

# Effect of a physical pre-treatment on drying kinetics and phenolic compounds in goji berries (*Lycium barbarum* L.)

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## Abstract

This work investigated the effect of a physical pretreatment on the Goji properties (drying kinetics, phenols) after drying. The pretreatment is based on the peel abrasion for the removal of the wax outer peel layer, which creates a barrier to the movement of moisture across the membrane. The drying kinetics were modeled by a Fick’s diffusion model in cylindrical coordinates. Model results showed the pretreatment is able to increase the effective diffusion coefficient of 2-3 times with respect to untreated gojis by decreasing the resistance to the moisture transport.

Moreover the shorter exposure time to high temperatures and to oxygen better preserve the phenolic content of the fruits, especially at 50 and 60 C.

## Keywords

goji berry, drying, pretreatment, phenols, mathematical model

## 1. INTRODUCTION

Goji berries, also known as wolfberries, are orange-red ovoid fruits of *Lycium barbarum* or *L. chinense* and belong to the *solanaceae* family (Kosin´ska-Cagnazzo et al., 2017a). These fruits have long been used in traditional Chinese medicine as anti-hypertension and anti-fatigue agents; moreover, they are believed to protect hepatic function and to be an effective remedy for the treatment of eye problems, skin rashes and diabetes (Kosin´ska-Cagnazzo et al., 2017b).

35 Since 2005, goji consumption have increased rapidly because these berries are viewed as functional  
36 food (Potterat, 2010; Rosa et al., 2017), or as an ‘exotic superfood’ by nutritionists (Rosa et al., 2017;  
37 Hummer et al., 2012). Through specialized health product stores, *L. barbarum* has entered the health  
38 food market with a total export of US\$ 120 million from China (Donno et al., 2016)

39 Researchers, consumers and food companies are taking more of an interest in goji berries because  
40 they are rich antioxidant components such as carotenoids and polyphenols, (Ignat et al., 2011),  
41 recognized as beneficial to prevent and treat several diseases (Szajdek & Borowska, 2008). In goji  
42 berries, the main phenols are phenolic acids and flavonoids (Szajdek & Borowska, 2008).

43 In recent years the cultivation of goji berries in Europe was due to the growing interest of the  
44 consumers for these berries, as well as alarming reports on the content of pesticides in fruits  
45 originating from China (Kosin´ska-Cagnazzo et al., 2017b; Hacker et al., 2010). The cultivation of  
46 goji berries in Romania (Mocan et al., 2014), Bulgaria (Dzhugalov et al., 2015), Spain and Italy  
47 (Donno et al. 2016; Fratianni et al., 2018) is reported in literature.

48 Since fresh goji berries have short shelf life, owing essentially to fungal decay (Mocan et al., 2014),  
49 they are mainly present on the European market as dry berries, especially originating from Ningxia  
50 province in China (Kosin´ska-Cagnazzo et al., 2017a). Dried berries are consumed as a snack or can  
51 be used for the production of functional food: in confectionary goods or in bakery products and soups  
52 (Hummer at al., 2012; Gao et al., 2008). To reduce water activity of fresh berries and prolong their  
53 shelf life, the most common preservation is the drying (Brasiello et al, 2011).

54 Traditionally, goji berries are harvested in late summer to autumn. After this operation, firstly, the  
55 berries are dried without sunlight until the skin shrinks, and then they are dried in the sun until the  
56 outer skin becomes hard but the pulp is still soft (Adiletta et al., 2015).

57 Goji drying is difficult because this berry contains a wax outer peel layer, which creates a barrier to  
58 the movement of moisture across the membrane. For this reason, the long exposure to high  
59 temperatures may reduce the nutritional value of the fruit (Adiletta et al., 2015). Different dipping  
60 techniques were applied to overcome this problem.

61 Wu et al. (2015) investigated the drying characteristics and quality of *Lycium barbarum* with a pre-  
62 treatment using 3% alkali. Li et al. (2014) evaluated the effect of dipping with sodium carbonate and  
63 sodium sulfite solution on the content of total flavonoid in sun-dried, hot-air-dried and freeze-dried  
64 goji. However, the chemical additive residue in the samples gives rise to food safety problems. Beside  
65 chemical pretreatment, some physical pre-treatments have also been developed for grapes (Adiletta  
66 et al., 2016) and plums (Cinquanta et al., 2002) to reduce drying time and preserve the quality of final  
67 products. In a previous paper, the effect of a physical pre-treatment on colour and carotenoids changes  
68 in dried goji, were studied (Fratianni et al., 2018).

The aim of this work is to study the effect of a peel abrasion, to remove the waxy layer from the fruit before drying, on drying kinetics at different temperatures and on phenolic compounds of dried goji berry (*Lycium barbarum* L.).

## 2. MATERIALS AND METHODS

### 2.1 Raw material

Italian fresh organic goji berries (*Lycium Barbarum* L.) were kindly provided by South Italy farmers joined in the "LYKION" organization. In order to use uniform samples, goji berries with the same size (length  $h=14.85 \pm 0.56$  mm and average radius  $r=8.07 \pm 1.10$  and weight  $0.91 \pm 0.07$  g) and without surface damage were chosen. The initial water content of samples was:  $3.36 \pm 0.10$  g /g (db), measured according to AOAC standards (1990).

Two different types of samples were compared in this study: untreated goji (UTR) and abraded goji (TR). Before drying, some of the samples (TR) were subjected to a physical abrasive pretreatment. A motorized rotating drum was used for the goji peel abrasion, as reported elsewhere (Adiletta et al., 2015).

### 2.2 Drying experiments

In a convective dryer (B80 FCV/E6L3, Termaks, Norway) the drying experiments on UTR and TR samples were carried out at 50, 60 and 70 °C with an air velocity at 2.1 m/s.

The weight of nine samples was continuously recorded using a weight sensor (Phidgets INC., Canada): a transducer that converts mechanical force into electrical signals. Moisture ratio ( $M_t/M_0$ ) was calculated as the ratio between the actual ( $M_t$ ) and the initial ( $M_0$ ) moisture content on dry basis. Goji samples were dried up to a final moisture value of  $0.03 \pm 0.02$  g /g (db) using different air temperatures (50, 60 and 70 °C). All drying experiments were carried out in triplicate.

