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The oxidability of krill lipids

ABSTRACT: The photo-oxidability of lipids taken from 32 samples of krill from different dates of catch has been examined for photooxidation. Relations were indicated between the rate of accumulation of peroxides in the process of lipids, exposure and content of lipids in krill, its iodine value and amount number of carotenoids.

Key words: Antarctic, krill, lipids.

Introduction

Krill lipids can be considered as a potential source of n-3-polyunsaturated fatty acids (PUFA). The quantity of these acids reaches 40% of the total amount of fatty acids in krill phospholipids (Lee, Fujimoto & Kaneda 1981), and phospholipids are the dominant fraction of krill lipids.

The positive influence of PUFA of fish lipids on health is not successful when the lipids are oxidated (Ziemlański et al. 1990). Despite the large quantity of PUFA the lipids of krill are thought to be resistant to oxidation (Yamagimoto et al. 1979). The addition of lipids extracted from the frozen stored krill inhabited the oxidation of β-carotene (Kosackina & Lobanowa 1981), and fatty acid methyl esters of safflower oil (Lee, Fujimoto & Kaneda 1981). These anti-oxidative properties of krill lipids are attributed to the presence of tocopherol (Lee, Fujimoto & Kaneda 1981, Seher & Löschner 1985) and to the abilities of the products of phospholipids hydrolysis to degradate of peroxides and to create coloured antioxidants (Lee, Fujimoto & Kaneda 1984). Lipids of freshly caught krill are susceptible to photooxidation similar to lipids of Antarctic fish (Kołakowska 1987). Storage of krill from few up to several hours since the moment of catch increases the susceptibility of lipids to photooxidation by many times. Probably it is due to the activity of products of phospholipids hydrolysis (Kołakowska 1989).

During the deep freeze storage krill, differences caused by the degree of freshness of the stored and frozen material increase. The lipids of krill frozen directly after catch, are the quickest to oxidate (Kołakowska 1989).

The composition of krill lipids shows seasonal fluctuations (Kołakowska, unpubl. data) and therefore it depends on many biological factors (Clarke 1980, Shibata 1983, Saether, Ellingsen & Mohr 1986, Kołakowska, in press). Therefore, it can be expected that the susceptibility of lipids to oxidation will also fluctuate.

The aim of this work to examine the susceptibility of lipids of freshly caught krill to oxidation. The influence of different dates of catch and of other biological factors was also taken under consideration.

Materials and methods

Material: krill (*Euphausia superba* Dana) was caught in 1984 and 1986 in the Admiralty Bay (South Shetlands). Immediately after the catch the whole krill was homogenized and lipids were taken for extraction. Extraction of lipids was done using Bligh-Dyer (1959) method. The contents of lipids were measured by vaporizing a defined quantity of extract. The composition of lipids was determined using thin layer chromatography method, in the way described in the previous work (Kołakowska 1986). Lipids were separated on the silica gel (G-60-254 Merck foil) in a mixture: n-hexane-ether ethylic-acetic acid. After visualized under UV lamp, fraction of phospholipids and waxes was cut off and developed in the 2-nd direction; phospholipids in chloroform-methanol--water (70:30:4), and waxes in n-hexane.

Chromatographs were visualized in iodine (15 min) and left for 24 hours. Particular fractions were taken into distilling flasks and heated with the sulphuric acid in the temperature of 125°C for 1 hour. Water was added to the samples in the proportion of 3:2, they were cooled in snow. The absorbancy was measured at 345 nm with the Pay Unicam spectrophotometer. Standard curves of the respective glicerols were used for: mono, 1,2- and 1,3-di and triacylglicerols. For phospholipids the standard curve of the mixture of phosphatidylcholine and phosphatidylethanolamine with the rests of palmityl and stearyl acids were used, and for free fatty acids — of linolenic acid.

Iodine value was estimated using Hanus method (Polska Norma 78/C--04281). Oxidation of lipids was carried out with 2 methods:

1) samples of krill from 1984 — extract of lipids (chloroform layer of Bligh-Dyer extract) was placed on strips of blotting paper (filter paper test) after being concentrated 10 times on vacuum evaporator in the temperature up to 30°C;

2) samples of krill from 1986 — extract as above, a quantity of 2 cm^3 was placed in Petri dish and it was left for 1 hour under ventilating hood to

vaporize chloroform; the quantity of sample (15—20 mg) and thickness of layer exposed was similar in both methods and amounted to about 0.005 mm.

