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Changes in the Fatty Acids Composition, Especially *Trans* Isomers, and Heat Stability of Selected Frying Fats Available on the Polish Market in the Years 1997 and 2008

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Key words: fatty acids composition, *trans* isomers, frying fats, Rancimat test

The aim of this work was to examine the fatty acids composition, especially *trans* isomers (TFA), and oxidative stability of frying fats available on the Polish market.

The quality of 23 frying shortenings of Polish origin or imported, produced in the years 1997 and 2008, was estimated in the study. Their fatty acid composition was determined with the GC.

The fats examined differed substantially in the content of TFA. Only about 33% of fats from 1997 and about 46% from 2008 contained very small contents of these acids (below 1%). Some of fats were characterised by a high concentration of TFA (about 50%), thus we could assume that these fats were based on raw materials modified by partial hydrogenation. A reduction of TFA content of the frying fats was noted from 1997 to 2008. It was found that an average TFA content in frying fats sold in Poland in 1997 was 21.4%, while in 2008 it was significantly lower and reached 12.2%. TFA had a positive, but PUFA a negative influence on induction period of fats.

INTRODUCTION

The frying process evokes complex chemical and physical changes in the frying medium, which affects the quality and safety of food and as a consequence human health [Gertz, 2001]. In frying fats generally three types of changes occur: oxidative, hydrolytic and polymeric ones. Oxidative changes are caused by the presence of oxygen, hydrolytic changes by the presence of water and polymeric changes are the result of a long-lasting effect of high temperature on fat [White, 1991]. The most dangerous for human health are polymers, which in most cases may cause diarrhoea or other stomach problems and even can be carcinogenic [Szukalska, 1995].

Nowadays, hydrogenated oils prevail, mainly for economic reasons. The second and the most often used oil is palm oil, which is frequently one of the components of other hardened fats assigned to frying, and it is responsible for improving their technological quality [Saguy & Dana, 2003]. Hydrogenation of oils is of a great worth for the technological reason, since it allows for a prolonged utilization of fats. Unfortunately, hardened fats are the main source of *trans* fatty acids (TFA) regarded as a factor increasing health risks, mainly the incidence of coronary heart disease [Willett & Ascherio, 1994; Juttelstad, 2004]. Consequently, frying products should be significantly reduced of *trans* fatty acids. It is also very important to note that fried food are consumed first of all by children.

Taking the negative opinions on the influence of TFA on human health into account [Oomen *et al*., 2001; Bray *et al*., 2002; Dlouhý *et al*., 2003; EFSA, 2004], FDA (The Food and Drug Administration) has decided that since the year 2006 all labels on food products and additives should contain information on the content of *trans* fatty acids. Such information has to be specified in a separate line below the information about saturated fatty acids [Yurawecz, 2004]. In 2003, the Danish Government stated that industrially produced TFA, those from partially hydrogenated oils, should be limited to 2% of the total amount of fat and oil in food [Leth *et al*., 2006]. Likewise in Denmark , the Health Canada's Trans Fat Task Force issued recommendations for regulating TFA (by declaring them on the nutrition label) in food supply to the Minister of Health in June 2006 [Astrup, 2006]. In contrast to Denmark and Canada, some countries, such as the Netherlands, have opted against government regulation, yet thus have made significant progress in reducing TFA in food supply [Katan, 2006].

The main aim of this work was to characterise and compare fats assigned to frying that were available on the Polish market in the years 1997 and 2008. Fats were examined for their fatty acids composition, with special regard to *trans* isomers content, as well as their resistance to oxidative changes

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at high temperature. A relationship between stability of fats and their fatty aids composition was examined as well.

MATERIALS AND METODS

Materials

Twenty three solid and liquid frying fats available on the Polish market were examined. All fats were produced on an industrial scale and originated from home factories or were imported and were offered for frying in Poland. Twelve products were examined in 1997 (samples 1–12) and the others (13–23) in 2008.

Fatty acids composition

Preparation of fatty acids methyl esters (FAMEs)

Fatty acids were converted into their methyl esters according to ISO standard method [ISO 5509:2000a].

Gas chromatography analyses (GC)

Gas chromatography of the FAMEs was performed according to ISO standard [ISO 5508:2000b]. Conditions were as follows: apparatus HP 6890 GC System with autosampler; column: SGE Capillary BPX 70, highly polar column, 60 m length, 0.22 mm internal diameter with 70% Cyanopropyl (equiv.) polysilphenylene-siloxane; pven: temperature program from 160 to 190°C, heating rate: 2.5°C/min; carrier gas: helium, flow rate 0.6 mL/min; injector: split-splitless 240°C; detector: a flame ionization detector (FID); flame gas: $H_{2;}$ software: HP Chemstation v. 3.11; sample: 1 micro liter in iso-octane.

