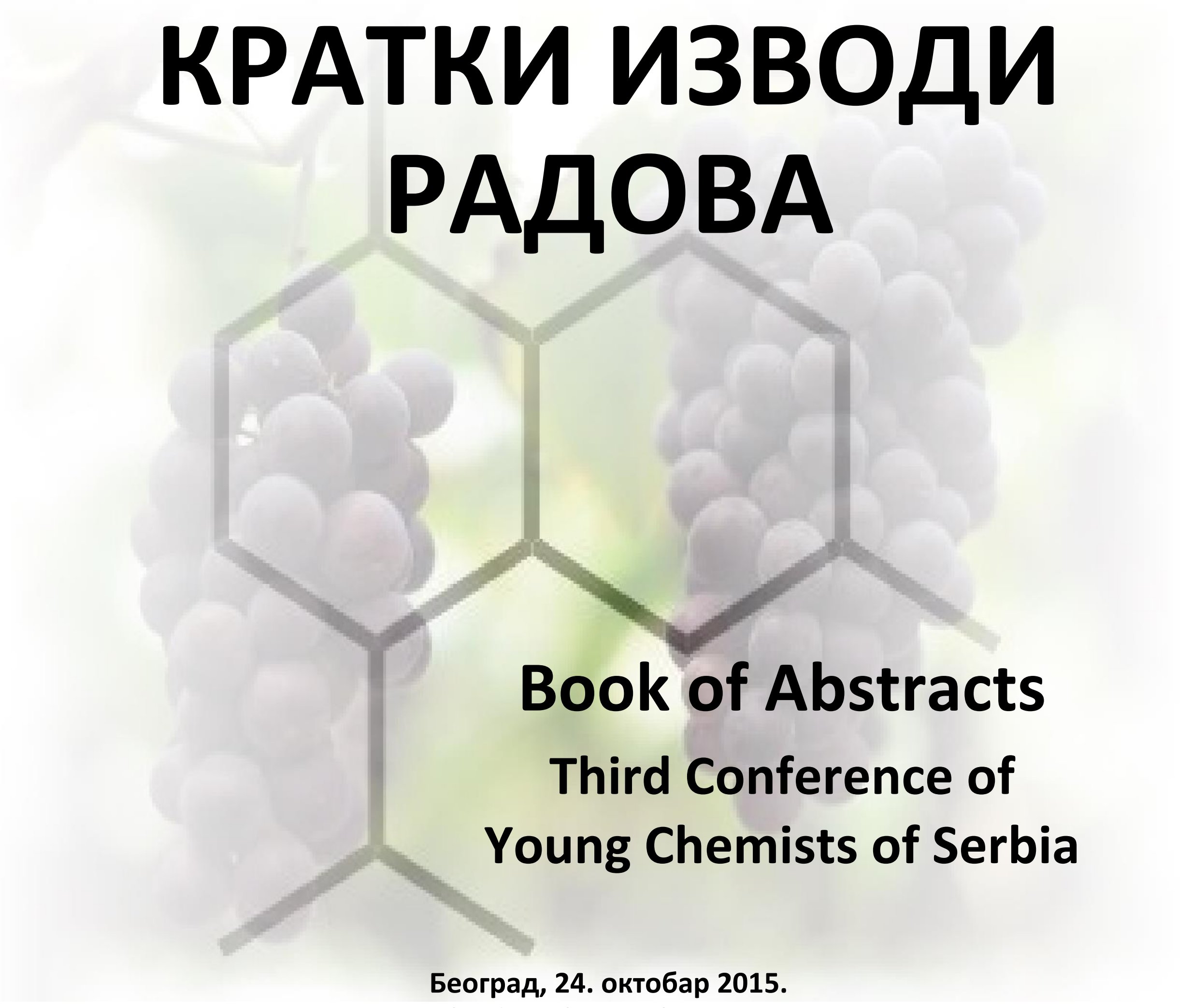
Serbian Chemical Society
Српско хемијско друштво
Клуб младих хемичара Србије
Serbian Young Chemists' Club

ТРЕЋА КОНФЕРЕНЦИЈА МЛАДИХ ХЕМИЧАРА СРБИЈЕ

КРАТКИ ИЗВОДИ РАДОВА



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КРАТКИ ИЗВОДИ РАДОВА

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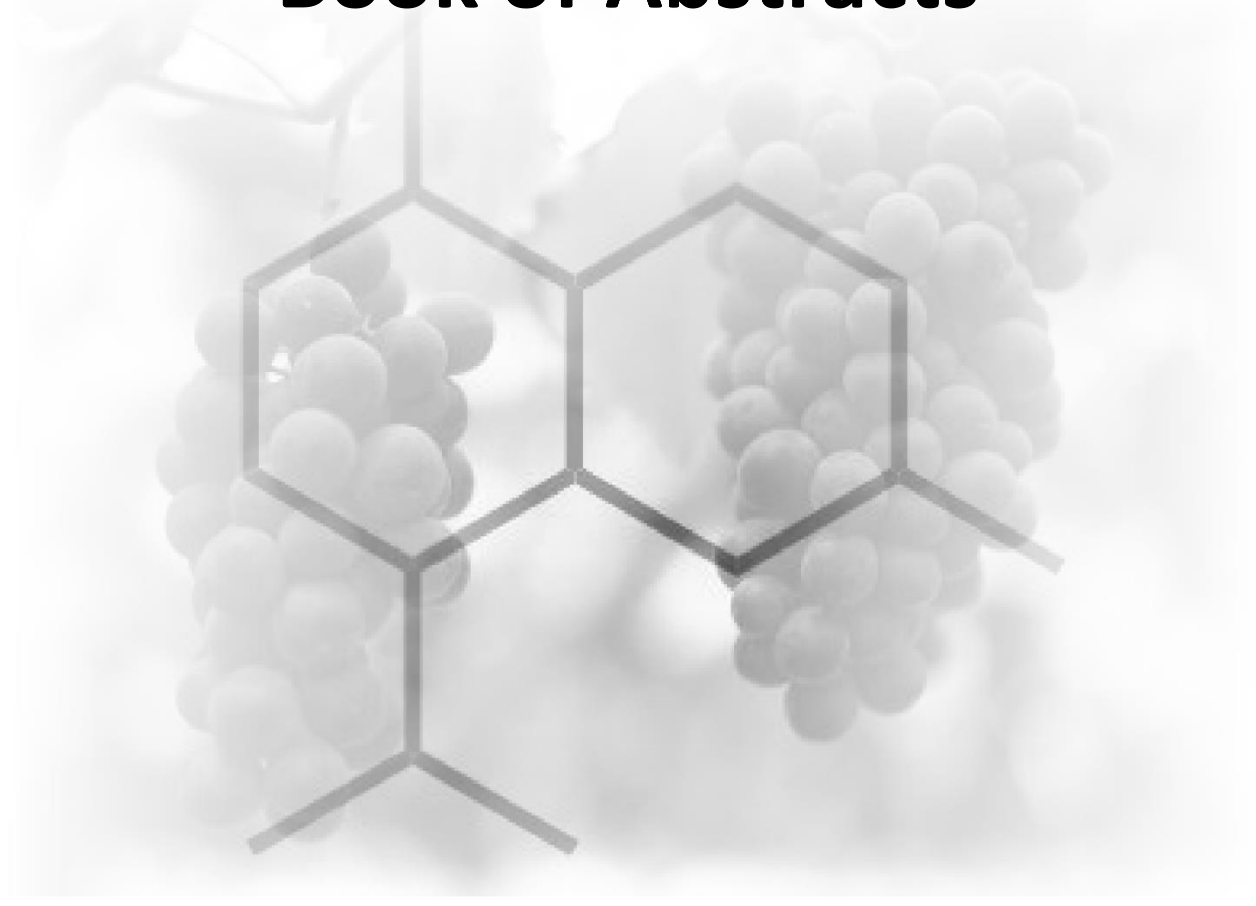

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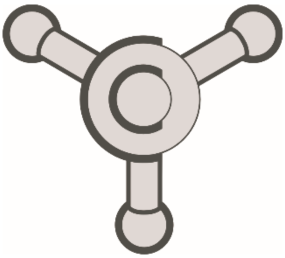

Serbian
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PP 01

HPTLC profili za određivanje autentičnosti propolisa

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Karakterizacija meda i drugih pčelinjih proizvoda primenom različitih analitičkih postupaka, u cilju određivanja krivotvorenja ili geografskog i botaničkog porekla, dugo zaokuplja pažnju naučnika zbog izraženog farmakološkog i nutritivnog dejstva ovih prirodnih proizvoda. Autentičnost i kvalitet hrane se vrlo često određuju na osnovu hromatografskih profila koji predstavljaju set karakterističnih hromatografskih signala, čije upoređivanje dovodi do prepoznavanja pojedinačnih uzoraka. Ceo hromatogram se tretira kao jedinstveni multivarijantni 'otisak prsta' uzorka, odnosno multivarijantni vektor, bez specijalne identifikacije pojedinačnih pikova. Visoko-efikasna tankoslojna hromatografija (Higth-performance thin-layer chromatography – HPTLC) kombinovana sa postupcima obrade slike i multivarijantne analize podataka može se koristiti za profilisanje i klasifikaciju uzoraka hrane. U ovom radu će biti prezentovan HPTLC u kombinaciji sa softverom za obradu slike koji su upotrebljeni za dobijanje fitohemijskog profila ekstrakata propolisa i prikupljanje podataka, kao i različite hemometrijske metode upotrebljene za njihovu klasifikaciju prema botaničkom i geografskom poreklu.

Zahvalnica: Ova istraživanja su podržana od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije (projekat br. 172017).

HPTLC profiling in authenticity assesments of propolis

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The analytical characterization of honey and other bee products in order to detect adulteration or to verify geographical or botanical origin has been a scientific long-time preoccupation due to their pronounced pharmacological and nutritional benefits. The chromatographic profile is usually taken into consideration for an assay of authenticity and quality of food. Fingerprint analysis of food samples could be defined as a set of characteristic chromatographic signals, which comparison leads to sample recognition. The entire chromatogram is treated as unique multivariate fingerprint, i.e. multidimensional vector, without special identification of single peaks. High-performance thin-layer chromatography (HPTLC) combined with image analysis and pattern recognition methods could be used for fingerprinting and classification of food samples. Current work will present HPTLC in combination with software for image processing applied for fingerprinting of propolis extracts and data acquisition, and pattern recognition methods applied for their classification according to botanical and geographical origin.

Acknowledgements: This research was supported by the Ministry of education, science and technological development of the Republic of Serbia (Grant No. 172017).

PP 02

Analiza dugotrajnih organskih zagađivača (POPs) – osnove i trendovi

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Kao što im ime kaže, dugotrajni organski zagađivači (POPs) predstavljaju grupu organskih jedinjenja koja se u prirodi (vodi, zemljištu i vazduhu) zadržavaju u nepromenjenom obliku dugi vremenski period, pri čemu se nagomilavaju u masnom tkivu i biokoncentruju u lancu ishrane, a pre svega su toksična za ljude i ekosistem. Pod okriljem Ujedinjenih nacija 2001. godine usvojena je Stokholmska konvencija kojom je 12 najupornijih zagađivača (12 žigosanih) svrstano u tri kategorije POPs-ova: pesticidi, industrijske hemikalije i nenamerno proizvedene hemikalije. Ovo predavanje će se biti fokusirano na dva koncepta gasno-masenih analiza: na analizi uzoraka iz životne sredine i na analizama ljudskog biomonitoringa ovih jedinjenja. Analize uzoraka iz životne sredine (pre svega vazduha i zemljišta) upošljavaju dobro poznate analize zasnovane na gasnoj hromatografiji sa različitim spektrom injektorskih sistema sa jedne strane i detektora sa druge strane.
Analiziranje humanih uzoraka na prisustvo tragova POPs-ova zahteva korišćenje najsavremenijih analitičkih instrumenata koji uvode unapređenja i u gasno-hromatografski, ali i u maseno-spektrometrijski deo. Tako se danas može rutinski postići osetljivost na femtogramskom nivou. Kompresovanje pomoću kriogene zone i promenljiva petlja (dvodimenzionalna gasna hromatografija) povezana masenim spektrometrima visoke rezolucije: magnetnim sektorskim analizatorom, orbitrapom i Q-TOF-om predstavljaće smer u kome će se kretati buduće analize ultra razblaženih humanih uzoraka ovih jedinjenja.

