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CHANGES IN LIPIDS AND THEIR EFFECT ON THE QUALITY OF FREEZE-DRIED MEAT MEALS

ZMIANY LIPIDÓW I ICH WPŁYW NA JAKOŚĆ LIOFILIZOWANYCH DAŃ MIĘSNYCH

Summary. Lipid oxidation is the main chemical reaction that determines stability of freeze-dried food. The aim of this research was to determine the quality of lipids in 10 types of freeze-dried food and in meals prepared from them. Lipids were extracted using the Bligh and Dyer method and the following parameters were determined: oxidation level (PV, AsV, CD), hydrolysis level (AV) and fatty acid composition (FA). An analysis of the level of oxidation and hydrolysis in freeze-dried food revealed a wide range of values for each analysed parameter – PV: 8-52 meq O_2 per 1 kg, AsV: 6-9 and AV: 3.5-9. Adding hot water to freeze-dried food resulted, for some of the samples, in further oxidation and hydrolysis of lipids. In general, preparing meals had no significant effect on the composition of FA. General desirability of prepared meals was relatively low (average score of 4.9 points). The characteristic that was evaluated to be the lowest was consistency (≈ 4.9), whereas colour received the highest score (≈ 6.8). Products near their expiry date can be a source of substantial amounts of lipid oxidation products and are characterised by very low general desirability.

Key words: freeze-dried food, lipid oxidation, hydrolysis, fatty acids

Introduction

One of the main difficulties for people engaging in active recreation, including mountaineering, is providing the body with adequate food. At high altitudes appetite and sense of taste are weakened, and along with hypoxia, it may result in feeling satiated even after limited meals. This effect of "mountain anorexia" can lead to significant loss of weight even for persons at about 3600 m altitude (WESTERTERP 2001). While a slight decrease in body weight can be attributed to acclimatisation, more substantial

loss of weight can even determine whether an entire expedition is successful or not. Weight loss may be limited if the food is tasty enough and is eaten in relatively comfortable conditions. Sometimes conditions of an expedition, such as the presence of steep icy slopes, narrow down the way of preparing meals to basic mixing the "concentrate" and hot water (PUGH 2004). The food that can be prepared in such a way must contain not only carbohydrates, which are the primary source of energy in the mountains, but also other ingredients, including vitamins and minerals. The only food that meets this criteria and, in addition, has low mass and volume, which is the decisive factor for choosing it, is freeze-dried food. In general it is characterised by high nutritional value and sensory qualities. One of the basic ingredients of food are fats, which, due to their composition, are among the most labile compounds. The ability of muscles to store carbohydrates is limited, so the human body may prefer energy in form of fat, especially during extensive exercise. Therefore, it is extremely important that the fat provided to the body is not only of adequate quality but is also adequately stable. Lipid oxidation is one of the major reactions limiting the stability of freeze-dried food (KAREL et AL. 1967). Lipid oxidation products are responsible for both deterioration of sensory qualities and reduction of both nutritional and health value of food. As a result, mere exposure to high altitude and exercise contribute to increased production of reactive forms of oxygen and nitrogen compounds (DOSEK et AL. 2007), all the more so the food should be free of lipid oxidation products. Long shelf life of freeze-dried products may raise some concerns about the quality of lipids. Wide access to freeze-dried food allows it to make its way into the provisions not only for typical high-mountain expeditions, but is also becoming "reserve food" for the average tourist. Although there is research data that report on the quality of freeze-dried foods, including lipids (SUN et AL. 2002, RAHMAN et AL. 2009, HĘŚ et AL. 2011), all this data involve material that had been controlled from the beginning of the research. There is no information in the available literature about the quality of ready-to-eat freeze-dried products available to consumers, and about the effects of the manner of preparing (adding hot water) meals on the quality of lipids. The main reason for choosing the research material was a significant share of the producer in the domestic freeze-dried food market, which provided a broad picture in terms of quality of lipids. The aim of the research was to determine the quality of lipids in both freeze-dried food and in ready-to-eat meals. The quality of lipids was determined by analyzing the level of oxidation, composition of fatty acids and by a sensory analysis of meals prepared from freeze-dried products.

