POLISH JOURNAL OF FOOD AND NUTRITION SCIENCES
Pol. J. Food Nutr. Sci. 2005, Vol. 14/55, No 4, pp. 381–387

CHANGES IN PHYTOSTEROLS AND THEIR OXIDATION PRODUCTS DURING FRYING OF FRENCH FRIES IN RAPESEED OIL

Magdalena Rudzińska, Józef Korczak, Erwin Wąsowicz

The August Cieszkowski Agricultural University of Poznań, Poznań

Key words: phytosterols, oxyphytosterols, deep frying, rapeseed oil, French fries

The goal of this study was to monitor changes in the composition of phytosterols and oxyphytosterols in rapeseed oil and French fries during multiple (14 times) deep-frying. Phytosterols (brassicasterol, campesterol, stigmasterol, β-sitosterol and avenasterol), after saponification, were separated by capillary GC. The oxidation products of campesterol, stigmasterol and sitosterol, such as: epimers of 7-hydroxy, 5,6-epoxy, 7-keto and triols, after transesterification and SPE fractionation, were identified by GC/MS and quantified by capillary GC.

Results of this research indicate that the content of phytosterols significantly decreased during deep frying of French fries in rapeseed oil (*ca.* 60%). In addition, the content of oxyphytosterols, particularly triol derivatives, significantly increased. The content of total phytosterols in fresh, good quality rapeseed oil was 5.4 mg/g and decreased after the 14th frying to 2.0 mg/g. French fries prepared in the first frying oil contained 2.9 mg of phytosterols in 1 g of extracted lipids, but after the 14th frying they had only 1.1 mg of phytosterols in 1 g of extracted lipids.

The level of total oxyphytosterols in fresh good quality rapeseed oil used for frying was 25.1 μg/g. After the 14th frying it increased to 197.1 μg/g. The content of oxyphytosterols in French fries during frying ranged from 16.8 to 147.6 μg/g of lipids extracted from the products. The dominating oxyphytosterols were epoxy- and 7-hydroxyphytosterols.

INTRODUCTION

Deep fat frying is a popular method for food preparation, especially in fast food restaurants. Physical and chemical changes of oil compounds, like oxidation [Finocchiaro & Richardson 1983; Pazoła *et al.*, 1985; Perkins, 1992; Lalas & Dourtoglou, 2003], sensory properties [Gemert, 1996; Raoux *et al.*, 1996; Xu *et al.*, 1999], volatile and nonvolatile compounds [Jeleń *et al.*, 2000 Mildner-Szkudlarz *et al.*, 2003], polar components [Perkins, 1992] have been widely studied. Oil absorption and distribution during frying of potatoes were the subjects of ample researches as well [Aguilera & Hernandez, 2000; Bouchon *et al.*, 2001, 2003]. Fatty acid composition was the main determining factor for the rate of lipid oxidation during frying operations. Various plant oils with different fatty acid composition have been used in deep-frying of French fries, both in industrial scale and at home [Pazoła *et al.*, 1987; Dobson *et al.*, 1996; Sèbèdio *et al.*, 1996]. Rapeseed oil is still the main source of commercial and household frying fats in Poland and some other countries. The production of refined rapeseed oil in Poland in 2002 year was *ca.* 350 thousands tons, and that of margarines *ca.* 370 thousands tons [POS, 2003]. In Poland, the sale of block confectionery fats in 2002 was *ca.* 30% higher than in 2001 year. The hydrogenated frying fats based on the rapeseed oil have modified the fatty acid composition. Yet, the heat stability of oils and fats depends not only on their fatty acid composition but also on the presence of non-glyceridic constituents such as phytosterols (plant sterols). These compounds are closely related by chemical structure to cholesterol, an animal origin sterol. The stability of phytosterols depends on the sterol structure, mainly on the unsaturation of the ring, temperature and composition of matrix [Yanishlieva *et al.*, 1980; Yanishlieva & Schiller, 1983; Yanishlieva-Maslarova & Marinova-Tasheva, 1986; Oehrl *et al.*, 2001; Piironen, 2001; Lampi *et al.*, 2002; Rudzińska *et al.*, 2002b].

Plant sterols naturally present in vegetable oils are not as resistant at higher temperatures as cholesterol [Przybylski *et al.*, 1999]. During simulated frying *ca.* 50% of sterols from canola oil and 60% of sterols from hydrogenated canola oil were transferred into other derivatives. However, no significant differences in the content of sterols were observed in the frying oils used for crisps after two days of frying operations [Dutta, 1997]. Research in recent years have proved that phytosterols play a role in fighting atherosclerosis. Increased phytosterol consumption is an effective way to contend hypercholesterolemia by decreasing cholesterol concentration in blood [Moreau *et al.*, 1999; Hicks & Moreau, 2001]. New findings indicate the antipolymerizing activity of these compounds in the process of food frying [Boskou, 1998; Blekas & Boskou, 1999]. Unprecedented

Author's address for correspondence: Magdalena Rudzińska, Department of Food Science and Nutrition, The August Cieszkowski Agricultural University of Poznań, Wojska Polskiego 31, 60-624 Poznań, Poland; tel.: (48 61) 848 72 76, fax: (48 61) 848 73 14; e-mail: magdar@au.poznan.pl

escalation of interest in phytosterols has been observed during the last 10 years. It has been proposed that some plant sterols act as antioxidants under frying conditions [Gordon & Magos, 1983; White & Armstrong, 1986]. Rapeseed oil and corn oil are characterised by the highest contents of phytosterols, as compared to other plant oils, hence they can be a good source of these compounds [Rudzińska *et al.*, 2001].