Analysis of Persistent Organic Pollutants (POPs) from basics to future trends

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Persistent Organic Pollutants (POPs) are group of carbon based pollutant that: remain intact for exceptionally long periods of time, wildly distributed all over the environment (soil, water and air), accumulate in the fatty tissue of living organisms including humans through process called bioaccumulation, and last but not the least they are toxic to humans and environment. The Stockholm Convention was adopted and put into practice by the United Nations Environment Programme (UNEP) in 2011. Initially, twelve POPs (The Dirty Dozen) have been recognized by the Stockholm Convention as toxic chemical for humans and the ecosystem and these can be placed in 3 categories: pesticides, industrial chemicals, and by-products. Nowadays, the Stockholm Convention has grown and covered 23 different POPs, and all are divided in three different annexes: A. Elimination, B. Restriction and C. Unintentional production.
This presentation will focus on two approaches. The first considers GC based POPs analysis of environmental sample and the second will cover ultra-trace levels of POPs analysis in the frame work of human biomonitoring. Sensitivity could be high enough for femtogram level analysis. Large volume injection, cryogenic zone compression and loop modulation coupled with HRMS (Magnetic sector, Orbitrap and Q-TOF) to measure POPs will be way were ultra level trace analysis will go.

Предавање по позиву / Invited Lecture

PPP 01

Flavanols and methylxanthines in chocolate and plant extracts

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Flavanols and their dimer procyanidins as well as methylxanthines are two groups of plant secondary metabolites which act in plants as protectors against herbivores and pathogens (bacteria, fungi). Flavanols and procyanidins are desired compounds in human diet because of their potential to prevent cardiovascular diseases, while methylxanthines have among positive effects (increasing attention, physical performance and muscular recovery etc.), in higher doses negative side effects (shivering, wakefulness, heart beating and even delirium). Flavanols and procyanidins can be found in different food of plant origin such as grape seeds, apples, barley, junipers seeds, while chocolate and cacao as a processed food are known as a higher amount of both groups of secondary metabolites.

The aim of our study was to develop analytical methods for fast screening and quantitative determination of flavanols, procyanidins and methylxanthines in chocolate samples and plant extracts. TLC on silica gel and cellulose plates using different developing solvents following derivatization with sensitive and selective detection reagent on the base of 4-dimethylaminocinnamaldehyde [1] were applied for qualitative and quantitative analyses of chocolate samples and plant extracts as well as to control the optimization steps of solid-phase extraction. HPLC separation of flavanols and procyanidins on ordinary RP column usually takes about 60 minutes in spite of gradient elution. To develop HPLC methods, which would enable faster separation of flavanols, procyanidins and methylxanthines in one run, we applied two C_{18} core-shell columns of different producers and mobile phases based on acetonitrile-water or methanol-water with addition of acetic or formic acid. The optimization, which included also the optimization of the gradient elution, the flow rate and the temperature resulted in the baseline separation of five flavanols (epigallocatechin, catechin, epicatechin, epicatehin gallate), three procyanidins (procyanidin B1, B2 and A2), three methylxanthines (theobromine, theophylline and caffeine) in less than 15 minutes. Both methods were validated, tested by use of the baking chocolate standard reference material SRM 2384 (National Institute of Standards and Technology) and applied to the analysis of the real samples.

1. V. Glavnik, B. Simonovska, I. Vovk, Densitometric determination of (+)-catechin and (-)-epicatechin by 4-dimethylaminocinnamaldehyde reagent, *J. Chromatogr. A*, **1216** (2009) 4485

Саопштења / Contributions

Hemija hrane - Food Chemistry

HH O 01

Dried fruits of *Sorbus aucuparia* L. 1753 as a new antioxidant agents

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Rowan (*S. aucuparia*) has been extensively used in folk medicine for different digestive disorders. Also, traditionaly prepared products are utilized as a treatments for anemia, edema, dyspersia, gout, diathesis and for normalizing metabolism. However, fruits of rowan have been poorly investigated regarding antioxidant potency. Consequently, the aim of this study was to define phenolic profile and antioxidant activity of water and methanol extracts of dried fruits. The content of 44 phenolics and quinic acid in extracts was determined using LC-MS/MS technique. In order to examine antioxidant potency, three *in vitro* assays were carried: DPPH (diphenylpicrylhydrazyl), NO (nitric oxide) and $O_2^{\bullet-}$ (superoxide anion radical) radical scavenging capacity. LC-MS/MS analyses of selected phenolics resulted in determination of 11 compounds. Among examined compounds, quinic acid (precursor of phenolics) was the most dominant in both samples, followed by chlorogenic and caffeic acid. In applied assays, both extracts showed potent antioxidant effect compared to propyl gallate (PG), a well known synthetic antioxidant. Overall, obtained results introduce fruits of *S. aucuparia* as a possible new source of phenolics and antioxidant agents.

The Ministry of Education and Science RS (Grant No.172058) supported this research work

Suvi plodovi vrste *Sorbus aucuparia* L. 1753 kao novi antioksidantni agensi

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Jarebika (*S. aucuparia*) se u narodnoj medicini obimno koristi za različite poremećaje sistema za varenje. Takođe, tradicionalno pripremljeni proizvodi upotrebljevaju se u lečenju anemije, otoka, dispersije, gihta, dijateze, kao i za normalizovanje metabolizma. Međutim, antioksidantni potencijal plodova jarebike je nedovoljno ispitan. Stoga, cilj prikazanih ispitivanja bio je određivanje fenolnog profila i antioksidantne aktivnosti vodenih i metanolnih ekstrakata suvog ploda. Sadržaj 44 odabrana fenolna jedinjenja i hinske kiseline ispitan je primenom LC-MS/MS tehnike. U cilju određivanja antioksidantnog potencijala sprovedena su tri *in vitro* testa: određivanje kapaciteta hvatanja DPPH (1,1-difenil-2-pikrilhidrazil), NO i $O_2^{\bullet-}$ (superoksid anjon radikal). LC-MS/MS analizom identifikovano je prisustvo 11 fenolnih jedinjenja. Hinska kiselina (prekursor fenola) je bila dominatna u oba ekstrakta, praćena hlorogenskom i kafenom kiselinom. U poređenju sa standardnim antioksidansom, propil galatom (PG), oba ekstrakta su pokazala dobru antikosidantnu aktivnost u primenjenim testovima. Uopšteno, dobijeni rezultati ukazuju na moguću primenu plodova *S. aucuparia* kao izvora fenolnih jedinjenja i antioksidantnih agenasa.

Rad je finansiran od strane Ministarstva prosvete i nauke RS (IO 172058)).

HH O 02

Optimizacija mikrotalasne ekstrakcije sporednog proizvoda od divlje jabuke (*Malus sylvestris*)

Tijana N. Hojan, Abdulhakim Naffati, Branimir Pavlić, Jelena Vladić
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Prilikom proizvodnje mešavine filter čaja, koji kao jednu od komponenata sadrži divlju jabuku, proizvede se oko 20-30% sprednog proizvoda/otpada od divlje jabuke, tzv. „herbalne ili voćne prašine“. To je materijal čije su čestice manje od prečnika pora na filter vrećici. Obzirom na visok sadržaj farmakološki aktivnih supstanci u nativnom materijalu divlje jabuke, pretpostavka je da bi se primenom odgovarajućih ekstrakcionih metoda iz ovakvog materijala moga dobiti visokokvalitetan proizvod. U tom cilju je primenjena i analizirana mikrotalasna ekstrakcija, pri čemu su varirani sledeći ekstrakcioni prametri: vreme ekstrakcije (15, 25 i 35 min), koncentracija etanola (40, 60 i 80%) i snaga mikrotalasnog zračenja (400, 600 i 800 W). U dobijenim tečnim ekstraktima divlje jabuke određeni su: sadržaj ukupnih fenola, sadržaj ukupnih flavonoida, antioksidativna aktivnost DPPH metodom i redukcioni kapacitet. Proces mikrotalasne ekstrakcije optimizovan je korišćenjem metode odzivnih površina (engl. *Response Surface Methodology, RSM)*. U dobijenim ekstraktima sadržaj suvog ostatka se kreće od 4,238 do 5,950 g/100 ml ekstrakta, sadržaj ukupnih fenola od 1,8140-3,6992 mg EGK/ml tečnog ekstrakta, a sadržaj flavnoida od 0,8195-1,5558 mg KE/ml. Zbog visokog sadržaja fenola ispitivani ekstrakti su pokazali visoke antioksidativne aktivnosti (IC50 od 0,3091 do 0,6209 µl/ml test smeše) i redukcione kapacitete (EC50 od 0,5004 do 1,5208 µl/ml test smeše).

Optimization of microwave extraction byproduct of wild apples (*Malus sylvestris*)

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When producing a mixture of filter tea as one of the components comprising the wild apple, produces about 20-30% sprednog product/waste of wild apples, so-called. "herbal or fruit dust". That is a material with a particle smaller than the diameter of the pores of the filter bag. Due to the high content of pharmacologically active substances in the native material of wild apples, the assumption is that the application of appropriate extraction method from such materials could get a high quality product. For this purpose, the microwave extraction applied and analyzed, wherein the extraction were varied: a drive parameters from the following: the time of extraction (15, 25 and 35 min), the concentration of ethanol (40, 60 and 80%) and the power of microwave irradiation (400, 600, and 800 W). The obtained liquid extracts of wild apples were determined: total phenol content, the content of total flavonoids, antioxidant activity DPPH method and reducing capacity. Microwave extraction process was optimized using Response Surface Methodology (RSM). In the obtained extract content of dry residue ranges from 4,238 to 5,950 g / 100 ml of extract total phenol content of from 1.8140 to 3.6992 mg EGK / ml of liquid extract, a content of from 0.8195 to 1.5558 mg flavnoida CE / ml. Due to the high content of phenols tested extracts showed high antioxidant activity (IC50 of 0.3091 to 0.6209 µl/ml of the test mixtures) and the reducing capacity (EC50 of 0.5004 to 1.5208 µl/ml of the test mixtures).

