The effect of microwave pre-treatment of rapeseed on the degradation kinetics of lipophilic bioactive compounds of the oil during storage

A. Rękas[a,✉], A. Siger[b] and M. Wroniak[a]

[a]Faculty of Food Sciences, Department of Food Technology, Warsaw University of Life Sciences, Nowoursynowska St. 159c, 02-787 Warsaw, Poland
[b]Faculty of Food Sciences and Nutrition, Department of Food Biochemistry and Analysis, Poznan University of Life Sciences, Wojska Polskiego St. 28, 60- 637 Poznan, Poland

✉Corresponding author: agnieszka_rekas@sggw.pl

SUMMARY: This study examined the storage stability of tocochromanols and carotenoids in the oils prepared from microwave pre-treated (MV) rapeseeds (2-10 min, 800W) during storage at 20 °C for 12 months. In line with lipophilic antioxidant degradation throughout the storage period, changes in the antioxidant capacity of the oil were monitored. Microwaving significantly affected the concentration of lipophilic antioxidants in the oil. After 10 min of MV pre-treatment the highest content of total tocochromanols (76.64 mg/100g) was achieved, whereas a maximum carotenoid concentration (861.28 μg/100g) was obtained following 6 min seed MV pre-treatment. The degradation kinetics for the tocochromanols and carotenoids followed a zero-order kinetic model. From the kinetic analysis, it was shown that the degradation rate constant (k) of both tocochromanols and carotenoids decreased with longer seed exposure to MV radiation. The kinetics of antioxidant capacity degradation during the storage of oils followed a zero-order reaction. The rate of antioxidant capacity degradation in the control oil was higher (k=9.1×10^{-2} mmol TEAC/l/month) compared with oils prepared from MV pre-treated seeds (k=6.8-8.0 ×10^{-2} mmol TEAC/l/month).

KEYWORDS: *Antioxidant capacity; Carotenoids; Degradation kinetics; Microwaving; Rapeseed oil; Tocochromanols*

RESUMEN: ***Efecto de pretratamientos con microondas a semillas de colza sobre la cinética de degradación de los compuestos bioactivos lipófilos del aceite durante el almacenamiento.*** En este estudio se determinó la estabilidad de tococromanoles y carotenoides de aceites preparados a partir de semillas de colza pretratadas con microondas (MV) (2-10 min, 800 W) durante el almacenamiento a 20 °C durante 12 meses. De acuerdo con la degradación de los antioxidantes lipófilos durante el periodo de almacenamiento, se monitorizó el cambio en la capacidad antioxidante del aceite. El microondas afectó significativamente a la concentración de antioxidantes lipofílicos en el aceite. Después de 10 minutos de pretratamiento con MV, se obtuvo el contenido más alto de tocromanoles totales (76,64 mg/100 g), mientras que se obtuvo una concentración máxima de carotenoides (861,28 g/100 g) después de un pretratamiento con MV de 6 minutos. La cinética de degradación para los tococromanoles y carotenoides siguió un modelo cinético de orden cero. A partir del análisis cinético, se demostró que la constante de velocidad de degradación (k) tanto de los tococromanoles como de los carotenoides disminuía con una exposición más prolongada de las semillas a la radiación de MV. La cinética de la degradación de la capacidad antioxidante durante el almacenamiento de los aceites siguió una reacción de orden cero. La tasa de degradación de la capacidad antioxidante en el aceite testigo fue mayor (k = 9,1 × 10^{-2} mmol TEAC / l / mes) en comparación con los aceites preparados a partir de semillas pretratadas con MV (k = 6,8-8,0 × 10^{-2} mmol TEAC / l /mes).

PALABRAS CLAVE: *Aceite de colza; Capacidad antioxidante; Carotenoides; Cinética de degradacion; Microondas; Tococromanoles*

ORCID ID: Rękas A https://orcid.org/0000-0001-5979-8430, Siger A https://orcid.org/0000-0002-3681-153X, Wroniak M https://orcid.org/0000-0002-8527-7185

1. INTRODUCTION

Natural antioxidants, such as tocopherols, carotenoids, phospholipids, and flavonoids, delay or inhibit lipid oxidation at low concentrations. Antioxidants prevent the auto-oxidation of oils by giving their hydrogen to free radicals formed in the initiation and propagation stages of autoxidation. Antioxidants prevent free radical-induced cell and biological target damage by preventing the formation of radicals, scavenging them, or by promoting their decomposition. Examples of antioxidants to scavenge free radicals are tocopherols, lignans, flavonoids, and phenolic acids, ubiquinone (coenzyme Q), carotenoids, ascorbic acids and amino acid (Choe and Min, 2009).

During the roasting of oilseeds and nuts some antioxidants are lost due to their heat instability (Yoshida *et al.*, 1999; Anjum *et al.*, 2006; Vujasinovic *et al.*, 2012; Cai *et al.*, 2013). Others are formed via chemical reactions such as Maillard reaction products (Shrestha *et al.*, 2013). The roasting of sesame seeds before oil extraction increases their sesamol content - the thermal degradation product of sesamolin, which is a more potent antioxidant than sesamolin (Lee *et al.*, 2010). Thermal pre-treatment of rapeseed leads to the formation of canolol (4-vinylphenol) - a decarboxylation product of sinapic acid (Shrestha *et al.*, 2013).

Rapeseed is an important crop worldwide. Crude rapeseed oil supplies comparable amounts of tocopherols to sunflower seed oil or soybean oil (Codex Alimentarius, 2013). It is rich in mono-unsaturated fatty acids (oleic acid) and polyunsaturated fatty acids (linoleic and α-linolenic essential fatty acids) and low in saturated fatty acids. Because of favorable polyunsaturated fatty acid contents with a 2:1 ratio of linoleic vs. linolenic fatty acid it is considered as one of the healthiest oil on the edible oil market. The storage stability of phytochemicals has been studied for olive oil (Krichene *et al.*, 2015), rice bran oil (Mezouari and Eichner, 2007) and rapeseed oil (Wroniak and Rękas, 2016).

