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Research of the Nutritional Value of Macrophytes of the Sea of Azov

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Abstract

The paper presents the results of research devoted to the nutritional value of macrophytes – green algae *Ulvarigida C. Ag.*, *Cladophora spp.*, red algae *Callithamnion corymbosum (Smith) Lyngb*. These typical representatives of the aquatic biocenoses of the coastal waters of the two seas, Cladophora spp., episodically dominate in the periphyton of the Sea of Azov. An analysis of the chemical composition made it possible to establish the predominance of the carbohydrate component (59.2 – 64.9 % absolute dry matter), the presence of pectin substances in significant quantities (% a.d.m.), namely in *U. rigida* – 12.1, *Cladophora sp.* – 7.5, *C. corymbosum* -- 6.0. The amino acid composition of algae proteins was studied; limiting essential amino acids were established. In the mineral composition of macrophytes, the presence of phosphorus, calcium, potassium, sodium, magnesium was determined; a high iodine content was noted in U. rigida (4.3 -- 4.6 %). All three types of algae belong to low-calorie raw materials (less than 90 kcal/100 g) and with a certain technological processing can be recommended in diets to reduce weight.

Keywords: macrophytes, green algae, red algae, *Ulva*, *Callithamnion*, *Cladophora*, nutritional value.

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1. Introduction

The commercial value of macrophytes of the Azov-Black Sea basin is insignificant. Maximum yield amount of algae *Zostera marina* L., *Z. noltei* Hornem was recoreded in 2006 -- 2009 (up to 2164.6 tonnes in 2009), peak yield of the golden *Cystoseira barbata* (Stackh.) C. Agardh. did not exceed 36.3 -- 36.4 tons in 2002 -- 2003. The water area of the growth of another previously commercial species -- *Phyllophora nervosa* (DC.) Grev. was granted the status of a national botanical reserve. Most macrophytes are not targets of fishing. Data on their chemical composition, nutritional value, and perspective methods of cultivation and processing are practically not available in the national literature. However, such representatives of red and green algae as pp. Callithamnion, Ulva,

Enteromorpha, Cladophora are abundant representatives of the aquatic biocenoses of the coastal waters of the two seas and even dominate the periphyton.

Green algae of the genus Ulva L. (Ulvophyceae) are cultivated on an industrial scale in waters of temperate latitudes. Representatives of this genus are more commonly known to the consumer under the name ``sea salad''. It should be noted that *Ulva rigida* C. Ag. (1823) is able to propagate two vegetative methods. Vegetative propagation of the attached form is carried out by germination of the cells of the basal disk with the formation of additional shoots, unattached form -- by fragmentation. Under favorable conditions (shallow water, even bottom topography), the detached plates continue to grow, but eventually lose the ability to form reproductive cells. Unattached ulva is often found in the Kerch Strait, Sevastopol Bay and in the estuaries of the Odessa coast [1]. The rapid growth of thallus, a large number of produced cells, and high specific production make the ulva an attractive marine aquaculture target species. Recent advances in the development of intensive marine aquaculture also allow talking about ulva exploitability as a target for polyculture [2].

Numerous species of the genus Cladophora Kütz. are ubiquitous representatives of the Ulvophyceae class [3, 4]. In 2017 and 2018, abundant reproduction of cladophores was observed on the coast of the Sea of Azov. It has been established that the growth rate of Cladophora is directly related to the level of phosphorus in the environment [4–6].

Red algae of the genus *Callithamnion Lyngb. (Ceramiaceae)* are delicate, light-purple bushes with a dichotomous arrangement of branches, tightly attached to stony ground with a disc-shaped base or creeping branched threads. *Callithamnion corymbosum* (Smith) Lyngb. (1819), the most common species, like all representatives of the *Rhodophycophyta* division, contains, in addition to chlorophyll, carotene and xanthophyll pigments, two additional pigments in the cells, namely phycoerythrin and phycocyan. The product of assimilation is red algae starch.

In modern nutritional science, algae are one of the most useful food products. Moreover, nutraceuticals and parapharmaceuticals based on them are involved in restoring nutritional balance and in complex overcoming metabolic disorders by forming a pool of substrates of essential substances.

The purpose of the research was to assess the nutritional value of macrophytes distributed in the coastal zone of the Kerch Strait (Sea of Azov).

2. Methods

The objects of research were samples of algae gg. Ulva, Cladophora, Callithamnion, taken in August and November 2018 in the water area of the Kerch Strait (45°35'N, 36°52'E).

