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Phytosterols in frying oils: evaluation of their absorption in pre-fried potatoes and determination of their destruction kinetics after repeated deep and pan frying

Panagiotis E. Igoumenidis, Maria A. Konstanta, Fotini N. Salta, Vaios T. Karathanos *

Department of Science of Dietetics-Nutrition, Laboratory of Chemistry, Biochemistry, Physical Chemistry of Foods, Harokopio University, 70 El. Venizelou Av., Kallithea, 17671, Athens, Greece (e-mail address: vkarath@hua.gr)

Abstract

The levels of β-sitosterol and total phytosterols were monitored in pre-fried potatoes during eight successive pan- and deep-frying sessions in five different commercial frying oils (virgin olive oil, sunflower oil, palm oil, cottonseed oil and vegetable shortening oil). The amount of these constituents that were transferred from the frying oils to the potatoes at the end of each frying session was determined prior and after frying by GC/FID. Except for the potato enrichment with phytosterols, the kinetics of the destruction of β-sitosterol and total phytosterols, mainly due to thermal oxidation of the oils, were evaluated for each of the five different types of oil. The experiments showed that in most cases the destruction of both β-sitosterols and total phytosterols followed first order kinetics with quite good correlation coefficients (R>0.92) and the reaction constant *k* was found to be at the range of 0.004 - 0.028 min^{-1}. Concerning the absorption of the two types of phytosterols in the fried potatoes during frying, they were found to be at the range (average) of 0.4-27% of their initial content in the oil at the beginning of each frying process (eight frying processes/session), depending on the type of oil and the constituent.

Keywords: frying; oils; phytosterols; absorption; kinetics.

1. Introduction

Fried potatoes are widely consumed worldwide and their way of preparation is used in both industrial and household cooking processes. Among other food products people favour this type of potatoes mainly because of their excellent taste, unique sensory characteristics as well as the easy and quick way of

* Corresponding author. Tel.: +30-210-9549224; fax: +30-210-9577050.
E-mail address:vkarath@hua.gr.

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cooking. Although they are generally considered as being a rather unhealthy type of food in the Western diet, studies have shown that frying appears to have the same or even less effect on nutrient losses compared to other cooking methods [2]. Furthermore the nutritive value of food may increase due to the absorption of frying oils which usually contain high quantities of useful constituents such as unsaturated fatty acids and vitamin E [3].

Phytosterols or plant sterols can be characterized as important dietary components which lower low density lipoprotein (LDL) cholesterol. Additionally they have been found to possess anti-cancer, anti-inflammatory, anti-atherogenic and anti-oxidative properties. Their dietary sources include vegetable oils (especially unrefined ones), nuts, seeds and grains [1]. Phytosterols are characterised by the fact that they compete with dietary cholesterol to be absorbed by the intestines, resulting in lower serum cholesterol levels and at the same time they offer protection against the oxidation of low-density lipoprotein (LDL) [4]. As they are considered to be unsaturated lipids, they normally undergo thermal oxidation during heating or frying, which leads to the formation of decomposition products such as phytosterol oxides [5]. In general, phytosterols' stability is influenced by frying temperature, frying time, sterol structure and lipid composition.

The main aim of this study was to measure the amounts of β-sitosterol and total phytosterols in the potatoes at the end of each of the eight consecutive frying sessions (deep- and pan-frying) that were carried out. B-sitosterol was chosen as it is considered to be the predominant sterol in common vegetable oils. Five different commercial types of frying oils were used for the experiments and the kinetics of the destruction of β-sitosterol and total phytosterols were evaluated concerning every type of oil.

2. Materials and Methods

The vegetable oils selected, namely sunflower oil (SFO), cottonseed oil (CSO), palm oil (PO), virgin olive oil (VOO) and a vegetable shortening oil (VSO) (consisting of sunflower oil, palm oil and cottonseed oil), are among the most popular frying oils and they were purchased from local stores. Pre-fried potatoes having approximate dimensions of 10 cm length and 1 cm thickness were purchased from a local store.