The degradation of tocopherols, plastochromanol-8 and canolol during the long-term storage (4° C) of rapeseed oil prepared from roasted seeds was investigated by Siger and Michalak (2016). Vaidya and Choe (2011b) studied the stability of tocopherols and lutein in oil extracted from roasted or unroasted mustard seeds during oil oxidation at 60 °C in the dark. The effect of rapeseed microwave pre-treatment on the stability of phenolic compounds during accelerated storage (60 °C, 10 weeks) was reported by Zheng *et al.*, (2014). So far, kinetic models have been developed to evaluate phenolic compound and tocopherol degradation during the storage of olive oil (Lavelli *et al.*, 2006; Krichene *et al.*, 2015). In our previous work (Rękas *et al.*, 2017), the degradation kinetics of phenolic compounds in the rapeseed oil obtained from microwave pre-treated seeds (*cv.* Monolit) during storage for 12 months at 20 °C were examined. The objective of this study was to determine the kinetic parameters for lipophilic antioxidants (tocochromanols and carotenoids) in rapeseed oil prepared from seeds exposed to microwave radiation for 2 to 10 min during storage at room temperature for 12 months.

2. MATERIALS AND METHODS

2.1. Experimental material

Seeds of the winter type rapeseed *cv.* Monolit were provided by the Plant Breeding Strzelce Ltd. Co. – IHAR Group, Poland. The seeds were harvested at optimum maturity, and did not contain any impurities or broken seeds. They were stored in paper bags under atmospheric conditions at 20 ± 1 °C. The moisture content of rapeseeds was 5.6%.

2.2. Reagents

Analytical standards of α-, β-, γ-, δ-tocopherols (≥ 95%) and carotenoids: lutein (≥ 97.0%), β-carotene (≥ 97.0%), (9-Z)-β-carotene (≥ 95.0%), (13-Z)-β-carotene (≥ 95.0%) and 1,4- dioxane were provided by Calbiochem-Merck Biosciences (Darmstadt, Germany). HPLC-grade n-hexane, methanol, ethyl acetate, 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) and (±)-6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.3. Sample moisturizing

The moisture content of seeds was determined based on a precision weighing balance, using Electronic Moisture Analyzer (Kern & Sohn GmbH, Germany). A 5 g sample was dried at 115 °C to constant mass and taken as a reference. The measurement accuracy of the analyzer was 0.05% wet basis. The seeds (batches of 500g) were sprayed with pre-calculated amount of water, mixed thoroughly, sealed in polyethylene bags and equilibrated at 4 ± 2 °C for 72 h. Based on the results presented in our previous work (Rękas *et al.,* 2017), the moisture level of seeds of 7.5% prevents the seeds from overheating during microwave pre-treatment, whereas seed moisturizing prior to cold-pressing to the moisture content of 8.5% enables the highest oil yield. For this reason, the seeds were moistened twice: to the moisture content of 7.5% prior to microwave pre-treatment and before cold-pressing to reach the required moisture content of 8.5%. After 72 h of

equilibration, the moisture content of the seeds was checked in order to verify whether homogeneous moisture distribution throughout the bulk of the seeds was reached.

2.4. Pre-treatment with microwaves

The rapeseeds were microwaved for 2, 4, 6, 8 and 10 min (2450 MHz, 800 W) following the procedure presented in an earlier work (Rękas *et al.*, 2017).

2.5. Oil extraction by cold-pressing

Pressing was carried out by applying a screw press (Farmet, Czech Republic), and the temperature of the out-flowing oil was kept below 40 °C. Once produced, the oil was stored at 4 °C overnight in the dark until analyzed.

2.6. Storage conditions

The oil samples were stored in 100-mL amber glass bottles, with no access to light at a temperature of 20 °C. In all samples, a nitrogen cushion was created by introducing an inert gas (N_2) into the headspace. The bottles were sealed with standard polypropylene threaded caps. Analyses were performed immediately after oil production (0 months of storage) and after 3, 6, 9 and 12 months of storage. For each oil sample, a series of three bottles was prepared. Samples were periodically withdrawn for scheduled analyses. Overall, 90 bottles were used in the study.

2.7. Tocopherol and plastochromanol-8 determination

To determine tocochromanols (α-, β-, γ-, and δ-tocopherol and PC-8), 200 mg of oil were dissolved in 10 ml of *n*-hexane and transferred to vials for further analysis. Separation was performed using a Waters HPLC system (Waters, Milford, MA, USA) coupled with a FLD detector (Waters 474), a PDA detector (Waters 2998), and a LiChrosorb Si 60 column (250 × 4.6 mm, 5 μm, Merck Millipore, Darmstadt, Germany). The mobile phase was a mixture of *n*-hexane with *1,4*-dioxane (96:4 v/v) at a flow rate of 1.0 mL·min⁻¹. The quantification of tocochromanols was conducted using data from the FLD with excitation/emission wavelengths of 295/330 nm, respectively. The plastochromanol-8 content was assayed and calculated following the method described by Siger *et al.,* (2014).

2.8. Carotenoid determination

In order to determine carotenoid content, samples of oils (2 g) were saponified using 60% KOH (2 mL), ethanol (20 mL) and pyrogallol (0.5 g).

The saponification was carried out at ethanol boiling point temperature (78 °C) for 30 minutes. After saponification, unsaponifiable substances were extracted using 50 mL n-hexane/ethyl acetate (90:10 v/v). The 20 mL mixture of unsaponifiable substances was dried using a rotary evaporator and the residue was dissolved in 2 mL of ethyl acetate. The identification and quantification of carotenoids were made using high performance liquid chromatography (HPLC – Waters, Milford, MA) equipped in a ODS2 C18 reversed-phase column (4.6 × 250 mm; 5 μm) (Waters, Milford, MA). A gradient program was used, combining solvent A (80% acetonitrile and 0,05% triethylamine) and solvent B (ethyl acetate) as follows: 100–65% A (35 min), 65–50% A (25 min), 50-100% A (5 min). The flow rate was 1.0 mL·min⁻¹. The injection volume was 10 μl while the column temperature was maintained at 30 °C. The signal was monitored at 200 - 600 nm with the diode array detector (DAD) (UV-VIS Waters, Milford, MA). The quantitative determination of carotenoids was carried out by comparing retention times and diode array spectral characteristics with corresponding standards.

2.9. Antioxidant capacity

The radical scavenging capacity (RSC) of the oil sample was analyzed using the DPPH radical-scavenging assay according to the method described by Tuberoso *et al.,* (2007). The antioxidant capacity of the oil (TF), hydrophilic (HF), and lipophilic (LF) fractions were measured at 517 nm using Spectronic Helios β UV-Vis spectrophotometer (Thermo Electron Corporation, Waltham, MA, USA). The results were expressed as a Trolox equivalent antioxidant capacity (TEAC, mmol/l), using a Trolox calibration curve in the range 0.02–4.00 mM.

