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Tocopherols and tocotrienols as free radical-scavengers in refined vegetable oils and their stability during deep-fat frying

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Abstract

The aim of this study was to assess the effect of total tocopherols and tocotrienols of refined vegetable oils on oil radical-scavenging activity and to investigate the stability of the various homologues during the deep-fat frying of French fries. Eight different refined vegetable oils were investigated, having variable levels of natural tocopherols and tocotrienols. A direct correlation between the radical-scavenging capacity of the oils, measured by the DPPH test, and the total content of natural tocopherols and tocotrienols was found. Frying experiments showed that the stability of the different tocopherols and tocotrienols present in the refined vegetable oils basically depend on two factors: the fatty acid composition of the oil, in particular polyunsaturated fatty acid content, and the kind of tocopherol and tocotrienol homologues present. The more oxidizable the oil, on the basis of fatty acid composition, the more stable were the tocopherolic antioxidants. Among the different homologues, γ-tocotrienol in palm super olein proved to be the least stable during the deep-fat frying, thus preserving the other homologues.

Keywords: Antioxidants; Deep-fat frying; DPPH; Radical-scavenging activity; Refined oils; Tocopherols; Tocotrienols

1. Introduction

Deep-fat frying may be defined as the process of cooking foods by immersing them in an edible oil or fat maintained at a temperature of about 150–200 °C (Yamsaengsung & Moreira, 2002). There are many types of oils and fats available for frying. The oil or fat used for frying becomes part of the food being fried; therefore, the quality of the frying oil is of great importance with regard to quality of the fried food (Kochhar, 2001). During frying, a complex series of various chemical reactions, such as thermoxidation, hydrolysis and polymerisation, takes place and the frying oil decomposes to form a variety of volatile compounds as well as monomeric and polymeric products. Several factors affect the overall performance of frying oils (Andrikopoulos, Kalogeropoulos, Falirea, & Barbagianni, 2002). In particular, each frying oil has a characteristic stability against autoxidation, depending on the composition of fatty acids and the content and composition of minor components. Actually, fatty acid composition alone may not adequately explain the stability of frying oils (Normand, Eskin, & Przybylski, 2001). Crude vegetable oils contain a variety of minor components, such as hydrocarbons, sterols, tocopherols, polyphenols, colour compounds and trace metals. Some of these components, e.g. tocopherols (particularly γ-tocopherol), phospholipids (at less than 100 mg/kg), carotenoids (at low levels), squalene, and certain sterols, are beneficial to oil stability during frying (Kochhar, 2001).

Natural tocopherols and tocotrienols are retained at considerable levels in finished refined vegetable oils (Karabulut, Topcu, Yorulmaz, Tekin, & Ozay, 2005; Norris, 1982; Rossi, Gianazza, Alamprese, & Stanga, 2001; Simonne & Eitenmiller, 1998). Since they are relatively thermal-resistant, so that only modest tocopherol losses are registered during deodorization/distillation phase (carried

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out at 220–260 °C) (De Greyt & Kellens, 2000; Rossi et al., 2001), their natural antioxidant activity should protect the refined oils against thermal oxidation (Simonne & Eitenmiller, 1998). Tocopherols and tocotrienols, while protecting the fat, are generally themselves first oxidized to quinones and dimers (Hoffmann, 1989).

There is some difficulty in adequately evaluating the antioxidant activity of tocopherols and tocotrienols, because this activity is frequently influenced by their concentration, the types of oils and fats used as substrates, and the method of evaluation (Yoshida, Kajimoto, & Emura, 1993). Moreover, the relative stabilities of the individual homologues, under simulated frying conditions, vary according to the oils under study (Simonne & Eitenmiller, 1998).

Antioxidant activity can be evaluated as total free radical-scavenging capacity, by spectrophotometrically measuring the disappearance of the free 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical. The DPPH· test has previously been successfully employed in assessing the antioxidant activity of crude oils (Ramadan, Kroh, & Morsel, 2003), in particular virgin olive oil (Gomez-Alonso, Fregapane, Salvador, & Gordon, 2003; Lavelli, 2002; Rotondi et al., 2004), but little is known about refined vegetable oils (Espín, Soler-Rivas, & Wichers, 2000).