### 2.3 Mathematical model

A diffusion model is developed to describe the drying process of goji berries. A three-dimensional model of mass transfer that assumes fruits as an isotropic, homogenous and continuous solid phase was adopted. In this model, an isothermal condition was considered since in drying conditions here analyzed, the characteristic time of thermal transient was far less than that of mass transport.

Goji berries shape can be approximated to that of a cylinder, so that the equation that describes the mass diffusion phenomenon (i.e. water during drying) in cylindrical coordinates was adopted:

$$\frac{\partial M}{\partial t} = \frac{1}{r} \left\{ \frac{\partial}{\partial r} \left( r D_{\text{eff}} \frac{\partial M}{\partial r} \right) + \frac{\partial}{\partial z} \left( r D_{\text{eff}} \frac{\partial M}{\partial z} \right) \right\} \quad (1)$$

102 where  $D_{\text{eff}}$  is the diffusion coefficient ( $\text{m}^2/\text{s}$ ) and  $M$  is the moisture content on a dry basis ( $\text{kg}/\text{kg}_{\text{d.b.}}$ ).

103 The initial condition is:

$$104 \quad M(r, z, t=0) = M_0 \quad \text{for } 0 < r < R_0, \quad 0 < z < h \quad (2)$$

105 The boundary conditions are:

$$106 \quad \frac{\partial M(r=0, z, t)}{\partial r} = \frac{\partial M(r, z=0, t)}{\partial z} = 0 \quad \text{for } t > 0 \quad (3)$$

107 and at  $r=R_0, z=h$  and for  $t>0$

$$108 \quad -D_{\text{eff}} \rho_s \frac{\partial M}{\partial r} = h_m \rho_s (M_{\text{sur}} - M_e) \quad (4)$$

$$109 \quad -D_{\text{eff}} \rho_s \frac{\partial M}{\partial z} = h_m \rho_s (M_{\text{sur}} - M_e) \quad (5)$$

110  $\rho_s$  is the solid density ( $\text{kg}/\text{m}^3$ ) and it is kept constant;  $h_m$  is the moisture transfer coefficient ( $\text{m}/\text{s}$ );

111  $M_{\text{sur}}$  is the moisture at the surface of the cylinder and  $M_e$  is the equilibrium moisture content  
 112 ( $\text{kg}/\text{kg}_{\text{d.b.}}$ ) (i.e. the moisture content necessary to maintain equilibrium with the surrounding  
 113 atmosphere).

114 Introducing the following dimensionless variables:

$$115 \quad \bar{r} = \frac{r}{R_0}, \quad \bar{z} = \frac{z}{R_0} \quad \text{and} \quad \bar{M} = \frac{M}{M_0} \quad \bar{M}_e = \frac{M_e}{M_0} \quad (6)$$

116 the equation (1) becomes:

$$117 \quad \frac{\partial \bar{M}}{\partial \tau} = \left( \frac{\partial^2 \bar{M}}{\partial \bar{r}^2} \right) + \left( \frac{\partial^2 \bar{M}}{\partial \bar{z}^2} \right) \quad (7)$$

118 where  $\tau$  is the dimensionless time  $\tau = \frac{t \cdot D_{\text{eff}}}{R_1^2}$

119 Furthermore, the initial and boundary conditions become:

$$\bar{M}(\bar{r}, \bar{z}, \tau = 0) = 1 \text{ for } 0 < \bar{r} < 1, 0 < \bar{z} < \frac{h}{R} \quad (8)$$

$$\frac{\partial \bar{M}(\bar{r} = 0, \bar{z}, \tau)}{\partial \bar{r}} = \frac{\partial \bar{M}(\bar{r}, \bar{z} = 0, \tau)}{\partial \bar{z}} = 0 \text{ for } \tau > 0 \quad (9)$$

$$\text{and at } \bar{r} = 1, \bar{z} = \frac{z}{R}, \text{ for } \tau > 0$$

$$\frac{\partial \bar{M}}{\partial \bar{r}} = -Sh(\bar{M}_{\text{sur}} - \bar{M}_e) \quad (10)$$

$$\frac{\partial \bar{M}}{\partial \bar{z}} = -Sh(\bar{M}_{\text{sur}} - \bar{M}_e) \quad (11)$$

The convective mass transfer coefficient and the effective diffusion coefficient are correlated with the dimensionless Sherwood number:

$$Sh = \frac{h_m \cdot R_0}{D_{\text{eff}}} \quad (12)$$

where  $R_0$  is the radius of the sample (m). It represents the ratio of the convective mass transfer to the rate of diffusive mass transport.

In order to determinate the optimum value of the  $D_{\text{eff}}$ , the coefficient of determination of the fit ( $R^2$ ), the reduced  $\chi$ -square of the fit ( $\chi^2$ ) and the root mean square error of the fit (RMSE) were used as targets.

The finite element method is applied to solve the non-linear partial differential equations (Eq. 7) subjected to the initial and boundary conditions (Eq. 8-11). Simulations were run adopting 4974 cells and 7877 nodes. The convergence criterion assumed at each node of the computational domain was  $|\bar{M}_k - \bar{M}_{k-1}| \ll 10^{-8}$  (where  $k$  represents the  $k$ -th iteration).

137

## 138 2.4 Titrable Acidity, pH, Aw

139 The pH measurements were obtained at 20°C using a pH meter (Model 2001, Crison, Barcelona,  
140 Spain). Total titrable acidity (g of malic acid /100g db) was determined by an alkaline solution (0.1M  
141 sodium hydroxide) to the end point at pH 8.1 (AOAC, 1990). The water activity ( $A_w$ ) was determined  
142 using a water activity meter (Testo 650, Testo Inc., USA) at 25 °C.

