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Title: Kinetics of carotenoids degradation and furosine formation in dried apricots (*Prunus armeniaca* L.)

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Abstract: The kinetics of carotenoid and color degradation, furosine formation and antioxidant activity were investigated in apricot fruits during convective heating at 50, 60 and 70°C. Degradation of carotenoids and color, expressed as total color difference (TCD), followed a first and zero order kinetic, respectively. The activation energy ( $E_a$ ) for carotenoids degradation ranged from 73.7 kJ/mol for 13-cis- $\beta$ -carotene to 120.7 kJ/mol for lutein, being about 91 kJ/mol for  $\beta$ -carotene. Violaxanthin and antheraxanthin were the most susceptible to thermal treatment. The furosine evolution was fitted at zero order kinetic model. The  $E_a$  for furosine formation was found to be 83.3 kJ/mol and the  $Q_{10}$  (temperature coefficient) varied from 1.59 to 4.14 at the temperature ranges 50-60°C and 60-70°C, respectively.

Dear Editor-in-Chief: A. Sant'Ana,

We submit the original paper “Kinetics of carotenoids degradation and furosine formation in dried apricots (*Prunus armeniaca* L.)”,

by A. Fratianni, S. Niro, M.C. Messina, L. Cinquanta, G. Panfili, D. Albanese, M. Di Matteo;

for publication in “*Food Research International*”, *Special Issue on “Carotenoids in food and health”*”

This study aimed at investigating the kinetics of color and carotenoid degradation and furosine formation, together with antioxidant activity, in apricot fruits, during convective heating.

We hope this paper is of sufficient interest and is worth of publication in: Special Issue on “Carotenoids in food and health”

Yours faithfully,

Prof. Luciano Cinquanta

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### **Highlights Fratianni et al.**

Kinetics of carotenoids degradation in dried apricots were evaluated

The activation energy  $E_a$  for carotenoids was 97 kJ/mol, higher than color evolution.

Violaxanthin and anteraxanthin were the most susceptible to thermal treatment

$Q_{10}$  values of furosine ranged from 1.59 to 4.14 at 50-60°C and 60-70°C, respectively



26 **Abstract**

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28 investigated in apricot fruits during convective heating at 50, 60 and 70°C. Degradation of carotenoids  
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31 cis- $\beta$ -carotene to 120.7 kJ/mol for lutein, being about 91 kJ/mol for  $\beta$ -carotene. Violaxanthin and  
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33 order kinetic model. The  $E_a$  for furosine formation was found to be 83.3 kJ/mol and the  $Q_{10}$   
34 (temperature coefficient) varied from 1.59 to 4.14 at the temperature ranges 50-60°C and 60-70°C,  
35 respectively.

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49 **Keywords:** Apricot; Carotenoids; Color; Drying; Furosine; Kinetics.



51 **1. Introduction**

52 Apricots are a good source of carotenoid compounds, which are beneficial for human health.  
53 Carotenoids are responsible for the color of a wide variety of foods and color is an important attribute,  
54 which significantly affects the consumer perception. Carotenoids are important, from a nutritional point  
55 of view, because some of them have provitamin A activity (Simpson & Chichester, 1981). Moreover,  
56 they are beneficial to human health, being scavengers of reactive species and thus showing antioxidant  
57 activity (Krinsky, 2001), protecting humans from serious disorders such as skin disorders,  
58 cardiovascular disease, several forms of cancer and age-related diseases of the eye (Meléndez-  
59 Martínez, Vicario, & Heredia, 2004). Color and carotenoid evolution are used as quality markers for  
60 several food products and processing (Fратиanni, Irano, Panfili, & Acquistucci 2005; Frатиanni,  
61 Cinquanta, & Panfili, 2010; Frатиanni, Di Criscio, Mignogna, & Panfili, 2012; Frатиanni, Giuzio, Di  
62 Criscio, Flagella, & Panfili, 2013a; Frатиanni, Albanese, Mignogna, Cinquanta, Panfili, & Di Matteo,  
63 2013b). The main pigment of apricot is  $\beta$ -carotene, the major important source of vitamin A,  
64 accounting for more than 50% of the total carotenoid content (Fратиanni et al., 2013b; Kurz, Carle, &  
65 Schieber, 2008; Sass-Kiss, Kiss, Milotay, Kerek, & Toth-Markus 2005). Degradation of carotenoids  
66 and color, together with their antioxidant activity is a common phenomenon during the thermal  
67 treatment that have been developed to extend the shelf life of fruit, vegetables and their products  
68 (Demiray, Tulek, & Yilmaz, 2013; Frатиanni et al., 2010; Frатиanni et al., 2013b, Yemiş, Bakkabaşı,  
69 Artik, 2012, Kamiloglu, Toydemir, Boyacioglu, Beekwilder, Hall, & Capanoglu, 2016; Saxena, Maity,  
70 Raju, and Bawa, 2012). Being highly unsaturated, carotenoids are very prone to oxidation, which  
71 causes color loss. Moreover, depending on different factors (food matrix, food structure and  
72 composition, pH, heat, oxygen tension, presence of other antioxidants) (Penicaud, Achir, Dhuique-  
73 Mayer, Dornier, & Bohuon, 2011) carotenoids are expected to undergo two types of changes:  
74 degradation and isomerization. Thermal treatment induces variable losses, depending on its severity

75 and length (Fратиanni, et al. 2010, 2013b; Gama & De Sylos, 2007) and leads to structural modifications  
76 such as cis-isomerization (Schieber & Reinhold, 2005). The thermal lability of carotenoids is also  
77 influenced by their chemical structure. Thus, carotenoid esters showed an increased stability compared  
78 to the corresponding non-esterified carotenoids (Schweiggert, Kurz, Schieber, & Carle, 2007). The  
79 carotenoids and  $\beta$ -carotene degradation during thermal treatment has been reported mainly as first-  
80 order kinetics and seldom as zero-order kinetics (Demiray et al., 2013; Di Scala & Crapiste, 2008;  
81 Saxena, et al., 2012). Quantitative kinetic models describing carotenoid and color changes as a function  
82 of process parameters are valuable tools for process optimization. Other process indicator that usually  
83 takes place during thermal processing of food is the Maillard reaction and the evaluation of the initial  
84 steps provides useful information for processing control. The formation of the “Amadori compounds”  
85 that takes place during the early stage of the Maillard reaction is considered as the key factor. To date  
86 the furosine assay, which is specific for  $\epsilon$ -N-deoxy-ketosyllysine (Amadori compound), remains the  
87 most sensitive and most accepted method for determining the extent of “early” Maillard reactions  
88 (Rufián-Henares, García-Villanova, & Guerra-Hernández, 2008). It is one of the most commonly used  
89 markers for evaluating the raw materials, the type and conditions of heat treatment, and the storage  
90 conditions (Acquistucci, Panfili, & Marconi, 1996; Caboni, Boselli, Messia, Velazco, Fratianni, Panfili,  
91 & Marconi, 2005; Marconi, Panfili, & Acquistucci, 1997; Marconi, E. Caboni, Messia, & Panfili,  
92 2002). Furosine (2-furoylmethyl-lysine) was the main 2-furoylmethyl derivative observed in dried  
93 apricot samples (Sanz, del Castillo, Corzo, & Olano, 2001) and in different vegetable and vegetable  
94 products, where the drying process can cause the non-enzymatic condensation of carbonyl and amino  
95 groups of sugars and protein (amino acids), leading to the browning of the product (Cardelle-Cobas,  
96 Moreno, Corzo, Olano, & Villamiel, 2005; Mendoza, Olano & Villamiel, 2002). The main objective of  
97 this study was to investigate the kinetic of carotenoid and color degradation together with the furosine

98 evolution, in order to use them as quality markers of thermal damage of dried apricots. In addition, the  
99 evolution of the antioxidant activity of both lipophilic and hydrophilic compounds was evaluated.