Phytosterols during deep-frying of plant oils, such as cholesterol during frying of animal fats [Lee *et al.*, 1984; 1985; Park & Addis, 1985; Zhang *et al.*, 1991], can be sources of their oxidation products [Dutta, 1997; Boskou, 1998; Przybylski & Eskin, 1991; Dutta & Appelqvist, 1997; Dutta *et al.*, 1997]. Literature data on the presence of oxyphytosterols in various kinds of food is scarce. However, evidence on their potential diverse biological effects has focused scientists' attention on these compounds nowadays. The cytotoxicity of oxyphytosterols has been studied in cultured macrophage-derived cell line [Adcox *et al.*, 2001]. Meyer and Spiteller [1997] showed the toxicity of epoxy derivatives of phytosterols and especially triols.

The goal of this research was to study changes in the content of sterols and oxyphytosterols in rapeseed oil and lipids extracted from French fries during frying under laboratory conditions.

MATERIALS AND METHODS

Fully refined rapeseed oil and potatoes, a special variety for French fries preparation, were purchased in local stores in Poznań.

Frying procedure. A commercial electric fryer containing 2 L of oil was used to prepare French fries. Potatoes were peeled, cut into homogenous strips and washed with water. The batch of 150 g was fried in oil for 1 min 45 s. The initial temperature was 180°C and no replenishments of oil were made. Then oil was cooled to room temperature and next frying started. French fries were dried on the laboratory blotting paper. The frying operations were repeated 14 times, which gave the total frying time of 24 min 30 s. Three replicates were done for the experiment.

Determination of sterol content. Sterol content of rapeseed oil and lipids extracted from French fries by Folch's method [1957] was determined by gas chromatography according to the method described by Rudzińska *et al.* [2001]. The method involved the saponification of samples with 1 N KOH in methanol and extraction of an unsaponifable fraction with diethyl ether. Then, the samples were silylated by BSTFA with 1% TMCS and analysed with a Hewlett-Packard 6890 gas chromatograph with split 1:25, FID detector and capillary column HP5 (30 m × 0.32 mm × 0.25 μm, J&W Scientific Inc., Folsom, CA, USA). Analysis parameters were as follows: oven temperature - 290°C, injector - 310°C, carrier gas – helium at a flow rate of 1.6 mL/min. As an internal standard use was made of 5-cholestane (500 μg/200 L of oil). Phytosterols were identified based on a comparative analysis of their retention times with those of authentic standards.

Determination of oxyphytosterol content. Oxidized derivatives of plant sterols (campesterol, stigmasterol and β-sitosterol) were determined as described earlier by Rudzińska *et al.* [2001]. The isolation of oxyphytosterols from a lipid mixture was performed following the procedure of enrichment by solid phase extraction on 360 mg NH_2 columns (Waters, Milford, MA., USA), as described previously [Schmarr *et al.*, 1996]. Then, the samples were silylated and analysed with GC/MS and GC/FID. The identification of phytosterol oxidation products was confirmed on a Hewlett-Packard HP 5890II gas chromatograph coupled with an MS Trace 2000/Finnigan-Polaris Q with a capillary column HP-5 (5% Phenyl Methyl Siloxane, 50 m × 0.2 mm × 0.32 μm, J&W Scientific Inc., Folsom, CA, USA). A quantitative analysis was carried out with GC/FID using the same parameters of analysis and column as those used in the GC/MS analysis. Analysis parameters were as follows: initial temperature 260°C (for 20 min), 0.5°C/min to 275°C (2 min), 3°C/min to 290°C (47 min), injector – 300°C, detector – 310°C, carrier gas – helium at a flow rate of 0.8 mL/min. 19-Hydroxy-cholesterol was used as internal standard. The selected 18 oxyphytosterols were identified using GC/MS [Rudzińska *et al.*, 2001]. As an internal standard, 10 μg of 19-hydroxy cholesterol was added to each sample.

Brassicasterol oxidation products were not determined because of difficulties in their identification.