Oxidation was carried out in temperature of 60°C for 110 hours, in darkness (termooxidation), exposed to the UV Camac lamp = 344 nm, at the distance of 14 cm, for several hours, most frequently for 3 hours, at the maximum for 8 hours (photooxidation).

After 15 minutes of exposition and next, every 30 minutes peroxide value (LN) was estimated using thiocyanate technique (Branżowa Norma 74/8020--07) by taking 3 strips of filter paper at a time or 3 Petri dishes to paralel determinations. Strips of filter paper were eluated with chloroform. Lipids in Petri dishes were dissolved in chloroform-metanol mixture in the proportion 2:1. The amount of carotenoids was determined by measuring absorbancy of lipids extract, as was done before (Kołakowska 1986). Statistical analysis of results was carried out separately, for samples examined with the use of filter paper test technique and separately for samples oxidated in Petri dishes.

The value of coefficient "b" of equation describing changes of peroxide value in the process of exposition of lipids was taken as a measure of photooxidation.

Results

Krill lipids were resistant to oxidation in temperature of 60°C but they were easily photooxidated (Fig. 1). The exposition time of lipids necessary to reach a defined peroxide value for example 40 mg 0/100 mg of lipids during exposition to light is measured in minutes, in heating it is measured in hours. Therefore, in further examination of susceptibility of krill to oxidation only exposition was applied. The lipids were examined directly after being extracted from the freshly cought krill, because longer storage of chloroform extracts of lipids or krill samples in frozen state had a decisive influence on length of induction period and on the photooxidation process (Fig. 1).

For the samples of krill caught in 1984 and 1986 somewhat different conditions of lipids exposition were used: on the filter paper (krill from 1984), and in Petri dishes (krill from 1986); different techniques had an influence on the results received. In Petri dishes (krill from 1986) the change of peroxide value of exposed lipids had exponential character, on the filter paper — linear character, and before the beginning of exposition lipids were more oxidated (Tab. 1). During the first 60 minutes of exposition about 90% of carotenoids contained in lipids underwent disintegration but in Petri absorbancy (A 470 nm) simultaneously increased as the result of accumulation of coloured products of oxidation (Tab. 3). Oxidation in Petri dishes was accompanied also by linear increase of absorbancy of lipids with the wave length 320 nm (Fig. 2). Due to the above mentioned differences the results concerning oxidation of

Table 1

Photooxidation of krill lipids (material of 1984, filter paper test); LN — peroxide value, LJ — iodine value; A and B — different catches from the same day; R — regression coefficient

Date	Material	Regression equation	Equation parameters			R	LN after 120 min	LN for 120 min	Contents of		LJ
			a	b	c				lipids % w.w.	caro-tenoids µg/g of lipids	
16.01.84.	whole krill	$y=a+bx+cx^2$	−44.64	3.89	−1.94	0.97	412	988	2.89	8.73	106
		$y=a+bx$	−44.78	3.89	—	0.97					
18.02.84.	whole krill	$y=a+bx+cx^2$	−57.12	5.99	−4.58	0.95	838	1264	4.91	609	109
		$y=a+bx$	200.82	2.98	—	0.92					
18.02.84.	females	$y=a+bx+cx^2$	−286.00	14.54	−1.64	0.98	1388	1844	6.10	720	115
		$y=a\cdot x^b$	85.21	0.52	—	0.81					
6.05.84.	whole krill	$y=a\cdot e^{bx}$	182.00	0.018	—	0.97	1678	4932	4.91	834	137
		$y=a\cdot x^b$	389.00	0.22	—	0.82					
12.05.84.	whole krill	$y=a+bx+cx^2$	−95.00	29.0	0.062	0.99	1841	4962	4.25	1048	131
		$y=a+bx$	169.73	12.0	—	0.96					
6.08.84.	whole krill	$y=a+bx+cx^2$	−45.76	20.07	−5.63	0.89	1515	3602	3.57	955	108
		$y=a+b\ln(x)$	766.00	111.0	—	0.82					
6.09.84.	large krill	$y=a+bx+cx^2$	51.45	15.73	−0.0288	0.97	1374	4121	5.46	528	101
		$y=a+bx$	360.94	7.24	—	0.93					
6.09.84.	small krill	$y=a+bx+cx^2$	11.01	16.51	−0.25	0.99	1512	3971	3.75	1012	119
		$y=a+bx$	284.50	9.0	—	0.96					