Studies of the chemical composition were carried out using standard methods adopted in a comprehensive chemical analysis, namely: the total content of nitrogenous substances – according to the Kjeldahl method using a FOSS auto-nitrogen analyzer; mineral substances – gravimetrically, after burning at a temperature of 600 – 700 °C, the composition of macro- and microelements – by capillary electrophoresis, pectin substances – by calcium-pectate method.

3. Results

The research results for chemical composition and calorific value are given in Table 1.

Table 1: Chemical composition of macrophytes *Callithamnion corymbosum*, *Cladophora sp., Ulvarigida*.

Target species	Moisture content, %	Mass percentage, %				Calorific value, kJ/100 g
		protein	ash	fat	carbohydrates	
August, 2018						
C. corymbosum	78.2	4.1	3.7	0.25	13.75	307.9
Cladophora sp.	87.5	1.6	3.2	0.30	7.40	161.8
*U. rigid*a	87.9	2.3	2.2	0.35	7.25	172.8
November, 2018						
C. corymbosum	80.2	4.3	3.9	0.3	11.8	272.1
*U. rigid*a	88.6	1.4	2.3	0.3	7.4	158.4

As it can be seen from the data presented, the algae sampled in the autumn period are more moist (water-logged); a significant part of their organic substances is represented by carbohydrates (in % absolute dry matter), namely in *C. corymbosum* -- 63.0, in *Cladophora sp.* -- 59.2, in *U. rigida* -- 59.9.

Table 2 provides the data as per pectin matters in the samples under research. Higher polysaccharide content is distinguished by *U. rigida* – 12.1 % a.d.m., versus 6.0 % for *C. corymbosum* and 7.5 % *Cladophora sp.*, while 55.5 – 63.8 % of their total content

can be found in the fraction of insoluble pectins. For comparison: the content of pectin in the traditional source of marine pectin Zostera marina L. is 11.0 -- 12.2 % a.d.m.

The mass fraction of nitrogenous substances in macrophytes on average is as follows: for *C. corymbosum* -- 0.7 %, *Cladophora sp.* -- 0.3 %, *U. rigida* -- 0.4 % (Table 1).

Table 2: Contents of pectins in macrophytes.

Target species	Percentage of pectins, %		
	Total contents	soluble	insoluble
August, 2018			
C. corymbosum	1.31	0.53	0.78
Cladophora sp.	0.94	0.34	0.60
*U. rigid*a	1.46	0.65	0.81
December, 2018			
C. corymbosum	1.03	0.52	0.51

The amino acid composition of the algae protein is unbalanced in composition: limiting amino acids for red algae *C. corymbosum* are tryptophan, valine and lysine, for *Cladophora sp.* -- tryptophan, methionine, *U. rigida* -- tryptophan, valine (Table 3, 4). *U. rigida* has a high methionine and phenylalanine content.

The algae samples under study contain the following mineral macroelements: potassium, sodium, calcium, phosphorus, magnesium (Table 5). The largest amount of iodine (4.3 -- 4.6 %) as the essential microelement entering the human body with food is found in *U. rigida*.

4. Discussion

The specification of the algal nutritional value implied an assessment of the complex of their useful properties, including the degree to which the physiological needs of a human are provided for in basic and essential nutrients, energy and organoleptic properties.

Green macroalga *Ulva rigida* is the most attractive in terms of use for food (% a.d.m.). The protein content is 19.0; carbohydrates predominate -- up to 64.9 with the content of pectin substances up to 12 %. It is known that the metabolic processes in algae in the summer and autumn are aimed at carbohydrates synthesis [8, 9]. The high iodine content (physiological norm for an adult is 130 --200 µg/a day) suggests the advisability

Table 3: Amino acid composition of proteins in macrophytes *Callithamnion corymbosum*, *Cladophora sp.*, *Ulvarigida*.