RESULTS AND DISCUSSION

During multiple deep frying of French fries under laboratory conditions, the total sterol content in rapeseed oil, used for frying, was decreasing systematically (Figure 1). At the beginning of frying in good quality rapeseed oil, the total sterol content was 5.4 mg/g, and after the 14th frying it dropped to 2.0 mg/g (Table 1). Still, contents of individual sterols varied, *i.e.* they reached 61% for sitosterol, 65% for campesterol, and 60% for brassicasterol. Comparatively, the highest decrease was noted for avenasterol and it was 67%. These changes were connected with changes in the percentage composition of a sterol fraction. At the beginning of frying, sitosterol constituted 47%; campesterol – 35%, and brassicasterol – 12% of the oil sterol fraction, whereas after the 14th frying they constituted 49%, 32% and 13% of the oil sterol fraction, respectively.

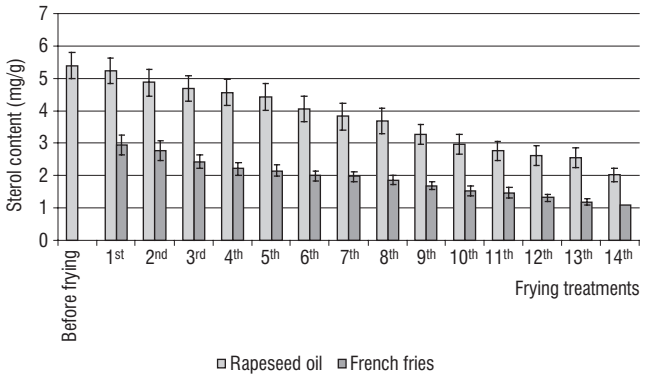

FIGURE 1. Changes of sterol content in rapeseed oil and in lipid fractions extracted from French fries fried 14 times.

TABLE 1. Changes of sterol content in rapeseed oil over 14 frying treatment (mg/g)*.

Sterols	Frying treatments														
	Before frying	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th	12th	13th	14th
Cholesterol	0.04	0.03	0.03	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Brassicasterol	0.66	0.65	0.64	0.60	0.60	0.58	0.56	0.55	0.50	0.46	0.42	0.36	0.32	0.31	0.27
Campesterol	1.87	1.84	1.56	1.46	1.39	1.34	1.26	1.14	1.13	1.12	1.10	1.10	0.99	1.01	0.65
Stigmasterol	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.04	0.03	0.03	0.03	0.03	0.02	0.02
β-Sitosterol	2.54	2.43	2.39	2.35	2.30	2.25	2.01	1.91	1.86	1.51	1.30	1.17	1.16	1.11	0.99
Avenasterol	0.24	0.22	0.19	0.19	0.19	0.18	0.17	0.15	0.15	0.13	0.09	0.09	0.08	0.08	0.08

* – mean of three replicates; the value of relation standard deviation (RSD) was below 10%; the authors available detailed data who need

It is interesting that in lipids extracted from French fries the amounts of sterols were always lower than in the rapeseed oil used for frying (Figure 1). French fries prepared in the first stage of frying contained 2.9 mg of sterols in 1 g of extracted lipids, and after the 14th frying the content of sterol dropped to as little as 1.1 mg/g (Table 2). A decrease in the content of individual sterols in lipids extracted from French fries was different than in the rapeseed oil and reached 64% for sitosterol, 51% for campesterol, and 65% for brassicasterol. The highest decrease was noted for the amount of avenasterol – 83%. In lipids extracted from French fries after the 1st frying, sitosterol constituted 46%, campesterol – 31%, and brassicasterol – 12% of a sterol fraction. After the 14th frying, the percentage composition of the sterol fraction changed and sitosterol was 44%, campesterol was 40%, and brassicasterol was 11%.

Differences in the chemical structure of phytosterols could be a source of differences in their decrease during frying. The highest decrease of avenasterol depends probably on the occurrence of two double bonds in a molecule. Differences in the percentage decrease of campesterol (65% in rapeseed oil and 51% in lipids extracted from French fries) during deep frying are probably due to greater absorption of this phytosterol by French fries. Dutta and Appelqvist [1996] showed that the contents of sterols in plant oils used for frying of crisps were always higher than the ones in lipids from crisps. However, such a great differences between the contents of phytosterols in the frying oil and the lipid fraction extracted from French fries during multiple deep frying have not been reported in literature. It is difficult to explain these differences by specific unabsorption of phytosterols by French fries from oil medium. It was likely that the method used to extract lipids from French fries was not enough to break complexes of phytosterols with other compounds of French fries.

The low amount of phytosterols in French fries is unfavourable from the nutritional point of view due to their capability to decrease the absorption of cholesterol and reduce low density lipoprotein in human blood [Piironen *et al.*, 2000]. In this situation, when the consumption of phytosterols is of great interest, the level of these compounds in food ought to be as high as possible. Moreover, the role of phytosterols against colon carcinogenesis has also been reported [Rao & Janezic, 1992]. The presented data showed that the content of phytosterols in French fries depends on the time of deep frying and that the differences are highly significant.