14.09.84.	(A)	$y = a + bx + cx^2$	1.24	11.89	−0.0053	0.99	1274	5310	4.83	738	110
		$y = a + bx$	37.55	10.6	—	0.99					
14.09.84.	(B)	$y = a + bx + cx^2$	92.46	13.3	−0.917	0.98	1483	5601	4.69	691	96
		$y = a + bx$	279.00	8.7	—	0.97					
5.10.84.	whole krill	$y = a + bx + cx^2$	−158.48	20.03	−3.30	0.99	2543	5789	3.10	1143	119
		$y = a + bx$	205.62	10.02	—	0.96					
12.10.84.	whole krill	$x = a + bx + cx^2$	17.41	15.60	−1.99	0.99	1850	4029	2.76	1173	114
		$y = a + bx$	154.00	10.87	—	0.99					
16.10.84.	whole krill	$y = a + bx + cx^2$	−78.93	12.76	−1.73	0.97	1726	4029	2.59	1395	195
		$y = a + bx$	106.53	7.67	—	0.96					
24.10.84.	whole krill	$y = a + bx + cx^2$	−43.76	21.44	−4.23	0.99	1854	2498	2.62	1063	201
		$y = a + bx$	417.20	8.76	—	0.91					
29.10.84.	whole krill	$y = a + bx + cx^2$	28.30	38.30	−0.124	0.99	2105	4709	2.35	1321	189
		$y = a \cdot x^b$	−632.86	0.26	—	0.91					
10.11.84.	whole krill	$y = a + bx + cx^2$	219.54	20.93	−4.40	0.97	2842	6782	1.15	2947	108
		$y = a \cdot x^b$	533.70	0.25	—	0.92					
16.11.84.	whole krill	$y = a + bx + cx^2$	95.77	19.80	−0.031	0.99	2075	5542	2.42	1622	140
		$y = a + bx$	312.53	12.30	—	0.98					

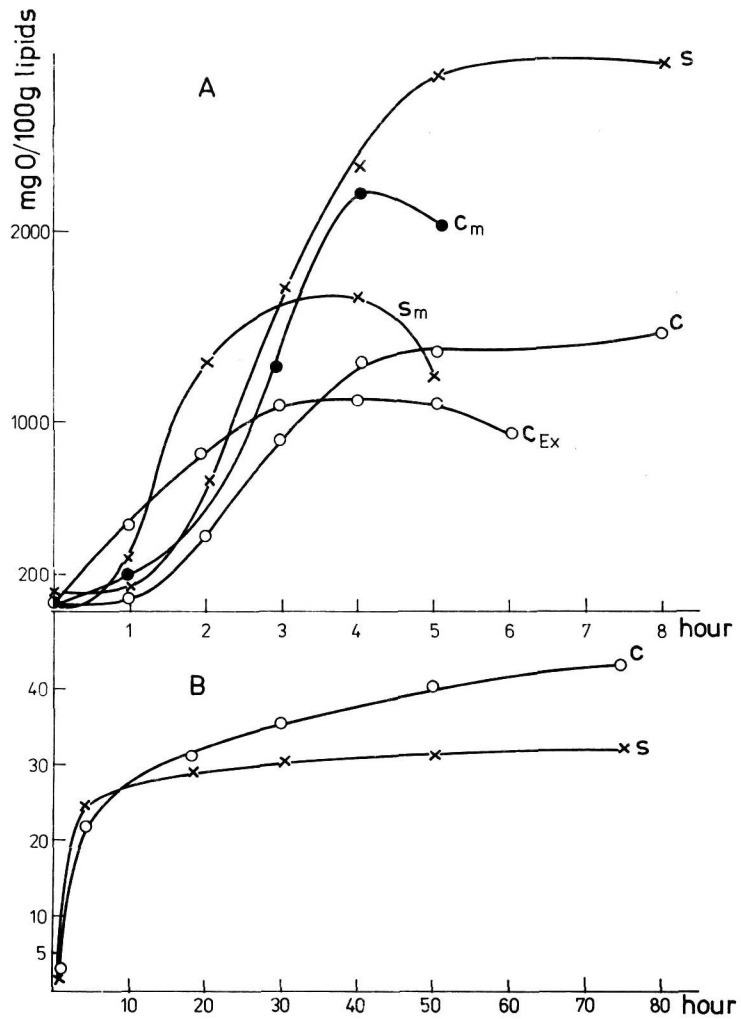

Fig. 1. Changes of the peroxide value during photooxidation (A) and termooxidation (B) of krill lipids;
C — whole sample, S — unsorted females, m — krill stored in the temp. −22°C for 4 months, Ex — the extract of lipids stored in the temp. 5°C for 4 months

krill lipids in catches from 1984 and from 1986 are discussed separately in this paper.