100

## 101 **2. Materials and methods**

### 102 *2.1 Materials*

103 Fresh, fully ripe apricots var. *Pellecchiella* (*Prunus armeniaca* L.) were obtained from the local  
104 farmer (Napoli, Italy). About 900 g apricots were halved and pitted. The apricots had a spherical shape  
105 with a diameter of about 6.0 cm and a thickness (halved apricot) of about 1.2 cm. One half was  
106 subjected to the drying treatment (HA), while the other half was used as time zero control and was  
107 immediately stored at  $-20^{\circ}\text{C}$ . Every couple was labeled for the following identification. Apricots were  
108 dried in a hot-air convective HA and oven at  $50^{\circ}\text{C}$  (HA50),  $60^{\circ}\text{C}$  (HA60) and  $70^{\circ}\text{C}$  (HA70). All  
109 experiments were performed in triplicate. Drying tests were performed in a hot-air convective oven  
110 (Zanussi FCV/E6L3, Zanussi Professional, Pordenone, Italy), with an air speed of 2.3 m/s. Drying was  
111 stopped, until a final content of relative moisture equal to about 20% was reached. After sampling,  
112 apricots were freeze dried by using a freeze dryer Genesis 25SES (VirTis Co., Gardiner, NY).

113

### 114 *2.2. Furosine determination*

115 Furosine content was determined by HPLC, according to Resmini, Pellegrino, and Battelli (1990). A  
116 sample amount, corresponding to about 30-70 mg of protein, was hydrolyzed under nitrogen with 8 ml  
117 of 8 N HCl at  $110^{\circ}\text{C}$  for 23 h. Afterwards, the hydrolyzate (0.5 ml) was purified on a Sep-Pak C18  
118 cartridge (Waters), diluted and analyzed by HPLC (Waters), equipped with an Alltech furosine-  
119 dedicated column (250 x 4.6 mm) (Alltech, Derfield, IL, USA). Furosine standard was purchased from  
120 Neosystem Laboratoire (Strasbourg, France).

121

122 *2.3. Color measurement*

123 Color of fresh and HA samples was measured, at regular time intervals, by using a tri-stimulus  
124 colorimeter CR-200 Chromometer (Minolta, Japan) having an aperture size of 10 mm. Hunter values  
125 ( $L^*$ ,  $a^*$ ,  $b^*$ ) were monitored on the surface of fresh and dried samples; nine set of data were obtained  
126 from the three replicates with three measurements for each replicate (Albanese, Cinquanta, & Di  
127 Matteo, 2007). Color parameters were  $L^*$  value (lightness),  $b^*$  value (yellowness and blueness) and  $a^*$   
128 value (redness and greenness). The total color difference (TCD), was used to express the overall color  
129 change during the thermal process and was calculated by using the Eq. 1 as in Saxena et al. (2012):

130

$$131 [(L - L_0)^2 + (a - a_0)^2 + (b - b_0)^2]^{1/2} \quad (1)$$

132

133 where  $L$ ,  $a$ ,  $b$  are the values at time  $t$ ;  $L_0$ ,  $a_0$ ,  $b_0$  are the values at time zero.

134

135 *2.4. Carotenoid extraction and determination*

136 Carotenoids were extracted according to the method reported by Panfili, Fratianni, and Irano (2004)  
137 and Fratianni et al. (2013b, 2015) with slight modifications: 0.5 g of freeze dried apricots was  
138 saponified under nitrogen in a screw capped tube by adding 5 mL of ethanolic pyrogallol (60 g/L) as  
139 antioxidant, 3 mL of ethanol (95%), 1 mL of sodium chloride (10 g/L), and 2 mL of potassium  
140 hydroxide (600 g/L). The tubes were placed in a 70°C water bath and mixed every 5–10 min during  
141 saponification. After alkaline digestion at 70°C for 45 min, the tubes were cooled in an ice bath and 15  
142 mL of sodium chloride (10 g/L) were added. The suspension was then extracted with 15 mL portions of  
143 n-hexane/ ethyl acetate (9:1, v/v) until it became colorless. Recovery tests made on samples and pure  
144 standards showed that the used saponification procedure did not cause isomerization/degradation of the  
145 investigated carotenoids (Fratianni et al., 2010; Panfili et al., 2004). The organic layers, containing

146 carotenoids, were collected and evaporated to dryness; the dry residue was dissolved in  
147 methanol:MTBE (50:50 v/v) and an aliquot of the carotenoid extract (25  $\mu$ l) was separated, as in  
148 Mouly, Gaydou, and Corsetti (1999), by a reverse-phase HPLC system. A HPLC Dionex (Sunnyvale,  
149 CA) analytical system consisting of a P680 solvent delivery system and a 25  $\mu$ l injector loop  
150 (Rheodyne, Cotati) was used. Separation was performed by a YMC (Hampstead, NC, USA) stainless  
151 steel column (250 $\times$ 4.6 mm i.d.), packed with 5  $\mu$ m silica spheres that were chemically bonded with  
152 C30 material, at a flow rate of 1 mL/min. The mobile phase was methanol:MTBE:water (v/v/v). The  
153 eluted compounds were monitored by a photo-diode array detector (Dionex, Sunnyvale) set at 430 nm.  
154 Data were stored and processed by a Dionex Chromeleon Version 6.6 chromatography system  
155 (Sunnyvale, CA).

156

### 157 *2.5. Carotenoid identification and quantification*

158 Antheraxanthin, lutein, zeaxanthin,  $\beta$ -cryptoxanthin, 9-cis- $\beta$ -carotene, 13-cis- $\beta$ -carotene and  $\beta$ -  
159 carotene were identified on the basis of diode array spectral characteristics, retention times, and relative  
160 elution order, compared with known commercially available standards. Violaxanthin, antheraxanthin,  
161  $\alpha$ -carotene, 9-cis- $\beta$ - carotene, and 13-cis- $\beta$ -carotene standards were purchased from CaroteNature  
162 (Lupsingen, Switzerland); lutein, zeaxanthin, and  $\beta$ -cryptoxanthin were from Extrasynthese (Z.I. Lyon-  
163 Nord, Genay, France), all-trans- $\beta$ -carotene was from Sigma Chemicals (St. Luis, MO, USA). Purity for  
164 all standards was above 95% (as certified by the suppliers), except for zeaxanthin, which was 90%  
165 pure. All carotenoid standards were spectrophotometrically quantified and diluted in methanol:acetone  
166 (2:1, v/v) to give a final concentration of 25  $\mu$ g/ml. The concentration range was 5– 25  $\mu$ g/ml for every  
167 carotenoid standard. Identified carotenoids were quantified using calibration curves of respective  
168 standard solutions. Total carotenoids were expressed as a sum of single quantified carotenoids.

