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Effect of processing on the drying kinetics and functional value of dried apricot

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Abstract

Apricots can be considered as a good source of phenolic compounds, which are beneficial for human health. Microwaves may be an alternative to the conventional sun or hot air drying techniques used to obtain dried apricot. Nevertheless, their impact on the functional compounds must be taken into account if they are to be recommended as an attractive drying option. This work compared the drying kinetics and the change in the organic acids, phenolic compounds and antioxidant activity of dried apricot when using hot air drying and microwave energy. Empirical (linear and Page) equations can be used to model the drying kinetics in air, combined air-microwave and microwave processes. From the obtained results, it can be concluded that the industrial processing of dried apricots may be improved by using microwave energy, as the drying time is considerably reduced, and the obtained fruit had a higher phenolic content, particularly of chlorogenic acid, catequin and epicatequin. Nevertheless, as the contribution of these phenols to antioxidant capacity was not significant, microwave dried samples maintained the same antioxidant capacity as the air-dried ones. When sulphite is added previous to the drying processes, care should be taken with the total phenols and the antioxidant capacity quantified as it may interfere with the results depending on the methodology used.

Keywords: hot air drying, microwave, drying kinetics, phenolic compounds, vitamin C, antioxidant capacity.

1. Introduction

Apricot fruits can be considered as a good source of phytochemicals such as polyphenols, carotenoids and vitamins, which significantly contribute to their taste, colour and nutritional and functional values. Currently there is a considerable interest in these biologically active components because of their antioxidant properties and ability to alleviate chronic diseases (Gardner, White, McPhail, & Duthie, 2000; Rice-Evans, Miller, & Paganga, 1997; Vinson, Hao, Su, & Zubik, 1998). In addition the growing demand for healthy and nutritive foods in the world today has made nutrient analyses a major area in quality control studies.

Dietary phenolic intakes, in particular, are known to reduce coronary heart diseases and cancer, as well as to act as anti-microbial, anti-allergic, anti-mutagenic and anti-inflammatory (Kim, Jeong & Lee, 2003). Phenolic acids are the dominant phenolic compound in apricots and, of these, the major one is chlorogenic acid (5-caffeoylquinic acid). Other phenolic acids present in this fruit are neochlorogenic acid, caffeic acid, p-coumaric acid, ferulic acid and their esters. Flavanols (+)-catechin and (–)-epicatechin and flavonols, which occur mostly as glucosides and rutinosides of quercetin and kaempferol, have also been determined in apricot fruits and their products (Arts, van de Putte, & Hollman, 2000; Dragovic-Uzelac, Pospisil, Levaj, & Delonga, 2005).

Vitamin C is known as the most important vitamin in fruits and vegetables for human nutrition (Lee & Kader, 2000). It is an efficacious free radical scavenger, playing the major non-enzymatic antioxidant role in the body. It may act independently, with specific activities such as anti-cancer or cardioprotective agents (Halliwell, 1994; Rice-Evans et al. 1997), or in combination and synergistically with other vitamins to enhance the overall antioxidant capacity of the body (Karatas & Kamish, 2007). A variety of methods have been used to quantify antioxidant activity in foods (Stratil, Klejdus,& Kuban, 2006). DPPH radical scavenging assays are widely used due to their stability, accuracy and reproducibility (Reddy, Sreeramulu & Raghunath, 2010).

Apricot is a climacteric fruit with a very short storage life due, in part, to a high respiration rate and a rapid ripening process. To extend the shelf life of apricot, different preservation methods have been developed including canning, freezing, drying and packing in controlled atmospheres (Jiménez, Martínez-Tomé, Egea, Romojaro, & Muricia, 2008). 40-45% of the total world apricot production is processed (Madrau, Piscopo, Sanguinetti, Del Caro, Poiana, Romeo, & Piga, 2009). Nowadays, there is an increasing demand for dried apricots in several parts of the world, such as the USA, the UK, Germany and Australia, thanks to the fact that it is known to be beneficial for human health, it holds an important position in world trade. As both the variety of apricot and where it has been cultivated are important parameters that influence the nutrient and mineral contents, some variety of apricots are especially suitable for drying to give high vitamin and mineral-rich products (Belloso & Barriobero, 2001).

The most commonly used method of drying apricots is sun drying, which requires little capital, simple equipment and low energy input (El Halouat and Labuza, 1987). To prevent both enzymatic and non-enzymatic browning, quality loss and microbial activity during drying and storage and to facilitate the drying process, sulphiting at low concentration is the most commonly used pre-treatment (Karabulut, Topcu, Duran, Turan, & Ozturk, 2007; Lewicki, 2006; Miranda, Berna, Salazar, & Mulet, 2009; Rossello, Canellas, Santiesteban, & Mulet, 1993;). The sun drying of sulphured fruit makes it possible to obtain apricots of an intense orange colour, translucent appearance and very good gumminess (El Halouat & Labuza, 1987). However, particular attention should be paid to two aspects: i) the process is slow, dependent on the weather conditions and the fruit is exposed to the open air when sun dried, which may lead to an unhygienic and inferior quality product, and; ii) due to any allergic reactions that high concentrations of sulphites may cause, there is an increasing demand for sulphur-free dried apricots. Though solar energy can also be used in a cabinet/tunnel drier, shortening the process time and giving a better quality product

under hygienic conditions (Singh, Paul, & Thapar, 1990), other techniques, such as hot air drying, microwave drying or its combination, may be efficient alternatives with even shorter processing times and, consequently, less impact on the nutritional value of the apricot (Karatas & Kamişli, 2007; Karabulut, et al., 2007; Mir, Hussain, Fouzia, & Rather., 2009). There is scarcely any data on alternative methods of drying apricot halves and their effect both on the kinetics and on a wide spectra of bioactive compounds and their relationship with the product's antioxidant activity. For this reason, this paper aims to evaluate the effect of using alternative methods to sun drying (hot air, microwave energy and a microwave energy-hot air combination) on the antioxidant capacity, the main organic acids, ascorbic acid, vitamin C, the main single polyphenols and the total phenol content of apricot.