The frying experiments were conducted in the same manner as the actual household cooking process. Pan-frying was performed in an uncovered stainless steel pan fryer (5.5 cm high, diameter 20.5 cm); 200 ± 10 g potatoes were fried each time in 0.3 L (270 g) of oil, for 6 min at 175 ± 5°C, using an electric plate of a conventional electric kitchen cooker equipped with a thermostat. The oil temperature was monitored with a digital thermometer attached to a steel probe. After cooling (approx. 30 min), the frying process was repeated eight times in the same oil, without replenishment. For deep-frying, a common domestic type electric fryer was used (Kenwood DF SSO, PK OOS/WGR, Havant, UK), equipped with a thermostat (170°C) and supplied with an inert cross-linked steel wire-mesh which allowed the food to be dipped into the oil, without coming in contact with the fryer's inner surface. In every frying session 400 ± 10 g potatoes were deep fried for 9 min in 2.0 L oil, without replenishment. Both the frying oil and potatoes were weighed before and after frying. Excess oil in French-fries was allowed to drain on a cross-linked steel wire-mesh and was added to the oil remaining in the fryer. The frying trials were performed in duplicate.

Samples of French-fries and frying oils from every frying operation were obtained. The potatoes were immediately frozen and lyophilized (for 48 h). Besides preservation, freeze-drying also served for determining the water content. The oil samples were placed into 10-mL screw capped vials, sealed under nitrogen and kept at -20°C until analysis. The freeze-dried potato samples (500 mg) were extracted with diethyl oxide (2x5 mL), in the first step by means of an Ultra-Turrax T25 homogenizer (Junkel & Kunkel, Staufen, Germany). The homogenates were centrifuged; the extracts were combined and, after removing the solvent under vacuum, the residue oil was weighted and it was treated as the oil samples. Since the lipid content of fresh potatoes is negligible, the ether extracts of the pre-fried and finish-fried potatoes also

served for the determination of the absorbed oil. Phytosterols were determined using a Gas Chromatography/FID method which is described in Salta et al. (2007).

3. Results and Discussion

3.1. Phytosterol content

The determination of β-sitosterol and total phytosterols in both the frying oils and the French fries was done by GC/FID. The contents of the above micro constituents in every oil and potatoes after each frying session are shown in Tables 1 and 2, respectively.

3.2. Study of phytosterol destruction kinetics

After having obtained all the necessary data concerning the content of phytosterols both in the frying oils and in the fried potatoes, we examined their reduction kinetics due to destruction of phytosterols inside each frying oil. In general, the reduction of β-sitosterol and total phytosterols, which further results in the deterioration of the quality of frying oils, can be attributed to two important factors. One of them is a serious amount of phytosterols, which enters the potatoes together with the oil absorption and at the end of each frying session it is removed from the remaining oil together with the fried potatoes. The other factor is the destruction of phytosterols during each frying session which happens mainly due to the thermal process. In this case an amount of phytosterols is decomposed probably due to their oxidation to oxy-sterols, which is a reaction favored both by the presence of heat and available surface oxygen. That is why the destruction of phytosterols seems to be more intense in the case of pan-frying than in deep-frying, as in pan frying there is a relatively higher concentration of available oxygen which is in contact with the frying oil. All the calculations needed by using the data of Tables 1 and 2, in order to estimate the kinetic model that fits best to the phytosterol deterioration rate in every frying oil, during the eight consecutive frying sessions, were done by using the Microsoft EXCEL program.

In particular, in this study we determined the reaction constants *k* concerning the destruction rate of β-sitosterol and total phytosterols for every sequence of eight consecutive frying sessions (both deep- and pan-frying cases) and for each of the five different types of oil. We calculated the *k* constants in each case after having done trials, supposing that the phytosterol deterioration reaction follows zero, first and second order kinetics, so that we can finally decide which of them fits best the experimental data. The most important parameter concerning choosing the order of the reaction kinetics was the correlation coefficients R which were greater, on the average, in the case that the deterioration followed first order kinetics compared to those estimated in the cases of zero and second order kinetics.