169

170 2.6. *ABTS assay*

171 The ABTS (2,2-Azino-bis (3-ethylbenzothiazoline-6-sulfonicacid) diammonium salt) antioxidant  
172 activity was determined using ABTS<sup>\*+</sup> radical cation decolorization assay (Re, Pellegrini, Proteggente,  
173 Pannala, Yang, & Rice-Evans, 1999). Proper dilutions of the lipophilic extracts for carotenoid analysis  
174 were added to 1 mL of diluted ABTS<sup>\*+</sup> solution; the mixture was vortexed and the absorbance was read  
175 after 1 min. The disappearance of ABTS<sup>\*+</sup> was determined by measuring the decrease of absorbance at  
176 734 nm for 20 min. The percentage inhibition of absorbance was calculated and plotted as a function of  
177 concentration. The blank was run with ethanol and the standard curve was prepared using 0-22 nmoles  
178 Trolox. Results were analyzed by reference to trolox and expressed as micromolar trolox equivalent  
179 antioxidant capacity (micromoles Trolox/g db). Each analysis was performed in triplicate.

180

181 2.7. *DPPH assay*

182 The antioxidant activity of the hydrophilic extract was measured with the DPPH assay as in  
183 Albanese, Cinquanta, Cuccurullo, and Di Matteo (2013).

184

185 2.8. *Kinetic Parameters*

186 The evolution of TCD, single carotenoids and total carotenoids (TCAR) during HA at 50, 60 and  
187 70°C, was modeled by Eqs. 2–3 for a zero and first-order reaction, respectively:

188

189  $C = C_0 \pm k_0 t$  (2)

190  $\ln C = \ln C_0 \pm k_1 t$  (3)

191

192 where C is the concentration (%) at time t; C<sub>0</sub>, the concentration (%) at time zero; k<sub>0</sub>, the zero order rate  
193 constant (h<sup>-1</sup>); k<sub>1</sub>, the first-order rate constant (h<sup>-1</sup>); t, the drying time (h). The efficacy of fitted model  
194 was determined by the highest correlation coefficient (R<sup>2</sup>).

195 Temperature dependence of carotenoid and TCD degradation and furosine formation was determined  
196 by the Arrhenius equation (Eq. 4) and Q<sub>10</sub> value (Eq. 5):

$$197 \quad k = k_0 \times e^{[-E_a/RT]} \quad (4)$$

198 where E<sub>a</sub>, the activation energy (kcal/mol); k, the rate constant; k<sub>0</sub>, the pre-exponential factor; R, the  
199 universal gas constant (8.314 J/(mol. K), T, the absolute temperature (K).

$$200 \quad Q_{10} = k_2/k_1^{10/T_2-T_1} \quad (5)$$

201 where k<sub>2</sub> is the rate constant of the furosine formation and TCD and carotenoid degradation at T<sub>2</sub>  
202 temperature; k<sub>1</sub> is the constant rate of the furosine formation and TCD and carotenoid degradation at T<sub>1</sub>  
203 temperature.

204

## 205 *2.9. Statistical analysis*

206 Drying tests, for all temperatures, were performed in triplicate. Data reported are means and  
207 standard deviations calculated from three replicates. The analysis of variance (ANOVA) was applied to  
208 the data. The least significant differences were obtained using an LSD test (P < 0.05). Statistical  
209 analysis was performed using an SPSS version 13.0 for Windows (SPSS, Inc., Chicago, IL, USA).

210

## 211 **3. Results and discussion**

### 212 *3.1. Drying curves*

213 In the early stages of convective drying sensible heating dominates while, in the later stages, the  
214 progressive reduction in the evaporation rates was responsible for the lower drying rates. When the  
215 internal resistance to the transport of liquid water to the surface increases, thereby lowering the drying  
216 rate, the falling rate period occurs. Hence, internal diffusion may be assumed as the mechanism  
217 responsible for water loss during the drying process. At lower drying temperatures (50 °C) a more  
218 uniform moisture distribution exists, which allows the sample to continue to shrink until the last stages  
219 of drying, ending after about 25 hours, with a low porosity (Fig. 1). On the contrary, at highest air  
220 temperatures (70°C) the drying process lasts about 10 hours, but case hardening of the surface may  
221 occur and the volume of the sample becomes fixed at an earlier stage, inducing less shrinkage and a  
222 more intensive pore formation (Bonazzi & Dumoulin, 2011).

223

### 224 3.2. *Furosine evolution*

225 The Maillard reaction is strongly influenced by the temperature and the moisture content of the food  
226 during drying (Labuza, & Saltmarch, 1991). In addition, also the reducing sugars play an important role  
227 in the furosine formation in some groups of vegetables (Rufían-Henares et al., 2008). Furosine values  
228 were determined at 2 h, at the middle and to the end of drying. The furosine evolution was fitted at zero  
229 order kinetic model (Fig. 2). During drying, furosine values went from 2.4 to 28.1 mg/100g protein,  
230 from 3.6 to 40.1 mg/100g protein and from 4.4 to 70.4 mg/100g protein for HA50, HA60 and HA70,  
231 respectively. The  $E_a$  for furosine formation was found to be 83.3 kJ/mol and the  $Q_{10}$  values went from  
232 1.59 to 4.14 at the temperature ranges 50-60°C and 60-70°C, respectively (Table 2). The parameter  $Q_{10}$   
233 describes the temperature dependence of a reaction as the factor by which the reaction rate is changed  
234 when the temperature is increased by 10°C. It can be concluded that the browning increases markedly  
235 when the temperature increases from 60 to 70°C.

236

237 *3.3. Impact of thermal treatment on color parameters and carotenoids*

238 Carotenoid profiles in fresh apricot showed seven different identified compounds, in the following  
239 elution order: (i) epoxy-carotenoids: violaxanthin, antheraxanthin, (ii) hydroxycarotenoids: lutein,  
240 zeaxanthin,  $\beta$ -cryptoxanthin and (iii) carotenes: 13-cis- $\beta$ -carotene, all-trans- $\beta$ -carotene and 9-cis- $\beta$ -  
241 carotene. Total carotenoid content in fresh fruits was 137.8 mg/kg db: the main compound was  $\beta$ -  
242 carotene (65%), followed by  $\beta$ -cryptoxanthin (11%), 13-cis- $\beta$ -carotene (9%), 9-cis- $\beta$ -carotene (7%),  
243 violaxanthin (5%), lutein (2%) and antheraxanthin (about 1%), according to Fratianni et al. (2013b).  
244 The amount of the main representative identified carotenoids in fresh and HA dried apricots at the end  
245 of the drying treatment are reported in Table 1. At the end of the drying treatments the total carotenoid  
246 (TCAR) content significantly reduced to about 40% and 45% from fresh fruit at 50°C and 60°C,  
247 respectively, while the extent of TCAR degradation increased at 70 °C, with about a 70% decrease. The  
248 reduction observed for  $\beta$ -carotene was similar to that of total carotenoids. In a previous work (Fratianni  
249 et al., 2013b) we observed a lower decrease in TCAR, about 20% for HA60 samples and 40% for  
250 HA70 samples. Violaxanthin and antheraxanthin were the most susceptible to thermal treatment;  
251 antheraxanthin, in particular, was found to significantly decrease ( $P < 0.05$ ) during the first hours of  
252 drying and to disappear at the end of drying in all HA samples. The high susceptibility of 5,6-  
253 epoxy-carotenoids (violaxanthin and antheraxanthin) was also observed in previous works (Fratianni et  
254 al., 2010; Fratianni et al., 2013b) and by other authors (Meléndez-Martínez, Britton, Vicario, &  
255 Heredia, 2008), which found also their isomerization into their corresponding 5,8-epoxyderivatives,  
256 however, this isomerization was not observed. Several studies report the decrease of trans  $\beta$ -carotene  
257 and the concomitant increase in cis isomers in vegetables subjected to thermal processes (Penicaud et  
258 al., 2011; Schieber & Reinhold, 2005). However, in our case no rising of cis isomers, 9-cis  $\beta$ -carotene  
259 and 13-cis  $\beta$ -carotene, was found during drying treatment, indicating the predominance of a higher  
260 degradation rate upon isomerization. The above reported different results could be due to the fact that