2.10. Kinetics of antioxidant lipophilic compounds and antioxidant capacity degradation

The degradation of tocopherols, plastochromanol-8, carotenoids and antioxidant capacity in rapeseed oils produced from microwave pre-treated seeds was calculated according to the standard equation from the zero-order reaction model. The degradation rate constant was determined by fitting Eq. (1) to the experimental data.

$$C_t = C_0 + kt \tag{1}$$

Where C_t is the studied compound concentration (α-, β-, γ-, δ-tocopherols, plastochromanol-8, lutein, β-carotene, 9-Z- β-carotene, 13-Z- β-carotene, antioxidant capacity of the oil (TF) and its lipophilic (LF), hydrophilic (HF) fraction) after *t* months of storage, C_0 is the initial

concentration of the studied compounds, *k* is the kinetic rate constant.

2.11. Statistical analysis

Data are expressed as Mean ± SD. To examine the effect of microwave pre-treatment of rapeseeds on the crude oil variables studied, one-way ANOVA was used when the variables fulfilled parametric conditions, and the Kruskal-Wallis test when they were nonparametric. Significance was established at a probability of $p < 0.05$, using Statistica 12.0 software (StatSoft, Inc., Tulsa, OK).

3. RESULTS AND DISCUSSION

3.1. Tocopherols

The initial contents of the individual tocopherol homologues in the analyzed oil samples are given in Table 1. The main components of the control oil sample were γ- and α-tocopherol (γ- and α-T) with the concentration of 31.19 and 27.36 mg·100g⁻¹, respectively, followed by plastochromanol-8 (PC-8), present at a concentration of 2.26 mg·100g⁻¹; whereas the sum of δ- and β-tocopherol (δ- and β-T) was 1.04% of the total tocochromanols. In the oils produced from MV pre-treated seeds, the level of total tocochromanols ranged from 60.84 to 76.64 mg·100g⁻¹. Similarly to the results presented by other authors (Yoshida *et al.*, 1999; Anjum *et al.,* 2006) the reduction in α-T content with longer seed exposure

to microwaves was observed. The amounts of γ-T increased with increasing MV time, the highest level of γ-T was found in the oil prepared from 10 min MV seeds (45.14 mg·100g⁻¹). An increase in γ-T was also found in the oils pressed from roasted rapeseeds (Siger *et al.*, 2015) and pumpkin seeds (Vujasinovi-*et al.*, 2012); whereas the roasting of pine nuts (Cai *et al.*, 2013) and sunflower seeds (Anjum *et al.*, 2006) resulted in a significant reduction in the γ-T concentration in the oil. β-T was almost unchanged by MV pre-treatment applications, while δ-T first increased and then decreased, depending on the time of seed exposure to MV radiation. The behavior of tocopherol homologues during thermal seed pre-treatment differed among one another due to their different thermo-stabilities. α-T was the most thermal sensitive, followed by β-T; whereas the highest thermo-stability was shown, equally, by δ- and γ-T (Valavanidis *et al.*, 2004). As shown by Moreau *et al.*, (1999) a significant amount of γ-T in corn hulls formed complexes with proteins or was linked to phosphates or phospholipids. An increase in γ-T in the oil prepared from thermally pre-treated corn may be a result of heat-induced degradation of these bonds. Wijesundera *et al.*, (2008) offered a possible explanation for the heat-induced increase in the levels of tocopherols, suggesting possible co-elution of tocopherols with other compounds formed during rapeseed roasting. Moreover, Matthäus (2012) suggested a potential role of canolol, formed during rapeseed thermal pre-treatment, in protecting the tocopherols from thermal degradation. The level

TABLE 1. Tocochromanol (mg·100g⁻¹) and carotenoid (μg·100g⁻¹) concentrations in rapeseed oil samples pressed from microwave treated seeds.

Compound	Microwave pretreatment time (min)					
	0	**2**	**4**	**6**	**8**	**10**
Tocochromanols (μg·100g⁻¹)						
α-Tocopherol	27.36 ± 0.25[b]	25.63 ± 0.13[a]	25.65 ± 0.11[a]	25.92 ± 0.07[a]	25.07 ± 0.07[a]	25.21 ± 0.09[a]
β-Tocopherol	0.10 ± 0.02[a]	0.10 ± 0.03[a]	0.08 ± 0.02[a]	0.09 ± 0.03[a]	0.09 ± 0.01[a]	0.10 ± 0.01[a]
γ-Tocopherol	31.19 ± 0.08[a]	31.20 ± 0.19[a]	32.79 ± 0.06[ab]	33.34 ± 0.17[b]	35.87 ± 0.07[b]	45.14 ± 0.08[c]
δ-Tocopherol	0.54 ± 0.03[c]	0.59 ± 0.03[c]	0.49 ± 0.03[b]	0.42 ± 0.02[a]	0.47 ± 0.02[b]	0.44 ± 0.01[a]
PC-8	2.26 ± 0.14[a]	3.31 ± 0.12[b]	4.70 ± 0.14[c]	5.09 ± 0.07[d]	5.72 ± 0.22[e]	5.75 ± 0.10[e]
Total tocochromanols	61.45 ± 0.27[b]	60.84 ± 0.23[a]	63.72 ± 0.07[b]	64.86 ± 0.22[b]	67.23 ± 0.14[c]	76.64 ± 0.15[d]
Carotenoids (μg ·100g⁻¹)						
Lutein	225.90 ± 0.55[b]	222.18 ± 0.58[a]	574.49 ± 0.99[e]	545.03 ± 1.77[d]	441.03 ± 0.22[c]	442.70 ± 0.82[c]
β-Carotene	115.01 ± 0.31[a]	116.53 ± 0.5[a]	171.52 ± 1.13[c]	219.06 ± 0.59[d]	157.89 ± 0.76[b]	172.94 ± 0.71[c]
9-Z-β-Carotene	45.00 ± 0.05[c]	41.52 ± 0.46[b]	40.58 ± 0.44[b]	66.40 ± 0.15[d]	35.81 ± 0.60[a]	37.99 ± 0.22[a]
13-Z-β-Carotene	20.51 ± 0.14[c]	17.69 ± 0.29[b]	22.46 ± 0.25[c]	30.79 ± 0.23[d]	18.61 ± 0.28[b]	15.58 ± 0.40[a]
Total carotenoids	406.42 ± 0.15[b]	397.92 ± 1.74[a]	809.04 ± 2.31[e]	861.28 ± 1.10[f]	653.34 ± 0.66[c]	669.21 ± 2.16[d]

Means in a row (a-e across microwaving time) followed by the same letter are not significantly different ($p < 0.05$).

of PC-8 in the oils prepared from MV seeds varied from 3.31 to 5.75 mg·100g^{-1}. PC-8 is an antioxidant that, together with tocopherols and tocotrienols, belongs to the group of tocochromanols. Recently, its antioxidant capacity has been documented to be similar to that of γ-tocotrienol and 1.5 times higher than of α-tocopherol (Siger *et al.,* 2014). According to Shrestha and De Meulenaer (2014) it is possible that a thermally-induced disruption of the internal structure of rapeseeds during roasting causes increased extractability of PC-8 from the seeds.

