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INFLUENCE OF *TRANS* UNSATURATED FATTY ACIDS CONTENT ON CHEMICAL CHANGES IN THE SHORTENING DURING BAKING AND STORAGE OF CAKES

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Key words: *trans* isomers, fatty acids, lipid peroxidation products, acid value, storage, shortcakes

The aim of this work was to determine the dependence between the content of fatty acids (especially *trans* isomers) and chemical changes occurring in fats during baking and storage of shortcakes.

The fats containing different fatty acids (*trans* isomers from 4.1 to 53.2%) were used to bake the cakes. The cakes were baked at 180ºC for 20 min and next stored for 6 weeks. Fat was extracted with the Kates' method and the composition of fatty acids was determined with gas chromatography.

It was found that *trans* isomers content in fats had no statistically significant effect on the oxidation and hydrolytic changes occurring in fats during baking of shortcakes. In all fats, irrespective of the content of *trans* isomers, the primary and secondary oxidation products appeared in small quantities. Temperature during baking had no influence on the content of saturated fatty acids. Considering *trans* isomers and polyunsaturated fatty acids in the product in comparison with initial fats, small changes appeared, but the changes were significant from the statistical point of view. Fats with a high content of *trans* fatty acids – although they do not cause hydrolytic and oxidation changes during baking and storage - should not be used for baking cakes, especially shortcakes with a high content of fat.

INTRODUCTION

A great deal of fats is very important in the production of shortcakes. High fat content has a favourable influence not only on taste of products but is also of key importance in providing proper structure of cakes [Meneger 1976; Confetti *et al*., 1997; Allen & Hamilton, 1989].

Most often used fats are: shortening and hard margarines in the production of cake products. A vast majority of these fats contain partly hydrogenated rapeseed oil. The process of hydrogenation results in the generation of *trans* isomers of fatty acids, which is disadvantageous for these fats [Haumann, 1994; Pedersen 2001; Beers & Mangnus, 2004]. These fats and their products are an important source of *trans* isomers of fatty acids. These acids and also saturated fatty acids are supposed to aggravate the risk of inducing heart diseases [Aro, 2001; Juttelstad, 2004]. High content of *trans* isomers in a diet increases the level of total cholesterol and as well its LDL fraction (Low Density Lipoproteins). Important factor is that the LDL fraction blocks blood vessels forming atherosclerotic plaques. It is said that it is the atherosclerotic effect of TFA [Van Duijn, 2000; De Roos *et al*., 2001]. As regards the HDL fraction (High Density Lipoproteins), an opposite situation is observed. These isomers - as opposed to saturated fatty acids – reduce its level [Müller *et al*., 1998; Aro, 2001; Sundram *et al*., 2003].

Trans isomers are able to build into phospholipid membranes. This may change the properties of these membranes which evoke neoplasmic diseases. But till now, there is no evidence that would confirm these suggestions [Bartnikowska & Obiedziński, 1997].

Furthermore *trans* isomers of fatty acids can interfere with the metabolism of other fatty acids (EFA) valuable from the nutritional point of view [Verschuren & Zevenbergen, 1990].

It is very important to realize that the chemical changes of fats take place during such processes as baking and storage of high-fat cakes. These changes can be evoked by hydrolysis of triacylglycerols, oxidation, polymerisation and cyclisation of unsaturated fatty acids. Thus, it is particularly significant for cake producers to establish the conditions of storage [Frankel, 1982].

The aim of this work was to determine the dependence between the content of fatty acids (especially *trans* isomers) and chemical changes occurring in fats during baking and storage of shortcakes.

MATERIALS AND METHODS

The evaluation of chemical properties of three fats was carried out in this investigation. Fats which were investigated contained different amounts of fatty acids especially *trans* isomers (from 4.1 to 53.2%).

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The following fats were determined: (1) fats used in the production of shortcakes, (2) fats extracted from the cakes after baking, and (3) fats extracted from cakes that had been stored.

The following fats (produced by ZPT in Warsaw) were used in the study: (A) a blend of palm and coco oil, (B) a blend of partly hydrogenated palm and rapeseed oil, and (C) hydrogenated rapeseed oil. The subsequent letters indicate a higher content of *trans* isomers.

The flour – type 500 (proper for shortcakes with the content of 32.2% gluten), fresh mass of eggs and salt were used in the research.