143

## 144 2.5 Phenolic compounds

145 The separation and identification of polyphenol compounds in goji extracts was performed by HPLC,  
146 (Agilent 1100 chromatograph, Santa Clara, USA) with a RP-Amide column (5  $\mu\text{m} \times 150 \text{ mm} \times 4.6$

mm) (Phenomenex, Torrance, USA). The mobile phase was water-acetic acid (98.6:1.4 v/v) (solvent A) and acetonitrile-acetic acid (98.6:1.4 v/v) (solvent B) with a flow rate of 1.0 ml/min. The solvent gradient was as follows: 4% B keeping isocratic condition during 10 min, reaching 63% B at 37 min, 100% B at 39 min, 4% B after 55 min. was used. The sample injection volume was 20 µl and the wavelengths used for the quantification of the goji extracts with the diode detector were 280 and 350 nm. Prior to HPLC injection samples and mobile phases were filtered through a 0.45 µm Millipore filter. Each sample was analysed in triplicate.

## 2.6 Antioxidant activity

The free radical scavenging capability of the extracts was determined using the stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay (Albanese et al., 2014; Adiletta et al., 2017). The extracts for analysis were those used previously for quantification of polyphenols.

Goji extracts in different concentrations were added to 6 x 10<sup>-5</sup>M methanol solution of DPPH. The mixture was shaken vigorously and, after 30 min of incubation at room temperature in the dark., the absorbance of remaining DPPH was recorded at 517 nm by a Perkin–Elmer lambda-Bio 40 (PerkinElmer Inc., Waltham, MA, USA). The absorbance of DPPH without antioxidant (control sample) was used for baseline measurements.

The free radical scavenging activity (AA) was calculated using the following equation:

$$\% \text{ inhibition of DPPH} = [(A_{\text{blank}} - A_{\text{sample}}) / A_{\text{blank}}] * 100 \quad (13)$$

where A<sub>blank</sub> is the absorbance of the control at t = 0 min and A<sub>sample</sub> is the absorbance of sample after 30 min. The free radical scavenging activity (AA) was expressed as the EC<sub>50</sub> value, which was defined as the mg of the extract sample concentration necessary to inhibit the initial DPPH radical activity by 50% during a 30-min incubation. The lower the EC<sub>50</sub>, the higher the antioxidant activity.

## 2.7 Statistical analysis

The means and standard deviations of experimental results were calculated from three replicates.

Statistical analyses were performed by one-way ANOVA (P< 0.05) followed by a Tukey test.

The tests were considered as significant with p values of less than 0.05

Principal component analysis (PCA) was applied to identify the principal components contributing to the majority of the variation within the main physicochemical properties of all goji samples. All analyses were performed using the SPSS software package, Version 20.0 (SPSS Inc., Chicago, IL, USA).

### 179 3 RESULTS AND DISCUSSION

#### 180 3.1 Drying kinetics and mathematical model

181 The same water content (about  $0.03 \pm 0.02$  g /g (db)) was obtained by the drying process at the  
182 following times: 45, 21 and 12 h at the air drying temperatures of 50, 60 and 70 °C, respectively, for  
183 the UTR samples. Corresponding values for the TR samples were 22, 15 and 5 h at the same respective  
184 temperatures.

185 Results of the model in cylindrical coordinates (equations 7-11) were compared with experimental  
186 data in terms of moisture ratio in figure 1 for the untreated samples, and in figure 2 for treated samples  
187 at the temperatures considered in this work (50-70°C).

188 **Figure 1**

189 **Figure 2**

190

191 The results showed that developed model in cylindrical coordinates is able to describe the  
192 experimental drying kinetics at 60 and 70 °C, but not those at 50 °C, especially for the untreated  
193 samples.

194 This behaviour is probably due to the fact that the model did not take into account the reduction of  
195 the volume of goji berries during drying. A better description of the experimental data could be  
196 obtained including the shrinkage effect on the drying kinetic in the model.

197 Table 1 reports the values of the  $D_{eff}$  estimated by the model and the corresponding values of fitting  
198 parameters.

199 **Table 1**

200

201 The value of the effective diffusion coefficient estimated by the model ranged from  $0.75 \cdot 10^{-8}$  to  
202  $4.20 \cdot 10^{-8}$  m<sup>2</sup>/s in the range of temperature 50-70 °C for untreated samples and from  $2.50 \cdot 10^{-8}$  to  
203  $1.20 \cdot 10^{-8}$  m<sup>2</sup>/s for TR samples. Values were significantly higher than those estimated by Xie et al.  
204 (2017). The effective moisture diffusivity can be related to with temperature by Arrhenius-type  
205 relationship:

206 
$$D_{eff} = D_0 \exp\left(-\frac{E_a}{RT}\right)$$

207 where  $D_0$  is the effective moisture diffusivity at 273.15K,  $E_a$  is the active energy, R is the universal  
208 gas constant with 8.314J/mol·K as its value, T is the drying temperature. The value of  
209 activation energy found in this work was 57.7 KJ/mol for the untreated samples and 99.4 KJ/mol for  
210 the treated samples.

211 The activation energy of goji berries was within the range 12.70-110.00 kJ/mol, which was reported  
212 for most agricultural materials (Xie et al., 2017). In drying, activation energy is the threshold energy,  
213 or the energy barrier must be overcome to initiate mass diffusion from the wet material. Hence, a  
214 material with lower  $E_a$  value, indicates that moisture diffusion coefficient is more susceptible to  
215 temperature effect during drying.

216

### 217 **3.2 Chemico- physical properties of fresh and dried goji berries**

218 Some chemico- physical qualitative data for fresh, dried UTR and TR samples are in Table 2. Fresh  
219 Italian goji berries showed a titrable acidity (TA), as malic acid, equal to 1.30% and a pH value close  
220 to 3.90.

221 After drying process at different temperatures, the pH values of samples did not change except for  
222 UTR samples dried at 60 and 70°C. Furthermore, all dried samples showed TA values higher than  
223 that of fresh one. The highest significantly different TA value was found for the UTR samples dried  
224 at 70 °C (1.93g malic acid/100 g) compared to the other ones.