261 isomerization and degradation processes could depend also on the structure and cellular organization of  
262 carotenoids in the food matrix, water activity (Lavelli, Zanoni, & Zaniboni, 2007), pH, oxygen  
263 occurrence and the interactions with other antioxidants (Dragovic-Uzelac, Levaj, Mrkic, Bursac, &  
264 Boras, 2007, Penicaud et al., 2011). Degradation of carotenoid content was found to follow first-order  
265 reaction kinetics, as reported in Figs 3 and 4 for  $\beta$ -carotene and TCAR, respectively, where the  
266 negative slope shows the degradation of content as a function of time. As for visual color, with the  
267 increase in time and temperature the lightness ( $L^*$  value) of all HA samples tended to decrease, while  
268 the  $b^*$  value (yellowness) decreases at 60°C and 70°C (data not shown). The alteration in total color  
269 difference (TCD) was modeled using the Eq. 1. Zero order kinetic plots, showing the change of TCD in  
270 function of time, are reported in Fig. 5. At the end of drying the TCD increases from 0 to 7.6, 13.1 and  
271 14.0 at 50, 60 and 70°C, respectively. Rate constants at different drying temperatures and  $Q_{10}$  values for  
272 single, total carotenoids (TCAR) and TCD are presented in Table 2.  $Q_{10}$  values for TCAR were similar  
273 at all the analyzed temperature ranges and close to those of TCD in the range 50-60°C.  $Q_{10}$  values for  
274 TCD were slightly lower in the range 60-70°C. From  $Q_{10}$  values for single carotenoids emerged that the  
275 most susceptible carotenoid to the temperature increase from 50 to 60°C was lutein. These data are in  
276 accordance with previous results (Fратиanni, et al., 2010) where lutein, together with violaxanthin, was  
277 found to be the most sensitive carotenoid to temperature changes. The  $E_a$  for change in TCD was found  
278 to be about 67 kJ/mol. The  $E_a$  for the degradation process of carotenoids was observed in the range  
279 from 73.7 kJ/mol for 13-cis- $\beta$ -carotene to 120.7 kJ/mol for lutein, being about 91 kJ/mol and 97 kJ/mol  
280 for  $\beta$ -carotene and TCAR, respectively. Several literature works show variable results, with a  $E_a$  range  
281 from 14 to 188 kJ/mol (Ahmed, Shivhare, & Sandhu, 2002; Penicaud et al., 2011; Saxena et al., 2012).  
282 The observed difference in susceptibility of carotenoid content to drying temperatures might be due to  
283 differences in processing, in type of fruit, degree of ageing and carotenoids composition. Moreover, the  
284  $\beta$ -carotene reaction may be influenced by the presence of co-substrates, which can be found in different

285 concentration in food matrices (Penicaud et al., 2011). A good correlation, at all drying temperatures,  
286 was found between the evolution of total carotenoid content and TCD ( $r > 0.90$ ), of TDC and furosine ( $r$   
287  $> 0.95$ ), and of total carotenoids and furosine ( $r > 0.95$ ).

288

### 289 *3.4. Impact of thermal treatment on the antioxidant capacity*

290 The antioxidant activity of lipophilic extracts (ABTS assay) of fresh samples, was found to be about  
291  $1.7 \mu\text{mol Trolox/g db}$ , while that of hydrophilic extract (DPPH assay) was found to be about 13.5 (%  
292 inhibition of DPPH  $\cdot \text{mg}^{-1} \text{db}^{-1}$ ). Similar decreases ( $P < 0.05$ ) in the antioxidant activity of hydrophilic  
293 extracts and lipophilic ones were observed at the end of drying, being about 35-40%, at all the applied  
294 temperatures, (Figs. 6A and 6B). In addition, the evolution of the antioxidant activity, with the  
295 exception of HA50 samples at the middle of the drying process, was the same for both extracts, showing  
296 a decrease until the middle of the drying time, followed by no further decreases until the end of the  
297 process. Decreases in the antioxidant activities under drying conditions have been found by different  
298 authors in several fruit and vegetable products (Duru, Karadeniz, & Erge, 2012; Kamiloglu et al., 2016;  
299 Sogi, Siddiq, & Dolan, 2015). In some case, different results were observed for dried apricots, with an  
300 increase in DPPH during processing, probably due to the formation of new compounds of antioxidant  
301 activity or to the presence of interfering substances, such as sulphites (Igual, García-Martínez, Martín-  
302 Esparza, Martínez-Navarrete, 2012).

303

## 304 **4. CONCLUSIONS**

305 On dependence of the applied drying temperatures, a statistically significant decrease of carotenoids,  
306 visual color (TCD) and antioxidant activities, together with an increase of furosine, occurred.  
307 Carotenoid degradation was adequately described by a first-order kinetic model, with activation energy

308  $E_a$  of 97 kJ/mol, higher than that of TCD, which was about 67 kJ/mol. In particular, among carotenoids,  
309 the epoxy-carotenoids violaxanthin and antheraxanthin confirmed to be adequate markers for the  
310 evaluation of drying process.

311

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454 **Figure legend**

455

456 **Fig.1.** Plots of the drying process of apricots at different temperatures. Squares, 50 °C; diamonds, 60  
457 °C; triangles, 70 °C

458 **Fig.2.** Furosine evolution during apricot drying at different temperatures. Squares, 50 °C; diamonds, 60  
459 °C; triangles, 70 °C

460 **Fig.3.** Kinetic plots of changes of  $\beta$ -carotene in apricots dried at different temperatures. Squares, 50 °C;  
461 diamonds, 60 °C; triangles, 70 °C.

462 **Fig.4.** Kinetic plots of changes of total carotenoids (TCAR) in apricots dried at different temperatures.  
463 Squares, 50 °C; diamonds, 60 °C; triangles, 70 °C.

464 **Fig.5.** Kinetic plots of changes of total color difference (TCD) in apricots dried at different  
465 temperatures. Squares, 50 °C; diamonds, 60 °C; triangles, 70 °C.

466 **Fig.6.** Effect of apricot drying at different temperatures on the antioxidant activity (A) DPPH (B)  
467 ABTS.