FAMEs were identified by comparing their relative and absolute retention times to those of authentic standards of FAMEs obtained from Sigma Chemical Co. All quantifications were done by a built-in data-handling program provided by the manufacturer of the gas chromatograph. The FA composition was reported as a relative percentage of the total peak area.

Oxidative stability by Rancimat measurements

The induction times for oxidation were measured using a Methrom Rancimat apparatus model 679 (Herisau, Switzerland). The oxidation process is monitored by measuring the change in conductivity of distilled water resulting from the formation of volatile oxidation products. Purified air is passed through a heated fat sample. The effluent air contains volatile organic acids which increase the conductivity. The fat stability index (induction period) is defined as the point of maximum change of the rate of oxidation [Wagner *et al.,* 2000]. The tests were carried out at 150°C with 2.5 g±0.02 of fat. Air flow rates were set at 20 dm^3/h. Determinations were conducted following standard ISO procedures [ISO 6886:1997]. The average induction time was given in hours.

Statistical analysis

Results obtained for the content of individual FA are given as mean values (wt % of total FA) and for summation of FA as mean±SD (g per 100 g sample). Coefficients of correlation between fatty acid composition of fats and induction times were computed. Differences were considered significant at $p<0.05$. Microsoft Excel 6.0 functions, SPSS package for Windows and Statgraphics plus 4.0 package (Statistical Graphics Corp., USA) were used for calculations.

RESULTS AND DISCUSSION

Fatty acid composition of the samples is provided in Table 1. The relative contents of *trans* fatty acids (TFA), saturated (SFA), *cis*-monounsaturated (MUFA), and *cis*-polyunsaturated fatty acids (PUFA) of the 23 samples are provided in Table 2.

During the deep frying process two-thirds of products' total fat content is absorbed from the fat used [Wagner *et al.,* 2000]. When using a partially hydrogenated fat the content of *trans* isomers of fried products increases. That means that the choice of the frying fat is responsible for differences in TFA levels in the end product.

The TFAs content is the sum of quantified *trans*–monounsaturated fatty acids with 18 (18:1) carbon atoms and the geometric isomers of linolenic acids (C18:2:t9t12, t9c12, c12t9 where c and t are *cis* and *trans* configurations). The highest content of TFA was found for *trans*-octadecenoic acid (C18:1t). The isomeric pattern of C18:1 TFA in frying fats is formed by technical hydrogenation. Likewise, in Karabulut & Turan's [2006] work, the *trans* isomers of 18:3 were not found in the fat samples examined. Therefore, the content of 18:3 may probably include a small amount of its *trans* isomers.

The content of TFAs was lower in frying fats from 1997 as compared to those from 2008 and the differences were significant ($p<0.05$). The frying fats examined differed substantially in the content of *trans* fatty acids, which are regarded as controversial for health reasons. Only about 33% of the examined fats from 1997 and about 46% from 2008 contained very small amounts of these acids (below 1%). The highest TFA content was 58% in fats from 1997 and 54% in the samples from 2008. This generally indicates that the Polish market offers two types of frying fats: those obtained from partial hydrogenated oils and those made with a high proportion of palm oil in combination with slightly hydrogenated vegetable oils. A reduction of TFA was also found in the presented frying fats. The mean TFAs content in frying fats used in 2008 in Poland (12.2%) was higher than those reported in Turkey (9%) [Karabulut & Turan, 2006] but lower than those reported in the Czech Republic (25.5) [Brat & Pokorny, 2000] and in Pakistan (23.1%) [Bhanger, 2004]. TFAs concentration in frying fats in some European countries ranges from 0.30 to 50.19% [Aro *et al*., 1998].

In the examined fats the total content of saturated fatty acids (SFAs) was between 12.5 and 60.6% in fats sold in Poland in 1997, and from 20.7 to 54.3% in these sold in 2008 (Table 2), with the highest concentration recorded for palmitic acid, *i.e.* from 6.1 to 53.6% and 14.1 to 46.5%, respectively. The content of myristic and stearic acids was much lower (for all samples), from 0.1 to 3.1% and from 3.5 to 22.4% (Table 1), respectively.