HH O 03

Uticaj prehrambenih aditiva na spektroskopske parametre Betanina

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Betanin, Cvekla crvena, E 162, je po hemijskom sastavu 4-(2-(2-karboksi-5-(β-D-glukopiranoziloksi)-2,3-dihidro-6-hidroksi-1H-indol-1-il)etenil)-2,3-dihidro-(S-R*,R*))-2,6-piridinedikarboksilna kiselina. Da bi se ispitalo da li pojedini aditivi, često prisutni u hrani, izazivaju promenu uticaja hromofore u molekulu boje i promenu njenog molarnog apsorpcionog koeficijenta izvršeno je ispitivanje o uticaju (vitamina C, limunske kiseline i aspartama) na spektroskopske karakteristike Betanina pomoću VIS spektrofotomertijske analize (350-700 nm). Merenjima je potvrđeno da vitamin C, limunska kiselina i aspartam, kao aditivi ne utiču na promenu u intenzitetu apsorpcionog maksimuma boje Betanina, niti na promenu njegovog položaja. Vrednost molarnog apsorpcionog koeficijenta izračunata na talasnoj dužini λ=535 nm iznosila je ε=107,38 $dm^3/mol\cdot cm$. Dobijeni rezultati i vrednosti spektroskopskih parametara potvrdili su mogućnost direktne primene VIS metode za kvantitativnu determinaciju ove prehrambene boje u namirnici u prisustvu određenih aditiva.

The influence of additives on the spectroscopic parameters of Betanin

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Betanin, Beetroot Red, E 162, is chemically 4-(2-(2-carboxy-5-(β-D-glucopyranosyloxy)-2,3-dihydro-6-hydroxy-1H-indol-1-yl)ethenyl)-2,3-dihydro-(S-(R*,R*))-2,6-pyridinedicarboxylic acid. In order to investigate whether particular additives often found in food cause change of chromophores influence in dye molecule and change of its molar absorptive coefficient, it was performed the investigation of influence (vitamin C, citric acid, aspartame) on spectroscopic characteristics of Food Blue 5 using VIS spectrophotometric analysis (350-700 nm). Vitamin C, citric acid and aspartame as an additives were confirmed in measurements that does not affect changes neither in intensity of maximum of absorption of dye Betanin, nor in its position. The value of molar absorption coefficient was calculated on wavelength λ=535 nm; it is ε=107.38 $dm^3/mol\cdot cm$. The obtained results together with the spectrocsopic parameters have confirmed the possibility of direct VIS method application to quantitatively determinef this food dye in foodstuff with certain additives present in them.

HH O 04

Characterisation and comparison of Croatian unifloral honeys according to micro and macro element content

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In this study twenty elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Pb, S, Zn) were determined in 12 lime (*Tilia* sp.), 13 chestnut (*Castanea sativa* Mill.) and 17 black locust (*Robinia pseudoacacia* L.) honey samples from Croatia by inductively coupled plasma atomic emission spectrometry (ICP-OES). Honey samples were prepared for analysis using microwave acid digestion procedure. Samples were collected during the 2014 harvesting season. Botanical origin of samples was determined by the combination of physicochemical, melissopalynological and sensory analyses. Potassium, calcium and phosphorus were the most abundant elements in all three honey types. Similar percentage shares (%) of potassium, calcium and phosphorus in the total micro and macro element content were found for lime and chestnut honey (K 79.0-91.1 and 86.4-90.9, Ca 4.2-14.5 and 4.9-7.8, P 1.8-5.2 and 1.5-2.2, respectively) while in black locust honey samples potassium share was lower and calcium and phosphorus share was considerably higher (K 57.1-77.7, Ca 7.5-25.0, P 7.4-12.5). Average manganese concentration in chestnut honey samples (20.77 mg kg^{-1}) was substantially higher in comparison with other two honey types (lime 1.04 mg kg^{-1} and black locust 0.16 mg kg^{-1}). Concentration of potentially toxic elements (As, Cr, Cd, Pb, Hg) was very low in all honey samples, with exception of one lime honey sample which beside high concentrations of chromium also had high concentrations of zinc, iron, and aluminium, indicating the possibility of storage or environmental contamination.

HH P 01

Polifenolni profil ploda evropskog koprivića

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Celtis australis L., poznatiji kao evropski koprivić, je listopadno drvo prvobitno svrstano u porodicu skrivenosemenica (Ulmaceae). Nedavna fizičko-hemijska ispitivanja omogućila su re-klasifikaciju ove biljke u porodicu konoplji (Cannabaceae). Zahvaljujući svojim antioksidativnim svojstvima ima različitu primenu u narodnoj medicini: kao lek za teška menstrualna krvarenja i grčeve, prelome kostiju, kontuzije, uganuća i bolove u zglobovima. S obzirom na nedovoljno proučen fitohemijski sastav koprivića, cilj ovog rada je bio da se utvrdi njegov polifenolni profil primenom ultraefikasne tečne hromatografije sa hibridnim linearni trap - orbitrap masenim analizatorom. Na osnovu odgovarajućih spektralnih karakteristika: masenog spektra, tačne mase, karakterističnih fragmenata i specifičnog retencionog vremena, u metanolnim ekstraktima ploda koprivića identifikovano je četrdeset devet fenolnih kiselina i flavonoida.

Polyphenolic profile of the fruit of the European hackberry

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Celtis australis L., better known as the European hackberry, is a deciduous tree previously placed in the family of angiosperms (Ulmaceae). Recent physicochemical researches supported the re-classification of this plant to the family of hemp (Cannabaceae). Thanks to its antioxidative properties European hackberry has various uses in folk medicine: as a cure for heavy menstrual bleedings and colic, as well as a cure for bone fracture, contusions, sprains and joint pains. Since the phytochemical composition of the hackberry is insufficiently studied, the aim of this study was to obtain its polyphenolic profile using ultra-performance liquid chromatography with hybrid linear trap - Orbitrap mass analyzer. According to the corresponding spectral characteristics: mass spectra, accurate mass, characteristic fragmentation, and characteristic retention time, forty nine phenolic acids and flavonoids were identified in the methanol extracts of the fruit of the European hackberry.

HH P 02

Fitohemijski "otisak prsta" obične planike

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Postoje epidemiološki dokazi da nedovoljan unos voća i povrća može dovesti do hroničnih poremećaja zdravlja, uključujući rak i kardiovaskularne bolesti. Fitohemikalije sa izraženim antioksidativnim svojstvima, kao što su polifenoli prisutni u voću i povrću, mogu učestvovati u prevenciji pomenutih bolesti, što dovodi do povećanog interesovanja za identifikaciju ovih komponenti u biljkama. Dobar izvor antioksidanasa jeste obična planika. Drvo obične planike (*Arbutus unedo* L., Ericaceae) je zimzeleno šiblje karakteristično za mediteransko područje. Listovi obične planike se koriste u narodnoj medicini u terapiji hipertenzije i dijabetesa. Cilj ovog rada je bio da se utvrdi detaljan polifenolni profil, tzv. "otisak prsta" uzoraka liofilizata lista obične planike iz Hrvatske. Polifenolni profil je dobijen primenom ultra-efikasne tečne hromatografije spregnute sa hibridnim linearni trap i orbitrap masenim analizatorom. Više od 40 fenolnih kiselina i flavonoida identifikovano je na osnovu odgovarajućih spektralnih karakteristika: masenog spektra, tačne mase, karakterističnih fragmenata i specifičnog retencionog vremena.

Phytochemical fingerprint of the strawberry tree

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There is epidemiological evidence that insufficient intake of fruit and vegetables can lead to chronic health problems, including cancer and cardiovascular diseases. Phytochemicals with strong antioxidant properties, such as polyphenols present in fruits and vegetables, may participate in the prevention of the above-mentioned diseases, which leads to an increased interest for identifying these components in plants. Good source of antioxidants is the strawberry tree (*Arbutus unedo* L., Ericaceae). It is an evergreen shrub typical for the Mediterranean area. Its leaves are used in folk medicine in therapies against hypertension and diabetes. The aim of this work was to establish a polyphenolic profile ("fingerprint") of the samples of lyophilisate of leaves of a strawberry tree from Croatia. A polyphenolic profile was obtained by using ultra-preformance liquid chromatography coupled to Orbitrap mass spectrometry. More than 40 phenolic acids and flavonoids, were identified according to the corresponding spectral characteristics: mass spectra, accurate mass, characteristic fragmentation, and characteristic retention time.

HH P 03

Korelacija između koncentracije ukupnih fenola i boje izabranih slovenačkih vina

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Ovim istraživanjem je pokušano da se utvrdi da li su boja vina i koncentracija ukupnih fenola u izabranim vinima u pozitivnoj korelaciji. Ispitano je pet vina proizvedenih u Sloveniji: dva bela (Svečinčan elegant - Turistična kmetija Jarc, Zgornja Kungota 2014 i Laški rizling – domaći 2014), jedan roze (Poletni Rose - Vinogradništvo in izletniška kmetija Leber, Kungota 2014) i dva crna (Efekt - Hiša vina Doppler Zg. Kungota 2014 i Cabernet Sauvignon - Quercus, Vinska klet Goriška brda z.o.o., Dobrovo 2014). Spektrofotometrijski je određen intenzitet boje izabranih vina, a koristeći Folin-Ciocalteau reagens u istim vinima je utvrđena i koncentracija ukupnih fenola u ekvivalentima galne kiseline. Rezultati pokazuju da su boja i koncentracija ukupnih fenola izabranih vina u značajnoj pozitivnoj korelaciji ($R=0,977$; $p<0,1$). Kako je ranije utvrđena pozitivna korelacija između fenolnog sadržaja i antioksidativne aktivnosti vina[1], rezultati istraživanja ukazuju da tamnija izabrana vina imaju i veću antioksidativnu aktivnost.

Correlation between the concentration of total phenols and colour of chosen Slovenian wines

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This investigation studied if the colour density and the concentration of total phenols is in positive correlation for five chosen wines made in Slovenia. The wines chosen varied in colour. The investigation was carried on two white wines (Svečinčan elegant - - Turistična kmetija Jarc, Zgornja Kungota 2014 and Laški rizling – homemade 2014), one rosé (Poletni Rose - Vinogradništvo in izletniška kmetija Leber, Kungota 2014) and two red wines (Efekt - Hiša vina Doppler Zg. Kungota 2014 and Cabernet Sauvignon - Quercus, Vinska klet Goriška brda z.o.o., Dobrovo 2014). The colour density was determined spectrophotometrically, as well as the concentration of total phenols expressed as gallic acid equivalents using the Folin-Ciocalteau's reagent. Results show that the colour density and the concentration of total phenols of five chosen Slovenian wines are strongly positively correlated ($R=0.977$, $p<0.1$). Since previous investigations showed a positive correlation between the phenolic content and the antioxidant activity in wines[1], the results of the investigation further imply that the chosen wines with darker colour have higher antioxidant activity, and vice versa.

Reference:

1. D. Di Majo, M. La Guardia, S. Giammanco, L. La Neve, M. Giammanco, *Food Chemistry*, **111(1)** (2008) 45-49

Hemijska analiza - Chemical Analysis

HA P 01

Priprema uzorka spanaća (*Spinacia oleracea*) za određivanje piridoksina HPLC metodom

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Piridoksin (4,5-bis(hidroksimetil)-2-metilpiridin-3-ol) se uz piridoksamin i piridoksal naziva vitamin B6. Piridoksin se u prirodnom uzorku, kao što je spanać (*S. oleracea*), nalazi kao slobodan piridoksin, ali često i kao piridoksin fosfat ili u kompleksima sa proteinima i aminokiselinama. Postoje razrađene procedure pripreme uzorka za određivanja ukupnog piridoksina HPLC metodom, kojima se hidrolizuju ovi oblici piridoksina. Međutim, korisno je i znanje o količini samog piridoksina u uzorku jer on ima najveću biodostupnost. Istraživanjem su ispitani tretmani uzorka spanaća sa hlorovodoničnom kiselinom (0,1 *M*), sumpornom kiselinom (0,1 *M*), trihlorosirćetnom kiselinom (5 %) i sulfosalicilnom kiselinom (5 %) kao načini pripreme za HPLC određivanje piridoksina. Rezultati su pokazali da je tretman sulfosalicilnom kiselinom pogodna metoda za određivanje čistog piridoksina u spanaću. Metodom se očuva oko 89 % početne količine piridoksina i dobija se jasan pik na hromatogramu, što omogućava dobijanje jasnih i preciznih podataka o količini slobodnog piridoksina u spanaću. Smatra se da ovakva ili slična metoda može biti odgovarajuća i za druge molekule slične piridoksinu (kao što su drugi molekuli koji pripadaju grupi vitamina B), ali i za uzorke slične spanaću po svom sastavu.

