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BAZYLI CZECZUGA

Karotenoidy u ryb. 21. *Percidae* z polskich wód

Carotenoids in fish. 21. *Percidae* from Polish waters

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Abstract — Using column and thin-layer chromatography the content and percent relations of carotenoids in gills, skin, muscles, liver, intestines, and eggs of perch, pike-perch, and ruff were investigated.

Three species of the *Percidae* family, occurring in Poland, are classified to three separate genera. They are perch, pike-perch, and ruff. Their economic importance is considerable, particularly of the two former species, since perch is among the most important fish caught by fishermen, while the economic importance of perch-pike is due to its rapid growth and high quality meat. They are predatory species, and so play a marked role in the biocenoses of water bodies.

Not only the content of basic constituents, i.e. protein, fats, or mineral salts, but also the presence of such biologically active compounds as carotenoids, which are vitamine A provitamines, are decisive for the consumption value of fish.

The aim of the work was to show the presence of particular carotenoids in the different organs of the three species of *Percidae* family; an attempt was also made at finding possible specific differences and at determining the dominating carotenoids in the individual organs of the investigated *Percidae* specimens from Polish waters.

Material and method

Specimens of perch (*Perca fluviatilis* (L.)) were collected at two periods; one group was composed of the two sexes collected from Lake Ełk in May while the second group, composed of female specimens only, was

collected from the River Supraśl also in May. Specimens of pike-perch (*Lucioperca lucioperca* (L.)) were sampled from the River Biebrza in June and the specimens of ruff (*Acerina cernua* (L.)) were collected from the pond Czechowice at Knyszyn in April 1975.

The collected material was flooded with 95% acetone in dark bottles and kept in nitrogen atmosphere in a refrigerator up to the moment of analysis. The carotenoid pigments were separated by means of column and thin layer chromatographies. Prior to the separation, the material was hydrolysed in nitrogen atmosphere at room temperature for 24 hrs. After hydrolysis the extract was passed through 15—25 cm column filled with Al_2O_3. The separated fractions were eluted through various systems of solvents; then the eluents were evaporated and the residue being dissolved in an appropriate solvent, an absorption curve was plotted. Its maxima were used also for identifying the separate carotenoids. The β-carotene and astaxanthin were determined by the standards of F. Hoffmann-La Roche, Basel. Unicam spectrophotometer and Specol were applied for the determination of the absorption maxima.

Besides column chromatography, the obtained acetone extract was separated into bands by means of thin-layer chromatography. On 14 × × 40 cm glass plates covered with silica gel the acetone extract was carried in with a micropipette on the starting line, various systems of solvents being also used. R_f values were determined according to common rules.

The identification of different carotenoids was based up on the absorption maxima of the separate fractions, R_f values, epoxide test, as well as upon the epiphase and hypophase ratios (Czeczuga, Czerpak 1976). Quantitative relations of the carotenoids were determined by Davies's method (1965).

Results

The carotenoids found in the investigated material are listed in Table I and the results of detailed chromatographic analyses of perch, pike-perch, and ruff in Tables II—V. Table II shows that as far as both sexes are concerned in gills of perch specimens three carotenoids occurred with the domination of astaxanthin which attained 78.4% of all carotenoids. The skin contained much more carotenoids, the dominants being also astaxanthin (45.9%) and canthaxanthin (44.1%). Similarly, in the muscles of the investigated specimens astaxanthin (41.0%) and canthaxanthin (42.1%) predominated. In gills and liver the highest content of astaxanthin

Tabela I. Występowanie karotenoidów u badanych gatunków okoniowatych

Table I. Carotenoid present in the investigated species of the Percidae

Nazwa karotenoidu Name of carotenoid	Perca fluviatilis (L.)	Lucioperca lucioperca (L.)	Acerina cernua (L.)
β-karoten β-carotene	+		
α-kryptoksantyna α-cryptoxanthin	+		+
β-kryptoksantyna β-cryptoxanthin	+	+	+
Luteina Lutein	+		
Luteina - epoksy Lutein - epoxide	+	+	+
Foenikoksantyna Phoenicoxanthin	+	+	+
Izozeaksantyna Isozeaxanthin	+	+	
Zeaksantyna Zeaxanthin	+	+	
Taraksantyna Taraxanthin	+	+	
Tunaksantyna Tunaxanthin	+	+	
4-hydroksy-4-keto- β-karoten 4-hydroxy-4-keto- β-carotene	+	+	+
Astaksantyna Astaxanthin	+	+	+
Astaksantyna ester Astaxanthin ester	+	+	

Tabela II. Zawartość stwierdzonych karotenoidów w badanych częściach ciała Perca fluviatilis (L.) (♀ i ♂) w %

Table II. Carotenoid content found in the investigated parts of the body of Perca fluviatilis (L.) (♀ and ♂) in %

