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1 **Absorption of phenolic acids in rice kernels after boiling in**
2 **spearment aqueous extracts of different concentrations. A diffusion**
3 **study**

4

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27 **ABSTRACT**

28 In this study, an attempt was made to fortify white milled rice grains with phenolic
29 compounds using a hydrothermal process and spearmint aqueous extracts of different
30 % w/v concentrations. In addition, a mathematical model was acquired in order to
31 simulate the diffusion of specific phenolic acids in rice kernels during boiling inside
32 the extracts. Results showed that the amount of phenolic acids in rice, the potential
33 equilibrium concentration values, as well as the diffusivity of these compounds in rice
34 material were positively affected by the increase in % w/v bulk concentration of the
35 aqueous extract. It was also shown that the diffusion process could be sufficiently
36 described by a Fickian model and the estimated diffusion coefficients ranged from
37 6.86×10^{-12} to 3.56×10^{-11} m²/s, with the p-coumaric acid presenting the highest average
38 diffusivity in boiling rice material among all examined compounds. The chemical
39 affinity of each phenolic acid to rice macromolecules was believed to play the most
40 important role concerning their diffusivity in rice during fortification process.

41

42 **Keywords:** hydrothermal process, diffusivity, fortification, Fickian, phytochemicals

43

44 **Practical Application**

45 Consumer's interest for functional food products is constantly growing during the last
46 decades. This study may act as preliminary for the production of fortified rice
47 products, possessing adjusted bioactive content, in industrial scale. The proposed
48 methodology for the production of quick-cooking or ready-to-eat fortified rice may be
49 adopted by rice industries and applied by only making slight modifications in their
50 existing parboiling units.

51 **1. Introduction**

52 White milled rice is a staple food which could either be cooked prior to its
53 consumption or undergo some treatment in order to get rich in health-promoting
54 compounds that could enhance its nutritional value. Our recent studies (Igoumenidis,
55 Lekka, & Karathanos, 2016; Igoumenidis & Karathanos, 2016) have shown that white
56 rice has the ability to absorb and maintain a significant amount of antioxidants, as
57 well as colors and aromas, after being boiled in *Mentha spicata* aqueous extracts.
58 Therefore, it could be considered a promising carrier of useful compounds after
59 fortification. Literature during the last couple of decades has mainly focused on white
60 rice fortification with nutrients coming from the outer layers of rough rice kernels
61 (bran, husk, etc) which has been extensively applied using the well known parboiling
62 process (Elbert, Tolaba, & Suarez, 2001; Sridhar & Manohar, 2003; Miah, Haque,
63 Douglass, & Clarke, 2002; Oli, Ward, Adhikari, & Torley, 2014). Most of these
64 studies aimed to clarify the phenomena occurring inside rice grains during parboiling,
65 among which are water diffusion and starch gelatinization within the grain, in order to
66 optimize the quality of parboiled rice by predicting the soaking behavior of the paddy.
67 There are also a number of other studies that concern rice enrichment with minerals,
68 such as Fe, Zn and iodine, either through germination or hydrothermal processes (Wei
69 et al., 2012; Wei et al., 2013; Tulyathan, Laokuldilok, & Jongkaewwattana, 2007) and
70 rice fortification with vitamins and aromatic substances by spraying and hydrothermal
71 processes (Kyritsi, Tzia, & Karathanos, 2009; Yahya, Fryer, & Bakalis, 2011).
72 However, none of them is dealing with the calculation of diffusivity of
73 microconstituents inside rice grains during fortification process.

74 Moisture absorption and modeling of its diffusion in rice kernels during
75 hydration using hydrothermal treatments have been studied extensively in the past.

76 Many researchers have applied either analytical (Ahromit, Ledward, & Niranjan,
77 2006; Cheevitsopon & Noomhorm, 2011; Bello, Tolaba, & Suarez, 2004) or
78 numerical techniques (Balbinoti, Jorge, & Jorge, 2018; Perez, Tanaka, & Uchino,
79 2011; Bakalis, Kyritsi, Karathanos, & Yanniotis, 2009), showing that the hydration of
80 rice during soaking in hot water or cooking at several different temperatures follows
81 Fick's second law for diffusion. A number of studies dealing with the diffusion of
82 constituents, such as sugars, salts, phenols and vitamins in foodstuffs other than rice
83 are also available in literature (Telis, Murari, & Yamashita, 2004; Lombardi &
84 Zaritzky, 1996; Rozek, Achaerandio, Guell, Lopez, & Ferrando, 2009; Rastogi &
85 Raghavarao, 1998). In particular, most of these studies focus on the mass transfer of
86 these compounds in food matrices and the calculation of their diffusion coefficients
87 during osmotic dehydration processes.

88 Phenolic acids constitute a major part of total phenolics contained in plant
89 tissues and can be classified in many different categories, the most important of which
90 are cinnamic, benzoic and phenylacetic acid derivatives, detected in plant and plant-
91 derived foods like fruits, vegetables, teas, spices and grains. Their presence inside
92 plant material has been associated with a variety of functions such as protein
93 synthesis, nutrient uptake and enzymatic action, as well as structural and protective
94 roles concerning plant cells (Stalikas, 2007). Phenolic acids have been found to
95 exhibit antioxidant properties, the strength of which depends on their structural
96 features, especially on the number and position of hydroxyl groups in the phenolic
97 ring, as studies on hydroxycinnamic, hydroxybenzoic and hydroxyphenylacetic acids
98 revealed (Rice-Evans, Miller, & Paganga, 1996). In addition, most of phenolic acids
99 present a good absorbance rate when ingested by human, particularly when they are
100 under their aglycone-free form, and except for having the ability to scavenge free

101 radicals and prevent oxidative stress, they can also prevent the appearance of chronic
102 diseases (Kroon & Williamson, 1999; Lafay, Morand, Manach, Besson, & Scalbert,
103 2006; Zhao & Moghadasian, 2010; Lafay & Gil-Izquierdo, 2008). For this reason,
104 phenolic acids could contribute to the enhancement of the nutritional value of a food
105 product, such as white milled rice, when they are used for fortification purposes.