2. Materials and methods

2.1. Raw material

Apricots (*Prunus armeniaca* L., Rojo de Carlet variety) were harvested in a patch located in Quatretonda, Valencia (Spain). To provide fruits with a uniform maturity, size and colour and with a firm texture, they were harvested the same day. The fruits were sorted to remove over-ripe and bruised fruits. After sorting, apricots were frozen at -18ºC until subsequent processing and analyses.

2.2. Treatments

Apricots were peeled, cut into halves, pitted and dipped in a sodium meta-bisulphite solution (1.5 g/L) for 1 h, drained and then dried either by using air drying at 40 and 60 ºC (HAD 40 and HAD 60 samples, respectively), microwave drying (MW, 100 W incident microwave power) or hot air-microwave combined drying (HAD-MW, 40ºC, 100 W until 40% water content was reached and 40ºC afterwards until the end of the drying process). HAD 40, HAD-MW and MW samples were obtained in a microwave (model

5141 AFW2, Moulinex, France) where hot air and microwave energy can be used independently or combined. In this case, the round-trip upward movement of air was considered. For 60ºC drying, a five perforated tray dehydrator with perpendicular upward circulation of air (model BY-FD600, Back To Basics, Zhejiang, China (Mainland)) was used. In each experiment around 120-150 g of apricot were used. All the samples were dried to 20-25 g water/100 g dried sample (as applied in commercial applications), which was controlled through the continuous control of the sample weight (recorded at 5 min interval) and taking the initial water content into account. Drying experiments were carried out in triplicate.

2.3. Analytical determinations

All the analyses described in this section were performed in triplicate. The results are expressed as the mean value with the standard deviation in bracket. Except for water content, ºBrix and water activity determination, dried apricots were rehydrated in water for 24 hours prior to analysis, while fresh samples were directly analyzed.

2.3.1. Water content

Water content was analysed by vacuum drying at 60 ºC until constant weight (AOAC, 1990).

2.3.2. Soluble solids

Total soluble solids were estimated as ºBrix using a refractometer (Abbe Atago 89553 by Zeiss, Japan) at 20 ºC.

2.3.3. Water activity

The water activity was determined at 25ºC by using a dew point hygrometer (GBX model FA-st, Bourg de Peage, France; 0.003 accuracy), after calibration with a K_2SO4 saturated solution (a_w=0.972).

142 *2.3.4. Organic acids*

143 HPLC (Jasco, Italy) was applied to the quantitative determination of citric (CA), malic
144 (MA) and tartaric acid (TA), according to Cen, Bao, He, & Sun. (2007). Samples were
145 centrifuged at 2,630 x g for 15 min and filtered by 0.22 μm membrane. HPLC method
146 and instrumentation was: Ultrabase-C18, 5 μm (4.6x250 mm) column (Spain); mobile
147 phase 0.01mol/L potassium dihydrogen phosphate solution, volume injection 20 μL,
148 flow rate 1mL/min, detection at 215 nm and at 25 ºC. Standard curves of each
149 reference acid (Panreac, Spain) were used to quantify.

150

151 *2.3.5. Ascorbic acid and total vitamin C*

152 Ascorbic acid (AA) and total vitamin C (ascorbic acid + dehydroascorbic acid) were
153 determined by HPLC (Jasco, Italy). To determine the ascorbic acid (Xu, Liu, Chen, Ye,
154 Ma & Shi, 2008), samples were homogenated and the mixture was centrifuged
155 (Selecta Medifriger-BL) at 2,630 x g for 10 min at 4 ºC. A 1 mL supernatant aliquot was
156 extracted with 9 mL 0.1% oxalic acid for 3 min. Then, the sample was immediately
157 filtered through a 0.45 μm membrane filter before injection. The procedure employed to
158 determine total vitamin C was the reduction of dehydroascorbic acid to ascorbic acid,
159 using DL-dithiothreitol as the reductant reagent (Sanchez-Mata, Cámara-Hurtado,
160 Diez-Marques, & Torija-Isasa, 2000; Sánchez-Moreno, Plaza, De Ancos & Cano,
161 2003). A 0.5 mL aliquot sample was taken to react with 2 mL of a 20 g/L dithiothreitol
162 solution for 2 h at room temperature and in darkness. Afterwards, the same procedure
163 as that used for the ascorbic acid method was performed. The HPLC method and
164 instrumentation was: Ultrabase-C18, 5 μm (4.6x250 mm) column (Spain); mobile phase
165 0.1 % oxalic acid, volume injection 20 μL, flow rate 1mL/min, detection at 243 nm and
166 at 25 ºC. AA standard solution (Panreac, Spain) was prepared.