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Figure  
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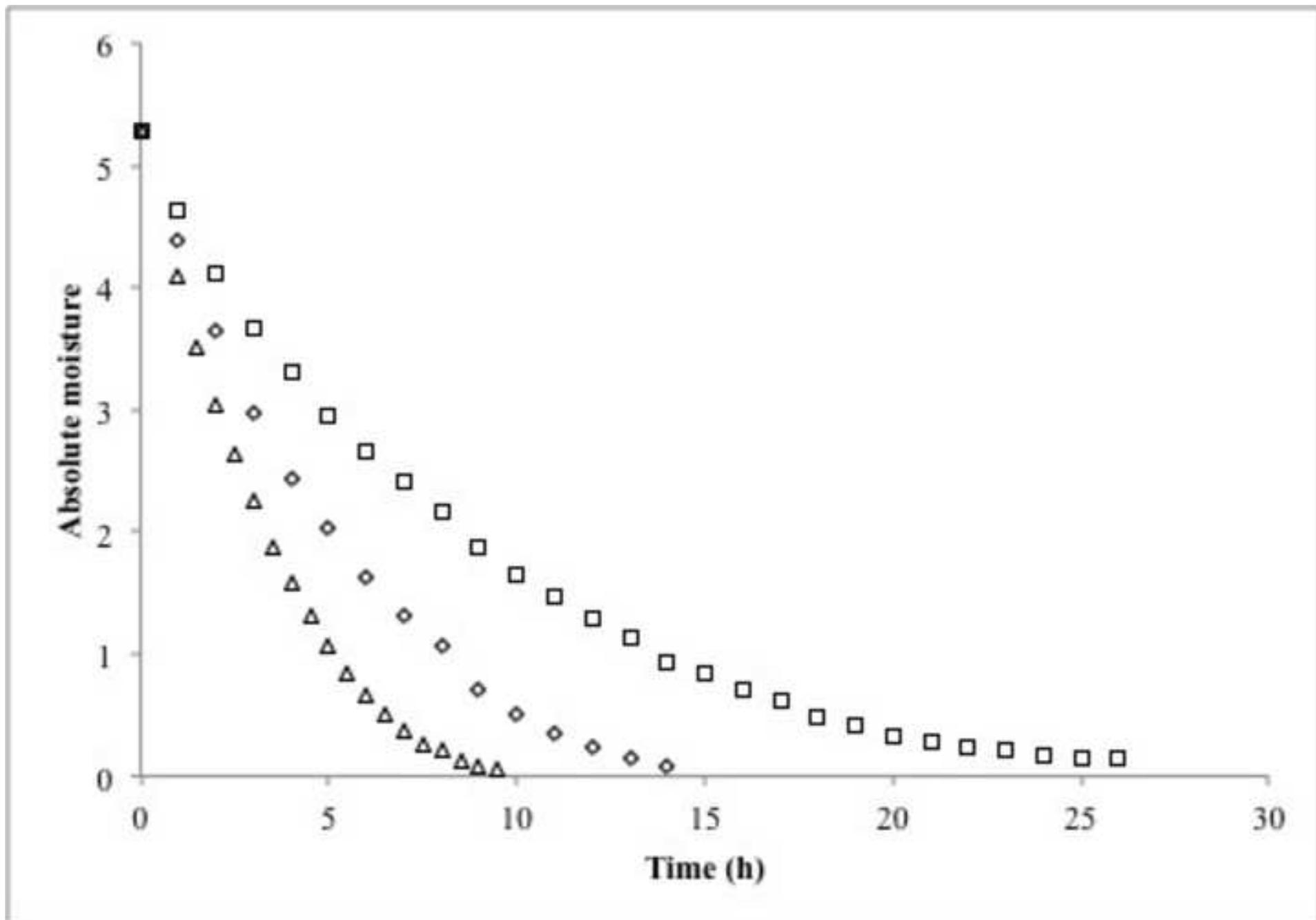


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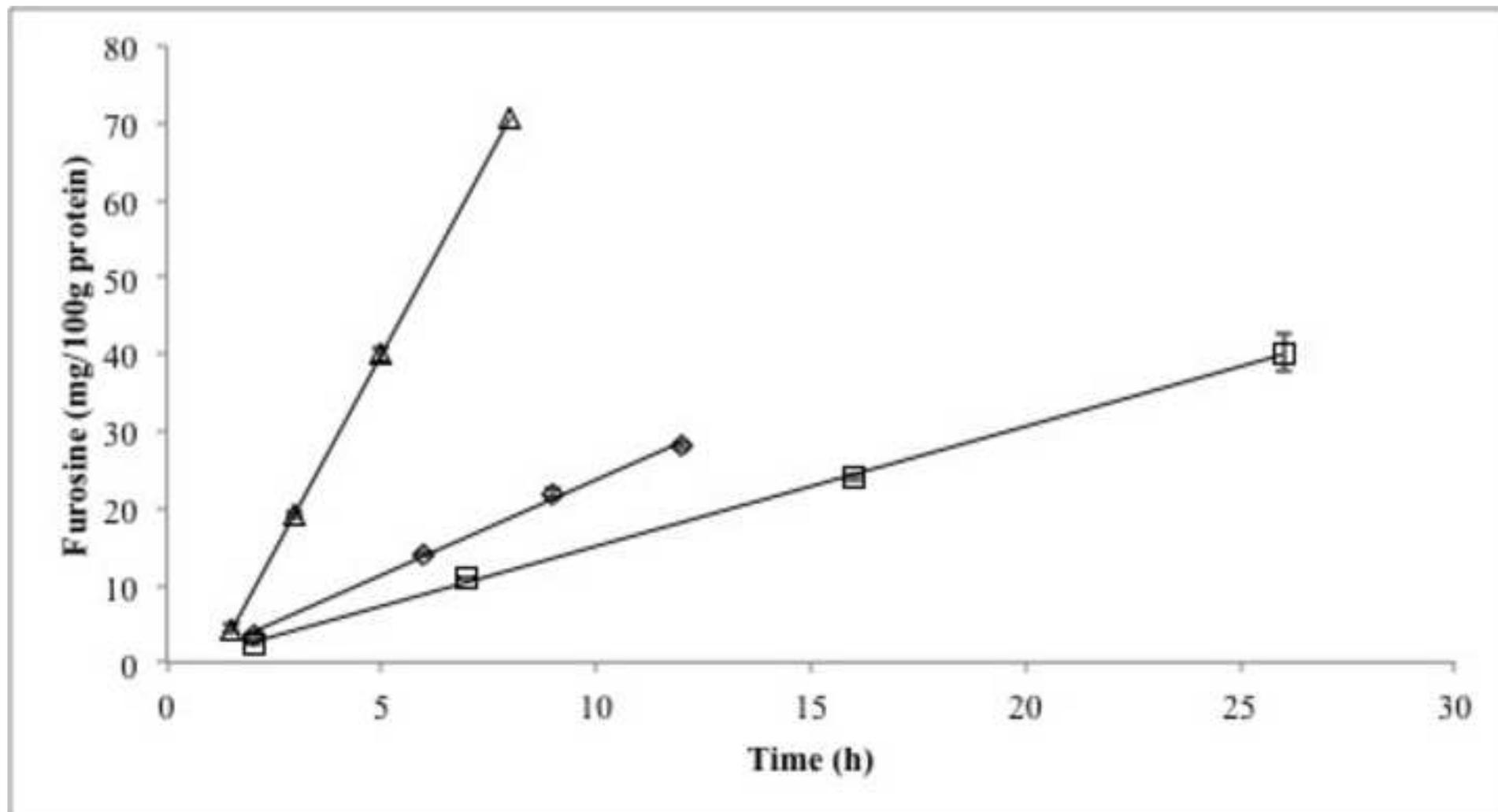