Material and methods

The research material consisted of 10 freeze-dried food samples and meals prepared from the food. All the examined products were within their shelf life. Eight products were purchased on the market and two products were obtained from the manufacturer. From each group four dishes there were examined. Meals were prepared following the instructions on the package, that is an appropriate amount of hot water was added and the product was left alone for 6-10 min. A standardised test samples of freeze-dried food and of cold prepared meals were collected for chemical analyses. Sensory analysis was performed immediately after preparing the meals (analysed all dishes). Lipids from

both freeze-dried food and meals were extracted using the BLIGH and DYER (1959) method; the extraction was performed twice. Lipid content was determined gravimetrically and expressed as gramms per 100 g wet weight. The quality of lipids in freeze-dried food and in prepared meals was determined by analysing: the peroxide value (PV) (PIETRZYK 1958), anisidine value (AsV) (ISO 6885 – 1988), conjugated dienes (CD) (OFFICIAL METHODS... 2004), acid value (AV) (OFFICIAL METHODS... 2004) and fatty acids (FA) composition, performed via gas chromatography. Fatty acid methyl esters (FAME) were prepared according to PN-ISO 5509 (1996) and separated via gas chromatography. Conditions of the separation are described in an earlier paper (DOMISZEWSKI and BIENKIEWICZ 2010). A team of six adequately instructed persons performed sensory evaluation of the prepared meals. The aim of the evaluation was to determine the desirability of the meals. The following distinguishing features were assessed: texture, taste, smell, colour and overall desirability. A 100 mm non-structured graphic scale with the ends labelled: very undesirable – very desirable, was used for the evaluation. The obtained results were assigned numerical values equal to the distance from the beginning of the scale to the marked point (BARYŁKO-PIKIELNA 1995). Also the intensity of rancid odour was evaluated, using a 10-point scale.

Statistical analysis

Numbers presented in tables and figures are the mean values of three concurrent iterations. The statistical analysis was based on the one-way analysis of variance, homogeneous groups were formed according to the Duncan test for $p < 0.05$. The data were statistically analysed using STATISTICA (data analysis software system) by StatSoft, Inc. (2005), version.

Results

Freeze-dried products are characterised in Table 1. Compositional analysis showed that: the meat in three of the products was poultry, four beef, two pork and one beef and pork. The main starch ingredient in the products was rice, buckwheat, potato flakes, or modified starch. All the analysed dishes also included vegetables, oils or hydrogenated fats and spices.

An analysis of the level of oxidation and the level of hydrolysis revealed that in eight samples (1-8), with the expiry date in 18-24 months each quality indicator fell within a narrow range, with minor deviations. The PV was between 8.5-12.32 meq O_2 per 1 kg, AsV between 5.3-8.25 and AV between 3.5-4.25 (Table 2). Larger deviations, in the 0.5--1.43 range were observed for conjugated dienes. Two samples (9, 10), which were near their expiry date, revealed the highest amount of peroxides and free fatty acids and the lowest CD value. Adding hot water to freeze-dried food caused a general increase in all quality indicators under analysis. In some cases, the observed increase was significant (Table 2). The highest increase, between 50 and 100%, was observed in the samples which were near their expiry date. In other cases, the increase amounted to about 4-15%.

Domiszewski Z., Plust D., Wasilewska K., 2013. Changes in lipids and their effect on the quality of freeze-dried meat meals. Nauka Przyr. Technol. 7, 3, #36.

Table 1. Characteristics of freeze-dried dishes
Tabela 1. Charakterystyka dań liofilizowanych

Product number Numer produk-tu	Number of analysed products Liczba analizowa-nych produktów	Net weight Masa netto (g)	Amount of added water Ilość dodanej wody (ml)	Number of months to the end of product shelf life Liczba miesięcy pozostałych do końca okresu przecho-wywania	Ingredients – Składniki
1	2	3	4	5	6
1	4	83	300	19	Barley, pork, vegetables, flour, canola oil, spices Jęczmień, mięso wieprzowe, warzywa, mąka, olej rzepakowy, przyprawy
2	4	150	20	22	Rice, chicken, bamboo shoots, soy bean sprouts, vegetables, mun mushrooms, soy sauce, mushrooms, flour, canola oil, spices Ryż, kurczak, pędy bambusa, kiełki soi, warzywa, grzyby mun, sos sojowy, grzyby, mąka, olej rzepako-wy, przyprawy
3	4	125	300	24	Rice, beef, maltodextrin, starch, hydrogenated oil, sour cream, mushrooms, dextrose, lactose, caramel colour, guar gum, yeast extract, soy sauce, spices Ryż, wołowina, maltodekstryna, skrobia, uwodorniony olej, śmietana, grzyby, dekstroza, laktoza, karmel, guma guar, ekstrakt drożdżowy, przyprawy, sos sojowy
4	4	140	380	18	Pasta, tomatoes, beef, palm oil, potato starch, onion, peas, milk, spices Makaron, pomidory, wołowina, olej palmowy, skrobia ziemniaczana, cebula, groch, mleko, przyprawy
5	4	140	500	21	Rice, soybean, chicken, vegetables, vegetable oil, milk powder, yoghurt powder, chicken flavour, fructose, spices Ryż, soja, kurczak, warzywa, olej roślinny, mleko w proszku, proszek jogurtowy, aromat kurczaka, fruktо-za, przyprawy
6	4	125	350	19	Rice, chicken, starch, vegetables, hydrogenated oil, butter powder, broth, whey, maltodextrin, mushrooms, herbs, spices Ryż, kurczak, skrobia, warzywa, uwodorniony olej, masło w proszku, bulion, serwatka, maltodekstryna, grzyby, zioła, przyprawy
7	4	125	300	22	Potatoes, beef, milk, vegetables, wheat flour, vegetable fat (hydrogenated), starch, yeast extract, mushrooms, lactose, maltodextrin, sunflower oil, spices Ziemniaki, wołowina, mleko, warzywa, mąka pszenna, tłuszcz roślinny (uwodorniony), skrobia, ekstrakt drożdżowy, grzyby, laktoza, maltodekstryna, olej słonecznikowy, przyprawy

