POLISH POLAR RESEARCH (POL. POLAR RES.) POLSKIE BADANIA POLARNE	2	3—4	95—107	1981

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Chemism of some species of Antarctic macroalgae of the genera Adenocystis, *Himantothallus*, *Leptosomia* and *Monostroma**)

ABSTRACT: It appears from the analysis of the chemical composition of macroalgae of the Antarctic: *Adenocystis utricularis* and *Himantothallus grandifolius* (brown algae), *Leptosomia simplex* (red algae) and *Monostroma hariotti* (green algae) that the examined algae, brown algae in particular (mainly *Adenocystis utricularis*), are rich in mineral components, primarily: sodium, potassium, hologens, and structural polysaccharides. Organic substances, such as: proteins, amino acids, lipids, fatty acids, saccharides reduction, chlorophylls and carotenoids, occur in the analysed algae in quantities much smaller in comparison with taxonomically similar macroalgae derived from marine environment having more favourable hydrochemical and climatic conditions.

Key words: Antarctic, Admiralty Bay, algae, *Adenocystis*, *Himantothallus*, *Leptosomia*, *Monostroma*, chemical composition, metabolism

1. Introduction

Chemical composition of the algae belonging to thallophytes showing high photosynthetic productivity, as compared with vascular plants, of a considerable economic and medical importance is not yet sufficiently well known, chiefly due to the vast taxonomic diversity and great variability under the influence of various environmental factors (Lewin 1962, Boney 1966, Barąškov 1972, Stewart 1974, Bonner and Varner 1976, Czerpak and Obrusiewicz 1977, Liaaen-Jensen 1977, Czeczuga 1979, Czerpak 1979).

*) These studies were carried out within the Research Project R-44 included into the Antarctic Research MR-II-16 Project sponsored by he Institute of Ecology, Polish Academy of Sciences.

The environmental factors producing the most essential effects on the chemism of the algae include: chemical composition of the environment together with water circulation, the type of light and its intensity, carbon dioxide contents and temperature (Lewin 1962, Starmach 1963, Boney 1966, Levring 1967, 1969, Stein 1973, Stewart 1974).

The review of the literature (Lewin 1962, Jensen 1966, Goedheer 1970, Baraškov 1972, Matucha, Zilka and Svihel 1972, Jeffrey and Humphrey 1973—1974, Stewart 1974, Liaaen-Jensen 1977, Yokohama et al. 1977, Kageyama and Yokohama 1978, Arnesen, Hallenstvet and Liaaen-Jensen 1979, Czeczuga 1979, Czerpak 1979) treating of the chemism of algae indicates that they are rich in mineral components, especially: sodium, potassium, chlorates, magnesium and calcium, and in organic substances, such as: proteins, exogenous amino acids, lipids, unsaturated fatty-acids, reserve and structural polysaccharides, vitamins, chlorophylls, carotenoids, amines, phytosterols, and terpenes. Among the various algal species the most abundant in mineral, organic and biologically active substances are blue-green, green, brown, red algae and diatoms (Lewin 1962, Baraškov 1972, Stewart 1974).

For quite a long time, now, the interests of many researchers (Lewin 1962, Boney 1966, Levring 1967, 1969, Baraškov 1972, Waaland 1973, Stewart 1974, Liaaen-Jensen 1977, Yokohama et al. 1977) has been concentrated on the problem of the chemism of algae. They were concerned mostly with marine macroalgae, occurring in the regions of temperate and tropical climates, on account of the high values of their productivity, great amounts of biomass and dry weight containing considerable quantities of various mineral and organic substances valuable for nutrition and for industrial use. On the other hand, chemism of the marine algae and especially that of the thallophytic forms from frigid climate zones is still known in the least (Rakusa-Suszczewski 1980).

2. Material and methods

The thallophytic algae of the Antarctic were collected at Admiralty Bay (King George Island, South Shetlands Islands), from the depth ranging from 4 to 25 m deep, at the end of the summer season 1979—1980 (8—20 Feb. 1980). The experimental material for the analyses of chlorophylls and carotenoids, directly after drying with tissue blotting paper, was treated with acetone and preserved in nitrogenous atmosphere, at the temperature of about 0°C. The algae used for examination of the intensity of photosynthesis and (dark chamber) respiration were kept under artificial conditions (aquariums) at the required temperature and light. For the remaining chemical analyses dry mass of algae was used. In the analysis of the chemical composition of macroalgae of the Antractic the following biochemical parameters were determined:

Dry weight was measured by weight after desiccation of algae at 105°C, for 3 hours (Stein 1973).

Ash content was determined gravimetrically by mineralization of algae

by ashing in a muffle at 550°C during 45—60 minutes (Skulmowski 1974). The total amount of organic substances was determined from the difference between the dry weight of algae and the weight of the obtained ash.

Total protein was calculated by multiplying total nitrogen content, expressed in per cents of dry weight algae, into the 6.25 conversion factor (Skulmowski 1974, Czerpak 1979).

Saccharides reduction i.e. dissoluble carbohydrates in water phase were determined spectrophotometrically with the Samogyi method, at the 520 nm wave length, described in detail by Hodge and Hofreiter (1962).

Lipids were determined with gravimetric method after extraction from dried algae with chloroform: methanol (2:1) and chloroform: petroleum ether (1:1) in sequence, at the temperature of 50—60°C (Skulmowski 1974).