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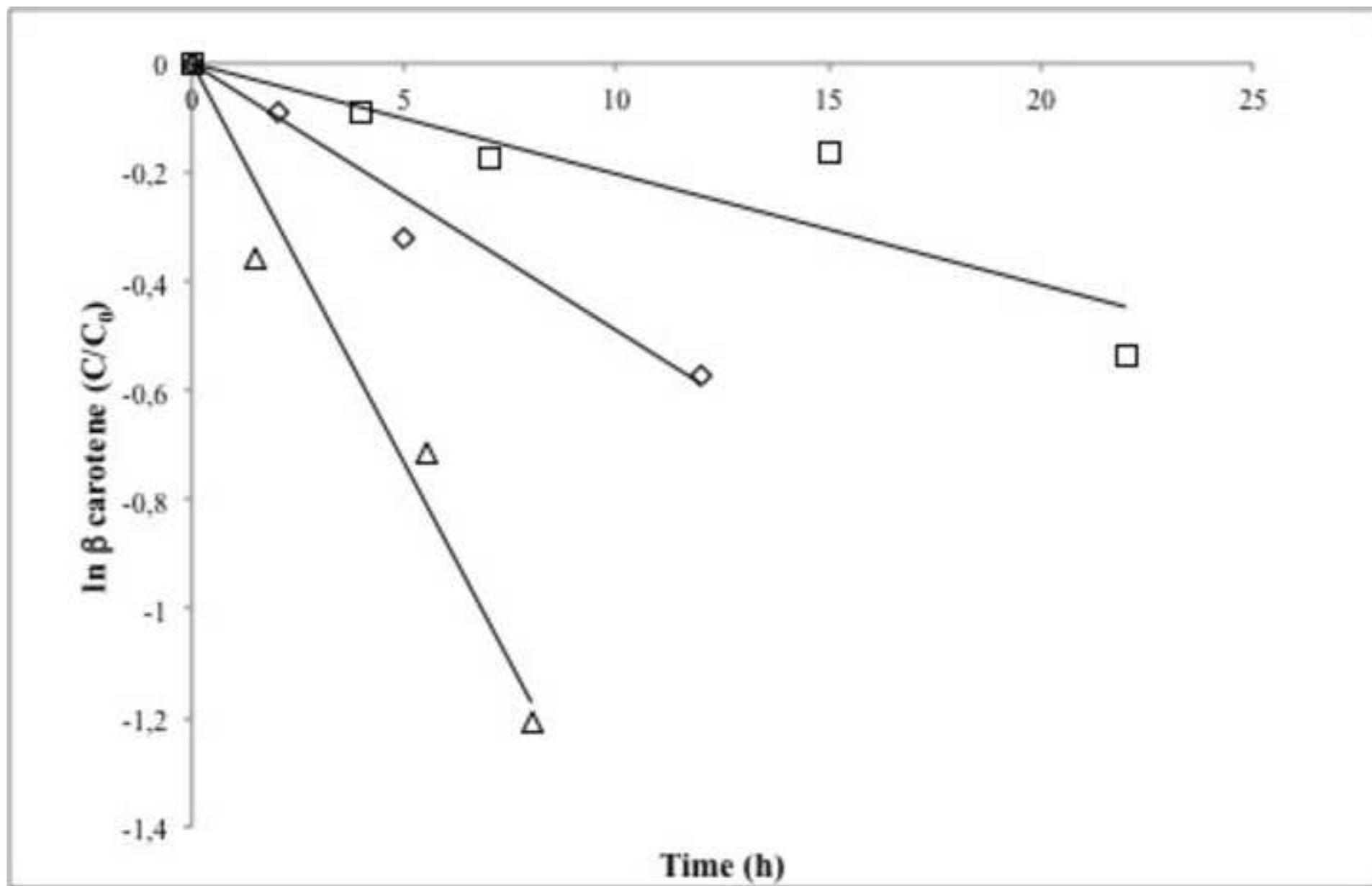


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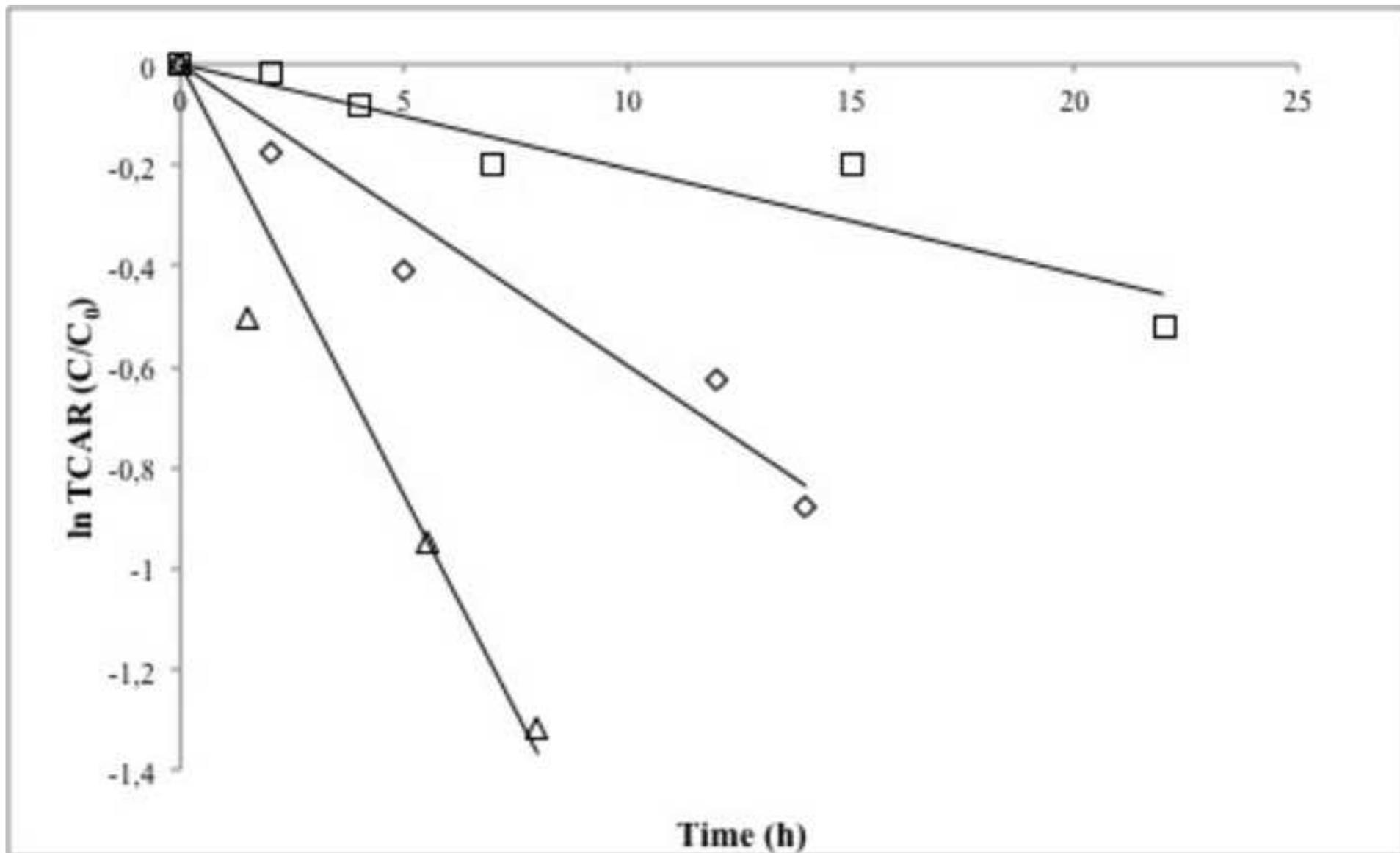
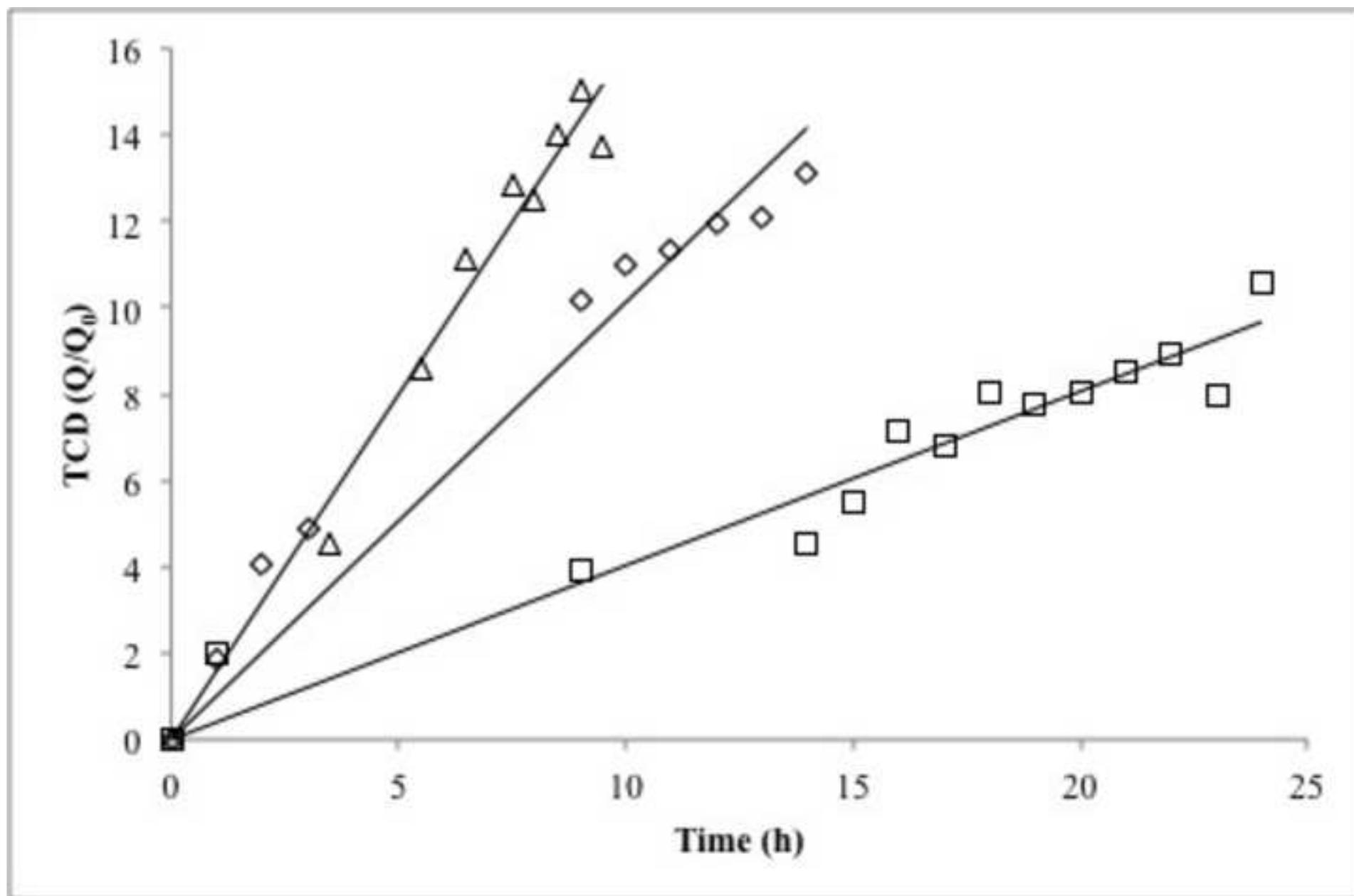


