)

¹Total phenolic content as mg GAE/g d.m.

²Total flavonoid content as mg QE/g d.m.

³Total anthocyanin content (TAC) as mg delphinidin-3-glucoside equivalent/g d.m.

⁴ORAC assay expressed in $\mu\text{mol TE/g d.m.}$

⁵DPPH assay expressed in $\mu\text{mol TE/g d.m.}$

drying), nevertheless, a longer drying time was necessary (several hours) compared to the time employed for vacuum drying in this work.

To estimate the antioxidant capacity, two different methodologies were employed: ORAC and DPPH. Table 3 illustrates the results of antioxidant capacity, where fresh maqui berries show a value of $616.1 \pm 3.1 \mu\text{mol TE/g d.m.}$ for ORAC and $240.3 \pm 6.23 \mu\text{mol TE/g d.m.}$ for DPPH. There is a noticeable decrease in the antioxidant capacity measured by ORAC, however, the antioxidant capacity determined by DPPH showed minor differences among dried samples with only three homogeneous groups.

The vacuum dried maqui berries at 50–70 °C showed a decrease in the antioxidant capacity by DPPH against fresh berries. In the antioxidant capacity measured by the ORAC assay a decrease was observed as compared to fresh samples throughout the whole temperature range evaluated (about 29–38% decrease as to fresh samples). This significant decrease ($p < 0.05$) observed by DPPH and ORAC is associated with a reduction in TPC, TFC and other non-polyphenol antioxidants. The results show that in terms of antioxidant phenolic compounds a temperature at 80 °C is suitable for this vacuum drying technology.

Phenolic compounds profile

The identified and quantified free phenolics were gallic, protocatechuic and ellagic acids. Table 4 shows that free gallic acid content has significant different groups where an increase at 40–50 °C and a decrease at 70–80 °C ($< 13\%$) were observed. There are no significant differences ($p > 0.05$) compared to the fresh fruit at 60 °C. This tendency might be produced because some of the phenolic acids are bound to insoluble cell wall material, and these

can be partially released with heat for example at 40–50 °C; however, when reaching higher temperatures (70–80 °C) those phenolic acids may be subjected to a thermal degradation (Yan and Kerr 2013).

In relation to free protocatechuic acid, a degradation of $< 10\%$ was noted when maqui berries underwent vacuum drying. On the other hand, the ellagic acid content represented about 51% of the three free phenolic acids identified in the fresh sample. This result agrees with Genskowsky et al. (2016) who reported that this acid is the main component of the maqui berries as a non-anthocyanin component. Ellagic acid shows a degradation percentage $< 38\%$ in the range 40–80 °C during vacuum drying.

The main free flavonoids identified in maqui berries were myricetin and quercetin (Table 4). These results agree with several authors who have reported the identification of the same flavonoids (Céspedes et al. 2010; Vidal et al. 2014; Brauch et al. 2016; Genskowsky et al. 2016). Table 4 shows some increase in these compounds, because they are commonly bound to sugars. Hence, it is possible that o-glucoside bond rupture is produced at temperatures > 40 °C generating a higher quantification.

Some bound phenolic compounds such as gallic, protocatechuic and ferulic acids were identified and quantified. In general, a statistically significant decrease ($p < 0.05$) was observed in all of them at all working temperatures, with degradations of 80, 30 and 43% for gallic, protocatechuic and *trans*-ferulic acids, respectively. These results show that the retention percentage in bound form varied from 57 to 77% for ferulic and over 70% catechuic acid. Hence it seems to be that both acids are relatively resistant to a heat treatment using vacuum drying technology, considering that gallic acid in a bound form was more affected than in a free form.

Table 4 Free and bound phenolic compounds profile ($\mu\text{g/g}$ d.m.)

