A C T A A L I M E N T A R I A P O L O N I C A
Vol. XVI (XL), No. 3-4 1990

ADAM SROCZYŃSKI
CELINA WIECZOREK*)

CHEMICAL CHANGES IN THE FAT FRACTION DURING STORAGE OF LONG LIFE SWEET BAKED PRODUCTS

Institute of Chemical Food Technology, Technical University, Łódź
*) Centralny Ośrodek Badawczo-Rozwojowy Przemysłu Gastronomicznego i Artykułów Spożywczych, Warszawa

Key words: fat changes, storage, long life sweet baked products.

Changes in the fat fraction of durable sweet baked products were assessed by determining contents of peroxides, cinnamic and malonic aldehydes, fatty acids, and the ester number. Three kinds of biscuits and one kind of wafer were studied in various temperature and air humidity conditions over a period of four months.

Long life sweet baked products are intended for storage over periods anywhere between one and 30 months. Maximum storage time of these products depends on their chemical composition, among other things. When their water content is 4-20% their qualitative features tend to remain fairly stable during prolonged storage. A low water content (1-5%) is conducive to autoxidation processes in fats [5, 6, 12, 14]. Some of the long life sweet baked products contain as much as 20-35% of fat, and this figure, together with the potentially long periods of storage suggest that the sensory quality of these products may be affected by chemical changes in the fat [4, 11, 13, 17].

MATERIAL AND METHODS

The experiments were performed with durable baked products containing over 20% of fat: layered biscuits with sugar-fat filling, chocolate biscuits, laminar biscuits, and layered wafers with sugar-fat filling. The products were packed in heat-sealed viscose foil. The fat indices were determined immediately after baking and then at four one-month intervals. The products were stored at +10, 20 and 30°C in relative air humidity of 50, 60, 70, 80 and 90%. Fat was extracted from the baked products with freshly distilled ethyl ether (34-35°C fraction) devoid of peroxides directly before chemical determinations.

Changes in the fat fraction were deduced from the following:

— peroxide number [16],
— reaction with benzidine [18] and thiobarbituric acid [3],
— amount of free fatty acids determined by the titration method [15],
— fatty acids composition [1],
— ester number[7].

RESULTS AND DISCUSSION

Increasing intensity of oxidation processes in the fat fraction of baked products, signalled by peroxides content, was due mainly to storage time and temperature. Increases of temperature additionally caused variously intense effects of humidity. The highert content of peroxides was found after four months of storage which means that it increases with the increase of storage time. At 10°C the peroxides content in the various stages of study was practically identical in all humidities within each particular group of products. At 20 and 30°C the peroxides content in the various humidities was more diversified. At 10 and 20°C