Table 1 – cont. / Tabela 1 – cd.

1	2	3	4	5	6
8	4	120	400	24	Beef, potatoes, milk, palm oil, broth, vegetables, starch, milk, spices Wołowina, ziemniaki, mleko, olej palmowy, bulion, warzywa, skrobia, mleko, przyprawy
9	4	100	400	1	Rice, pork, peppers, mushrooms, corn, vegetables, soup vegetables, oil Ryż, wieprzowina, papryka, pieczarki, kukurydza, warzywa, włoszczyzna, olej
10	4	100	400	1	Sauerkraut, cabbage, beef, pork, bacon, sausage, vegetables Kiszona kapusta, kapusta, wołowina, wieprzowina, bekon, kiełbasa, warzywa

Table 2. Oxidation and hydrolysis level of lipids in freeze-dried food and in prepared meals
Tabela 2. Poziom utlenienia i hydrolizy lipidów w liofilizatach i daniach gotowych

Product number Numer produktu	Peroxide value (meq O_2 per 1 kg of lipids) Liczba nadtlenkowa (meq O_2 na 1 kg lipidów)		Anisidine value Liczba anizydynowa		Conjugated dienes Skoniugowane dieny (%)		Acid value (mg KOH per 1 g of lipids) Liczba kwasowa (mg KOH na 1 g lipidów)	
	freeze-dried food liofilizat	meal danie	freeze-dried food liofilizat	meal danie	freeze-dried food liofilizat	meal danie	freeze-dried food liofilizat	meal danie
1	12.32^{Ae}	13.45^{Bc}	6.23^{Ac}	6.75^{Bc}	1.23^{Ag}	1.35^{Bf}	4.03^{Ab}	4.36^{Abc}
2	8.78^{Aab}	8.99^{Ab}	7.32^{Ab}	7.52^{Ad}	0.54^{Ac}	0.92^{Bb}	3.52^{Ac}	3.81^{Aa}
3	10.21^{Abcd}	11.63^{Ba}	8.25^{Aa}	8.73^{Bab}	0.76^{Ae}	0.82^{Ae}	3.96^{Aab}	4.35^{Abc}
4	8.58^{Aa}	9.01^{Ab}	5.28^{Af}	5.62^{Ae}	1.02^{Ab}	1.09^{Ac}	3.75^{Aad}	4.92^{Bd}
5	14.19^{Af}	15.03^{Bc}	7.92^{Aae}	8.43^{Ab}	1.43^{Ah}	1.65^{Bg}	4.25^{Ae}	4.52^{Ac}
6	11.21^{Ade}	11.55^{Aa}	8.32^{Aa}	9.25^{Ba}	1.03^{Ab}	1.11^{Ac}	3.84^{Aab}	4.01^{Aab}
7	9.62^{Aabc}	9.81^{Aab}	6.42^{Acd}	7.01^{Bcd}	0.65^{Ad}	0.72^{Bd}	3.81^{Aab}	4.12^{Aabc}
8	10.43^{cd}	11.22^{a}	8.01^{Aa}	9.18^{Ba}	0.85^{Af}	0.94^{Bb}	3.54^{Acd}	3.72^{Aa}
9	52.30^{Bh}	95.0^{Ad}	7.40^{Abe}	9.25^{Ba}	0.15^{Aa}	0.23^{Ba}	8.98^{Ag}	19.15^{Bf}
10	46.46^{Ag}	146.0^{Be}	6.9^{Abd}	8.60^{Bb}	0.17^{Aa}	0.25^{Ba}	6.51^{Af}	14.91^{Be}

Values represented by the same capital letters in row for the same parameter are not significantly different at $p < 0.05$.