Sample preparation for HPLC determination of pyridoxine in spinach (*Spinacia oleracea*)

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Pyridoxine (4,5-bis(hydroxymethyl)-2-methylpyridin-3-ol), together with pyridoxamine and pyridoxal is considered as vitamin B6. In natural sources, such as spinach (*S. oleracea*), pyridoxine can be found as free pyridoxine, but it is commonly found as pyridoxine phosphate or bound to proteins or amino acids. Current methods for HPLC determination of total pyridoxine consider hydrolysing these other forms of pyridoxine, so only free pyridoxine is present for analysis. However, knowledge about the amount of initial free pyridoxine in a sample is useful since this form has the highest bioavailability. The investigation examines the treatment of spinach sample with hydrochloric acid (0.1 *M*), sulphuric acid (0.1 *M*), trichloroacetic acid (5 %) and sulfosalicylic acid (5 %) as a method for preparing the sample for HPLC analysis. The results show that the treatment with sulfosalicylic acid is suitable method for preparing the sample for determining the free pyridoxine in spinach. The procedure gave recovery of approximately 89 % and the resulting peak assigned to pyridoxine is clear and sharp on the chromatogram. This enables for a clear and precise determination of free pyridoxine in spinach. Presumably, the method can also be applied for molecules similar to pyridoxine (other molecules from group of vitamin B, for example) and on samples similar to spinach by their composition.

HA P 02

Ekstrakcija nezasićenih masnih kiselina iz semena *Trigonella foenum-graceum* L. natkritičnim ugljenik(IV)-oksidom primenom različitih procesnih uslova

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Nezasićene masne kiseline su jedinstvena grupa jedinjenja sa širokim spektrom dejstava na biološke sisteme, kako su to pokazala brojna istraživanja, pri čemu je od posebnog interesa njihovo dobijanje iz prirodnih sirovina, kao što je seme *Trigonella foenum-graecum* L. (grčko seme). Natkritična ekstrakcija ugljenik(IV)-oksidom iz grčkog semena je optimizovana u cilju izolovanja nezasićenih masnih kiselina, identifikovanih i kvantifikovanih nakon derivatizacije gasnohromatografski (GC/FID i GC/MS). Prinos ekstrakta nezasićenih masnih kiselina je analiziran pri različitim uslovima procesnih parametara natkritične ekstrakcije uključujući pritisak, temperaturu i vreme u cilju optimizacije efikasnosti procesa, praćenjem kinetike procesa.

Unsaturated fatty acids from seeds of *Trigonella foenum-graceum* L. obtained by supercritical carbon (IV) oxide extraction using different process conditions

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Unsaturated fatty acids (UFA), as a unique class of food constituents, have been known for their wide range of biological activities. Up to day the numerous research studies regarding their presence and distribution within plants were performed. The seeds of *Trigonella foenum graecum* L. (fenugreek seeds) were considered as interesting natural source of UFA. The aim of this study was to develop a specific supercritical extraction method for UFA from fenugreek seeds. The characterization of fenugreek seed oil UFA composition was achieved using gas chromatography (GC/FID and GC/MS) after derivatization of seed oil. The yield of fatty acids was studied for various process parameters of supercritical extraction, such as pressure, temperature and extraction time, in order to optimize the extraction efficiency.

HA P 03

Neočekivana pojava multipleta drugog reda u proton-kuplovanom ^{13}C NMR spektru 5-aminosalicilne kiseline

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Pretragom literature je utvrđeno da su NMR spektralni podaci amino- i/ili hidroksi-supstituisanih benzoevih kiselina (antranilne, 3-hidroksiantranilne, 5-hidroksiantranilne, salicilne, 4-aminosalicilne, 5-aminosalicilne kiseline) nepotpuni, neasignirani ili čak i pogrešno asignirani. Zato su snimljeni ^{1}H- i ^{13}C-NMR spektri pomenutih jedinjenja u perdeutriodimetilsulfoksidu (DMSO-d_6) i izvršena je njihova potpuna asignacija kombinovanjem 1D- i 2D-eksperimenata, uključujući ^{1}H-^{1}H COSY, NOESY, HSQC i HMBC eksperimente. U proton-kuplovanom ^{13}C NMR spektru 5-aminosalicilne kiseline su uočeni "neočekivani" multipleti drugog reda. Signali na 117,1 ppm i 123,7 ppm, dodeljeni ugljenicima C-3 i C-4, za koje se očekivalo da budu signali prvog reda, javili su se kao asimetrični multipleti (deo multipleta na jačem polju se razlikovao od dela multipleta na slabijem polju). Ako bi se C-3-H-3-H-4 i C-4-H-4-H-3 sistemi posmatrali kao ABX spinski sistemi, pojava multipleta višeg se može objasniti time što je razlika hemijskih pomeranja protona (u Hz) po vrednosti bliska razlici ^{13}C-^{1}H sprezanja kroz jednu i više veza.

Unexpected second-order effects in proton-coupled ^{13}C NMR spectra of 5-aminosalicylic acids

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A literature survey on the NMR data of amino- or/and hydroxy-substituted benzoic acids: anthranilic, 3-hydroxyanthranilic, 5-hydroxyanthranilic, salicylic, 4-aminosalicylic and 5-aminosalicylic acids revealed that there are limited, unassigned or even incorrectly assigned spectral data for these benzoic acid derivatives. In order to amend the situation, a complete assignment of ^{1}H- and ^{13}C-NMR spectra of these compounds, recorded in perdeuteriodimethyl sulfoxide (DMSO-d_6), based on a combination of 1D- and 2D-NMR experiments, including ^{1}H-^{1}H COSY, NOESY, HSQC and HMBC, was performed. In the proton-coupled ^{13}C NMR spectrum of 5-aminosalicylic acids "unexpected" second-order multiplets were observed, although initially first-order ones were expected. The signals at 117.1 ppm and 123.7 ppm, assigned to C-3 and C-4, respectively, appeared as asymmetric multiplets; the high-field parts of the multiplets arising from one bond and longer-range couplings differed from the low-field halves. The observed phenomenon could be explained, with reference to the ABX spin system as a model, as being due to the near equality of the relative proton shift, in frequency units, to the difference between one-bond and long-range ^{13}C-^{1}H couplings.

HA P 04

Izolovanje i određivanje strukture diterpena jatrofanskog tipa iz biljne vrste *Euphorbia glareosa* L.

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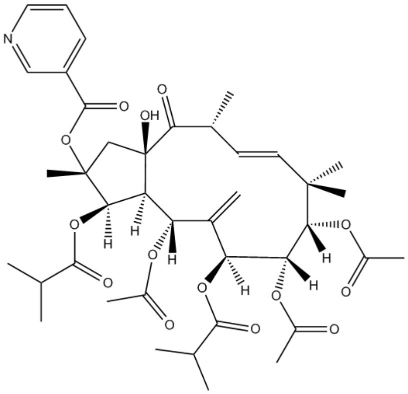
U ovom radu opisan je postupak izolovanja i određivanja strukture diterpena jatrofanskog tipa iz biljne vrste *Euphorbia glareosa* L. prikupljene na Zagajičkim brdima (Deliblatska peščara). Biljni materijal je ekstrahovan n-heksanom, a zatim frakcionisan i prečišćavan hromatografskim tehnikama. Izolovano jedinjenje je 5,8,9-triacetoksi-15-hidroksi-3,7-diizobutanoiloksi-2-nikotinoiloksijatrofa-6(17), 11*E*-dien-14-on. Struktura jedinjenja određena je primenom spektropskopskih meteda, 1D i 2D NMR (COSY, HSQC i HMBC), i HR-ESI-ToF MS. Izolovano jedinjenje je novo jedinjenje i nije do sada opisano u literaturi.



Isolation and characterisation of jatrophane diterpene from *Euphorbia glareosa* L.

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In this study, we reported isolation and characterisation of jatrophane diterpene from plant *Euphorbia glareosa* L., collected on Zagajicka hill (Deliblato sands). The plant material extracted with n-hexane and than fractioned and purified by chromatografic techniques. The isolated compound is 5,8,9-triacetoxy-15-hydroxy-3,7-diisobutanoyloxy-2-nicotinoyloxyjatropha-6(17), 11*E*-dien-14-one. The structure of compound determined using spectroscopic methods, including 1D and 2D NMR (COSY, HSQC and HMBC), and HR-ESI ToF MS. The isolated compound is new compound and it is not described in the literature up to now.

HA P 05

Uticaj rastvarača na ekstrakciju aktivnih komponenti sremuša (*Allium ursinum* L.)

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Sremuš, *A. ursinum* ili divlji luk, je lekovita biljka koja sadrži različite grupe farmakološki aktivnih jedinjenja među kojima su najznačajnija iz grupe polifenolinh jedinjenja, sumporna jedinjenja, kao i različite aromatične komponente. Zbog svog sastava, ispitan je uticaj rastvarača u cilju dobijanja što boljeg prinosa ekstrakcije, ukpnih fenola i ukupnih flavonoida u ekstraktu. Prilikom ekstrakcije u trajanju od 24 sata na sobnoj temperaturi uz mešanje, odnos droge i rastvarača je bio konstantan (1:5). Kao rastvarači prilikom ekstrakcije se korišćeni voda, 30%, 50%, 70% i 90% etanol. Najveći prinos ekstrakcije (36,32%) i ukupnih fenola (2,80g GAE/100g DW) je dobijen korišćenjem vode kao rastvarača (36,32%), dok je najveći prinos ukupnih flavonoida (0,21g CE/100g DW) detektovan korišćenjem 90% etanola kao rastvarača. Najmanji prinos ekstrakcije (16, 03%) i ukupnih fenola (0,30g GAE/100g DW) je dobije koršćenjem 90% etanola kao ekstragensa i 30% etanola za ukupne flavonoide (0,07g CE/100g DW). Ratvarači kao što je 30%, 50% i 70% etanol su imali sličan uticaj na prinos ekstrakcije i ekstrahovane komponente.

Solvent influnece on extraction of active compounds of wild garlic (*Allium ursinum* L.)

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Wild garlic, Allium ursinum is medicinal herbal plant containing various health benefit compounds as are polyphenols, sulphur compounds and various aromatic compound. Due to its health benefit composition, solvent influence was examined in order to obtain better extraction yield, total phenolics and total flavonoids in extracts. Extractions were set at room temperature with agitation. Drug and solvent ration was constant in all experiments (1:5). As an extraction solvents, water, 30%, 50%, 70% and 90% ethanol were used. The highest extraction yield (36.32%) and total phenols (GAE 2.80g / 100g DW) was obtained using water as a solvent, while the highest yield of total flavonoids (0.21g CE/ 100g DW) was detected using 90% of ethanol as a solvent. The lowest yield of extraction (16.03%) and lowest total phenols content (0.30g GAE / 100g DW) was obtained using 90% ethanol as extraction solvent and 30% ethanol for total flavonoids (CE 0,07 g / 100 g DE). Solvents as are 30%, 50% and 70% ethanol had a similar impact on the yield of extraction and extracted compounds.

