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Quantification of Organochlorine Pesticides in Selected Food Samples by GC/ECD

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Keywords:

GC/ECD;
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Abstract: Some of organochlorine pesticides (OPCs) are widely used in agronomy. Nowadays most of them are banned by EU legislation and proper MRL values are established. Fifteen different OCPs: four isomers of HCH (α , β , γ and δ), heptachlor epoxide, heptachlor, aldrin, dieldrin, endrin, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT, α and β isomer of endosulphane, endosulphane sulphate were analyzed. The samples of oranges, lemons, strawberries, lettuces, apples and wheat that were obtained from local markets were analyzed. Extraction of OCPs and cleaning of extracted samples were performed by QuEChERS dispersive SPE method. The samples were analyzed by GC/ECD. Multiple pesticides were found in some samples, and value of investigated OCPs was higher than MRL values directed by EFSA. The most contaminated was lemon bark. In that sample four pesticides, γ -HCH, β -HCH, heptachlor epoxide and endrin, exceeded MRL values.

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Sažetak

Neki od organohlorinih pesticida (OCPs) imaju široku upotrebu u agronomiji. Većina njih je zabranjena odgovarajućim propisima Evropske unije sa uspostavljenim MRL vrijednostima. Petnaest različitih OCPs: četiri izomera HCH (α , β , δ , γ), heptahlor epoksid, heptahlor, aldrin, dieltrin, endrin, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT, α i β izomer endosulfana i endosulfan sulfat su analizirani. Ispitivani uzorci su bili: naranča, limun, zelena salata, jagoda, jabuka i pšenica. Ekstrakcija i prečišćavanje dobijenih uzoraka izvršeno je disperznom SPE po QuEChERS metodi. Uzorci su analizirani GC/ECD metodom. U pojedinim uzorcima je pronađeno više vrsta OCPs pesticida, i te vrijednosti su bile veće od dozvoljenih vrijednosti propisanih od strane EFSA. Najviše kontaminiran uzorak je limun, i to kora limuna. U tom uzorku su pronađena četiri pesticida, γ -HCH, β -HCH, heptahlor epoksid i endrin čije izmjerene vrijednosti prelaze vrijednosti MRL.



Determination of Certain Phenolic Compounds in *Crataegus monogyna* and *Crataegus microphylla* by HPLC-ED

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Keywords:

Crataegu monogyna Jacq.,
Crataegus microphylla C. Koch,
flavonoids,
phenolic acids,
HPLC-ED.

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Abstract: Investigations of *Crataegus* species is typically focused on the identification and quantification of flavonoids, phenolic acids and anthocyanins, which have been shown to have pharmacological activity. The main flavonoids and phenolic acids found in *Crataegus* species are hyperoside, vitexin, quercetin, rutin, chlorogenic acid, gallic acid and caffeic acid. The aim of the work was to determine the content of some phenolic compounds of two *Crataegus* species growing in Bosnia and Herzegovina. In this study, ethanolic extracts of fruits, leaves and flowers of *Crataegus monogyna* and *Crataegus microphylla* were prepared by Soxhlet and ultrasonic extraction. The content of hyperoside, caffeic acid and gallic acid were determined by HPLC method with electrochemical detection.

The content of hyperoside in the investigated extracts varied from 0 to 19.28 mg g⁻¹ of extract while content of gallic acid ranged from 0.015 to 1.76 mg g⁻¹ of extract, and caffeic acid whose content varied from 0.16 to 2.72 mg g⁻¹ extract.

Sažetak

Istraživanja vrsta roda *Crataegus* fokusirana su na identifikaciju i kvantifikaciju flavonoida, fenolskih kiselina i antocijanina, koji su pokazali da imaju farmakološko dejstvo. Glavni flavonoidi i fenolske kiseline pronađeni u vrsta roda *Crataegus* su hiperozid, viteksin, kvercetin, rutin, hlorogenska kiselina, galna kiselina i kafena kiselina. Cilj rada bio je određivanje sadržaja nekih fenolskih spojeva u različitim vrstama roda *Crataegus* koje rastu u Bosni i Hercegovini. U ovom istraživanju, etanolni ekstrakti plodova, lišća i cvijetova *Crataegus monogyna* i *Crataegus microphylla* su pripremljeni Soxhlet i ultrazvučnom ekstrakcijom. Sadržaj hiperozida, kafene kiselina i galne kiselina određen je HPLC metodom sa elektrohemijском detekcijom. Sadržaj hiperozida u ispitivanim ekstraktima je varirao od 0 do 19.28 mg g⁻¹ ekstrakta, galne kiselina se kretao od 0.015 do 1.76 mg g⁻¹ ekstrakta, a kafene kiselina od 0.16 do 2.72 mg g⁻¹ ekstrakta.



Tyrosinase and Lipxygenase Inhibition and Antioxidant Activity of an Aqueous Extract from *Epilobium angustifolium* L. Leaves

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Keywords:

Epilobium angustifolium L.,
tyrosinase,
lipxygenase inhibitory activities
and antioxidant effects.

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Abstract: Herbs have been utilized to treat acute and chronic disorders since thousand years. *Epilobium angustifolium* L. (Onagraceae) is used as herbal and digestive plant all over the world. The *Epilobium* extracts are reported to have analgesic, antimicrobial, antimotility, antiproliferative, antiinflammatory, antitumor and antiandrogenic activities. Phytochemical screenings of aerial parts of *Epilobium* species revealed the presence of steroids, triterpenes, fatty acids, phenolic acids, macrocyclic tannins and flavonoids. In the present study, the antioxidant activity and tyrosinase, lipxygenase inhibitor activities of *E. angustifolium* L. have been examined. Total phenolic and total flavonoid content, reducing power, superoxide anion radical scavenging, hydroxyl radical scavenging, 2,2-diphenyl-1-picryl-hydrazyl (DPPH) radical scavenging, 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) radical scavenging activities were used to evaluate the antioxidant activities. The results were compared with natural and synthetic antioxidants. The aqueous extract of *E. angustifolium* exhibited strong tyrosinase ($EC_{50} = 33.03 \pm 3.71 \mu\text{g/ml}$) and lipxygenase inhibitory activities ($EC_{50} = 0.57 \pm 0.06 \mu\text{g/ml}$). The extract also showed good antioxidant activity in all antioxidant tests. According to these results, *E. angustifolium* may be considered as an important source for pharmaceutical, cosmetic and food manufactures due to its tyrosinase, lipxygenase inhibitory activities and antioxidant effects.

Sažetak

Ljekovito bilje se koristi za liječenje akutnih i hroničnih poremećaja već hiljadama godina. *Epilobium angustifolium* L. (Onagraceae) je biljka koja se koristi u prehrani i liječenju širom svijeta. Kako navode izvještaji *Epilobium* ekstrakti imaju analgetsku, antimikrobnu, antidijaroijsku, antiproliferativnu, antiupalnu, antitumornu i antiandrogenu aktivnost. Fitohemijske provjere nadzemnih dijelova *Epilobium* vrsta otkrile su postojanje steroida, triterpena, masnih kiselina, fenolnih kiselina, makrocikličnih tanina i flavanoida. U ovom istraživanju antioksidativna i inhibitorska aktivnost tirozinaze i lipoksigenaze *E. angustifolium* L. je istražena. Ukupni sadržaj fenola i flavonoida, reduksijska moć, istiskivanje superoksidnog anionskog radikala, istiskivanje hidroksil radikala, istiskivanje 2,2-difenil-1-pikril-hidrazil (DPPH) radikala, istiskivanje 2,2'-azino-bis(3-etilbenzotiazolin-6-sulfonska kiselina) (ABTS) radikala su aktivnosti korištene za određivanje antioksidativne aktivnosti. Rezultati su uspoređeni sa prirodnim i sintetskim antioksidansima. Vodeni ekstrakt *E. angustifolium* je pokazao jaku tirozinazu ($EC_{50} = 33.03 \pm 3.71 \mu\text{g/ml}$) i lipoksigenazu inhibitorsku aktivnost ($EC_{50} = 0.57 \pm 0.06 \mu\text{g/ml}$). Ekstrakt je također pokazao dobru antioksidativnu aktivnost u svim antioksidativnim ispitivanjima. Sukladno ovim rezultatima, *E. angustifolium* se može smatrati kao značajan izvor za farmaceutsku, kozmetičku i prehrambenu proizvodnju zbog inhibitorske aktivnosti i antioksidativnih efekata tirozinaze i lipoksigenaze.



Total Polyphenols, Flavonoids and Antioxidant Activity of Methanolic Extracts of Some *Crataegus* Fruits

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Keywords:

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Antioxidant activity.

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Abstract: Fruits of two *Crataegus* species (*C. monogyna* and *C. rhipidophylla*) from natural populations were analyzed for total polyphenols, total flavonoids and antioxidant activity using aqueous methanol and acidified aqueous methanol extraction mixtures. Phenolic and flavonoid content were determined using standard spectrophotometric assays. Results for total polyphenols were expressed as gallic acid equivalents and for total flavonoids, rutin and quercetin were used as standards. Generally, in both extraction systems higher content of total polyphenols and total flavonoids was found for *C. monogyna*. In aqueous methanol extracts total polyphenols ranged between 23.66–28.50 mg GAE/g DW; total flavonoids ranged between 0.99–1.689 mg RE/g DW and 0.436–0.806 mg QE/g DW. In acidified aqueous methanol extracts total polyphenols ranged between 24.93–28.62 mg GAE/g DW; total flavonoids ranged between 0.964–1.530 mg RE/g DW and 0.151–0.213 mg QE/g DW. The highest antioxidant activity determined by DPPH showed *C. monogyna* with higher values in acidified methanolic extracts. The highest correlation was determined between total polyphenols and antioxidant activity in aqueous methanol extracts. The results obtained in this study indicate that investigated hawthorn fruits can be considered as a natural source of phenolic compounds with good antioxidant capacity.