Total chlorophyll content was determined spectrophotometrically in the extract from algal biomass in 80% acetone at the wave lengths corresponding to the absorption maxima i.e. 645, 652 and 663 nm (Strain, Sherma and Grandolfo 1968, Jeffrey and Humphrey 1973—1974).

Carotenoids in algae were analized using the methods of extraction, column and thin-layer adsorption chromatography and spectophotometry (Petraček and Zechmeister 1956, Czeczuga and Czerpak 1966, Opieńska-Blauth and Trojanowski 1967, Strain, Sherma and Grandolfo 1968, Foppen 1971, Isler, Gutmann and Solms 1971, Goodwin 1976, Czerpak 1977).

Total nitrogen was determined with Kjeldahl method, based on volumetric analysis, after wet mineralization in a Kjel-Foss Automatic 16210A/S, Danemark, autoanalyser (Czerpak 1979).

Total phosphorus was determined spectrophotometrically with Fiske-Subbarov method, after dry mineralization of algae, at the 660 nm wave length (Skulmowski 1974).

Total sulphur was determined gravimetrically in $BaSO_4$, after dry mineralization of algae (Skulmowski 1974).

Halogens — the total content reduced to chlorine, after extraction from algae into re-distilled water, was determined by titration after Volhard method (Just and Hermanowicz 1964, Skulmowski 1974).

Iodine was determined volumetrically in an aqueous extract from algae by titration with thiosulphate in the presence of an amyloceous indicator (Just and Hermanowicz 1964).

Metals (sodium, potassium, magnesium, calcium, iron, zinc, copper, manganese), after wet mineralization of dried algae, were determined with atomic absorption spectrometry using a Perkin-Elmer 300, USA, spectrometer (Printa 1977).

Amino-acids composition was analysed in dry weight algae hydrolyzed with 6N HCL at 115°C for 45—50 hours. The content of various amino acids (except of tryptophane) in appropriately prepared algal hydrolyte were determined in a JOEL JLC-6 AH, Japan, autoanalyser (Spackman, Stein and Moore 1958).

Percentile composition of fatty-acids in lipids extracted from dried algae was determined chromatographically after esterifying with sodium methanol

in a Varian model 2100, USA, gas-chromatographer (Schlenk et al. 1960, Matucha, Žilka and Svihel 1972).

Calorific value of dry weight algae was determined by combustion in oxygen atmosphere in a KL-3 type of calorimeter with water jacket (Górecki 1965).

The rate of growth of the thalluses of algae was determined gravimetrically, measuring every week the increment of fresh and dry weight (Waaland 1973).

Intensity of photosynthetic activity and intensity of respiration of algae in the dark chamber were determined using Winkler method for measurements of the content of oxygen produced in photosynthesis and utilized by algae in respiration (King and Schramm 1976, Zelitch 1977, Zurzycki and Michniewicz 1977, Merril and Waaland 1979).

3. Results and discussion

The results of the investigations (Table I) show that among the analysed algae *Monostroma harriotti* (green algae) has the highest content of dry weight organic substances, reduction saccharides, chlorophylls and carotenoids content and the highest calorific values of dry weight and intensity of photosynthesis. *Adenocystis utricularis* (brown algae) shows the highest ash and lipids content and highest dynamics of the increase of biomass and intensity of respiration in dark chamber. *Leptosomia simplex* shows the highest total protein content and highest quotient of photosynthesis: respiration (dark chamber) ratio.

The lowest dry weight content was noted in *Himantothallus grandifolius* (brown algae), whereas the lowest quantities of organic substances, total protein and carotenoids, the lowest dry weight calorific value and the lowest quotient of photosynthesis: respiration ratio was recorded in *Adenocystis utricularis*. The lowest content of reduction saccharides, lipids and lowest values of the intensity of photosynthesis and dark-chamber respiration were noted in *Leptosomia simplex* and the smallest quantity of asch — in *Monostroma hariotti*. It is clearly evident from the results obtained that the analysed thallophytic algae of the Antarctic, brown algae in particular (32.5—46.0% of ash in the dry weight material), are a rich source of mineral substances.

Against the background of the data from the literature treating of the chemical composition of algae (Lewin 1962, Levring 1967, 1969, Baraškov 1972, Waaland 1973, Stewart 1974, Czerpak and Obrusiewicz 1977, Zelitch 1977, Arnesen, Hallenstvet and Liaaen-Jensen 1979, Czeczuga 1979, Merril and Waaland 1979) it appears that among all the analysed algae *Monostroma hariotti* has relatively high content of dry weight material, while *Leptosomia simplex* as well as *Monostroma hariotti* contain considerable quantities of total protein, ranging from 15.5 to 23.5% of dry weight. For all that, the content of the remaining biochemical parametres, the dynamics of the increase of fresh and dry weight and intensity of photosynthesis and respiration are much lower in Antarctic

Table I.