The content of palmitic, myristic, and lauric acids, which elevate blood cholesterol [Mensink *et al.* 1992], in frying fats sold in Poland in 2008, was much lower (mean 13.0%) than the 40.37% reported by Bhanger & Anwar [2004] in Pakistan

TABLE 1. Fatty acids composition (as percentage of total fatty acids) of Polish frying fats (mean±SD).

No	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1t	C18:1	C18:2t	C18:2	C18:3	C20:0	C20:1	C22:1	C24:0
							1997							
1	0.3±0.01	1.0±0.01	41.6±3.21	0.1±0.00	10.2±0.89	24.3±3.02	21.0±2.81	0.1±0.02	0.4±0.02	–	0.4±0.07	0.1±0.00	–	0.1±0.00
2	–	0.1±0.00	12.0±1.08	0.1±0.01	22.4±2.13	39.9±4.11	23.3±2.76	0.2±0.01	0.4±0.01	–	0.5±0.05	0.2±0.01	–	0.1±0.01
3	0.9±0.21	0.5±0.02	12.5±3.02	0.1±0.01	8.7±0.09	45.4±4.75	28.5±2.94	0.8±0.03	1.0±0.03	–	0.4±0.02	0.6±0.03	–	0.1±
4	0.2±0.02	1.2±0.07	53.6±4.18	0.1±0.02	4.9±0.10	0.1±0.00	32.1±2.98	0.3±0.01	6.3±0.19	0.1±0.00	0.4±0.01	0.2±0.01	–	0.1±0.01
5	0.4±0.00	1.2±0.02	43.9±3.11	0.2±0.01	4.5±0.09	0.1±0.01	38.9±3.18	0.5±0.02	9.1±0.89	0.1±0.01	0.4±0.00	0.2±0.02	–	0.1±0.01
6	–	0.1±0.01	6.1±0.02	0.2±0.02	11.9±0.12	50.7±6.01	25.4±2.08	1.0±0.07	0.8±0.21	–	0.8±0.11	1.4±0.18	0.7±0.03	0.1±0.00
7	0.4±0.02	1.0±0.07	38.4±4.02	0.1±0.00	12.4±1.01	15.7±1.12	29.6±2.19	0.7±0.03	0.5±0.11	–	0.5±0.03	0.2±0.03	–	0.1±0.01
8	0.1±0.00	0.3±0.02	12.2±0.18	0.2±0.01	5.2±0.07	10.1±1.27	59.3±4.98	3.8±0.51	5.5±0.37	0.7±0.02	0.5±0.04	1.5±0.04	0.2±0.01	0.1±0.02
9	0.5±0.11	1.2±0.08	45.6±6.10	0.2±0.01	4.5±0.09	0.1±0.00	38.6±4.01	0.4±0.03	7.7±0.52	0.1±0.01	0.4±0.01	0.2±0.01	–	0.1±0.01
10	0.3±0.03	1.1±0.03	42.8±4.37	0.2±0.00	4.1±0.03	0.1±0.01	40.6±3.03	0.3±0.01	9.0±1.00	0.3±0.01	0.4±0.01	0.2±0.01	–	0.1±0.00
11	0.2±0.02	0.2±0.00	6.3±0.08	0.3±0.01	5.0±0.12	56.4±4.18	24.3±3.81	1.2±0.17	1.5±0.18	0.2±0.02	0.6±0.03	1.7±016	1.2±0.13	0.1±0.01
12	0.4±0.01	1.1±0.08	40.2±2.33	0.2±0.02	4.9±0.09	4.9±0.09	37.0±3.17	0.2±0.01	9.0±0.78	0.6±0.03	0.4±0.02	0.3±0.02	0.1±0.01	0.1±0.01
							2008							
13	7.2±1.20	3.1±0.18	25.1±1.27	0.1±0.01	4.9±0.09	–	36.9±3.27	0.2±0.00	16.0±2.18	3.5±0.13	0.5±0.02	0.8±0.03	0.2±0.00	0.1±0.01
14	0.2±0.01	0.8±0.01	35.6±2.21	0.1±0.00	6.5±0.09	34.7±3.17	19.3±2.02	0.9±0.18	0.5±0.01	–	0.5±0.02	0.3±0.01	–	0.1±0.00
15	0.7±0.02	0.1±0.00	7.8±1.01	0.3±0.02	10.4±0.27	53.7±3.09	20.1±0.89	0.3±0.02	1.4±0.12	0.2±0.01	0.8±0.03	1.5±0.07	1.3±0.03	0.2±0.01
16	1.5±0.80	0.9±0.07	16.1±1.17	0.1±0.00	16.5±0.89	15.9±1.13	42.2±1.13	0.4±0.01	3.2±0.01	0.1±0.01	0.8±0.03	0.4±0.02	–	0.1±0.02
17	1.9±1.02	1.0±0.03	14.1±1.18	0.1±0.01	11.5±0.91	23.1±1.28	43.4±2.18	–	2.1±0.07	0.2±0.01	0.6±0.01	0.6±0.03	–	0.1±0.01
18	0.4±0.02	1.0±0.01	33.5±2.22	0.2±0.01	3.5±0.03	–	47.2±5.21	–	13.5±1.12	0.2±0.01	0.3±0.01	0.2±0.01	–	–
19	0.4±0.01	1.0±0.02	39.6±3.41	0.2±0.01	4.1±0.05	0.1±0.00	43.2±4.05	–	10.7±0.87	0.2±0.01	0.3±0.02	0.1±0.00	0.1±0.00	–
20	0.2±0.01	1.0±0.01	44.0±4.02	0.2±0.00	4.3±0.02	0.2±0.01	39.8±6.01	–	9.8±2.13	0.2±0.00	0.3±0.00	0.1±0.01	–	–
21	0.6±0.02	1.3±0.04	46.5±4.08	0.1±0.02	5.5±0.03	1.6±0.05	36.9±4.31	0.4±0.01	6.4±0.93	0.2±0.02	0.3±0.00	–	0.1±0.01	–
22	0.2±0.01	1.0±0.01	46,1±6.01	0.0±0.00	5.0±0.05	1.2±0.02	36.1±5.24	0.8±0.02	8.3±0.87	–	0.4±0.01	0.3±0.02	0.2±0.01	0.1±0.00
23	0.4±0.03	0.9±0.02	39.7±5.32	0.1±0.01	4.2±0.03	0.4±0.01	41.3±6.01	–	12.7±2.17	0.2±0.00	0.4±0.02	0.1±0.01	0.1±0.00	–