225

**Table 2**

226

### 227 **3.3 Phenolic compounds and AA**

228 A total of eight phenolic compounds were identified from the goji fruits tested, mainly catechins (379  
229 mg/kg), belonging to flavonoid class, present in similar high concentrations in green tea and apple  
230 (Gadkaria et al., 2014). Even though catechins are not essential to human nutrition, they help in  
231 improving human health by preventing various diseases. Catechins decreased in all dried samples  
232 (Fig. 3), since they are sensitive to oxidation by polyphenol oxidase enzyme, acid and heat. The  
233 cinnamic acids, mostly present in coffee (Panusa et al., 2017), represented the second class of  
234 phenolic compounds present in the analyzed goji fruits. They were detected, at decreasing  
235 concentration as follow: ferulic, caffeic, chlorogenic and p-coumaric acids. The radical scavenging  
236 activity on DPPH decreased in the order caffeic acid > ferulic acid > p-coumaric acid, while in an  
237 ethanol–buffer solution of linoleic acid, ferulic acid was most effective among the tested phenolic  
238 acids (Kikuzaki et al., 2002). The drying always caused a significant reduction in the content in  
239 cinnamic acids of fresh fruit of goji. However, the abrasive pre-treatment better preserved the content  
240 in caffeic and chlorogenic acids due to the lower exposure times to high temperatures and oxygen  
241 compared to the reference samples (Tab. 3). Rutin is a glycoside of the flavonoid quercetin with  
242 beneficial role in controlling various diseases, including the ones related to lipid metabolism  
243 (Ravirajsinh et al., 2014); among flavonoids, rutin was reported as the most frequent compound in  
244 goji (Mikulic-Petkovsek et al., 2012; Protti et L., 2017). Its content in goji fruits always reduced



245 significantly after goji drying. Finally, low amounts of quercetin and kaempferol were found in fruits  
246 (Tab. 3).

247 In addition, increasing the drying temperature resulted in a decrease in the antioxidant activity (an  
248 increment in terms of EC<sub>50</sub> value). In details, TR samples dried at 50 and 60°C always showed a low  
249 EC<sub>50</sub> value respect to all untreated samples.

250

### 251 **3.4 Principal component analysis**

252 Some of the co-authors of this work investigated the effects of abrasive pre-treatment on carotenoids  
253 and colour in dried goji used in this trial (Fратиanni et al., 2018); therefore, we added such data to the  
254 PCA to better evaluate the results obtained. Fresh gojis and TR samples dried at 50°C and at 60°C  
255 were located on the positive side of the PC1 that explained 50.2% of the overall variation with  
256 phenolic content attribute. The groups of phenols considered (catechins, cinnamic acids and rutin)  
257 and the main carotenoid (zeaxanthin dipalmitate) were very close in the positive quadrant of PC1.  
258 Color parameters, in particular a\* (redness index) were at the PC2 boundary.

259 It is to underline that after drying, small but significant carotenoid losses (15–20%) were observed in  
260 all samples [12]. On the biplot, EC<sub>50</sub>, which comprised both samples dried at 70°C, and TPC, which  
261 included TR 50°C and TR 60°C samples, segregated in opposite directions, meaning these two factors  
262 were negatively correlated.

263

264

## 265 **CONCLUSIONS**

266

267 The developed model in cylindrical coordinates was able to describe the experimental drying kinetics  
268 especially at 60 and 70 °C and a better fitting was obtained for treated samples. Phenolic compounds  
269 undergone significant reductions in fresh gojis following drying, however samples pre-treated by  
270 abrasion showed high antioxidant activity. In fact, they better preserved phenols content, such as  
271 caffeic and chlorogenic acids, due to the lower exposure times to high temperatures and oxygen  
272 compared to the reference samples.

273 By the PCA, treated and untreated samples dried at 70°C were segregate in opposite directions,  
274 respect to the samples treated at 50°C and 60°C, that were on the positive side of the PC1 that  
275 explained over 50%, of the overall variation in phenolic compounds.

276

## 277 **REFERENCES**

278 Kosin'ska-Cagnazzo, A., Bocquel, D., Marmillod, I., Andlauer, W., 2017a. Stability of goji bioactives  
 279 during extrusion cooking process. Food Chemistry 230, 250–256.  
 280

281 Kosin'ska-Cagnazzo, A., Webera, B., Chablaisb, R., Vouillamoz, J.F., Moln'ar, B., Crovadore, J.,  
 282 Lefort F., Andlauer W., 2017. Bioactive compound profile and antioxidant activity of fruits from six  
 283 goji cultivars cultivated in Switzerland. Journal of Berry Research 7(1), 43-59.  
 284

285 Potterat, O., 2010. Goji (*Lycium barbarum* and *L. chinense*): phytochemistry, pharmacology and  
 286 safety in the perspective of traditional uses and recent popularity. Planta Medica 76, 7–19.  
 287

288 Rosa, A., Maxia, A., Putzu, D., Atzeri, A., Era, B., Fais, A., Sanna, C., Piras A., 2017. Chemical  
 289 composition of *Lycium europaeum* fruit oil obtained by supercritical CO2 extraction and evaluation  
 290 of its antioxidant activity, cytotoxicity and cell absorption. Food Chemistry 230, 82–90.  
 291

292 Hummer, K.E., Pomper, K.W., Postman, J., Graham, C.J., Stover, E., Mercure, E. W., ... Zee, F.  
 293 (2012). Emerging fruit crops. In M. L. Badenes & D. H. Byrne (Eds.), Fruit breeding, handbook of  
 294 plant breeding (pp. 97–147). New York: Springer.  
 295

296 Donno, D., Mellano, M.G., Raimondo, E., Cerutti, A.K., Prgomet, Z., Beccaro, G.L., 2016. Influence  
 297 of applied drying methods on phytochemical composition in fresh and dried goji fruits by HPLC  
 298 fingerprint. Eur Food Res Technol 242, 1961–1974.  
 299

300 Ignat, I., Volf, I., Popa, V.I., 2011. A critical review of methods for characterisation of polyphenolic  
 301 compounds in fruits and vegetables. Food Chem 126, 1821–1835.  
 302

303 Szajdek, A., Borowska, E.J., 2008. Bioactive Compounds and Health-Promoting Properties of Berry  
 304 Fruits: A Review. Plant Foods Hum Nutr 63, 147–156.  
 305

306 Hacker, K., Bauer, N., Schu"le, E., Wieland, M., Scherbaum, E., 2010. Goji Berries – A Natural Fruit?  
 307 Pesticide Residues in Dried Goji Berries. Chem. Veterinäruntersuchungsamt Stuttg.  
 308

309 Mocan, A., Vlase, L., Vodnar, D., Bischin, C., Hanganu, D., Gheldiu, A.M, et al., 2014. Polyphenolic  
 310 Content, Antioxidant and Antimicrobial Activities of *Lycium barbarum* L. and *Lycium chinense* Mill.  
 311 Leaves. Molecules 19(100), 56-73.