167

168 *2.3.6. Phenolic composition*

169 The extraction of polyphenols (Tomás-Barberán, Gil, Cremin, Waterhouse Hess-Pierce
170 & Kader, 2001) consisted of homogenizing 35 g of the homogenate sample (T25 Janke
171 and Kunkel turrax) for 5 min with 40 mL of methanol, 10 mL of bidistilled water and NaF
172 to inactivate polyphenol oxidases and prevent phenolic degradation. The homogenate
173 was centrifuged (2,630 x g, 10 min, 4 ºC) to obtain the supernatant which was filtered
174 by 0,45 µm membrane filter. The HPLC (Jasco, Italy) method and instrumentation was:
175 Ultrabase-C18, 5 µm (4.6x250 mm) column (Spain); the mobile phase was made up of
176 of (A) methanol and (B) water and a linear gradient elution was performed starting at
177 30:70 to reach 100:0 at 70 min, volume injection 25 µL, flow rate 1mL/min.
178 Chromatograms were recorded at 286, 276 and 254 nm and at 25 ºC. Standard curves
179 of each reference phenolic acid (gallic, caffeic and chlorogenic acid) and flavonoids
180 (catechin, epicatechin and kaempferol) (Extrasyntesis, France) were used to quantify
181 the polyphenols. Naphthalene was used as internal standard (Peiró, 2007).
182
183 *2.3.7. Total phenols*
184 Total phenols (TP) were analysed by using the method reported by Selvendran &
185 Ryden (1990) and Benzie & Strain (1999) based on the Folin-Ciocalteu method, which
186 involves the reduction of the reagent by phenolic compounds with the concomitant
187 formation of a blue complex. The extraction procedure was the same as described in
188 section 2.3.6 for individual phenolic compound. 15 mL of distilled water and 1.25 mL of
189 Folin CIocalteu reagent (Sigma-Aldrich, Germany) were added to 25 µL of the extract.
190 The samples were mixed and allowed to stand for 8 min in darkness before 3.75 mL of
191 7.5 % sodium carbonate aqueous solution was added. Water was added to adjust the
192 final volume to 25 mL. Samples were allowed to stand for 2 h at room temperature
193 before absorbance was measured at 765 nm in a UV-visible spectrophotometer
194 (Thermo Electron Corporation, USA). The total phenolic content was expressed as mg
195 of gallic acid equivalents (GAE) (Sigma-Aldrich, Germany) per g of sample.
196

197 *2.3.8. Antioxidant capacity*

198 Antioxidant capacity was assessed using the free radical scavenging activity of the
199 samples evaluated with the stable radical DPPH•, as described by Puupponen,
200 Hakkinen, Aarni, Suortti, Lampi, Eurola, Piironen, Nuutila, & Oksman-Caldentey (2003).
201 Briefly, apricot samples were homogenized and centrifuged (Selecta Medifriger-BL) at
202 2,630 x g for 10 min at 4 ºC. 0.1 ml of supernatant diluted in methanol was added to
203 3.9 ml of DPPH• (0.030 g/L, Sigma-Aldrich, Germany) in methanol. A Thermo Electron
204 Corporation spectrophotometer (USA) was used to measure the absorbance at 515 nm
205 at 0.25 min intervals until the reaction reached a plateau (time at the steady state). The
206 changes in absorbance were measured at 25 ºC. Appropriately diluted samples were
207 used on the day of preparation. The percentage of DPPH• (%DPPH•) was calculated
208 by means of equation (1):

209 $$\%DPPH\bullet = \frac{(A_{control} - A_{sample})}{A_{control}} \quad (1)$$

210

211 where $A_{control}$ is the absorbance of the control (initial time) and A_{sample} the absorbance of
212 the sample (time at the steady state).

213

214 *2.3.9. Statistical analysis*

215 Significant differences between treatments and storage time ($p<0.05$) were studied by
216 means of the analysis of variance (ANOVA). The correlation between antioxidant
217 activity and all the studied components with a 95 % significance level was analysed. All
218 statistical analyses were performed using Statgraphics Plus 5.1 (Statgraphics Plus 5.1,
219 for Windows, 2000).

220

221 **3. Results and discussion**

The mean fresh apricot physicochemical characteristics were: water content (X_w) 0.870 (0.010) g/g sample (6.7 (0.6) g/g dry mass), soluble solid content (X_s) 0.12 (0.02) g/g sample (0.923 (0.013) g/g dry mass) and water activity (a_w) 0.977 (0.003). After drying, apricot samples presented X_w of 0.329 (0.002) g/g dry mass, X_s of 0.719 (0.05) g/g dry sample and a_w of 0.786 (0.005). The water activity values were above the threshold for microbial growth, but since the sugar content is high, an increase in microbes is unlikely.

3.1. Drying kinetics

Fig. 1 shows an example of the drying rate curves obtained from the different process conditions. The drying rate was calculated as $\Delta X_w/\Delta t$, considering the decrease in the apricot`s moisture content (ΔX_w) at each drying time related to the previous control (Δt). From an examination of these curves, it is evident that kinetic behaviour was dependent on the drying method. In HAD samples, the drying rate falls continuously as the moisture rate decreases (X_w/X_{wo} in Fig.1), showing that diffusion is the dominant physical mechanism governing the movement of moisture in the apricot halves (Chemkhi & Zagrouba, 2005; Doymaz, 2004; Karathanos & Belessiotis, 1997; Riva et al., 2005). Hence, mass transfer is governed both by intrinsic product properties and the internal resistance to water diffusion (Mulet, 1994). Different authors obtained similar results when working on the hot air drying of whole apricots (Doymaz, 2004; Toğrul & Pehlivan, 2003). However, the drying rate remained constant when microwaves were applied (MW treatment, Fig. 1), revealing that the evaporation of water to the product-air interface seems to take place at a similar rate to water diffusion from the product's interior to its surface. It is known that the volumetric, internal and fast heating caused by microwaves implies a water phase transition from a liquid to gaseous state inside the product (Constant & Moyne, 1996). This vapour partial pressure gradient could act as an additional driving force to the water diffusion and, consequently, similar rates to those of surface evaporation could be reached. In the