The dough was prepared according to Ambroziak [1994] formula, and contained 31% of fats (200 g). Other ingredients were flour – 300 g, sugar 100 g, eggs – 50 g. Cakes were baked in a convectional oven (Electrolux AR 85) at 180°C for 20 min. The temperature was measured during baking in the middle of cake. The measurements were carried out by an EMT-08 type thermometer coupled with a temperature sensor (series 200K. NiCr – NiAl). The final temperature in the cakes was 135°C. Four series of cake's baking were carried out.

The shortcakes have been stored at 25°C without packing for six weeks.

The investigated fats were determined for the composition of fatty acids using GC; Gas Chromatography procedure followed the method recommended by International Standard [EN ISO: 5508 2000] under the following conditions: apparatus HP 6890 GC System with autosampler; column: SGE Capillary BPX 70, highly polar column, 60 m in length, 0.22 mm in diameter with 70%, cyanopropyl (equiv.) polysilphenylene-siloxane; oven: temperature program from 160 to 190°C, heating rate: 2.5°C/min; carrier gas: helium applied at a flow rate of 0.6 mL/min, injector: split-splitless 240°C, detector: FID 250°C; flame gas: H_2; software: HP Chemstation v. 3.11; sample: 1 μL in iso-octane; preparation of methylester according to ISO 5509 [2000]. Additional analyses included assays of: acid value [ISO 660, 1996], peroxide value [ISO 3960, 1996], anisidine value [EN ISO 6885, 2000], and Totox index of Patterson [1992]

Kates method [Rutkowski & Krygier, 1979] was used to extract fat from cakes. The following solvents were used: dichloromethane, methanol, and water.

Investigations were carried out by using Statgraphics Plus 4.1 software. The evaluation of differences of between the results was done by using Duncan test at $p<0.05$.

RESULTS AND DISCUSSION

Temperature is one of the factors that can cause disadvantageous changes in fats [Viera & Regitano-d'Arce, 2001]. Changes in the content of the most important groups of fatty acids (*trans* isomers – TFA, saturated fatty acids – SFA, essential fatty acids – EFA) in fats occurring during baking are shown in Figure 1. Regulska-Iłow *et al*. [2000, 2001] carried out research into the influence of baking temperature on the content of fatty acids in shortcakes and yeast cakes, which were baked by conventional method and using the microwave. The authors demonstrated that the content of fatty acids was not changed on the basis of their results. As in the work of Regulska–Iłow *et al*. [2000, 2001], the tendency of changes of the disadvantageous *trans* isomer content varied (both increasing and decreasing tendency was noticed).

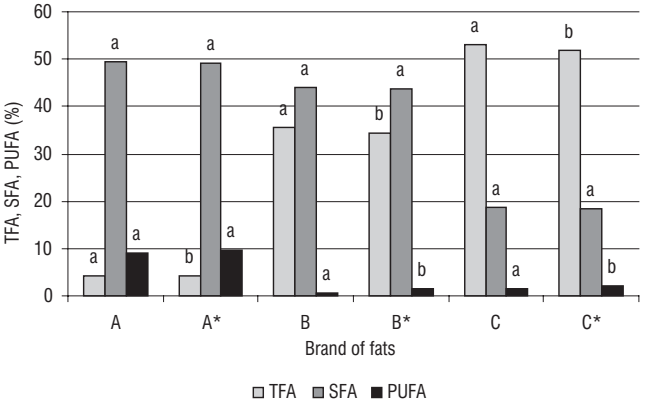

FIGURE 1. The content of main groups of fatty acids in the raw fatty material and extracted fat after baking the cakes.
A, B, C fats before baking; A*, B* ,C* fats after baking; the mean values denoted with the same letters are not significantly different at $p<0.05$.

An insignificant decrease (from 53.2 to 51.9%) was noticed in the fat with the highest content of TFA (C). For the fat with medium content of TFA (B) the increase was 3.7%, and for the fat with a very low content of TFA (A) it was 2.3%. The differences were small, but statistically significant ($p<0.05$), (Figure 1). It is important that in the extracted fat there was additionally fat from flour and eggs.

According to expectations baking did not cause statistically significant changes in the content of saturated fatty acids. The changes were not statistically significant and were equal to 0.3 unit (fat A).