312

313 Dzhugalov, H., Lichev, V., Yordanov, A., Kaymakaov, P., Dimitrova, V., Kutoranov, G, et al., 2015.

314 First results of testing goji berry (*Lycium barbarum* L.) in Plovdiv region, Bulgaria. Sci Pap-Ser B

315 Horti, 47-50.

316

317 Fratianni, A., Niro, S., Alam, M.D.R., Cinquanta, L., Di Matteo, M., Adiletta, G., Panfili, G., 2018.

318 Effect of a physical pre-treatment and drying on carotenoids of goji berries (*Lycium barbarum* L.)

319 LWT - Food Science and Technology 92, 318–323.

320

321 Gao, Z., Ali, Z., Khan, I.A., 2008. Glycerogalactolipids from the fruit of *Lycium barbarum*.

322 Phytochemistry 69, 2856–2861.

323

324 Brasiello, A., Crescitelli, S., Adiletta, G., Di Matteo, M., Albanese, D., 2011. Mathematical modeling

325 with shrinkage of an eggplant drying process, Chemical Engineering Transactions 24, 451-456.

326

327 Adiletta, G., Alam, Md R., Cinquanta, L., Russo, P., Albanese, D., Di Matteo, M., 2015. Effect of

328 abrasive pretreatment on hot dried goji berry. Chemical Engineering Transactions 44, 127–132.

329

330 Wu, Z., Li, W., Zhao, L., Shi, J., Liu, Q., 2015. Drying characteristics and product quality of *Lycium*

331 *barbarum* understages-varying temperatures drying process. Trans. Chin. Soc.Agric. Eng. 31 (11),

332 287–293.

333

334 Li, P.L., Liao, R.Y., Wang, X., Gong, Y., Liu, D.H., 2014. Effect of different drying method and wax

335 removers on total flavonoid from *Lycium barbarum* L. Food Technol. 39 (5), 79–83.

336

337 Adiletta, G., Russo, P., Senadeera, W., & Di Matteo, M. (2016). Drying characteristics and quality of

338 grape under physical pretreatment. Journal of Food Engineering 172, 9-18.

339

340 Cinquanta, L., Di Matteo, M., Esti, M., 2002. Physical pre-treatment of plums (*Prunus domestica*).

341 Part 2. Effect on the quality characteristics of different prune cultivars, Food Chemistry 79, 233-238.

342

343 AOAC (1990) Official methods of analysis, 16th edn. Association of Official Analytical Chemists,

344 Washington, DC

345

346 Zhang, Q., Chen, W., Zhao, J., Xi, W., 2016, Functional constituents and antioxidant activities of  
 347 eight Chinese native goji genotypes. *Food Chemistry* 200, 230–236  
 348

349 Adiletta, G., Petriccione, M., Liguori, L., Pizzolongo, F., Romano, R., Di Matteo, M., 2018. Study of  
 350 pomological traits and physico-chemical quality of pomegranate (*Punica granatum* L.) genotypes  
 351 grown in Italy. *European Food Research and Technology* 244, 1427–1438.  
 352

353 Albanese, D., Adiletta, G., D'Acunto, M., Cinquanta, L., Di Matteo, M., 2014. Tomato peel drying  
 354 and carotenoids stability of the extracts. *International Journal of Food Science & Technology* 49 (11),  
 355 2458-2463.  
 356

357 Adiletta, G., Liguori L., Albanese, D., Russo, P., Di Matteo, M., Crescitelli, A., 2017. Soft-Seeded  
 358 pomegranate (*Punica granatum* L.) varieties: preliminary characterization and quality changes of  
 359 minimally processed arils during storage. *Food Bioprocess Tech* 10, 1631–1641.  
 360

361 Zhao, J., Li, H., Xi, W., An, W., Niu, L., Cao, Y., Wang, H., Wang, Y., Yin, Y., 2015. Changes in  
 362 sugars and organic acids in wolfberry (*Lycium barbarum* L.) fruit during development and  
 363 maturation. *Food Chemistry* 173, 718–724.  
 364

365 Zheng, G.Q., Zheng, Z.Y., Xu, X., Hu, Z.H., 2010. Variation in fruit sugar composition of *Lycium*  
 366 *barbarum* L. and *Lycium chinense* Mill. of different regions and varieties. *Biochemical Systematics*  
 367 *and Ecology* 38, 275–284.  
 368

369 Carranza-Concha, J., Benlloch, M.M., Camacho, M., Martínez-Navarrete, N., 2012. Effects of drying  
 370 and pretreatment on the nutritional and functional quality of raisins. *Food and Bioproducts Processing*  
 371 90 (2), 243-248.  
 372

373 Gadkaria, P.V., Balaraman, M., 2015. Catechins: Sources, extraction and encapsulation: A review.  
 374 *Food and Bioproducts processing* 93, 122–138.  
 375

376 Kikuzaki, H., Hisamoto, M., Kanae Hirose, K., Akiyama, K., Hisaji Taniguchi H., 2002.  
 377 Antioxidant Properties of Ferulic Acid and Its Related Compounds. *Journal of Agriculture and Food*  
 378 *Chemistry*, 2002, 50 (7), 2161–2168.  
 379  
 380

381 Ravirajsinh, N.J., Ranjitsinh, V.D., 2014. Polyphenols in Chronic Diseases and their Mechanisms of  
 382 Action. Polyphenols in Human Health and Disease. Edited by: Ronald Ross Watson, Victor R. Preedy  
 383 and Sherma Zibadi.

384

385 Mikulic-Petkovsek, M., Slatnar, A., Stampar, F., Veberic, R., 2012. HPLC–MS<sup>n</sup> identification and  
 386 quantification of flavonol glycosides in 28 wild and cultivated berry species. Food Chemistry 135  
 387 (4), 2138-2146.