In the literature, much information is available on the deterioration of frying oils (Andrikopoulos et al., 2002; Du Plessis & Meredith, 1999; Gomez-Alonso et al., 2003; Negishi, Nishida, Endo, & Fujimoto, 2003; Saguy & Dana, 2003; Singh & Tyagi, 2001), whereas few studies (Andrikopoulos et al., 2002; Barrera-Arellano, Ruiz-Mendez, Velasco, Marquez-Ruiz, & Dobarganes, 2002; Du Plessis & Meredith, 1999; Gordon & Kourimska, 1995; Normand et al., 2001; Simonne & Eitenmiller, 1998) have been done on the stability of tocopherols and tocotrienols during deep-fat frying. Besides, some studies have been carried out under simulated frying conditions, in the absence of food (Barrera-Arellano et al., 2002; Simonne & Eitenmiller, 1998).

The aim of this study was to assess the effect of the total tocopherol and tocotrienol contents of selected refined vegetable oils on their radical-scavenging activity, measured by the DPPH test, and to investigate the stability of the various homologues during the deep-fat frying of French fries.

2. Materials and methods

2.1. Chemicals and reagents

HPLC-grade hexane and stabilized 2,2-diphenyl-1-picrylhydrazyl, an artificial free radical, were purchased from Sigma–Aldrich (Steinheim, Germany); α-, γ- and δ-tocopherols were purchased from Calbiochem-Merck KGaA (Darmstadt, Germany); HPLC-grade ethyl acetate was purchased from Merck.

2.2. Materials

Samples of eight different refined vegetable oils were investigated in this work: three palm oils (PO1, PO2 and PO3) and two palm super oleins (double fractionated; PSO1 and PSO2) directly provided by a local refinery (Industria Grassi e Oli Raffinati, Orzinuovi, Italy); one olive oil (OO), one sunflower oil (SO) and one organic frying oil (SHO) made of a blend of sunflower and hazelnut oils, all purchased at local supermarkets. Samples PO1, PO3, PSO1 and OO were only analysed as fresh oils, while PO2, SO, PSO2 and SHO were also used for frying experiments. Two different retail-bought varieties of potato were used for frying experiments: "Vittoria" (from Belgium) and "Bintje" (from Holland). One hour before use, potatoes were manually peeled and cut into sticks (9 mm × 9 mm × 60 mm). Subsequently, the sticks were washed for 5 min in flowing water and then dried for 5 min between two sheets of blotting paper. Finally, they were stored in an air-tight polystyrene container to avoid moisture loss before frying.

2.3. Frying experiments

Two groups of frying experiments were carried out. In the first group, PO2 and SO oils were used for 12 h, frying Vittoria potatoes; in the second group, PSO2 and SHO oils were used for 18 h, frying Bintje potatoes. Experiments were carried out using a domestic deep-fat fryer equipped with a removable stainless steel wire basket and a thermostat. The operative conditions were as follows: actual frying temperature, 175 °C; potato cooking time, 8 min; break time between two successive fryings, 7 min. A low and constant potatoes to oil ratio of 25 g:1 l (Simonne & Eitenmiller, 1998) was used, in order to avoid excessive cooling of the oil at the moment of food immersion and to have enough oil for all sampling, also taking into account the oil uptake by food. Frying sessions lasted continuously for 6 h/day with no oil make up. After each frying session, the fryer was switched off and the oil covered and left at room temperature until the next session.

2.4. Sampling

Oil sampling for analysis (100 ml) was performed during frying every 3 h, for both groups of experiments. For the second group, oil was also sampled after 1 and 2 h of frying. Samples were stored at −20 °C prior to analysis.