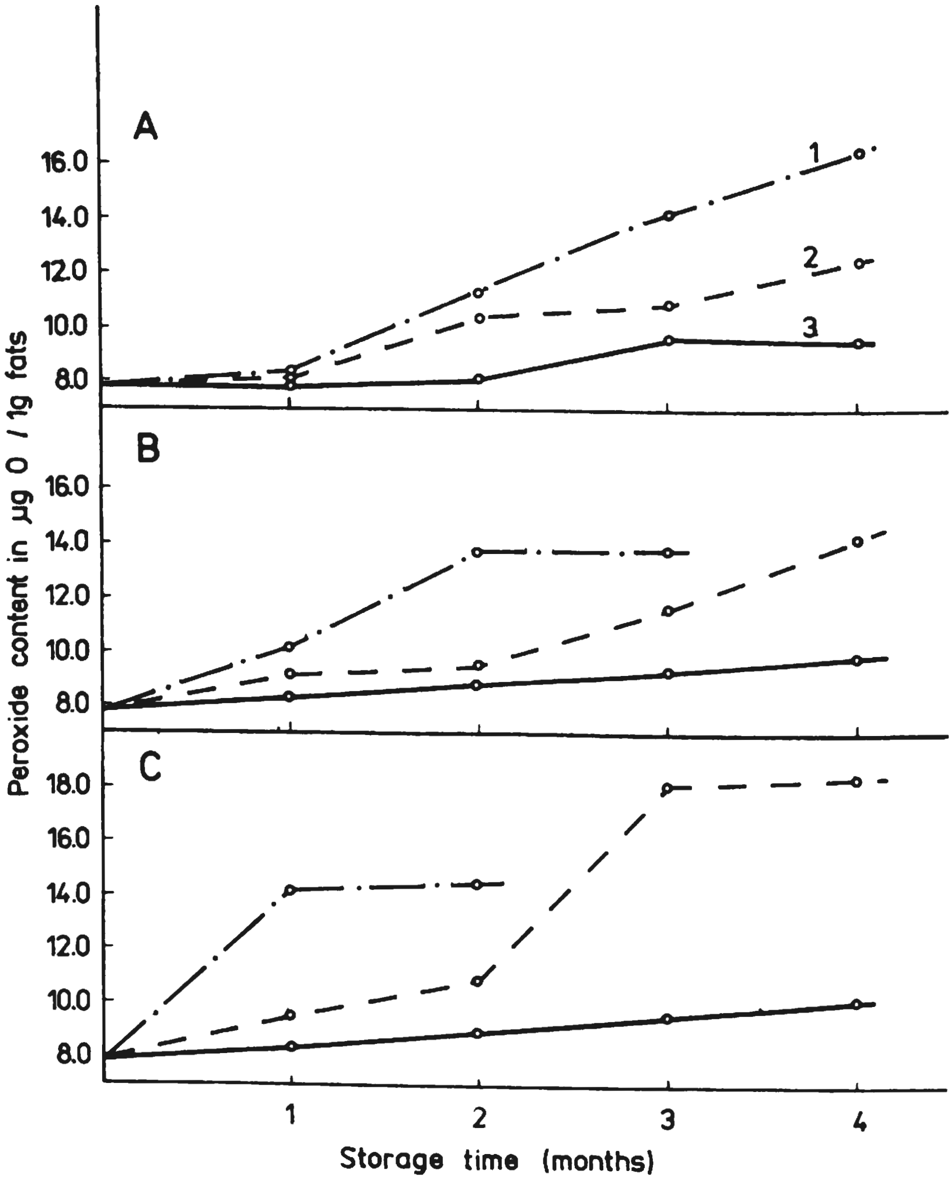

Fig. 1. Dependence between peroxides content in chocolate biscuits and storage time at constant relative air humidity and various temperatures; A — relative humidity 50%, B — relative humidity 70%, C — relative humidity 90%; 1 — 30°C, 2 — 20°C, 3 — 10°C

changes in humidity brought about random variations of this content, while at 30°C it was correlated with air humidity. Fig. 1 shows that in chocolate biscuits the peroxides contents for each humidity level differed, increasing with the increase of temperature and humidity. This proportional dependence between peroxides content on the one hand and temperature and humidity on the other reflected the general tendency of changes in all the studied products, despite several departures from the rule in some stages of the studies. An increase of humidity caused greater increments of peroxides in the initial stages of storage which indicate greater dynamics of oxidation. For comparison, we give results of peroxide content studies in four kinds of sweet baked products stored for four