Same order of reaction kinetics was chosen by Krokida et al. (2000) who came to the conclusion that the mass transport phenomena, which happen during frying and concern both the loss of moisture and the oil absorption, are considered to follow a first order kinetic model. Additionally in other cases of international literature a first order kinetic model was developed for the description of oil absorption rates [6, 8].

Table 1. Phytosterol content in fresh and fried oils in mg/100 g oil [3]

Frying Session	CSO		SFO		VSO		PO		VOO	
	Pan	Deep	Pan	Deep	Pan	Deep	Pan	Deep	Pan	Deep
	β-Sitosterol									
0*	349.5	349.5	177.0	177.0	287.3	287.3	71.2	71.2	141.0	141.0
1	166.2	345.0	92.6	157.0	239.5	242.4	57.8	64.6	137.5	141.3

2	151.6	336.5	91.1	149.5	201.1	208.0	54.5	62.6	116.8	136.1
3	138.0	328.0	77.2	146.6	157.3	203.5	54.3	61.4	103.0	120.7
4	133.9	320.0	77.0	119.4	140.6	195.7	53.9	59.1	100.9	119.9
5	123.9	309.8	75.9	111.3	125.5	207.6	51.5	40.8	91.0	118.4
6	121.2	256.1	80.0	106.9	116.9	208.7	50.8	35.5	90.1	94.1
7	117.2	236.0	74.7	102.9	73.3	194.5	46.0	35.9	86.2	90.1
8	86.6	213.6	73.4	102.2	63.8	109.3	44.3	35.0	82.4	86.8
Total Phytosterols										
0*	402.6	402.6	225.4	225.4	356.5	356.5	115.3	115.3	179.2	179.2
1	194.5	395.8	116.0	198.5	289.6	303.4	92.2	105.5	170.2	174.5
2	177.5	385.0	115.7	187.7	242.1	260.5	86.5	93.7	145.0	166.5
3	162.4	373.6	97.3	182.4	192.2	253.6	83.3	90.6	129.3	148.7
4	157.5	364.3	97.2	153.1	171.0	244.9	81.4	84.9	126.4	147.0
5	146.7	351.5	95.1	142.4	150.5	255.7	78.3	63.7	113.8	145.0
6	143.3	295.4	101.4	135.9	139.8	256.0	76.7	57.6	111.0	113.8
7	138.2	272.9	96.0	128.6	91.4	239.1	70.3	55.9	105.5	107.8
8	103.3	246.9	93.8	126.5	80.6	139.6	67.8	54.2	98.4	99.7

* Frying session 0 represents the content in fresh oils. The content for the rest of frying sessions (fried oils) stands for the average value of two phytosterol determinations.

The values of destruction rate constants *k* concerning both β-sitosterol and total phytosterols together with the respective correlation coefficients R are presented in Table 3. For the calculation of constants *k* we used the equation which describes the model of first order kinetics:

$$ln(C/C_0) = -k*t$$

where C_0 is the phytosterols' content of fresh oils, C is the phytosterols' content of the fried oils at the end of each of the eight concecutive frying sessions, after having supposed that it is reduced compared to C_0 only by the amount which represents the destruction of phytosterols and not the amount of reduction due to the absorption in the potatoes, *k* is the phytosterol destruction rate constant in every frying oil and t is the cumulative time of the consecutive frying sessions after taking into consideration that each pan-frying session lasts 6 min and each deep-frying session 9 min.

After having applied the above equation for every type of oil and for both deep- and pan-frying sessions, we took eight pairs of values [$ln(C/C_0)$, t] (one for each of the eight consecutive frying sessions) by which we produced certain diagrams using the Microsoft EXCEL program. Based on the eight pairs of values in each diagram we drew a trend line which best fits all of these pairs and its slope is equal, according to the equation, to the value of constant *k* concerning every sequence of frying sessions.