Polyunsaturated fatty acids (PUFA) were determined as the sum of α-linolenic and linolic acid in this work. For fat A (the smallest content of TFA) the change of PUFA was not statistically significant. In contrast, the change of polyunsaturated fatty acids for fats B and C was significant. For fat B the increase of the content in the above-mentioned acids was equal to 150% (from 0.6% in comparison with initial fat to 1.5% in the fat of cakes after baking). For fat C the increase amounted to 0.7 unit. That means 47% more than in the initial fats. It is likely that fats from flour and eggs have affected these results.

The content of polyunsaturated fatty acids was higher in all extracted fats than in the initial fats. This tendency is similar to findings reported by Regulska–Iłow *et al*. [2000, 2001] .

The acid values (AV) of extracted fats from cakes after baking (without storage) were similar to those noted for fat added to cakes (Table 1). This means a slower increase of free fatty acids in fats during baking cakes. The biggest increase of free fatty acids (about 0.01 units) occurred both for fats with a lower content of TFA and the highest content TFA.

Greater differences were observed in oxidative changes (Table 1). Baking caused an increase of initial oxidative products in all types of fats. In the fat with the highest content of TFA the difference between the peroxide value in the initial fat and extracted fat was the highest and was equal to 0.4 units. High temperature during baking can cause the degradation of peroxides and hydroperoxide to carbonyl com-

TABLE 1. Changes of AV, PV, AnV, Totox in fats during baking of shortcakes.

Brand of fats	Acid value (mgKOH/g)	Peroxide value (mEqO/kg)	Anisidine value	Totox
A	0.15±0.01	1.49±0.04	1.9±0.03	4.9±0.04
A*	0.16±0.02	1.41±0.03	2.2±0.06	5.0±0.05
B	0.33±0.01	0.63±0.01	1.6±0.04	2.9±0.03
B*	0.33±0.01	0.69±0.01	1.7±0.03	3.1±0.02
C	0.28±0.02	0.38±0.01	1.8±0.01	2.6±0.01
C*	0.29±0.02	0.78±0.02	1.9±0.02	3.5±0.02

A, B, C fats before baking; A*, B* ,C* fats after baking

pounds and that is why fats with a high degree of oxidative degradation can have quite low peroxide value (PV) [Kafel, 1987]. Drzewicka & Biernat [2001] obtained higher peroxide values in extracted fats from different cake products. This might have been caused not only by high temperature during baking but also by the changes occurring in fats during storage of products.

The increase of secondary products of oxidation was insignificant in all the analysed fats, without reference to the content of *trans* isomers. The biggest increase of anisidine value was found for the fat with the lowest content of TFA (0.3 units) (Table 1). The number of secondary products of oxidation was rather small (below 3) in all analysed fats before and after baking, which proved the good quality of fat after thermal processing [Podmore, 1992]. The biggest increase in AnV occurred in the fat with the highest content of PUFA. These observations confirm earlier research carried out on the mechanism of oxidation of fatty acids. It was claimed that hydroperoxides arising in the oxidation of linolenic acid could decompose easier than those which had arisen in the oxidation of oleic acid [Ziemlański & Budzyńska-Topolowska, 1991; Frankel, 1982].

Totox index was calculated on the basis of the content of primary and secondary products of oxidation. The highest value of Totox index after baking (5.0) was obtained for the fat with the lowest content of TFA (Table 1). Allen & Hamilton [1989] showed that the maximum value of the Totox index is 10 and this value determines good quality of edible fat. It was found that the analysed fat (initial and after baking) had been oxidized insignificantly. The increase of the content of free fatty acids and the oxidation products (which was caused by heating cakes during baking) was very low and had no influence on the quality of fat in the products. No statistically significant correlations were found between the content of TFA in the initial fats and the hydrolytic and oxidative changes (which appeared because of baking in the extracted fat from shortcakes).

It was pointed out that the acid value for all fats had not exceeded 0.50 mg KOH/g during the storage of shortcakes for 21 days (Figure 2). It was noticed that there was a relatively large increase of acid value for fat A from cakes after 21 days of storage. The initial value was 0.17 unit and 21 days after baking it was 0.46. The increase was equal to 170%. For fats B (35.5% TFA) and C (53.2%TFA) over the entire time of storage of cakes the increase of free fatty acids was rather slower. The increase was 21% after 21 days and 37.9% after 42 days.

