

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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Received October 14, 2017 / Accepted October 30, 2017

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 previously⁵). 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** | <i>F. vesiculosus</i> | <i>P. pavonica</i> |
|-------------------|------|-----------------------|--------------------|
| 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 |
| Lignocericinic | 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 studies⁶. 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 acid⁷. 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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