The decrease in phytosterol content of plant oils could be caused by some different factors, like polymerization, degradation or oxidation. The autoxidation is a source of cytotoxic substances, oxyphytosterols [Adcox *et al.*, 2001]. As expected the content of total oxyphytosterols increased during frying in both rapeseed oil and lipids extracted from French fries, *ca.* 8 and 9-times, respectively (Figure 2). Although the contents of oxyphytosterols in rapeseed oil and lipids extracted from French fries were similar when

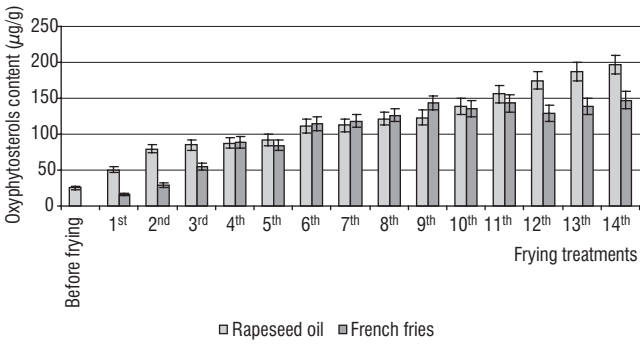

FIGURE 2. Changes of total oxyphytosterols content in rapeseed oil and in lipid fractions extracted from French fries fried over 14 frying treatments.

TABLE 2. Changes of sterol content in lipids extracted from French fries over 14 frying treatments (mg/g)*.

Sterols	Frying treatments													
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th	12th	13th	14th
Cholesterol	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.01
Brassicasterol	0.34	0.31	0.28	0.24	0.22	0.23	0.22	0.20	0.19	0.17	0.15	0.16	0.15	0.12
Campesterol	0.90	0.86	0.84	0.80	0.79	0.77	0.77	0.69	0.63	0.57	0.57	0.50	0.45	0.44
Stigmasterol	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	nd	nd	nd
β-Sitosterol	1.35	1.27	1.01	0.92	0.92	0.82	0.81	0.80	0.73	0.66	0.62	0.58	0.52	0.48
Avenasterol	0.30	0.30	0.26	0.21	0.19	0.16	0.15	0.15	0.10	0.10	0.09	0.07	0.06	0.05

nd - not detected; * – mean of three replicates; the value of relation standard deviation (RSD) was below 10%; the authors available detailed data who need

expressed in μg/g, their content in relation to the phytosterol fraction was higher by 100%in lipids from French fries than in the rapeseed oil. During frying, the dominating oxyphytosterols in rapeseed oil were epimer epoxysterols (Figure 3). From the 1st to 14th frying the total amount of epoxy derivatives of campesterol, sitosterol and stigmasterol increased rapidly from 10 μg/g up to 69 μg/g. Epoxysterols constituted from 34% to 48% of the total oxyphytosterols in the analysed rapeseed oil. In the research presented, the level of triols in rapeseed oil was observed to increase rapidly. The content of triols in rapeseed oil before frying accounted for *ca.* 1 μg/g and after the 14th frying it increased to *ca.* 59 μg/g (30% of the total oxyphytosterol fraction – Figure 3). The level of 7-hydroxy derivatives in rapeseed oil grew up from 7 μg/g to 36 μg/g. In rapeseed oil there dominated epoxy and 7hydroxy derivatives with β-configuration. Their contents increased during frying from 10 μg/g to 62 μg/g, whereas those of derivatives with β-configuration – from 8 μg/g to 50 μg/g.

Epoxy derivatives of phytosterols dominated also in lipids extracted from French fries. Their content increased from 5 μg/g of lipids extracted from French fries after the 1st frying to 51 μg/g of lipids extracted from French fries after the 14th frying (Figure 4). Epoxysterols constituted from 32% to 45% of the total oxyphytosterols in lipids extracted from French fries.

The content of triols in French fries was also observed to increase very rapidly during frying, but after the 14th frying it was lower than that in the rapeseed oil, reaching *ca.* 33 μg/g of lipids extracted from French fries. The level of 7-hydroxy derivatives grew rapidly from 7 μg/g to 45 μg/g. Lipids extracted from French fries were dominated by epoxy and 7-hydroxy derivatives with β-configuration. Their contents increased during frying from 8 μg/g to 60 μg/g, while those of derivatives with α-configuration – from 4 μg/g to 47 μg/g.

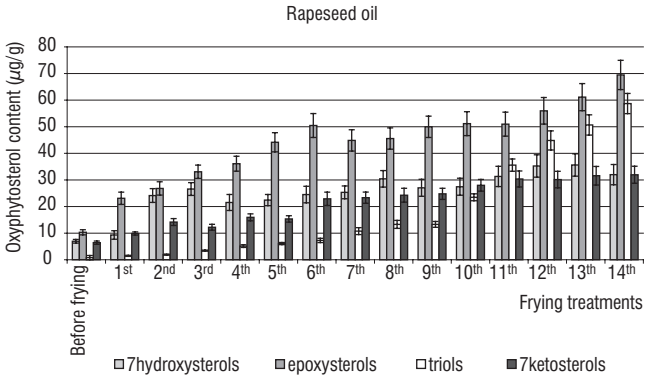

FIGURE 3. Changes of the content of oxyphytosterol fractions in rapeseed oil over 14 frying treatments.