Biochemical composition of the thallophytic algae of the Antarctic *)

Analysed parametres	*Monostroma harriotti* (green algae)	*Adenocystis utricularis* (brown algae)	*Himantothallus grandifolius* (brown algae)	*Leptosomia simplex* (red algae)
Dry weight (percent of biomass)	17.46(±3.59)	12.87(±4.26)**)	11.39(±1.83)	11.46(±1.78)
Total ash (percent of dry weight)	25.06(±4.08)	45.98(±3.42)	32.49(±3.27)	26.12(±2.13)
Organic substances (percent of dry weight)	74.94(±5.97)	54.02(±4.66)	67.51(±4.95)	73.88(±3.19)
Total protein (percent of dry weight) ***)	18.32(±2.83)	8.65(±1.58)	10.16(±1.34)	22.21(±1.27)
Reduction saccharides (percent of dry weight) ****)	0.99(±0.44)	0.57(±0.21)	0.73(±0.28)	0.31(±0.07)
Lipids (percent of dry weight)	1.03(±0.23)	1.18(±0.26)	0.81(±0.19)	0.53(±0.11)
Chlorophylls (g percent of biomass)	0.101(±0.020)	0.039(±0.008)	0.019(±0.003)	0.017(±0.002)
Carotenoids (mg percent of biomass)	8.37(±0.42)	1.10(±0.07)	1.51(±0.09)	3.75(±0.19)
Calorific value ($J \cdot g^{-1}$ dry weight)	14649.4(±203.3)	7137.6(±139.5)	11261.0(±533.8)	12981.4(±199.3)
Increment of biomass (g per week)	0.042	0.060		
Increment of dry weight (g per week)	0.014	0.011		
Intensity of photosynthesis (mg $0_2 \cdot h^{-1}$ per g wet weight) *****)	4.57	4.06		1.46
Intensity of dark chamber respiration (mg $0_2 \cdot h^{-1}$ per g wet weight) *****)	3.22	3.45		0.23
Photosynthesis respiration ratio (dark chamber)	1.42	1.18		6.35

*) mean values from 3–5 analyses

**) dry weight was determined after removal of fluid from the follicles of the thalluses of algae

***) total nitrogen content expressed gravimetrically in percent of dry weight multiplied by 6.25 — conversion coefficient for protein

****) carbohydrates dissoluble in aqueous phase after homogenization of the algae

*****) experiments under artificial conditions at the temperature 0°C and light intensity 5000 lx.

Table II.

Occurrence of some elements in thallophytic algae of the Antarctic*)

Element content (% of dry wt.)	*Monostroma hariotti* (green algae)	*Adenocystis utricularis* (brown algae)	*Himantothallus grandifolius* (brown algae)	*Leptosomia simplex* (red algae)
Nitrogen	2.85(±0.47)	1.76(±0.26)	1.83(±0.29)	4.05(±0.33)
Phosphorus	1.76(±0.31)	1.15(±0.22)	1.39(±0.18)	1.98(±0.27)
Sulphur	0.32(±0.03)	0.42(±0.04)	0.63(±0.07)	0.37(±0.03)
Halogens (F,Cl,Br,J)	4.57(±1.96)	2.32(±1.14)	2.13(±1.38)	3.35(±1.43)
Iodine	0.39(±0.23)	0.67(±0.24)	0.61(±0.25)	0.74(±0.43)
Sodium	2.96(±0.75)	13.55(±4.56)	9.55(±3.88)	0.61(±0.20)
Potassium	0.91(±0.29)	8.21(±2.55)	2.94(±0.79)	1.95(±0.39)
Magnesium	0.58(±0.16)	2.58(±0.63)	0.75(±0.34)	0.22(±0.12)
Calcium	0.32(±0.05)	2.24(±0.44)	0.39(±0.14)	0.12(±0.04)
Iron	0.081(±0.042)	0.085(±0.029)	0.067(±0.028)	0.065(±0.021)
Zinc	0.012(±0.004)	0.028(±0.009)	0.031(±0.012)	0.030(±0.008)
Copper	0.0027(±0.0004)	0.0042(±0.0011)	0.0037(±0.0010)	0.0041(±0.0011)
Manganese	0.0011(±0.0008)	0.0022(±0.0015)	0.0016(±0.0011)	0.0028(±0.0018)

*) mean values from 3—4 analyses

macroalgae than in the algae growing under more favourable environmental conditions.

Out of the analysed chemical elements (Table II) the content of nonmetals: nitrogen, phosphorus, and iodine was the highest in *Leptosomia simplex*, of halogens in *Monostroma hariotti*, of sulphur in *Himantothallus grandifolius*. The lowest content of nitrogen and phosphorus was noted in *Adenocystis utricularis*, of sulphur and iodine in *Monostroma hariotti*, of halogens in *Himantothallus grandifolius*.

From the analyzed metals the greatest quantities of sodium, potassium, magnesium, calcium, iron and copper were found in *Adenocystis utricularis*, of zinc in *Himantothallus grandifolius* and of manganese in *Leptosomia simplex*, whereas the lowest content of sodium, magnesium, calcium and iron was noted in *Leptosomia simplex* and the lowest content of potassium, zinc, copper and manganese in *Monostroma hariotti*.

In the analysed brown algae (*Adenocystis utricularis* and *Himantothallus grandifolius*) and green algae (*Monostroma hariotti*) the content of sodium is much higher than potassium content; in red algae (*Leptosomia simplex*) this relation is inverse.