Krill caught in 1984 was very variable as regards to the amount of lipids (from 1.15 to 6.0% wet weight), iodine value (from below 100 to 200) and to the number of carotenoids extracted together with lipids (from about 500 to almost 3000 μg/g of lipids).

Oxidability of these lipids was also variable (Tab. 1). It was higher when content of krill lipids was lower (r = 0.59; Tab. 6). Iodine value did not have

any decisive influence upon the rate of photooxidation. The presence of carotenoids increased the amount of peroxides during the exposure of lipids on the filter paper (Tab. 6). As results from the data included in table 4 the increase in the amount of peroxides cannot be connected explicity with the rate of carotenoids disintegration.

Lipids of krill caught at the end of October and in November showed maximum rate of photooxidation. Krill at that time had its alimentary tract filled with phytoplankton, it was so called "green" krill. Lipids of females were more susceptible to oxidation than those from the whole bulk of krill from the same catch (Tab. 1).

Krill caught in 1986 came mainly from October and November and it was not differentiated to such extent as regards to the amount of lipids, as well as its iodine value and carotenoids (Tab. 2). The oxidability of lipids measured by the amount of peroxides was positively correlated ($r = 0.76$; Tab. 6) with the amount of lipids in krill, but fluctuated within narrow range from 1.48 to 3.44% wet weight (Tab. 2). The presence of carotenoids in lipids increased initial amount of peroxides (coefficient "a" of regression equation), but it inhibited the rate of photooxidation (coefficient "b" of the same equation) and amount of peroxides after long period of oxidation. These relations, however, were very weak (Tab. 6); correlation coefficient "r" does not exceed 0.55.

Induction period, accepted as time needed to reach the peroxide value of 100 mg 0/100 g of lipids, fluctuated depending on the date of catch from 7 to 63 min, most frequently amounting to 30 min (Tab. 2). It was not directly replated to the content of lipids in krill, their iodine value and amount of carotenoids. No statistically substantial correlation was observed between the length of induction period and the rate of oxidation, although it precisely depended on the initial amount of peroxides and had an influence on their number after a longer time of oxidation (Tab. 7).

The lipids of "green" krill caught in November were characterized by the shorest induction time. It also manifested by the comparison of photooxidation rate in "green" krill lipids of krill sample caught on 19.10.1990 with the lipids of unsorted krill (Tab. 2, Fig. 2). "Green" krill had lipids less resistant to oxidation, induction period was shorter, higher peroxide value and its more rapid increase as well as increase of absorbancy at A_{320} and A_{470} nm (Fig. 2, Tab. 3). "Green" krill contained slightly more lipids of similar content, lower iodine value and fewer carotenoids (Tabs. 2 and 5) than unsorted krill.

Spectrum of carotenoids was similar and, in both cases, it was very remote from spectrum of plankton lipids (Figs. 3 and 4). However, as regards the lenght of waves responsible for the presence of chlorophyl (Fig. 4) essential differences occurred concerning the absorbancy of lipids in "green' and unsorted krill. The estimated amount of chlorophyl calculated on such basis, was three times higher in "green" krill (Tab. 5).

Table 2

Photooxidation of krill lipids (material of 1986, Petri dishes test); equation: $y = a \cdot e^{bx}$; x — time of UV exposition in min, y — theoretic peroxide value, LN — peroxide value obtained in the experiment, R — regression coefficient, LJ — iodine value