Sažetak

Plodovi dvije vrste gloga (*C. monogyna* i *C. rhipidophylla*) iz prirodnih populacija analizirani su na sadržaj ukupnih polifenola, ukupnih flavonoida i antioksidacijsku aktivnost u vodeno-metanolnim i zakiseljenim vodeno-metanolnim ekstraktima. Sadržaj fenola i flavonoida je određen standardnim spektrofotometrijskim metodama. Rezultati za ukupne polifenole su izraženi u ekvivalentima galne kiseline dok su rutin i kvercetin korišteni kao standardi u određivanju ukupnih flavonoida. Generalno, u oba ekstrakciona sistema veći sadržaj ukupnih polifenola i ukupnih flavonoida je određen za *C. monogyna*. U vodeno-metanolnim ekstraktima sadržaj ukupnih fenola je bio između 23.66–28.50 mg GAE/g s.u; ukupnih flavonoida između 0.99–1.689 mg RE/g s.u. i 0.436–0.806 mg QE/g s.u. U zakiseljenim vodeno-metanolnim ekstraktima sadržaj ukupnih fenola je bio između 24.93–28.62 mg GAE/g s.u; ukupnih flavonoida između 0.964–1.530 mg RE/g s.u i 0.151–0.213 mg QE/g s.u. Najveću antioksidacijsku aktivnost, određenu DPPH metodom, imali su zakiseljeni metanolni ekstrakti *C. monogyna*. Najveća korelacija je određena između sadržaja ukupnih polifenola i antioksidacijske aktivnosti za vodene metanolne ekstrakte. Rezultati dobiveni u ovoj studiji ukazuju da se plodovi ispitivanih vrsta glogova mogu smatrati prirodnim izvorom fenolnih jedinjenja sa dobrom antioksidacijskom aktivnošću.

Total Monomeric Anthocyanins, Proanthocyanidins and Antioxidant Activity of Methanolic Extracts of Some *Crataegus* Fruits

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Keywords:

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Abstract: Fruits of two *Crataegus* species (*C. monogyna* and *C. rhipidophylla*) from natural populations were analyzed for total monomeric anthocyanins, total proanthocyanidins and antioxidant activity using aqueous methanol and acidified aqueous methanol extraction mixtures. Anthocyanins were determined by a pH differential method, proanthocyanidins with acid butanol assay, and results were expressed as cyanidin-3-glucoside equivalents and cyanidin chloride equivalents, respectively. In both extraction systems, higher anthocyanin content and proanthocyanidin content were obtained for *C. monogyna*. In aqueous methanol extracts total monomeric anthocyanins ranged from 0.580 to 0.686 mg CGE/g DW, and proanthocyanidins from 12.892 to 14.187 mg CE/g DW. In acidified aqueous methanol extracts total monomeric anthocyanins ranged from 0.628 to 0.688 mg CGE/ g DW, and proanthocyanidins from 13.575 to 15.451 mg CE/g DW. The highest antioxidant activity determined by DPPH showed *C. monogyna* in both extraction systems. The highest correlation was determined between proanthocyanidins content and antioxidant activity in aqueous methanol extracts. Overall results showed that investigated fruits can serve as good source of bioactive compounds in human diet, food and pharmaceutical industry.

Sažetak

Plodovi dvije vrste glogova (*C.monogyna* i *C. rhipidophylla*) iz prirodnih populacija analizirani su na sadržaj ukupnih monomernih antocijanina, ukupnih proantocijanidina i antioksidacijsku aktivnost u vodeno-metanolnim i zakiseljenim vodeno-metanolnim ekstraktima. Antocijanini su određeni pH diferencijalnom metodom, a kiselinsko-butanolna metoda je korištena za određivanje ukupnih proantocijanidina. Rezultati su izraženi u ekvivalentima cijanidin-3-glukozida, odnosno ekvivalentima cijanidin hlorida. U oba ekstrakciona sistema veće vrijednosti sadržaja antocijanina i proantocijanidina su dobivene za *C. monogyna*. U vodeno-metanolnim ekstraktima sadržaj ukupnih monomernih antocijanina je bio u opsegu od 0.580 do 0.686 mg CGE/g s.u. i proantocijanidina od 12.892 do 14.187 mg CE/g s.u. U zakiseljenim metanolnim ekstraktima sadržaj ukupnih monomernih antocijanina se kretao od 0.628 do 0.688 mg CGE/ g s.u., i proantocijanidina od 13.575 do 15.451 mg CE/g s.u. Najveća antioksidacijska aktivnost, određena DPPH metodom, izmjerena je u ekstraktima *C. monogyna*. Najveća korelacija je određena između sadržaja proantocijanidina i antioksidacijske aktivnosti u vodenim metanolnim ekstraktima. Sveukupni rezultati ukazuju da plodovi ispitivanih vrsta gloga mogu poslužiti kao dobar izvor bioaktivnih jedinjenja u ishrani kao i prehrambenoj i farmaceutskoj industriji.



Synthesis of Some Coumarins and Comparison of Their Antioxidant Activities

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Keywords:

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Abstract: Coumarins are naturally occurring benzopyrone derivatives and found in nature in a great variety of plants where they have an important effect on plant biochemistry and physiology. Recently, coumarins and their derivatives were extensively studied for their antioxidative and enzyme inhibitory properties. Furthermore, the coumarin derivatives, used as selective MAO inhibitors, are also widely reported. Pechmann, Perkin, Knoevenagel, Reformatsky and Wittig reactions are some of the commonly employed reactions for the syntheses of coumarins and its derivatives. The Pechmann's reaction is widely used in the synthesis of 4-substituted coumarins in good yields. In these reactions, mineral acids, Lewis acids, ionic liquids and etc. have been employed as catalyst. In this work; 4-methyl-7-hydroxy-, 4-propyl-7-hydroxy- and 4-methyl-7-methoxy- coumarin compounds were synthesized by using oxalic acid or bismuth nitrate as catalysts. They were purified either crystallization or column chromatography. Structures of these products were characterized by spectroscopic methods (IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, MS). Furthermore, the obtained coumarins were compared according to antioxidant activity by DPPH method. 4-Methyl-7-methoxy coumarin showed the best activity.

Sažetak

Kumarini su benzopironski derivati zastupljeni u prirodi u velikom broju biljaka, gdje pokazuju značajan uticaj na biohemiju i fiziologiju biljaka. Nedavno su izvršena opsežna proučavanja antioksidativnih i enzimskih inhibitorskih svojstava kumarina i njihovih derivata. Nadalje, derivati kumarina su korišteni kao selektivni MAO inhibitori, što stoji u mnogim izvještajima. Reakcije Pechmanna, Perkina, Knoevenagala, Reformatskog i Wittiga su često korištene reakcije za sintezu kumarina i njihovih derivata. Pechmann-ova reakcija se naširoko koristi za sintezu 4-substituiranih kumarina, sa dobrim prinosima. U ovim reakcijama kao katalizatori se koriste mineralne kiseline, Lewisove kiseline, jonske tečnosti itd. U ovom radu 4-metil-7-hidroksi-, 4-propil-7-hidroksi- i 4-metil-7-metoksi-kumarinski spojevi su sintetizovani uz korištenje oksalatne kiseline ili bizmut nitrata kao katalizatora. Prečišćeni su kristalizacijom ili hromatografijom na kolonama. Struktura ovih produkata okarakterizirana je spektroskopskim metodama (IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, MS). Nadalje, antioksidativna aktivnost dobijenih kumarina je uspoređena DPPH metodom. Najbolju aktivnost je pokazao 4-metil-7-metoksi kumarin.



Catecholase-Mimetic Activity of Fe(II) Complex with New N₂O₂ Donor Schiff Base Ligand

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Keywords:

Schiff base,
catecholase-mimetic activity,
3,5-Di-*tert*-butylcatechol,
Michaelis-Menten kinetics.

Abstract: There is continuing interest in the biomimetic catalytic activity of transition metal complexes, which may serve as structural and functional models for various metalloenzymes. The chemistry of mononuclear iron(II) complexes has aroused considerable interest as iron has been found in active sites of the large number of metalloenzymes. Metal complex based functional metalloenzyme models are of considerable interest both as sources of mechanistic information on enzyme reactions and as possible starting points for developing biomimetic catalysts for synthetic applications. In this study, a new N₂O₂ donor Schiff-base and its Fe(II) complex were synthesized by condensation of 2-aminobenzylamine with 6-formyl-7-hydroxy-5-methoxy-2-methylbenzopyran-4-one and by using an appropriate Fe(II) salt, respectively. The prepared compounds were characterized by elemental analysis, FT-IR, and NMR. The catecholase-mimetic activity of the Schiff Base Fe (II) complex was performed for the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) in methanol at 25 °C, where the electronic spectra were recorded at different time intervals. The yield of the quinone (3,5-DTBQ) was determined from the measured absorbance at 400 nm of the resulting solution. The compatibility of catalytic reaction with Michaelis-Menten kinetics was also investigated.

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Sažetak

Stalan je interes za biomimetske katalitičke aktivnosti kompleksa prijelaznih metala koji mogu poslužiti kao strukturni i funkcionalni modeli za razne metaloenzime. Razlog velikog interesovanja za hemiju kompleksa mononuklearnog željeza (II) je prisustvo željeza na aktivnim mjestima velikog broja metaloenzima. Funkcionalni modeli metaloenzima zasnovani na metalnim kompleksima su važni dvojako, kao izvori informacija o mehanizmu enzimskih reakcija i kao osnove za početak i razvoj biomimetskih katalizatora za sintetičke aplikacije. U ovom istraživanju sintetiziran je novi N₂O₂ donor Schiffove baze i njegov Fe (II) kompleks kondenzacijom 2-aminobenzilamina sa 6-formil-7-hidroksi-5-metoksi-2-metilbenzopiran-4-onom koristeći odgovarajuću Fe (II) sol, redom. Pripremljeni spojevi su karakterizirani elementarnom analizom, FT-IR-om i NMR-om. Kateholazno-mimetska aktivnost kompleksa Schiffove baze Fe (II) je izvedena za oksidaciju 3,5-di-*tert*-butilkatehola (3,5-DTBC) u metanolu na 25 °C a elektronski spektri su bilježeni pri različitim vremenskim intervalima. Prinos hinona (3,5-DTBQ) je određen mjerenjem apsorbancije otopine na 400 nm. Ispitivana je i usklađenost katalitičke reakcije sa kinetikom Michaelis-Menten-ove reakcije.