Values represented by the same small letters in column are not significantly different at $p < 0.05$.

Wartości oznaczone tymi samymi dużymi literami w wierszu w obrębie tego samego czynnika nie różnią się istotnie dla $p < 0,05$.

Wartości oznaczone tymi samymi małymi literami w kolumnie nie różnią się istotnie dla $p < 0,05$.

Lipid content in freeze-dried food varied in a fairly wide range between 8.47 and 35 g per 100 g of product (Table 3). Analysis of the composition of fatty acids in freeze-dried food revealed that in six samples the dominant group were monounsaturated fatty acids (MUFA), which accounted for approximately 40% of total fatty acids (FA).

The dominant group in four other samples were saturated fatty acids (SFA) (Table 3). The smallest group were polyunsaturated fatty acids (PUFA), whose content varied from 5 to as high as 32% of FA, depending on the sample. In all freeze-dried food samples oleic acid accounted for nearly 90% of MUFA, whereas SFA were domi-

Table 3. Lipid content and fatty acids content of freeze-dried food and in prepared meals
Tabela 3. Zawartość tłuszczu oraz zawartość kwasów tłuszczowych w liofilizatach i daniach gotowych

	Product number – Numer produktu																			
	1		2		3		4		5		6		7		8		9		10	
	freeze-dried food liofilizat	meal danie	freeze-dried food liofilizat	meal danie	freeze-dried food liofilizat	meal danie	freeze-dried food liofilizat	meal danie	freeze-dried food liofilizat	meal danie	freeze-dried food liofilizat	meal danie	freeze-dried food liofilizat	meal danie	freeze-dried food liofilizat	meal danie	freeze-dried food liofilizat	meal danie	freeze-dried food liofilizat	meal danie
Lipid content (g per 100 g) – Zawartość tłuszczu (g w 100 g)																				
	35.22^{b}	8.95^{a}	15.12^{b}	3.82^{a}	8.47^{b}	3.11^{a}	11.25^{b}	3.84^{a}	19.34^{b}	6.52^{a}	15.77^{b}	3.87a	12.51^{b}	4.01^{a}	22.11^{b}	5.98^{a}	14.78^{b}	5.37^{a}	35.01^{b}	9.02^{a}
Fatty acid content (%) – Zawartość kwasów tłuszczowych (%)																				
C 12:0	–	–	–	–	0.02	0.01	0.03	0.04	0.02	0.02	–	–	–	–	–	0.01	0.19	0.21	0.22	0.19
C 14:0	1.68	1.54	0.63	0.57	1.75	1.84	2.28	2.20	1.32	1.18	0.69	0.65	2.89	3.03	1.82	1.74	1.65	1.11	1.84	1.03