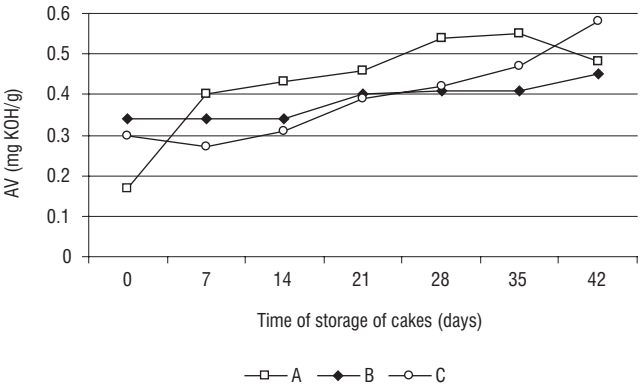

FIGURE 2. Changes of free fatty acids content in extracted fat from shortcakes during their storage.
Explanations: see Fig. 1.

No statistically significant correlations were noticed between the *trans* isomer content in the initial fats and the increase of acid value in the extracted fats from the shortcakes during storage (r=-0.15).

During the storage of cakes for 21 days (for fat A – 4.1% TFA) the peroxide value exceeded 3 mEqO/kg. This is the peak value of peroxides acceptable for shortening (Figure 3) [PN-A--86902, 1997]. A reduction of peroxide value appeared after 35 days of storage of cakes in fat B. This situation shows the degradation of peroxides and hydroperoxides to carbonyl compounds – which proves that fats with a high oxidation-induced degree of degradation can have low peroxide value [Kafel, 1987].

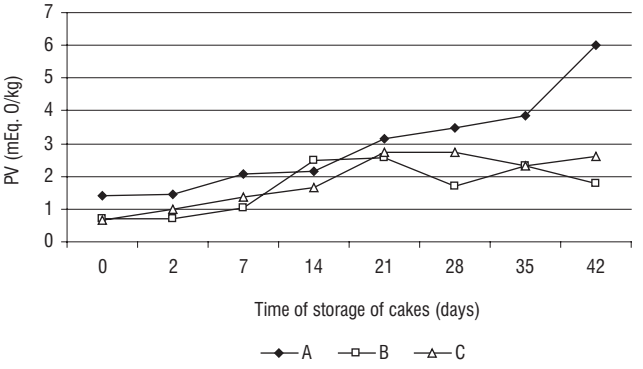

FIGURE 3. Changes of peroxide products content in extracted fat from shortcakes during their storage.
Explanations: see Fig. 1.

The statistical results of analysis proved that there was no significant correlation between the content of *trans* isomers in the initial fat and the peroxide values of extracted fats from cakes during storage for 42 days (r=-0.21).

On January 1, 2003, Canada as the first country in the world introduced labelling of the content of *trans* fatty acids (TFAs) in food products [Stender & Dyerberg, 200].

On July 11, 2003, the Food and Drug Administration (FDA) published its regulations on nutrition labelling. These require that TFAs be declared in the nutrition label of conventional foods and dietary supplements on a separate line immediately under the line for the declaration of saturated fatty acids, to be effective by January 1, 2006. FDA has

decided not to distinguish between industrially produced *trans* fatty acids and TFAs of ruminant origin. Consequently dairy products will be labelled with the content of TFAs [Yurawecz, 2004].

In the EU, processed and packaged food should be labelled with a list of ingredients ranked according to the amounts in grams in the products. If the products contain some partially hydrogenated fat, it should appear on the label, but not how much TFAs it contains.

If food is provided with a health claim concerning its content of industrially produced TFAs, *e.g.* "free of trans fatty acids", a declaration is required of fat composition in the product, stating the amounts of mono-, poly-, and saturated fatty acids [Stender & Dyerberg, 2004; Mojska *et al*., 2006].

In March 2003, after consultations with the Member States of the EU, the Danish Government decided that oils and fats with more than 2% content of industrially produced TFAs would not be sold in Denmark after January 1, 2004 [Anonymous, 2006].

CONCLUSIONS

1. It was found that *trans* isomers content in fats did not affect scientifically the oxidative and hydrolytic changes occurring in fats during baking of shortcakes. In all fats, irrespective of the content of *trans* isomers, the primary and secondary oxidation products appeared in small quantities.

