SHORT COMMUNICATION

Carboxylic acids from brown algae *Fucus vesiculosus* and *Padina pavonica*

Karboxylové kyseliny z hnědých řas *Fucus vesiculosus* a *Padina pavonica*

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Summary

Using the gas chromatographic–mass spectrometric method, the content of 28 carboxylic acids was determined in the thalli of *Fucus vesiculosus*, palmitic, oxalic and malic acids predominating. In the thalli of *Padina pavonica*, the content of 27 carboxylic acids was determined. Palmitic, oxalic and oleic acids prevail.

Key words: brown algae • *Fucus vesiculosus* • *Padina pavonica*, carboxylic acids • gas chromatography • mass spectrometry.

Souhrn

S použitím metody plynové chromatografie-hmotnostní spektrometrie byl ve stélkách chaluhy bublinaté (*Fucus vesiculosus*) stanoven obsah 28 karboxylových kyselin. Převládají kyselina palmitová, šťavelová a jablečná. Ve stélkách řasy *Padina pavonica* bylo zjištěno 27 karboxylových kyselin. Převládají kyselina palmitová, šťavelová a olejová.

Klíčová slova: hnědé řasy • *Fucus vesiculosus* • *Padina pavonica* • karboxylové kyseliny • plynová chromatografie • hmotnostní spektrometrie

Introduction

Fucus vesiculosus L. (Fucaceae) and *Padina pavonica* (L.) Gaill. (Dictyotaceae) belong to the class of brown algae (Phaeophyceae). *F. vesiculosus* is widespread throughout the Atlantic Ocean, in the eastern and western areas of the Mediterranean Sea; in Russia – in the White Sea, the Barents Sea, the Kara Sea, and the Baltic Sea. *P. pavonica* grows along the coasts of Southern Europe and along the Atlantic coasts of Central America. Industrial harvesting of raw material is possible in the Mediterranean Sea. The most studied compounds of brown algae are polysaccharides of the fucan type and alginates. The literature has shown that fucans and fucoidans possess anti-inflammatory, antibacterial, antiviral, immunomodulatory, antithrombotic, anticoagulant, fibrinolytic, hepatoprotective, antitumor effects; derivatives of alginic acid remove radionuclides from the body, have hemostatic, antitumor, antimicrobial, immunomodulatory, anti-inflammatory and antispasmodic effects[1–3].

We have already studied amino acid, polysaccharide, macro- and microelement composition of *F. vesiculosus* and *P. pavonica* earlier[1, 4]. The purpose of this paper was to study carboxylic acids of the thalli of *F. vesiculosus* and *P. pavonica*.

Experimental part

The thalli of *F. vesiculosus* and *P. pavonica* were harvested in July 2015 in the coastal strip of the Mediterranean Sea near the city of Tyre, Lebanon. The identification of raw material was carried out based on the algae herbarium stored in the herbarium fund of the Department of Botany at the National University of Pharmacy (Sample No. 518, Ass. Prof. Seraya L. is responsible for the identification). Carboxylic acids were determined using an Agilent Technologies 6890 chromatograph with a 5973 mass-spectrometric detector. Samples for the analysis were prepared by the method described previously[5]. For the identification of components, mass spectra libraries NIST05 and WILEY 2007 with a total number of spectra > 470000 in a combination with the programs for identification AMDIS and NIST were used. For quantitative calculations, the internal standard method was used. The results of the study are presented in Table 1.

Results and discussion

The content of 28 carboxylic acids was determined in the thalli of *F. vesiculosus* (2 hydroxy acids, 5 dibasic, 7 aromatic, 13 fatty acids, 1 keto acid), from which palmitic (4249.4 mg/kg), oxalic (1274.0 mg/kg) and malic (1177.5 mg/kg) acids predominate. In the thalli of *P. pavonica*, the content of 27 carboxylic acids (2 hydroxy

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*Table 1. Content of Carboxylic Acids of Thalli of F. vesiculosus and P. pavonica, mg/kg**

Acid	RI**	*F. vesiculosus*	*P. pavonica*
Caproic	1120	3.8	116.5
Oxalic	1359	1274.0	2996.9
Malonic	1477	213.1	643.6
Levulinic	1501	99.1	167.8
Fumaric	1516	–	7.3
Succinic	1575	273.9	576.0
Benzoic	1600	2.6	30.2
Glutaric	1686	82.8	–
Phenylacetic	1746	7.1	28.4
Salicylic	1757	3.6	–
Lauric	1793	57.6	23.8
Myristic	1994	97.2	515.7
Malic	2008	1177.5	414.5
Pentadecanoic	2101	159.7	70.9
Azelaic	2114	130.9	77.1
Palmitic	2204	4249.4	4387.5
Palmitoleic	2223	109.4	103.2
Margaric	2292	–	12.5
Citric	2367	403.3	483.3
Stearic	2384	100.1	333.5
Oleic	2402	195.3	1253.8
Linoleic	2443	44.9	65.9
Linolenic	2490	46.5	48.6
Vanillic	2522	4.9	16.0
2-Hydroxypalmitic	2542	–	101.1
Arachidic	2543	60.0	92.7
Behenic	2698	79.2	–
Syringic	2793	7.3	–
p-Coumaric	2801	–	395.4
Gentisic	2805	13.9	8.0
Lignocerinic	2843	51.0	25.5
Ferulic	2919	83.1	–

**Of air-dried raw material mass, **Retention index of acid methyl ester*

acids, 5 dibasic, 5 aromatic, 14 fatty acids, 1 keto acid) was determined. Palmitic (4387.5 mg/kg), oxalic (2996.9 mg/kg) and oleic (1253.8 mg/kg) acids prevail. The total content of carboxylic acids in the thalli of *F. vesiculosus* is 0.9 %, 58 % of which are fatty acids. The total content of carboxylic acids in the thalli of *P. pavonica* is 1.3 %, 55 % of which are fatty acids. If the composition of fatty acids of the thalli of these algae has been studied earlier, the composition of the other carboxylic acids has not been studied sufficiently[1, 6, 7]. Wahbeh M. I. reported that in the thalli of *P. pavonica* unsaturated oleic and hexadecadienoic acids predominated among the fatty acids, whereas in the present study saturated palmitic and unsaturated oleic acids predominate, which coincides with earlier studies[6]. In the studies of Jones A. L. and Harwood J. L., as in our studies, saturated palmitic acid prevailed in the thalli of *F. vesiculosus*, and oleic acid was the dominant monounsaturated acid[7]. We have identified in the thalli of *F. vesiculosus* a dibasic glutaric acid and aromatic salicylic, syringic and ferulic acids; and in the thalli of *P. pavonica*, dibasic fumaric acid and aromatic p-coumaric acid. These substances can serve as chemomarkers in the identification of raw materials. The results of the chromatography-mass spectrometric study of the thalli of *F. vesiculosus* and *P. pavonica* show the prospects of further phytochemical and pharmacological research.

Conflicts of interest: none.

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