Phenolic compounds	Temperatures ($^{\circ}\text{C}$)					
	Fresh	40	50	60	70	80
Free						
Gallic acid	640.24 ± 19.76^a	721.40 ± 41.94^b	777.94 ± 29.74^c	653.88 ± 7.86^a	555.85 ± 37.63^d	576.73 ± 19.19^d
Protocatechuic acid	309.06 ± 11.34^a	294.57 ± 13.98^{ab}	298.31 ± 6.10^{ab}	310.77 ± 6.65^a	280.61 ± 19.23^b	315.90 ± 12.28^a
Ellagic acid	1009.47 ± 82.83^a	633.79 ± 51.94^b	619.87 ± 16.52^b	852.76 ± 22.08^c	808.22 ± 21.29^c	811.34 ± 54.80^c
Myricetin	19.74 ± 1.85^a	25.68 ± 1.04^b	24.44 ± 0.59^{bc}	30.76 ± 0.23^d	19.45 ± 0.43^a	22.92 ± 0.68^c
Quercetin	14.44 ± 0.60^a	15.93 ± 0.37^b	15.62 ± 0.31^b	31.38 ± 0.48^c	15.95 ± 0.35^b	21.02 ± 0.58^d
Bound						
Gallic acid	251.95 ± 20.39^a	49.29 ± 7.22^b	62.58 ± 5.05^b	168.54 ± 8.21^c	392.20 ± 16.03^d	210.92 ± 5.66^e
Protocatechuic acid	147.64 ± 9.58^a	103.53 ± 9.95^b	112.66 ± 9.80^b	108.09 ± 4.42^b	105.72 ± 11.03^b	112.75 ± 7.68^b
Trans-ferulic acid	348.87 ± 26.31^a	232.22 ± 6.79^{bc}	267.51 ± 13.99^d	253.44 ± 8.11^{cd}	199.64 ± 13.43^e	216.60 ± 3.80^{be}

Different letters in the same row indicate a significant statistical difference ($p < 0.05$)

In brief, if the goal is to keep some specific phenolic compounds, a vacuum drying temperature at 60°C would be the most adequate one.

Sugars

The nutritional quality and health aspects of a food must consider a balance between antioxidant compounds and nutrients such as dietary fiber and simple sugars. In this sense a fruit should have a high content of antioxidants and dietary fibers as well as a low content of simple sugars like fructose and glucose. Figure 2 shows that only fructose and glucose were identified and quantified. The sugar content of the fresh berry was 46.1 ± 2.9 and 78.8 ± 1.6 mg/g d.m., for fructose and glucose, respectively. The glucose content value was close to that one reported by Quispe-Fuentes et al. (2016b) for convective dried maqui berries, but Brauch et al. (2016) reported higher values for these sugars on the same fruit. This difference can be due to

sugar composition in berries depending on fruit ripening state. These results show a fructose and glucose content lower than other fruits such as Corinthian currant (*Vitis vinifera*) (Nikolidaki et al. 2016). Figure 2 shows that no significant differences were observed among temperatures (40 , 50 and 80°C) for both glucose and fructose. However, there is a decrease ($p < 0.05$) at 60 – 70°C against other treatments. Figure 2 shows the fructose content in fresh berry, a slight increase in the dried samples was obtained, probably due to a bond rupture of this type of sugar attached to phenolic compounds allowing sugar release.

Conclusion

In this study, the kinetic modelling and quality parameters on vacuum maqui berries drying at five different temperatures were evaluated. The Weibull model was used to model the experimental data and an adequate fit was obtained. The Total Dietary Fiber seems not to be so influenced by vacuum drying temperature, where the most of the TDF corresponded to the insoluble one. Vacuum drying of maqui at 80°C is a convenient temperature to preserve its TPC, TFC, TAC and sugars. Therefore, vacuum drying is a good alternative to maqui drying compared to other drying methods avoiding a long drying time and maintenance of its natural antioxidants.

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Compliance with ethical standards

Conflict of interest The authors declare having no conflict of interest.

Fig. 2 Sugars (fructose and glucose) in vacuum dried maqui berries. Different letters above the bars indicate that values are significantly different ($p < 0.05$)

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