Date	Material	Equation parameters		R	LN after 120 min	ΣLN for 120 min	Induction time (min)	Contents of		LJ
		a	b					lipids % w.w.	caro-tenoids µg/g of lipids	
30.09.	whole krill	40.24	0.027	0.97	1988	2984	32	3.44	876	118
3.10.	— „ —	54.14	0.021	0.95	784	1909	35	2.49	1296	110
3.10.	abdomen	43.96	0.019	0.93	680	1432	45	2.40	656	86
6.10.	whole krill	45.99	0.022	0.98	789	1633	42	2.34	1415	109
10.10.	— „ —	61.78	0.021	0.91	1153	2222	45	2.36	1423	125
19.10.	— „ —	45.01	0.019	0.93	914	1451	63	2.33	1226	127
19.10.	"green" krill	49.08	0.022	0.93	1280	2188	32	2.72	924	99.9
23.10.	whole krill	80.88	0.018	0.96	1316	2276	17	1.89	1385	114
25.10.	— „ —	77.86	0.014	0.99	490	1123	22	1.48	2263	108
28.10.	— „ —	77.66	0.015	0.98	630	1291	25	1.50	2120	110
20.11.	— „ —	104.98	0.020	0.95	1957	3444	8	2.54	1380	145
22.11.	— „ —	126.46	0.018	0.91	1420	3587	7	2.63	1341	130
5.12.	— „ —	47.52	0.023	0.98	1229	2064	41	3.40	1974	155
5.12.	abdomen	39.53	0.022	0.88	687	1512	35	2.75	576	130
5.12.	cephalothorax	59.84	0.017	0.86	580	1333	28	3.90	1215	135
	X±	63.71	±0.020		1059.8	2030	31.8	2.54	1398	120
		±25.46	±0.003		±473.7	±776.7	±14.8	±0.67	±489	±17.7

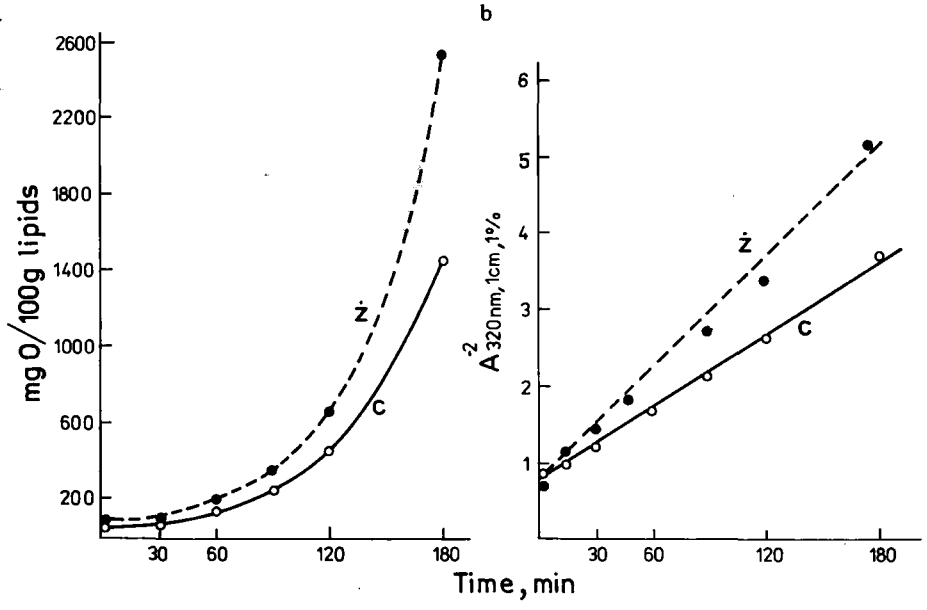

Fig. 2. Photooxidation of krill lipids;
a — peroxide value, b — absorbance at 320 nm, c — unsorted krill, z — krill with filled digestive tract (green)

Lipids isolated from the abdomen were more susceptible to oxidation than lipids from the whole krill or from cephalothorax. They contained less than half of the number of carotenoids which could be found in lipids extracted from the whole krill (Tabs. 2 and 3).

Discussion

Lipids extracted from fresh krill during long storage (many hours) in temperature of 60°C showed a light increase in peroxide value. It confirms earlier information on lipids of frozen krill (Yamagimoto et al. 1979, Lee, Fujimoto & Kaneda 1981, 1984, Seher & Löschner 1985) showing that krill lipids are resistant to thermooxidation.

Lipids extracted from the whole krill and also from abdomen or cephalothorax easily undergo photooxidation. They are susceptible to this type of oxidation because krill lipids have a high content of polyunsaturated fatty acids. Moreover, the presence of double bonds makes photooxidation easier than autooxidation (Gustone 1984). The existance of sensitizers has the same effect. Probably, it is chlorophyl from phytoplankton which plays this role in krill lipids. Exceptionally high susceptibility to oxidation of lipids extracted from the whole "green" krill testifies this fact.