The comparison of the obtained results with the data from the literature (Lewin 1962, Baraškov 1972, Steward 1974, Czerpak and Obrusiewicz 1977) indicates that the analysed macroalgae of the Antarctic, especially brown algae of the genera *Adenocystis* and *Himantothallus* are much richer in mineral components (25—46% of ash in dry weight material), most of all in sodium, potassium and halogens, than the thallophytic algae from other climatic zones. On the other hand they are very scant of nitrogen and poor in sulphur, except *Himantothallus grandifolius*, and in magnesium and calcium, except *Adenocystis utricularis*. It is known from the reports

of Baraškov (1972) that halogens (chlorine, bromine and iodine in particular) form numerous compounds in combine with organic substances and their content in marine thallophytic algae of the brown, green, and red algae group may amount to 10 per cent or more.

From the analysed amino acids (Table III) in the examined species of algae the following are predominant: in *Monostroma hariotti* — Gly, Ala, Leu, Asp, Glu, and Pro; in *Adenocystis utricularis* and *Himantothallus grandifolius* — Ala, Asp, Glu; in *Leptosomia simplex* — Gly, Ala, Val, Leu, Ile, Asp, Glu, Arg, Lys and Phe. The smallest quantities of the following amino acids were noted: in *Monostroma hariotti* — Ser, Thr, Cys, Met, His and Tyr; in *Adenocystis utricularis* — Ser, Thr, Cys, Met, Pro, His and Tyr; in *Himantothallus grandifolius* — Ile, Ser, Thr, Cys, Arg, His and Tyr; in *Leptosomia simplex* — Ser, Cys, His and Tyr.

Table III.

Amino-acids composition of thallophytic algae of the Antarctic*)

Amino-acids content (% of dry wt.)	*Monostroma hariotti* (green algae)	*Adenocystis utricularis* (brown algae)	*Himantothallus grandifolius* (brown algae)	*Leptosomia simplex* (red algae)
Glycine (Gly)	1.03(±0.03)	0.35(±0.04)	0.39(±0.05)	1.34(±0.08)
Alanine (Ala)	1.29(±0.02)	0.90(±0.16)	1.03(±0.11)	1.55(±0.12)
Valine (Val)	0.86(±0.04)	0.41(±0.10)	0.46(±0.05	1.18(±0.10)
Leucine (Leu)	1.06(±0.03)	0.45(±0.08)	0.48(±0.02)	1.29(±0.07)
Isoleucine (Ile)	0.61(±0.02)	0.41(±0.07)	0.29(±0.03)	1.12(±0.05)
Serine (Ser)	0.37(±0.05)	0.14(±0.03)	0.16(±0.04)	0.50(±0.05)
Threonine (Thr)	0.42(±0.05)	0.17(±0.02)	0.21(±0.05)	0.72(±0.07)
Cysteine (Cys)	0.40(±0.06)	0.23(±0.03)	0.25(±0.03)	0.36(±0.06)
Methionine (Met)	0.48(±0.04)	0.28(±0.06)	0.32(±0.04)	0.83(±0.05)
Asparaginic acid (Asp)	1.32(±0.07)	0.83(±0.09)	0.76(±0.02)	2.21(±0.18)
Glutaminic acid (Glu)	1.46(±0.20)	0.89(±0.08)	0.97(±0.08)	2.03(±0.13)
Arginine (Arg)	0.81(±0.08)	0.32(±0.03)	0.30(±0.03)	1.44(±0.08)
Lysine (Lys)	0.78(±0.05)	0.37(±0.05)	0.45(±0.06)	1.18(±0.05)
Proline (Pro)	1.55(±0.14)	0.28(±0.04)	0.34(±0.04)	0.75(±0.09)
Histidine (His)	0.23(±0.03)	0.15(±0.03)	0.19(±0.02)	0.33(±0.03)
Phenylalanine (Phe)	0.71(±0.10)	0.33(±0.05)	0.38(±0.05)	1.19(±0.10)
Tyrosine (Tyr)	0.29(±0.07)	0.19(±0.04)	0.22(±0.03)	0.47(±0.04)
Total	13.67(±1.08)	6.70(±1.00)	7.20(±0.75)	18.49(±1.35)

*) mean values from 2—3 samples of the analysed algae

Quantitatively, *Leptosomia simplex* (red algae) is the richest in amino acids, *Monostroma hariotti* (green algae) is poorer (by 25—30%) and still poorer (by 60—65%), as compared with red algae, are brown algae (*Adenocystis utricularis* and *Himantothallus grandifolius*).

Referring to the data from the literature (Lewin 1962, Baraškov 1972, Stewart 1974) the Antarctic macroalgae under investigation, especially brown algae as compared with the marine thallophytic algae of tropical and temperate climates, are quantitatively much poorer in amino acids, particularly in such as: Ser, Thr, Cys, Met, Pro, His and Tyr.

Table IV.