250 case of HAD-MW, drying rate curves had a first period where the drying velocity was
251 close to constant (similar behaviour to MW dried apricot halves but with higher drying
252 rates), followed by a second falling drying rate period (similar behaviour to HAD
253 treatments). Initial constant period starts from the initial moisture content and ends at
254 the moisture content of approximately 1.87 kg water per kg dry mass (in Fig. 1
255 corresponds to a reduced water content, X_w/X_{wo} of 0.28). This pattern reveals that, in
256 the first step, microwaves play a relevant role while hot air facilitates the removal of the
257 evaporated water from the fruit surface, leading to higher drying rates when compared
258 to those obtained using the MW treatment.
259 Some semi-theoretical drying models that have been widely used to describe falling
260 drying rates in the literature are the Newton, the Henderson and Pabis, the
261 Logarithmic, and the Page models. These models are generally derived by simplifying
262 general series solutions of Fick's second law and considering a direct relationship
263 between the average water content and the drying time (Doymaz, 2004). They neglect
264 the fundamentals of the drying process and their parameters have no physical meaning
265 (Simal, Femenia, Garau, & Rossello, 2005). Despite this, Page's model (Page, 1949)
266 has been used to describe the drying kinetics of various agricultural materials such as
267 grapes, plums, apricots, strawberry, apple, kiwi, figs and currants in convective and
268 microwave-convective drying (Bozkir, 2006; Contreras, Martin-Esparza, Chiralt, &
269 Martínez-Navarrete, 2008; Doymaz & Pala, 2002; Jasna, Sander & Skansi, 2001;
270 Karathanos & Belessiotis, 1999; Prabhanjan, Ramaswamy & Raghavan, 1995; Sharma
271 & Prasad, 2001; Simal, Femenia, Garau, & Rossello, 2005).
272 By considering the different patterns for the obtained drying rate curves of HAD, MW
273 and HAD-MW drying treatments, the semi-empirical Page equation (Eq.(2)) was used
274 to reproduce the falling drying rate periods observed in HAD (the entire process) and
275 HAD–MW (second period) treatments while the constant drying rate period (occurring
276 in MW and first period of HAD–MW treatments) was fitted to a simple linear equation
277 (Eq. (3)), as described by Contreras et al. (2008). When fitting Page's equation to the

second period of combined drying, the critical water content (X_w^c), at which the drying rate values change from constant to decreasing, was considered as the initial water content and the corresponding time was recalculated as ($t-t_c$), t_c being the critical time at which the critical water content was reached.

$$\frac{(X_w^t - X_w^e)}{(X_w^o - X_w^e)} = \exp(-k * t^n) \quad (2)$$

$$X_w^t = X_w^o - a * t \quad (3)$$

where X_w^t, X_w^e and X_w^o are the water content (dry basis) at any time, in thermodynamic equilibrium with the surrounding medium and at the initial time, respectively; and *a* and *k* are the corresponding constants of drying kinetics (h^{-1}) and *n* is the dimensionless drying exponent which moderates the time thus improving moisture loss prediction (Azzouz, Guisan, Jomaa, & Belghith, 2002). As in the drying experiments carried out in this work, the values of the equilibrium water content are expected to be much smaller than X_w^o, X_w^e may be assumed to be zero. Non-linear regression (Statgraphics Plus 5.1. for Windows, 2000) was used to obtain *k* and *n* parameters.

The model constants obtained for each period (a, k and n) are listed in Table 1 as the average values for all the experiments. Both the critical water content and critical drying time for the HAD-MW sample and the drying times necessary to achieve the desired final water content in the apricot halves are also shown in Table 1. The obtained kinetic parameters were related to the process variables by statistical analysis. During convective drying, Page's drying constant k was not significantly affected ($p>0.05$) when applying the highest air temperature. In fact, despite the shortest drying time was obtained at 60ºC, the difference compared to drying at 40 ºC was not significant ($p>0.05$).

The time required to obtain the desired final water content was greatly reduced when applying microwave energy, either alone or combined with hot air. The existence of a constant-rate period and the fact that the k values obtained for the falling-rate period

304 are higher when compared to those of convective drying, support these results. The
305 highest drying rate was obtained for HAD-MW treatments (constant-rate period).
306 The precision of the fit between the experimental data and the predicted values was
307 evaluated using the coefficient of determination (r^2) and the root mean square deviation
308 (Sopade et al., 1992), described by Eq. 4, the higher the r^2 value and the lower the
309 RMSD value, the better the fit (Doymaz, 2004). The obtained values are shown in
310 Table 1. The best fit was obtained for HAD-MW treatments.