HA P 06

Elektrohemijska detekcija vitamina B_6 upotrebom borom dopovane dijamantske elektrode

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Predložena je, po prvi put, elektroanalitička metoda za detekciju vitamina B_6 korišćenjem diferencijalne pulsne polarografije (DPP) i borom dopovane dijamantske (BDD) elektrode u uzorcima urina. Najbolji oblik pika, kao i najjači intenzitet struje se dobija u Briton-Robinsonovom puferu na pH 6. Ispitani su DPP parametri i uticaj interferirajućih supstanci, kao što su vitamin C, dopamin i mokraćna kiselina. Konstruisana je kalibraciona kriva koja pokazuje linearnost u opsegu od 7 do 47 μM sa odgovarajućom jednačinom I (μA) = -0.043 + 0.008 c (μM) (R^2 = 0.9912) i detekcionim limitom (LOD) od 3.76 μM. Relativna standardna devijacija sedam merenja pri koncentraciji vitamina B_6 od 9 μM je 3.6 % što nam govori da je reproduktivnost metode odlična, tako da se ova metoda može koristiti u analizi realnih uzoraka.

Electrochemical detection of Vitamin B_6 by using boron-doped diamond electrode

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It was proposed, for the first time, electroanalytical method for detection of Vitamin B_6 by using differential pulse polarography (DPP) and boron-doped diamond (BDD) electrode, in human urine samples.The vitamin B_6 provides well defined and the highest current peak in Britton-Robinson buffer solution pH 6. DPP parameters and influence of interferences, as Vitamin C, dopamine and uric acid, were examined. Calibration curve was found to be linear in the range from 7 to 47 μM with corresponding equation I (μA) = -0.043 + 0.008 c (μM) (R^2 = 0.9912) and detection limit of 3.76 μM. Relative standard deviation of seven measurements was 3.6 % for concentration of 9 μM which verified excellent reproducibility of proposed method, so that this method could be applied in real samples analyses.

HA P 06

Uporedna analiza epikutikularnih alkana biljnih vrsta *Primula veris* L. i *Primula vulgaris* Huds. (Primulaceae)

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Rod *Primula* L. (Primulaceae) obuhvata više od 400 vrsta jedno- i višegodišnjih jagorčevina koje su rasprostranjene u umerenim i hladnim delovima severne hemisfere. Dostupna fitohemijska literatura o vrstama ovog roda se bavi farmakološki aktivnim saponinima prisutnim u podzemnim delovima ovih biljaka. Iako je poznato da neke vrste roda *Primula* produkuju egzudate, epikutikularna jedinjenja su znatno manje ispitivana. U ovom radu, po prvi put, analiziran je hloroformski ispirak sa površine listova dve vrste ovog roda: *Primula veris* L. i *Primula vulgaris* Huds. Biljni materijal vrste *P. veris* je sakupljen na Suvoj planini, a materijal *P. vulgaris* u blizini sela Gornja Slatina, pored Leskovca (jugo-istočna Srbija). Hromatografsko razdvajanje ispiraka je dalo frakciju koja se sastojala od isključivo *n*-, *izo*- i *anteizo*-alkana. Međutim, alkani iz *P. veris* i *P. vulgaris* su se međusobno razlikovali i kvalitativno i kvantitativno. Oba alkanska profila su bila tipična za više biljke u pogledu odnosa parnih i neparnih alkana, među kojima su dominirali *n*-alkani sa maksimumom na C_{29}. Kod *P. veris* je nađeno da biosintetiše alkane dužeg ugljovodoničnog lanaca (C_{23}-C_{35}) u odnosu na *P. vulgaris* (C_9-C_{33}). Zanimljivo je bilo i to što su račvasti alkani bili značajno zastupljeni kod obe vrste: približni odnos *n*- : *izo*- : *anteizo*- alkana je bio 67:24:9 i 53:35:12 kod *P. veris* i *P. vulgaris*.

Comparative study of epicuticular alkane profiles of *Primula veris* L. and *Primula vulgaris* Huds. (Primulaceae)

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The genus *Primula* L. (Primulaceae) encompases more than 400 species of both annual and perennial plants distributed in temperate and cold regions of the Northern hemisphere. Most of the available literature on *Primula* species phytochemistry concerns the hypogeal saponins, due to their known pharmacological properties. Although some *Primula* sp. are known to produce farinas and/or exudates, the epiculticular compounds have received much less attention. In this work, for the first time, we analyzed the chloroform leaf surface washings of two species from this genus: *Primula veris* L. and *Primula vulgaris* Huds. The plant material of *P. veris* was collected on mountain Suva planina and that of *P. vulgaris* in the vicinity of the village Gornja Slatina, near Leskovac (SE Serbia). A chromatographic separation of the washings yielded a fraction representing a mixture of solely *n*-, *iso*- and *anteiso*-alkanes. However, both qualitatively and quantitatively, the composition of the alkanes differed between *P. veris* and *P. vulgaris*. Both alkane profiles were dominated by *n*-alkanes with the usual higher plant odd-even ratio, and showed a maximum at C_{29}. *P. veris* was found to produce longer chain-length alkanes (C_{23}-C_{35}) when compared to *P. vulgaris* (C_9-C_{33}). Interestingly, the branched alkanes were present in a significant share with the approximate ratio of *n*- : *iso*- : *anteiso*-alkanes 67:24:9 and 53:35:12, for *P. veris* and *P. vulgaris* respectively.

Acknowledgments. This work was supported by the Ministry of Education and Science of the Republic of Serbia (Project No. 172061).

HA P 08

Hemijski sastav etarskog ulja biljne vrste *Senecio vernalis* Waldst. et Kit

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Rod Senecio je važan zbog mnogih botaničkih, fitohemijskih, farmakoloških i toksikoloških osobina, tako da je predmet ovog rada bilo odredjivanje hemijskog sastava vrste *Senecio vernalis* Waldst. et Kit, koja pripada rodu Senecio, a u cilju provere tih karakteristika. Etarsko ulje biljne vrste *S. vernalis* dobijeno je hidrodestilacijom i analizirano pomoću GC/MS. Prinos etarskog ulja svežih nadzemnih delova biljke *S. vernalis* u fazi punog cvetanja od 0,20% (w/w) svrstava ovu biljnu vrstu u vrste siromašne etarskim uljima. U etarskom ulju je identifikovano 17 komponenata, pri čemu su ugljovodonični i oksigenovani seskviterpeni najzastupljenije klase jedinjenja, a osim seskviterpena identifikovani su i monoterpeni. Najzastupljenija komponenta u etarskom ulju biljke *S. vernalis* je α-humulen (59,94%), koji čini 3/5 od ukupne količine etarskog ulja. Germakren D, (E)-kariofilen, δ-kadinen i α-zingiberen su komponente koje su takođe prisutne u značajnoj meri u ispitivanom uzorku (11,69%, 9,69%, 6,10%, 4,10%, respektivno).

Chemical composition of *Senecio vernalis* Waldst. et Kit essential oil

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The genus Senecio is important because of many botanical, phytochemical, pharmacological and toxicological properties, so the subject of this study was to determine the chemical composition of the species *Senecio vernalis* Waldst. et Kit, which belongs to the genus Senecio, in order to verify these characteristics. The essential oil of plant species S.vernalis obtained by hydrodistillation was analyzed by GC/MS. The yield of essential oil of fresh aerial parts of S. vernalis in the full bloom of 0.20% (w/w) classifies this species in species that are poor with essential oils. Seventeen compounds were identified in the essential oil, wherein the sesquiterpene hydrocarbons and the oxygenated sesquiterpenes were the most common classes of compounds, and in addition to sesquiterpenes, monoterpenes were also identified. The most abundant component of the essential oil of the plant S. vernalis is α-humulene (59.94%), which accounted for 3/5 of the total oil. Germacrene D, (E)-caryophyllene, δ-cadinene and α-zingiberene are the components that are also present in a significant percentage in the tested sample (11.69%, 9.69%, 6.10%, 4.10%, respectively).

HA P 08

Novi estri *trans*-sabinola iz etarskog ulja biljne vrste *Achillea serbica* Nym. (Asteraceae): sinteza i detaljna spektralna analiza

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Achillea serbica Nym. (srpska hajdučica; *syn. A. ageratifolia* (Sm.) Boiss. var. *serbica* (Nyman) Hayek) je slabo ispitana vrsta hajdučke trave, endemska za oblast centralnog Balkanskog poluostrva. Analizom etarkog ulja izolovanog iz suvih nadzemnih delova (4 uzoraka iz 2 populacije iz okoline Niša, jugo-istočna Srbija), kombinacijom hromatografskih i spektralnih metoda, identifikovano je ukupno 324 sastojka koji su činili 95,8–97,2% ulja. U etarskom ulju su dominirali *trans*-sabinol i njegovi estri, uključujući dva potpuno nova prirodna proizvoda: *trans*-sabinil-nonanoat i *trans*-sabinil-dekanoat. Struktura svih estara *trans*-sabinola detektovanih u ovom ulju je nedvosmisleno potvrđena sintezom ovih jedinjenja i ko-injekcijom uzoraka etarskog ulja i sintetisanih estara. Novi estri su potpuno spektralno okarakterisani (NMR (1D i 2D), IR i MS), a stereohemija ovih jedinjenja je proučavana na osnovu NMR spektara snimljenih sa dodatkom lantanidnih reagenasa hemijskog pomeranja.

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New esters of *trans*-sabinol from the essential oil of *Achillea serbica* Nym. (Asteraceae): synthesis and structural elucidation

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Achillea serbica Nym. (Serbian Yarrow; *syn. A. ageratifolia* (Sm.) Boiss. var. *serbica* (Nyman) Hayek) is a poorly investigated yarrow species, endemic to the Central Balkan Peninsula area. A combination of chromatographic and spectroscopic techniques enabled the identification of, in total, 324 constituents (comprising 95.8–97.2% of the total oil composition) from the essential oils of the dry aerial parts (four samples from two populations collected from the vicinity of the city of Niš, SE Serbia) of *A. serbica*. The oil compositions were dominated by *trans*-sabinyl derivatives including two completely new natural products: *trans*-sabinyl nonanoate and *trans*-sabinyl decanoate. The identity of these new esters was unambiguously confirmed by co-injection of the oil samples with synthesized standards and their structure was elucidated by NMR (1D and 2D), IR and MS, whereas the stereochemistry of the esters was studied by an NMR methodology that employed lanthanide induced shifts reagents.

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HA P 10

Diferencijacija plavog i crnog mastila hemijskih olovaka

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Mastilo koje se nalazi u hemijskim olovkama se sastoji od nekoliko industrijsih boja koje se mešaju u odgovarajućem odnosu i daju različitu nijansu mastila. Svako mastilo ima odgovarajući otisak kada se analizira visoko efikasnom tankoslojnom hromatografijom. Cilj ovog rada je da obezbedi brzu i što efikasniju metodu razdvajanja plavih i crnih mastila različitih hemijskih olovaka sa papira. Analizirane su 42 hemijske olovke različitih proizvođača (20 plavih i 22 crnih). Poređeno je razdvajanje boja metodom HPTLC pri čemu su korišćena četiri sistema rastvarača. Mastila su analizirana i UV/VIS spektroskopijom. Razultati dobijeni HPTLC tehnikom pokazuju postojanje razlike između hemijskih olovaka različitih proizvođača.