106 The main aim of the present study was to examine the correlation between the
107 concentration of specific phenolic acids, contained in an herbal extract medium, and
108 their rate of absorption in boiling rice grains. Diffusion phenomena in rice kernels
109 during hydration were modeled by using Fick's second law, and the diffusion
110 coefficients of each compound were estimated by fitting the model to experimental
111 absorption data. In addition, potential equilibrium concentrations for each compound
112 were also obtained from fortified rice flour samples. Finally, an attempt was made to
113 correlate the calculated diffusivity of the examined compounds with their chemical
114 structure and affinity to boiling rice material.

115 **2. Materials and methods**

116 *2.1. Materials*

117 White milled long grain rice of type "nychaki" of Greek origin and dried
118 spearmint leaves of Egyptian origin, in coarse powder form, were purchased from a
119 local market. Folin-Ciocalteu reagent and methanol (analytical grade) were purchased
120 from Merck (Darmstadt, Germany). Bis-(trimethylsilyl)-trifluoroacetamide reagent
121 (BSTFA) and 3-(4-hydroxyphenyl)-1-propanol were obtained from Aldrich Chemie
122 GmbH (Steinheim, Germany). Caffeic, protocatechuic and 3,4-dihydroxyphenylacetic
123 acids were purchased from Fluka (Steinheim, Germany). P-coumaric and gallic acids
124 were obtained from Sigma (Steinheim, Germany).

125 *2.2. Preparation of spearmint aqueous extracts*

126 Deionized water (15 L) was used for the preparation of spearmint aqueous
127 extract. After water was heated up to its boiling point, it was removed from the
128 heating source and dry spearmint leaves' powder (2 kg) was soaked and remained
129 fully immersed in it for 10 min. The aqueous herbal extract produced following the
130 above procedure was then infiltrated, collected and cooled down to room temperature.
131 Three samples (10 ml) of aqueous extract were stored in plastic tubes till freeze-
132 drying for further analysis. Afterwards, the extract was properly diluted using
133 deionized water and 4 aqueous solutions were produced, each one containing a
134 different concentration of phytochemical components. The final content in dry
135 spearmint extract of the 4 aqueous solutions was 0.33% w/v, 0.66% w/v, 1% w/v and
136 2% w/v.

137 *2.3. White milled rice and rice flour boiling in aqueous herbal extracts of different*
138 *concentrations.*

139 A specific volume (2 L) of each of the 4 spearmint aqueous extracts was
140 heated up using a conventional cooker and when it reached boiling temperature white
141 milled rice (50 g) was added in order to be cooked. The initial moisture content of rice
142 was 0.11 kg water/kg dry matter and the dimensions of 20 white milled rice grains
143 were measured by using a calliper. The initial length of rice grains was found to be
144 6.98 ± 0.29 mm, while their initial two diameters of the kernels, considered as ellipse,
145 were found to be 1.93 ± 0.06 and 1.78 ± 0.06 mm, respectively. The cooking process
146 lasted 20 min and took place under continuous stirring. The final moisture content of
147 rice was 2.92 kg water/kg dry matter. Samples of cooked rice (approx. 10 g) were
148 collected at 4 min time intervals (t_4 , t_8 , t_{12} , t_{16} , t_{20}) and then freeze dried before
149 undergoing extraction with methanol and further analysis.

150 The above experiments were repeated for white rice flour for much longer
151 time (90 min, to simulate a fortifying process of infinite duration), in order to achieve
152 equilibrium which may not be achieved with rice kernels. Thus, white rice flour
153 granules, produced by grinding the same rice source ('nychaki'), were boiled in
154 spearmint aqueous extracts containing same phytochemical component concentrations
155 by following the technique used for rice kernels. Cooked rice flour samples were
156 removed at the following time steps (subscripts indicate minutes): t_{30} , t_{60} , t_{70} , t_{80} , t_{90}
157 and then freeze-dried. All rice samples' cooking processes and analyses were
158 performed in triplicate.

159 *2.4. Analyses of individual phenolic compounds and total polyphenol content*

160 After freeze drying, the samples of the initial pure aqueous herbal extract were
161 accurately weighed (5 ± 0.1 mg) and diluted in methanol (5 mL) in order to be
162 analyzed by GC/MS. The techniques used for the extraction of phenolic compounds
163 from fortified rice and rice flour samples have been previously described in
164 Igoumenidis et al. (2016). In particular, a total of 20 mL MeOH/g of freeze-dried
165 sample was used for the extraction procedure. Dried MeOH extracts of each fortified
166 rice and rice flour sample were diluted in 1 mL of MeOH and led to further analyses.

167 The detection of 4 common phenolic acids in aqueous spearmint extract, as
168 well as in methanolic extracts of cooked fortified rice and rice flour samples was
169 performed by GC/MS analysis, as described by Kalogeropoulos, Konteles,
170 Troullidou, Mourtzinou, & Karathanos (2009). Briefly, a Selective Ion Monitoring
171 (SIM) method was employed for the analysis of 4 target phenolic acids, which were
172 transformed in their respective trimethyl-silyl-ether forms. In addition, the
173 quantification of all examined components in every sample was made by using 3-(4-
174 hydroxyphenyl)-1-propanol as internal standard. Results were expressed in μg of

175 phenolic acid/g dry rice or dry rice flour and in μg of phenolic acid/g of dry aqueous
176 spearmint extract.

177 The total polyphenol content of fortified rice flour methanolic extracts was
178 also determined by applying the Folin-Ciocalteu photometric method as being adapted
179 to microscale by Arnous, Makris, and Kefalas (2002). The results concerning total
180 polyphenol content were presented as mg of Gallic Acid Equivalents (GAE)/g of dry
181 rice flour.

182 *2.5. The diffusion model*

183 A mathematical model was used to simulate the diffusion of the investigated
184 phenolic acids in rice kernels during their boiling inside spearmint aqueous extract
185 media of 4 different concentrations in diluted solids (w/w). The agitation of the
186 boiling medium during rice fortification process was natural, sufficient though, so
187 surface resistance to phenolic mass transport was considered to be small and only the
188 internal resistance of rice grains was taken into consideration. In addition, phenolic
189 acid concentration gradient between the surface and the center of rice kernels was
190 supposed to be the driving force for the diffusion of the compounds in rice and also
191 Fickian diffusion was assumed to be the predominant mechanism of phenolic mass
192 transfer inside the kernels. The geometry of rice grain has been simplified to an
193 equivalent sphere with equivalent radius $R_{eq} = 2 \times 10^{-3}$ m. The simplification was done
194 by following the same assumptions, equations and procedures as in the study of
195 Chapwanya and Misra (2015) for the transformation of the elliptical geometry of a
196 grain to an equivalent spherical geometry. According to Gastón et al. (2004) the
197 geometry deviation in diffusion coefficients for the above transformation is expected
198 to be about 15%. The equivalent radius was calculated by using data and assumptions

199 corresponding to hydration of rice grains (including expansion parameter during
200 boiling) from a previous study (Bakalis et al., 2009).

