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CHEMICAL CHARACTERIZATION OF BROWN SEAWEED – *CYSTOSEIRA BARBATA*

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Abstract

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The aim of this study is to make chemical characterization of one type brown seaweed (*Cystoseira barbata*) obtained from several points in Black Sea near to city of Varna and to make comparative analysis at obtained samples. In order to make this characterization quantity of several major substances has been determined. We analyzed content of proteins, carbohydrates, fats, phenols, alginic acid, some heavy metals as Pb, Cd, As, and some essential elements as P, Ca, Mg. In addition, ash and water content has been determined.

Key words: brown seaweed, chemical characterization, essential elements, polysaccharides

Introduction

Currently biodiversity of seaweed in Bulgarian aquatory is represented by 165 species referred to the three genuses. Most numerous are red seaweed (Rhodophyta), followed by green (Chlorophyta) and brown (Phaeophyta). Studying of macro-algae grew up interest because their ability for purification of associated ecosystems, and their role as bioindicators. They are markers for presence of negative changes in coastal marine ecosystems due to the accumulation of pollutants in their talus. Another aspect in their study is accumulation of bioactive compounds with application in various types of industry. Cultivated algae and products produced by them have implementation in medicine, pharmacy, food, textile industry, for purification of wastewater, and in livestock farming (Dimitrova-Konaklieva, 2000). Species from genus Phaeophyta (classis Phaeophyceae, ordo Fucales, familia *Cystoseiraceae*), *Cystoseira barbata* (Agardh, 1821) is one of largest seaweed in black see aquatory. *C. barbata* reaches maximum length of 170 cm. Studying association of *C. barbata* is used for biomonitoring, for calculation of indexes that help to determine ecological status and eutrophication level of given habitat. *Cystoseira barbata* is indicator for purity of water. Aquatories with dominating *Cystoseira* are known with highest quality of water (Orfandis, 2001; Dencheva, 2008). *Cystoseira* is second most used species with economical value in black sea region. Since mid 60s in Bulgaria, chemical direction of studying marine algae has been built up. Species has been investigated due high content of alginic acid. (Dimitrova-Konaklieva, 2000). The first in our studies and quantitative distribution and supply of *Cystoseira* in Bulgarian coastal are (Petrova-Karadzhova, 1975). This seaweed is recognized as valuable raw material both for industry and agricultural (Petrova-Karadzhova, 1975). As industry raw material, both alginic acid

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nad its salts had been extracted, as representatives of most valuable products produced by seaweeds at all. They had almost universal implementations in various types of industry, and nonindustrial manufacturing (Petrova-Karadzhova, 1967). Alginic acid is contained in cellular walls of *Cystoseira barbata* as calcium and magnesium alginate. The principle of extraction lies in modification of insoluble alginates (calcium and magnesium salts) into soluble ones(sodium and potassium salts). This is performed by treatment of insoluble salts (or raw material as brown seaweeds) with alkaline solution (Bashford et al., 1950).

$$CaAlg_2 + 2\ Na^+ + 2\ NaAlg + Ca^{2+}$$

Manny authors established that treatment of raw materials with mineral acid (sulfur or hydrochloric) improves extraction (Haug, 1964; Myklestad, 1968a; 1968b; Secconi, 1967). Alginic acid yield varies between 18.3% – 26.6% in dependence from dry weight and preliminary treatment. It is found (Moen et al., 1997a; 1997b) that natural endogenous alginate lyase enzymes catalyze influence of natural polyphenols contained in brown seaweed, resulting alginate degradation. It is well known that marine algae are rich in minerals, and some biological active compounds, such as polysaccharides, proteins, lipids, and polyphenols, with antibacterial, antivirus and antifungal activity. (Arasaki, 1983), (Kumar et al., 2008b). Water content in fresh seaweed is high and can reach up to 94%. Content of nutrients varies in dependence of season, species, and location.

Aim of this investigation is to provide chemical characterization and comparative analysis between for samples of brown seaweed (*Cystoseira barbata*) taken from for different location in black see near to city of Varna.

Materials and Methods

Used metods:

– Protein determination: БДС 14431-78

Protein content is determined by measure of nitrogen content by Kjeldahl method. (Pearson, 1970).

– Lipids determination: БДС 6997-84

Content of fats is measured by extraction of lipids with petroleum ether by soxhlet method. (Manirakiza et al., 2001)

– Determination content of reducing sugars: БДС 7169-89

– Dry weight measurement: БДС EN 12145-2000

– Determination of ash content: БДС 7646-82

– Polyphenols determination:

Content of polyphenols is measured by Folin-Ciocalteu method.

– Determination content of chemical elements:

Content of few important chemical elements are determined trough ICP-OES spectroscopy by method validated in FRDY-Plovdiv.

– Alginic acid determination:

Is Determined by high thermal alkaline extraction (Perez, 1992; Haug, 1974 ; Suzuki, 1953**)**

Materials and reagents

Samples *Cystoseira barbata* was obtained from few different regions of black see near city of Varna by method of squares (Kalugina-Gutnik, 1975).

Used reagents where supplied by SIGMA – ALDRICH.

Equipment

ICP – OES Spectroflame Modula.