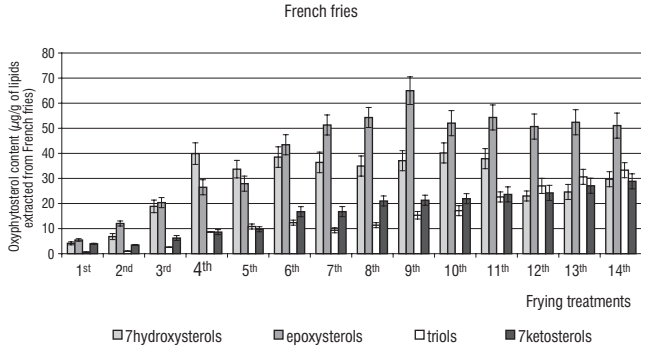

FIGURE 4. Changes of the content of oxyphytosterol fractions in lipid fractions extracted from French fries over 14 frying treatments.

It should be emphasized that oxyphytosterols were detected in good quality refined plant oils [Rudzińska *et al.*, 2001]. The lowest total oxyphytosterol content was determined in rapeseed oil before frying. It was about 25 μg/g (Figure 2) and the major sterol oxides were epoxy derivatives of campesterol and sitosterol, whose amount reached *ca.* 10 μg/g (Figure 3). Phytosterol oxidation products were determined in different varieties of rapeseeds [Rudzińska *et al.*, 2003]. Their content ranged from 10 to 15 μg/g of seeds. During the production of rapeseed oil the content of oxyphytosterols increased up to 100–240 μg/g depending on industrial conditions [Rudzińska *et al.*, 2002a]. For this reason, the presence of oxyphytosterols in rapeseed oil before frying was expected. Still, their increase during deep frying under model conditions was very high.

Though the content of phytosterols in rapeseed oil was always higher than in French fries during frying, the level of oxyphytosterols in both was alike. Especially alarming was the increase of epoxy derivatives, which are referred to as primary phytosterol oxidation products. Numerous studies have indicated that epoxides are linked with atherosclerosis and mutagenicity [Guardiola *et al.*, 1996; Morin *et al.*, 2000; Grandgirard, 2002]. They could be better metabolized *in vivo* than the other phytosterol oxidation products and they could be transformed to triols under acidic conditions of the stomach or subjected to the action of an epoxide hydralase in the intestinal cells [Grandgirard, 2002; Aringer & Eneroth, 1974; Hwang & Kelsey, 1978; Maerker *et al.*, 1988]. In the next step of autoxidation, epoxides are transformed to triol derivatives, which are expected to be the most cytotoxic [Meyer *et al.*, 1998]. For this reason, the monitoring of epoxyphytosterols increase during deep fat frying is very important.

Domination of α-epimers in rapeseed oil and β-epimers in lipids extracted from French fries has not been elucidated so far. Still, Aringer and Eneroth [1974] reported that α-epimers of oxyphytosterols could be preferentially transformed to triols. Numerous studies have shown that thin layer of oil on the surface of French fries is mostly oxidized during the cooling period [Aguilera & Hernandez, 2000; Bouchon *et al.*, 2003]. It could explain the high level of triols in lipids extracted from French fries and the domination of α-epimers. Dutta and Appelqvist [1996] also detected a higher level of α-epimers in frying plant oils compared to that of β-epimers. They did not suggest any sources of that phenomenon. Lee *et al.* [1985] analysed French fries and demonstrated that the level of 7β-hydroxy-sterols was much higher than that of 7α-hydroxy-sterol. Smith [1996] suggested that Δ^5-7α-hydroperoxides undergo rearrangement and turn spontaneously into epimers of 7β-hydroperoxides, but the reverse epimerization has not been observed. The 7α-peroxyl radical is transformed to epimeric 7β-peroxyl radical by a dissociative mechanism. The higher level of

epimers 7β-hydroxy-sterols could implicate higher formation of epimers β-epoxysterols, especially during the cooling of French fries. 7-Hydroperoxides are unstable under conditions involving a heat agent.

CONCLUSIONS

The content of phytosterols decreased significantly during deep frying of French fries in rapeseed oil. In the same time, the content of oxyphytosterols, particularly triol derivatives, increased significantly.

The content of total phytosterols in fresh, good quality rapeseed oil was 5.4 mg/g and decreased after the 14th frying to 2.0 mg/g. French fries prepared in the first frying oil contained 2.9 mg of phytosterols in 1 g of extracted lipids, but after the 14th frying they had only 1.1 mg of phytosterols in 1 g of extracted lipids. The level of total oxyphytosterols in fresh good quality rapeseed oil used for frying was 25.1 μg/g. After the 14th frying it increased to 197.1 μg/g. During frying, the content of oxyphytosterols in French fries ranged from 16.8 to 147.6 μg/g of lipids extracted from the products.