Differentiation of blue and black ballpoint pen inks

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Ballpoint pen ink is a mixture of few different industrial dyes. Different rates of this dyes gives a ink lot of varieties of painting. High-performance thin-layer chromatography analysis reports that every ballpoint pen ink poses a different fingerprint. Aim of this study is to provide fast and more efficient method for differentiation of blue and black ballpoint pen inks written on paper. We had analyzed 42 ballpoint pens from different manufacturer (20 blue and 22 black ones). HPTLC method and four mobile phases were used to observe ink colors separation. Also, inks were analyzed with UV/VIS spectroscopy. Results obtained from HPTLC method indicate that there was difference between ballpoint pens from different manufacturers.

HA P 11

Primena sterola kao biomarkera za identifikaciju izvora fekalnog zagađenja rečnih sedimenata u Srbiji

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U slivu reke Dunav fekalno zagađenje poreklom iz antropogenih izvora je prepoznato kao ključni problem. Reka Dunav i njene pritoke su izložene uticaju raznih tačkastih i netačkastih izvora zagađenja, kao što su izlivi tretiranih ili netretiranih otpadnih voda, kao i spiranja sa urbanih i poljoprivrednih površina, koji doprinose pogoršanju kvaliteta vode i sedimenata. U ovom radu izvršena je procena fekalnog zagađenja rečnih sedimenata Dunava i njenih pritoka (Tise, Save i Morave) u Srbiji primenom odnosa sterola. Uzorci sedimenata su pripremljeni optimizovanom ultrazvučnom ekstrakcijom i dobijeni ekstrakti su prečišćeni na silika gel/anhidrovani Na_2SO_4 kertridžu. Za analizu tragova dvadeset hormona, humanih/životinjskih i biljnih sterola primenjena je metoda tečne hromatografije–tandem masene spektrometrije. Studija je pokazala široku rasprostranjenost sterola, u opsegu koncentracija 22–1907 ng g^{-1}. U najvećoj koncentraciji je detektovan koprostanol, biomarker humanog zagađenja. Mestranol i 17α-estradiol su bili hormoni detektovani u uzorcima, u koncentracijama od 11 ng g^{-1} i 13 ng g^{-1}. Na osnovu izračunatih odnosa sterola većina ispitivanih sedimenata je prepoznata kao zagađena humanim fekalnim materijalom. Za dva uzorka je utvrđen kombinovan uticaj zagađenja komunalnim otpadnim vodama i prirodnih izvora sterola poreklom od biljojeda.

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Application of sterol biomarkers for identification of fecal contamination sources in river sediments in Serbia

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Fecal pollution from anthropogenic sources was identified as a crucial problem throughout the Danube River Basin. The Danube River and its tributaries are affected by various point and non-point pollution sources, such as discharges of treated or untreated sewage as well as urban and agricultural run-off, which contribute to the deterioration of water and sediment quality. In this work, fecal contamination assessment of sediments of the Danube River and its tributaries (the Tisa, the Sava and the Morava) in Serbia was performed using sterol ratios. Sediment samples were prepared by optimized ultrasonic extraction and silica gel/anhydrous Na_2SO_4 extract clean up. Liquid chromatography–tandem mass spectrometry method was applied for the trace analysis of twenty hormones and human/animal and plant sterols. The study showed a widespread occurrence of sterols, in the range 22–1907 ng g^{-1}. Coprostanol, human-associated fecal biomarker, was detected at the highest concentration. Hormones detected in the samples were mestranol and 17α-estradiol, at the concentrations of 11 ng g^{-1} and 13 ng g^{-1}, respectively. According to the calculated sterol ratios, the majority of the investigated sediments was recognized as human fecal polluted. Two samples were found to be affected by a combination of sewage and herbivore sources.

HA P 12

Izolovanje i identifikacija novog triterpena iz kore drveta *Alnus viridis* (Chaix) DC. ssp. *viridis*

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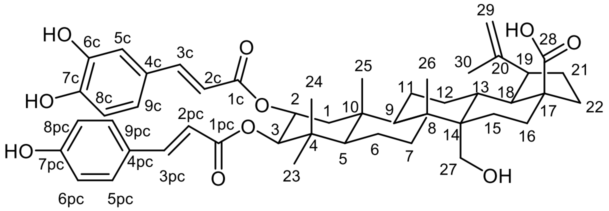
U ovom radu prikazano je izolovanje i strukturno određivanje novog sekundarnog metabolita iz kore drveta *Alnus viridis* ssp. *viridis*. Novo jedinjenje je izolovano kolonskom hromatografijom na silika gelu i semipreparativnom HPLC hromatografijom sa DAD detekcijom. Struktura je određena na osnovu 1D (^{1}H, ^{13}C) i 2D NMR (HSQC, HMBC, COSY, NOESY) i HRESIMS spektara. Derivat alfitolične kiseline sa kafeinskom i *p*-kumarinskom kiselinom u položajima 2 i 3 redom, je prepoznat na osnovu spektroskopskih podataka i literaturnih podataka za slična jedinjenja.



Isolation and identification of the novel triterpene from the bark of *Alnus viridis* (Chaix) DC. ssp. *viridis*

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In this work isolation and structure elucidation of the novel secondary metabolite from the bark of *Alnus viridis* ssp. *viridis* has been presented. Isolation of the novel compound has been made using silica gel column chromatography followed by semipreparative HPLC with DAD detection. The structure elucidation has been done using 1D (^{1}H, ^{13}C) and 2D NMR (HSQC, HMBC, COSY, NOESY) and HRESIMS spectra. Alphytolic acid derivative with caffeic acid and *p*-coumaric acids in positions 2 and 3, respectively, has been recognized according to the spectroscopic data and literature data for similar compounds.

HA P 13

Elektrohemijsko ponašanje biološki aktivnih jedinjenja edda-tipa

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Redoks hemija biološki aktivnih jedinjenja je poslednjih godina izuzetno zastupljena oblast istraživanja u bioneorganskoj hemiji. Njen značaj se prvenstveno ogleda u mogućnosti selekcije potencijalno aktivnog jedinjenja sklonog ka selektivnoj redukciji u hipoksičnoj sredini.

U tom smislu, ispitana su oksido-redukciona svojstva biološki aktivnih dialkil (Me, Et, *n*Pr, *n*Bu) estara *N*,*N*'-metilen-(*S*,*S*)-etilendiamin-*N*,*N*'-di-2-(3-cikloheksil)propanske kiseline metodom ciklične voltametrije. Ciklovoltamogrami jedinjenja su snimljeni u različitim oblastima elektrodnih potencijala ($-2 < E < 0$ V i $-1,2 < E < 1,0$ V). Dobijene I-E krive upućuju na reverzibilan proces pri čemu jasno pokazuju da na položaj pika najviše utiče voluminoznost liganada. Naime, produžavanje alkil lanca estarskog dela liganada dovodi do primetnog pomeranja oksidacionog pika ka pozitivnijm vrednostima elektrodnih potencijala koje je istovremeno praćeno smanjenjem pika (od $E = -0,97$ V do $E = -0,49$ V). Isti trend je vidljiv i u slučaju redukcionog pika koji se s produžetkom alkil niza pomera ka negativnijm vrednostima potencijala (od $E = -1,26$ V do $E = -1,34$ V). U oblasti pozitivnijih potencijala ($-1,2 < E < 1,0$ V) dolazi do pojave oksidacionog pika na $E = -0,54$ V koji se povećava s produžavanjem alkil niza i koji je najizraženiji za *n*Bu-estar.

Na osnovu dobijenih elektrohemijskih podataka može se zaključiti da su ispitivana jedinjenja stabilna u datom opsegu elektrodnih potencijala.

Electrochemical behavior of biologically active edda-type of compounds

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Redox chemistry of biologically active compounds is widely present research area in bioinorganic chemistry in the last few years. Its importance is primarily reflected in the possibilty for a selection of a potentially active compound, proned to a selective reduction in hypoxic medium.

In that sense, oxidoreductive features of biologically active dialkyl (Me, Et, *n*Pr, *n*Bu) esters of *N*,*N*′-methylene-(*S*,*S*)-ethylenediamine-*N*,*N*′-di-2-(3-cyclohexyl)propanoic acid were investigated. Cyclic voltammograms of the compounds were recorded in different ranges of electrode potentials ($-2 < E < 0$ V i $-1,2 < E < 1,0$ V). Obtained I-E plots indicate on reversible process showing that ligands bulkiness mainly affect on a position of the peak. Thus, extending the alkyl chain of ligands ester's part leads to noticable shifts of the oxidation peak toward positive vaules of electrode potentials followed by peak decreasement (from $E = -0,97$ V to $E = -0,49$ V). The same trend is obvious for the reduction peak which shifts toward more negative values of electrode potentials with the alkyl chain extension (from $E = -1,26$ V to $E = -1,34$ V). In the area of positive potentials ($-1,2 < E < 1,0$ V) an oxidative peak is found at $E = -0,54$ V which increases with extending of alkyl chain and is the most noticable for *n*Bu ester.

Based on obtained electrochemical data it is concluded that compounds of interest are stable in the investigated range of electrode potentials.

HA P 14

Primena lantanidnih regenasa hemijskih pomeranja za identifikaciju prirodnih proizvoda direktno iz složenih smeša bez prethodnog razdvajanja identifikacija elemenala iz biljne vrste *Inula helenium* L. (Asteraceae)

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Seskviterpenski aldehid iz hromatografske frakcije etarskog ulja biljne vrste *Inula helenium* sa snažnom antistafilokokalnom aktivnošću nije mogao da bude izolovan u čistom stanju iz složenog matriksa frakcije (masa frakcije je bila *ca.* 5 mg). Nakon brojnih 1D- i 2D-NMR eksperimenata na datom složenom uzorku rasvetljeni su samo delovi strukture ovog molekula. U ovom radu je ispitana moguća primena lantanidnih reagenasa hemijskog pomeranja za identifikaciju ovog metabolita diretno iz smeše bez dodatnog razdvajanja. Postepeni dodatak $Eu(fod)_3$ je doveo do značajnog pojednostavljenja NMR spektara (npr. rezolucije signala u ^{1}H NMR spektru koji potiču od pojedinačnih sastojaka ove složene smeše i uklanjanja degeneracije hemijskih pomeranja), a što je omogućilo dobijanje krucijalnih podataka o strukturi i konformaciji ovog sekundarnog metabolita. Primenom ove nove metode utvrđeno je da je reč o elemenalu (elema-1,3,11(13)-trien-12-al), seskviterpenu koji ima veoma ograničenu rasprostranjenost u prirodi.

Lanthanide-induced shift reagents enable structural elucidation of natural products in inseparable complex mixtures The case of elemenal from *Inula helenium* L. (Asteraceae)

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A sesquiterpene aldehyde from *Inula helenium* with a possible potent antistaphylococcal activity remained unidentified due to the impossibility to separate the compound from its complex matrix available in very low amount (*ca.* 5 mg). Detailed analyses of 1D- and 2D-NMR spectra of this original complex sample allowed access to a very limited amount of structural data for the unknown aldehyde. Thus, we tested the usefulness of lanthanide-induced shift reagents for the resolution and assignation of overlapped ^{1}H-NMR signals originating from individual components of this inseparable mixture. The incremental addition of $Eu(fod)_3$ led to a simplification of NMR spectra in terms of signal overlap and removal of chemical shift degeneracy, so the crucial data was inferred from the shifted NMR spectra. The application of this new structural elucidation methodology based on the analyses of shifted 1D- and 2D-NMR spectra of the mentioned mixture revealed that the unknown compound was a rare sesquiterpene - elemenal (elema-1,3,11(13)-trien-12-al).