After 12 months of storage, the level of total tocochromanols in the control oil decreased from 61.45 to 43.67 mg·100g^{-1} (28.9% loss) (Table 2). Throughout the entire storage period, 33.4% of γ-T, 27.4% of α-T, 25.0% of δ-T and PC-8 degraded (Fig. 1a-c); whereas β-T was undetectable after 9 months of storage (data not shown). The results presented by Wroniak and Rękas (2016) showed 59.7 and 84.3% loss in γ- and α-T after 12 months of storage of cold-rapeseed oil in the dark at room temperature. The storage of olive oil in closed glass bottles at room temperature for 9 months resulted in the degradation of 80.90% α-T (Samaniego-Sánchez *et al.*, 2012). In crude rice bran oil after 240 days of storage (20 °C, in the dark) the total tocopherol level decreased by about 72% (Mezouari and Eichner, 2007).

During 12 months' storage of the oils, the total amount of tocochromanols decreased by 26.0, 23.2, 23.0, 23.5 and 22.1%, respectively, for oils pressed from seeds MV for 2, 4, 6, 8 and 10 min. (Table 2). The percentage loss in individual tocopherol homologues and PC-8 was dependent on the seeds' MV pre-treatment time (Fig. 1a-c). After 12 months of storage, the level of α-T was reduced by 24.5, 20.4, 21.2, 18.8 and 17.6%, in the oils pressed from seed MV for 2 to 10 min, respectively. For PC-8, the highest reduction (54.6%) was observed in the oil pressed from 2 min MV seeds, while 4 and 10 min seeds exposure to MV resulted in the lowest loss in PC-8 (17.2 and 18.2%, respectively) in the oil. The losses in γ-T in the oils prepared from MV seeds were comparable to that of the control oil (25% loss), and were within the range of 23.6-24.3%. Unlike other tocopherol homologues, after 12 months of storage, a decrease in δ-T in the oils pressed from MV seeds was, in most cases, higher than that observed in the control oil (27.4%), and ranged from 18.4 to 41.5%. After 3 months of storage, β-T was undetectable in the oils produced from seed MV for 6-10 min, and was reduced to zero in all the oil samples after a storage period of 9 months (data not shown). Similarly to our results, a higher storage stability of tocopherols was reported by Vaidya and Choe (2011a), who investigated the effect of mustard seed roasting (160 °C) on the stability of tocopherols during oil oxidation at 60 °C in the dark for 12 days.

The linear relationship between tocochromanol contents in the analyzed rapeseed oil and storage period followed zero-order kinetics (Eq. 1). The estimated values of the determination coefficients (R^2) and the degradation rate constants (k) for the oils prepared from the control and MV seeds are presented in Table 3. The degradation rate constant of individual tocochromanols varied significantly, depending on the tocopherol homologue. As shown in Table 3, k values obtained for α-T decreased with longer seed MV pre-treatment time (0.763-0.369 mg/100g/month), longer seed MV resulted in a higher degradation rate of γ-T (0.631-0.935 mg/100g/month), whereas the degradation of δ-T was almost

TABLE 2. Tocochromanol (mg·100g^{-1}) and carotenoid (μg·100g^{-1}) concentrations in rapeseed oil samples pressed from microwave treated seeds.

Storage period (months)	Microwave pre-treatment time (min)					
	0	2	4	6	8	10
Total tocochromanols (μg·100g^{-1})						
0	61.45 ± 0.41[c]	60.84 ± 0.35[c]	63.40 ± 0.15[c]	64.71 ± 0.29[c]	66.23 ± 0.17[c]	70.64 ± 0.08[c]
3	55.95 ± 0.14[b]	58.50 ± 0.16[b]	60.38 ± 0.34[bc]	60.49 ± 0.30[c]	60.73 ± 0.32[bc]	71.30 ± 0.26[c]
6	54.12 ± 0.12[b]	54.91 ± 0.22[b]	59.21 ± 0.38[b]	57.35 ± 0.22[b]	58.25 ± 0.26[b]	68.19 ± 0.36[b]
9	47.89 ± 0.24[a]	49.19 ± 0.18[a]	53.36 ± 0.34[ab]	54.44 ± 0.15[b]	56.32 ± 0.37[b]	64.70 ± 0.28[b]
12	43.67 ± 0.40[a]	45.03 ± 0.20[a]	48.91 ± 0.12[a]	49.95 ± 0.14[a]	51.46 ± 0.22[a]	59.58 ± 0.16[a]
Total carotenoids (μg·100g^{-1})						
0	406.42 ± 0.15[e]	397.92 ± 1.74[e]	809.04 ± 2.31[e]	861.28 ± 1.10[e]	653.34 ± 0.66[e]	669.21 ± 2.16[e]
3	367.73 ± 1.49[d]	364.74 ± 0.91[d]	738.94 ± 5.00[d]	797.86 ± 5.91[d]	624.65 ± 14.67[d]	579.40 ± 5.59[d]
6	317.75 ± 2.54[c]	300.25 ± 2.58[c]	632.25 ± 6.20[c]	670.97 ± 4.64[c]	574.86 ± 2.27[c]	533.23 ± 4.42[c]
9	243.60 ± 0.71[b]	231.58 ± 0.69[b]	522.02 ± 3.81[b]	542.15 ± 6.45[b]	535.02 ± 6.05[b]	455.54 ± 2.41[b]
12	207.77 ± 0.64[a]	198.62 ± 0.98[a]	446.32 ± 1.01[a]	477.62 ± 1.89[a]	513.67 ± 3.86[a]	385.02 ± 4.03[a]