2. Temperature during baking had no influence on the content of saturated fatty acids. Considering *trans* isomers and polyunsaturated fatty acids in the product in comparison with initial fats, small changes appeared, but from the statistical point of view, the changes were significant.

3. No statistically significant dependences were noticed between the *tran*s isomers content of fats and the oxidative and hydrolytic changes in fats during shortcakes storage.

4. Fats with a high content of trans fatty acids, although they do not cause hydrolytic and oxidative changes during baking and storage, should not be used to bake cakes, especially shortcakes with a high content of fat.

REFERENCES

1. Allen J., C. Hamilton R.J., Rancidity in Foods. 1989, Elsevier Science Publishers London, pp. 30–34.
2. Ambroziak Z., ed, Ciastkarstwo także dla piekarzy. Receptury, normy, porady i przepisy prawne. 1994, Wyd. Spółdzielcze Warszawa, pp. 2–27. (in Polish).
3. Anonymous, Unilever Canada takes the „trans" out of fat. Food Navigator, 2004 [http://www.foodnavigator.com/news/science.asp].
4. Aro A., Complexity of issue of dietary trans acids. The Lancet, 2001, 375, 9258, 732–733.
5. Bartnikowska E., Obiedziński M., Unsaturated trans fatty acids – nutritional problem? Pol. J. Food Nutr. Sci., 1997, 47, 1–20.
6. Beers A., Mangnus G., Hydrogenation of edible oils for reduced trans-fatty acid content. INFORM, 2004, 15, 404–405.
7. Confetti FD., Charles SA., Duncan SE., Evaluation of a carbohydrate – based fat replace in a fat – reduced baking powder biscuit. J. Food Qual., 1997, 20, 247–256.
8. De Roos N.M., Schouten E.G.,. Katan M.B., Consumption of a solid fat rich in lauric acid results in a more favourable serum lipid profile in healthy men and women than consumption of a solid fat rich in trans-fatty acids. Am. Soc. Nutr. Sci., 2001, 242–245.
9. Drzewicka M., Biernat J., Estimation of the extent of oxidation of fatty acids and of their content in commercial pastries. Bromat. Chem. Toksykol., 2001, 2, 91–97 (in Polish; English abstract).
10. EN ISO 5508: 2000. Animal and vegetable fats and oils – Analysis by gas chromatography of methyl esters of fatty acids.
11. EN ISO 6885: 2000. Edible vegetable fats. Determination of anisidine value.
12. Frankel E.N., Lipid oxidation. Progress in Lipid Research. 1982, 19, 1–2, 1–22.
13. ISO 5509: 2000. Animal and vegetable fats and oils- Preparation of methyl esters of fatty acids.
14. ISO 660: 1996. Animal and vegetable fats and oils. Determination of acid value and acidity.
15. ISO 3960: 1996. Animal and vegetable fats and oils. Determination of peroxide value.
16. Haumann F.B., Questions remain over hydrogenated fats. INFORM, 1994, 5, 4, 358-363.
17. Juttelstad A., The marketing of trans fat- free foods. Food Technol., 2004,1, 58, 20.
18. Kafel S., Significance of unsaturated fats in carcinogenesis. Żyw. Człow. Metab., 1987, 14, 117–120 (in Polish; English abstract).
19. Meneger A., Technologic and nutritional aspects of fats and emulsifiers in baked goods. 1976, *in:* Lipids, Technology, Vol. 2, 1st ed. (eds. R. Paoletti, G. Jacini, R. Porcellati). Raven Press, New York, USA, pp. 419–424.
20. Mojska H., Gielecińska I., Balas J., Pawlicka M., Szponar L., *Trans* fatty acids in food in Poland: Monitoring study. Żyw. Człow. Metab., 2006, 33, 2, 107–122 (in Polish).
21. Müller H., Jordal O., Kierulf P., Kirkhus B., Pedersen J.I., Replacement of partially hydrogenated soybean oil by palm oil in margarine without unfavorable effects on serum lipoproteins. Lipids, 1998, 33, 9, 879–887.
22. Patterson H.B., Bleaching and Purifying Fats and Oils. Theory and Practice. 1992, AOCS Press, Champaign, Illinois, p. 220.
23. Pedersen J.I., More on trans fatty acids. Brit. J Nutr., 2001, 85, 249–250.
24. Podmore J., Recent Advances in Chemistry and Technology of Fats and Oils. 1992, Elsevier Applied Science Publishers, London, p. 172.
25. PN-A-86902. 1997. Animal and vegetable oil and fats - Bakery and confectionery fats.
26. Regulska–Iłow B., Iłow R., Chnges in selected fats during conventional and microwave banking of yeast cakes. Bromat Chem. Toksykol. 2000, 2, 119–124 (in Polish; English abstract).
27. Regulska–Iłow B., Iłow R., Biernat J., Changes in fats during conventional and microwave banking of cakes. Bromat. Chem. Toksykol. 2001, 34, 99–104 (in Polish; English abstract).
28. Rutkowski A., Krygier K., Technologia i analiza tłuszczów jadalnych. 1979, Wyd. SGGW Warszawa, pp. 128–129 (in Polish).
29. Stender S., Dyerberg J., Influence of trans fatty acids on health, Ann. Nutr. Metab., 2004, 48, 61–66.
30. Sundram K., French M.A., Clandinin M.T., Exchanging partially hydrogenated fat for palmitic acid in the diet increases LDL-cholesterol and endogenous cholesterol synthesis in normocholesterolemic women. Europ. J. Nutr., 2003, 42, 88–194.
31. Verschuren P.M., Zevenbergen J.L., Safety evaluation of hydrogenated oils. Food Chem. Toxicol., 1990, 11, 28, 755–757.
32. Van Duijn G, Technical aspects of trans reduction in margarines. Oléagineux Corps Gras Lipides, 2000, 7, 1, 95–98
33. Viera T.M.S., Regitano-d'Arce M.A.B., Canova oil thermal oxidation during oven test and microwave heating. Lebensm. Wiss. Technol., 2001, 34, 215–221.
34. Yurawecz M.P., FDA requires mandatory labelling of trans fat. INFORM, 2004, 15, 184.
35. Ziemlański Ś, Budzyńska-Topolowska J., Nutritional quality of oxidized fats. Przem. Spoż. 1991, 4, 98–100 (in Polish).