201 Diffusion of phenolic acids through the rice grain was described using Fick's
202 second law:

$$203 \quad \frac{\partial C_i}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[D_i r^2 \frac{\partial C_i}{\partial r} \right], \forall r \in (0, R) \quad \text{Eq. 1}$$

204 where C_i ($\mu\text{g/g}$ dry rice) and D_i (m^2/s) are the concentration and the effective mass
205 diffusivity, respectively, of each phenolic acid, r (m) is the radial coordinate and t (s)
206 is the boiling time.

207 The boundary condition imposed at $r = 0$ (rice kernel center) followed from
208 the symmetry of the system:

$$209 \quad \frac{\partial C_i}{\partial r}(0, t) = 0 \quad \text{Eq. 2}$$

210 while at the external boundary $r = R$ ($= R_{eq}$, grain surface) the compound
211 concentration was defined as the equilibrium one $C_{i,\infty}$ ($\mu\text{g/g}$ dry rice flour):

$$212 \quad C_i(R, t) = C_{i,\infty} \quad \text{Eq. 3}$$

213 The equilibrium concentration was estimated by taking the mean experimental
214 concentrations of phenolic acids in rice flour during the last time steps of the
215 fortification process.

216 The experimental concentrations of phenolic acids in the rice prior to its
217 fortification $C_{i,0}$ ($\mu\text{g/g}$ dry rice) were used to define the corresponding initial
218 conditions for each phenolic compound:

$$219 \quad C_i(r, 0) = C_{i,0} \quad \text{Eq. 4}$$

220 The predicted concentrations of phenolics were obtained as volume average according
221 to the following equation (Chapwanya and Misra, 2015; Ruiz et al 2008):

$$222 \quad C_i(t) = \frac{3}{R_{eq}^3} \int_0^{R_{eq}} r^2 c(x, t) dr \quad \text{Eq. 5}$$

223 where $C_i(t)$ is the volume averaged concentration of phenolic compound i and $c(x,t)$ is
224 the spatially distributed concentration, given as output of the numerical model.

225 2.5.1. Dimensionless transformations

226 The dimensionless concentration of each compound was defined as:

$$227 \quad \check{C}_i = \frac{C_i - C_{i,0}}{C_{i,\infty} - C_{i,0}} \quad \text{Eq. 6}$$

228 The time scale of the diffusion phenomena for each compound is given by the Fourier
229 number:

$$230 \quad \tau = \frac{tD_i}{R^2} \quad \text{Eq. 7}$$

231 while the dimensionless independent spatial variable is defined as:

$$232 \quad \check{r} = \frac{r}{R} \quad \text{Eq. 8}$$

233 2.5.2. Dimensionless formulation

234 The dimensionless form of the governing equation is given by:

$$235 \quad \frac{\partial \check{C}_i}{\partial \tau} = \frac{1}{\check{r}^2} \frac{\partial}{\partial \check{r}} \left(\check{r}^2 \frac{\partial \check{C}_i}{\partial \check{r}} \right), \forall \check{r} \in (0,1) \quad \text{Eq. 9}$$

236 with boundary:

$$237 \quad \frac{\partial \check{C}_i}{\partial \check{r}}(0, \tau) = 0 \quad \text{Eq. 10}$$

$$238 \quad \check{C}_i(1, \tau) = 1 \quad \text{Eq. 11}$$

239 and initial conditions:

$$240 \quad \check{C}_i(\check{r}, 0) = 0 \quad \text{Eq. 12}$$

241 2.5.3. Numerical simulations

242 The model formed by Eqs. 6-12 has been solved using the Finite Element (FE)
243 method (commercial software COMSOL Multiphysics 4.3b[®]). A uniform spatial
244 mesh consisting of 121 elements has been employed in all the numerical simulations.

245 2.5.4. Mass diffusivity estimation

246 The effective mass diffusivity coefficient D_i (m^2/s) for each compound and for
247 each extract concentration was estimated by minimizing the sum squared of the
248 difference between experimental and simulated concentrations (Least Square method
249 implemented in MATLAB 2013). The goodness of the fitting has been evaluated
250 using the value of the coefficient of determination R^2 , while the 95% Confidence
251 Intervals (CI) for the diffusivity constants were calculated using the Bootstrap method
252 (Efron & Tibshirani, 1993).

253 **3. Results & Discussion**

254 The content of the spearmint aqueous extract in four major phenolic acids (i.e.
255 caffeic, 3-4 di-OH-phenylacetic, protocatechuic and p-coumaric) detected by GC/MS
256 is presented in Table 1. Caffeic acid seems to be the predominant one as its
257 concentration surpasses the levels of 3000 $\mu g/g$ of dry extract, while most of the other
258 examined compounds present much lower concentrations in dry extract (see Table 1).
259 As shown in a previous study (Igoumenidis et al., 2016) the concentration of phenolic
260 acids in a similar type of spearmint extract (*Mentha spicata*) did not present
261 significant changes after being boiled for at least 40 minutes, so the values of
262 concentrations listed in Table 1 could be considered as being quantitatively stable
263 throughout the whole rice fortification process.