388

389 Protti, M., Gualandi, I., Mandrioli, R., Zappoli, S., Tonelli, D., Mercolini, L., 2017. Analytical  
 390 profiling of selected antioxidants and total antioxidant capacity of goji (*Lycium spp.*) berries. J.  
 391 Pharm. Biomed. Anal. 143, 252-260.

392

393 Xie, L., Mujumdar, A.S., Fang, X.M., Wang, J., Dai, J.-W., Du, Z.-L., Xiao, H.-W., Liu, Y., Gao, Z.-  
 394 J., 2017. Food and Bioproducts Processing, 102, 320–331.

395

396 A. Panusa, R. Petrucci, R. Lavecchia, A. Zuorro, “UHPLC-PDA-ESI-TOF/MS metabolic profiling  
 397 and antioxidant capacity of arabica and robusta coffee silverskin: antioxidants vs phytotoxins”, Food  
 398 Research International, 99, 155-165, 2017

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413 **Figure Captions**

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415 Figure 1. Experimental and predicted moisture ratio for untreated samples (UTR).

416 Figure 2. Experimental and predicted moisture ratio for treated samples (TR).

417 Figure 3. Principal phenolic acids in fresh and dried samples.

418 Figure 4. 2D-principal component analysis plot of the main physicochemical and nutritional  
419 characteristics in fresh and dried goji samples.

420 **UR**: moisture; **pH**: pH; **TA**: total titratable acidity; **TS**: total sugars; **L\***: lightness; **a\***: red index; **b\***: yellow  
421 index; **TPC**: total phenols content; **Lut**: lutein; **Zeax**: zeaxanthin; **EC50**: antioxidant activity; **Cinnamic ac**:  
422 cinnamic acids; **Rutin**: rutin; **Catec**: catechin.; **Fresh**: fresh sample; **UTR50**: untreated sample dried at 50°C;  
423 **UTR60**: untreated sample dried at 60°C; **UTR70**: untreated sample dried at 70°C; **TR50**: treated sample dried  
424 at 50°C; **TR60**: treated sample dried at 60°C; **TR70**: treated sample dried at 70°C.

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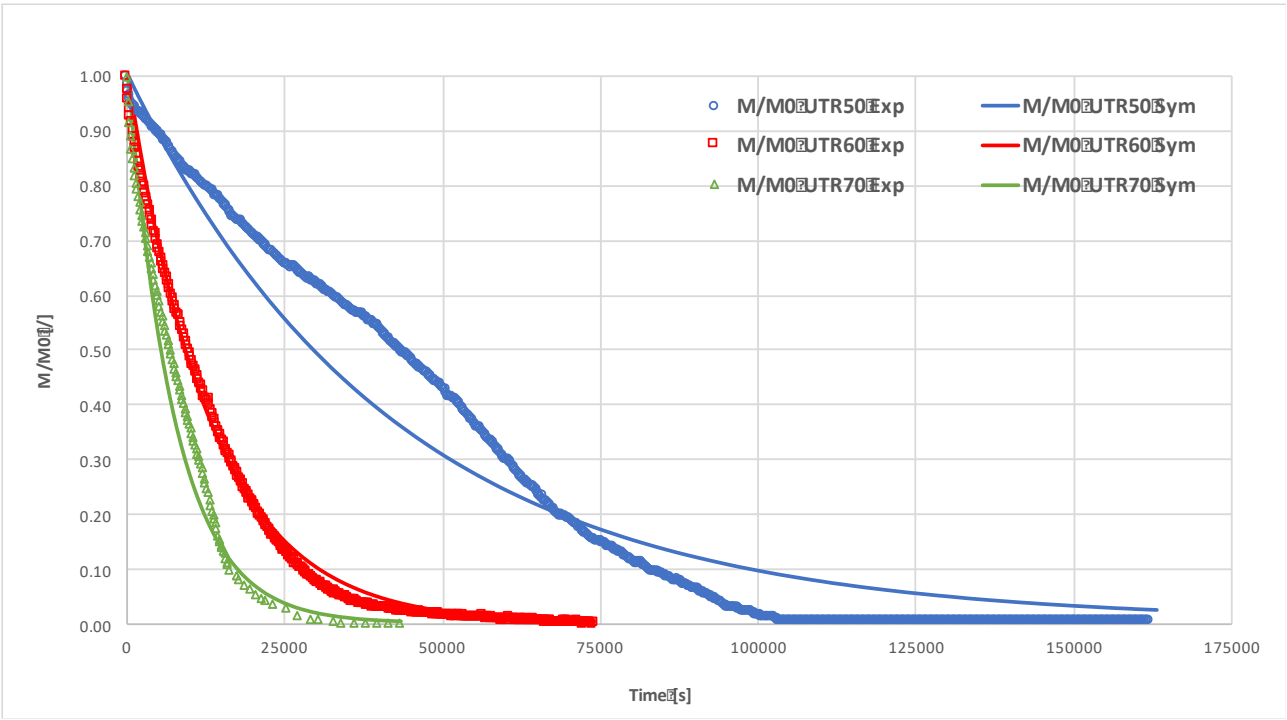