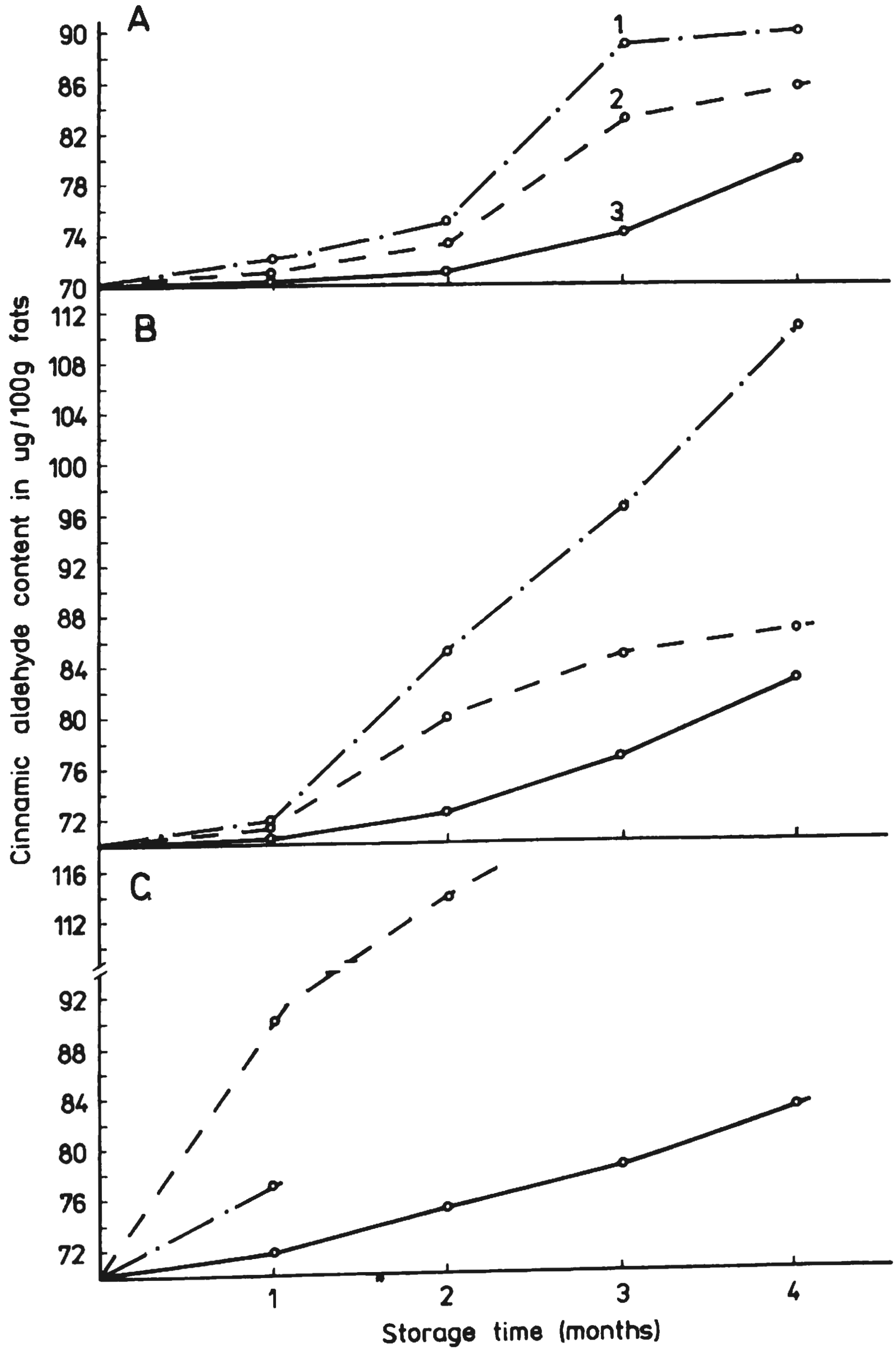

Fig. 2. Dependence between benzidine number in layered biscuits and storage time at constant relative air humidity and various temperatures. For explanations see Fig. 1

Table 1. Changes in malonic aldehyde content during storage of sweet baked products at various temperatures and air humidities

Product	Storage time (months)	Initial malonic aldehyde content	Temperature (°C)										
			10			20					30		
			Relative air humidity (%)										
			50	70	90	50	60	70	80	90	50	70	90
			µg malonic aldehyde/1 g dry substance of baked product										
layered biscuits	0	1.63											
	1		1.64	1.66	1.66	1.66	1.64	1.67	1.69	1.69	1.64	1.72	2.16*)
	2		1.66	1.72	1.68	1.69	1.72	1.75	1.79	2.52*)	1.69	1.79	—
	3		1.80	1.83	1.87	1.69	1.78	1.82	1.82	—	1.75	1.82	—
	4		1.78	1.83	1.88	1.83	1.86	1.94	1.95	—	1.86	1.86	—
chocolate biscuits	0	1.13											
	1		1.16	1.13	1.15	1.15	1.13	1.15	1.16	1.15	1.20	1.23	1.24
	2		1.32	1.40	1.25	1.23	1.22	1.24	1.32	1.33	1.24	1.26	1.89*)
	3		1.43	1.42	1.47	1.34	1.36	1.33	1.34	1.44	1.36	1.33	—
	4		1.45	1.48	1.55	1.38	1.40	1.42	1.43	2.48*)	1.41	1.50	—
laminar biscuits	0	1.58											
	1		1.65	1.66	1.68	1.63	1.67	1.67	1.66	1.72	1.63	1.65	2.66*)
	2		1.69	1.69	1.76	1.70	1.70	1.76	1.76	1.75	1.66	1.72	—
	3		1.71	1.75	1.79	1.77	1.76	1.79	1.85	1.77	1.73	1.90	—
	4		1.80	1.80	1.87	1.85	1.85	1.89	1.95	1.97	1.87	1.99	—
layered wafers	0	1.37											
	1		1.39	1.45	1.47	1.39	1.43	1.41	1.44	1.44	1.43	1.45	1.84*)
	2		1.48	1.45	1.54	1.42	1.43	1.45	1.48	1.56	1.50	1.51	—
	3		1.53	1.56	1.58	1.50	1.46	1.55	1.54	3.45*)	1.56	1.52	—
	4		1.60	1.62	1.67	1.59	1.58	1.62	1.65	—	1.66	1.73*)	—