Table 2. Phytosterol content in French fries in mg/100 g of potatoes [3]

Frying Session	CSO		SFO		VSO		PO		VOO	
	Pan	Deep	Pan	Deep	Pan	Deep	Pan	Deep	Pan	Deep
β-Sitosterol										
0*	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
1	42.9	49.3	7.6	34.9	26.7	11.9	7.9	13.5	11.4	13.2
2	41.1	48.1	7.5	34.2	16.8	11.0	7.2	8.7	8.5	12.6

3	39.4	47.5	7.4	33.7	16.3	8.6	6.4	8.1	7.8	10.1
4	39.1	47.0	7.1	32.9	15.6	5.2	5.4	8.0	7.6	7.4
5	35.2	45.7	6.1	24.6	15.0	3.9	4.9	7.9	7.2	6.7
6	33.3	43.0	6.1	24.3	14.1	3.4	4.1	6.8	6.9	6.1
7	33.2	39.7	6.0	23.0	10.2	2.9	3.5	6.4	4.6	6.0
8	31.2	38.4	5.8	21.8	4.9	2.1	1.5	5.5	3.8	4.8
					Total Phytosterols					
	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3
1	50.2	59.9	9.8	45.9	34.5	14.9	14.2	20.8	17.5	17.6
2	48.3	56.5	9.6	44.5	22.1	13.8	11.6	14.0	13.1	16.6
3	46.5	55.6	9.4	43.9	21.2	10.5	10.3	12.4	12.1	12.9
4	46.2	54.7	9.0	41.7	20.1	6.8	8.7	12.1	11.7	9.9
5	41.9	53.1	7.7	32.1	19.2	5.3	7.4	11.5	11.2	9.2
6	39.8	50.3	7.6	31.5	18.1	4.7	6.1	10.3	10.6	8.3
7	39.6	46.7	7.5	29.9	13.4	3.9	5.1	9.6	8.1	8.2
8	37.5	45.1	7.2	28.2	6.5	3.0	2.4	8.2	7.2	6.9

* Frying session 0 represents the content in the initial pre-fried potatoes. The content for the rest of frying sessions (fried potatoes) stands for the average value of two phytosterol determinations.

Table 3. Destruction rate constants *k* for β-sitosterol and total phytosterols during frying (hypothesis of 1st order kinetics)

Frying Oil	Deep/Pan-Frying	β-sitosterol		Total phytosterols	
		k	R	*k*	R
VOO	Deep-	0.0092	0.976	0.0101	0.980
	Pan-	0.0279	0.993	0.0232	0.996
SFO	Deep-	0.0043	0.935	0.0044	0.957
	Pan-	0.0204	0.893	0.0212	0.897
CSO	Deep-	0.0049	0.926	0.0049	0.943
	Pan-	- *	- *	- *	- *
PO	Deep-	0.0102	0.946	0.0103	0.978
	Pan-	0.0193	0.977	0.0181	0.985
VSO	Deep-	0.0101	0.850	0.0102	0.868
	Pan-	0.0203	0.989	0.0226	0.990

* The *k* and R values for pan-frying in CSO could not be accepted and that is why they were not included in this table