311 $$RMSD = \frac{1}{n}\sqrt{\sum_{i=1}^{n}(X_{w,exp,i} - X_{w,pre,i})^2} \quad (4)$$

312 where $X_{w,exp,i}$ and $X_{w,pre,i}$ are the experimental and predicted water contents at each
313 control time, respectively, and n is the number of observations. The consistency of the
314 fit is illustrated in Fig. 2, where it is possible to observe the close agreement between
315 the experimental and predicted data for every drying condition. Therefore, the
316 proposed equations can be considered adequate to predict the drying curves and
317 drying times for the hot air (40 and 60ºC), microwave (100 W) and combined air-
318 microwave (40ºC-100 W) drying of apricot halves. This may be very useful for the
319 optimization of the drying conditions and the further design of industrial dryers.
320
321 3.2. Effect of drying treatment on the functional compounds of dried apricot
322 In order to compare the phytochemical composition of frozen and dehydrated apricot,
323 the results of the dried samples have been referred to the corresponding frozen sample
324 used in the drying process. Fig. 3 shows the organic acid content of frozen and dried
325 apricot. MA was determined to be the predominant organic acid in the Rojo de Carlet
326 apricot variety, coinciding with what the literature has reported for other varieties (Akin,
327 Karabulut, & Topcu., 2008; Versari, Parpinello, Mattioli, & Galassi, 2008). TA content
328 was around 400 mg/100 g, higher than CA. The identification of the quantitative
329 analysis of the major organic acids present in fruits is considered to be of great

importance both for food technology and quality evaluation. These acids not only influence fruit flavour, but also their stability, nutrition, acceptability and keeping quality (Versari et al., 2008). They have been proposed as an index of maturity, ripeness or spoilage in fruits (Hasib, Jaouad, Mahrouz, & Khouili, 2002). In particular, malic and citric acids are correlated to the perception of sourness in peach and apricot (Versari et al., 2008). As can be seen in Fig. 3, the drying treatments led to a significant decrease ($p<0.05$) in MA and TA content, with no significant differences found between the treatments. HAD drying did not affect the CA content, while microwave application implied a significant decrease. A depletion in organic acids in thermally treated fruit and vegetables could be explained by the consumption of these compounds as reactants in the Maillard reactions (Belitz & Grosch, 1997; Nicoli, Anese & Parpinel,1999).

Literature provides no abundant, comparative measures for the AA content of apricot varieties. Its content depends mainly on the ripening stage (Karatas & Kamish, 2007). As regards fresh apricot, other authors reported that the AA value in the Red Carlet variety was 2.8 (0.3) mg/100 g (Kevers, Falkowski, Tabart, Defraigne, Dommes, & Pincemail., 2007), and literature points to low contents of this acid being found in other apricot varieties, too (2-10 mg/100g) (Akin et al., 2008; Munzuroglu, Karatas, & Geckil, 2003). In our case, neither frozen nor dried apricot showed any AA or vitamin C content, which may indicate that frozen storage prior to drying destroyed the low amount of this vitamin present in the frozen fruit. A large amount of literature deals with ascorbic acid degradation as a consequence of freezing (Ibanez 1996; Klimezka & Irzyniec, 1997; Sahari, Boostani & Hamidi, 2004).

The nutritional composition and the phytocompounds present in apricots, such as polyphenols, lead to them being ascribed among the functional foods, as are other fruits, whose dietary intake is becoming more and more indicative of healthy lifestyles (Leccese, Bartolini, & Viti, 2008). The amount of each individual phenolic compound analysed in apricots is presented in Table 2. Chlorogenic acid was the predominant phenolic acid in the apricot under study, as is consistent with the literature consulted

(Dragovic-Uzelac, Levaj, MrvicIC, Bursac & Boras, 2007; Dragovic-Uzelac et al., 2005). Gallic (4.02 mg/100 g) and caffeic (4.4 mg/100g) acids were also found. Other phenolic compounds, flavonols, were present, of which epicatequin and catechin stand out due to their high content (13.9 mg/100g and 8.3 mg / 100g, respectively). It also contains kampferol, but in smaller amounts.

Hot air drying treatments, combined or not with microwave energy, significantly decreased ($p<0.05$) the amount of gallic acid to a greater extent than when only microwave energy was employed. However, all the dried samples showed a significant decrease ($p<0.05$) in caffeic acid with no significant differences among variable treatments. Other authors also observed a decrease in the phenolic acids content during the drying and storage of dried plums, mainly attributed to enzymatic oxidation (Del Caro, Piga, Pinna, Fenu, & Agabbio, 2004). In this sense, many authors have described the rapid degradation of phenolic compounds after being subjected to high temperatures and oxygen, as occurs during drying (Mazza & Miniati, 1993). As regard flavonols, they are not direct substrates of the PPO enzyme, and they are usually more sensitive to temperature, thus tending to decrease more rapidly as the processing temperature rises (Del Caro et al., 2004). In general, the obtained flavonol values were of the same order as those reported by other authors (Garcia-Alonso, De Pascual-Teresa, Santos-Buelga, & Rivas-Gonzalo, 2004). MW significantly increased ($p<0.05$) the epicatequin and catechin content. Moreover, a combination of HAD - MW significantly increased ($p<0.05$) catechin to a greater degree than MW alone, while epicatequin decreased to the same degree as when hot air drying was applied. Every drying method caused the total loss of kampferol. When the sum of the individual phenolic compounds was analyzed, there seems to be an effect of the temperature reached by the sample; the higher the temperature, the greater the total phenolic content. If the air temperature is higher and MW is applied, the samples are heated to a greater extent. This may be related with the fact that, the more they have been heated,