*) denotes mold growth on samples

—/ dash denotes lack of data (elimination of moldy samples)

Table 2. Changes in acid number of fat during storage of longlife sweet baked products at various temperatures and air humidities

Product	Storage time (months)	Initial acid number	Temperature (°C) 10			20					30		
			Relative air humidity (%)										
			50	70	90	50	60	70	80	90	50	70	90
			KOH/1 g fat										
layered biscuits	0	1.4											
	1		1.4	1.4	1.4	1.4	1.4	1.4	1.5	1.6	1.4	1.5	3.7*)
	2		1.4	1.4	1.5	1.5	1.5	1.5	1.6	5.3*)	1.5	1.5	—
	3		1.4	1.5	1.5	1.5	1.5	1.5	1.6	—	1.5	1.6	—
	4		1.4	1.5	1.5	1.5	1.6	1.6	1.7	—	1.5	1.8	—
chocolate biscuits	0	1.3											
	1		1.3	1.3	1.3	1.3	1.3	1.4	1.4	1.4	1.3	1.3	1.6
	2		1.3	1.4	1.4	1.3	1.4	1.6	1.5	1.5	1.3	1.5	6.4*)
	3		1.3	1.4	1.5	1.4	1.5	1.6	1.7	1.5	1.5	1.7	—
	4		1.3	1.5	1.5	1.4	1.5	1.7	1.9	32.5*)	1.5	1.8	—
laminar biscuits	0	1.4											
	1		1.4	1.4	1.5	1.4	1.4	1.4	1.5	1.6	1.4	1.5	54.8*)
	2		1.5	1.5	1.5	1.4	1.5	1.5	1.6	1.9	1.5	1.6	—
	3		1.5	1.6	1.5	1.5	1.5	1.5	1.6	1.9	1.6	1.7	—
	4		1.5	1.6	1.6	1.6	1.6	1.6	1.9	2.0	1.6	1.7	—
layered wafers	0	1.0											
	1		1.0	1.0	1.0	1.0	1.1	1.0	1.2	1.2	1.0	1.0	50.4*)
	2		1.0	1.1	1.0	1.0	1.1	1.1	1.3	1.7	1.1	1.4	—
	3		1.1	1.1	1.2	1.2	1.1	1.2	1.3	60.7*)	1.2	1.4	—
	4		1.1	1.1	1.1	1.2	1.3	1.3	1.5	—	1.3	31.0*)	—

*) denotes mold growth on samples

— (dash denotes lack of data / elimination of moldy samples) months at 20°C and relative air humidity of 70%. The peroxides content (expressed in μg O_2/1 g fat) was 14.3 in chocolate biscuits, 20.7 in layered biscuits, 47.7 in laminar biscuits, and 51.4 in layered wafers. The initial benzidine number (expressed in mg cinnamic aldehyde per 100 g fat) was 20.4 in chocolate biscuits, 70.0 in layered biscuits, 85.1 in laminar biscuits, and 90.1 in layered wafers. The benzidine number increased dynamically in time and in most cases attained its peak value at the end of storage (after four months). Increments of this number were in general proportional to increases of temperature and air humidity. The greatest differences in cinnamic aldehyde contents at the various temperatures occurred when humidity was high; as humidity decreased, so did the effect of temperature (Fig. 2). After four months of storage at 20°C and relative air humidity of 70%, the values of the benzidine number were 27.9 for chocolate biscuits, 86.7 for layered biscuits, 95.2 for laminar biscuits, and 97.2 for layered wafers. The contents of malonic aldehyde in the freshly baked products ranged from 1.13 to 1.63 μg per 1 g dry substance. The content of this aldehyde was found to be affected very slightly by time of storage, temperature and air humidity, the exception being samples showing signs of microbiological decay (Table 1).Our studies show that the reaction with benzidine is a better indicator of changes occurring in stored baked products than the reaction with thiobarbituric acid.