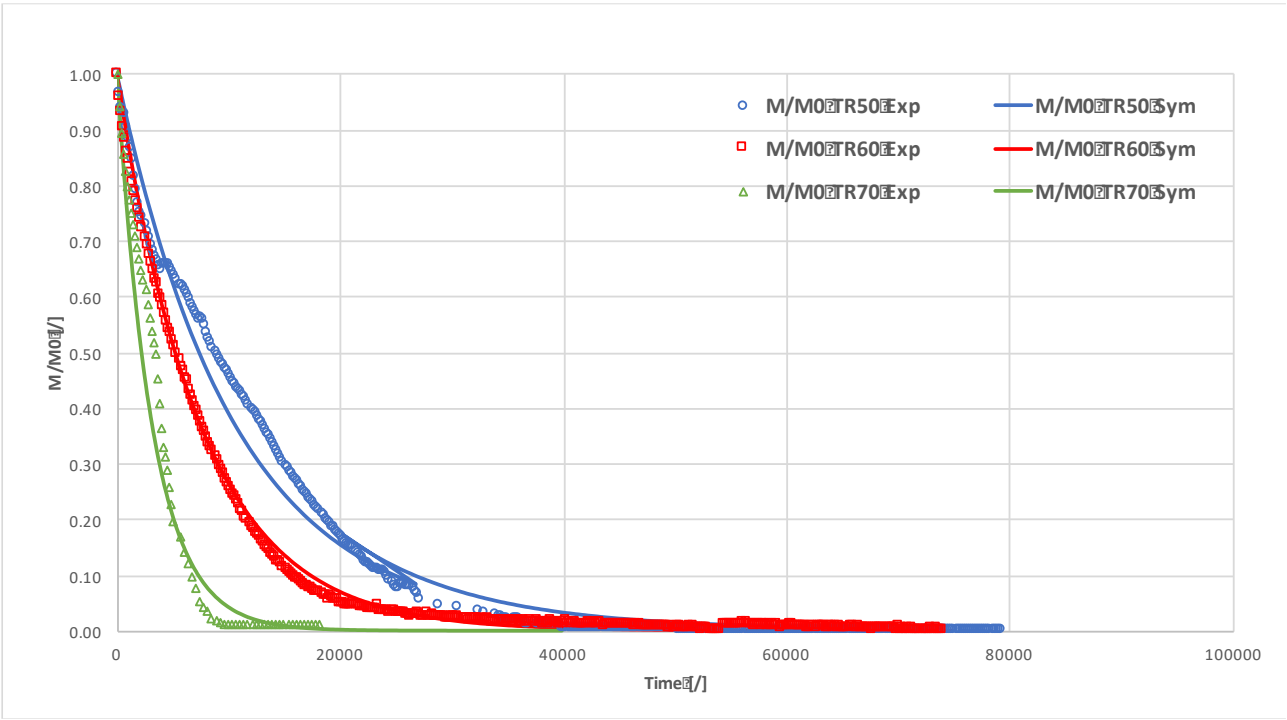
Figure 1

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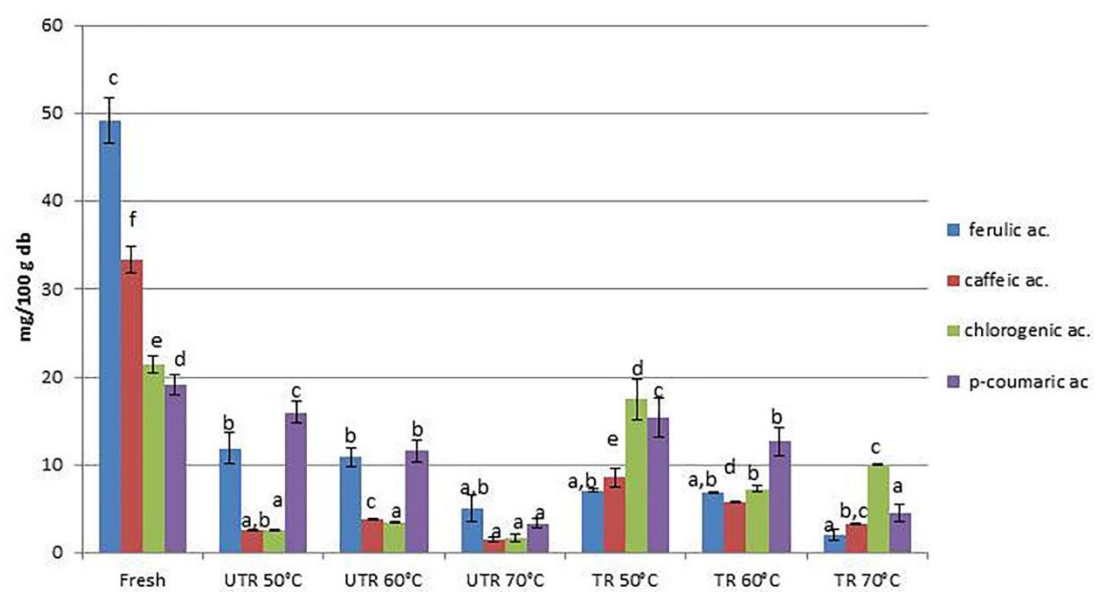
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Figure 2





**Figure 3**

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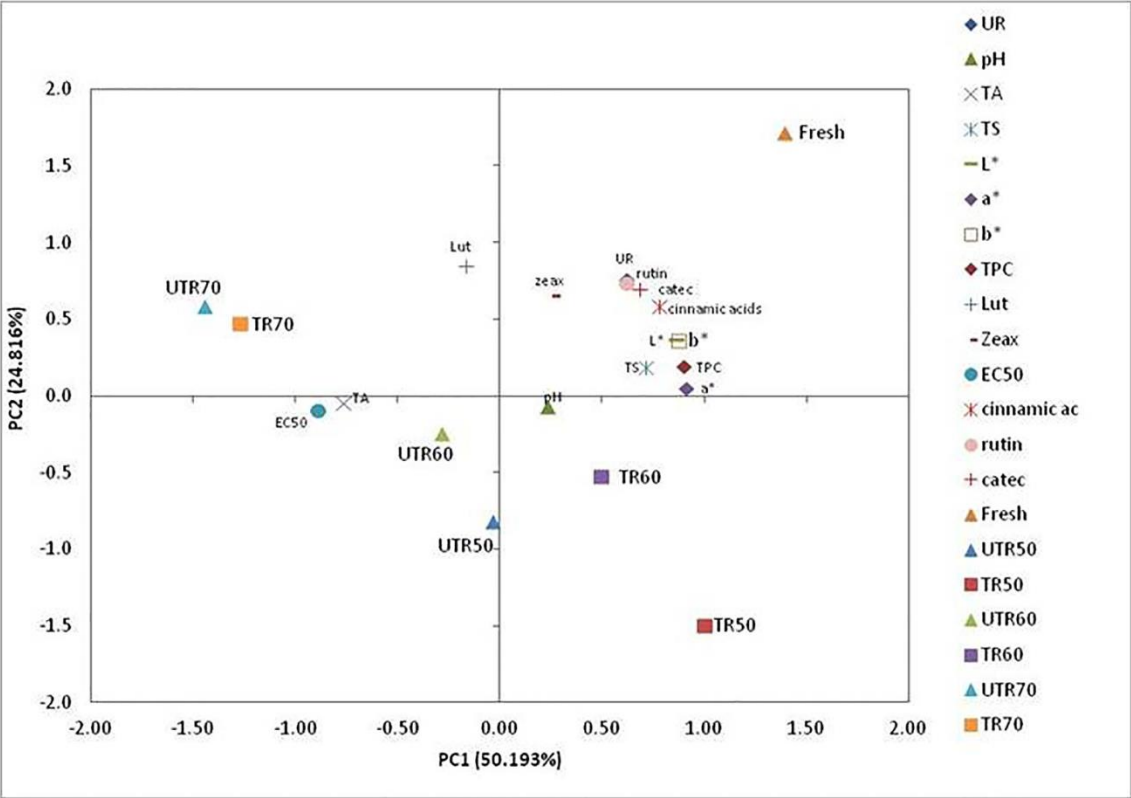