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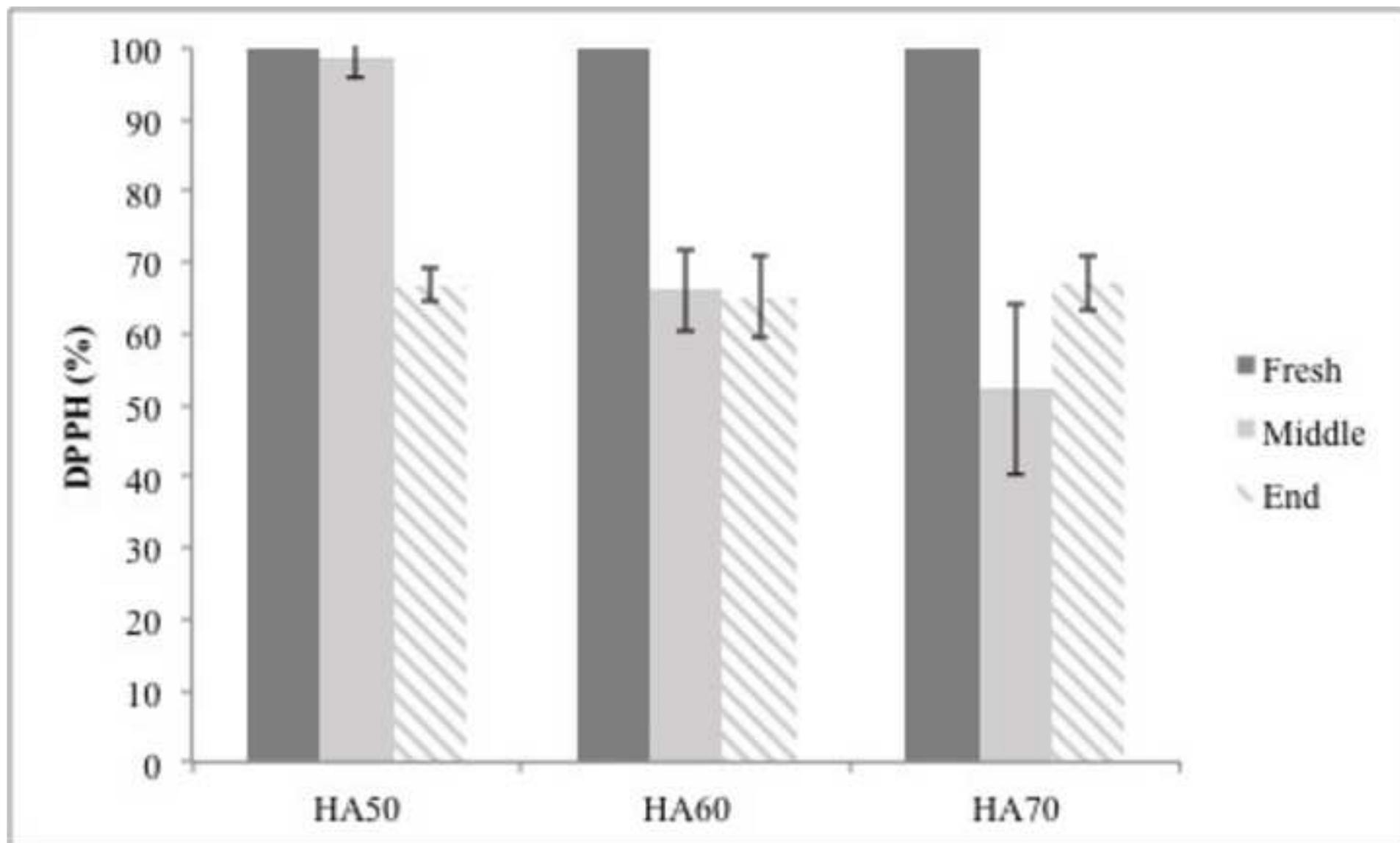
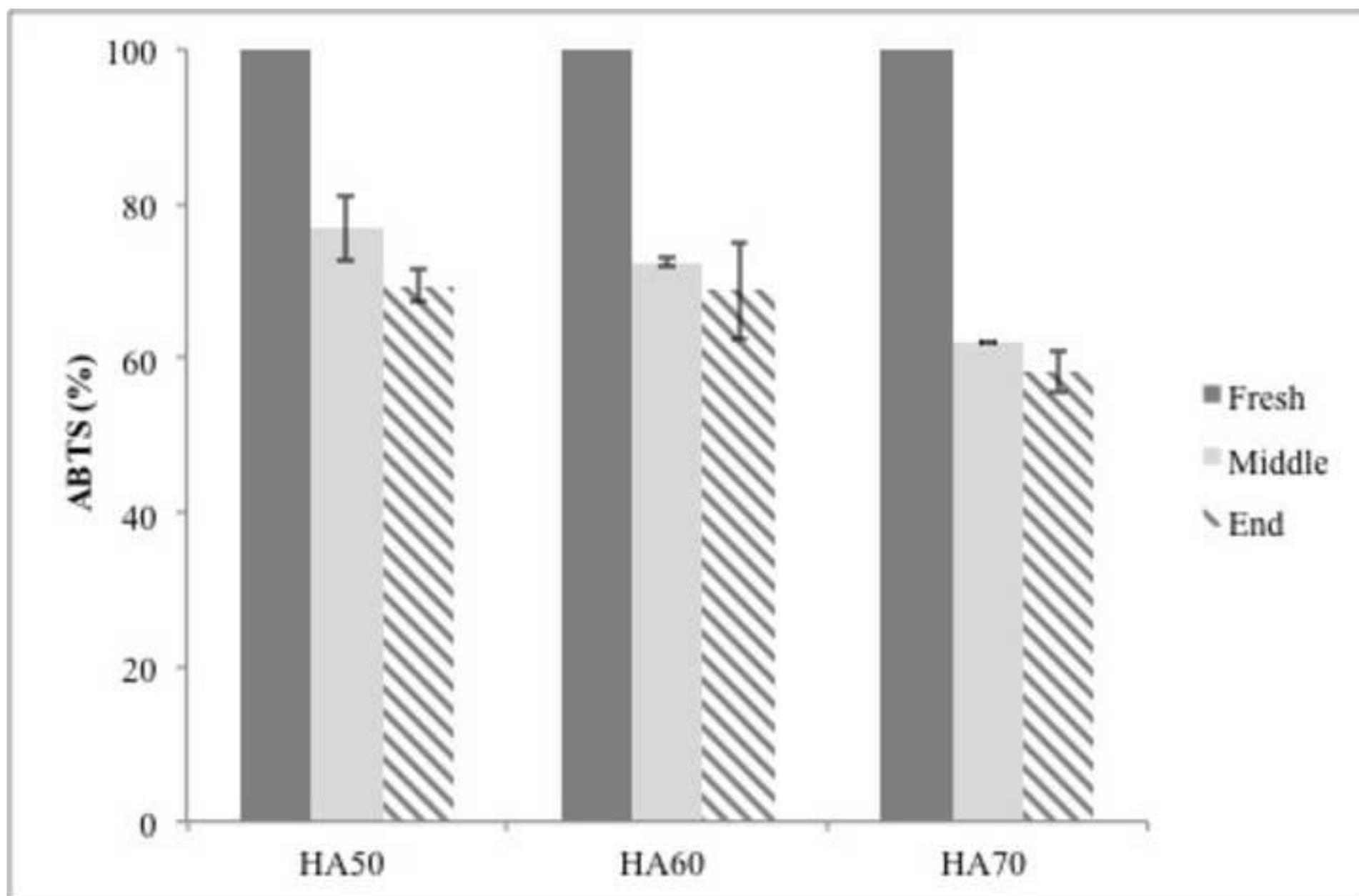