Means in a column (a-e across storage period) followed by the same letter are not significantly different ($p < 0.05$).
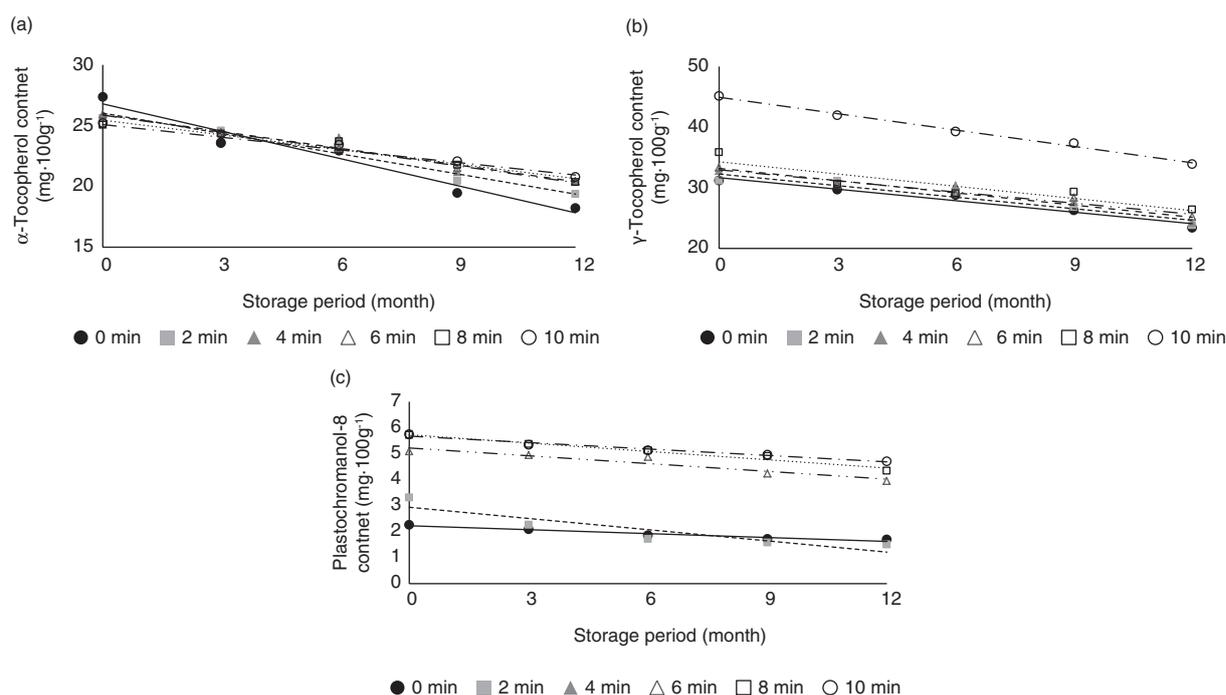
FIGURE 1. Concentrations of α- and γ-tocopherol and plastochromanol-8 (mg·100g⁻¹) in rapeseed oil samples pressed from microwave-treated seeds stored at 20 ˚C in the dark for 12 months.

unchanged by the seed thermal pre-treatment prior to oil cold-pressing. The k values of PC-8 showed that the degradation of this compound proceeded at a faster rate in the oil samples pressed from MV seeds than in the control oil. Overall, the degradation rate of total tocochromanols in the oils prepared from MV seeds was slightly lower than that of the control oil (k=1.482 mg/100g/month), with k values of 1.317, 1.234, 1.243, 1.314 and 1.412, for seed pre-treatment for 2-10 min, respectively. In a study of virgin olive oil storage for 18 months at temperatures of 5-50 °C, the degradation of α-T was found to follow zero-order kinetics (Krichene *et al.*, 2015). Lavelli *et al.,* (2006), concluded that a *pseudo* first-order kinetic model was suitable to describe the reduction in α-T in the extra virgin olive oil stored for 8 months (25 and 40 °C).

3.2. Carotenoids

The effect of rapeseed MV pre-treatment on the concentration of carotenoids in presented in Table 1. A total of 4 carotenoids (lutein, β-carotene, 9-Z-β-carotene and 13-Z-β-carotene) were detected in the control rapeseed oil. Lutein was the predominant carotenoid (225.90 μg/100g), followed by β-carotene (115.01 μg·100g⁻¹) and its isomers, 9-Z-β- and 13-Z-β-carotene, were present at a concentration of 45.00 and 20.51 μg·100g⁻¹, respectively. Total and individual carotenoid contents in the oil were significantly ($p < 0.05$) altered by

the seed MV pre-treatment (Table 1). The highest level of total carotenoids in the oils prepared from MV-treated seeds was achieved after seed exposure to MV for 4 and 6 min (809.04 and 861.28 μg/100g, respectively). At first, the total carotenoid contents in the oil decreased by 2.1% after 2-min seed MV, and then increased by 99.1, 111.9, 62.6 and 64.7%, after seed MV pre-treatment for 4-10 min, respectively. As suggested by Vaidya and Choe (2011a), increased carotenoid contents in oils produced from heated seeds may be partially explained by the fact that carotenoids are bound to proteins and form thermo-stable carotenoid–protein complexes. A thermally induced process of destruction of the internal seed cell structure, including protein denaturation, increases the oil's accessibility to lipid-soluble carotenoids. The highest concentration of lutein in the oil was achieved after 4 min seed MV (574.49 μg·100g⁻¹), 6-min seed exposure to MV was found to cause the highest increase in β-carotene contents in the oil (219.06 μg·100g⁻¹). Thermal degradation leads to β-carotene oxidation, the first step comprises its conversion to Z-isomers. The behavior of β-carotene in the oil oxidation process depends on its concentration and on the lipid medium, exposure to light, presence or absence of other antioxidants and pro-oxidants (Zeb, 2012). Thermal degradation of all-E-β-carotene, 9-Z-β-carotene, lycopene and lutein during safflower oil heating at 75, 85 and 95 °C showed degradation rates in the following order: lycopene > all-E-β-carotene ≈

TABLE 3.   Kinetic parameters from zero-order reaction kinetics for the tocochromanol and carotenoid degradation during the storage of rapeseed oils pressed from microwave treated seeds.