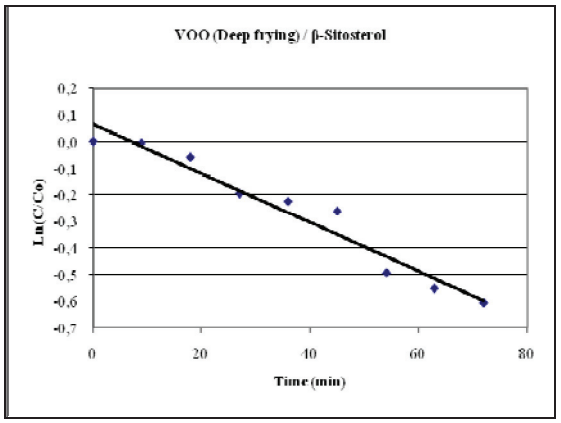
In Table 3 it is noticed that the calculated values of R were satisfactory for the majority of frying cases (70%) R>0.92. After having followed a first order kinetic model the R values were on the average greater than the resulted R values after applying zero or second order kinetic models. For this reason calculations for the constant *k* were made by choosing a first order kinetic model.

In addition, the destruction rate constants *k*, concerning both β-sitosterol and total phytosterols during deep frying sessions, were all found to be in a relatively short range of values (0.0043-0.0103 min^{-1}). The minimum *k* value in deep-frying was found for the Sunflower oil (SFO) and the maximum *k* value for Palm oil (PO). This means that SFO undergoes the slowest deterioration due to destruction of β-sitosterol and total phytosterols among all the oils used and PO the fastest one for a certain amount of time. In pan-

frying cases the destruction rate constants *k* were again found to be in a short range of values (0.0181-0.0279 min^{-1}) and the minimum *k* value was found for PO, while the maximum was for VOO. This shows that during pan-frying PO undergoes the slowest deterioration, while VOO the fastest one for a certain amount of frying time.

The data of Table 3 showed that the destruction rate constant *k* presented a higher value in pan-frying cases than in deep-frying ones, when using the same type of oil. This indicates that the rate in which phytosterols are lost, because of their destruction, during pan-frying is greater than the rate during deep frying using the same oil type. The same conclusion was partially drawn by Salta et al. (2007), who found out that pan-frying generally resulted in higher phytosterol total reduction than deep-frying for specific amounts of frying times.

Figures 1 and 2 show the deterioration rate of β-sitosterol during a sequence of eight consecutive deep- and pan-frying sessions in VOO respectively, while Figures 3 and 4 present the deterioration rate of total phytosterols during the above deep- and pan-frying sessions.



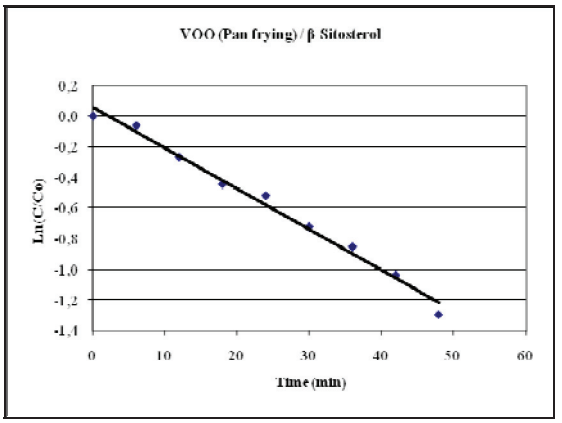
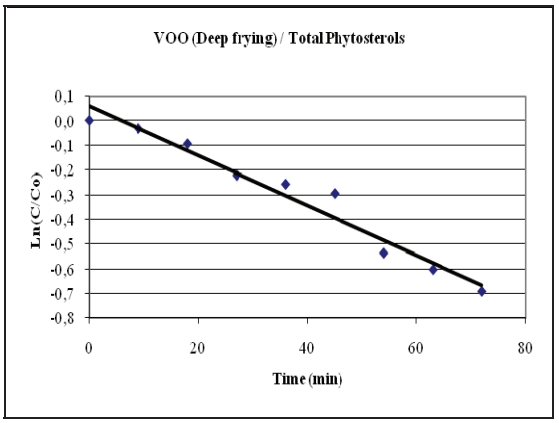


Fig. 1, 2. Deterioration rate of β-sitosterol in virgin olive oil during deep- and pan-frying, respectively