2.5. Fatty acid composition

The relative percentage of fatty acids in the fresh oils was determined by capillary gas chromatography on fatty acid methyl esters (FAMEs) obtained according to Liebich, Wirth, and Jakober (1991). Gas chromatographic analysis

of FAMEs was carried out as reported by Colonello, Rossi, and Amelotti (1996), using a Carlo Erba HRGC 5160 instrument equipped with a Supelco SP-2340 capillary column (60 m length, 0.25 mm internal diameter, and 0.25 μm phase thickness). The operative conditions were as follows: carrier, H_2 (90 kPa); oven temperature, 177 °C for 18 min, increased to 205 °C (2.3 °C/min), 205 °C for 2 min, increased to 210 °C (2 °C/min), 210 °C for 30 min; injection temperature was 240 °C; flame ionisation detector temperature, was 250 °C.

2.6. Tocopherol and tocotrienol content

The concentrations of the different tocopherol and tocotrienol homologues in fresh and fried oils were determined by normal phase HPLC analysis, as reported by Rossi et al. (2001). Oil samples were diluted with HPLC-grade hexane using a dilution ratio of 1:15 (w/v), and filtered through a 0.22 μm GV membrane (Millipore Co., Bedford, MA). Calibration curves were prepared by analysing standard solutions in hexane of the following: α-tocopherol in the range 9–53 mg/l, γ-tocopherol in the range 4–45 mg/l, and δ-tocopherol in the range 8–40 mg/l. The curves were linear within the concentration range considered ($r \geqslant 0.998$). α-, γ- and δ-tocotrienols were identified by comparing retention times with the previous study (Rossi et al., 2001) and quantified using the same response factors as the corresponding tocopherol homologues according to the AOCS Ce 8-89 method (2001).

2.7. Radical-scavenging capacity

The total free radical-scavenging capacity of fresh oils was evaluated by measuring the disappearance of the stabilized 2,2-diphenyl-1-picrylhydrazyl artificial free radical (DPPH·) at 515 nm according to the method of Espín et al. (2000), with minor modifications. A 6.1×10^{-5} M DPPH· ethyl acetate solution, adjusted to an absorbance of 0.670 AU, was used. A dose–response curve was built, using, for each point, a mixture of 1900 μl DPPH· solution and 100 μl sample diluted with HPLC-grade ethyl acetate at five different ratios. Mixture absorbance was read after 30 min of reaction at 25 ± 1 °C. Results are reported as $1/I_{50}$, where I_{50}, extrapolated from the rectilinear part of the dose–response curve, is the volume of fresh oil (in μl) required to lower the initial DPPH· concentration by 50%.

All the above analyses were performed in duplicate.

2.8. Calculated oxidizability (Cox) of oils

The Cox value of oils was calculated by the percentage of unsaturated C18 fatty acids, applying the formula proposed by Fatemi and Hammond (1980):

$$\text{Cox} = [1(18{:}1\%) + 10.3(18{:}2\%) + 21.6(18{:}3\%)]/100.$$

2.9. Statistical analysis

A Pearson correlation matrix was performed using Systat 5.03 software for Windows (Systat Inc., USA).

3. Results and discussion

Table 1 lists the fatty acid composition, the ratio between unsaturated and saturated fatty acids and the Cox value of the refined vegetable oils considered. It can be observed that the palm oils (PO1, PO2 and PO3) and the palm super oleins (PSO1 and PSO2) can be distinguished from the other oils due to their high concentration of saturated fatty acids, palmitic acid (C16:0) in particular. Consequently, the ratio between unsaturated and saturated proves to be the lowest in these oils. SO stands out for its high linoleic acid content (C18:2) and its low saturated fatty acid content, which make it particularly prone to oxidation. Indeed, of the oils considered, SO shows the highest Cox value. OO and SHO are characterized by a very high concentration of oleic acid (C18:1) and a low content of saturated fatty acids. SHO is a blend of sunflower oil (primary ingredient) and hazelnut oil; given the fatty acid composition of the blend, it can be hypothesized that a sunflower oil high in oleic fatty acid was used in its formulation, although this was not stated on the label. Even though SHO presents the highest ratio of unsaturated to saturated fatty acids, its Cox value is not particularly high, as the predominant unsaturated acid is the monounsaturated oleic acid which has a lower weight, in the Cox calculation, than the polyunsaturated linoleic and linolenic acids (C18:3), since its oxidation rate is far below those of the other C18 unsaturated acids (Gunstone & Hilditch, 1946).