Kinetic Studies on Catecholase-like Activity of New Schiff Base Cu(II) Complex

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Keywords:

Schiff base,
catecholase activity,
3,5-Di-*tert*-butylcatechol,
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Abstract: The oxidation of organic substrates with molecular oxygen under mild conditions is of great interest for industrial and synthetic processes. Active copper and iron centers dominate the field of biological oxygen chemistry and play a vital role in catalysis. Catechol oxidase is a type III active site protein containing copper which catalyzes the oxidation of *o*-diphenols to the corresponding *o*-quinones in a process known as catecholase activity.

In this study, a new Schiff-base and its Cu(II) complex were synthesized by condensation of 2-aminobenzylamine with 6-formyl-7-hydroxy-5-methoxy-2-methylbenzopyran-4-one and by using an appropriate Cu(II) salt, respectively. The prepared compounds were characterized by elemental analysis, FT-IR, and NMR. In order to determine the kinetics parameters of catechol oxidase-like activity of Schiff base Cu(II) complex, the oxidation of the 3,5-di-*tert*-butylcatechol (3,5-DTBC) was measured at 25°C by monitoring the increase of the absorption band at 390-400 nm of the product 3,5-di-*tert*-butylcatequinone (3,5-DTBQ). The compatibility of catalytic reaction with Michaelis-Menten kinetics also investigated by the method of initial rates by monitoring the growth of the 390-400 nm band of 3,5-DTBQ as a function of time.

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Sažetak

Oksidacija organskih supstrata s molekularnim kisikom pod blagim uvjetima reakcije je od velikog interesa za industrijske i sintetičke procese. Aktivni bakar i željezo centri dominiraju u području biološke kemije kisika i igraju vitalnu ulogu u biohemijskoj katalizi. Katehol oksidaze je tip III protein sa aktivnim mjestom koja sadrži bakar i koji katalizira oksidaciju *o*-difenola u odgovarajuće *o*-kinon u procesu poznatom kao kateholna aktivnost. U ovom istraživanju, nova Schiffova baza i kompleks sa Cu (II), je sintetiziran kondenzacijom 2-aminobenzilamina sa 6-formil-7-hidroksi-5-metoksi-2-metilbenzopiran-4-ona i uz pomoć odgovarajuće Cu (II) soli. Pripremljeni spojevi su karakterizirani pomoću elementarne analize, FT-IR i NMR. Da bi se odredili kinetički parametri kompleksa Schiffove baze sa Cu (II) koji djeluje kao katehol oksidaza, oksidacija 3,5-di-*tert*-butilkatehol (3,5-DTBC) je mjerena na 25°C praćenjem povećanja apsorpcije proizvoda 3,5-di-*tert*-butylcatequinone (3,5-DTBQ) na 390-400 nm. Kompatibilnost katalitičke reakcije sa Michaelis-Mentenovom kinetikom, također istraživana metodom početne brzine reakcije praćenjem povećanja apsorpcije 3,5-DTBQ na 390-400 nm u funkciji vremena.



Electrochemical synthesis and characterization of poly [Co(salabza)] on Platinum electrode

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Keywords:

Schiff base metal complex,
electropolymerization

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Abstract: Conducting polymer films have a wide variety of applications in many fields including electroanalysis, electrocatalysis, biosensors and corrosion protection. These films have been generally produced by electrochemical way. Electropolymerization allows uniform coating on irregular surfaces and easy electrochemical control of the film thickness. Interest in building conducting polymers containing complexed transition metals is ever-increasing, especially because metal centres can be electrically connected via the polymer skeleton. Such applications as for electrode modifiers, electrocatalysis and sensors, are especially interesting, since one can expect the electrochemical conversion of a whole multi-layer electroactive film. In recent years, the electropolymerization of various Schiff base-metal complexes have been investigated. Researchers have incorporated Schiff base complexes into polymers, generating new materials with useful mechanical, thermal, chemical and electronic properties.

In this study, electrochemical polymerization of Co(II)-(N,N'-bis(salicylidene)-2-aminobenzylamine (poly[Co(salabza)]) have been achieved by Cyclic Voltammetry (CV) technique on the platinum electrode in non-aqueous acetonitrile solution consist 0.15 M LiClO₄ as supporting electrolyte. The characterization of the polymers was done by using FT-IR, UV-vis, CV, Scanning Electron Microscopy (SEM) techniques.

Sažetak

Provodljivi polimeri imaju široku primjenu u oblastima elektroanalize, elektrokatalize, biosenzora i zaštite od korozije. Polimerni filmovi se uglavnom dobijaju elektrohemijskim putem. Elektropolimerizacija omogućava ravnomjerno nanošenje filma na neravne površine i lahko elektrohemijsku kontrolu debljine filma. Sve je veći interes za stvaranje provodljivih polimera koji sadrže prelazne metale u kompleksu zbog mogućnosti da se metalni centri mogu elektro-vezati preko polimernog kostura. Pogotovo je zanimljiva njihova primjena kao elektrodnih modifikatora, senzora u elektrokatalizi jer se može očekivati elektrokemijska konverzija višeslojnog elektroaktivnog filma. U posljednje vrijeme istraživana je elektropolimerizacija raznih metalnih kompleksa sa Schiff-ovim bazama. Istraživači su inkorporirali komplekse sa Schiff-ovim bazama u polimere, stvarajući nove materijale s korisnim mehaničkim, termičkim, hemijskim i elektronskim osobinama. Elektrokemijska polimerizacija Co(II)-(N,N'-bis(salicylidene)-2-aminobenzilamina (poli[Co(salabza)]) postignuta je cikličnom voltametrijom (CV) na platinskoj elektrodi u nevodenoj otopini acetonitrila sa 0,15 M LiClO₄-om kao pomoćnim elektrolitom. Polimeri su karakterizirani FT-IR-om, UV-Vis-om, CV-om i SEM tehnikom (skenirana elektronska mikroskopija).



Total Phenolic and Flavonoid Content and Antioxidant Activity of Two *Crataegus* Species from Bosnia

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Keywords:

Crataegus
Total phenolics
Flavonoids
Antioxidant activity
ABTS
DPPH

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Abstract: Hawthorn is the common name for *Crataegus* species in *Rosaceae* family. There are over 1000 species of *Crataegus* distributed primarily in Asia, Europe and North America.

The aim of this work is to determine the total phenolic and total flavonoid content as well as antioxidant activity of two *Crataegus* species; *C. monogyna* and *C. microphylla* growing wild in Bosnia. Extracts of leaves and flowers (LF), and berries (B) were prepared by ultrasound-assisted extraction using ethanol as solvent. Total phenolic content was determined by Folin-Ciocalteu method and content varied from 51,50 mgGAE/g for *C. monogyna* (B), to 66.25 mgGAE/g for *C. monogyna* (LF). Total flavonoid content was determined using AlCl₃ method. The lowest content of flavonoids was found for *C. microphylla* (B), 0.22 mgQE/g, and the highest for *C. monogyna* (LF), 8.74 mgQE/g. Two spectrophotometric methods, DPPH and ABTS, were used for determination of the antioxidant activity of the samples. The best antioxidant was sample of *C. microphylla*, by both antioxidant methods applied. Extract from the leaves and the flowers (LF) had IC₅₀ value of 1.09 mg/mL for DPPH, and extract from the berries (B) had IC₅₀ of 0.41 mg/mL for ABTS method. There was no correlation between total phenolic and flavonoid content and antioxidant activity.

Sažetak

Glog je uobičajeno ime za vrste roda *Crataegus*, porodice *Rosaceae*. Postoji preko 1000 vrsta *Crataegus* rasprostranjenih uglavnom u Aziji, Evropi i Sjevernoj Americi. Cilj ovog rada je da se odredi sadržaj ukupnih fenola i flavonoida kao i antioksidacijska aktivnost dvije vrste roda *Crataegus*; *C. monogyna* i *C. microphylla* koje divlje rastu u Bosni. Ultrazvučna ekstrakcija listova i cvjetova (LF) i plodova (B) urađena je uz etanol kao rastvarač. Ukupan sadržaj fenolskih spojeva je određen Folin-Ciocalteu metodom i njihov sadržaj je varirao od 51,50 mgGAE/g za *C. monogyna* (B), do 66.25 mgGAE/g za *C. monogyna* (LF). Sadržaj flavonoida je određen metodom sa AlCl₃. Najniži sadržaj imao je uzorak *C. microphylla* (B), 0.22 mgQE/g, a najviši uzorak *C. monogyna* (LF), 8.74 mgQE/g. Dvije spektrofotometrijske metode, DPPH i ABTS, su korištene za određivanje antioksidacijske aktivnosti uzoraka. Najbolji antioksidans, po obje metode, je bio uzorak *C. microphylla*. Ekstrakt listova i cvjetova (LF) je imao IC₅₀ 1.09 mg/mL za DPPH, a ekstrakt plodova (B) vrijednost IC₅₀ od 0.41 mg/mL za ABTS metod. Nije nađena korelacija između sadržaja ukupnih fenola i flavonoida i antioksidacijske aktivnosti.



Chemical Composition and Antioxidant Activity of Four Asteraceae Essential Oils

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Keywords:

Essential oil
Achillea millefolium L.
Arnica montana L.
Artemisia absinthium L.
Artemisia annua L.
Antioxidant activity

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Abstract: Hydrodistilled volatile oils from the aerial parts of four plants of Asteraceae family, *Achillea millefolium* L., *Arnica montana* L., *Artemisia absinthium* L., and *Artemisia annua* L. were analyzed by GC/MS. More than one hundred and fifty compounds were identified in all samples, ranging from 71.5%-97.8% of the total oil. Essential oils showed significant differences in their content and chemical composition. The yield of oil varies from 0.07% for *A. montana* to 0.18% for *A. annua*. A high percentage of oxygenated monoterpenes is the main characteristic of *A. millefolium* and *A. absinthium* essential oils with camphor (19.2%) and *iso*-ascaridol (21.9%) as the major constituents, respectively. In contrast, the main component of *A. annua* oil was oxygenated sesquiterpene selina-3,11-dien-6- α -ol (9.6%), while the chemical composition of *A. montana* oil was characterized by a high content of saturated fatty acids with *n*-hexadecanoic acid (15.5%) as the main constituent. Antioxidant activity was tested using four different methods, DPPH, ABTS, Reducing power, and Phosphomolybdenum Assay. The highest antioxidant activity had essential oil of *A. montana* using DPPH and ABTS method, while *A. absinthium* oil showed the best ability to reduce Fe ions. In addition, it was found that all essential oils analyzed are significantly weaker antioxidants than chlorogenic acid used as a standard.