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WPŁYW ZAWARTOŚCI IZOMERÓW *TRANS* NIENASYCONYCH KWASÓW TŁUSZCZOWYCH NA ZMIANY CHEMICZNE ZACHODZĄCE W TŁUSZCZACH PIEKARSKICH W TRAKCIE WYPIEKU I PRZECHOWYWANIA CIASTEK

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Celem pracy było określenie wpływu składu kwasów tłuszczowych (szczególnie izomerów *trans*) na zmiany chemiczne zachodzące w tłuszczach podczas obróbki termicznej i przechowywania ciastek kruchych. Do wyrobu ciast zastosowano tłuszcze różniące się składem kwasów tłuszczowych (zawartość izomerów *trans* od 4,1 do 53,2%). Ciastka wypiekano w temp. 180°C przez 20 min, a następnie przechowywano przez okres 6 tygodni. Tłuszcz ekstrahowano metodą Katesa i oznaczono w nim, metodą chromatografii gazowej, skład kwasów tłuszczowych.

Stwierdzono, że zawartość izomerów *trans* kwasów tłuszczowych nie wpływa w sposób istotny na zmiany oksydacyjne i hydrolityczne, zachodzące w tłuszczach podczas wypieku i podczas przechowywania ciastek. We wszystkich tłuszczach, niezależnie od zawartości izomerów *trans*, następował bardzo mały wzrost pierwotnych i wtórnych produktów utleniania. Temperatura w czasie wypieku nie wpływała na zawartość nasyconych kwasów tłuszczowych. W przypadku izomerów *trans* i NNKT w produkcie gotowym, w odniesieniu do surowca, następowały nieznaczne, ale statystycznie istotne zmiany. Tłuszcze o tak dużej zawartości kwasów tłuszczowych *trans*, mimo że nie wywołują zmian hydrolitycznych i oksydacyjnych podczas pieczenia i przechowywania, nie powinny być w ogóle stosowane do pieczenia ciast, a zwłaszcza do pieczenia ciast kruchych o dużej zawartości tłuszczu.