C 16:0	21.53	20.77	16.85	15.74	23.99	23.43	30.25	29.76	14.56	13.96	18.29	17.79	19.85	20.22	21.88	21.62	38.91	43.59	38.16	43.55
C 17:0	–	0.00	0.12	0.11	1.03	0.95	1.01	1.08	0.11	0.08	0.08	0.07	0.88	0.81	0.91	0.88	–	–	–	–
C 17:1	–	0.00	0.01	0.02	0.75	0.67	0.74	0.76	0	0.01	0.01	0.01	0.51	0.57	0.61	0.62	–	–	–	–
C 16:1	3.12	2.96	3.46	3.33	1.89	1.99	2.29	2.33	2.21	2.38	2.22	2.34	1.52	1.70	2.15	2.09	–	–	–	–
C 18:0	12.11	10.79	5.38	4.81	17.23	16.76	16.12	16.69	4.96	4.53	8.52	8.14	14.86	14.57	14.99	15.26	15.58	6.08	16.79	8.11
∑C 18:1	43.72	44.80	48.38	48.85	40.51	40.37	42.55	41.50	43.4	41.50	46.54	46.85	39.98	38.35	42.04	41.58	37.79	39.31	36.72	37.87
C 18:2 n-6	12.56	13.15	18.68	19.48	11.23	11.71	3.94	4.12	28.32	30.79	18.36	18.80	18.35	18.97	12.76	12.83	4.91	8.96	5.07	8.66
C 18:3 n-3	2.63	2.72	4.62	4.92	0.69	0.83	0.36	0.40	3.59	4.13	2.88	2.97	0.33	0.39	1.75	1.79	0.33	0.51	0.41	0.37
C 20:1	1.32	1.24	0.81	0.88	0.8	0.81	0.31	0.34	0.57	0.61	1.34	1.40	0.75	0.81	0.79	0.81	0.64	0.23	0.77	0.17
C 20:4 n-6	1.12	1.58	0.85	1.17	0.11	0.12	0.12	0.14	0.77	0.88	0.89	0.94	0.08	0.10	0.10	0.11	–	–	0.02	0.05
C 22:1	0.21	0.46	0.21	0.37	–	–	–	0.00	0.17	0.19	0.18	0.19	–	–	0.2	0.19	–	–	–	–
∑ SFA	35.32^{b}	33.10^{a}	22.98^{b}	21.23^{a}	44.02^{b}	42.98^{a}	49.69^{a}	49.77^{a}	20.97^{b}	19.77^{a}	27.58^{a}	26.65^{a}	38.48^{a}	38.63^{a}	39.60^{a}	39.51^{a}	56.33^{b}	50.99^{a}	57.01^{a}	52.88^{b}
∑ MUFA	48.37^{a}	49.46^{a}	52.87^{a}	53.45^{a}	43.95^{a}	43.83^{a}	45.89^{b}	44.94^{a}	46.35^{a}	44.69^{a}	50.29^{a}	50.77^{a}	42.76^{b}	41.43^{a}	45.79^{a}	45.28^{a}	38.43^{a}	39.54^{b}	37.49^{a}	38.04^{a}
∑ PUFA	16.31^{a}	17.45^{b}	24.15^{a}	25.57^{b}	12.03^{a}	12.66^{b}	4.42^{a}	4.66^{a}	32.68^{a}	35.79^{b}	22.13a	22.71^{a}	18.76^{a}	19.46^{b}	14.61^{a}	14.73^{a}	5.24^{a}	9.47^{b}	5.50^{a}	9.08^{b}
∑ n-6 PUFA	13.68^{a}	14.73^{b}	19.53^{a}	20.65^{b}	11.34^{a}	11.83^{b}	4.06^{a}	4.26^{a}	29.09^{a}	31.67^{b}	19.25^{a}	19.74^{a}	18.43^{a}	19.07^{b}	12.86^{a}	12.94^{a}	4.91^{a}	8.96^{b}	5.09^{a}	8.71^{b}
∑ n-3 PUFA	2.63^{a}	2.72^{a}	4.62^{a}	4.92^{b}	0.69^{a}	0.83^{b}	0.36^{a}	0.40^{b}	3.59^{a}	4.13^{b}	2.88^{a}	2.97^{a}	0.33^{a}	0.39^{b}	1.75^{a}	1.79^{a}	0.33^{a}	0.51^{b}	0.41^{a}	0.37^{a}
n-6/n-3	5.20	5.41	4.23	4.20	16.43	14.29	11.28	10.76	8.10	7.67	6.68	6.65	55.85	48.89	7.35	7.23	14.88	17.57	12.41	23.54