Sažetak

Esencijalna ulja izolirana hidrodestilacijom iz nadzemnih dijelova četiri biljne vrste porodice Asteraceae, *Achillea millefolium* L., *Arnica montana* L., *Artemisia absinthium* L. i *Artemisia annua* L., analizirana su primjenom GC/MS. Više od stotinu i pedeset komponenata je identificirano u svim uzorcima, što predstavlja 71.5%-97.8% ukupnog ulja. Esencijalna ulja pokazuju značajne razlike u sadržaju i hemijskom sastavu. Prinosi ulja se razlikuju od 0.07% za ulje *A. montana* do 0.18% za ulje *A. annua*. Visok procenat oksigeniziranih monoterpena je glavna karakteristika esencijalnih ulja *A. millefolium* i *A. absinthium*, sa kamforom (19.2%), odnosno *izo*-askaridolom (21.9%), kao glavnim konstituentom. Nasuprot tome, glavna komponenta esencijalnog ulja *A. annua* je oksigenizirani seskviterpen selina-3,11-dien-6- α -ol (9.6%), dok je hemijski sastav ulja *A. montana* karakteriziran visokim sadržajem zasićenih masnih kiselina, sa *n*-heksadekanskom kiselinom (15.5%) kao glavnim konstituentom. Antioksidativna aktivnost je određena primjenom četiri različite metode, DPPH, ABTS, redukcijaska moć i fosfomolibdatnom metodom. Najbolju antioksidativnu aktivnost, primjenom DPPH i ABTS metode, imalo je esencijalno ulje *A. montana*, dok je ulje *A. absinthium* pokazalo najbolju sposobnost da reducira jone Fe. Uz navedeno, nađeno je da su sva esencijalna ulja znatno slabiji antioksidansi od hlorogenske kiseline koja je korištena kao standard.



Synthesis and Characterization of 1,4-naphthoquinone Derivatives

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Keywords:

naphthoquinones,
sulfanyl naphthoquinones,
amino naphthoquinones

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Abstract: The chemistry of quinones is of considerable interest since this class of compounds includes many natural products and numerous important synthetic products. The naphthoquinone chromophore has been found to possess potent antimalarial, antifungal, antibacterial, anti-inflammatory, and antitumor activities. Reactions of various nucleophiles such as thiols or amines with naphthoquinones represent a common synthetic route to many fused heterocyclic rings which have been used as synthetic intermediates in medicinal chemistry and for dyestuffs. In consideration of these, herein, a series of some interesting 1,4-naphthoquinone derivatives have been synthesized from the reactions of 2,3-dichloro-1,4-naphthoquinone with nucleophiles in the presence of triethylamine or Na₂CO₃ in ethanol at room temperature or reflux. The structures of novel compounds were determined by micro analysis, FTIR, ¹H NMR, ¹³C NMR, and MS.

Sažetak

Hemija kinona je prilično interesantna budući da ova klasa spojeva uključuje mnoge prirodne produkte i važne brojne sintetske produkte. Nađeno je da kromofor naftokinona posjeduje jaku antimalaričnu, antifungalnu, antibakterijsku, antiupalnu i antitumornu aktivnost. Reakcije raznih nukleofila kao što su tioli ili amini sa naftokinonima predstavljaju opći sintetski put za mnoge spregnute heterociklične prstenove koji se koriste kao sintetički intermedijeri u medicinskoj hemiji i u sredstvima za bojenje. Uzimajući ovo u obzir, serija od nekoliko interesantnih 1,4-naftokinonskih derivata je sintetizirana u reakciji 2,3-dihlor-1,4-naftokinona sa nukleofilima, u prisustvu trietilamina ili Na₂CO₃ u etanolu pri sobnoj temperature ili refluksu. Strukture novih spojeva određene su mikroanalizom, FTIR, ¹H NMR, ¹³C NMR, i MS.



Investigation of Commercial Peppermint Oils of Japan and Turkey Origin by Chiral GC/MS

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Keywords:

Commercial Peppermint oil,
essential oil,
GC-MS

Abstract: Peppermint oil is isolated from the plant *Mentha piperita* L, which is an aromatic perennial herb belonging to the family of Lamiaceae found all over the world. Peppermint oils of several mentha species can be used for pharmaceutical and nutritional aspects, as natural additives in medicine, drugs, foods, mouthwash, toothwash, chewing gum and confectionary because of their antiviral, antibacterial, antifungal, pesticidal, antiinflammatory and antimicrobial properties and pain decreasing and immunity increasing activities.

The aim of this study was to investigate the difference of the chemical composition of several commercial peppermint oils because their pharmaceutical activities such as muscle, head, nerve, rheumatic pain and spasms relieving effects are not equal. According to the literature survey, the best medicinal therapy is obtained with Japanese peppermint oil, but this mint oil is very expensive. The desire to know what is the effective criterion between the Turkish and Japanese peppermint oil. Chemical composition of these mint oils were investigated by GC/MS, chiral GC/MS, IR and determination by optical rotation, in order to find out which chemical substances may cause this difference.

Three commercial Japanese oil samples, bought in Germany, one Turkish commercial oil sample, and one nutritional peppermint oil obtained by Clevenger method from the mint leaves were used for this investigation.

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Sažetak

Ulje pepermintu je izolirano iz biljke *Mentha piperita* L, koja je aromatska cjelogodišnja biljka iz porodice Lamiaceae i koja se može pronaći diljem svijeta. Pepermint ulja od nekoliko vrsta mente se mogu koristiti u farmaceutske i prehrambene svrhe, kao prirodni aditivi u medicini, lijekovima, hrani, vodici za ispiranje usta, pastama za zube, žvakaćim gumama i konditorskim proizvodima, ali i zbog svojih antivirusnih, antibakterijskih, antiglivičnih, pesticidalnih, antiupalnih i antimikrobnih svojstava kao i zbog smanjenja bolova i jačanja imuniteta. Cilj ovog istraživanja je da se ispita razlika između hemijskog sastava nekoliko komercijalnih pepermint ulja zbog toga što njihovo farmaceutsko djelovanje kao što je ublažavanje mišićne boli, glavobolje, bolova živaca, reumatskih bolova i efekti ublažavanja grčeva nije isto. U skladu s literaturnim pretraživanjem, najbolja medicinska terapija se dobije sa Japanskim pepermint uljem, ali ovo ulje je veoma skupo. Želja je bila da se spozna šta je efektivni kriterij između turskog i japanskog pepermint ulja. Hemijski sastav ovih mentinih ulja ispitan je sa GC/MS, hiralnim GC/MS, IR i određena je optička rotacija, u cilju da se otkrije koja hemijska tvar čini razliku. Tri uzorka komercijalnog japanskog ulja, kupljenih u Njemačkoj, jedan uzorak komercijalnog turskog ulja i jedan uzorak pepermint ulja dobijen Clevengerovom metodom iz lišća mente su korišteni za ispitivanje. Dobijeni su različiti rezultati sa IR, hiralnim GC/MS i optičkom rotacijom zbog razlike u hemijskom sastavu ovih pet uzoraka ulja mente.



Antiacetylcholinesterase, Antielastase and Antioxidant Activities of Some Ketoxime Tetradecanoic Acid Methyl Ester Isomers

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Keywords:

Acetylcholinesterase,
elastase,
antioxidant,
inhibitor,
ketoxime esters.

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Abstract: Oximes and *O*-substituted oximes are important compounds in organic and medicinal chemistry due to their practical applications in several drugs, biologically active compounds and as therapeutic immuno-agents. Recently, biological activity of oxime compounds has attracted more interest. In this study, we aimed to investigate the inhibition effect to both acetylcholinesterase, and elastase, and antioxidant activities of some ketoxime tetradecanoic acid methyl ester isomers. With this aim, the mentioned ketoxime ester isomers were synthesized and characterized for the first time from their corresponding keto ester isomers. According to literature survey, there is no data about the inhibition of acetylcholinesterase which is an important criteria in Alzheimer disease by these ketoxime esters. Besides, the antielastase and antioxidant activities of these ketoxime esters were not studied until today. All the test compounds exhibited antiacetylcholinesterase, antielastase and antioxidant activities in this study. The enzyme inhibitory and antioxidant activities of these mentioned isomers were found to increase dose dependently. According to the experimental results of this study, the mentioned ketoxime esters may be used as a drug in Alzheimer disease and in pharmacy industry with their excellent antiacetylcholinesterase, antielastase and antioxidant activities tested in this study.

Sažetak

Oksimi i *o*-substituirani oksimi su važna jedinjenja u organskoj i medicinskoj hemiji zbog praktičnih aplikacija u lijekovima, biološki aktivnim jedinjenjima i terapeutskim imuno-agentima. Biološka aktivnost oksima privlači sve više pažnje. U ovoj studiji ispitivali smo inhibicioni uticaj acetilholinesteraze i elastaze kao i antioksidativne osobine nekih ketoksim tetradekanoičnih kiselih metilnih esterskih izomera. Da bi se izveo ovaj eksperiment, ketoksim esterski izomeri su po prvi put sintetizirani i karakterizirani od odgovarajućih keto ester izomera. Pregled literature je pokazao da nema podataka o inhibiciji acetilholinesteraze koja je važan parametar u Alzheimerovoj bolesti i koja je povezana sa ketoksim esterima. Također, nema podataka o prethodnim studijama na antielastazama i o antioksidativnoj aktivnosti ketoksim estera. Sva testna jedinjenja u ovom radu su pokazala antiacetilholinesterazu, antielastazu i antioksidativnu aktivnost. Enzimske inhibitorne i antioksidativne aktivnosti pomenutih izomera su se povećavale sa dozom. Eksperimentalni podaci rada su pokazali da se steri ketoksima mogu koristiti kao lijekovi u liječenju Alzheimerove bolesti i u farmaceutskoj industriji na osnovu svojih odličnih antiacetilholinesteraznih, antielastaznih i antioksidativnih osobina proučavanih u ovom radu.