Fatty-acids content of thallophytic algae of the Antarctic*)

Fatty acids (percent of the total)	*Monostroma hariotti* (green algae)	*Adenocystis utricularis* (brown algae)	*Himantothallus grandifolius* (brown algae)	*Leptosomia simplex* (red algae)
Caprinoic $C_{10:0}$	1.59(±0.61)	0.66(±0.11)	—	1.76(±0.61)
Lauric $C_{12:0}$	1.66(±0.16)	2.22(±0.46)	1.20(±0.37)	3.55(±0.35)
Myristic $C_{14:0}$	4.62(±0.28)	5.19(±0.53)	4.97(±0.69)	6.63(±0.57)
Palmitic $C_{16:0}$	14.64(±1.18)	17.99(±1.37)	15.90(±1.50)	18.27(±2.33)
Palmitoleic $C_{16:1}$	6.08(±0.21)	4.53(±1.06)	6.86(±0.56)	9.97(±1.67)
Stearic $C_{18:0}$	4.83(±0.49)	5.03(±0.73)	5.48(±0.24)	4.58(±0.96)
Oleic $C_{18:1}$	8.57(±0.71)	5.57(±1.68)	8.38(±0.32)	8.42(±0.58)
Linoleic $C_{18:2}$	2.77(±0.14)	5.80(±0.24)	2.75(±0.57)	5.26(±1.02)
Linolenic $C_{18:3}$	2.16(±0.10)	2.97(±0.75)	0.65(±0.10)	1.81(±0.49)
Eicozenic $C_{20:1}$	2.90(±0.50)	4.56(±0.61)	1.12(±0.20)	3.19(±0.28)
? $C_{20:2}$	3.61(±0.71)	5.94(±0.53)	2.18(±0.12)	2.15(±0.65)
? $C_{20:4}$	1.68(±0.38)	5.38(±0.21)	4.52(±0.28)	4.51(±1.07)
Eurucic $C_{22:1}$	11.33(±0.24)	6.19(±1.17)	—	7.80(±0.68)
? $C_{22:2}$	—	—	7.39(±0.93)	—
? $C_{22:3}$	3.13(±0.53)	4.95(±0.97)	9.59(±0.99)	2.63(±0.13)
? $C_{22:4}$	—	4.35(±0.60)	—	—
Lignoceric $C_{24:0}$	19.13(±0.74)	—	—	—
? $C_{24:1}$	—	18.67(±1.13)	25.83(±2.19)	19.47(±1.53)
? $C_{24:2}$	11.30(±1.81)	—	—	—
? $C_{24:4}$	—	—	3.18(±0.94)	—
Saturated acids	46.47(±3.46)	31.09(±3.20)	27.55(±2.80)	34.79(±4.82)
Unsaturated acids	53.53(±5.33)	68.91(±8.95)	72.45(±7.20)	65.21(±8.10)

*) Mean values of three analyses

The following fatty-acids were identified in the examined species of Antarctic algae (Table IV): $C_{10:0}$, $C_{12:0}$, $C_{14:0}$, $C_{16:0}$, $C_{16:1}$, $C_{18:0}$, $C_{18:1}$, $C_{18:2}$, $C_{18:3}$, $C_{20:1}$, $C_{20:2}$, $C_{20:4}$, $C_{22:1}$, $C_{22:2}$, $C_{22:3}$, $C_{22:4}$, $C_{24:0}$, $C_{24:1}$, $C_{24:2}$, $C_{24:4}$. From the analysed fatty-acids the greatest quantities of: $C_{16:0}$, $C_{18:1}$, $C_{22:1}$, $C_{24:0}$ and $C_{24:2}$ were found in *Monostroma hariotti;* $C_{16:0}$, $C_{22:1}$, and $C_{24:1}$ in *Adenocystis utricularis;* $C_{16:0}$, $C_{16:1}$, $C_{18:1}$, $C_{22:2}$, $C_{22:3}$ and $C_{24:1}$ in *Himantothallus grandifolius;* $C_{16:0}$, $C_{16:1}$, $C_{18:1}$, $C_{22:1}$, and $C_{24:1}$ in *Leptosomia simplex*. Among the fatty-acids occurring in smallest quantities were: $C_{10:0}$, $C_{12:0}$ and $C_{20:4}$ in *Monostroma hariotti*; $C_{10:0}$, and $C_{12:0}$ in *Adenocystis utricularis;* $C_{12:0}$, $C_{18:3}$, $C_{20:1}$ and $C_{\cdot\cdot}$ in *Himantothallus grandifolius;* $C_{10:0}$, $C_{18:3}$ and $C_{20:2}$ in *Leptosomia simplex*.

The content of unsaturated fatty acids is much higher than the content of saturated fatty acids in the analysed algae. The quotient of unsaturated: saturated acids ratio is the highest in brown algae, amounting to 2.63 in *Himantothallus grandifolius* and 2.22 in *Adenocystis utricularis;* much lower, about 1.59, in red algae (*Leptosomia simplex)*; the lowest, hardly 1.15, in green algae (*Monostroma hariotti*). On the whole, the analysis shows the highest content of the following fatty acids: $C_{16:0}$, $C_{16:1}$, $C_{18:1}$, $C_{22:1}$, $C_{22:3}$, $C_{24:0}$, $C_{24:1}$, $C_{24:2}$ and the lowest content of: $C_{10:0}$, $C_{12:0}$, $C_{18:3}$, $C_{20:1}$, and $C_{20:2}$.

