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POLYSACHARIDY RIAS A ICH FUNKCIA VLÁKNINY POTRAVY
ALGAL POLYSACCHARIDES AND THEIR FUNCTION AS DIETARY FIBER

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Abstract: Algal products became popular as functional foods and nutraceuticals due to presence of many bioactive compounds. Algal polysaccharides are mainly crucial component of their cell walls, and many of them have many biological functions. In this paper, values of dietary fiber in freshwater green alga – *Chlorella pyrenoidosa* (Chlorophyta) and blue-green alga – *Spirulina pacifica* (Cyanobacteria), and six seaweeds – *Palmaria palmata* and *Porphyra tenera* (Rhodophyta), *Eisenia bicyclis*, *Hizikia fusiformis*, *Laminaria japonica* and *Undaria pinnatifida* (Phaeophyceae) were studied by different analytical methods. The brown seaweed products were established as a higher source of dietary fiber than freshwater algal products. Algal polysaccharides are mostly responsible for enormous capacity of algae to absorb toxic elements, for that reason Pb, Cd and Hg were also determined. In all samples, toxic elements were presented in very low concentrations that did not exceed French limits: ≤ 5.0 mg.kg^{-1} dw for Cd, Pb and ≤ 0.1 mg.kg^{-1} dw for Hg, in this study.
Keywords: freshwater algae, seaweed, polysaccharides, dietary fiber, toxic elements

INTRODUCTION

Algal polysaccharides introduce a wide group of compounds and they have been used for numerous commercial applications. Key and economically important seaweed products are hydrocolloids presented by alginates, agars, carrageenans, ulvanes and fucoidans, which have been widely used in the food and pharmaceutical industry and also in other branches of industry (**MacArtain *et al.*, 2007**). Diverse chemical composition of dietary fiber polysaccharides is responsible for their different physicochemical properties, such as their ability to be fermented by the human colonic microbiota resulted in health benefit effects (**Anttila *et al.*, 2004**). Moreover, algal polysaccharides have been widely investigated due to their chemical properties and important biological effects in recent years. Most of them carry sulphate groups. Generally, biological activities of sulphated polysaccharides are related to their different composition and extent of sulphation, and they have been associated with many significant biological activities such as antioxidant, anticoagulant, antithrombotic and antiviral activities including anti-HIV infection, herpes and hepatitis viruses (**Jiménez-Escrig and Sánchez-Muniz, 2000**).

Freshwater algae and seaweeds have high capacity to bind trace metals; their cellular walls are rich in sulphated polysaccharides in which hydroxyl, sulphate and carboxyl groups are strong ion-exchangers, and therefore they are important complexation sites for hard transition metal cations (**Vasconcelos *et al.*, 2001**).

MATERIAL AND METHODS

Nine samples of algal food products from freshwater algae and seaweeds (Table 1) were homogenized with a mixer (Vorwerk Thermomix TM 31, Wuppertal, Germany) up to a size of particle of 1 mm and used for analyses. All used chemicals were of p.a. purity and originated from Lach-Ner, Lachema Brno and Merck.

Dietary fiber analysis.

a) **Henneberg-Stohmann (H-S)** method is based on the subsequent hydrolysis of samples with diluted 0.255 M H_2SO_4 and 0.313 M NaOH followed by gravimetric determination of the residue after drying.

Table 1 Food products from freshwater algae and seaweeds

Product	Indication of samples	Producer	Provenance	Alga
Chlorella Tabs	C	Chlorella centrum, CZ	Taiwan	*Chlorella pyrenoidosa*
Spirulina Pacifica	S	Nutrex, Inc., USA	Hawai	*Spirulina pacifica*
Dulse flakes Bio	D	Lifefood, CZ	USA	*Palmaria palmata*
Nori flakes	NV	Sunfood, CZ	Japan	*Porphyra tenera*
Arame	A	Country life, CZ	Japan	*Eisenia bicyclis*
Hijiky	H	Country life, CZ	Japan	*Hizikia fusiformis*
Kombu	K	Country life, CZ	Japan	*Laminaria japonica*
Wakame	W	Country life, CZ	Japan	*Undaria pinnatifida*
Wakame-instant	WI	Country life, CZ	Japan	*Undaria pinnatifida*

b) **TDF** – according to AOAC methods (AOAC, 1997) by using Total Dietary Fiber Assay Kit (Megazyme, NOACK ČR, spol. s r.o.).

c) **Crude fiber (CF), acid-detergent fiber (ADF), neutral-detergent fiber (NDF), and acid-detergent lignin (ADL)** by using an Ankom^{220} Fibre Analyzer; according to Ankom^{220} Fibre Analyzer manufacturer methodologies (ANKOM Technology, New York, USA) **(Mišurcová, 2008; Mišurcová *et al.*, 2010).**

Toxic elements analyses.