Values represented by the same letters in row for the same sample are not significantly different at $p < 0.05$.
Wartości oznaczone tymi samymi literami w wierszu dla tej samej próby nie różnią się istotnie dla $p < 0,05$.

nated in 80-90% by the sum of palmitic and stearic acids. The main acid among PUFA was linoleic acid, which accounted for 50-60% of total PUFA. Regardless of the freeze-dried food sample under analysis, four acids: C16:0, C18:0, C18:1 and C18:2 formed on average 90% of FA as well. Depending on the sample, the ratio of n-6 to n-3 PUFA ranged from 5.2 to as high as 55. The only acid of the n-3 family that was found in freeze-dried food was linolenic acid, whose percentage ranged between 0.3 and 4.5% (Table 3). Preparing meals (adding hot water) caused a decrease in fat content to 3-9 g per 100 g of product. With the exception of certain products, for which a substantial increase in PUFA was observed, preparing meals did not significantly alter the composition of fatty acids.

The results of the consumer desirability analysis and the analysis of intensity of rancid odour are shown in Table 4. Generally, with the exception of two samples stored for the longest time (9, 10), the overall desirability of dishes ranged from 4.8 to 6.8.

Table 4. Consumer assessment results of the desirability of meals and intensity of rancid odour of meals
Tabela 4. Wyniki konsumenckiej oceny pożądalności dań oraz intensywność zapachu jełkiego w daniach

Product number Numer produktu	Texture Tekstura	Taste Smak	Smell Zapach	Colour Barwa	General desirability Ogólna pożądalność	Intensity of rancid odour Intensywność zapachu jełkiego
1	6.2^{a}	4.9^{a}	7.2^{ab}	6.3^{bc}	6.4^{b}	1.0^{a}
2	3.8^{be}	6.8^{bc}	6.5^{a}	7.5^{ac}	6.0^{b}	1.2^{a}
3	4.3^{bce}	7.6^{c}	6.8^{ab}	8.3^{a}	4.8^{a}	1.0^{a}
4	4.5^{bc}	5.6^{ab}	7.3^{ab}	7.9^{a}	5.5^{ab}	1.3^{a}
5	6.9^{a}	7.8^{c}	8.6^{c}	8.2^{a}	5.9^{ab}	1.0^{a}
6	5.4^{abc}	6.4^{abc}	7.2^{ab}	7.5^{ac}	6.8^{b}	1.3^{a}
7	6.5^{a}	5.6^{ab}	8.5^{bc}	6.3^{bc}	5.6^{ab}	1.1^{a}
8	5.8^{ac}	4.6^{a}	6.8^{ab}	5.9^{bcd}	6.2^{b}	1.0^{a}
9	2.8^{d}	2.1^{d}	2.5^{d}	5.6^{bd}	1.9^{c}	4.3^{b}
10	2.2^{d}	2.3^{d}	1.8^{d}	4.3^{d}	0.9^{c}	4.6^{b}

Values represented by the same letters in column are not significantly different at $p < 0.05$.
Wartości oznaczone tymi samymi literami w kolumnie nie różnią się istotnie dla $p < 0,05$.

The lowest score among all evaluated characteristics was given to texture – 4.84 points on average, and the highest to colour – 6.78 points. Average values for taste and smell were, respectively 5.37 (±2.08) and 6.32 (±2.40). As in the case overall desirability, the samples stored for the longest time received the lowest scores for all the evaluated characteristics. Smell and colour of the eight remaining products were characterized

by the lowest coefficient of variation, which did not exceed 18%. Rancid odour was detected only in samples 9 and 10. A statistical analysis showed a weak but significant correlation between the individual characteristics and certain chemical lipid values. A high correlation of 0.84-0.92 was found between overall desirability and such characteristics as texture and smell (Table 5).

Table 5. Correlation coefficients between the individual measures
Tabela 5. Współczynniki korelacji między poszczególnymi zmiennymi

	PV (peroxide value) LN (liczba nadtlenkowa)	AsV (anisidine value) LA (liczba anizydynowa)	CD (conjugated dienes) SD (skoniugowane dieny)	AV (acid value) LK (liczba kwasowa)	Texture Tekstura	Taste Smak	Smell Zapach	Colour Barwa	General desirability Ogólna pożądalność
AsV (anisidine value) LA (liczba anizydynowa)	0.34								
CD (conjugated dienes) SD (skoniugowane dieny)	–0.75*	–0.31							
AV (acid value) LK (liczba kwasowa)	0.90*	0.34	–0.77*						
Texture Tekstura	–0.67*	–0.10	0.69*	–0.68*					
Taste Smak	–0.74*	–0.07	0.66*	–0.77*	0.66*				
Smell Zapach	–0.86*	–0.28	0.75*	–0.86*	0.90*	0.86*			
Colour Barwa	–0.62	–0.06	0.53	–0.55	0.56	0.91*	0.76*		
General desirability Ogólna pożądalność	–0.86*	–0.17	0.73*	–0.85*	0.84*	0.79*	0.92*	0.72*	
Rancid odour Zapach jełki	0.75*	0.47	–0.67*	0.72*	0.51	0.76*	0.73*	0.65*	0.64*

*Correlation coefficient significant at $p < 0.05$.
*Współczynnik korelacji istotny dla $p < 0,05$.