In comparison with the data from the literature (Lewin 1962, Baraškov 1972, Matucha, Zilka and Svihel 1972, Waaland 1973, Stewart 1974, Czerpak and Obrusiewicz 1977), dealing with the chemism of lipids in tallophytic marine algae from the temperate and tropical climatic zones, the macroalgae from the Antractic inshore waters are very rich in unsaturated fatty, acids, containing more than 20 atoms of carbon: $C_{22:(1-4)}$ and $C_{24:(1-4)}$ and considerably poorer in fatty acids: $C_{10:0}$, $C_{12:0}$, $C_{14:0}$, $C_{18:1}$ and $C_{18:3}$.

In result of chromatographic and spectrophotometic analyses (Table V) the following carotenes: β, β-, β, ε-, β, ψ- and ε, ε-carotene and xanthophylls: 2-hydroxy-β-carotene, α-and β-cryptoxanthin, lutein, siphonaxanthin, siphonein, zeaxanthin and neoxanthin, were identified in *Monostroma hariotti* (green algae). The following carotenes: β, β- and ε, ε-carotene and xanthophylls: echinenone, β-cryptoxanthin, diatoxanthin, lutein, fuco-xanthinol, fucoxanthin, zeaxanthin, antheraxanthin, diadinoxanthin, neofucoxanthin and neoxanthin, were detected in brown algae (*Adenocystis utricularis* and *Himantothallus grandifolius)*. The presence of β, β- and β, ε-carotene and such xanthophylls as: echinenone, β-cryptoxanthin, lutein, zeaxanthin, antheraxanthin, violaxanthin, fucoxanthin and neoxanthin, was noted in *Leptosomia simplex* (red algae). The highest values of carotenes, especially of β, β- and β, ε-carotene were recorded in green algae, lower by a half in red algae and the lowest in brown algae (1/8—1/13 of the values for green algae). Xantophylls predominating in *Monostroma hariotti* are: siphonaxanthin (43% of the total value of carotenoids), siphonein, neoxanthin and zeaxanthin; in *Adenocystis utricularis* and *Himantothallus grandifolius* — fucoxanthin (27—43% of the total value of carotenoids), lutein, fucoxanthinol, and antheraxanthin; in *Leptosomia simplex* — zeaxanthin (55% of the total value of carotenoids), β-cryptoxanthin and lutein.

Qualitatively, the richest in carotenoids are the analysed species of brown and green algae, the poorest — red algae. As regards the total content of carotenoids the greatest quantities were noted in green algae (ca. 85% $\mu \cdot g^{-1}$ wet weight), considerably smaller in red algae (ca. 40 $\mu g \cdot g^{-1}$ wet weight) and the smallest in brown algae (10—15 $\mu g \cdot g^{-1}$ wet weight). Our studies and the data from the literature (Lewin 1962, Jensen 1966, Goedheer 1970, Baraškov 1972, Stewart 1974, Goodwin 1976, Czerpak 1977, Liaaen-Jensen 1977, Yokohama et al. 1977, Kageyama and Yokohama 1978, Arnesen, Hallenstvet and Liaaen-Jensen 1979, Czeczuga 1979) show that thallophytic algae of the Antractic — green and red algae and especially brown algae — are quantitatively poor in carotenoids (carotenes and xanthophylls) as compared with similar taxonomical groups from considerably warmer and more photic climatic zones.

The results from our studies compared with the data from the literature (Lewin 1962, Baraškov 1972, Stewart 1974, Czerpak and Obrusiewicz 1977, Liaaen-Jensen 1977, Yokohama et al. 1977, Czeczuga 1979) indicate hat the analysed thallophytic algae of the Antarctic, especially brown algae (above all *Adenocystis utricularis*) are most aboundant in mineral elements, in particular sodium, potassium and halogens. A high dry weight content, about 17.5% of the biomass on the average, is noted

in green algae (*Monostroma hariotti*), while in brown and red algae this value is in the range of 11—13% of the biomass. Moreover, macroalgae of the Antarctic have very high content of structural and may be also reserve polysaccharides, in the analysed brown algae amounting to 40—60%, in red algae 45—55% and in green algae — 50–60%. The remaining organic substances, such as: proteins, amino acids, lipids, fatty acids, reduction saccharides, chlorophylls, and carotenoids occur in the analysed thallophytic algae of the Antarctic in small quantities as compared with taxonomically analogical algae from marine environments with more favourable hydrochemical and climatic conditions.

4. Summary

Chemical composition of the following species of the Antarctic macroalgae: *Adenocystis utricularis* and *Himantothallus grandifolius* (brown algae), *Leptosomia simplex* (red algae) and *Monostroma hariotti* (green algae) was examined using the methods of gravimetric and volumetric analyses, extraction, wet and dry mineralization, gas and adsorption (thin-layer and column) chromatography, autoanalyses, spectrophotometry and spectrometry of atomic absorption.

The results of the studies show (Table I) that *Monostroma hariotti* has very high dry weight content (ca. 17.5% of wet weight), whereas the total protein content of *Leptosomia simplex* is higher (22.21% of dry weight) than that of *Monostroma hariotti* (18.32% of dry wieght). The analysed brown algae, *Adenocystis utricularis* in particular, are very rich in mineral elements (32.5—46.0% of ash in dry weight algae, Table I), especially in sodium, potassium, magnesium, calcium, iodine and sulphur (Table II).

The content of amino acids, especially of Gly, Ala, Val, Leu, Ile, Asp, Glu, Arg, and Lys, is the highest in *Leptosomia simplex* (Table III), as compared with the values for other investigated algae.