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**Table 1.**

Main carotenoid composition and content ( $\mu\text{g}/100\text{ g db}$ ) in fresh and HA dried apricots at the end of the drying treatment at different temperatures (mean of 3 determinations).

Compound	Fresh	End of treatment*		
		50°C	60°C	70°C
Violaxanthin <sup>§</sup>	674.5 <sup>a</sup>	16.6 <sup>b</sup>	0.0	0.0
Anteraxanthin	122.3 <sup>a</sup>	0.0	0.0	0.0
Lutein	311.7 <sup>a</sup>	187.0 <sup>b</sup>	155.8 <sup>c</sup>	0.0
$\beta$ -criptoxanthin	1457.1 <sup>a</sup>	1129.0 <sup>b</sup>	852.2 <sup>c</sup>	413.1 <sup>d</sup>
13-cis- $\beta$ -carotene	1221.3 <sup>a</sup>	791.2 <sup>b</sup>	817.2 <sup>b</sup>	470.0 <sup>c</sup>
$\beta$ -carotene	9011.2 <sup>a</sup>	5270.1 <sup>b</sup>	6029.2 <sup>c</sup>	3468.1 <sup>d</sup>
9-cis- $\beta$ -carotene	984.1 <sup>a</sup>	577.8 <sup>b</sup>	361.9 <sup>c</sup>	219.2 <sup>d</sup>
Totals	13782.2 <sup>a</sup>	7971.7 <sup>b</sup>	8216.3 <sup>c</sup>	4570.4 <sup>d</sup>

\* 22 h for 50°C; 12 h for 60°C; 8 h for 70°C.

<sup>§</sup> Different letters in the same raw indicate a significant difference ( $P < 0.05$ ).

**Table 2.**

Rate constants, activation energy ( $E_a$ ) and  $Q_{10}$  values of carotenoid, TCD formation and furosine evolution during apricot drying at different temperatures.

	Rate constant ( $\text{min}^{-1}$ )	$R^2$	Rate constant ( $\text{min}^{-1}$ )	$R^2$	Rate constant ( $\text{min}^{-1}$ )	$R^2$	$E_a$ (kJ/mol)	$Q_{10}$	
	50°C		60°C		70°C			50-60°C	60-70°C
<i>Carotenoids</i>									
Violaxanthin	0.0812	0.939	0.1570	0.956	nd	--	nd	1.93	nd
Anteraxanthin	0.0490	0.916	0.1591	0.841	0.3174	0.861	86.20	3.24	2.02
Lutein	0.0170	0.883	0.1237	0.901	0.2312	0.958	120.74	7.27	1.86
$\beta$ -criptoxanthin	0.0146	0.859	0.0575	0.826	0.1697	0.895	120.61	3.93	2.95
9-cis- $\beta$ -carotene	0.0213	0.820	0.0895	0.898	0.1872	0.980	100.34	4.20	2.09
13-cis- $\beta$ -carotene	0.0247	0.876	0.0350	0.815	0.1237	0.940	73.72	1.41	3.53
$\beta$ -carotene	0.0203	0.84	0.0490	0.908	0.1465	0.965	90.85	2.41	2.98
TCAR*	0.0208	0.892	0.0598	0.934	0.1710	0.933	96.95	2.88	2.86
TCD**	0.3770	0.913	1.0124	0.941	1.5978	0.974	66.70	2.69	1.58
<i>Furosine</i>	1.5560	0.999	2.4731	0.997	10.247	0.999	83.30	1.59	4.14

\*Total carotenoids.

\*\* Total color difference.