In Table 2, the composition and the total content (as the sum of all the identified homologues) of tocopherols and tocotrienols of the various refined oils considered are shown, together with their radical-scavenging capacities expressed as $1/I_{50}$ multiplied by 100.

SO, OO and SHO principally contain α-tocopherol (α-T), whereas the palm-derived oils are also characterized by the presence of α-tocotrienol (α-T3), γ-tocotrienol (γ-T3) and δ-tocotrienol (δ-T3). More specifically, γ-T3 proved to be the most abundant, while the other homologues were found in different ratios according to the oil considered. The tocopherol and tocotrienol contents were fairly high, confirming the resistance of these natural antioxidants to refining operations. Actually, the average tocopherol and tocotrienol contents of crude olive oil, sunflower oil, hazelnut oil and palm oil are 199, 1008, 455, and 800 mg/kg, respectively (O'Brien, 2004; Souci, Fachmann, & Kraut, 2000). Therefore, disappearance due to degradation and/or stripping in the refining processes ranges from 25% to 65% of the total content. The oils richest in tocopherols and tocotrienols were the two palm super oleins, which actually also showed the highest values for antiradical activity. The weakest radical-scavenging activity was

Table 1
Fatty acid composition (%) of the refined vegetable oils considered

Fatty acids	OO	SO	SHO	PO1	PO2	PO3	PSO1	PSO2
C8:0	Absent	Absentabsent	Absent	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.01	Traces
C10:0	Absent	Absent	Absent	Traces	Absent	Absent	Traces	Traces
C12:0	Traces	Absent	Absent	0.43 ± 0.02	0.32 ± 0.07	0.30 ± 0.07	0.41 ± 0.02	0.27 ± 0.02
C14:0	Traces	0.07 ± 0.01	0.04 ± 0.01	1.19 ± 0.03	1.23 ± 0.18	1.07 ± 0.17	1.11 ± 0.02	0.96 ± 0.06
C15:0	Absent	Absent	Traces	0.05 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.04 ± 0.01
C16:0	12.8 ± 0.3	6.07 ± 0.03	3.99 ± 0.01	46.3 ± 0.50	47.2 ± 2.02	45.0 ± 2.05	35.8 ± 0.15	33.9 ± 0.51
C16:1*n*9	0.11 ± 0.01	Traces	0.03 ± 0.01	Traces	Traces	Traces	0.04 ± 0.01	0.04 ± 0.01
C16:1*n*7	1.01 ± 0.02	0.08 ± 0.01	0.11 ± 0.01	0.16 ± 0.01	0.15 ± 0.01	0.14 ± 0.01	0.22 ± 0.01	0.20 ± 0.01
C17:0	0.07 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.10 ± 0.01	0.10 ± 0.01	0.08 ± 0.01	0.07 ± 0.01	0.07 ± 0.01
C17:1	0.13 ± 0.01	Traces	0.04 ± 0.01	Traces	Traces	Traces	Traces	0.03 ± 0.01
C18:0	2.49 ± 0.04	3.12 ± 0.01	2.66 ± 0.02	3.99 ± 0.05	3.93 ± 0.20	3.71 ± 0.08	3.41 ± 0.06	3.42 ± 0.01
C18:1*n*9 *trans* + C18:19*n*7 *trans*	Absent	Absent	Traces	0.10 ± 0.02	0.20 ± 0.01	0.18 ± 0.01	0.07 ± 0.01	0.06 ± 0.01
C18:1*n*9 + C18:1*n*7	72.5 ± 0.25	24.5 ± 0.11	79.0 ± 0.02	38.2 ± 0.33	37.4 ± 1.50	39.8 ± 1.78	45.0 ± 0.18	47.4 ± 0.42
C18:2*n*6 *cis–trans*	0.04 ± 0.01	0.48 ± 0.01	Traces	0.31 ± 0.01	0.11 ± 0.01	0.10 ± 0.01	0.17 ± 0.01	0.11 ± 0.01
C18:2*n*6 *trans–cis*	Traces	0.41 ± 0.01	Traces	0.30 ± 0.01	0.10 ± 0.01	0.09 ± 0.01	0.16 ± 0.01	0.10 ± 0.01
C18:2*n*6	9.51 ± 0.11	64.1 ± 0.15	12.7 ± 0.10	8.16 ± 0.07	8.61 ± 0.31	8.94 ± 0.42	12.7 ± 0.07	12.6 ± 0.19
C20:0	0.37 ± 0.01	0.20 ± 0.01	0.23 ± 0.01	0.30 ± 0.01	0.28 ± 0.04	0.27 ± 0.03	0.29 ± 0.01	0.31 ± 0.01
C18:3*n*3 + C20:1*n*11	0.83 ± 0.01	0.19 ± 0.02	0.40 ± 0.01	0.19 ± 0.01	0.24 ± 0.02	0.24 ± 0.02	0.37 ± 0.01	0.40 ± 0.01
C22:0	0.10 ± 0.01	0.52 ± 0.01	0.60 ± 0.03	0.05 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	0.06 ± 0.01
C24:0	0.04 ± 0.01	0.19 ± 0.02	0.23 ± 0.02	0.05 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	0.06 ± 0.01
Unsaturated/saturated	5.30	8.79	11.85	0.90	0.88	0.98	1.42	1.56
Cox value	1.89	6.89	2.18	1.27	1.31	1.37	1.84	1.86