* C8:0 for sample no.16 – 0.2%,17 – 0.3%; C10:0 for 3,16 -0.1%, 16,17- 0.2% and for 13 -0.5%; C13:0 for 13–0.4%; C15:0 for 1,4,5,7,9,10,12 – 0.1%; C22:0 for 17,21,23–0.1, 13,22 – 0.2, 15–0.4, 17- 0.7%; C24:1 for 8,11 -0.1%, **C17:0 for all fats 0.1%.
(-) not detected (<0.1%)

TABLE 2. Fatty acid profiles (%) and induction times of frying fats examined.

Sample no.	TFA	SFA	SFA+TFA	MUFA *cis*	PUFA *cis*	Induction times (h)
1997						
1	24.4	53.8	78.2	21.2	0.4	8.95
2	40.1	35.2	75.3	23.6	0.4	8.27
3	46.2	23.4	69.6	29.2	1.0	6.90
4	0.4	60.6	61.0	32.4	6.4	2.30
5	0.6	50.7	51.3	39.3	9.2	2.08
6	51.7	19.2	70.9	27.7	0.8	4.00
7	16.4	53.1	69.5	29.9	0.5	5.55
8	13.9	18.5	32.4	61.4	6.2	2.47
9	0.5	52.5	53.0	39.0	7.8	1.50
10	0.4	49.0	49.4	41.0	9.3	2.07
11	57.6	12.5	70.1	27.7	1.7	3.80
12	5.1	47.3	52.4	37.6	9.6	4.00
2008						
13	0.2	42.1	42.3	38.0	19.5	0.30
14	35.6	44.0	79.6	19.7	0.5	5.11
15	54.0	20.7	74.7	23.2	1.6	3.90
16	16.3	37.1	53.4	42.7	3.3	5.11
17	23.1	29.9	53.0	44.1	2.3	4.90
18	–	38.0	38.0	48.0	13.0	nd
19	0.1	45.4	45.5	43.7	10.9	nd
20	0.2	50.0	50.2	40.1	10.0	nd
21	2.1	54.3	56.4	37.1	6.6	2.59
22	2.0	52.9	54.9	36.6	8.3	1.56
23	0.4	45.7	46.1	41.6	12.3	nd
Mean 1997	21.4[b]	39.7[a]	61.1[a]	34.2[a]	4.4[a]	4.32[a]
Mean 2008	12.2[a]	41.8[a]	50.4[b]	37.7[b]	8.0[b]	3.35[b]

[a,b,c] different superscripts indicate mean values that differ statistically significantly at $p<0.05$. nd – not determined.