264 Experimental results for rice fortification with four different phenolic acids
265 contained in spearmint aqueous extract are presented in Figure 1. All the investigated
266 compounds seem to follow an increase in their content in rice grains with boiling
267 time, as well as an increase with the % w/v concentration of spearmint extract used in
268 the hydrothermal process. Figure 1 also shows that by increasing the concentration of
269 phenolic acids in the aqueous extract, this is, their availability at the surroundings of
270 rice grains during boiling, their content inside fortified rice kernels keeps on

271 increasing from the beginning until the end of the hydrothermal process (20 min).
272 However, there is no indication of approaching equilibrium levels (saturation) in their
273 concentrations in rice grains. In fact, these equilibrium levels of phenolic acid
274 concentrations could probably be reached under different experimental conditions, i.e.
275 by changing boiling time, temperature, pressure, concentration of aqueous extract
276 medium or even size and shape of rice grains. That is why a number of experiments
277 was repeated at the same conditions in rice flour (instead of rice kernels) of much
278 smaller size so that the potential equilibrium content of each phenolic acid in rice
279 material could be estimated. In this way, it would be easier to understand the diffusion
280 mechanism of phenolic acids in rice grains during fortification and also to clarify
281 whether or not Fick's second law for diffusion is followed in this case, as it happens
282 in the case of water diffusion in rice, according to a number of studies (Balbinoti et
283 al., 2018; Bakalis et al., 2009; Bello et al., 2004).

284 Regarding the total polyphenol content of fortified rice flour, Figure 2 shows
285 that it approaches equilibrium levels after being boiled at different % w/v aqueous
286 extract concentrations for an equivalent of infinite boiling time (90 min). The same
287 pattern was followed (data not shown) when the concentrations of the four specific
288 phenolic acids in fortified rice flour were measured as a function of boiling time. In
289 particular, the equilibrium levels of the examined phenolic compounds in rice material
290 appear to be depending on the % w/v concentration of the aqueous extract boiling
291 medium, as data in Table 2 suggest.

292 Data in Table 3 correspond to the fitted diffusion coefficient values of the
293 examined compounds in rice kernels during the fortification process. According to
294 these results, the diffusivity coefficient of phenolic acids in rice during boiling seems
295 to be almost 2 levels of magnitude lower than the diffusivity of water in rice ($7.5 \times 10^{-}$

296 10^{-10} m²/s, according to Bakalis et al., 2009) after following a similar hydrothermal
297 process. This could be attributed to the much larger molecular size of the examined
298 phenolic acids, in comparison to the size of water molecules, which could probably
299 cause a relative decrease in their ability to penetrate rice material and/or a decrease in
300 their molecular mobility inside rice grains. In addition, Table 3 also shows a
301 noticeable increase in the diffusivity of the examined phenolic acids in rice kernels
302 with the concentration of spearmint aqueous extract. Similar dependence of the
303 diffusivity coefficient on concentration can be found in studies looking at moisture
304 diffusivity in gelatinized foods or air drying processes. In such cases the effective
305 diffusivity of water has been found to present increased values at high moisture
306 contents, compared to the diffusivity at lower moisture contents, during dehydration
307 (Zogzas, Maroulis, & Marinos-Kouris, 1996; Maroulis, Kiranoudis, & Marinos-
308 Kouris, 1995). Moreover, there are studies that correlate moisture diffusivity with
309 starch gelatinization rate and moisture content in starchy foods during hydrothermal
310 treatment. In general, gelatinization is considered to be a first-order reaction that
311 normally restricts the transport of water in foods, while the degree of gelatinization
312 has been found to have a significant effect on water diffusion during soaking
313 processes (Gomi, Fukuoka, Mihori, & Watanabe, 1998; Elbert et al., 2001).
314 Dependence of penetrant diffusivity on its concentration has also been noted in
315 studies related to materials other than foods. In particular, this phenomenon is quite
316 common in polymer science, e.g. solvent absorption by a polymer in glassy state and
317 subsequent swelling (Danner, 2014; Vrentas & Vrentas, 1998; Thomas & Windle,
318 1980).

319 One of our recent studies (Igoumenidis, Zoumpoulakis, & Karathanos, 2018)
320 showed that caffeic acid presents the ability to interact with rice starch after applying

321 a hydrothermal treatment similar to that followed in our current study. In particular,
322 the addition of the phenolic acid in rice starch – water matrix, during heating, seemed
323 to have a significant effect on gelatinization properties, with stronger effects as the
324 concentrations of caffeic acid in the mixture increase. Similar results have been also
325 reported in literature (Karunaratne & Zhu, 2016; Zhu, 2015; Wu, Lin, Chen, & Xiao,
326 2011), showing that phenolic compounds interact with starch molecules during
327 gelatinization, reduce its degree and alter its thermal properties probably by
328 interfering with the starch - water matrix. The potential interaction of phenolic extract
329 constituents with the rice starch - water matrix during boiling may be a possible
330 explanation for the concentration dependent apparent diffusivity of the examined
331 phenolic acids in rice kernels being observed in Table 3.

332 According to the results listed in Table 3, the average effective diffusivity of
333 the examined compounds in all experimental conditions (0.33%, 0.66%, 1% and 2%
334 w/v of aqueous extract media) follows the order: $D_{p\text{-Coumaric}} > D_{\text{Caffeic}} > D_{\text{Protocatechuic}} >$
335 $D_{3\text{-}4\text{ diOH Phenylacetic}}$. During fortification process the spherical rice grains of our study
336 could be considered as porous networks of low porosity that absorb water molecules
337 quickly and maintain a rubbery state until the end of hydrothermal processing
338 (Biliaderis, Page, Maurice, & Juliano, 1986; Thuc, Fukai, Truong, & Bhandari, 2010;
339 Bertotto, Gaston, Batiller, & Calello, 2018). Given that the main components of these
340 membranes are amylopectin and water molecules (>70% w/w), the diffusivity of
341 phenolic acids through them is therefore affected by the nature of the porous network,
342 as well as by the nature of the penetrating molecules, e.g. the size and shape of
343 penetrating molecules, and also the chemical affinity between the components
344 contained in the membranes and the diffusing molecules. Regarding the chemical
345 affinity factor, it has been reported that the greater the attraction is between the

346 penetrants and the constituents of the porous network, the lower is the penetrating
347 ability and the diffusivity of the former through the polymeric membrane. (George &
348 Thomas, 2001; Cu & Saltzman, 2009; Dury-Brun, Chali er, Desobry, & Voilley, 2007)

349 In this study, the difference found in diffusivities of four phenolic acids in rice
350 grains (Table 3) may not be explained by the difference in molecular size and shape
351 of the examined molecules, as they could be considered to be of similar MW
352 (between 154 and 180) and structure (1 benzene ring per molecule). In addition, the
353 permeability through a porous network (i.e. rice material) is greatly affected by the
354 size and shape of the penetrating molecules only in case that the membrane is in its
355 glassy state (George & Thomas, 2001). In our case, the structural characteristics of
356 phenolic acids may not have a significant effect on their diffusivity as the boiling rice
357 grains are mostly found in their rubbery state during fortification treatment.