Figure 4

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Untreated			Treated	
T °C	D <sub>eff</sub> (m <sup>2</sup> /s)	R <sup>2</sup>	D <sub>eff</sub> (m <sup>2</sup> /s)	R <sup>2</sup>
50	7.50*10 <sup>-09</sup>	0.964	2.50*10 <sup>-08</sup>	0.977
60	2.20*10 <sup>-08</sup>	0.997	4.20*10 <sup>-08</sup>	0.998
70	4.20*10 <sup>-08</sup>	0.972	1.20*10 <sup>-07</sup>	0.971

Table 1 Values of the D<sub>eff</sub> estimated by the model and the corresponding values of fitting parameters.

Samples	Moisture (db)	a <sub>w</sub>	pH	Tritable Acidity (g malic acid /100g db)
Fresh	3.36 ± 0.10 <sup>b</sup>	0.92±0.01 <sup>d</sup>	3.90±0.01 <sup>b</sup>	1.30±0.02 <sup>a</sup>
UTR 50°C	0.026±0.002 <sup>a</sup>	0.42±0.01 <sup>c</sup>	3.89±0.01 <sup>b</sup>	1.47±0.07 <sup>b,c</sup>
TR 50°C	0.026± 0.002 <sup>a</sup>	0.40 ±0.02 <sup>a,b,c</sup>	3.96 ±0.01 <sup>b</sup>	1.42±0.01 <sup>b</sup>
UTR 60°C	0.025±0.002 <sup>a</sup>	0.41±0.01 <sup>b,c</sup>	3.78±0.05 <sup>a</sup>	1.49±0.07 <sup>b,c</sup>
TR 60°C	0.024±0.002 <sup>a</sup>	0.38±0.02 <sup>a</sup>	3.91±0.02 <sup>b</sup>	1.52±0.03 <sup>b,c</sup>
UTR 70°C	0.023±0.002 <sup>a</sup>	0.39±0.02 <sup>a,b</sup>	3.79±0.05 <sup>a</sup>	1.93±0.02 <sup>d</sup>
TR 70°C	0.025±0.002 <sup>a</sup>	0.37±0.02 <sup>a</sup>	3.95±0.05 <sup>b</sup>	1.56±0.04 <sup>c</sup>

Table 2 Physico-chemical properties of fresh and dried goji samples.

UTR: dried untreated berries, TR- Abr: dried abraded berries. Different letters in the same column are significantly different according to Tukey test at p<0.05.

	<b>Total phenols content (mg/g db)</b>	<b>Catechins (mg/100g db)</b>	<b>Rutin (mg/100g db)</b>	<b>Quercetin (mg/100g db)</b>	<b>Kaempferol (mg/100g db)</b>	<b>Antiox activity EC 50 (mg/ml)</b>
Fresh	21.47 ±4.02 <sup>b</sup>	379.15 ±24.37 <sup>d</sup>	29.07 ±1.43 <sup>c</sup>	0.66 ±0.03 <sup>d</sup>	0.70 ±0.04 <sup>c</sup>	28.59 ±0.15 <sup>a</sup>
UTR 50°C	9.49 ±0.25 <sup>a</sup>	46.65 ±0.73 <sup>b,c</sup>	4.27 ±0.47 <sup>b,c</sup>	0.13 ±0.01 <sup>c</sup>	0.22 ±0.06 <sup>b</sup>	85.01 ±0.35 <sup>e</sup>
UTR 60°C	6.51 ±0.14 <sup>a</sup>	20.46 ±1.94 <sup>a</sup>	3.14 ±0.58 <sup>ab</sup>	0.07 ±0.00 <sup>b</sup>	0.07 ±0.01 <sup>a</sup>	90.14 ±0.22 <sup>f</sup>
UTR 70°C	5.55 ±0.04 <sup>a</sup>	19.75 ±2.105 <sup>a</sup>	1.01 ±0.08 <sup>a</sup>	0.00 <sup>a</sup>	0.00 <sup>a</sup>	120.25 ±0.27 <sup>g</sup>
TR 50°C	18.51 ±0.10 <sup>b</sup>	72.51 ±1.77 <sup>c</sup>	6.15 ±0.6 <sup>c,d</sup>	0.12 ±0.02 <sup>c</sup>	0.03 ±0.00 <sup>a</sup>	32.10 ±0.20 <sup>b</sup>
TR 60°C	16.97 ±1.91 <sup>b</sup>	49.99 ±1.18 <sup>b,c</sup>	4.1 ±0.02 <sup>b,c</sup>	0.12 ±0.01 <sup>c</sup>	0.03 ±0.01 <sup>a</sup>	53.47 ±0.23 <sup>c</sup>
TR 70°C	7.19 ±0.16 <sup>a</sup>	38.14 ±1.61 <sup>ab</sup>	7.25 ±1.20 <sup>d</sup>	0.00 <sup>a</sup>	0.00 <sup>a</sup>	81.99 ±0.36 <sup>d</sup>

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513 Table 3 Total phenols content, catechin, rutin, quercetin, kaempferol and antioxidant activity in fresh  
514 and dried samples