385 the easier it is to extract the phenols from the samples, as other authors have also
386 found for carotenoid compounds in apricot (Karabulut, et al., 2007).
387 Considering that phenolic compounds are potent antioxidants in fruits, the total
388 phenolic content of frozen and dried apricot was further analysed (Table 2). TP of
389 frozen samples were within the range described by other authors for fresh apricots of
390 different Italian varieties (Leccese et al., 2008). Nevertheless, a TP value lower than
391 that corresponding to the sum of the individual phenolic compounds analyzed in frozen
392 apricot was obtained. From this point of view, the Folin method seems to
393 underestimate the total phenolic content. TP values reported in literature for other fruits
394 of the same *Prunus* family were around 9 mg GAE/100g in peaches and nectarines
395 (Akin et al., 2008). In this sense, the apricot can be considered as a fruit with a high
396 total phenol content compared to other fruits of the same botanical family.
397 In general, all the dried samples showed a significant increase ($p<0.05$) in TP content
398 after the drying treatment, ranging from 60 to 81 mg GAE/100 g. MW sample presented
399 the highest content, which may be related with the increase in chlorogenic acid,
400 catequin and epicatequin increase. This increase may be due to the sulphite added for
401 the drying processes. It has been described that this reagent interferes in the Folin
402 method for the determination of total phenols, providing positive error values (Güçlü,
403 Altun, Ozyurek, Karademir, & Apak, 2006).
404 The DPPH scavenging activity of frozen apricot was 2.4% DPPH and it significantly
405 increased for dried apricot, ranging from 3.5 to 3.8 % (Table 2). This increase observed
406 may be explained by the formation during the drying procedures of new compounds
407 with antioxidant activity, such as Maillard reaction products (Del Caro et al., 2004;
408 Nicoli et al.,1999). In addition, sulphite has also been described to interfere in the
409 quantification of the antioxidant capacity in all the analytical methods based on electron
410 transfer, as is the case of DPPH. In this sense, other studies have also observed an
411 increase in the antioxidant capacity of dried apricots, as compared with fresh ones. The
412 authors concluded that this is an indication that apricots had been treated with sulphate

413 during drying (Güçlü et al., 2006; Halvorsen, Holte, & Myhrstad, 2002). For fruits which
414 are relatively poor in vitamin C, significant antioxidant activity is generally thought to
415 arise from flavonoids and phenolic acids (Güçlü et al., 2006). As regards the
416 importance of phenols as antioxidants, it is a result of their ability to provide electrons
417 or hydrogen, with the consequent formation of stable radical intermediates (Belitz &
418 Grosch, 1997). Pearson's statistical correlation analysis was used to establish
419 correlations between the antioxidant capacity and total phenols and individual phenolic
420 compounds. The obtained results showed that the most significant contribution to
421 antioxidant capacity was provided by total phenol content (0.9642, $p<0.05$), followed by
422 caffeic acid (0.9140, $p<0.05$), kaempferol (0.6874, $p<0.05$) and gallic acid (0.6235,
423 $p<0.05$). The results coincide with the references in the literature to fresh and frozen
424 apricot (Jiménez et al., 2008; Karakaya, El & Taç, 2001; Leccesse et al., 2008). The
425 same trend has been observed by other authors working on peaches and plums
426 (Leccese et al., 2008) and grapefruit (Igual, García-Martínez, Camacho, & Martínez-
427 Navarrete, 2010).
428

429 **Conclusion**

430 Page's model satisfactorily fits the experimental drying kinetics data observed in both
431 air drying processes and in the falling rate period of combined drying process and a
432 close agreement was obtained when applying a linear model to microwave drying or to
433 the initial rate observed in combined drying process. Microwave application significantly
434 reduced the drying time. The phenols in the samples were easier to extract when a
435 higher temperature was reached. In this sense, microwave dried samples had the
436 highest phenol content, with particularly high amounts of chlorogenic acid, catequin
437 and epicatequin. Nevertheless, no significant effect was observed on the antioxidant
438 capacity, as the most significant contribution of phenols to antioxidant capacity was
439 provided by caffeic acid, kaempferol and gallic acid. The sulphite added for the drying

processes interferes in both the Folin method for the determination of total phenols and in the quantification of the antioxidant capacity through the DPPH reactive. Taking all these considerations into account, the industrial processing of dried apricots may be improved by using microwave energy, as the drying time is considerably reduced and the obtained fruit had a higher phenolic content while maintaining antioxidant capacity.

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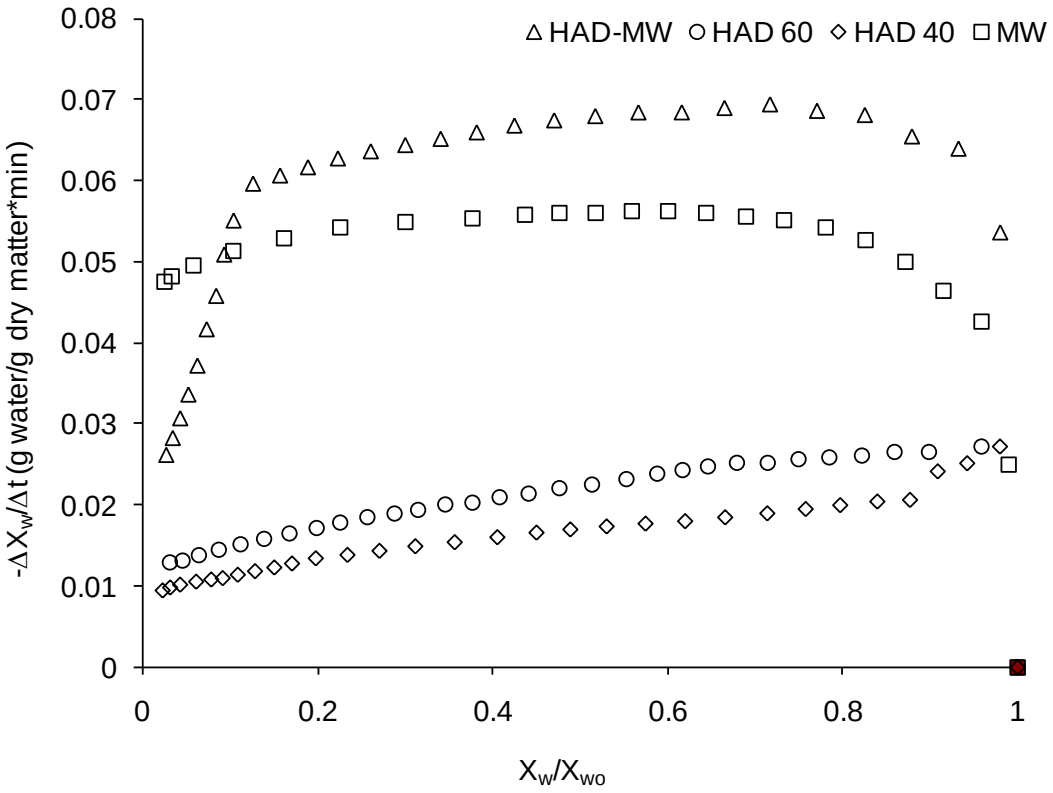