Traces = $\leqslant$ 0.02%.

Table 2
Tocopherol and tocotrienol contents and radical-scavenging activity (average ± s.d.) of the different oil samples analyzed

Sample	α-T (mg/kg)	α-T3 (mg/kg)	γ-T3 (mg/kg)	δ-T3 (mg/kg)	Total tocol-derived compounds (mg/kg)	$1/I_{50} \times 10^2$ (μl^{-1})
OO	148 ± 6	–	–	–	148	1.67 ± 0.07
SO	475 ± 11	–	–	–	475	5.12 ± 0.04
SHO	393 ± 14	–	–	–	393	2.79 ± 0.14
PO1	63.7 ± 0.7	62.8 ± 1.2	167 ± 2	62.8 ± 4.8	356	1.65 ± 0.09
PO2	63.4 ± 11.5	74.9 ± 2.7	138 ± 7	86.8 ± 5.4	276	1.89 ± 0.08
PO3	134 ± 9	163 ± 8	295 ± 14	72.0 ± 3.4	688	4.99 ± 0.13
PSO1	200 ± 9	192 ± 3	390 ± 14	99.8 ± 12.9	881	9.79 ± 1.01
PSO2	246 ± 10	259 ± 5	438 ± 6	122 ± 2	1064	9.08 ± 0.16

found for OO and PO1, where it was almost six times lower than the average value for the two super oleins.

The radical-scavenging activity proved to be significantly correlated ($P < 0.001$) with the total content of tocopherols and tocotrienols (Fig. 1). This proves that these compounds play a predominant role in determining the antioxidant characteristics of refined vegetable oils in which other kinds of natural antioxidants (e.g. polyphenols and carotenoids) have been removed or destroyed by the refining treatments (Andrikopoulos et al., 2002; Nergiz, 1993; Rossi et al., 2001). Moreover, as regards the various homologues, significant correlations were obtained between oil radical-scavenging activity and the contents of γ-T3 ($P < 0.01$) and α-T3 ($P < 0.05$), whilst no correlation was found for α-T and δ-T3. Indeed, in the literature, it is reported that α-T has the lowest antioxidant activity, even though its biological activity, as vitamin E, is the greatest (Belitz & Grosch, 1999), whereas γ-T3 has the highest antioxidant activity (Theriault, Chao, Wang, Gapor, & Adeli, 1999).