Amino acid nomenclature	Contents, %		
	Callithamnion corymbosum	*Cladophora sp.*	*Ulvarigida*
Valine	0.18 ± 0.07	0.09± 0.03	0.01± 0.004
Isoleucine+Leucine	0.43 ± 0.11	0.25 ± 0.07	0.26± 0.07
Lysine	0.17 ± 0.06	0.09± 0.03	0.12± 0.04
Methionine	0.26 ± 0.09	0.03 ± 0.01	0.14± 0.05
Threonine	0.24 ± 0.09	0.09± 0.03	0.09± 0.04
Phenylalanine	0.18 ± 0.05	0.09± 0.03	0.13 ± 0.04
Tyrosine	0.07 ± 0.02	0.08 ± 0.02	0.09± 0.03
Histidine	0.22 ± 0.11	Not detected	Not detected
Arginine	0.07 ± 0.03	0.12 ± 0.01	0.03 ± 0.01
Proline	0.13 ± 0.03	0.09± 0.03	0.11 ± 0.03
Serine	0.34 ± 0.09	0.09± 0.02	0.12 ± 0.03
Glycine	0,19 ± 0.06	0.10 ± 0.04	0.13 ± 0.04
Alanine	0.08 ± 0.02	0.13 ± 0.03	0.2 ± 0.05

Table 4: Comparative Composition of Essential Amino Acids in Macrophyte Proteins.

Nomeclature of essential amino acid	Contents, g/100 g of protein			Amino acid content, g/100 g of ideal protein [7]
	Callithamnion corymbosum	*Cladophora sp.*	*Ulvarigida*	
Val	4.2	5.6	0.7	5.0
Ile + Leu	10.0	15.6	18.2	4.0+7.0
Lys	4.0	5.6	8.4	5.5
Met	6.0	1.9	9.8	3.5
Thr	5.6	5.6	6.3	4.0
Phe + Tyr	5.8	10.6	15.4	6.0

of introducing *U. rigida* as a functional food ingredient. Furthermore, biological features of growth and high specific production make *U. rigida* an attractive mariculture target species in the Azov-Black Sea basin, which makes it possible to consider this species in the future as an accessible raw material source.

Table 5: Composition of minerals in macrophytes *Callithamnion corymbosum*, *Cladophora sp., Ulva rigid*a.

Target species	Percentage, %					
	potassium	sodium	magnesium	calcium	phosphorus	iodine
August, 2018						
C. corymbosum	1.23 ± 0.25	1.62 ± 0.32	0.08 ± 0.02	0.63 ± 0.13	0.036 ± 0.01	1.9
Cladophora sp.	0.86 ± 0.01	1.21 ± 0.24	0.07 ± 0.01	0.54 ± 0.10	0.013± 0.01	1.7
*U. rigid*a	0.31 ± 0.06	0.60 ± 0.12	0.20 ± 0.04	0.26 ± 0.05	0.019 ± 0.01	4.3
November, 2018						
C. corymbosum	1.35 ± 0.27	1.58 ± 0.32	0.09 ± 0.02	0.63 ± 0.13	0.042 ± 0.01	0.7
*U. rigid*a	0.5 ± 0.10	1.42 ± 0.30	0.25 ± 0.05	0.42 ± 0.08	0.021 ± 0.01	4.6

In the crown structure of the red alga *Callithamnion corymbosum*, the upper boundary zone (up to 57 % of the plant mass) is distinguished. It is characterized by high values of photosynthesis intensity and low biomass density [10]. This part of the alga also has a more delicate branch structure that does not require severe heat treatment. A comparative analysis of the chemical composition allows noting the high values of the carbohydrate component (59.6 -- 60.0 % a.d.m.), protein (18.8 -- 21.7 % a.d.m.) and mineral substances (17.0 -- 19.7 % a.d.m.). The amount of iodine in summer makes up 1.9 %, being physiologically significant. In East Asian countries, soups are cooked with *C. corymbosum*; it is also consumed dried or candied.

Among all the target species under research, the appearance of green algae Cladophora spp. is the least attractive, algae form ooze in the mass. By the chemical composition Cladophorasp stands out for the high content of minerals -- 25.6 % of a.d.m. and relatively low protein -- 12.8 % a.d.m. as compared to other macrophytes. It is likely that biotechnological methods for processing raw materials may be promising during treatment.

All three types of algae can be attributed to low-calorie raw materials, since the energy value of the samples did not exceed 376 kJ/100 g (90 kcal), namely *C. corymbosum* -- 309, *Cladophora sp*. --162, *U. rigida* -- 173. With certain technological processing they can be recommended in diets for weight loss.

5. Conclusion

The studies have shown the feasibility of finding new sources of raw materials of marine origin for the creation of food products and nutrients with certain physiological aims.

Ulva rigida and *Callithamnion corymbosum* are the most promising raw materials among the examined macrophytes from the coastal part of the Sea of Azov due to their rich carbohydrate component, the availability of iodine, and low calorie content. It should be noted that all three types of algae need additional mechanical and culinary processing.

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Conflict of Interest

The authors have no conflict of interest to declare.

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