Table 3. Fatty acids composition in fat of layered wafers

Fatty acid	Initial sample	Conditions of layered wafers storage during four months/tenperature and relative air humidity			
		10°C. 50%	10°C. 90%	30°C. 50%	30°C. 90%*)
		Fatty acids content			
C_{10}^{0}	0.1	0.1	0.1	0.1	0.1
C_{12}^{0}	0.2	0.2	0.2	0.2	0.2
C_{14}^{0}	1.6	2.1	2.0	2.0	1.6
C_{14}^{1}	traces**)	0.0	0.0	0.0	traces**)
C_{15}^{0}	0.1	0.3	0.2	0.2	0.2
C_{16}^{0}	9.6	9.8	9.9	10.0	10.0
C_{16}^{1}	1.9	1.4	1.5	1.6	1.3
C_{17}^{0}	0.2	0.2	0.3	0.2	0.3
C_{18}^{0}	5.2	5.5	5.5	5.4	5.4
C_{18}^{1}	28.2	30.5	30.8	29.6	29.6
C_{18}^{2izo}	0.6	0.3	0.2	0.2	0.4
C_{18}^{2}	5.7	6.1	6.2	5.8	6.2
C_{x}	0.2	0.3	0.3	0.2	0.3
$C_{18}^{3}+C_{20}^{0}$	3.8	4.0	3.9	3.8	3.7
C_{20}^{1}	7.2	7.0	7.1	7.2	6.8
C_{22}^{0}	2.5	2.1	1.9	1.9	2.0
C_{22}^{1}	32.8	30.1	29.9	31.6	31.2

*) one month of storage
**) below 0.1%

The chromogene absorbing light at 532-535 nm is a product of condensation of thiobarbituric acid with malonic aldehyde or unsaturated aldehydes, mainly 2,4-alkadienes and, to a lesser degree, with alken-2-als [8, 9]. One may thus conclude that changes in the contents of malonic aldehyde and unsaturated aldehydes during storage of long life sweet baked products are not fully positively correlated with the course of oxidation. This may be due to a low content of polyunsaturated fatty acids (Table 3) or to the formation of bonds between unsaturated aldehydes with active amino acid groups, or to changes in the degree of unsaturation of some of the aldehydes caused by their oxidation [2, 6]. The results collected in Table 2 illustrate the small changes in free fatty acids content during storage of sweet baked products. At 10°C, humidity had no effect on the fat's acid number which remained very stable in the investigated conditions. At 20°C the differences in this number were connected with humidity. Greater changes in the acid number were observed at higher values of humidity (80-90%), whereas at relative humidities of 50-70% the number remained practically at the same level. The results at 30°C were clearly diversified, in proportion to humidity and time of storage.

In our experiments we found that the differentiation of fatty acids composition in the fat of layered wafers due to extreme parameters of storage was slight (Table 3). There were also no significant differences between fatty acids contents in the initial sample and in fat samples from stored wafers. In all fat samples the following acids occurred in the highest content erucic (29.9-32.8%), oleic (28.2-30.8%), and in the middle quantities palmitic (9.6-10.0%), eicosenic (6.8-7.2%), linoleic (5.7-6.2%) and stearic (5.2-5.5%). In the investigated conditions most samples of the baked products had a similar ester number: ca. 180 mg KOH/1 g fat. The ester number changed significantly only when microbiological processes became apparent.

CONCLUSIONS

1. Peroxides content and benzidine number tended to rise in sweet baked products with the increase of storage time, in proportion to temperature and relative air humidity.

2. The changes in lipids of stored long life sweet baked products are better defined by the reaction with benzidine than with thiobarbituric acid.

3. The storage of long life sweet baked products affects only slightlly the thiobarbituric number, the content of free fatty adids, and the composition of all fatty acids.