Oxyphytosterols are absorbed by humans and their subsequent metabolic conversions may be of toxicological significance. The toxic effects of oxyphytosterols on the intestinal tissue should not be ignored. The food technologists have to be aware of the oxyphytosterols' level in food products.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the State Committee for Scientific Research for financing this research under the project No. PBZ-KBN-094/P06/2003.

REFERENCES

1. Adcox C., Boyd L., Oehrl L., Allen J., Fenner G., Comparative effects of phytosterol oxides and cholesterol oxides in cultured macrophage-derived cell lines. J. Agric. Food Chem., 2001, 49, 2090–2095.
2. Aguilera J.M., Hernandez H.G., Oil absorption during frying of frozen parfried potatoes. J. Food Sci., 2000, 65, 476–479.
3. Aringer L., Eneroth P., Formation and metabolism *in vitro* of 5,6-epoxides of cholesterol and β-sitosterol. J. Lipid Res. 1974, 15, 389–398.
4. Blekas G., Boskou D., Phytosterols and stability of frying oil. 1999, *in*: Frying of Food. (eds. D. Boskou, J. Elmadfe) Technomic Publishing, Lancaster-Basel, pp. 205–221.
5. Boskou D., Frying temperatures and minor constituents of oils and fats. Grasas y Aceites, 1998, 49, 326–330.
6. Bouchon P., Aguilera J.M., Pyle D.L., Structure oil-absorption relationships during deep-fat frying. J. Food Sci., 2003, 68, 2711–2716.
7. Bouchon P., Hollins P., Pearson M., Pyle D.L., Tobin M.J., Oil distribution in fried potatoes monitored by infrared microspectroscopy. J. Food Sci., 2001, 66, 918–923.
8. Dobson G., Christie W.W., Dobarganes M.C., Changes in molecular species of triacylglycerols during frying. Grasas y Aceites, 1996, 47, 34–37.
9. Dutta P.C., Appelqvist L.Å., Sterols and sterol oxides in the potato products, and sterols in the vegetable oils used for industrial frying operations. Grasas y Aceites, 1996, 47, 38–47.
10. Dutta P.C., Appelqvist L.Å., Studies on phytosterol oxides. I. Effect of storage on the content in potato chips prepared in different vegetable oils. J. Am. Oil Chem. Soc., 1997, 74, 647–657.
11. Dutta P.C., Przybylski R., Appelqvist L. Å., Eskin N.A.M., Formation and analysis of oxidized sterols in frying fat. 1997, *in*: Deep Frying. Chemistry, Nutrition and Practical Applications (eds. E.G. Perkins, M.D. Erickson). AOCS Press, Champaign, IL, pp. 112–150.
12. Dutta P.C., Studies on phytosterol oxides. II. Content in some vegetable oils and in French fries prepared in these oils. J. Am. Oil Chem. Soc., 1997, 74, 659–666.
13. Finocchiaro E.T., Richardson T., Sterol oxides in foodstuffs: a review. J. Food Prot., 1983, 46, 917–925.
14. Folch J., Lees M., Stanley G.H.S., A simple method for the isolation and purification of total lipids from animal tissue. J. Biol. Chem., 1957, 726, 497.
15. Gemert L.J., Sensory properties during storage of crisps and French fries prepared with sunflower oil and high oleic sunflower oil. Grasas Aceites 1996, 47, 75–80.
16. Gordon M.H., Magos P., The effect of sterols on the oxidation of edible oils. Food Chem., 1983, 10, 141–147.
17. Grandgirard A., Biological effects of phytosterol oxidation products, future research areas and concluding remarks. 2002, *in*: Cholesterol and Phytosterol Oxidation Products: Analysis, Occurrence, and Biological Effects (eds. F. Guardiola, P.C. Dutta, R. Codony, G.P. Savage). AOCS Press, Champaign, IL, pp. 375–382.
18. Guardiola F., Codony R., Addis P.B., Rafecas R., Boatella J., Biological effects of oxysterols: Current status. Food. Chem. Toxicol., 1996, 34, 193–211.
19. Hicks K.B., Moreau R.A., Phytosterol and phytostanols: Functional food cholesterol busters. Food Technol., 2001, 55, 63–67.
20. Hwang K.K., Kelsey M.I., Evidence of epoxide hydrase activity in human intestinal microflora. Cancer Biochem. Biophys., 1978, 3, 31–35.
21. Jeleń H.H., Obuchowska M., Zawirska-Wojtasiak R., Wąsowicz E., Headspace solid-phase microextraction use for the characterization of volatile compounds in vegetable oils of different sensory quality. J. Agric. Food Chem., 2000, 48, 2360–2367.
22. Lalas S., Dourtoglou V., Use of rosemary extract in preventing oxidation during deep-frying of potato chips. J. Am. Oil Chem. Soc., 2003, 80, 583.
23. Lampi A.M., Juntunen L., Toivo J., Piironen V., Determination of thermo-oxidation products of plant sterols. J. Chromat. B, 2002, 777, 83–92.
24. Lee K., Herian A.M., Highley N.A., Sterol oxidation products in French fries and in stored potato chips. J. Food Prot., 1985, 48, 158–161.
25. Lee K., Herian A.M., Richardson T., Detection of sterol epoxides in foods by colorimetric reaction with picric acid. J. Food Prot., 1984, 47, 340–342.