Compound Parameter		α-Tocopherol		γ-Tocopherol		δ-Tocopherol		PC-8		Total tocochromanols	
		k	R^2	k	R^2	k	R^2	k	R^2	k	R^2
Microwave pre-treatment time (min)	0	0.763	0.9578	0.651	0.9558	0.012	0.9172	0.047	0.9443	1.482	0.9818
	2	0.522	0.9626	0.615	0.9178	0.021	0.8914	0.151	0.8160	1.317	0.9797
	4	0.436	0.9418	0.714	0.9331	0.010	0.9156	0.067	0.9844	1.234	0.9568
	6	0.459	0.9970	0.675	0.9560	0.006	0.9156	0.096	0.9047	1.243	0.9925
	8	0.394	0.9545	0.789	0.8365	0.009	0.9156	0.115	0.9697	1.314	0.9565
	10	0.369	0.9631	0.935	0.9932	0.012	0.9156	0.087	0.9730	1.412	0.9912

Compound Parameter		Lutein		β-Carotene		9-Z-β-Carotene		13-Z-β-Carotene		Total carotenoids	
		k	R^2	k	R^2	k	R^2	k	R^2	k	R^2
Microwave pre-treatment time (min)	0	8.576	0.9833	5.487	0.9848	2.152	0.9690	0.340	0.9788	16.555	0.9872
	2	8.519	0.9720	5.777	0.9725	1.876	0.9714	0.435	0.9705	16.608	0.9843
	4	20.113	0.9942	8.173	0.9908	1.615	0.9988	0.326	0.4892	30.227	0.9942
	6	15.767	0.9737	11.816	0.9551	3.748	0.9717	0.640	0.8388	31.971	0.9846
	8	4.335	0.9856	5.922	0.9949	1.015	0.6671	0.367	0.5590	11.639	0.9850
	10	12.088	0.9931	9.330	0.9669	1.854	0.9613	0.410	0.9826	23.682	0.9933

k – kinetic rate constant (mg/100g/month, for tocochromanols; μg/100g/month, for carotenoids); R^2 – coefficient of determination

9-Z-β-carotene > lutein (Henry *et al.*, 1998). In a study of heat-induced degradation of carotenoids in crude paprika oleoresins diluted with high oleic or high linolenic oil, the conversion E to Z isomers was initially higher than the degradation of Z-isomers (Pérez-Gálvez and Mínguez-Mosquera, 2004). In our study, the degradation of β-carotene Z-isomers was observed after 8 min of MV seeds pre-treatment. Achir *et al.,* (2010) found all E-lutein to be more resistant to degradation than all E-β-carotene during palm olein and Vegetaline heating at 120-180 °C. Achir *et al.,* (2011) stated that 9-Z-β-carotene could be a good degradation indicator during oil storage or processing.

The levels of total and individual carotenoids in the control oil were significantly reduced ($p < 0.05$) during storage for 12 months (Table 2, Fig. 2). After the entire storage period, total carotenoid concentration was reduced by 48.9% (a decrease from 406.42 to 207.77 μg·100g^{-1}). In this oil, β-carotene and 9-Z-β-carotene showed the greatest losses of 57.2 and 57.4%, respectively. The respective losses in lutein and 13-Z-β-carotene were 45.6 and 19.9% (Fig. 2).

During 12 months of storage, a decrease in lutein in the oils pressed from MV pre-treated seeds was lower than in the control oil; while the percentage loss in β-carotene and its isomers exceeded that observed in the control oil (Fig. 2a,b). The only exception was the oil prepared from seed MV for 8 min, in which the lowest reduction in individual carotenoids was found. In this oil, after a storage period of 12 months, the amounts of lutein,

β-carotene and 9-Z-β-carotene decreased by 11.8, 45.0 and 46.7%, respectively. Vaidya and Choe (2011a,b) found that the increased thermo-oxidative stability of mustard oil prepared from roasted seeds was highly correlated with improved heat stabilities for both tocopherols and lutein.

When the total carotenoid retention of rapeseed oil was plotted against storage period, R^2 was higher than 0.98, thus a decrease in carotenoids followed zero-order reaction kinetics (Eq. 1). The k values of lutein, β-, 9-Z- β- and 13-Z-β-carotene in the control oil were 8.576, 5.487, 2.152, 0.340 μg/100g/month, respectively. As can be seen from Table 3, the degradation rate of individual carotenoids in the analyzed oil was significantly affected by the applied MV pre-treatment. The loss in lutein progressed at the fastest rate in the oil pressed from 4, 6 and 10 min MV seeds (k=20.113, 15.767, 12.088 μg/100g/month, respectively); while after 8 min seed exposure to MV, the stability of lutein was the highest, as k was 4.335 μg/100g/month. The degradation rate of β-carotene in the oils from 2 and 8 min MV seeds (k = 5.777 and 5.922 μg/100g/month, respectively) was comparable to that of the control oil (k = 5.487 μg/100g/month). MV pre-treatment for 4, 6 and 10 min resulted in a significant increase in β-carotene degradation when compare to the control oil. In general, the degradation of 9-Z-β-carotene in the oils pressed from heated seeds progressed at a lower rate when compare to the control oil (with the exception of oil from 6 min MV seeds); while 13-Z-β-carotene loss rate was comparable to that of the control oil (Fig. 2c,d). The degradation of
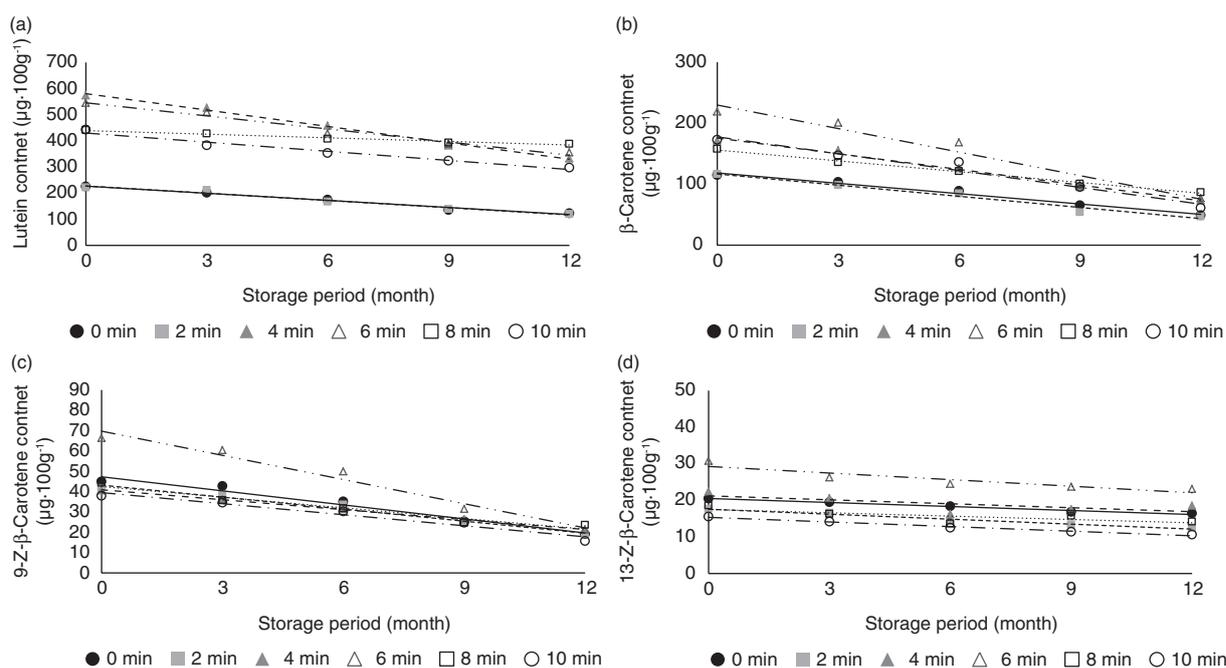
FIGURE 2. Concentrations of lutein, β-carotene, 9-Z-β-carotene and 13-Z-β-carotene (µg·100g⁻¹) in rapeseed oil samples pressed from microwave-treated seeds stored at 20 °C in the dark for 12 months.