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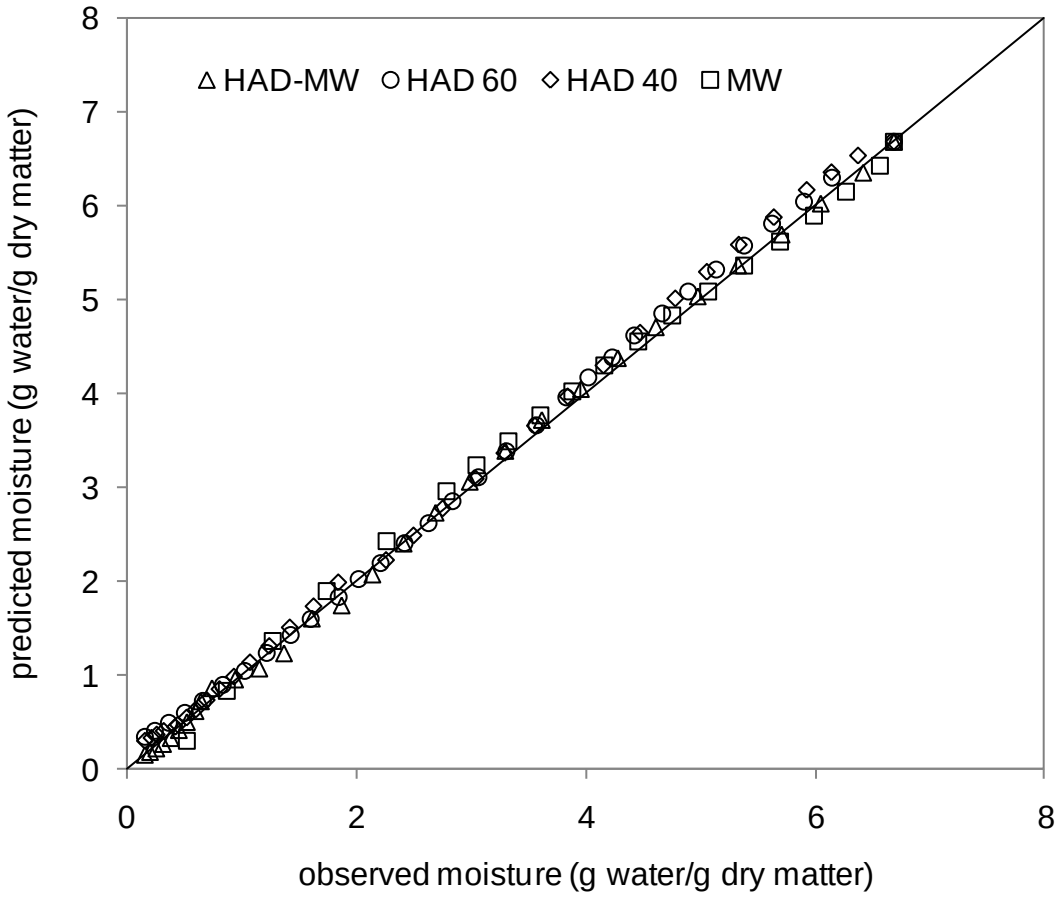
711 Fig. 1. Drying rate vs reduced water content of hot air (HAD), microwave (MW) and

712 combined hot air-microwave (HAD-MW) dried apricots

713



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715 Fig. 2. Experimentally determined and predicted moisture of hot air (HAD), microwave