26. Maerker G., Nungesser G.H., Bunick F.J., Reaction of cholesterol 5,6-epoxides with simulated gastric juice. J. Am. Oil Chem. Soc., 1988, 23, 761–765.
27. Meyer W., Jungnickel H., Jandke M., Dettner K., Spiteller G., On the cytotoxicity of oxidized phytosterols isolated from photoaututrophic cell cultures of *Chenopodium rubrum* tested on meal-worms *Tenebrio molitor*. Phytochem., 1998, 47, 789–797.
28. Meyer W., Spiteller G., Oxidized phytosterols increase by ageing in photoautotrophic cell cultures of *Chenopodium rubrum*. Phytochem., 1997, 45, 297–302.
29. Mildner-Szkudlarz S., Jeleń H.H., Zawirska-Wojtasiak R., Wąsowicz E., Application of headspace – solid phase microextraction and multivariate analysis for plant oils differentiation. Food Chem., 2003, 83, 515–522.
30. Moreau R.A., Norton R.A., Hicks K.B., Phytosterols and phytostanols lower cholesterol. Inform, 1999, 10, 572–577.
31. Morin R.J., Hu B., Peng S.K., Sevanian A., Cholesterol oxidation and cancer. 2000, *in*: Biological Effects of Cholesterol Oxides (eds. S.K. Peng, R.J. Morin). CRC Press, London, pp. 191–202.
32. Oehrl L.L., Hansen A.P., Rohrer C.A., Fenner G.P., Boyd L.C., Oxidation of phytosterols in a test food system. J. AM. Oil Chem. Soc., 2001, 78, 1073–1078.
33. Park S.W., Addis P.B., HPLC determination of C-7 oxidized cholesterol derivatives in foods. J. Food Sci., 1985, 50, 1437–1441.
34. Pazoła Z., Buchowski M., Korczak J., Grześkowiak B., Effect of some antioxidants on fat stability during deep frying and storage of fried potato products. II. French Fries. Ernährung, 1987, 11, 546–550 (in German).
35. Pazoła Z., Gawęcki J., Buchowski M., Korczak J., Jankun J., Grześkowiak B., Choice of the simple methods for quality control of frying fat during deep frying of potato products. Fette, Seifen, Anstrichmittel, 1985, 87, 190–193.
36. Perkins E.G., Effect of lipid oxidation on oil and food quality in deep frying. 1992, *in*: Lipid Oxidation in Food (ed. Allen J.St. Angelo). ACS Symposium Series 500, pp. 310–321.
37. Piironen V., Lindsay D.G., Miettinen T.A., Toivo J., Lampi A.M., Plant sterols: biosynthesis, biological function and their importance to human nutrition. J. Sci. Food Agric., 2000, 80, 939–966.
38. Piironen V., Puupponen-Pimiä R., Toivo J., Lampi A.M., Stability of plant sterols in foods and model systems. Bioactive compounds in plant foods. 2001, *in*: Proceedings of the European Scientific Conference COST Action 916, 26-28 April 2001, Tenerife, Spain, 26–28 April 2001, pp.197–198.
39. Polish Official Statistics – 2003.
40. Przybylski R., Eskin N.A.M., Formation of phytosterol oxides in fried oil products. 1991, *in*: Proceedings of the 8th International Rapeseed Congress (ed. D.I. McGregor). GCRIC, 9-11 May 1991, Saskatoon, pp. 888–893.
41. Przybylski R., Zambiazi R., Li W., Kinetics of sterols changes during storage and frying of canola oils. 1999, *in*: Proceedings of the 10th International Rapeseed Congress, 26–29 September 1999, Canberra, Australia, pp. 837–841.
42. Rao A.V., Janezic S.A., The role of dietary phytosterols in colon carcinogenesis. Nutr. Cancer, 1992, 18, 43–52.
43. Raoux R., Morin O., Mordret F., Sensory assessment of stored French fries and crisps fried in sunflower and high oleic sunflower oils. Grasas y Aceites, 1996, 47, 63–74.
44. Rudzińska M., Banaszak S., Wąsowicz E., Phytosterol oxidation products in rapeseeds and rapeseed oil during its production. Proceedings XXIV Scientific Conference „Oilseed crops", Poznań 16-17 April 2002a, pp. 72–73 (in Polish).
45. Rudzińska M., Jeleń H., Wąsowicz E., The content of phytosterols and their oxidized derivatives in heated plant oils. Pol. J. Food Nutr. Sci. 2002b, 11/52, SI 1, 129–134.
46. Rudzińska M., Kazuś T., Wąsowicz E., Sterols and their oxidized derivatives in refined and cold pressed seed oils. Rośl. Oleiste, 2001, 22, 477–494 (in Polish).
47. Rudzińska M., Muśnicki C., Wąsowicz E., Phytosterols and their oxidized derivatives in winter rapeseeds. Rośl. Oleiste, 2003, 24, 59–74 (in Polish).
48. Schmarr H.G., Gross H.B., Shibamoto T., Analysis of polar cholesterol oxidation products: Evaluation of a new method involving transesterification, solid phase extraction, and gas chromatography. J. Agric. Food Chem., 1996, 44, 512–517.
49. Sébédio J.L., Dobarganes M.C., Márquez G., Wester L., Christie W.W., Dobson G., Zwobada F., Chardigny J.M., Mairot Th., Lahtinen R., Industrial production of crisps and prefried French fries using sunflower oils. Grasas y Aceites, 1996, 47, 5–13.
50. Smith L.L., Review of progress in sterol oxidation: 1987-1995. Lipids, 1996, 31, 453–488.
51. White P.J., Armstrong L.S., Effect of selected oat sterols on the deterioration of heated soybean oil. J. Am. Oil Chem. Soc., 1986, 63, 525–529.
52. Xu X.Q., Tran V.H., Palmer M., White K., Salisbury P., Chemical and physical analyses and sensory evaluation of six deep-frying oils. J. Am. Oil Chem. Soc., 1999, 76, 1091–1099.
53. Yanishlieva N., Schiller H., Effect of sitosterol on autoxidation rate and product composition in a model lipid system. J. Sci. Food Agric., 1983, 35, 219–224.
54. Yanishlieva N., Schiller H., Marinowa E., Autoxidation of sitosterol. II. Main products formed at ambient and high temperature treatment with oxygen. Riv. Ital. Sostanze Grasse, 1980, 57, 572–576.
55. Yanishlieva-Maslarova N., Marinova-Tasheva M., Effect of the unsaturation of lipid media on the autoxidation of sitosterol. Grasas y Aceites, 1986, 37, 343–347.
56. Zhang W.B., Addis P.B., Krick T.P., Quantification of 5α-cholestane-3β,5,6β-triol and other cholesterol oxidation products in fast food French fried potatoes. J. Food Sci., 1991, 56, 716–718.