The Investigation of Reactions Between Polyhalogenated Dienes and Aliphatic Mercaptans

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Keywords:

Mercaptans,
polyhalogenated dienes,
S-substituted-1-buten-3-yne,
S-substituted polyhalogenobuta-
1,3-diene

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Abstract: As it is known polyhalogenated diene compounds possess a broad spectrum of useful properties such as good dielectrics, refrigerant and heat-transfer agents, and also aerosol, lubricant and floatation agents and hold algicidal, bactericidal and fungicidal activities. Various polyhalogenated dienes express high antitumour activity. The formation of C-S bonds is one of the most important reactions in numerous synthesis of intermediates and targets with biological and pharmaceutical impact, and in molecular precursors for the development of materials. The aim of this study is to investigate the reactions between aliphatic mercaptans and polyhalogenated dienes such as 1,1,2,4,4-pentachlorobuta-1,3-diene and 1-bromo-1,2,4,4-tetrachlorobuta-1,3-diene. The reactions were investigated with different molar ratio of mercaptans. Even though it was planned on yielding the S-substituted polyhalogenobuta-1,3-diene compounds, the S-substituted-1-buten-3-yne compounds were also formed as a product of the reactions.

Sažetak

Polihalogenirani dieni posjeduju široki spektar korisnih osobina kao što su dobre dielektrične, rashladne osobine kao i osobinu prevođenja toplote, mogu se koristiti kao aerosol, mazivo i plutajući agenti te posjeduju algicidalnu, baktericidalnu i fungicidalnu aktivnost. Različiti polihalogenirani dieni pokazuju visoku anticancer aktivnost. Nastanak C-S veza je jedna od najvažnijih reakcija u brojnim sintezama međuprodukata i targetiranju sa biološkim i farmaceutskim impaktom kao i molekularni prekursori u razvoju novih materijala.

Cilj ove studije je bio ispitati reakciju između alifatskih merkaptana i polihalogeniranih diena kao što su 1,1,2,4,4-pentachlorobuta-1,3-dien i 1-bromo-1,2,4,4-tetrachlorobuta-1,3-dien. Reakcija je ispitana sa različitim molarnim udjelima merkaptana. Iako je očekivano povećanje prinosa S-supstituiranih polihalogenobuta-1,3-dienskih jedinjenja, S-substituirani-1-buten-3-in jedinjenja su također nastala kao produkti reakcije.



Elastase and Collagenase Inhibitory Activities of Ethanolic Extract from *Epilobium angustifolium* L. Leaves

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Keywords:

Epilobium angustifolium L.,
elastase and collagenase inhibitory
activities.

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Abstract: The genus *Epilobium* is widely distributed all over the world and consists of over 200 species. Various members of the genus *Epilobium* have been used in folk medicine internally for prostate disease, menstrual and gastrointestinal disorders, rectal bleeding and externally as antiphlogistic. In Russia, due to a sweet and pleasant taste, it is usually consumed as tea for the treatment of stomach ulceration, gastritis and sleeping disorders. Elastase is the only enzyme capable of degrading elastin, an insoluble elastic fibrous protein of animal connective tissue. Elastase is known to cause rheumatoid arthritis, pulmonary emphysema, and other chronic inflammatory diseases by the protein degradation of human tissues. And also collagenases are endopeptidases that digest native collagen in the triple helix region. Collagens are the major fibrous component of animal extracellular connective tissue. Of particular interest is the relationship between collagenase and rheumatoid arthritis, metastasis, wound debridement, herniated disc treatment, angiogenesis, tissue repair, and cirrhosis. In this study, we have investigated the elastase and collagenase inhibitory activities of the ethanolic extract from *E. angustifolium* L. for the first time. The enzyme inhibitory activities of this extract were found to increase dose dependently. For this reason, this extract can be used in cosmetic industries due to their excellent elastase and collagenase activities observed in this study.

Sažetak

Rod *Epilobium* je raširen širom svijeta i sadrži preko 200 vrsta. Različiti članovi roda *Epilobium* koriste se u narodnoj medicini, interno za liječenje bolesti prostate, menstrualnih i stomačnih poremećaja, krvarenja rektuma i za vanjsku upotrebu protiv upala. U Rusiji zbog slatkog i ugodnog ukusa, često se koristi kao čaj za liječenje čireva u stomaku, gastritisa i poremećaja sna. Elastaza je jedini enzim koji je u stanju da razgradi elastin, nerastvorljivi elastični vlaknasti protein u vezivnim tkivima životinja. Poznato je da elastaza uzrokuje reumatoidni artritis, plućni emfizem i druge hronične upalne bolesti usljed razgradnje proteina ljudskih tkiva. Kolagenaze su također endopeptidaze koje razgrađuju prirodni kolagen u području trostrukog heliksa. Kolageni su glavne vlaknaste komponente životinjskog vanćelijskog vezivnog tkiva. Od značajnog interesa je veza između kolagenaze i reumatoidnog artritisa, metastaza, uklanjanja mrtvog tkiva sa rane, liječenja diskus hernije, angiogeneze, zacjeljivanja tkiva i ciroze. U ovom radu, ispitana je inhibitorna aktivnost elastaze i kolagenaze etanolskog ekstrakta iz *E. angustifolium* L., po prvi put. Nađeno je da inhibitorske aktivnosti oba enzima ovog ekstrakta povećavaju dozu ovisno jedan od drugog. Zbog ovoga, ekstrakt se može koristiti u kozmetičkoj industriji usljed odličnih aktivnosti elastaze i kolagenaze ispitanih u ovom radu.



Biomarkers for Alzheimer's Disease, amyloid beta peptide (1-42) and total tau protein, highly increased in CSF of patients with hydrocephalus-postoperation status

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CSF Biomarkers,
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Alzheimer's Disease,
ELISA.

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Abstract: Cerebrospinal fluid (CSF) used to be the most informative fluid in biomarkers discovery for neurodegenerative disease prognosis as is in direct, physical contact with brain. Some products of brain specific activities are reflected in CSF. The core candidate CSF biomarkers proteins β -amyloid 1–42 (A β 42) and total tau protein (T-tau) have a high performance to identify AD, as well as other neurodegenerative diseases and impaired mental function such Hydrocephalus (Hyd). Both proteins are linked to hallmark lesions of AD, amyloid plaques, and neurofibrillary tangles. We investigated levels of the A β 42 and T-tau in lumbar punctured CSF samples collected from 47 Controls, 23 AD and 10 Hydrocephalus age matched patients and 10 ventricular CSF samples of patients in early childhood using ELISA-s, specifically constructed to measure tau isoforms and β -amyloid containing both the 1st and 42nd amino acids. Comparing with Control values for T-tau (287 \pm 49 pg/ml) and A β 42 (645 \pm 52 pg/ml) high concentrations of T-tau (619 \pm 37pg/ml), ($p < 0,001$) and low concentration of A β 42 (382 \pm 42 pg/ml) ($p < 0,01$) in the AD patients where detected. In elderly and in early childhood of patients with Hyd postoperation status, both biomarkers where highly significantly increased ($p < 0,001$) compared with C and AD. Combination of both biomarkers differentiate AD from controls and other pathochemical conditions even in early stage. The fact that the T-tau and A β 42 are present in CSF of very young patients with AD like pathology, may help early prediction for development of neurological disorders.

Sažetak

Cerebrospinalna tekućina (CSF) od svih fluida daje najviše podataka pri otkrivanju biomarkera za predviđanje neurodegenerativnih bolesti jer je u direktnom kontaktu sa mozgom. Neki produkti specifičnih moždanih aktivnosti se prenose u CSF. Glavni kandidati za CSF biomarkere β -amiloid 1–42 (A β 42) i ukupni tau protein (T-tau) imaju visoku sposobnost identificiranja AD, drugih neurodegenerativnih bolesti i oštećenja mentalne funkcije poput hidrocefalusa (Hyd). Oba biomarkera ukazuju na AD lezije, amiloidne plakove i neurofibrilarna klubad. Ispitivali smo nivoe A β 42 i T-tau u lumbalno punktiranim uzorcima CSF 47 kontrolna, 23 AD i 10 pacijenata sa Hyd slične starosne dobi i 10 ventrikularnih CSF uzoraka pacijenata rane životne dobi (novorođenčad), koristeći ELISA metodu specifično dizajniranu za mjerenje tau izoformi i β -amiloida sa obje 1. i 42. aminokiselinom. U odnosu na kontrolne vrijednosti za T-tau (287 \pm 49 pg/ml) i A β 42 (645 \pm 52 pg/ml), kod AD su nađene visoke koncentracije T-tau (619 \pm 37 pg/ml), ($p < 0,001$) i niske koncentracije A β 42 (382 \pm 42 pg/ml) ($p < 0,01$). Kod starijih kao i kod veoma mladih pacijenata sa Hyd postoperativnim statusom oba biomarkera su izrazito značajno uvećana ($p < 0,001$) u odnosu na kontrolu i AD. Kombinacijom vrijednosti oba biomarkera diferencira se AD od kontrolnih i drugih patohemijskih slučajeva čak i u ranoj fazi. Činjenica da su T-tau i A β 42 prisutni i u CSF veoma mladih pacijenata-novorođenčadi sa patologijom sličnom AD, može pomoći u ranoj predikciji razvoja neurodegenerativnih poremećaja.



¹H NMR study of *trans,trans*-2,5-distyryl-furans and 2,5-distyryl-thiophenes

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Abstract: Organic molecules with delocalized π -electrons and electron donor and electron acceptor groups at the two opposite ends have been widely investigated owing to their ability to absorb light and to generate charge separation. The design and study of these *push-pull* systems have attracted our attention because of their properties to perform useful photoinduced functions such as fluorescent sensing, solar energy conversion, optical information storage and effects of non-linear optics. ¹H NMR spectral study of *trans, trans* isomers of 2,5-distyryl-furans and 2,5-distyryl-thiophenes, bearing an electron acceptor (nitro) and an electron donor (methoxy or dimethylamino) groups have been made. The ¹H NMR resonances of ethylenic protons in positions 2 and in position 5 of the furan/thiophene ring are discussed. Chemical shifts of ethylenic nuclei are influenced by the electronic effect of substituents causing shielding or deshielding of adjacent hydrogens. Comparison of chemical shifts was made with model compounds.