TABLE 3. Coefficients of correlation between fatty acids content and stability of frying fats (n=19).

	Stability of frying fats
TFA	0.54(*)
SFA	-0.13
TFA+SFA	0.70(*)
PUFA *cis*	-0.77(*)
MUFA *cis*	-0.54(*)

*Significant correlation at $p<0.05$.

fats and lower than the 33.8% reported by Karabulut & Turan [2006] in Turkey, and than the 28.70% reported a few years earlier in Danish frying fats [Ovesen *et al*., 1998]. A significant relationship was found between the contents of total TFA and SFA. Generally, samples low in SFA were high in TFA.

The total mean content of SFA and TFA in the examined fats from 1997 was 61.1% and in these from 2008 it reached 50.4%, and the difference was significant (Table 2).

The content of *cis* MUFA of presented products from 1997 ranged from 21.2 to 61.4% and in these from 2008 from 19.7 to 48.0%.

The total content of *cis* polyunsaturated fatty acids (linoleic and linolenic acids), which are more desirable for human health, for the majority of all samples, was between 0.4 and 19.5%. This value of *cis* PUFA for shortenings marketed in Poland was higher than that reported by Bhanger & Anwar [2004] in samples from Pakistan (2.73 to 7.04%) but slightly lower than the value of 13.7–23.0% reported by Karabulut & Turan [2006] in the Turkish fats and than 2.5–25.7% reported for Czech fats [Brat & Pokorny, 2000]. The content of *cis* PUFA seemed to increase in the frying fats from 1997 to 2008 and the differences were significant (Table 2).

About 33% of the examined fats presented on the Polish market in 1997 but about 64% of the samples from 2008 had a high level (above 5%) of PUFA, whose oxidation is quicker than oleic or other fatty acids. The transformation of fats caused by oxidation is the main source of undesirable food changes. High temperature and quite a long time of the frying process mean that the fat used for frying should be resistant to oxidation and polymerization. These changes are mostly dependent on the content of PUFA. The initial content of these compounds defines oxidative stability during heating and frying [Gertz, 2000, 2001; Ericsson & Frey, 1994].

Oxidative stability (Rancimat, 150°C) of all examined fats differed in a great range from 0.3 to 8.95 h. The mean induction period of presented fats sold in Poland in 2008 (4.32) was shorter (Table 2) than the stability index of the samples from 1997. The shortest induction times were shown by fats with the highest content of PUFA, and the longest induction times were shown by samples with the highest total content of SFA and TFA (r=0.70) and lower PUFA content (r=-0.77). The statistical analysis showed a significant positive relationship between TFA content and stability of frying fats (r=0.54) too (Table 3).

This means that a large proportion of fats (about 70%) offered for frying seems to be unsuitable for frying, with the induction period below 5 hours.

CONCLUSION

Some of the examined fats contained very high amounts of unsaturated fatty acid *trans* isomers (about 50%), but those with low amounts of this undesirable form (under 1%) were found as well. Therefore, it can be stated that meeting the nutritional requirements (by technological and material changes) and achieving the maximum reduction of *trans* isomers in fats used for frying are possible.

The examined frying fats were deeply heterogeneous in fatty acid composition. The majority of them were characterised by a high content of *trans* isomers, up to 54%, which can even be dangerous for human health. Therefore it is crucial to follow the changes, and the obtained results are very helpful. However, fats with the high TFA content were characterised by higher oxidative stability. On the other hand, the content of saturated fatty acid was very high, up to 54.3%.

Fats with low contents of *trans* isomers were characterised by a high concentration of palmitic acid, which may indicate that their main source was palm oil. The sum of the TFA and SFA of frying fats significantly influenced their oxidative stability. Induction time of fats scored higher with a higher TFA+SFA content in the examined fats and lower PUFA content. Moreover, the oxidative stability of the fats from 2008 was shorter (3.35) than the stability index of fats from 1997 (4.32).

A reduction of TFA content was noted from 1997 to 2008. It was found that TFA content in frying fats sold in Poland in 1997 ranged from 0.4 to 57.6% (mean 21.4%), and in 2008 from 0 to 54%, which was significantly less (12.2%). The sum of TFA and SFA was significantly different between the frying fats from these years (61.1 and 50.4% respectively).

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