Received February 2005. Revision received and accepted July 2005.

ZMIANY FITOSTEROLI I ICH POCHODNYCH UTLENIONYCH ZACHODZĄCE PODCZAS SMAŻENIA FRYTEK

Magdalena Rudzińska, Józef Korczak, Erwin Wąsowicz

Akademia Rolnicza im. Augusta Cieszkowskiego w Poznaniu, Poznań

Celem pracy było zbadanie zmian zawartości fitosteroli i ich pochodnych utlenionych podczas wielokrotnego (14 razy) smażenia frytek w oleju rzepakowym. Zawartość fitosteroli (brassikasterol, kampesterol, stigmasterol, β-sitosterol i awenasterol) oznaczano, po uprzednim zmydleniu, techniką kapilarnej chromatografii gazowej. Pochodne utlenione kampesterolu, stigmasterolu i β-sitosterolu, takie jak: epimery 7-hydroksy, 5,6-epoksy, 7-keto i triole, po transestryfikacji i oczyszczeniu metodą SPE, identyfikowano za pomocą GC/MS i oznaczano ilościowo techniką GC/FID.

Podczas smażenia frytek w oleju rzepakowym poziom fitosteroli znacznie zmniejszył się (60%). W tym samym czasie nastąpił istotny wzrost zawartości ich pochodnych utlenionych, a zwłaszcza trioli. W oleju rzepakowym przed smażeniem zawartość fitosteroli wynosiła 5,4 mg/g i po 14 cyklach smażenia zmniejszyła się do 2,0 mg/g. We frytkach smażonych w pierwszym cyklu było 2,9 mg fitosteroli/g wyekstrahowanego tłuszczu, a po 14 cyklach – tylko 1,1 mg/g (tab. 1, 2, rys. 1).

Poziom oksyfitosteroli wzrósł w oleju rzepakowym podczas smażenia od 25,1 μg/g przed smażeniem do 197,1 μg/g po 14 cyklach smażenia. We frytkach, po pierwszym cyklu smażenia, zawartość tych związków wynosiła 16.8 μg/g, a po czternastu cyklach wzrosła do 147,6 μg/g wyekstrahowanego tłuszczu. We frakcji tej dominowały pochodne epoksydowe i epimery 7-hydroksysteroli (rys. 3, 4).

Obecność oksyfitosteroli we frytkach na tak wysokim poziomie jest zjawiskiem niepokojącym i należy zwrócić uwagę na stosowany często, w punktach zbiorowego żywienia, proces wielokrotnego smażenia zanurzeniowego. Zastosowanie tłuszczów smażalniczych zamiast oleju rzepakowego i dodatek przeciwutleniaczy może opóźnić proces oksydacji fitosteroli, ale wymaga to dalszych badań.