358 The diffusivity of the examined compounds can also depend on their chemical
359 affinity to rice main constituents, which could be expressed by chemical properties
360 such as polarity and hydrophobicity. In particular, hydrophobicity of a compound is
361 defined as its liquid-liquid partition coefficient (P) between octanol and water and it is
362 expressed on log scale as logP. Hydrophobic molecules are generally characterized by
363 positive values of logP while negative values of logP are characteristic of hydrophilic
364 compounds (Dury-Brun et al., 2007). The results in Table 3 show that p-coumaric
365 acid presents the highest average diffusivity in rice grains during fortification process,
366 followed by caffeic, protocatechuic and 3,4-diOH phenylacetic acids. The same trend
367 is also followed by the estimated logP values of the investigated phenolic acids
368 (Supplementary Table 1). Assuming that hydrated rice mainly consists of amylopectin
369 molecules - which have an estimated logP value of -10.6 - and water, boiled rice
370 could be considered as a rather hydrophilic material. This indicates that the diffusion

371 of more hydrophobic compounds such as p-coumaric acid was favored, while more
372 hydrophilic ones (3,4-diOH phenylacetic acid) may present a stronger attraction to
373 rice matrix components, chemically interact with them and result in lower diffusion
374 coefficients.

375 The goodness of fit of the Fickian model, together with the estimated D_i
376 values, is illustrated in Table 3 (columns presenting R^2 values) and Figure 1, where
377 the predicted evolution of the phenolic acids concentrations along time is compared to
378 the experimental results. Overall, there is a good agreement between model and
379 measurements ($R^2 > 0.9$), with the exception of the p-coumaric acid at the lowest
380 extract concentrations. This suggests that the diffusion of the investigated phenolic
381 acids during hydrothermal fortification processes can be overall well described by a
382 Fickian model.

383 To confirm Fickian diffusion of the phenolic acids during the fortification
384 process, the dimensionless concentrations of acids \check{C}_i were plotted against the square
385 root of Fourier time $\sqrt{\tau}$ in Figure 3a. This revealed a linear relationship between
386 phenolic acid concentrations (\check{C}_i) at much lower levels than $C_{i,\infty}$ (i.e. $\check{C}_i < 0.35 \ll 1$) and
387 small Fourier times τ (far away from the equilibrium state). According to Peppas and
388 Brannon-Peppas (1994), a linear correlation between dimensionless concentration of
389 the diffusive species and $\sqrt{\tau}$ during the first stages of an absorption process is a
390 reliable indicator of Fickian diffusion. Finally, Figure 3b presents the correlation
391 between the dimensionless concentration (\check{C}_i) of phenolic acids in fortified rice and
392 Fourier times τ . As shown, experimental results from all phenolic compounds and
393 concentrations collapse onto a characteristic Fickian master curve.

394 **4. Final remarks**

395 In general, our study showed that the proposed methodology could result in
396 the production of fortified rice grains presenting the ability to achieve an adjusted-
397 predicted concentration of particular nutrients in their mass. This could be based on
398 the selection of a combination of aqueous herbal extract bulk concentration, time of
399 rice hydrothermal processing and source of specific herb. For example, it is well
400 known that prolonged boiling times, as well as the need for drying of the fortified
401 product, usually have a detrimental effect on the sensory attributes and the structure of
402 the final product. So the production of a ready-to-eat fortified rice product of a
403 desirable phytochemical content, which does not require a drying step, may be
404 preferably done by applying a standard % w/v bulk concentration of herbal aqueous
405 extract together with relatively high boiling times. On the other hand, the production
406 of a quick-cooking fortified rice product, of same phenolic acid content as the ready-
407 to-eat one, would probably require the application of a much higher % w/v bulk
408 concentration of herbal aqueous extract together with a shorter boiling time, as the
409 production of such products includes a drying as well as a rehydration step which
410 usually act at the expense of the sensory quality of the final product. The rice industry
411 could possibly adopt the proposed technique and select appropriate herbal extracts of
412 relatively stable phytochemical content to produce optimal fortified rice products,
413 concerning phytochemical content and sensory characteristics, according to
414 consumers' needs. In addition, the launch of such products in the market could
415 promote both the nutritional and commercial value of white milled rice.

416 **5. Conclusions**

417 The use of various % w/v concentrations of aqueous herbal extract for the
418 enrichment of rice grains with phenolic acids during boiling (20 min) showed that
419 there was a significant increment in the amount of phenolic acids absorbed in rice for

420 higher % w/v concentrations of extract. In addition, the relative diffusivities of the
421 examined phenolic acids in rice during boiling were found to be dependent on the
422 chemical affinity of each compound to rice material. The proposed application of rice
423 fortification through hydrothermal process, described in this study, seems to be quite
424 interesting for the food industry, as it may offer the opportunity to produce fortified
425 rice of either quick-cooking or ready-to-eat type which could contain adjusted
426 portions of phenolic acids, together with an optimum final product appearance. This
427 could probably be achieved by utilizing existing parboiling units of rice industries,
428 after making slight modifications, and selecting the proper aqueous herbal extracts, as
429 sources of phytochemicals or bioactive compounds of known diffusivities in rice
430 material. However, extra work would be needed to predict the diffusivities of other
431 health-promoting compounds (i.e. flavonoids, trace elements, vitamins, natural
432 pigments) in rice, as well as their stability during hydrothermal processing.

433 **Author Contributions**

434 S. Bakalis and V. T. Karathanos designed the study, contributed to the interpretation
435 of the results and reviewed the manuscript. P. E. Igoumenidis conducted the
436 experiments, analyzed data, interpreted the results and wrote the manuscript. S. V.
437 Iosifidis carried out the experiments and participated in data analysis. E. Lopez-
438 Quiroga did the mathematical modeling and contributed to the revision of the final
439 manuscript. V. T. Karathanos supervised the whole project.