total carotenoids in the oil obtained from 2 min MV seeds was almost the same as in the control oil (k = 16.608 and 16.555 µg/100g/month, respectively). The slowest degradation rate of total carotenoids over the entire storage period was noted for the oil pressed from 8 min MV seeds (k=11.639 µg/100g/month); while the highest loss rate was found after 4, 6 and 10 min seed exposure to heat pre-treatment (k=30.227, 31.971 and 23.682 µg/100g/month, respectively).

3.3. Antioxidant capacity

The results of the antioxidant capacity measured for the oil (TF) and its hydrophilic (HF) and lipophilic (LF) fractions are reported in Table 4. The HF of vegetable oil, also known as the polar fraction, contains most of the phenolic antioxidants, lignans and seco-iridoids (Valavanidis *et al.*, 2004). In our earlier work (Rękas *et al.*, 2017), it was shown that the rapeseed oil of the Monolit variety contained 6 phenolic compounds, *trans*-sinapic acid, ferulic acid, *p*-coumaric acid, sinapine, sinapic acid methyl ester and canolol, where the latter accounted for as much as 90% of the total phenolics. The TEAC value of HF of the control oil was 0.67 mmol/l. This was changed by seed microwaving prior to pressing. After 10 min of seed MV, the antioxidant capacity of HF increased from to 0.84 to 5.83 mmol TEAC/l, for oil pressed from 2 and 10 min MV pre-treated seeds, respectively. A significant correlation between total phenolics and the antioxidant capacity in the rapeseed oil pressed from MV pre-treated seeds was obtained by Zheng *et al.,* (2014). According to Oliviero *et al.,* (2009) nut

roasting increases oil hydrophilic antioxidant capacity due to Maillard browning reactions and/or the release of previously bound phenolic compounds (Talcott *et al.,* 2005). Maillard rection products formed between carbohydrates and amino acids are very polar; whereas the Maillard type reaction products involving amino phospholipids like phosphatidylethanolamine (PE) are more lipophilic (Zamora *et al.,* 2011). This would explain the potential role of the Maillard reaction products in protecting the tocopherols from thermal degradation during roasting or microwaving (McDaniel *et al.,* 2012).

The LF of oils contains mostly tocopherols, triglycerides and phospholipids. The antioxidant capacity of LF results from the tocopherol concentration, in addition to their efficiency as antioxidants. δ-T shows the highest antioxidant efficiency, followed by γ-T ≈ β-T, whereas α-T is the least efficient antioxidant (Valavanidis *et al.,* 2004). In this study, the control oil exhibited a TEAC value of LF of 1.58 mmol·L⁻¹. As MV time increased from 2 to 10 min, the TEAC values of LF increased from 1.74 to 4.81 mmol·L⁻¹, respectively. Although carotenoids are known as highly lipophilic antioxidants, the concentration of these compounds in all the variants of oils studied did not exceed 1 mg·100g⁻¹, and thus, their impact on the oil's antioxidant capacity of LF was much smaller when compared to the tocopherols. As pointed out by Shrestha *et al.,* (2013), the increase in oil oxidative stability linked to the increase in tocopherol and lutein during seed roasting is insufficient to explain the increased oxidative stability

TABLE 4. The effect of microwave pre-treatment of rapeseed on the changes in antioxidant capacities (mmol TEAC/l) of oil samples during 12 months of storage.

Oil fraction	Storage Period (months)	Microwave pre-treatment time (min)					
		0	2	4	6	8	10
HF	0	0.67 ± 0.05^d	0.84 ± 0.02^c	0.93 ± 0.05^c	1.71 ± 0.03^d	4.52 ± 0.06^d	5.83 ± 0.04^c
	3	0.45 ± 0.04^c	0.72 ± 0.06^c	0.81 ± 0.02^c	1.68 ± 0.05^d	4.51 ± 0.06^d	5.74 ± 0.05^c
	6	0.32 ± 0.02^b	0.53 ± 0.04^b	0.69 ± 0.03^b	1.55 ± 0.06^c	4.39 ± 0.04^c	5.65 ± 0.02^b
	9	0.26 ± 0.03^b	0.34 ± 0.04^a	0.54 ± 0.02^a	1.32 ± 0.04^b	4.18 ± 0.04^b	5.42 ± 0.05^b
	12	0.14 ± 0.05^a	0.21 ± 0.04^a	0.43 ± 0.04^a	1.18 ± 0.04^a	3.98 ± 0.05^a	5.23 ± 0.07^a
LF	0	1.58 ± 0.04^c	1.74 ± 0.02^c	1.89 ± 0.03^d	2.01 ± 0.03^d	2.05 ± 0.04^d	4.81 ± 0.04^d
	3	1.42 ± 0.04^{bc}	1.49 ± 0.04^b	1.56 ± 0.07^c	1.92 ± 0.02^c	1.84 ± 0.05^c	4.67 ± 0.14^c
	6	1.38 ± 0.02^b	1.48 ± 0.04^b	1.52 ± 0.03^c	1.86 ± 0.06^c	1.73 ± 0.04^c	4.41 ± 0.02^{bc}
	9	1.12 ± 0.04^a	1.28 ± 0.04^a	1.38 ± 0.04^b	1.59 ± 0.06^b	1.59 ± 0.01^b	4.24 ± 0.04^b
	12	0.93 ± 0.34^a	1.12 ± 0.04^a	1.22 ± 0.08^a	1.34 ± 0.05^a	1.39 ± 0.06^a	4.11 ± 0.06^a
TF	0	2.33 ± 0.11^d	2.63 ± 0.95^d	3.07 ± 0.94^d	3.79 ± 0.04^c	6.77 ± 0.03^d	9.95 ± 0.04^e
	3	2.21 ± 0.04^d	2.58 ± 0.14^{cd}	2.94 ± 0.06^d	3.66 ± 0.09^c	6.58 ± 0.07^{cd}	9.74 ± 0.05^d
	6	1.84 ± 0.02^c	2.42 ± 0.07^c	2.79 ± 0.03^b	3.48 ± 0.06^b	6.43 ± 0.04^c	9.57 ± 0.12^c
	9	1.45 ± 0.07^b	2.19 ± 0.11^b	2.57 ± 0.04^b	3.25 ± 0.11^b	6.21 ± 0.03^b	9.29 ± 0.04^b
	12	1.24 ± 0.06^a	1.68 ± 0.08^a	2.11 ± 0.02^a	2.88 ± 0.06^a	5.96 ± 0.06^a	9.01 ± 0.04^a