4. The ester number remains very stable in various conditions of storage of long life sweet baked products.

5. The proper chemical indices of deterioration of long life sweet baked products during storage are the peroxides content and the total amount of the saturated and unsaturated carbonyl compounds.

LITERATURE

Pren 7.16 = 20.740,-

1. Branżowa Norma. Oznaczanie składu kwasów tłuszczowych w roślinnych tłuszczach jadalnych i w nasionach rzepaku metodą chromatografii gazowej. BN-80/8050-05.
2. Franzke C. and others: Die Nahrung Food 1973, **17** (4), 429.
3. Holland D.C.: J. Ass. Off. Anal. Chem., 1971, **54** (5), 1024.
4. Hunger R.H.: Getreide u. Mehl 1981 (5), 139.
5. Horubała A.: Przemysł Spożywczy 1980, **34** (6), 208.
6. Janicek G. and others: Chemia żywności, WNT, Warszawa 1977, 29.
7. Krauze S. and others: Podręcznik laboratoryjny analityka żywnościowego, PZWL, Warszawa 1962, 294.
8. Masłowska J., Bazylak G.: Gospodarka Mięsna 1981, **33** (3), 12.
9. Marcuse R., Johanson L.: J. Amer. Oil Chem. Soc., 1973, **50** (10), 387.
10. Mikke H.: Metody badania wskaźników jełczenia tłuszczu w środkach spożywczych, PZH, Warszawa, 1979, 2.
11. Newburg D.S., Conoon J.M.: J. Food Sci., 1980, **45** (6), 1681.
12. Pijanowski E. and others: Ogólna technologia żywności, WNT, Warszawa 1984, 449.
13. Podstolski J.: Chłodnictwo 1985, **20** (5), 22.
14. Pokorny J.: Rev. Fr. Cor. Gras., 1981, **28** (4), 151.
15. Polska Norma. Oznaczanie liczby kwasowej. PN-60/A-86921.
16. Polska Norma. Oznaczanie zawartości nadtlenków. PN-84/A-86918.
17. Sobina J., Heller Z.: Przemysł Spożywczy 1984, **38** (3), 94.
18. Töth W.: Fleischwirtschaft 1970, **50** (6), 849.

Manuscript received: March 1988
Authors address: 90-924 Łódź, Stefanowskiego 4/10
**) 02-001 Warszawa, Al. Jerozolimskie 87*

A. Sroczyński, C. Wieczorek)*

ZMIANY CHEMICZNYCH WSKAŹNIKÓW TŁUSZCZU W PROCESIE PRZECHOWYWANIA TRWAŁEGO PIECZYWA CUKIERNICZEGO

Instytut Chemicznej Technologii Żywności, Politechnika, Łódź
*) Centralny Ośrodek Badawczo-Rozwojowy Przemysłu Gastronomicznego i Artykułów Spożywczych, Warszawa

Streszczenie

Zbadano zakres zmian chemicznych zachodzących w lipidach trwałego pieczywa cukierniczego, to jest trzech rodzajach herbatników, przekładanych, czekoladowanych i laminowanych oraz waflach przekładanych. Badania przeprowadzono w okresach jednego, dwóch, trzech i czterech miesięcy przy różnych parametrach przechowywania, tzn. w temp. 10, 20, 30°C i wilgotności względnej powietrza od 50% do 90%. Zmiany zachodzące we frakcji tłuszczowej wymienionych wyrobów kontrolowano na podstawie analizy zawartości nadtlenków, aldehydów cynamonowego i malonowego, wolnych kwasów tłuszczowych, składu wszystkich kwasów tłuszczowych oraz liczby estrowej. Badane wskaźniki chemiczne tłuszczu ujawniły częściowo korelację z postępującymi w czasie przechowywania pieczywa cukierniczego procesami degradacyjnymi. Zawartość nadtlenków (rys. 1) i liczba benzydynowa wyrażona zawartością aldehydu cynamonowego (rys. 2) wykazały z upływem czasu przechowywania tendencje wzrostowe, tym większe im wyższa temperatura i wilgotność względna powietrza. Charakterystyczne są małe zmiany liczby tiobarbiturowej wyrażonej zawartością aldehydu malonowego (tab. 1), liczby kwasowej tłuszczu (tab. 2) oraz składu ilościowego wszystkich kwasów tłuszczowych (tab. 3).