440 **Nomenclature**

441	t	boiling time (s)
442	D_i	mass diffusivity of phenolic acids in rice kernels (m^2/s)
443	R	radius of fortified rice grain sphere (m)
444	R_{eq}	equivalent radius of rice grain (m)
445	r	radial coordinate (m)
446	C_i	phenolic acid concentration in rice grains ($\mu g/g$ dry rice)
447	$C_{i,0}$	initial concentration of specific phenolic acids in rice ($\mu g/g$ dry rice)
448	$C_{i,\infty}$	potential equilibrium concentration of phenolic acids in rice grains
449		($\mu g/g$ dry rice flour)
450	$c(x,t)$	spatially distributed concentration of phenolic acids in rice grains ($\mu g/g$
451		dry rice)
452	$C_i(t)$	volume averaged concentration of phenolic compound i ($\mu g/g$ dry rice)
453	\check{C}_i	dimensionless concentration of individual phenolic acids in spherical
454		rice grains
455	\check{r}	dimensionless radius of rice grain
456	τ	dimensionless Fourier number

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620

621 **Table 1:** Concentration of examined phenolic acids in spearmint aqueous extract at
622 the beginning (t=0) of boiling process ($\mu\text{g/g}$ of dry extract). All measurements are
623 presented in mean values \pm Standard Deviation (n=3)

Major phenolic acids in spearmint dry extract ($\mu\text{g/g}$)			
Caffeic	3-4 di-OH-Phenylacetic	Protocatechuic	p-Coumaric
3373.1 \pm 159.3	1983.3 \pm 166.2	180.8 \pm 14.1	171.3 \pm 3.9

624 **Table 2:** Estimated equilibrium concentration of major phenolic acids in fortified rice
 625 flour ($\mu\text{g/g}$ dry rice flour) as a function of spearmint aqueous extract concentration (%
 626 w/v). All concentrations are presented in mean values \pm Standard Deviation (n = 3).

Spearmint aqueous extract concentration	Equilibrium phenolic concentrations in fortified rice flour ($\mu\text{g/g}$ dry rice flour)			
	3,4 di-OH-Phenylacetic	Caffeic	Protocatechuic	p-Coumaric
0.33% w/v	144.1 \pm 26.3	85.7 \pm 8.0	19.1 \pm 2.7	5.9 \pm 1.2
0.66% w/v	255.7 \pm 31.7	112.9 \pm 6.5	25.4 \pm 2.2	9.1 \pm 0.6
1% w/v	337.3 \pm 29.9	149.8 \pm 17.1	27.5 \pm 2.8	11.2 \pm 0.8
2% w/v	388.3 \pm 34.0	200.8 \pm 18.6	33.8 \pm 4.4	14.6 \pm 1.2

627 **Table 3:** Fitted values of the diffusion coefficient (D_i) of the examined phenolic acids in rice grains during boiling in spearmint extract media.

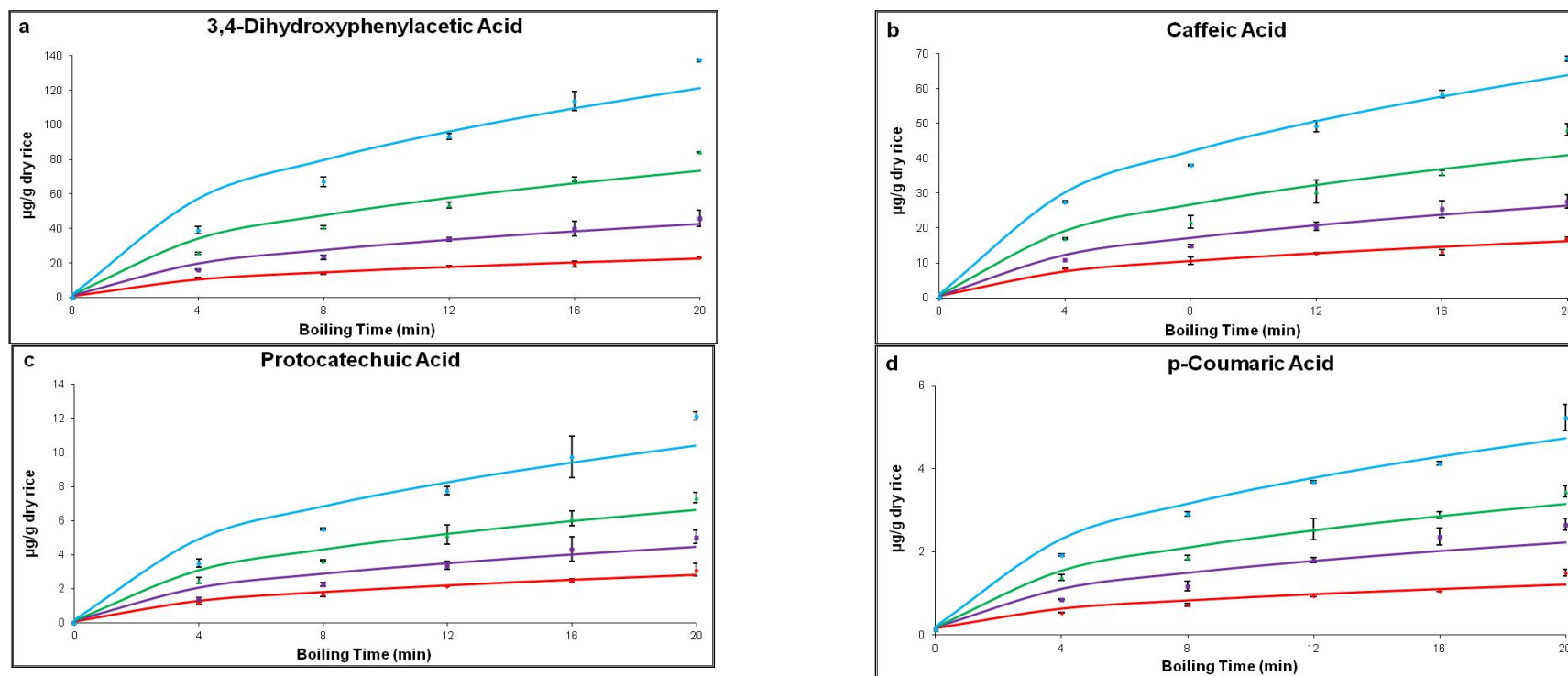
628 Correlation coefficient R^2 shows how good the fitting of simulated results with experimental data is. CI are the 95% confidence intervals.