UV/VIS spectrometer „Thermo „EVOLUTION 201“

Laboratory balance „Sartorius A120S“

Glassware with accuracy class „A“

Results and Discussions

In results represented in Table 1 can be seen that highest amount of dry weight have algae from Rusalka region, and ash content in st. Atanas region. Lowest dry weight content has algae from Shabla region, and ash content from Carevo. Dry weight in algae from Rusalka is 1.5 times more than one from Shabla, and ash content in algae taken from st. Atanas is 6 times more than one taken from Carevo.

Regarding content of proteins, sugars and fats it can be seen that highest protein content has algae from Shabla – 25.6 $g.kg^{-1}$; fats, from st. Atanas – 10.3 $g.kg^{-1}$, and sugars from Rusalka – 9.6 $g.kg^{-1}$. Lowest content of proteins and fats has algae from Rusalka 12.6 and 6.4 $g.kg^{-1}$; accordingly, and sugars from Carevo – 2.3 $g.kg^{-1}$.

When we consider polyphenols and alginic acid

Table 1
Physical and chemical composition of brown seaweed – *Cystoseira barbata* obtained from different regions in Black Sea

Seaweed	*Cystoseira barbata*	*Cystoseira barbata*	*Cystoseira barbata*	*Cystoseira barbata*
Type	Brown	Brown	Brown	Brown
Region	Shabla	St. Atanas	Rusalka	Carevo
Dry weight, $g.kg^{-1}$	187.6	254.0	272.7	262.9
Ash content, $g.kg^{-1}$	87.9	162.8	45.9	26.9
Proteins, $g.kg^{-1}$	25.6	24.7	12.6	20.4
Fats, $g.kg^{-1}$	6.9	10.3	6.4	8.9
Sugars, $g.kg^{-1}$	3.8	6.5	9.6	2.3
Alginic acid, %/dry weight	26.6	19.6	18.3	19.0
Polyphenols, $g.kg^{-1}$ GAE	14.3	16.8	16.4	66.9
Mg, $mg.kg^{-1}$	199.39	1669.67	1782.21	1803.26
P, $mg.kg^{-1}$	131.12	95.63	106.88	79.28
As, $mg.kg^{-1}$	5.55	3.85	3.92	4.08
Cd, $mg.kg^{-1}$	0.13	0.15	0.20	0.19
Pb, $mg.kg^{-1}$	0.93	1.10	1.47	0.56

content, algae taken from Carevo has highest amount of polyphenols – 66.9 $g.kg^{-1}$ GAE, and these taken from Shabla has highest alginic acid content – 26.6% / dry weight. Lowest amount of polyphenols is detected in algae from – 14.3 $g.kg^{-1}$ GAE; and alginic acid in algae from– 18.3% / dry weight.

Data shows that algae from Shabla with lowest amount of polyphenols contain highest amount of alginic acid. That can be explained with synergy between polyphenols and alginate lyase.

Regarding data for inorganic composition, highest content of magnesium can be seen in algae from Carevo – 1803.26 – $mg.kg^{-1}$; which is 9 times higher than one from Shabla. With phosphorus we can see opposite pattern, highest amount is in Shabla – 131.12 $mg.kg^{-1}$; and lowest in – 79.28 $mg.kg^{-1}$.

Regarding heavy metal content, highest amount of arsenic can be seen in algae from Shabla – 5.5 $mg.kg^{-1}$; for other regions content is very close. Highest amount of cadmium contain algae from Rusalka and Carevo, and lowest from Shabla. Highest content of lead has algae from Rusalka, and lowest from Carevo. In Bulgarian legislation there are not regulations regarding content of toxic metals in algae used in food industry. If we make comparison with other seafood as fish, shellfish, and crabs we see that content of toxic metals in algae are lower than regulations for such foods, but we can see strong regional variation regarding lead content. Algae taken from Shabla and Carevo we observe lead content bellow regulations for shellfish, but above those for crabs, until algae from Rusalka and st. Atanas contain lead bellow regulations for crabs regarding cadmium we observe smaller regional variations than lead, and in all regions content is lower than regulations for all seafood excluding meat from some types of fish. Regarding arsenic we observe relative constant content around 4 $mg.kg^{-1}$, excluding algae from Shabla where we observe 5.55 $mg.kg^{-1}$. Content for arsenic is higher than regulations for shellfish, but lower than one for fish meat, excluding algae taken from Shabla which content is higher even from regulations for fish meat.

Conclusions

In result of upper results, we can list following conclusions.

Highest content of proteins have algae from Shabla region, of fats from st. Atanas, and of sugars from Rusalka.

It has been established that algae with higher content of polyphenols contain lower content of alginic acid.

It has been established that brown algae accumulate toxic metals from seawater, but their content in most cases is not higher than allowance for seafood. Brown algae are not intended for direct consumption, but for raw materials for food and feed industry, whish allows us higher tolerance regarding heavy metal contamination than seafood intended for direct consumption. Samples under this study did not present concern regarding toxic metal exposure, but their content mast be taken into account during next technological treatment.

Accumulation of heavy metals gives us ground to use brown algae as biomarkers for ecological investigations.

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