Nazwa karotenoidu Name of carotenoid	Płetwy Fins	Skóra Skin	Mięśnie Muscles	Skrzela Gills	Wątroba Liver	Jelita Intestine
β-karoten β-carotene			4.2			
Kantaksantyna Canthaxanthin	15.6	44.1	42.1	8.4		
β-kryptoksantyna β-cryptoxanthin				2.6		2.1
Luteina - epoksy Lutein - epoxide				4.7		2.2
Izozeaksantyna Isozeaxanthin		4.1	1.8		7.9	
Zeaksantyna Zeaxanthin	6.0		10.9	29.8	24.2	
Taraksantyna Taraxanthin		0.4				
4-hydroksy-4-keto- β-karoten 4-hydroxy-4-keto- β-carotene		3.2		4.4		
Astaksantyna Astaxanthin	78.4	45.9	41.0	50.1	67.9	89.9
Astaksantyna ester Astaxanthin ester		2.3				5.8

Tabela III. Zawartość stwierdzonych karotenoidów w badanych częściach ciała samicy Perca fluviatilis (L.) w %

Table III. Carotenoid content found in the investigated parts of the body of female Perca fluviatilis (L.) in %

Nazwa karotenoidu Name of carotenoid	Płetwy Fins	Skóra Skin	Mięśnie Muscles	Wątroba Liver	Jelito Intestine	Ikra Eggs
β-karoten β-carotene				7.3		
Kantaksantyna Cantoaxanthin	47.0	4.1		31.1	7.3	
β-kryptoksantyna β-cryptoxanthin		4.9	57.2	19.7	18.9	18.0
α-kryptoksantyna α-cryptoxanthin	11.8	8.6			23.8	
Fenikoksantyna Phoenicoxanthin				13.5		
Luteina Lutein	7.8					
Luteina - epoksy Lutein - epoxide	15.0					
Tunaksantyna Tunaxanthin		12.4				
Astaksantyna Astaxanthin	7.9					4.5
Astaksantyna ester Astaxanthin ester		63.9			39.7	63.5
Nieznane Unknown	10.5	6.1	42.8	28.4	10.3	14.0
Ogólna zawartość w µg/g żywej wagi Total content in µg/g fresh weight	1.697	0.340	0.040	1.504	3.894	0.359

and zeaxanthin was found, astaxanthin amounting to more than 50%. In the intestine astaxanthin was also found to dominate (89.9%).

The females of perch were also separately investigated. The obtained results are given in Table III. Canthaxanthin dominated in gills and liver while an astaxanthin ester in skin, intestine, and eggs. In the muscles β-cryptoxanthin dominated (57.2%). Moreover α-cryptoxanthin, phoenicoxanthin, and tunaxanthin, which were not found in the mixed population, occurred in the investigated females.

Chromatographic analyses of the separate organs of pike-perch yielded results as listed in Table IV, containing 11 carotenoids found in the investigated material. In gills the greatest amounts of astaxanthin (48.2%), phoenicoxanthin (22.3%), and taraxanthin (20.1%) were noted, while muscles and skin contained the greatest amounts of taraxanthin (50.7%) and astaxanthin (the total of the ester and pure form 38.7%). Astaxanthin dominated in liver, intestine, and eggs, its content ranging from 73.2% (liver) to 87.3% (eggs).

Table V contains the results of analyses of ruff's organs. In gills only two carotenoids, lutein-epoxide (35.1%) and α-cryptoxanthin (44.9%). were noted. Slightly more carotenoids were found in the skin, the dominant being cantaxanthin (40.3%). The chief carotenoids of ruff muscles were canthaxanthin (55.5%) and α-cryptoxanthin (30.1%) and in the liver also α-cryptoxanthin (46.6%), canthaxanthin (21.4%), and lutein-epoxide (23.1%). The dominant carotenoid of the intestine was also α-crypto-

Tabela IV. Zawartość stwierdzonych karotenoidów w badanych częściach ciała Lucioperca lucioperca (L.) w %

Table IV. Carotenoid content found in the investigated parts of the body of Lucioperca lucioperca (L.) in %

Nazwa karotenoidu Name of carotenoid	Płetwy Fins	Mięśnie ze skórą Muscles and skin	Wątroba Liver	Jelita Intestine	Ikra Eggs
β-kryptoksantyna β-cryptoxanthin		1.4			
Kantaksantyna Canthaxanthin		4.5	14.6	1.9	
Foenikoksantyna Phoenicoxanthin	22.3			1.9	
Luteina - epoksy Lutein - epoxide	3.2				
4-hydroksy-4-keto- β-karoten 4-hydroxy-4-keto- β-carotene					5.6
Izozeaksantyna Isozeaxanthin		3.2			1.9
Zeaksantyna Zeaxanthin				2.6	
Taraksantyna Taraxanthin	20.1	50.7			
Tunaksantyna Tunaxanthin	6.2	1.5	10.8		5.2
Astaksantyna Astaxanthin	48.2	21.1	73.2	86.4	87.3
Astaksantyna ester Astaxanthin ester		17.6	1.4	7.2	

xanthin (61.6%). 5 carotenoids were noted in the eggs of ruff, canthaxanthin (28.8%) and cryptoxanthin (25.7%) occurring in the greatest amounts, while such carotenoids as phoenicoxanthin, lutein-epoxide, and astaxanthin amounted to several percent in the eggs.