Total mercury was determined directly from untreated samples in the special device for mercury determination TMA-254 (Tesla, CZ). Before determination of Pb and Cd by flameless atomic absorption spectrometry ET–AAS with the usage of graphite cuyvette GTA 120 – Varian AA 2402 (Varian, Inc., Australia), samples were decomposed by microwave furnace Mars Xpress (Varian, Inc., Australia) **(Mišurcová, 2008; Mišurcová *et al.*, 2009)**. Standards of Pb, Cd and Hg were originated from Merck.

RESULTS AND DISCUSSION

Definition of dietary fiber has been evaluated for many years. Initially, dietary fiber was defined as "the skeletal remains of plant cells in the diet, which are resistant to hydrolysis by human digestive enzymes". As follows, in the term of dietary fiber there were included "all polysaccharides (cellulose, hemicelluloses, oligosaccharides, pectins, gums), waxes and lignin, which are not digested by endogenous secretions of the human digestive tract" **(Bach Knudsen, 2001).** The definition of dietary fiber has been continuously modified also in dependence on analytical methods used for its determination **(AACC Report, 2001)**. Originally, the crude fiber method according to Henneberg and Stohmann has been the most commonly used method which is based on the subsequent hydrolysis of samples with diluted acid and alkali followed by gravimetric determination of the residue after drying. However,

only a small and variable fraction of fiber components (structural polysaccharides and lignin) can be established by this method as can be concluded from results in Table 2. Further, detergent methods have been developed by **Van Soest (1963).** They are based on determination of the fiber fractions which are insoluble in various detergents. Neutral detergent fiber (NDF) covers hemicelluloses, cellulose and lignin that are established as insoluble residues after hydrolysis in neutral detergents. Whereas, acid detergent fiber (ADF) that includes cellulose and lignin is determined as insoluble residues after acid detergent hydrolysis. By the reason of dissimilar solubility of different parts of dietary fiber, it could be measured as soluble and also insoluble fiber. The soluble fractions of fiber include pectin, xyloglucans and galactomannan hemicelluloses, gums and waxes, whereas the insoluble fractions involve cellulose, arabinoxylan hemicelluloses and lignin (Bach Knudsen, 2001). Dietary fiber is mostly determined as total dietary fiber (TDF) according to that includes both soluble (SF) and insoluble (IF) fractions.

In this study, different values of dietary fiber contents, depending on the hydrolysis method of the sample were found (Table 2). It is evident, that analytical methods, used for determination of dietary fiber, considerably affect its results. Generally, according to Henneberg-Stohmann, lower values of dietary fiber (H-S) were analyzed and they were similar as results of CF by ANKOM by the reason of ability of these methods to determine only structural polysaccharides and lignin. On the other hand, higher values were established by the detergent method using an Ankom^{220} Fibre Analyzer (NDF) and TDF by AOAC (1997), where both, soluble and insoluble fibers were determined. Further, obtained results have shown that contribution of different algal species to dietary fiber composition was also significant. High difference of dietary fiber level was established even between two samples Wakame and Wakame instant from the same brown seaweed *Undaria pinnatifida* (Table 2). Generally, seaweeds contain higher amounts of dietary fiber than freshwater algae; the highest amounts were determined in brown seaweeds.

Table 2 Values (%) of dietary fiber according to Henneberg-Stohmann (H-S), TDF by AOAC and CF, NDF, ADF, ADL by Ankom^{220} Fibre Analyzer in algal products ($\overline{x}$ ± S.D.)