Sažetak

Organske molekule s delokaliziranim π elektronima koje na suprotnim krajevima sadrže elektron donorske i elektron akceptorske skupine, predmet su brojnih istraživanja zbog svojih fotoapsorpcijskih sposobnosti i generiranja nosioca naboja pa stoga i mogućnosti da obavljaju korisne fotoinducirane funkcije kao što su pohranjivanje optičkih informacija, pretvorba solarne energije i fluorescentno osjećanje iona. Ovdje je prikazana ¹H NMR analiza *trans, trans* izomera 2,5-distirilfurana i 2,5-distiriltiofena funkcionaliziranih elektron akceptroskom grupom (nitro) i elektrondonorskom grupom (metoksi ili dimetilamino) s naglaskom na pomake etilenskih protona u položaju 2 i 5 na furanskom odnosno tiofenskom prstenu. Napravljena je i usporedba kemijskih pomaka s modelnim spojevima.



Determination of Gas-phase Basicity of Selected Amines, Guanidines and Phosphazenes Using Trichotomy Formula

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amini, gvanidini,
fosfazeni,
bazičnost,
teorija funkcionala gustoće,
protonski afiniteti.

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Abstract: Three groups of organic bases: amines, guanidines and phosphazenes together with three known proton sponges: 1,8-bis(dimethylamine)naphthalene (DMAN), 1,8-bis(tetramethylguanidine)naphthalene (TMGN) and 1,8-bis(hexamethyltriaminophosphazanyl)naphthalene (HMPN) were analyzed using trichotomy formula. Geometries and energies of neutral, protonated and cation-radical forms of molecules were calculated using DFT and *ab initio* methods. In all three investigated groups of organic bases, presence of aliphatic substituents resulted in proton affinity increase, lower values for Koopmans' energy and medium increase in relaxation energy. Aromatic substituents have resulted in almost similar values of proton affinities for amines and guanidines, while they had lower values for selected phosphazenes. Results of trichotomy analysis for proton sponges, when compared to monosubstituted naphthalenes, have shown an increase of proton affinity values by ~20, ~14 i ~24 kcal mol⁻¹ compared to DMAN, TMGN and HMPN, which led to lower values of Koopmans' ionization energies and increase of formation energies of the protonated form in the reaction between cation-radical and neutral hydrogen. Relaxation energy did not have a significant influence.

Sažetak

Trihotomnom analizom ispitane su tri skupine organskih baza: amini, gvanidini i fosfazeni, te poznate tri protonske spužve: 1,8-bis(dimetilamino)naftalen (DMAN), 1,8-bis(tetrametilgvanidino)naftalen (TMGN) i 1,8-bis(heksametiltriaminofosfazetil)naftalen (HMPN). Geometrijske strukture i energije neutralne, protonirane i kation-radikalne forme molekule računane su korištenjem DFT i *ab initio* modela. Kod sve tri skupine baza, alifatski supstituenti povećavaju protonski afinitet tako što dolazi do izraženog smanjenja Koopmansove energije i umjerenog povećanja energije relaksacije. Aromatski supstituenti rezultirali su protonskim afinitetima koji su ostali približno nepromijenjeni kod amina i gvanidina, odnosno umjereno sniženi kod fosfazena. Kod protonskih spužvi, trihotomna analiza u odnosu na odgovarajuće monosupstituirane naftalene pokazala je povećanje PA koje iznosi ~20, ~14 i ~24 kcal mol⁻¹ za DMAN, TMGN i HMPN što je bila posljedica smanjivanja Koopmansovih energija ionizacije, kao i povećanja energije nastanka protonirane forme u reakciji spajanja kation-radikala i neutralnog vodika, dok energija relaksacije nije imala značajniji utjecaj.



Determination of Ascorbic Acid and Total Anthocyanin Content in Four *Crataegus* Species Growing Wild in Bosnia

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Keywords:

Crataegus monogyna Jacq.,
Crataegus microphylla,
C. Koch,
ascorbic acid,
total anthocyanins.

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Abstract: Plants of the genus *Crataegus*, Rosaceae, are widely distributed and have long been used in folk medicine for the treatment of various ailments such as cardiovascular disorders, as well as disorders of central nervous system and immune system diseases. The aim of this work was to determine content of ascorbic acid and total anthocyanins in some *Crataegus* species (*C. monogyna* Jacq., *C. microphylla* C. Koch, *C. macrocarpa* Hegetschw. and *C. subsphaericea* Gand). The content of ascorbic acid was done by iodometric titration. Plant extracts were prepared by maceration with acetic acid. The highest content of ascorbic acid (10.47 mg/100 g dry sample) was obtained for the sample of *C. subsphaericea* (berries). Total anthocyanin content was determined by the pH differential method, which is a rapid and simple spectrophotometric method. It is based on the anthocyanin structural transformation that occurs with a change in pH (colored at pH 1.0, and colorless at pH 4.5). Extracts of the investigated samples were prepared by Soxhlet, ultrasonic extraction, maceration with buffer, and maceration with ethanol. The most efficient method of extraction was maceration with ethanol. The results showed that the highest concentration of total anthocyanin (10.59 mg/100 g dry sample) was found in the sample of *C. subsphaericea* berries.

Sažetak

Biljke roda *Crataegus*, Rosaceae, su dosta raširene i imaju dugu tradiciju u narodnoj medicini za tretman različitih bolesti kao što su oboljena srca (kardiovaskularna oboljenja), oboljenja centralnog nervnog i imunog sistema. Cilj ovog rada jeste da se odredi sadržaj askorbinske kiseline i ukupni antocijanini u nekim biljnim vrstama roda *Crataegus* (*C. monogyna* Jacq., *C. microphylla* C. Koch, *C. macrocarpa* Hegetschw. i *C. subsphaericea* Gand). Sadržaj askorbinske kiseline je određivan titracijom sa jodom. Priprema uzoraka je izvršena maceriranjem sa acetatnom kiselinom. Najveći sadržaj askorbinske kiseline (10.47 mg/100 g suhog uzorka) je dobiven u *C. subsphaericea* (plod). Sadržaj ukupnih antocijanina je određivan pH diferencijalnom metodom koja je brza i jednostavna spektrofotometrijska metoda. Bazirana je na strukturnoj transformaciji antocijanina koja se dešava sa promjenom pH (obojeno pri pH 1.0 i bezbojno pri pH 4.5). Ekstrakti ispitivanih uzoraka su pripremljeni Soxhlet i ultrazvučnom ekstrakcijom, maceracijom sa puferom i etanolom. Najefikasnija metoda ekstrakcije je maceracija sa etanolom. Rezultati pokazuju da je najveći sadržaj ukupnih antocijanina nađen u *C. subsphaericea* (plod) (10.59 mg/100 g suhog uzorka).



Spectrophotometric Determination of Ascorbic Acid with 2,6-dichlorophenolindophenol in Selected Pharmaceutical Preparations

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Abstract: The physiological functions of ascorbic acid (AA also named vitamin C) are largely dependent on the oxido-reductive properties of this vitamin. In view of the widespread use of AA, a large number of methods have been developed for quantifying AA content in natural and fortified food samples and pharmaceuticals. The aim of this paper was to determine the content of AA with 2,6-dichlorophenolindophenol (2,6-DCPIP) in some pharmaceutical samples of vitamin C. The method is based on the reaction between AA and 2,6-DCPIP where the blue form of 2,6-DCPIP is reduced to a colourless compound 2,6-DCPIPH₂, and AA is oxidized to dehydroascorbic acid (DHAA). The reaction was monitored spectrophotometrically by measuring the absorbance intensity at 588 nm. The linear range of AA concentration from $2.90 \times 10^{-6} \text{ mol L}^{-1}$ to $4.76 \times 10^{-3} \text{ mol L}^{-1}$. Also the influence of interfering substances such as citric acid and D-(-)-sorbitol were investigated. Comparative evaluation of the method is made with the iodometric titration. The results obtained by spectrophotometric method are in a good agreement with the results obtained by titration as well as the values on the label of the investigated samples. The proposed method is simple, cheap and fast for determination of AA in pharmaceutical samples.

Sažetak

Uloga askorbinske kiseline (AK takođe poznata i kao vitamin C) u organizmu vezuje se za učešće ovog vitamina u oksido-redukcionim procesima. Zbog široke upotrebe AK, razvijen je veliki broj metoda za njeno određivanje u uzorcima hrane, hrane obogaćene sa AK i u farmaceutskim preparatima. Cilj ovog rada je određivanje AK u izabranim farmaceutskim preparatima vitamina C sa 2,6-dihlorfenolindofenolom (2,6-DCPIP). Metoda je bazirana na reakciji između AK i 2,6-DCPIP pri čemu se plavo obojeni 2,6-DCPIP reducira do bezbojnog spoja (2,6-DCPIPH₂), a AK se oksidira do dehidroaskorbinske kiseline (DHAK). Reakcija je praćena spektrofotometrijski mjerenjem intenziteta apsorbanse na 588 nm. Dobivena je linearna zavisnost u području koncentracija $2,90 \times 10^{-6} \text{ mol L}^{-1}$ do $4,76 \times 10^{-3} \text{ mol L}^{-1}$. Kao poredbena metoda korištena je titracija sa jodom. Također je ispitivan uticaj interferirajućih supstanci kao što su limunska kiselina i D-(-) sorbitol. Dobiveni rezultati spektrofotometrijskom metodom pokazali su dobro slaganje sa rezultatima dobivenim jodometrijskom titracijom kao i sa vrijednostima na deklaraciji. Predložena metoda je jednostavna, jeftina i brza za određivanje AK u farmaceutskim preparatima.



Essential Oil Composition of *Laserpitium latifolium* L.