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HA P 15

^{1}H NMR iterativna potpuna spinska analiza pruža uvid u konformacioni prostor estara *endo*-fenhola

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endo-Fenhol je monoterpenol koji se široko upotrebljava zbog svojih organoleptičkih osobina; njegovi estri se takođe odlikuju prijatnim mirisom. Iznenađujuće, u literaturi ima malo podataka koji se tiču njihovih NMR spektralnih osobina. Iz tog razloga smo, prateći *Steglich*-ovu proceduru, sintetisali biblioteku od 10 *endo*-fenhil-estara C_1-C_7 alifatičnih kiselina (neka od njih su nova jedinjenja), izvršili njihovu detaljnu 1D i 2D NMR analizu i DFT molekulsko modelovanje. Geometrije svih estara su optimizovane korišćenjem B3LYP/6-31G metode. Za svako jedinjenje, nađena su po dva energetska minimuma sa različitnim orijentacijama C=O u odnosu na metilensku grupu mosta. ^{1}H NMR hemijska pomeranja (δ) i konstante kuplovanja (J) svih konformera su izračunata GIAO metodom, primenom specijalno parametrizovanog WP04 funkcionala i aug-cc-pVDZ *basis* seta. Polazeći od izračunatih vrednosti za δ i J, izvršena je ^{1}H NMR iterativna potpuna spinska analiza (HIPSA) delimično preklopljenih multipleta spinskih sistema višeg reda, prisutnih u protonskim spektrima ispitivanih jedinjenja. HIPSA je omogućila određivanje vrednosti za δ i J i ukazala na dominantnu konformaciju ovih jedinjenja u rastvoru, koja je odgovorna za njihovu specifičnu aromu (npr. interakcije sa olfaktornim receptorima).

^{1}H NMR Iterative Full Spin Analysis provides an insight into the conformational space of *endo*-fenchyl esters

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endo-Fenchol is a monoterpenol widely used as a flavoring agent; its esters are also contributed with a pleasant aroma. Surprisingly, the available NMR spectral data on these compounds are scarce. For that reason, employing Steglich procedure, we synthesized a library of 10 *endo*-fenchyl esters of C_1-C_7 aliphatic acids (some of these are new compounds), performed their detailed 1D and 2D NMR analysis and DFT molecular modelling. Geometries of all esters were optimized using B3LYP/6-31G method. All compounds displayed two energetic minima with a differing orientation of C=O relative to the bridging methylene group. ^{1}H NMR chemical shifts (δ) and coupling constants (J) for all conformers were calculated by GIAO method with the specially parametrized WP04 functional and using the aug-cc-pVDZ basis set. The calculated δ and J served as a starting point for an ^{1}H NMR iterative full spin analysis (HIFSA) of the partially overlaped, second order spin system multiplets observed in the proton spectra of the studied compounds. HIFSA enabled the assessment of the values of δ and J and gave an insight in the predominant conformation of these compounds in solution, important for their flavoring characteristics (e.g. interactions with olfactory receptors).

Acknowledgement: The authors are grateful to the Ministry of Education, Science and Technological Development, Republic of Serbia (Project number 172061).

Hemijska sinteza - Chemical Synthesis

HS P 01

Sinteza, karakterizacija i pro-apoptotska aktivnost tiokarbohidrazona na matičnim ćelijama adenokarcinoma pankreasa (AsPC-1)

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Matične ćelije raka (CSCs) su subpopulacija ćelija raka koja prouzrokuje rezistenciju prema terapiji i pojavu recidiva tumora. S obzirom na to da trenutni tretmani ne dovode do eliminacije CSCs, strateški cilj istraživanja novih lekova je usmeren ka supstancama koje će inicirati apoptozu ili diferencijaciju CSCs. U našoj grupi sintetisan je veći broj mono- i bis(tiokarbohidrazona), pretežno derivata *N*-heteroaromatičnih karbonilnih jedinjenja (NHK). Testiranje citotoksične aktivnosti sintetisanih jedinjenja na matičnim ćelijama adenokarcinoma pankreasa (AsPC-1), poznatim po svojoj otpornosi na standardne citostatike, je pokazalo da su samo bis(tiokarbohidrazoni) NHK pokazali dobru pro-apoptotsku aktivnost. U cilju određivanja potencijalnih proteinskih meta izračunati su AQVN/EIIP deskriptori sintetisanih jedinjenja i utvrđeno je da se njihove vrednosti nalaze u oblasti karakterističnoj za flavonoide. Poznato je da prirodni flavonid fizetin indukuje apoptozu kod AsPC-1 ćelija inhibirajući enzim ciklin-zavisnu kinazu 6 (CDK6). Kako je kristalna struktura CDK6 u kompleksu sa inhibitorom poznata (PDB ID 4P41), preklapanjem strukture najaktivnijeg bis(tiokarbohidrazona) sa antagonistom – derivatom piperazina, utvrđena je velika strukturna sličnost. Dobijeni rezultati predstavljaju osnov za dizajniranje novih biološki aktivnih NHK bis(tiokarbohidrazona).

Synthesis, characterization and pro-apoptotic activity of thiocarbohydrazones on pancreatic adenocarcinoma stem cells (AsPC-1)

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Cancer stem cells (CSCs) are a subpopulation of tumor cells that causes resistance to therapy and tumor relapse. Since current cancer treatments cannot efficiently eliminate CSCs, the strategic goal of the drug research is directed towards substances which are capable to trigger apoptotic death or differentiation of CSCs. We have synthesized and characterized a large number of mono- and bis(thiocarbohydrazones), predominantly derivatives of *N*-heteroaromatic carbonyl compounds (NHK). Results of evaluation of cytotoxic activity of synthesized compounds on highly resistant pancreatic adenocarcinoma (AsPC-1) stem cell line showed that only bis(thiocarbohydrazones) derived from NHK possess good pro-apoptotic activity. In order to determine possible protein targets of thiocarbohydrazones, the AQVN/EIIP descriptors were calculated. Their values were in the range of standard flavonoids. It is known that natural flavonoide fisetin induces apoptosis in AsPC-1 cells by blocking the enzyme CDK6 (cyclin-dependent kinase 6). Since the crystal structure of CDK6 in a complex with inhibitor is reported (PDB ID 4P41), the alignment of the most active bis(thiocarbohydrazone) with the antagonist – piperazine derivative reveals good structural similarity. Results of this study represent a good basis for design of novel biologically active bis(thiocarbohydrazones).

HS P 02

Sinteza i kristalna struktura kompleksa cinka(II) sa 2-hinolinkarboksaldehid-selenosemikarbazonom

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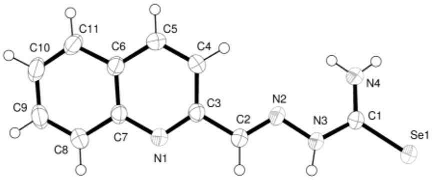

U cilju dobijanja biološki aktivnih kompleksnih jedinjenja sa biometalima, sintetisan je i strukturno okarakterisan novi kompleks cinka(II) sa ligandom 2-hinolinkarboksaldehid-selenosemikarbazonom (Hqasesc). Kompleks je sintetisan reakcijom Hqasesc sa $Zn(ClO_4)_2 \times 6H_2O$, a prekristalisan iz etanolnog rastvora. Templatnom sintezom dobijen je identičan proizvod. Kako su i ligand i kompleks dobijeni u obliku monokristala struktura im je određena primenom rendgenske strukturne analize. Kompleks $[Zn(Hqasesc)_2](ClO_4)_2\times$ EtOH ima distorgovanu oktaedarsku geometriju, pri čemu su za Zn(II) tridentatno koordinovana dva Hqasesc liganda u neutralnom obliku, preko hinolinskog i azometinskog atoma azota i atoma selena. U spoljašnjoj sferi kompleksa nalaze se dva perhloratna anjona i jedan molekul etanola. Koordinovani ligandi nisu kristalografski ekvivalentni. Kristalno pakovanje liganda i kompleksa zasnovano je na velikom broju vodoničnih veza.

Synthesis and crystal structure of zinc(II) complex with 2-quinolinecarboxaldehyde selenosemicarbazone

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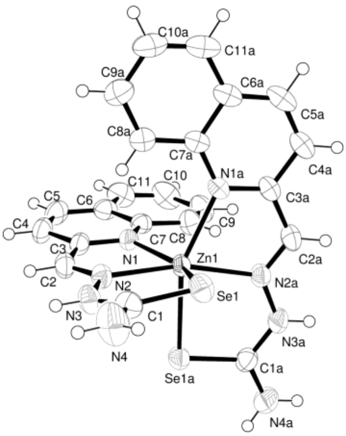

In order to obtain biologically active complexes with biometals, zinc(II) complex with the ligand 2-quinolinecarboxaldehyde selenosemicarbazone (Hqasesc) was synthesized and characterized. The complex was obtained by reaction of Hqasesc with $Zn(ClO_4)_2 \times 6H_2O$, and it was recrystallized from ethanol solution. The same product was also obtained by template reaction. The lignad and the complex were obtained as single crystals and the structure of both compounds was solved by X-ray structural analysis. The complex $[Zn(Hqasesc)_2](ClO_4)_2\times$ EtOH has distorted octahedral geometry with two neutral Hqasesc ligands coordinated tridentately *via* hquinoline and azomethine nitrogen atoms and selenium atom. In outher sphere of the complex there are two perchlorate ions and etanole solvent molecule. The coordinated ligands are not crystallographicaly equivalent. Crystal packings of both compounds are based on numerous hydrogen bonds. Investigation of biological activity of the synthesized compounds is still in progress.

HS P 03

Ponašanje okso derivata žučnih kiselina u uslovima Grignard-ove reakcije

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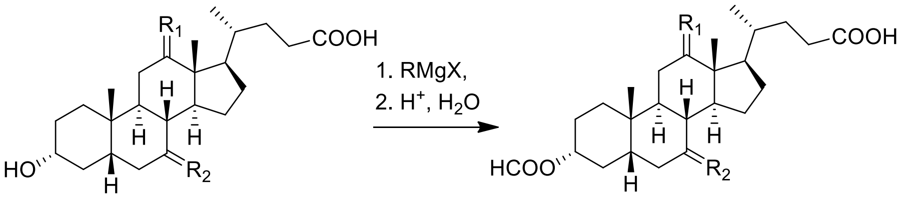
Pored poznate fiziološke fukcije žučnih kiselina u transportu lipida, liposolubilnih vitamina i eliminaciji holesterola iz organizma, novija istraživanja[1] otkrivaju hormonsku ulogu žučnih kiselina. Henodeoksiholna kiselina je prirodni ligandi za nuklearni FXR receptor i za membanotropni TRG5 receptor, koji učestvuju u lipidnoj, ugljeno-hidratnoj i energetskoj homeostazi. Sintetski, alkil derivati žučnih kiselina su agonisti FXR i TRG5 receptora.[2]

Sinteza alkil derivata žučnih kiselina Grignar-ovom reakcijom obično zahteva zaštitu karboksilne funkcije, što povećava broj koraka u sitezi i smanjuje prinos reakcije. Mi ovde želimo da prijavimo ponašanje različitih okso derivata žučnih kiselina u reakciji sa različitim Grignard-ovim reagensima, bez prethodne zaštite karboksilne funkcije.



1 R_1= α–OH, β–H; R_2= O
2 R_1= O; R_2= α–OH, β–H

3 R_1= α–OH, β–H; R_2= ξ-OH, ξ-alkil
4 R_1= α–OH, β–H; R_2= α–OH, β–H

Zahvalnica: Ovaj rad je finansiran od strane Ministarstva prosvete, nauke i tehnološkog razvoja (Projekat ON172021).