	H-S			AOAC (1997)			ANKOM											
	CF			TDF			CF			NDF			ADF			ADL		
	$\overline{x}$	±	S.D.	$\overline{x}$	±	S.D.	$\overline{x}$	±	S.D.	$\overline{x}$	±	S.D.	$\overline{x}$	±	S.D.	$\overline{x}$	±	S.D.
C	3.28	±	0.16	10.86	±	0.16	1.97	±	0.38	2.21	±	0.83	6.25	±	1.52	2.71	±	0.34
S	2.25	±	0.25	8.49	±	0.86	0.18	±	0.30	4.68	±	2.79	0.12	±	0.12	4.56	±	3.15
D	1.40	±	0.28	32.55	±	0.61	1.49	±	0.23	15.13	±	0.62	3.12	±	0.31	0.44	±	0.69
NV	3.44	±	0.48	46.73	±	0.33	3.24	±	0.17	28.18	±	2.33	12.38	±	0.45	4.36	±	0.42
A	8.05	±	1.29	59.81	±	0.02	7.30	±	0.29	14.55	±	0.79	19.28	±	0.38	3.45	±	0.66
H	10.80	±	0.33	57.50	±	1.24	12.55	±	0.27	20.66	±	0.81	29.36	±	1.20	7.51	±	0.81
K	3.78	±	0.26	39.15	±	4.01	5.45	±	0.46	22.08	±	2.70	13.83	±	1.05	0.43	±	0.67
W	3.44	±	0.30	42.57	±	1.47	3.11	±	0.55	13.90	±	4.02	16.19	±	1.87	2.93	±	0.70
WI	5.61	±	0.72	50.95	±	3.12	2.94	±	0.06	34.88	±	6.10	19.83	±	0.69	4.46	±	1.36

Algal polysaccharides, especially sulphated polysaccharides, have ability to absorb minerals from environment and they could positively influence the high concentration of toxic elements in algal biomass **(Vasconcelos *et al.*, 2001)**. From results presented in the Table 3 can be concluded, that concentration of Cd, Pb and Hg was determined in a small amounts. There are no standards for toxic elements in seaweeds for human consumption in the Czech Republic and the European Union. However, France has limits for Cd, Pb ≤ 5.0 mg.kg^{-1} dw and for Hg ≤ 0.1 mg.kg^{-1} dw in seaweeds **(Mabeau *et al.*, 1993)**. None of the samples exceeded these limits in this study.

Table 3 Values (mg.kg^{-1} dw) of toxic elements (Hg, Pb, Cd) in products from freshwater algae and seaweeds ($\overline{X}$ ± S.D.)

	Cd			Pb			Hg		
	$\overline{X}$		S.D.	$\overline{X}$		S.D.	$\overline{X}$		S.D.
C	0.027	±	0.004	0.586	±	0.091	0.011	±	0
S	0.071	±	0.004	0.415	±	0.011	0.019	±	0.002
D	0.387	±	0.027	0.375	±	0.062	0.006	±	0.001
NV	0.386	±	0.072	0.957	±	0.136	0.025	±	0
A	0.079	±	0.012	0.456	±	0.079	0.030	±	0
H	0.609	±	0.058	0.262	±	0.045	0.029	±	0
K	0.322	±	0.064	0.182	±	0.038	0.016	±	0
W	0.271	±	0.066	0.183	±	0.049	0.011	±	0
WI	1.010	±	0.105	0.959	±	0.266	0.037	±	0

CONCLUSION

The high content of polysaccharides in algal cell walls, undigested by human, is the reason why they are considered to be an abundant source of dietary fiber, from the nutrition point of view. Various surroundings of algae are responsible for enormous algal diversity which results in diverse chemical composition that varies in dependence on algal species, time of collection, geographic area and the environmental conditions such as water temperature, light intensity irradiation and nutrient concentration in a habitat. Determination of dietary fiber could be provided by different analytical methods. In this study, dietary fiber was conducted by Henneberg-Stohmann method, enzymatic method by AOAC and by Ankom^{220} Fibre Analyzer. The order of contents of dietary fiber in products from freshwater algae and seaweed has been found to be as: H > WI > A > NV > W > K > D > C > S.

Efforts to reduce human and environmental exposure to toxic elements must be prioritized because of the adverse health and environmental effects. Thus constant monitoring of the environment and food is essential. The amounts of Pb, Cd and Hg in algal samples were determined in a very low concentrations and the order of contents of toxic elements were found: Pb > Cd >Hg.

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