Phenolic Acids	Spearmint aqueous extract concentration											
	0.33% w/v			0.66% w/v			1% w/v			2% w/v		
	D (m ² /s)	CI	R ²	D (m ² /s)	CI	R ²	D (m ² /s)	CI	R ²	D (m ² /s)	CI	R ²
3,4 di-OH Phenylacetic	7.7298E-12	7.7289E-12, 7.7554E-12	0.99	8.87E-12	8.8329E-12, 8.8785E-12	0.96	1.57E-11	1.5664E-11, 1.5699E-11	0.93	3.42E-11	3.3368E-11, 3.4232E-11	0.92
Caffeic	1.1443E-11	1.1442E-11, 1.1446E-11	0.98	1.81E-11	1.8145E-11, 1.8174E-11	0.97	2.55E-11	2.4967E-11, 2.5542E-11	0.92	3.56E-11	3.5420E-11, 3.5641E-11	0.98
Protocatechuic	6.859E-12	6.8433E-12, 6.8616E-12	0.97	9.84E-12	9.5958E-12, 9.8571E-12	0.91	1.95E-11	1.9407E-11, 1.9584E-11	0.95	3.32E-11	3.1216E-11, 3.3217E-11	0.91
p-Coumaric	1.2229E-11	1.2224E-11, 1.2230E-11	0.88	2.06E-11	2.0141E-11, 2.0599E-11	0.86	2.60E-11	2.5618E-11, 2.6086E-11	0.97	3.50E-11	3.4624E-11, 3.5100E-11	0.96

629

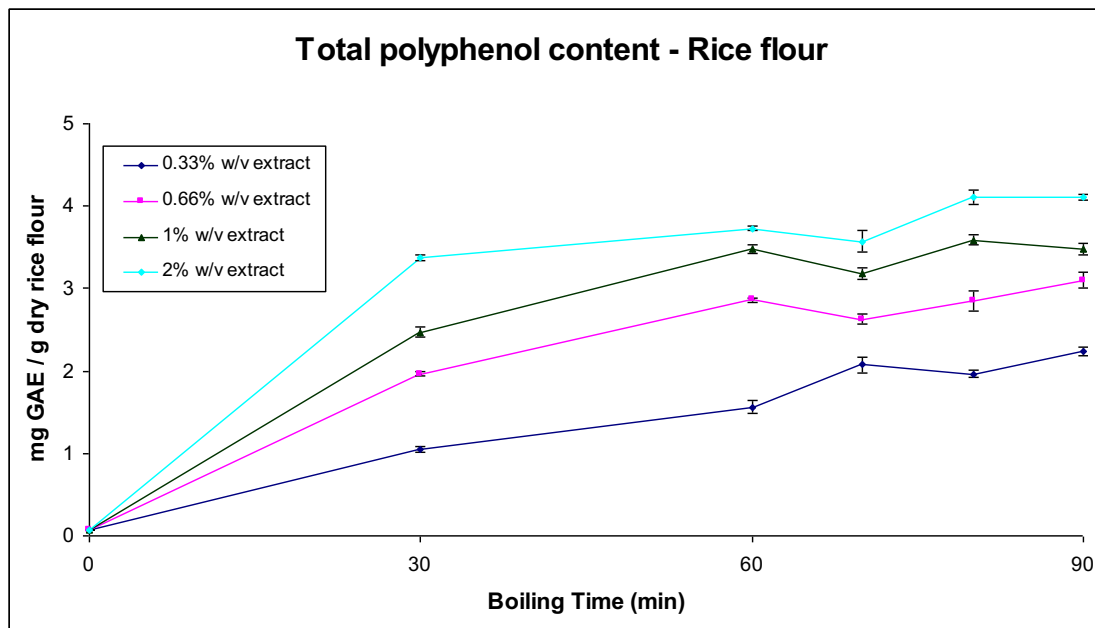
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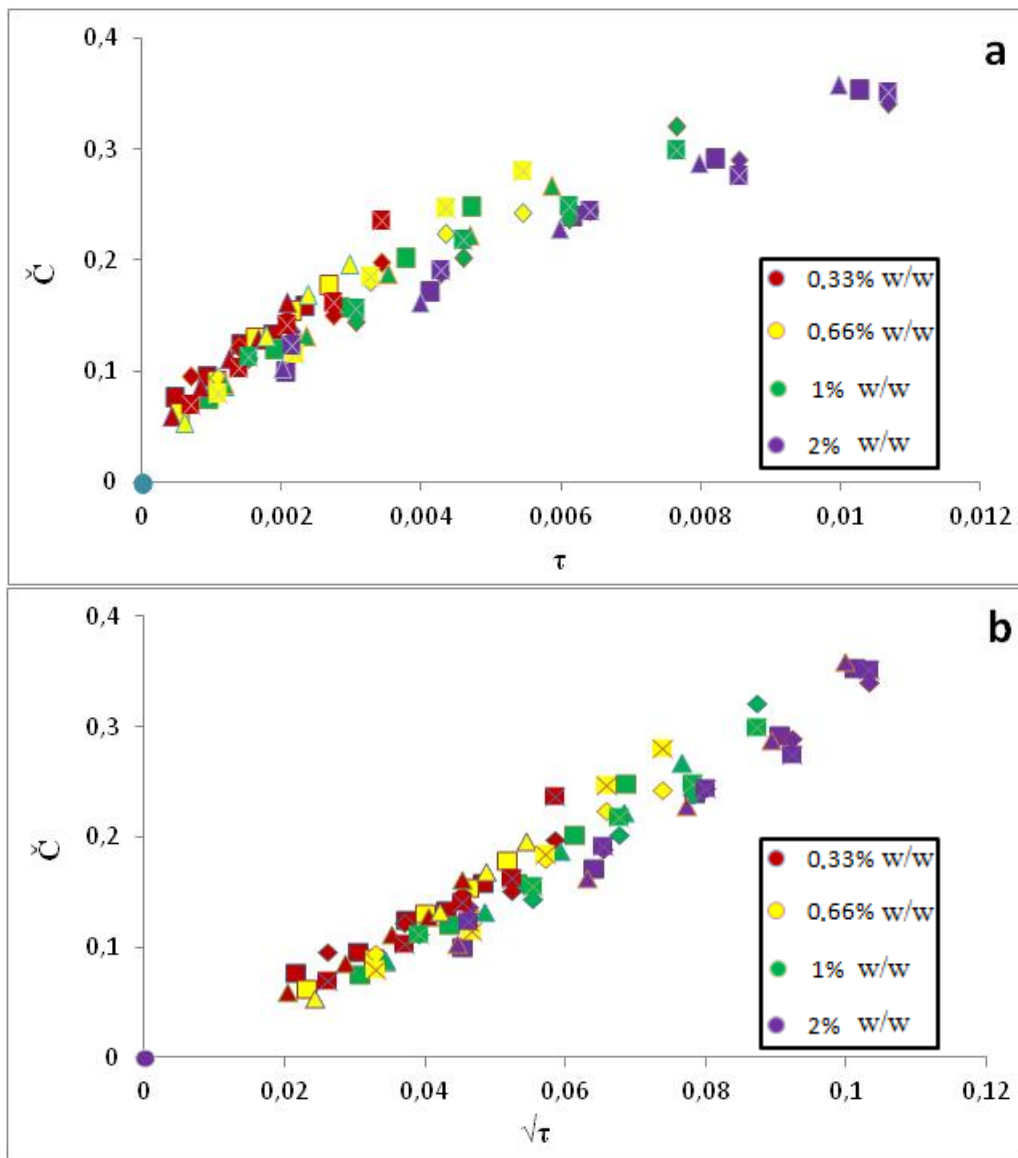
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633 **Figure 1:** Comparison of the experimental concentrations of 3,4-dihydroxyphenylacetic (a), caffeic (b), protocatechuic (c) and p-coumaric (d) acids in
634 rice grains (dots) with the simulation results (solid lines) obtained using the fitted D_i values. Dots and lines corresponding to boiling in 0.33% w/v
635 concentration of spearmint extract are in red, while results concerning 0.66%, 1% and 2% w/v concentrations of extract are presented in purple, green
636 and light blue, respectively. Error bars represent the standard deviation of the samples (n=3).



