



**UN FOOD
CONFERENCE**
University of Belgrade
210th Anniversary
OCTOBER 5-6 2018

**PROGRAM
I
ZBORNIK RADOVA**

*Programme
&
Book of Abstracts*

Beograd, 5 i 6 oktobar 2018
Belgrade, Octobre 5-6, 2018

CIP-Kategorizacija u publikaciji
Narodna biblioteka Srbije, Beograd

Univerzitet u Beogradu
UNIFOOD CONFERENCE (2018; Beograd)
Program; i zbornik radova= Programme; & Book of Abstracts/
Beograd, 5 i 6 oktobar 2018 = Belgrade, Octobre 5-6 2018
[organizator] Univerzitet u Beogradu; [organized by] University of Belgrade
[urednici, editors Marina Soković, Živoslav Tešić] Beograd, Univerzitet u Beogradu

Radovi na srp i engl. jeziku – Tekst ćir i lat- Tiraž

ISBN 978-86-7522-060-2

UNIFOOD Konferencija, Beograd, 5-6 oktobar 2018
PROGRAM I ZBORNIK RADOVA

UNIFOOD Conference, Belgrade Octobre 5-6 2018
Programme and Book of Abstracts

Izdaje / Published by

Univerzitet u Beogradu / University of Belgrade

Studentski trg 1, 11000 Beograd

Tel/fax ; www.bg.ac.rs, email

Za izdavača / For Publisher

Vladimir Bumbaširević, rektor

Urednici / Editors

Marina Soković

Živoslav Tešić

Dizajn korica i kompjuterska obrada teksta / Cover Design Layout

Tomislav Tosti

Tiraž / Circulation

ISBN 978-86-7522-060-2



Sadržaj fenolnih jedinjenja i antioksidativna aktivnost dve vrste roda *Asplenium* u različitim fazama životnog ciklusa

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Papрати su kroz istoriju smatrane značajnim izvorom lekovitih sirovina, hranljivih materija i vlakana. I pored toga, one su nedovoljno istražene u fitohemijskom smislu, a naročito haploidni gametofit koji se odlikuje krhkom građom i mikroskopskim dimenzijama, što otežava prikupljanje dovoljne količine biljnog materijala za hemijske analize. S ciljem da se opravda etnofarmakološki značaj paprati iz roda *Asplenium*, ovo istraživanje je fokusirano na karakterizaciju fenolnih jedinjenja i analizu antioksidativnih svojstava sporofita i gametofita vrsta *Asplenium adiantum-nigrum* L. i *A. ruta-muraria* L., koje su široko rasprostranjene u Evropi. Metanolni ekstrakti gametofita i sporofita (listova, rizoma i korenova) su podvrgnuti UHPLC/DAD/(-)HESI-MS/MS analizi, nakon čega je utvrđena njihova antioksidativna aktivnost (ABTS i DPPH test).

Sastav fenolnih jedinjenja i antioksidativna aktivnost analiziranih vrsta ukazuju na species-specifične profile koji su uslovljeni fazom životnog ciklusa paprati. Identifikovana fenolna jedinjenja pripadaju klasama fenolnih kiselina (hidroksibenzoične i hidroksicimetne kiseline), flavonoidima (flavan-3-oli, flavonoli), i ksantonima. Sporofiti *A. adiantum-nigrum* su bogat izvor ksantona (mangiferina i mangiferin glikozida), koji predstavljaju potentne bioaktivne agense. Pored ksantona, gametofiti ove vrste sadrže značajne količine flavan-3-ola (epigalokatehin i epigalokatehin galat). Flavan-3-oli su prepoznati kao dominantna fenolna jedinjenja u sporofitima (galokatehin galat i epigalokatehin galat) i gametofitima (galokatehin i katehin) kod vrste *A. ruta-muraria*. Izražena antioksidativna aktivnost ekstrakata rizoma *A. adiantum-nigrum* i listova *A. ruta-muraria* može se pripisati visokom sadržaju ksantona i flavan-3-ola. Rezultati ukazuju na veliki antioksidativni potencijal ove dve vrste, čime je podržana njihova upotreba u tradicionalnoj medicini.

Phenolics content and antioxidant activity of two *Asplenium* species: life cycle-specific patterns

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Historically, ferns have been an important source of drugs, food, and fibers. Nevertheless, very few works have been done on their phytochemical characterization. Moreover, the haploid gametophyte phase of ferns has, probably due to the fragile structure, microscopic dimensions, and difficult collection, only rarely been the subject of phytochemical investigations. With the aim to support the ethnopharmacological importance of *Asplenium* species, the present work focuses on evaluating the phenolic content and antioxidant properties of sporophytes and gametophytes of *Asplenium adiantum-nigrum* L. and *A. ruta-muraria* L., two fern species widely distributed in Europe. Methanol extracts of gametophytes and sporophytes (fronds, rhizomes and roots) were subjected to UHPLC/DAD/(-)HESI-MS/MS analysis, and further to the evaluation of their scavenging capacities against ABTS^{•+} and DPPH[•].

Phenolics content and antioxidant activity of analyzed *Asplenium* species showed species-specific and life cycle-specific patterns. Identified phenolic compounds belong to the classes of phenolic acids (hydroxybenzoic and hydroxycinnamic acids), flavonoids (flavan-3-ols, flavonols), and xanthenes. Sporophytes of *A. adiantum-nigrum* are especially rich in xanthenes (mangiferin and mangiferin glycoside), potent bioactive compounds. Besides xanthenes, gametophytes contain significant amounts of flavan-3-ols (epigallocatechin and epigallocatechin gallate). Flavan-3-ols are also recognized as the major phenolic compounds in both *A. ruta-muraria* sporophytes (galocatechin gallate and epigallocatechin gallate) and gametophytes (galocatechin and catechin). The excellent antioxidant activity of *A. adiantum-nigrum* rhizomes and *A. ruta-muraria* fronds, against both DPPH and ABTS radicals, could be ascribed to the high content of xanthenes and flavan-3-ols, respectively. The results of the present study candidate these two fern species as potent antioxidant agents, thus supporting their traditional use.