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Discussion

The highest peroxide content in freeze-dried food samples 9 and 10 was probably the result from a long time of storage and their high fat content. As the samples were analysed in the last month of their shelf life, it is likely that they had been stored for about two years. Samples 1-8, which were analysed 18-24 months before their expiry date, showed substantially lower peroxide content. An increased level of lipid oxidation was observed during storage of freeze-dried: beef (SUN et AL. 2002), pork (HĘŚ et AL. 2011), chicken (WILKINSON et AL. 2001) and fish (RAHMAN et AL. 2009). Due to high porosity and extended contact surface with oxygen, freeze-dried food is prone to oxidation (ESTÉVEZ and CAVA 2006). This susceptibility is linked to both the product's composition and the conditions of storage. Generally, product's with higher fat content are more prone to oxidation (WASZKOWIAK and DOLATA 2007). A relatively high level of lipid oxidation was confirmed by the amount of dienes. During the oxidation of PUFAs containing methylene substituted dienes and polyenes, there is a shift in the position of the double bond due to isomerisation and conjugate bond formation (conjugated dienes). This is accompanied by increased UV absorption at 234 nm. It is an indicator of autooxidation and is reported to increase with uptake of oxygen and formation of peroxides, during the early stages of oxidation. Low amounts of dienes in the samples that were stored the longest was probably the result of decomposition of these unstable compounds. Substantial discrepancies between the analysed samples in the observed level of oxidation could be the result of both varying conditions and time of storage of the samples and of the amount of water and its activity. A research by RAHMAN et AL. (2009) showed that storing freeze-dried fish with water content of 5% and 20% at a temperature of –40°C did not substantially alter the peroxide value. Significant changes were found when storing the same samples at –20, 5, 25 and 40°C. A research by SUN et AL. (2002) showed that the freeze-dried beef samples stored at 49°C which revealed lower water activity also had higher thiobarbituric acid (TBA) content. Samples stored at 25°C showed no such correlation. Although samples 9 and 10 were stored for the longest period of time, the amount of secondary oxidation products was similar to that observed in samples stored for shorter periods of time. It is unlikely that secondary oxidation products were not formed in these samples during such a long storage. It is more likely that secondary oxidation products interacted with other components of food. All lipid oxidation products can react with primary and secondary protein and amino acid products of meat, also the ones produced by technological processes (POKORNY et AL. 2010). The relatively high content of free fatty acids (FFA) in all analysed samples is probably due to still active lipases. Although water activity (a_w) in freeze-dried food is relatively low, lipases may still be active at a_w of 0.1 (BANTLE et AL. 2009). The accumulated FFA could also, to a certain extent, contribute to the degree of lipid oxidation, as they oxidise faster than molecules embedded in acylglycerol molecules. The results of an analysis of the composition of fatty acids of freeze-dried food samples were typical for their main ingredients and raw materials (mainly oils and fats). The proper ratio of n-6/n-3 fatty acids of about 3-5:1, was found in only two freeze-dried food samples (1, 2). This was due to the presence of rapeseed oil, which may contain relatively large amounts of α-linolenic acid (ALA). This research also showed that, for some samples, the process of preparing food (adding hot water), caused a significant increase of the amount of

peroxides and FFA. This process was particularly evident in the samples with the highest level of oxidation and hydrolysis. The observed increase in the amount of peroxides could be the result of either a rapid induction process caused by a sudden increase in temperature to about 90-100°C or a process of hydrolysis, which facilitated oxidation of the FFA. With the increase in temperature the rate of oxidation also rises whereas the period of induction is shortened. Lipoxygenase present in vegetables and spices, which catalyses oxidation of free or esterified fatty acids could also contribute to increasing the level of oxidation in ready-to-eat dishes (BARANIAK and SZYMANOWSKA 2006). Scientific data indicate that short-duration heat treatment, including conventional boiling of meat, generally does not cause a significant increase of neither PV nor TBA (RODRIGUEZ-ESTRADA et AL. 1997). This is probably due to the predominance of antioxidants over prooxidants in the matrix that is meat tissue (KOŁAKOWSKA and BARTOSZ 2010). Proteins and peptides, owing to their capability to scavenge free radicals and to chelate metals, are claimed to be important antioxidants in meat (ELIAS et AL. 2007). Research conducted by SERPEN et AL. (2012) for boiled meat showed that during the first 15 min of heat treatment antioxidant activity, measured with the ABTS and FRAP methods, was significantly higher than in raw meat. The observed different effects of adding hot water to freeze-dried food on peroxide content could be attributed to different levels of antioxidant activity of the entire system, which consists mainly of proteins, enzymes and products of the Maillard reaction. Antioxidants present in vegetables and spices, included in each product, probably had substantial effect on antioxidant activity as well (GAWLIK-DZIKI 2012). Presence of tocopherol in poultry feed significantly contributed to the reduction of the amount of cholesterol oxidation products in freeze-dried chicken breast during 4-month storage (LI et AL. 1996). Freeze-drying alone generally does not cause any losses in the amount of vitamins or in the extent of antioxidant activity (SHOFIAN et AL. 2011). The research conducted by BUI and COAD (2011) showed that, when storing freeze-dried chicken products for 24 months, the most stable of all fortified vitamins was by vitamin C (16% loss) followed by vitamin A (50% loss) and vitamin E (80% loss). When storing freeze-dried onion for 6 months no decrease in the amount of flavonols and anthocyanins was observed (PÉREZ-GREGORIO et AL. 2011).