Among the fatty acids the content of $C_{16:0}$, $C_{16:1}$, $C_{18:1}$, $C_{22:1}$, $C_{22:3}$, $C_{24:0}$, $C_{24:1}$, and $C_{24:2}$ is the highest in the analysed algae; the quotient of saturated: unsaturated acids ratio is the highest in brown algae averaging 2.22—2.63 (Table IV).

Qualitatively and quantitatively, brown algae and green algae are the richest in carotenoids, especially in: β, β-caroten, β, ε-caroten, fucoxanthin, fucoxanthinol, siphonaxanthin, siphonein, and lutein: whereas the total content of carotenoids is the highest (ca. 85 $\mu g \cdot g^{-1}$ of biomass) in *Monostroma hariotti* (Table V).

The obtained results indicate that the analysed macroalgae of the Antarctic, brown algae in particular, are most abundant in mineral elements and polysaccharides of structural or reserve character, but considerably poorer in the remaining organic substances, as compared with taxonomically similar algae growing in more favourable hydrochemical and climatic conditions.

5. Резюме

Применяя метод весового и объёмного анализа экстракции мокрой и сухой минерализации, хрометографии газовой и адсорбционной (тонкослоевой и колонной), автоанализа, спектрофотометрии и атомной спектрометрии адсорбции исследовано химический состав следуёщих видов макроальг Антарктики: *Adenocystis utricularis* и *Himantothallus grandifolius* (бурые водоросли), *Leptosomia simplex* (красные водоросли) и *Monostroma hariotti* (зелёные водоросли).

Table V.

Chromatographic distribution and spectrophotometrical qualitative-quantitative characteristic of carotenoids in thallophytic algae of the Antarctic *)

Eluents used in adsorption column chromatography **)	Maxima absorption of carotenoids in dif-ferent solvents (nm)	Mole coefficients of extinction ($E_{1\%} \cdot cm^{-1}$) ***)	Identified carotenoids	Carotenoids content ($\mu g \cdot g^{-1}$ of biomass)			
				Monostroma hariotti (green algae)	*Adenocystis utricularis* (brown algae)	*Himantothallus grandifolius* (brown algae)	*Leptosomia simplex* (red algae)
100% petroleum ether (boiling point 40—50°C)	421,451,478 (en)	2600 (en)	β,β-carotene	16.42(±0.89)	2.80(±0.11)	1.79(±0.06)	9.45(±0.16)
0.5—1% of acetone in petroleum ether	420,445,474 (en)	2800 (en)	β,ε-carotene	5.45(±0.41)	—	—	3.02(±0.13)
1—1.5% of acetone in petroleum ether	413,440,470 (h)	2900 (h)	ε,ε-catorene	1.12(±0.07)?	0.09(±0.02)	0.07(±0.01)	—
1.5—2% of acetone in petroleum ether	436,460,495 (en)	3000 (en)	β,ψ-carotene	1.16(±0.09)	—	—	—
4—5% of acetone in petroleum ether	430,459,480 (h)	2360 (h)	2-hydroxy-β-carotene	0.36(±0.03)?	—	—	—
5—7% of acetone in petroleum ether	458 (en)	2158 (en)	echinenone	—	0.07(±0.01)	0.08(±0.02)	0.15(±0.02)
8—9% of acetone in petroleum ether	422,446,475 (h)	2625 (h)	α-cryptoxanthin	0.23(±0.02)	—	—	—
10—12% of acetone in petroleum ether	425,452,481 (h)	2460 (h)	β-cryptoxanthin	0.38(±0.03)	0.15(±0.02)	0.23(±0.03)	1.56(±0.12)
15—20% of acetone in petroleum ether	431,451,483 (en)	2050 (en)	diatoxanthin	—	0.41(±0.03)	0.56(±0.06)	—
35—40% of acetone in petroleum ether	419,444,473 (en)	2550 (en)	lutein	0.61(±0.05)	1.96(±0.12)	2.84(±0.09)	1.24(±0.07)
50—60% of acetone in petroleum ether	415,447,469 (en)	1980 (en)	siphonaxanthin	35.97(±1.48)	—	—	—
60—75% of acetone in petroleum ether	400,421,449 (en)	2140 (en)	fucoxanthinol	—	1.23(±0.08)	0.73(±0.05)	—
90—100% of acetone in petroleum ether	429,450,478 (a)	2250 (a)	zeaxanthin	3.36(±0.17)	0.21(±0.01)	0.19(±0.03)	20.65(±1.24)
2—4% of n-propanol in acetone	421,443,471 (h)	2310 (h)	antheraxanthin	—	—	1.15(±0.11)?	0.28(±0.03)?
5—7% of n-propanol in acetone	451,474 (en)	1870 (en)	siphonein	13.92(±0.78)	—	—	—
8—10% of n-propanol in acetone	418,445,473 (h)	2400 (h)	diadinoxanthin	—	0.52(±0.04)?	—	—
12—15% of n-propanol in acetone	428,454,483 (b)	2215 (b)	violaxanthin	—	—	—	0.25(±0.03)
25—30% of n-propanol in acetone	426,446,475 (en)	2420 (en)	fucoxanthin	—	2.93(±0.17)	6.46(±0.35)	0.61(±0.04)
100% of methanol	427,449,476 (en)	2380 (en)	neofucoxanthin	—	0.34(±0.03)?	0.63(±0.05)?	—
5—7% of acetic acid in ethyl ether	417,438,467 (h)	2270 (h)	neoxanthin	4.75(±0.21)	0.25(±0.02)	0.36(±0.03)	0.29(±0.04)
			Total carotenoids	83.73(±4.23)	10.96(±0.66)	15.09(±0.89)	37.50(±1.88)