Table 3

Changes of the absorbancy (A_{470nm}, 1 cm, 1%) of krill lipids during photooxidation; samples of 1986

Date	Material	Time of exposition (min)							
		0	15	30	45	60	90	120	180
23.10.86	whole krill	2.8	—	0.15	0.16	0.18	0.33	0.41	0.44
25.10.86	— „ —	4.66	0.23	0.237	0.29	0.38	0.45	0.45	1.06
28.10.86	— „ —	4.06	0.21	0.19	0.29	0.36	0.38	0.42	0.65
20.11.86	— „ —	3.0	0.20	0.19	0.196	0.23	0.39	0.77	0.82
22.11.86	— „ —	2.5	0.2	0.2	0.2	0.22	—	0.48	0.53
5.12.86	— „ —	1.34	0.15	0.12	0.09	0.019		0.032	—
	abdomen	0.9	—	0.07	0.07	0.05	0.053	0.02	0.02
	cephalothorax	1.89	0.24	0.26	0.27	0.23	0.06	0.22	0.1
19.10.86	whole krill	2.45	0.84	0.67	1.27	0.95	1.83	3.12	2.9
	"green" krill	1.87	0.91	0.93	1.49	1.56	1.91	3.64	3.85

Table 4

Changes of the absorbancy (A_{470nm}, 1 cm, 1%) of krill lipids during photooxidation, samples of 1984; A, B — different catches from the same day

Date	Material	Time of exposition (min)							
		0	15	30	60	120	180	240	300
06.09.84	large krill	1.53	0.23	0.076	0.015	0.010	—	—	—
	small krill	1.69	0.49	0.26	0.03	0.02	—	—	—
14.09.84	(A)	1.51	0.31	0.15	0.04	0.16	0.007	0.007	0.006
	(B)	1.40	0.39	0.11	0.027	0.015	0.007	0.008	0.0095
		Degradation of carotenoids (in %)							
6.09.84	large krill	0	—	67	93.3	—	—	—	—
	small krill	0	—	47	93.3	—	—	—	—
14.09.84	(A)	0	—	51.7	87.3	94.7	98.1	98.1	—
	(B)	0	—	72.1	92.86	96.2	98.0	97.8	97.5

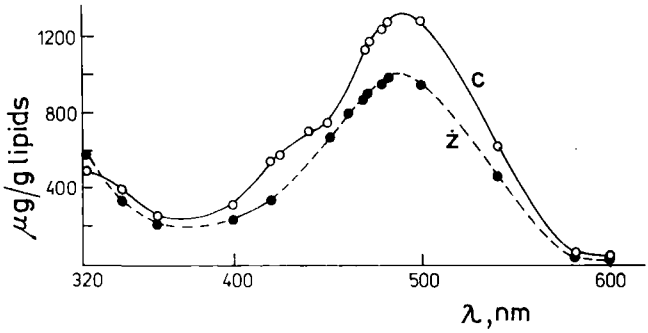

Fig. 3. Spectrum of chloroform solution of krill lipids;
C — unsorted krill, Z — krill with filled digestive tract (green)