As previously mentioned the process of preparing the meals also contributed to the increase in the FFA content, observed mainly in samples stored the longest. This increase was probably a result of thermal hydrolysis of lipids and/or lipase activity. The study by HERNANDEZ et AL. (1999) demonstrated that when boiling pork an increase in FFA was caused by thermal hydrolysis and the activity of endogenous lipases. Neutral esterase (pH 7.5) from adipose tissue was very active in the temperature range 45-75°C (MOTILVA et AL. 1992). Also the process of preparing meals generally did not affect the composition of fatty acids. An increase in the percentage of PUFA in some products was likely the result of these acids being released from the complexes formed by interactions of lipids with proteins and/or starch (POKORNY et AL. 2010). The research by BIENKIEWICZ and KOŁAKOWSKA (2003) showed that PUFA play a preferential role in the interactions. It was mainly texture and taste that contributed to the relatively low overall desirability of freeze-dried food. Texture is one of the most important characteristics determining the quality of food and influencing consumer acceptance of food products. During this research it was demonstrated that texture was the lowest ranked characteristic, with an average score of 4.9 points. Majority of the dishes resembled

mush rather than a typical meal for dinner. It does not seem likely that the texture of dishes was influenced by storage and the process of freeze drying. Presumably such texture was a result of a high degree of fragmentation of individual components of a product. Very low scores for taste and smell of samples 9 and 10 can probably be attributed to the presence of aldehydes and ketones. While the AsV of lipids was at a similar level in all analysed products, these samples, however, had an intense rancid odour. Rancidity developed from the autoxidation of lipids leads to unacceptability of the product by the consumers depending on the oxidation level occurred. Low molecular weight compounds including mainly aldehydes and ketones are believed to be responsible for the characteristic odour and taste of rancid fat (LADIKOS and LOUGOVOIS 1990). The formation of these compounds in sample 9 and 10 is presumably the result of a long storage period of these freeze-dried food samples.

In this study no correlation was found between smell or taste and AsV and no correlation was found between these characteristics and PV. It can be attributed to the fact that the system under analysis was a fairly complex system, in which there is usually no such correlation, since, as it is generally believed, peroxides are chemical compounds that do not influence sensory characteristics of fat (FRANKEL 1998). On the basis of the carried out research and the unpublished data it can be concluded that the obtained results of both the sensory analysis and the analysis of the oxidation level depended on the quality of the fat derived mostly from the meat and oil. Even though from the perspective of food safety and to obtain better sensory qualities it is preferable to use freeze-dried food based only on meat, this food, due to its relatively low fat content, does not provide enough calories. It is, therefore, necessary to "fortify" meat-based freeze-dried food with oils. For this reason freeze-dried food safety should not have 2-3 year shelf life.

Conclusions

Long-term storage of freeze-dried food has a negative effect on the level of lipid oxidation and hydrolysis, which is reflected by low overall desirability of a meal. The "mush" texture of meals contributed to the relatively low overall desirability. Adding hot water to freeze-dried food can contribute to further oxidation and hydrolysis of lipids, especially in products near their expiry date. The high ratio of n-6/n-3 PUFA indicates low biological value of fat.

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ZMIANY LIPIDÓW I ICH WPŁYW NA JAKOŚĆ LIOFILIZOWANYCH DAŃ MIĘSNYCH

Streszczenie. Utlenianie lipidów jest główną reakcją determinującą stabilność żywności liofilizowanej. Celem pracy była ocena jakości lipidów w 10 liofilizatach oraz daniach z nich przygotowanych. W lipidach wyekstrahowanych metodą Bligha i Dyera oznaczono poziom utlenienia (LN, LA, CD), hydrolizy (LK) oraz skład kwasów tłuszczowych (KT). Analiza poziomu utlenienia i hydrolizy w liofilizatach wykazała szeroki zakres poszczególnych wskaźników, który wyniósł dla LN: 8-52 meq O w 1 kg, dla LA: 6-9 i dla LK: 3,5-9. Zalanie liofilizatów gorącą wodą spowodowało w niektórych próbach dalsze rozwinięcie utlenienia i hydrolizy lipidów. Przygotowanie dań generalnie nie miało istotnego wpływu na skład KT. Ogólna pożądalność dań gotowych była stosunkowo mała (średnio 4,9 pkt.). Najgorzej ocenionym wyróżnikiem była konsystencja (≈ 4,9) a najlepiej barwa (≈ 6,8). Dania w końcowym okresie przydatności do spożycia mogą być źródłem znacznych ilości produktów utlenienia lipidów oraz charakteryzują się bardzo słabą pożądalnością ogólną.

Słowa kluczowe: żywność liofilizowana, utlenienie lipidów, hydroliza, kwasy tłuszczowe

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