*) mean values from 3—4 analyses

**) macherey Nagel and Düren Co. (DDR) neutral adsorbent Al_2O_3 was used

***) mole coefficients after: Jensen (1960), Foppen (1971), Isler, Gutmann and Solms (1971), Goodwin (1976) (a) acetone, (b) benzene, (en)petroleum ether, (h) hexane, ? identification not completely certain

В проведенных исследованиях доказано, что *Monostroma hariotti* содержит большие количества сухой массы около 17,5% свежей массы (таблица I), зато значительные количества общих белок (таблица I) у *Leptosomia simplex* — 22,21% и *Monostroma hariotti* - 18,32% сухой массы. Зато анализованные бурые водоросли особенно *Adenocastis utricularis* являются очень богатыми минеральными элементами (32,5—46,0% пепела в сухой массе водорослей, таблица I), особенно натрий, калий, молний, кальций, лид, серу (таблица II).

Содержание аминокислот, особенно Gly, Ala, Val, Leu, Ile, Asp, Glu, Arg и Lys самое большое среди исследованных водорослей и *Leptosomia simplex* (таблица III).

В анализованных водорослях констатировано самое большое содержание жировых кислот $C_{16:0}$, $C_{16:1}$, $C_{18:1}$, $C_{22:1}$, $C_{22:3}$, $C_{24:0}$, $C_{24:1}$ и $C_{25:2}$ при чём отношение ненасыщенных по насыщенных кислот самое большое у бурых водорослей в пределах 2,22—2,63 (таблица IV).

В качественно-количественном отношении, самые богатые каротеноидами особенно β, β-каротин, β, ε-каротин, фукоксантин, фукоксантинол, сифонаксантин, сифонеин и лютеин бурые водоросли и зелёные водоросли, зато их сумарное содержание самое большое у *Monostroma hariotti* около 85 $\mu g \cdot g^{-1}$ биомассы (таблица V).

Полученные итоги указывают, что анализированные макроальги Антарктики особенно бурые водоросли очень богаты минеральными элементами, а также полисахаридели со строительным и запасным характером а остальные органические субстанции значительно беднее по сравнению с похожими таксономическими водорослями проживающими в более благоприятных климатических и гидрохимических условиях.

6. Streszczenie

Stosując metody analizy wagowej i objętościowej, ekstrakcji, mineralizacji na mokro i sucho, chromatografii gazowej i adsorpcyjnej (cienkowarstwowej i kolumnowej), autoanalizy, spektrofotometrii oraz spektrometrii atomowej absorpcji, badano skład chemiczny następujących gatunków makroalg Antarktyki: *Adenocystis utricularis* i *Himantothallus grandifolius* (brunatnice), *Leptosomia simplex* (krasnorost) i *Monostroma hariotti* (zielenica).

W efekcie przeprowadzonych badań wykazano, że *Monostroma hariotti* zawiera spore ilości suchej masy (około 17,5% świeżej masy (tabela I), zaś znaczne ilości białka ogólnego (tabela I) u *Leptosomia simplex* — 22,21% i *Monostroma hariotti* — 18.32% suchej masy. Natomiast analizowane brunatnice zwłaszcza *Adenocystis utricularis* są bardzo zasobne w składniki mineralne (32.5—46.0% popiołu w suchej masie glonów, tabela I), szczególnie w sód, potas, magnez, wapń, jod i siarkę (tabela II).

Zawartość aminokwasów, zwłaszcza Gly, Ala, Val, Leu, Ile, Asp, Glu, Arg, i Lys jest największa spośród badanych glonów u *Leptosomia simplex* (tabela III).

W analizowanych glonach stwierdzono największą zawartość kwasów tłuszczowych $C_{16:0}$, $C_{16:1}$, $C_{18:1}$, $C_{22:1}$, $C_{22:3}$, $C_{24:1}$ i $C_{24:0}$, przy tym stosunek nienasyconych do nasyconych kwasów jest największy u brunatnic w granicach 2,22—2,63 (tabela IV).

Pod względem jakościowo-ilościowym najbogatsze w karotenoidy zwłaszcza β, β-karoten, β, ε-karoten, fukoksantynę, fukoksantinol, syfonaksantynę, syfoneinę i luteinę są brunatnice i zielenice, zaś sumaryczna ich zawartość jest największa u *Monostroma hariotti* — około 85 $\mu g \cdot g^{-1}$ biomasy (tabela V).

Uzyskane wyniki wskazują, że analizowane makroalgi Antarktyki, szczególnie brunatnice, są bardzo zasobne w składniki mineralne, a także polisacharydy o charakterze budulcowym bądź zapasowym, zaś w pozostałe substancje organiczne są znacznie uboższe w porównaniu do podobnych taksomicznie glonów żyjących w bardziej sprzyjających warunkach klimatycznych i hydrochemicznych.

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Paper received 5 December 1980

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