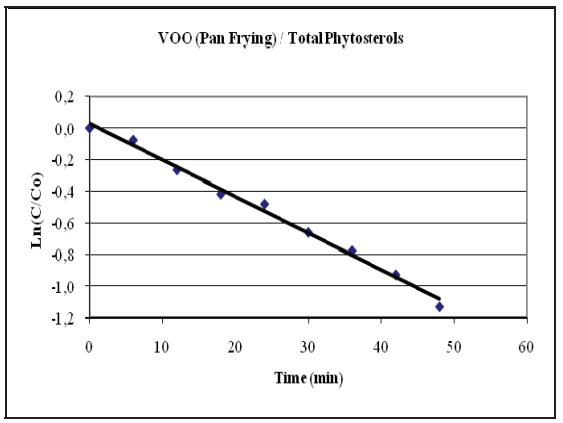


Fig. 3, 4. Deterioration rate of total phytosterols in virgin olive oil during deep- and pan-frying, respectively

3.3. Determination of phytosterol absorption

Except for destruction kinetics the amount of the absorption of β-sitosterol and total phytosterols in frying potatoes was also studied. This was calculated separately for each frying oil, frying type (deep- or pan-) and frying session. Table 4 shows the range of % absorption of phytosterols inside the fried potatoes at the end of each frying session as well as the average values of % absorption per sequence of eight consecutive frying sessions. These values represent the ratio of the phytosterol content in fried potatoes at the end of each frying session to the phytosterol content in the frying oil at the beginning of the same frying session.

Table 4. Phytosterol % absorption limits in potatoes and average values / frying session.

Frying Oils		β-Sitosterol		Total Phytosterols	
		Range of % absorption / frying session	Average % absorption / sequence	Range of % absorption / frying session	Average % absorption / sequence
VOO	Deep	0.3-1.5%	0.82%	0.4-1.5%	0.86%
	Pan	0-4.4%	2.79%	3.5-6%	4.47%
SFO	Deep	3.9-4.6%	4.35%	4-4.7%	4.40%
	Pan	1.6-3.9%	3.16%	1.5-3.5%	2.66%
CSO	Deep	2.9-3.9%	3.24%	2.9-3.9%	3.26%
	Pan	8.5-45.5%	27.00%	8.5-45.5%	26.76%
PO	Deep	1.2-3%	1.80%	1.3-3%	1.89%
	Pan	0.6-4.6%	3.05%	1-5.8%	3.90%
VSO	Deep	0-0.7%	0.40%	0-0.6%	0.37%
	Pan	2.8-10.5%	6.83%	2.4-11%	7.05%

The results presented in Table 4 show that the average absorption of micro constituents (both β-sitosterol and total phytosterols) in potatoes was greater when frying in CSO (27%) among all pan-frying sequences. On the other hand, the lowest average absorption ratios for the pan-frying sequences were found in the case of VOO (2,8%) concerning β-sitosterol and SFO (2,7%) concerning total phytosterols. The average values for the deep-frying sequences indicated that there is greater phytosterol absorption when using SFO (4,4%) and lower when using VSO (0,4%).

4. Conclusion

In this study we used a first order kinetic model to describe the reduction rate of phytosterols, due to thermal oxidation, in certain types of oil after deep- and pan-frying. We chose this model as it was found to be more accurate, on the average, concerning the values of constant k and coefficient correlation R, compared to the values taken when applying zero or second order kinetic models.

In general, raw potatoes are rather poor sources of phytosterols and other antioxidants. By studying the amounts and the rates in which such substances can be absorbed by fried potatoes, or be destroyed due to the heating process, and correlating these phenomena to the initial content of these constituents in each frying oil, the number of frying sessions in order to achieve an effective absorption of phytosterols by the potatoes may be judged. Moreover, even in cases of using oils, enriched with antioxidants, someone can predict the behavior and the transfer rate of these substances from the oil to the fried potatoes after a specific number of frying sessions according to their absorption and destruction kinetics.

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