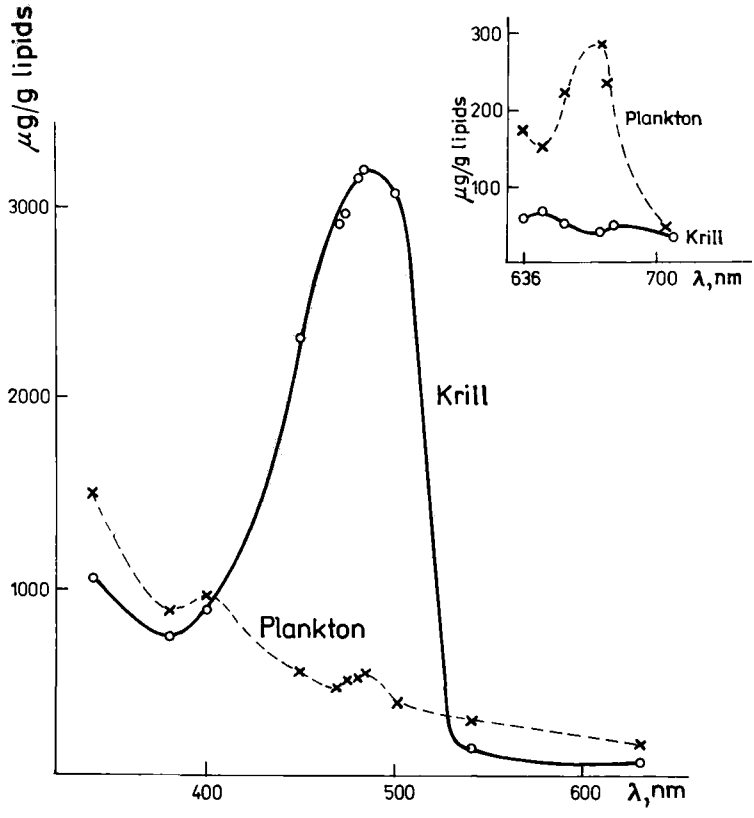

Fig. 4. Spectrum of chloroform solution of krill lipids and phytoplankton lipids

Table 5

Lipid composition of krill caught on 19.10.1986

Material	Classes of lipids (% of total lipids)						chlorophyll μg/g
	phospho-lipids	diacyl-glicerols + cholesterol	1,3-diacyl-glicerols	free fatty acids	triacyl-glicerols	waxes	
unsorted krill	71.5	3.6	2.7	2.9	7.1	4.8	0.46
"green" krill	71.8	3.1	1.9	2.9	10.7	4.0	1.59

Table 6

Statistical analysis of relations between the susceptibility to oxidation and other features of krill lipids
(zl — lipid contents in krill (% w.w.), zk — carotenoid contents in lipids (μg/g); a, b, c — equation parameters, a — significance coefficient; LN — peroxide value, LJ — iodine value)

Material	Relation		Regression equation	Equation parameters			a
	y	x		a	b	c	
Krill caught in 1984	LN	zl	$y = a+b \ln x$	2539	−739.8	—	0.001
	after	zk	$y = a+b \ln x$	−2454	589.3	—	0.001
	120 min	LJ	$y = a+bx+cx^2$	−3763	75.99	−0.25	0.05
	LN	zl	$y = a+b \ln x$	7021.6	−1272	117.7	0.02
	for	zk	$y = a+b \ln x$	−8379	1803	0.54	0.001
	120 min		$y = a+bx$	2855	1.09	—	0.001
		LJ	unsignificant				
Krill caught in 1986	LN	zl	$y = a+bx+cx^2$	−453	909	−123	0.05
	after	zk	$y = a+bx+cx^2$	377	1.40	-5.82^{-04}	0.05
	120 min	LJ	$y = a+b \ln x$	−9023	2087	0.84	0.01
	LN	zl	$y = a+bx+cx^2$	−2622	3451	−599	0.01
	for	zk	$y = a+bx+cx^2$	−72.53	3.61	-1.36^{-03}	0.01
	120 min	LJ	unsignificant				
		zl	$y = a+bx+cx^2$	-8.07^{-03}	1.98^{-02}	-3.25^{-03}	0.001
			$y = a+b \ln x$	1.31^{-02}	7.70^{-03}		
	a from equation	zk	$y = a+bx$	2.46^{-02}	-3.5^{-06}	—	0.01
	$y = a \cdot e^{bx}$, where: y = LN,	LJ	unsignificant				
	x = exposition time (min)	zl	$y = a+bx$	92.96	−11.5	—	0.1
	b	zk	$y = a+b \ln x$	−138.68	28.27	—	0.01
		LJ	$y = a+b \ln x$	−111.07	36.7	—	0.1

Table 7

The relation between induction time and other parameters of krill lipids photooxidation

		a from the equation: $y = a \cdot e^{bx}$ where: y = LN, x — exposition time	b	LN for 120 min
Regression equation		$a \cdot x^b$	$a+bx+cx^2$	$\frac{a \cdot b \cdot x}{1+bx}$
Equation parameters	a	324.7	1.56^{-02}	1475
	b	−0.51	2.29^{-04}	−0.25
	c	—	$-2.47^{-0.6}$	—
Regression coefficient	R	0.93	0.38	0.74
Significance coefficient	α	0.001	—	0.001