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639 **Figure 2:** Total polyphenol content of rice flour as a function of boiling time and
640 initial concentration of spearmint extract. All values are expressed as mean values of
641 mg GAE/g dry rice flour and error bars represent the standard deviation of samples
642 (n=3).



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645 **Figure 3:** Master curves indicating the correlation between dimensionless
 646 concentration (\check{C}) of examined compounds in rice grains during hydrothermal
 647 treatment and dimensionless time of the process (either τ (a) or $\sqrt{\tau}$ (b)). Symbols
 648 correspond to: 3,4-DiOH phenylacetic acid (squares), Caffeic acid (rhombus),
 649 Protocatechuic acid (triangles) and p-Coumaric acid (squares with X). Points
 650 corresponding to the 0.33% w/v herbal extract concentrations are in red. Yellow
 651 represents the 0.66% w/v data, while green and purple are for the 1% w/v and 2% w/v
 652 concentrations, respectively.

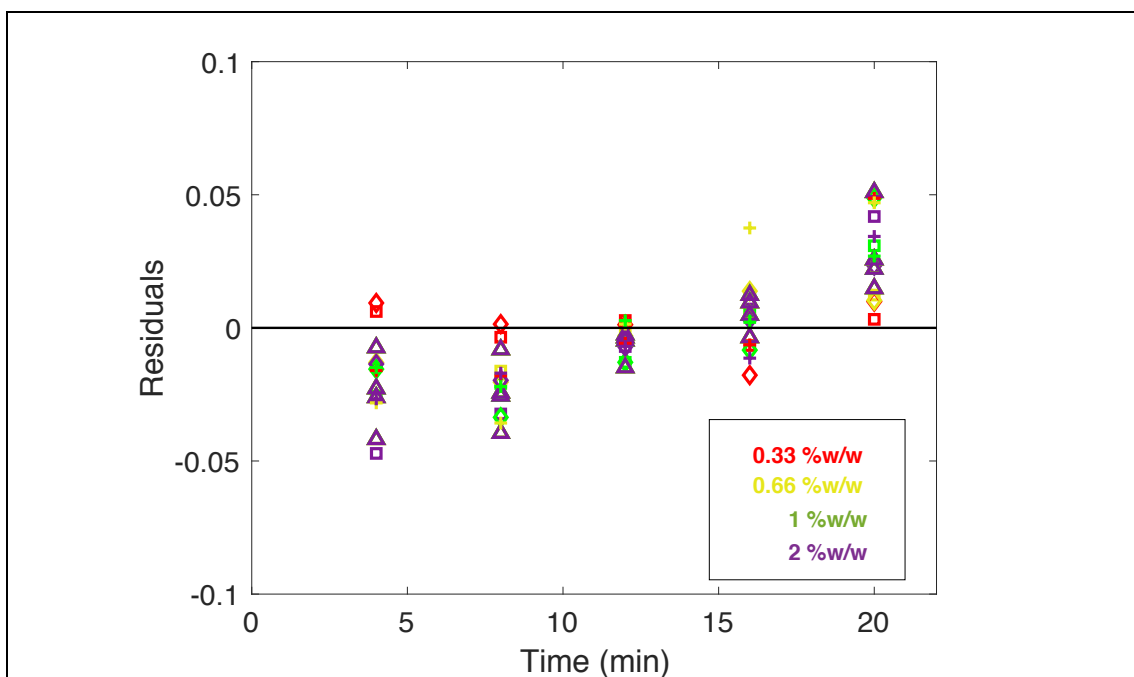
653

654 **Supplementary Table 1:** Molecular weight and hydrophobicity factor ($\log P$) of
655 major phenolic acids adsorbed in rice grains (Source: PUBCHEM). By P is
656 symbolized the partition coefficient of each compound in a biphasic system of liquid solvents,
657 one polar solvent (water) and a non-polar solvent (*n*-octanol).

Phenolic acids	Molecular Weight	Estimated value of $\log P$
Caffeic	180	1,2
3,4 di-OH Phenylacetic	168	0,5
p-Coumaric	164	1,5
Protocatechuic	154	1,1

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661 **Supplementary Figure 1:** Residuals of the fitted data along time, for all the
 662 concentrations and compounds.

663 Legend: 3,4-DiOH phenylacetic acid (squares), Caffeic acid (rhombus),
 664 Protocatechuic acid (triangles) and p-Coumaric acid (crosses).

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