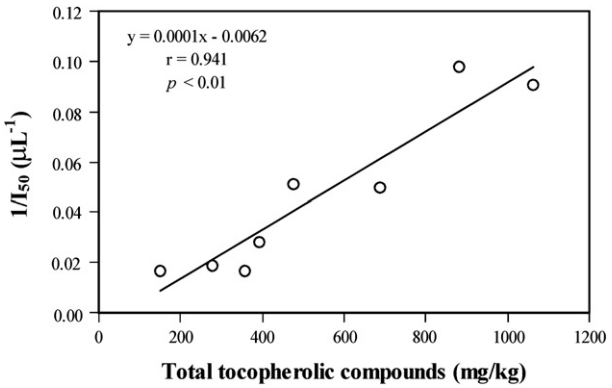

Fig. 1. Correlation between the total tocopherol and tocotrienol content and the radical-scavenging activity of the refined vegetable oils analyzed.

SO, PO2, PSO2 and SHO were utilized to perform the deep-fat frying experiments for the cooking of French fries, over a period of 12 or 18 h. During the frying experiments, the degradation kinetics of tocopherols and tocotrienols in the oils considered were studied.

Table 3
Tocopherol and tocotrienol contents (average ± s.d.) of PSO2 at different frying times

Time (h)	α-T (mg/kg)	α-T3 (mg/kg)	γ-T3 (mg/kg)	δ-T3 (mg/kg)
0	246 ± 10	259 ± 5	438 ± 6	122 ± 2
1	245 ± 10	258 ± 5	415 ± 11	122 ± 2
2	231 ± 1	236 ± 1	404 ± 26	118 ± 0
3	193 ± 2	212 ± 7	322 ± 3	113 ± 4
6	205 ± 9	214 ± 1	245 ± 2	121 ± 8
9	205 ± 7	214 ± 24	152 ± 5	112 ± 5
12	195 ± 8	199 ± 10	75.3 ± 2.8	100 ± 2
15	182 ± 2	174 ± 2	n.d.	82.5 ± 2.2
18	66.7 ± 4.7	n.d.	n.d.	n.d.

n.d., not detectable as a consequence of peak deformation due to superposition of newly-formed degradation compounds.

Table 3 shows contents of the various homologues in PSO2 at different frying times. As can be seen, in the first 2 h of frying, all the tocopherols and tocotrienols were resistant to thermoxidation, with negligible decreases recorded. Instead, starting from the third hour, a more significant reduction was observed, in particular for γ-T3, whose relatively rapid disappearance could be related to its greater antioxidant activity. Indeed, since the mechanism of the radical-scavenging reaction of tocopherols and tocotrienols requires that they lose their mobile hydrogen atoms in the hydroxyl group, forming more stable free radicals than those of the fatty acids, it follows that a faster oxidation of tocopherols and tocotrienols corresponds to a greater antioxidant power (Hoffmann, 1989).