716 (MW) and combined hot air-microwave (HAD-MW) dried apricots

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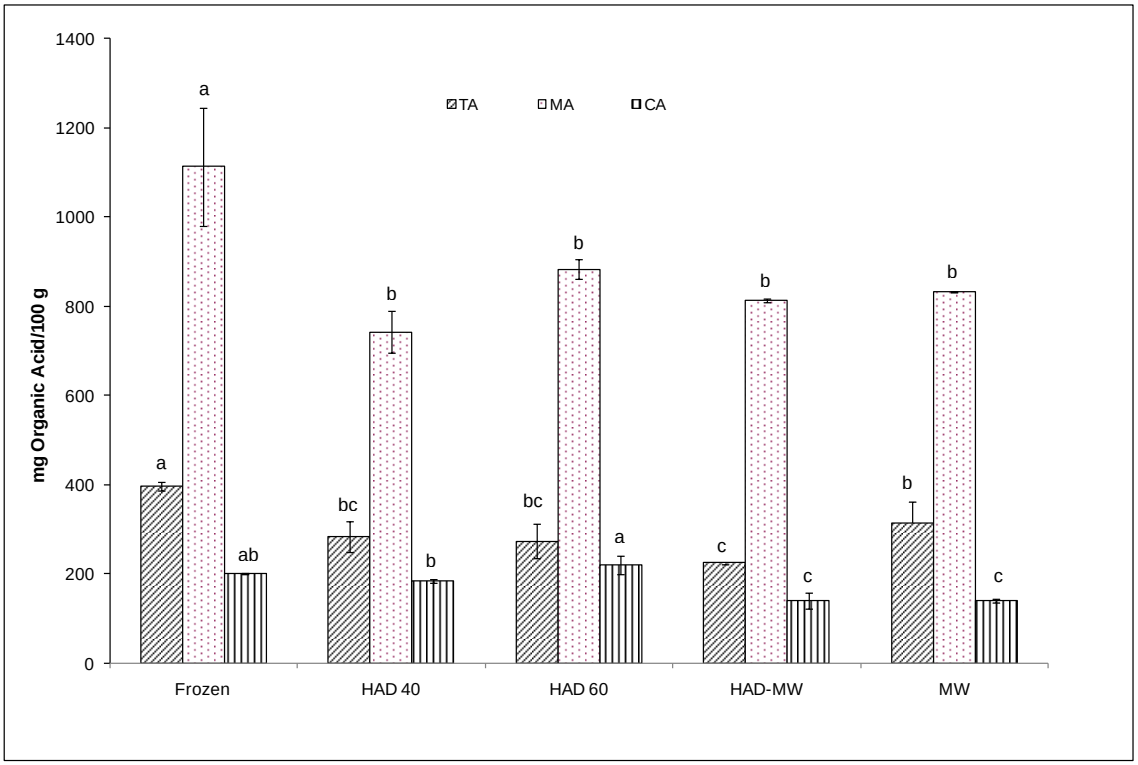
Fig 3. Organic acid content of frozen and dried apricot.



741 **Table 1.** Average values (standard deviation) of the obtained kinetic parameters,
742 critical moisture content and time, final drying time and root mean square deviation of
743 each drying treatment

	Drying treatments			
	HAD 40	HAD 60	HAD-MW	MW
a	-	-	0,067 (0,002)[a]	0,056 (0,003)[b]
k	0,0035 (0,0009)[b]	0,0041 (0,0012)[b]	0,08197 (0,0139)[a]	-
n	1,021 (0,051)[a]	1,031 (0,046)[a]	0,692 (0,076)[b]	-
X_w^c	-	-	1,64 (0,03)	-
t_c	-	-	78,33 (2,89)	-
t_d	10,9 (0,4)[a]	9,08 (0,82)[a]	3,2 (0,4)[c]	2,1 (0,1)[c]
r^2	0,994	0,993	0,999	0,995
RMSD	0,156 (0,08)	0,166 (0,02)	0,006 (0,001)	0,02 (0,005)

744 Within rows, same letters indicate non-significant differences ($p<0.05$)

745 a (min^{-1}): kinetic parameter for constant drying rates (linear model)
746 k (min^{-1}), n: kinetic parameters for falling drying rates (Page's model)
747 X_w^c (g water/g dry matter): critical moisture content
748 t_c (min): critical drying time
749 t_d (h): drying time necessary to reach the final moisture content
750 r^2: coefficient of determination
751 RMSD: root mean square deviation
752

753 **Table 2.** Mean values in mg/100 g frozen fruit (with standard deviation) of individual phenolic
754 compounds, total phenols (mg gallic acid equivalent /100g) and antioxidant capacity (%DPPH)
755 analysed in frozen and dried apricot. The sum of individual phenolic compounds (∑IP) appears
756 also in the table.

757

		Drying treatments			
Compound	Frozen apricot	HAD 40	HAD 60	HAD-MW	MW
Gallic acid	4.02 (0.02)^{a}	1.8(0.7)^{b}	2.4 (0.2)^{b}	2.6(0.5)^{b}	3.7 (0.5)^{ab}
Caffeic acid	4.4 (0.2)^{a}	1.9(0.7)^{b}	2.3 (0.2)^{b}	2.1(0.3)^{b}	1.84 (0.05)^{b}
Chlorogenic acid	4.57 (0.09)^{b}	4(1)^{b}	5.2 (0.3)^{ab}	5.9(0.9)^{ab}	9 (2)^{a}
Catequin	8.3 (0.2)^{c}	0.71(0.12)^{e}	3.4 (0.5)^{d}	13.71(0.03)^{a}	10 (1)^{b}
Epicatequin	13.9 (0.3)^{b}	2.5 (0.7)^{c}	3.9 (0.3)^{c}	4.9 (0.4)^{c}	21 (3)^{a}
Kaempherol	0.56 (0.04)^{a}	0^{b}	0^{b}	0^{b}	0^{b}
∑IP	35.75	10.91	17.20	29.21	45.54
Total phenols	16.6 (0.2)^{c}	64.73(0.06)^{b}	64.9 (0.6)^{b}	60(3)^{b}	81 (2)^{a}
% DPPH	2.4 (0.3)^{b}	3.8 (0.2)^{a}	3.7 (0.2)^{a}	3.7 (0.2)^{a}	3.5 (0.3)^{a}

758 In rows, different letters denote significant differences ($p<0.05$)

759

760