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Essential oil

GC/MS/MS triple quadrupole
system

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Abstract: *Laserpitium latifolium* L. (family Apiaceae), common name broad-leaved surmounting, is perennial plant. It is widespread in most of Europe and it has aromatic substances which make it useful as a medicinal, especially for animals. The root has been believed to strengthen the stomach and is able to lower fevers. As a medicinal plant it has been transplanted outside its natural habitat. Essential oil was obtained by hydrodistillation in a Clevenger's apparatus for 3 h and chemical composition analysis was performed by a GC/MS/MS triple quadrupole system. The identification was done by comparing the retention time, retention indices and mass fragmentation pattern of the peaks with literature or standard compounds run under the same conditions. Quantitative analysis of each oil component, expressed in relative percentages of area, was carried out by peak area normalization measurements. The essential oil content in the *Laserpitium latifolium* was found to be 0.164% based on the dry weight. Twenty six constituents, representing 98.9% of the oil were identified. The chemical composition of the oil is characterized by high amount of monoterpenes, of which hydrocarbons were 88.6% and oxygenated monoterpenes 7.6%. The main constituents identified in *L. latifolium* essential oil were sabinene (47.8%), α -pinene (25.0 %) and β -pinene (7.1%).

Sažetak

Laserpitium latifolium (porodica Apiaceae), u narodu poznata kao javorak, je višegodišnja biljka. Široko je rasprostranjena u većem delu Evrope, s obzirom da sadrži aromatične komponente ima lekovito dejstvo posebno za životinje. Veruje se da koren ove biljke pomaže pri stomahnim oboljenjima i pri smanjenju groznice. Kao lekovitija biljka presađena je sa svog prirodnog staništa. Etarsko ulje ove biljke dobijeno je hidrodestilacijom u trajanju od 3 h u aparaturi po Klevendžer-u, a hemijska analiza urađena je GC/MS/MS metodom sa triple tandem kvadripol detektorom. Identifikacija komponenata vršena je poređenjem retencionih vremena, retencionih indeksa i masama fragmentisanih osnovnih pikova sa literaturom ili standardima snimljenim pod istim uslovima. Kvantitativna analiza svake komponente ulja prikazana je kao relativan procenat površine pika, pritom je vršena normalizacija merenja površine ispod pika. Prinos etarskog ulja *L. latifolium* je 0,164% računajući na suhu biljku. U ulju je identifikovano 26 komponenti što predstavlja 98,9% ulja. Hemijski sastav ulja karakteriše veliki sadržaj monoterpena od čega su ugljovodonični 88,6% i oksidovani monoterpeni 7,6%. Dominantne komponente u etarskom ulju *L. latifolium* su: sabinen (47,8%), α -pinen (25,0 %) i β -pinen (7,1%).



Synthesis and biological activity of new derivatives based on aminoanthraquinones

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amino acid,
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tyrosine kinase activity,
antimicrobial activity.

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Abstract: In spite of the well-studied chemistry of dyes and anticancer drugs based on 9,10-anthraquinone, many anthraquinone derivatives remain still unknown. Therefore, the aim of our work was synthesis and investigation of biological activity of new N-benzoyl-N'-(9,10-dioxo-9,10-dihydroanthracen-1-yl)-thioureas, N-(9,10-dioxo-9,10-dihydroanthracene-1-yl)-2-(N-benzoylimino) thiazoles, [(5-phenyl-4H-1,2,4-triazol-3-yl)amino]anthracene-9,10-diones, and amino acid derivatives of 2-chloro-N-(9,10-dioxo-9,10-dihydroanthracene-1-yl)acetamide. The influence of new derivatives of the 9,10-anthraquinone with benzoylthiourea, thiazole, triazole and amino acid fragments on the activity of membrane-associated tyrosine kinase was investigated. Inhibitors of protein tyrosine kinase activity of the membrane fraction, as promising agents to search for new potential anticancer agents among the studied compounds were discovered. Compounds with antioxidant properties and effect on lipid peroxidation and oxidative modification of protein were found among new derivatives of the 9,10-anthraquinone. Substances with antibacterial and antifungal activities against the test-cultures *S. aureus*, *M. luteum* and *A. niger* have identified among amino acid derivatives of the 9,10-anthraquinone.

Sažetak

Iako je hemija boja I anticancer lijekova zasnovanih na 9,10-antrakinonu jako proučavana, još uvijek je mnogo derivata antrakinona nije poznato. Zbog toga je cilj ovog rada bio sinteza i proučavanje biološke aktivnosti novih N-benzoil-N'-(9,10-diokso-9,10-dihidroantracen-1-il)-tiourea, N-(9,10-diokso-9,10-dihidroantracen-1-il)-2-(N-benzoilimino)tiazole, [(5-fenil-4H-1,2,4-triazol-3-il)amino]antracen-9,10-diona, i derivata amino kiselina 2-hloro-N-(9,10-diokso-9,10-dihidroantracene-1-il)acetamida. Uticaj novih derivata 9,10-antrakinona sa benzoiltioureom, tiazolnim, triazolnom i fragmentima amino kiselina na aktivnost tirozin kinaze povezane sa membranom je ispitivana. Među testiranim jedinjenjima su pronađeni novi inhibitori aktivnosti protein tirozine kinaze kao dijela membrane, koji se mogu koristiti kao potencijalna antikancer jedinjenja. Jedinjenja sa antioksidativnim osobinama i uticajem na lipidnu peroksidaciju i oksidativne modifikacije proteina su također pronađene među novim derivatima 9,10-antrakinona. Jedinjenja sa antibakterijskom i antifungalnom aktivnošću protiv testnih kultura *S. aureus*, *M. luteum* i *A. Niger* su identificarene među amino kiselinskim derivatima 9,10-antrakinona.



The importance of determining metals from human hair

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Keywords:

hair samples,
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Medical and forensic significance

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Abstract: In this study, is described the determination of the concentrations metals Zn, Cd and Cd in hair of subjects residing in the city of Sarajevo. The analysis of the metals in hair, has been done in a group of sixteen subjects of different sexes and different age. The group is made up of an equal number of respondents of both sexes. The results of the determination of the concentrations metals Zn, Cd and Pb give a general picture of the contents this metals in the hair and body of the subjects from the area of Sarajevo. Concentration of these metals allows us to gain an insight into the quality of food, the quality of the environment (air, water, ground), possible ways of contamination by toxic metals (Cd, Pb). The content of zinc in the hair of the respondents is in direct correlation with the concentration of lead and cadmium. Results of the analysis enable undertaking of lifestyle changes, so level of Zn can be normalized. Also, undertaking a detox program or measures to avoid intoxication in cases of elevated toxic metals content (Cd, Pb). Undertaking measures to correct the content of metals in the body can directly impact on the health of the respondents.

Sažetak

U ovom radu je opisano određivanje koncentracije metala Zn, Cd i Pb u kosi ispitanika koji žive u gradu Sarajevu. Analiza metala u kosi vršena je u grupi od šesnaest ispitanika različitih spolova i različite životne dobi. Grupa je sačinjena od jednakog broj ispitanika oba spola. Rezultati ispitivanja koncentracije metala Zn, Cd i Pb daju opću sliku o sadržaju navedenih metala u kosi odnosno organizmu grupe ispitanika sa područja Sarajeva. Izmjerene koncentracije ovih metala omogućavaju sticanje uvida u kvalitet ishrane, kvalitet životne sredine (zrak, voda, tlo), načine moguće kontaminacije toksičnim metalima (Cd, Pb). Koncentracija cinka u kosi ispitanika je u direktnoj korelaciji sa koncentracijom olova i kadmija. Rezultati analize omogućuju poduzimanje mjera za normaliziranje nivoa cinka u slučajevima narušenog balansa. U slučajevima povišenog sadržaja toksičnih metala (Cd, Pb), moguće je poduzimanje mjera kojim bi se toksikacija izbjegla ili izvršila detoksikacija. Poduzimanjem mjera radi korekcije sadržaja metala u organizmu, moguće je direktno uticati na zdravstveno stanje ispitanika.



Antioxidant Activity of Chlorogenic Acid and Ester Analogues

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Keywords:

Antioxidant activity,
Chlorogenic acid,
Chlorogenic acid derivatives,
Structure-activity relationship

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Abstract: Chlorogenic acid (3-CQA), an ester of caffeic acid and quinic acid, is a major phenolic compound in coffee and well known as a potent antioxidant. In this study two 3-CQA derivatives were prepared. Chlorogenic acid was esterified with methanol over Amberlite IR120-H to obtain methyl chlorogenate (Me-CQA), while 3',4'-dimethoxy methyl chlorogenate (3',4'-diMeO-Me-CQA) was prepared from 3-CQA by treatment with diazomethane. The structure of these derivatives was confirmed by spectroscopic methods (NMR, MS, IR). These compounds were tested for antioxidant properties to find a relationship between structure and antioxidant activity. Eight methods were selected in order to cover a diversity of mechanistic approaches: DPPH (2,2-diphenyl-1-picrylhydrazyl) radical scavenging, Galvinoxyl radical scavenging, ABTS [2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)] method, DMPD (*N,N*-dimethyl-*p*-phenylene-diamine) method, Phosphomolybdenum Assay, Reducing Power, Metal Chelating Activity and ORAC-_{OH} (Oxygen Radical Absorbance Capacity). In most of these tests 3-CQA showed the highest antioxidant activity in comparison to its derivatives.

Sažetak

Hlorogenska kiselina (3-CQA), ester kafene kiseline i kinske kiseline, glavni je fenolski spoj u kafi i poznata kao moćan prirodni antioksidans. U ovom radu pripremljena su dva derivata 3-CQA. Da bi se priredio metil hlorogenat (Me-CQA), 3-CQA je esterificirana metanolom preko Amberlita IR120-H, a za pripremanje 3',4'-dimetoksi metil hlorogenata (3',4'-diMeO-Me-CQA), 3-CQA je tretirana diazometanom. Struktura ovih derivata je potvrđena spektroskopskim metodama (NMR, MS, IR). Za ove spojeve određivan je antioksidativni kapacitet kako bi se našla veza između strukture i antioksidativne aktivnosti. Ukupno je korišteno osam metoda kako bi se obuhvatila raznolikost mehanističkog pristupa i to: "hvatanje" slobodnih radikala DPPH (2,2-difenil-1-pikrilhidrazil) i galvinoksil, ABTS [(2,2'-azino-bis(3-etilbenzotiazolin-6-sulfonska kiselina)] metoda, DMPD (*N,N*-dimetil-*p*-fenilendiamin) metoda, fosfomolibdatna metoda, moć redukcije, sposobnost helatacije i ORAC (kapacitet apsorpcije radikala kisika). U većini ovih testova, 3-CQA je pokazala veću antioksidativnu aktivnost u odnosu na svoje derivate.