As far as the relative stability of the various homologues is concerned, in the case of PSO2 the following order was observed (comparing the residual percentages after 9 h of frying): δ-T3 > α-T ⩾ α-T3 > γ-T3. This order should correspond to an inverse order of antioxidant activity. Simonne and Eitenmiller (1998) reported a slightly different order of stability (α-T > δ-T3 > α-T3 > γ-T3) for palm olein, in simulated frying tests, and a different oxidizability for tocopherols and tocotrienols, according to the type of oil considered. The same phenomenon was also observed in this study and was brought out particularly by the data relating to SHO and SO. These two oils, which principally contain α-T, showed totally different degradation kinetics (Fig. 2). In SO, α-T proved to have a very high stability; after 12 h of frying, 90% of it was still present. Instead, in SHO, the α-T content plummetted during the 18 h of frying. Already, after 3 h, it had fallen by approximately 50% and, after 9 h of frying, only 6.6% remained. The considerable difference between the behaviours of α-T in SHO and SO may be attributable to the different Cox values (Table 1) (approximately three times higher in SO). As already observed by Simonne and Eitenmiller (1998), tocopherols and tocotrienols seem to degrade more quickly in the oils with a high saturated fatty acid content. Actually, one could suppose that, in the case of oils containing higher levels of polyunsaturated fatty acids, the double bonds which determine unsaturation compete with the tocopherols and tocotrienols as substrates for oxidation, determining a less rapid decrease of these antioxidants. Instead, in the case of oils low in polyunsaturated fatty acids, tocopherols and tocotrienols constitute the substrates that more easily react with oxygen. Indeed, it is reported in the literature that, in the propagation phase of the reaction, the fatty acid peroxy free radicals react preferentially with the phenolic hydrogen of the tocopherol molecule (Hoffmann, 1989).

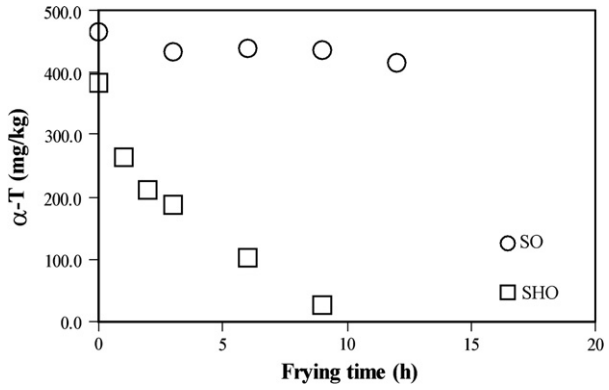

Fig. 2. α-Tocopherol content in SO and SHO during frying.

The degradation rate of α-T in SHO is far greater even than that observed in PSO2, even though the two oils have similar Cox values (1.86 for PSO2 and 2.18 for SHO). Actually, the half time for α-T in SHO (calculated by interpolation of the curve in Fig. 2) is 2.6 h while it is 17.1 h in PSO2 (calculated by interpolation of the data in Table 3). In this case, since the Cox value cannot justify such a different degradation speed for α-T, the quality and quantity of the other homologues present in the oils take on a prominent role. In the case of PSO2, the high levels of tocotrienols, in particular γ-T3, proved to be of fundamental importance in preserving the α-T from degradation. Indeed, the tocotrienols are better antioxidants than are the corresponding tocopherols, devoid of double bonds in the side chain (Theriault et al., 1999). In the case of SHO, the α-T degrades so rapidly because it is the only tocopherol present and, thus, the only one able to act as an antioxidant.

During the frying of PO2, which has a low Cox value, slightly below that of PSO2, and a lower tocopherol and tocotrienol content, a rapid degradation of all the homologues takes place. All of them already disappear after 3–6 h of frying (data not shown).

This study has shown that, in actual frying conditions, the stability of the different homologues of the natural tocopherols and tocotrienols present in the refined vegetable oils basically depends on two factors: the oxidizability of the oil, which is connected with the polyunsaturated fatty acid content, and the kind of tocopherolic compounds present. In particular, tocopherols and tocotrienols, acting as radical scavengers, play an important antioxidant role, since the presence of other antioxidants is negligible. The more oxidizable the oil, on the basis of fatty acid composition, the more stable are the natural tocopherols and tocotrienols present in the oil. As regards the effect of the

different tocopherolic compounds, the presence of γ-T3 preserves the other homologues, in particular α-T, with which the greatest vitamin E activity is associated.

The DPPH· test, carried out on different refined vegetable oils, showed the existence of a direct correlation between the radical-scavenging capacity of the oils and the total content of natural tocopherols and tocotrienols.

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