Tabela V. Zawartość stwierdzonych karotenoidów w badanych częściach ciała Acerina cernua L.) w %

Table V. Carotenoid content found in the investigated parts of the body of Acerina cernua (L.) in %

Nazwa karotenoidu Name of carotenoid	Płetwy Fins	Skóra Skin	Mięśnie Muscles	Wątroba Liver	Jelito Intestine	Ikra Eggs
β-kryptoksantyna β-cryptoxanthin		4.9	5.3	9.1		
α-kryptoksantyna α-cryptoxanthin	44.9	20.6	30.1	46.4	61.6	25.7
Kantaksantyna Canthaxanthin		40.3	55.5	21.4	10.6	28.8
Foenikoksantyna Phoenicoxanthin						12.0
Luteina - epoksy Lutein - epoxide	55.1	10.4	9.1	23.1	13.8	15.1
4-hydroksy-4-keto- β-karoten 4-hydroxy-4-keto- β-carotene		5.0			14.0	
Astaksantyna Astaxanthin		18.8				18.4
Ogólna zawartość w µg/g żywej wagi Total content in µg/g fresh weight	8.616	2.042	0.601	8.030	5.078	4.013

Discussion

The comparison of results obtained for three representatives of *Percidae* of Polish fresh waters, shows that with regard to quality, the most similar results were obtained for pike and pike-perch, with the exception of tunaxanthin and phoenicoxanthin which were not found in pike but occurred in pike-perch, while, on the contrary, β-carotene occurred in the investigated specimens of pike and did not in pike-perch. In the specimens of ruff the amounts of one carotene were much greater than either in pike or in pike-perch: it was a α-carotene derivative such as α-cryptoxanthin.

With regard to quantitative relations, the respective analyses were carried out for pike and ruff. The results show that all organs of ruff contained much greater amounts of carotenoids than the organs of pike, e.g. the muscles of pike contained 0.040 μg/g of carotenoid biomass and those of ruff 0.601 μg/g, while, as we know, fishermen regard the ruff as weed and this fish is not economically utilized. It seems that this species should be properly utilized, being rich in biologically active constituents, i.e. carotenoids which are the source of vitamin A. This was also the case of *Leucaspius delineatus* (Czeczuga, Czerpak 1976), whose specimens contain much more carotenoids and vitamin A as compared to *Carassius carassius*. Other instances can also be quoted: it is known that *Coregonus autumnalis migratorius* plays an important role in Lake Baikal in spite of the fact that the carotenoid content in its muscles amounts merely to 0.063 μg/g of body weight, while some species of *Cottidae*, showing considerably greater content of carotenoids, have no economic importance. Such are *Paracottus kessleri* (with the carotenoid content of 4.276) and *P. kneri* (with 0.835 μg/g of body weight) (Czeczuga 1976).

Differences were also observed between pike and pike-perch on the one hand and ruff on the other with regard to the domination of the particular carotenoids. In pike and pike-perch the β-carotene derivatives (astaxanthin, astaxanthin ester, and canthaxanthin) dominated while great amounts of α-carotene derivatives (α-cryptoxanthin, and lutein-epoxide) were also noted in ruff specimens. Only in the skin, muscles, and eggs of ruff considerable content of canthaxanthin (β-carotene derivative) was found. The occurrence of greater amounts of α-carotene was already noted by the authors in *Silurus glanis* and also in this case as in ruff specimens, low content of astaxanthin was observed (Czeczuga 1977).

STRESZCZENIE

Autor stosując chromatografię kolumnową i cienkowarstwową badał występowanie poszczególnych karotenoidów w płetwach, skórze, mięśniach, wątrobie, jelitach i w ikrze okonia, sandacza i jazgarza.

W wyniku badań ustalono obecność takich karotenoidów, jak: β-karotenu, kantaksantyny, α-kryptoksantyny, β-kryptoksantyny, luteiny, luteiny epoksy, foenikoksantyny, izozeaksantyny, zeaksantyny, taraksantyny, tunaksantyny, astaksantyny (formy czystej i estrowej) oraz 4-hydroksy-4-keto-β-karotenu. Podano również stosunki procentowe poszczególnych karotenoidów dla badanych części ciała ww. gatunków okoniowatych. Między innymi mięśnie jazgarza okazały się bardziej zasobne w karotenoidy, aniżeli mięśnie okonia.

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Adres autora — Author's address

Prof. dr hab. Bazyli Czeczuga

Zakład Biologii Ogólnej, Akademia Medyczna, ul. Kilińskiego 1, 15-230 Białystok