Antioxidant Activity of Rosmarinic Acid, Gallic Acid and Their Derivatives

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Keywords:

Antioxidant activity
Rosmarinic acid
Gallic acid

Abstract: Phenolic acids are widespread phytochemicals that possess prominent antioxidant activity. Gallic acid is found in almost all plants, while rosmarinic acid, an ester of caffeic acid and 3,4-dihydroxyphenyllactic acid, is found mainly in plants of Lamiaceae family.

The aim of this work was to determine antioxidant activity of rosmarinic acid (RA), gallic acid (GA), and their derivatives obtained by methylation with diazomethane. The structure of the resulting derivatives was confirmed by NMR and MS. Determination of antioxidant activity was performed by five different methods, DPPH, ABTS, Phosphomolybdenum Assay, Reducing Power, and Metal Chelating Activity. Gallic acid was more effective antioxidant than rosmarinic acid in most of the assays applied, while their methylated derivatives had very low or no antioxidant activity. Gallic acid had better antioxidant activity in DPPH, ABTS and Reducing Power method, while rosmarinic acid had better antioxidant activity in Phosphomolybdenum Assay. All samples analyzed did not show ability to chelate metal ions and validity of the method was confirmed using EDTA as a positive probe.

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Sažetak

Fenolske kiseline su široko rasprostranjena vrsta fitohemikalija koje posjeduju značajnu antioksidacijsku aktivnost. Galna kiselina se nalazi u gotovo svim biljkama, dok se ruzmarinska kiselina, ester kafeinske i 3,4-dihidroksifenilmlječne kiseline, nalazi uglavnom u biljkama porodice Lamiaceae. Cilj ovog rada je bio odrediti antioksidacijsku aktivnost ruzmarinske kiseline, galne kiseline i njihovih derivata dobivenih metiliranjem diazometanom. Struktura nastalih derivata potvrđena je primjenom NMR i MS. Određivanje antioksidacijske aktivnosti vršeno je pomoću pet metoda, DPPH, ABTS, fosfomolibdatnom, metodom redukcijske moći i sposobnosti helatiranja. Galna kiselina se pokazala kao efikasniji antioksidans od ruzmarinske kiseline u većini primjenjenih testova, dok su njihovi metilirani derivati imali veoma nisku ili nikakvu antioksidacijsku aktivnost. Galna kiselina je imala bolju antioksidacijsku aktivnost kod DPPH, ABTS i metode redukcijske moći, dok je ruzmarinska kiselina pokazala bolju aktivnost primjenom fosfomolibdatne metode. Ispitivani uzorci nisu pokazali sposobnost helatiranja, a valjanost metode je potvrđena upotrebom EDTA kao pozitivne probe.



Synthesis and Characterization of Sulfur Containing Ethoxy

1,4-Benzoquinones

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Keywords:

Sulfur-containing 1,4-benzoquinones,
Nucleophilic reactions of quinones,
thiols.

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Abstract: In recent years, the nucleophilic reactions of substituted-1,4-benzoquinones have been a central focus of general interest in organic chemistry because of the fact that it is a convenient way to obtain new compounds that are building blocks have some principal molecular properties that make them attractive to the organic chemists. Sulfur-containing 1,4-benzoquinones are well known to be used for the construction of biologically important compounds which possess antitumor, antibacterial, antifungal, antimalarial and cytotoxic activities. We aimed at discovering new 1,4-benzoquinone derivatives possessing sulfur atoms in the side chain since chemical modifications of this class of compounds with sulfur groups lead to diverse biological properties. New sulfur-containing ethoxy-1,4-benzoquinone scaffold such as 2,6-Diethoxy-3,5-di(thio)-1,4-benzoquinone promising new biologically active compounds were synthesized from the reactions of substituted-1,4-benzoquinones and thiols with a base and solvent at room temperature. Various spectroscopy techniques (FT-IR, ^1H NMR, ^{13}C NMR, MS) have been employed to clarify the structures of obtained compounds.

Sažetak

Posljednjih godina nukleofilne reakcije supstituiranih-1,4-benzokinona su u centralnom fokusu i od općeg interesa u organskoj hemiji zbog činjenice da predstavljaju pogodan način za dobijanje novih spojeva koji su gradivni blokovi i imaju neka od osnovnih molekulskih svojstava zbog čega su privlačni organskim hemičarima. Dobro je poznato da se 1,4-benzokinoni, koji sadrže sumpor upotrebljavaju u izgradnji važnih bioloških spojeva koji posjeduju antitumorne, antibakterijske, antifungalne, antimalarijske i citotoksične aktivnosti. Ciljali smo da otkrijemo nove 1,4-benzokinonske derivate koji sadrže atome sumpora u bočnom lancu, pošto hemijska modifikacija ove klase spojeva sa sumpornim grupama vodi ka raznolikim biološkim svojstvima. Novi etoksi-1,4-benzokinon koji sadrži sumpor, kao što je 2,6-dietoksi-3,5-di(tio)-1,4-benzokinon je obećavajući biološki aktivni spoj sintetiziran u reakciji supstituiranih 1,4-benzokinona i tiola uz bazu i rastvarač pri sobnoj temperaturi. Različite spektroskopske tehnike (FT-IR, ^1H NMR, ^{13}C NMR, MS) su korištene radi pojašnjenja strukture dobijenih spojeva.



Mechanism of s-n Bond Formation in Oxidative Condensation of Aliphatic Amine and Mercaptothiazolil Anion by Natrium-hypochlorite

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Keywords:

morpholine,
electrophilic, complex,
aliphatic amines.

Abstract: The mechanism of the S-N bond formation is the reaction between thiazolyl disulphide and morpholine has been studied. Most of the reactions were performed in aqueous suspension of thiazolyl disulphides with sodium hypochlorite and morpholine. It was confirmed that the S-N bond formation in the reaction between morpholine and thiazolyl disulphite is not a two-steps reaction, S_N1 like reaction, and that the heterolytic breaking of the S-S bond in disulphide is not the first step of the reaction. The S-N bond formation can be explained as a nucleophilic substitution of di-coordinated sulphur assisted by the effect of the electrophile. In the first step of the reaction, the electrophilic species attack by morpholine. The structure of the complex and transition state for nucleophilic displacement at the di-coordinated sulphur atom are given, according to the „three atoms in the line“ theory.

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Sažetak

U ovom radu ispitivan je mehanizam stvaranja S-N veze u reakciji između 2,2-benz-tiazolil disulfida i morfolina. Većina reakcija izvođena je u vodenoj suspenziji tiazolil disulfida sa natrijum hipohloritom i morfolinom. Utvrđeno je da stvaranje S-N veze u reakciji tiazolil disulfida i morfolina nije dvostepena reakcija i da ne obuhvata heterolitičko raskidanje S-S veze kao prvu fazu reakcije. Formiranje S-N veze okarakterisano je kao nukleofilna supstituciona reakcija na di-koordinativnom sumporu kod tiazolil disulfida koja je potpomognuta efektom elektrofila. U prvoj fazi reakcije elektrofilna vrsta napada disulfidnu vezu gradeći kompleks, koji zatim podliježe nukleofilnom napadu morfolina. Data je vjerovatna struktura kompleksa kao i prelazno stanje za nukleofilnu supstituciju na di-koordinativnom sumporovom atomu koji se uklapa u teoriju „linearnosti tri atoma“ u prelaznom stanju.



Interactions of Melatonin and copper(II) melatonin complex with pUC19 DNA

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Keywords:

Melatonin
pUC19 DNA
antioxidant

Abstract: Melatonin (N-acetyl-5-methoxytryptamine) is the main secretory product of the pineal gland of mammals. It is well known as a free radical scavenger and antioxidant involved in different biological and physiological regulation such as modulation of circadian rhythms, seasonal reproduction, retinal physiology and sleep regulation. Earlier studies have shown that melatonin protects DNA from oxidative stress and free radicals attack. In this study, the interaction of melatonin, copper and synthesized complex of copper and melatonin with supercoiled plasmid pUC19 DNA was investigated by spectroscopic methods and agarose gel electrophoresis. Absorption titration with melatonin and pUC19 DNA showed that no major difference was observed in the value of λ_{\max} of pUC19 DNA alone and pUC19 DNA in the presence of different melatonin concentrations. The electrophoretic results indicated the slower migration speed for pUC19 DNA treated with 200 μM melatonin solution only. Bands were not completely resolved indicating interaction of melatonin with pUC19 DNA but with low cleavage efficiency.

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Sažetak

Melatonin (N-acetil-5-metoksitriptamin) je glavni produkt sekretorne pinealne žlijezde kod sisara. Poznat je kao antioksidant i „hvatač“ slobodnih radikala, te je uključen u različite biološke i fiziološke reakcije, regulira dnevni bioritam organizma, reprodukciju, fiziologiju vida, te ciklus spavanja i buđenja. Ranija istraživanja su pokazala da melatonin štiti DNA od oksidativnog stresa i uticaja slobodnih radikala. U ovom istraživanju posmatran je uticaj melatonina, bakra i ranije sintetiziranog kompleksnog spoja bakra i melatonina, sa plazmidnom DNA (pUC19 DNA), posmatranom spektroskopskom metodom i agaroznom gel elektroforezom. Titracija melatonina sa pUC19 DNA nije pokazala značajne promjene naksimalne abosrbanse same pUC19 DNA i pUC19 DNA u prisustvu različitih koncentracija melatonina. Elektroforetska migracija je sporija u odnosu na sam pUC19 DNA, tretiran sa 200 μM melatoninom. Trake nisu u potpunosti razdvojene što ukazuje na interakciju melatonina s pUC19 DNK, ali s niskom učinkovitosti cijepanja pUC19 DNK