Antioxidant capacity of: hydrophilic fraction (HF); lipophilic fraction (LF) and oil (TF)
Means in a column (a-e across storage period) followed by the same letter are not significantly different ($p < 0.05$).

of oil. They concluded that phospholipids and its Maillard type browning reaction products together with the canolol formed during seed roasting were primarily responsible for the high oxidative stability of the roasted mustard seed oil samples. A marked increase in the oxidative stability of the oil with increasing phospholipid content in the range of 0 to 200 ppm was also reported in a study of rapeseed (Prior *et al.,* 1991) and pumpkin seed roasting (Vujasinovic *et al.,* 2012). Phospholipids and its browning reaction products could show antioxidant activity by multiple mechanisms like chelating agent, emulsifier, hydrogen transfer, reducing agent, free radical scavenger, or peroxide breakdown (Zamora *et al.*, 2011).

Storage of the control oil was found to significantly (p < 0.05) decrease the antioxidant capacity of TF and the oil fractions (HF and LF). After 12 months of storage, the TEAC values of TF, HF and LF in the control oil decreased by 79.1, 41.1 and 46.8%, respectively. A percentage decrease in antioxidant capacity was lower in the oils prepared from the MV pre-treated seeds when compare to the control oil. After 12 months of storage, the oil prepared from seed MV for 10 min lost approx. 10, 15 and 9% of its antioxidant capacity measured for HF, LF and TF, respectively. The reduction in the antioxidant capacity of TF of other oils obtained after seed MV for 2 to 8 min was within the range of 36.1-12.0%, respectively. The rate of degradation

of the antioxidant capacity of cold-pressed rapeseed oil versus oil produced from MV pre-treated rapeseed was examined by Zheng *et al.,* (2014). It was concluded that approx. 80% and 40% of the antioxidant capacity of the untreated oil and oil pressed from MV pre-treated (7 min, 800W) seeds degraded during the 10 weeks of the autoxidation test at 60 ºC.

In order to explain the phenomena of antioxidant capacity changes, the data were fitted using kinetic models (Eq. 1). As shown in Table 5, a zero-order kinetic model adequately described the antioxidant capacity of the oil and its fractions. Although the degradation rate of antioxidant capacity of both hydrophilic and lipophilic oil fractions was similar in all the oil variants studied, the rate of TF degradation was lower in the oils pressed from MV pre-treated seeds than in the control oil. The respective *k* value of TF calculated for the control oil was 9.1×10^{-2} mmol TEAC/l/month; whereas in oils pressed from seed MV for 2, 4, 6, 8 and 10 min, *k* values were $(7.9, 8.0, 7.6, 6.8, 7.8) \times 10^{-2}$ mmol TEAC/l/month, respectively.

4. CONCLUSIONS

Rapeseed microwave pre-treatment significantly affected the concentrations of lipophilic compounds in the oil. With longer seed exposure to MV, the level of α-T in the oil was found to decrease; whereas the

TABLE 5. Kinetic parameters from zero-order reaction kinetics for the antioxidant capacity degradation during the storage of rapeseed oils pressed from microwave-treated seeds.

Oil fraction	HF		LF		TF	
Kinetic parameter	$k \times 10^{-2}$	R^2	$k \times 10^{-2}$	R^2	$k \times 10^{-2}$	R^2
0	4.4	0.9936	5.4	0.9569	9.1	0.9759
2	5.3	0.9534	5.2	0.9536	7.9	0.8766
4	4.2	0.9981	5.6	0.9231	8.0	0.9240
6	4.4	0.9463	5.6	0.9871	7.6	0.9595
8	4.5	0.9463	5.5	0.9891	6.8	0.9915
10	5.0	0.9590	5.8	0.9871	7.8	0.9898

(Row label for the "0–10" column group: **Microwave pretreatment time (min)**)

k – kinetic rate constant (mmol TEAC/l/month); R^2 – coefficient of determination

amounts of γ-T and PC-8 increased with increasing MV time. Maximum lutein and β-carotene concentrations were obtained after 4 and 6 min of seed MV pre-treatment, respectively. Moreover, during microwaving, the thermal degradation of β-carotene took place, which led to the formation of 9-Z- and 13-Z-β-carotene. The kinetics of tocochromanol and carotenoid degradation during the storage of rapeseed oil pressed from MV pre-tretaed seeds followed a zero-order reaction. The application of seed MV pre-treatment prior to oil pressing slowed down the degradation rate of tocochromanols and carotenoids. The antioxidant capacity, as evaluated by using the 2,2-diphenyl-1-picrylhydrazyl radical, decreased following a zero-order kinetic. Although the degradation rate of the antioxidant capacity of both hydrophilic and lipophilic oil fractions was similar in all the oil variants studied, the rate of TF degradation was lower in the oils pressed from MV pre-treated seeds than in the control oil.

Abbreviations: HF: hydrophilic fraction; **LF**: lipophilic fraction; **PC-8**: plastochromanol-8; **TF**: antioxidant capacity of the oil, **α-T**: alpha tocopherol; **β-T**: beta-tocopherol; **γ-T**: gamma-tocopherol; **δ-T**: delta-tocopherol.

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