The process of photooxidation in krill lipids can be described using peroxide value and absorbancy (A_{320} nm). Their changes are closely correlated with lipids exposure time for at least 3 hours. In that time peroxide value reaches at least several thousands mg 0/100 g of lipids, i.e. value which exceeds by many times the ones encountered in lipids. The absorbancy increase at 320 nm confirms the argmentation of amount of coupling bonds during the process of photooxidation. On the other hand, the use of carotenoids disintegration as a method of measuring lipids oxidation, which has recently been frequently applied to model systems (Nowak, Zadernowski & Kozłowska 1990), can be questioned since in the process of krill lipids photooxidation carotenoids disintegration is accompanied by simultaneous accumulation of coloured products (Kołakowska 1988). They may arise both from the pigment disintegration and from the Maillard type reactions, and they may influence the oxidation (Pokorny et al. 1974).

Irrespectively of methodological discrepancies it has been proved that susceptibility of krill lipids to oxidation fluctuates significantly even during one spring fishing season. Stability of lipids may differ by many times depending on the date of krill fishing. The existence of correlation, although not direct, has been shown between the oxidability and the content of lipids in krill, whereas, the lack of correlation with iodine value was observed. In the case of the Baltic herring lipids, there exists a close correlation between these parameters (Kołakowska, Kwiatkowska & Czerniejewska-Surma 1989).

Krill lipids oxidation slightly differs as compared with photooxidation of Baltic herring lipids (Kołakowska, Kwiatkowska & Czerniejewska-Surma 1989, Kołakowska & Kwiatkowska 1990). In very similar conditions of oxidation (Petri dishes, the same equipment) krill lipids oxidate according to exponential equation, whereas oxidation of herring lipids can be described by

few equations of regression out of which none is exponential. Accumulation of coloured products cannot be observed in herring lipids during photooxidation process, they appear, however, during the thermooxidation process. The peroxide value of the oxidated herring lipids and krill lipids does not differ as much as one should expect from so remote species and different components of lipids.

It is worth noticing, however, that differences in susceptibility of lipids to photooxidation between different samples of the same species (particularly herring) are considerable, largely depending on the date of catch.

The presence of extremely high number of carotenoids, amounting to 0.1% has probably an influence on complication of photooxidation in krill lipids. This amount fluctuates on a large scale. From the results obtained from krill caught in 1984 and in 1986 it is obvious that small amounts of carotenoids accelerate photooxidation, above all, through the increase of the initial number of peroxides value. Within the range up to about 1500 μg/g together with the increase of their number in lipids the level of oxidation increases as well. The increase in the number of carotenoids in lipids, more or less above this level causes the inhibition of photooxidation. Frankel (1989) states that in the case of vegetable oils the value 1000 ppm is an effective antioxidation value of β-carotene. In krill carotenoids astaxantine dominates and β-carotene does not. Besides, it contains far fewer of tocopherols (Sugii & Kinumaki 1982), therefore the required amount of carotenoids as a protection of lipids against oxidation may be higher.

The study of photooxidation of "green" krill lipids indicate the role of a substances contained in phytoplankton lipids. Lipids of phytoplankton itself do not reach such a high level of oxidation as krill lipids (Kołakowska 1989) but probably through chlorophyl, which they have in greater quantities, they indicate photooxidation of krill lipids by creation of singlet oxygen (Hamilton 1983). It seems that lipophilic substances facilitating Maillard type reactions can also be found in phytoplankton.

The explanation of the seasonal variability of the lipid oxidability would need further studies on seasonal variation of the composition of lipids and especially on the amount of pro and anti- oxidants.

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Streszczenie

Lipidy kryla mogą być źródłem działających leczniczo n-3 wielonienasyconych kwasów tłuszczowych. Ponieważ utlenianie niszczy tę ich aktywność biologiczną, badano podatność lipidów kryla na fotooksydację. Stwierdzono istotne, nawet 6-krotne różnice w podatności na utlenianie, w zależności od daty połowu kryla. Fotooksydację lipidów kryla opisano równaniem wykładniczym, w którym szybkość (współczynnik „b" równania) zależy przede wszystkim od zawartości lipidów w krylu, a początkowa zawartość produktów utleniania (współczynnik „a" równania) od ilości karotenoidów. Wykazano wpływ stopnia wypełnienia przewodu pokarmowego kryla na przebieg fotooksydacji wyizolowanych z niego lipidów.