Bile acid oxo derivatives behavior in Grignard reaction conditions

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In addition to the known physiological function of bile acids in the transport of lipids, fat-soluble vitamins and the elimination of cholesterol from the body, recent studies[1] reveal hormonal role of bile acids. Henodeoxycholic acid is the natural ligand for the nuclear receptor FXR and for membanotropic, TRG5 receptor that participate in the lipid, carbohydrate and energy homeostasis. Synthetic, bile acid alkyl derivatives are agonists of FXR TRG5 receptors.[2]

The synthesis of bile acid alkyl derivatives by Grignard's reaction typically require the protection of the carboxylic function, which increases the number of steps in the synthesis, and reduces overall yield. Herein we want to report the behavior of various bile acid oxo derivatives in the reaction with a different of Grignard reagents, without the protection of carboxylic functions.

1. Wang H., Chen J., Hollister K., Sower L. C, Forman B. M. (**1999**): *Mol Cell.* 3: 543–553.
2. Pellicciari R., Costantino G., Camaioni E. (**2004**): *J. Med. Chem.* 47: 4559–4569.

HS P 04

Sinteza i karakterizacija kompleksa paladijuma(II) sa kondenzacionim derivatom etil hidrazinoacetata i 2-benzoilpiridina

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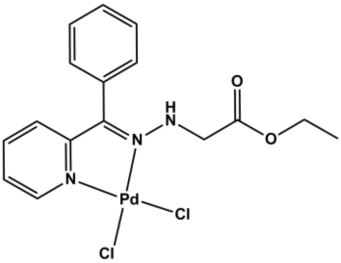

Sintetisan je novi kompleks Pd(II) sa bphaOEt ligandom koji predstavlja kondenzacioni derivat etil hidrazinoacetata i 2-benzoilpiridina. Kompleks je dobijen templatnom reakcijom polazeći od navedenih reaktanata i $K_2[PdCl_4]$ u smeši etanol/voda. Sastav novodobijenog kompleksa utvrđen je elementalnom analizom, dok je merenjem molarne provodljivosti utvrđeno da je u pitanju neelektrolit. Uzimajući u obzir navedeno pretpostavljena formula kompleksa je $[PdCl_2(bphaOEt)]$. Kompleks je dijamagnetičan, što odgovara kvadratno-planarnoj geometriji oko Pd(II) jona. Poređenjem ^{1}H i ^{13}C NMR spektralnih podataka za novi kompleks sa podacima dobijenim za komplekse Pd(II) sa strukturno sličnim *N*-heteroaromatičnim derivatima etil hidrazinoacetata, utvrđeno je da je bphaOEt ligand bidentatno koordinovan za metal preko iminskog i piridinskog atoma azota. Treće i četvrto koordinaciono mesto zauzimaju joni hlora. Sintetisani kompleks predstavlja strukturni Pd(II) analog cisplatine. Stoga će dalja istraživanja biti usmerena ka ispitivanju biološkog dejstva ovog kompleksa, posebno njegovog citotoksičnog dejstva.

Synthesis and characterization of palladium(II) complex with condensation derivative of ethyl hydrazinoacetate and 2-benzoylpyridine

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Novel Pd(II) complex with bphaOEt ligand, the condensation derivative of ethyl hydrazinoacetate and 2-benzoylpyridine, was synthesized by template reaction of the reactants and $K_2[PdCl_4]$ in ethanol/water mixture. The composition of the complex was obtained by elemental analysis, while molar conductivity measurements showed that the complex is non-electrolyte. Based on these data the formula $[PdCl_2(bphaOEt)]$ of the complex can be anticipated. The complex is diamagnetic in nature with square-planar geometry around Pd(II). Comparison of ^{1}H and ^{13}C NMR spectral data for the novel complex with the data obtained for other Pd(II) complexes, with structurally similar *N*-heteroaromatic derivatives of ethyl hydrazinoacetate, showed that the ligand bphaOEt is bidentately coordinated to Pd(II) *via* pyridine and imine nitrogen atoms. Other two coordination sites are occupied by chlorido ligands. The obtained complex represents Pd(II) structural analog of cisplatin. Thus our further research will focus on evaluation of biological activity of novel complex, especially cytotoxic activity.

HS P 05

Dobijanje petočlanih i šestočlanih heterocikličnih β-keto-estara modifikovanom Dieckmann-ovom kondenzacijom

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Petočlani i šestočlani karbociklični i heterociklični β-keto-estri mogu se dobiti u dobrim prinosima Dieckmann-ovom kondenzacijom, dok se aciklični analozi dobijaju Claisen-ovom kondenzacijom, uglavnom uz produženo zagrevanje sa alkoksidima u aromatičnim rastvaračima. Alternativno, acilovanje se može izvesti i u prisustvu Lewis-ovih kiselina. Takođe je u literaturi je opisano nekoliko primera deprotonovanja, acilovanja i/ili ciklizacije ketona, diestara ili dinitrila u DMSO, koristeći NaH kao bazu, na povišenim temperaturama (50-90 °C).

U našim preliminarnim eksperimentima, za ciklizaciju različitih amino-diestara, primenili smo Dieckmann-ovu kondenzaciju koristeći alkoksidne baze. Pod reakcionim uslovima: refluks reakcione smese od 3-5 sati u toluenu ili ksilenu dobijeni su, heterociklični β-keto-estri u prinosu od 70-90%. Pored toga, pod navedenim reakcionim uslovima veliki broj polaznih amino-diestara gradio je guste gelove, čime se značajno smanjivao prinos i čistoća proizvoda.

U ovom radu razvijena je veoma efikasna opšta preparativna metoda za Dieckmann-ovu kondenzaciju diestara i amino-diestara. Petočlani i šestočlani karbociklični i *N*-heterociklični β-keto-estri dobijeni su u visokom prinosu (> 80%), koristeći *in situ* generisanu smesu NaH/alkoksid u DMSO na ~20 °C u toku od 30 minuta.

Synthesis of five- and six- memebered heterocyclic β-keto esters by modified Dieckmann condensation

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Dieckmann condensation of various diesters provides good yields of 5 and 6 membered carbocyclic or heterocyclic β-keto esters, while acyclic analogues result from Claisen ester condensation typically after prolonged heating in aromatic solvents with alkoxides. Alternatively, the acylation is promoted by Lewis acids. Also, several examples of deprotonation, acylation and/or cyclization of ketones, diesters, or dinitriles in DMSO, using NaH at elevated temperatures (50-90°C), have been reported previously.

In our preliminary experiments we applied the Dieckmann condensation for cyclization of various amino-diesters, using alkoxide bases. Often it afforded heterocyclic β-keto esters in 70-90% yields and requred 3-5 hours of reflux in toluene or xylenes. More significantly, under the reaction conditions, a number of the starting amino-diesters formed thick gels, greatly reducing the isolated yields and purity of the products.

In this work we developed highly efficient general preparative procedure for Dieckmann condensation of diesters and amino-diesters. Five and six-membered carbocyclic or *N*-containing heterocyclic β-keto esters were synthesized in good yields (> 80%), using *in situ* generated NaH/alkoxide mixture in DMSO at ~20 °C, during half an hour.

HS P 06

Poboljšana metoda za sintezu β-keto-estara uz pomoć *in situ* aktiviranog natrijum hidrida u dimetil sulfoksidu

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β-Keto-estri su važni sintetički prekursori, koji se ekstenzivno koriste u laboratorijskoj i industrijskoj sintezi. Ova jedinjenja se najčešće dobijaju acilovanjem preformranih keton enolata, pomoću reagenasa kao što su Weinreb-ovi amidi, alkil-cijanoformati ili 1-Boc-imidazol, kao i alkil-karbonati na povišenim temperaturama.

U ovom radu opisana je efikasna preparativna metoda za acilovanje ketona. U okviru našeg istraživanja, sintetisali smo multigramske količine različitih karbocikličnih β-keto- estara. Eksperimentalno je utvrđeno da se suspenzija NaH u DMSO jako aktivira u prisustvu alkohola. Nastajanje smese NaH/alkoksid *in situ* omogućava brzo i potpuno deprotonovanje i acilovanje različitih cikličnih ketona alkil karbonatima na sobnoj temperaturi. U poređenju sa postupcima opisanim u literaturi, metoda koju smo razvili ima brojne prednosti; DMSO je netoksičan i nezapaljiv rastarač, dostupan na tržištu po relativno niskim cenama i ne zagađuje životu sredinu. Kvantitativno se uklanja vodenom ekstrakcijom.

Jednostavnost, efikasnost i ekonomičnost, kao i mogućnost primene za dobijanje različitih β-keto-estara na velikoj skali, pokazuju superiornost ove metode.

Improved method for preparation of β-keto esters using *in situ* activated sodium hydride in dimethyl sulfoxide

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**Faculty of Agriculture,University of Belgrade*

β-Keto esters are important synthetic precursors, widely used in laboratory and industrial syntheses. The compounds are very often prepared by the acylation of preformed ketone enolate anions using reagents such as Weinreb amides, alkyl-cyanoformates or 1-Boc-imidazole as well as alkyl carbonates at elevated temperature.

Herein we report an efficient and high yielding general preparative method for the ketone acylation. In connection with our research projects, we prepared multigram quantities of various carbocyclic and heterocyclic β-keto esters. It was found that NaH suspension in DMSO was highly activated when reacted with an alcohol. The *in situ* generated NaH/alkoxide mixture permitted very rapid and complete deprotonation and acylation of various cyclic ketones with alkyl carbonates at ambient temperature. In comparation with literature procedures, the advantages of our method are numerous; DMSO is non-toxic, non-flammable solvent which is relatively inexpensive and environmentally friendly. It is quantitatively removed by simple aqueous extraction.

In terms of expediency, yields and the operational simplicity, it compares favorably with previously reported methods. Besides, it is inexpensive and suitable for large scale preparations of various β-keto esters.

HS P 07

Hofmann-ovo premeštanje primenom N-bromacetamida

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Hofmann-ovo premeštanje predstavlja korisnu metodu za konverziju karboksamida u amine i njihove derivate sa jednim ugljenikovim atomom manje od reaktanta. Reakcija podrazumeva nastajanje izocijanata, korisnih sintetičkih intermedijera koji se mogu izolovati ali najčeće odmah reaguju sa prisutnim nukleofilima (voda, alkoholi).

Mi smo našli da se Hofmann-ovim premeštanjem različitih primarnih karboksamida, uz pomoć N-bromacetamida dobijaju metil- i benzil- karbamati u visokom prinosu. Reakcija zahteva prisustvo litijum hidroksida ili litijum metoksida za optimalne rezultate. Alifatični karbamati su dobijeni u sličnim prinosima upotrebom N-bromsukcinimida u prisustvu istih baza, ali aktivirani aromatični karboksamidi bili su ekstenzivno bromovani pod tim uslovima. Petočlane ciklične uree su dobijene stereospecifično iz β-fenilamino amida. Amid cimetne kiseline reagovao je novim tandemskim preocesom koji uključuje Hofmann-ovo premeštanje i 1,2-dimetoksilovanje dvostruke veze. $NBA/LiOH{\cdot}H_2O$ je na visokom nivou u pogledu prinosa i čistoće proizvoda, kao i ekonomičnosti u poređenju sa drugim reagensima za Hofmann-ovo premeštanje. Dobijanje reagensa je jednostavno i jeftino. Za manje osteljive supstrate $NBS/LiOH{\cdot}H_2O$ daje slične rezultate. Oba reagensa često omogućavaju jednostavno izolovanje proizvoda bez potrebe za hromatografskim prečišćavanjem. Sporedni proizvodi ovih reakcija su netoksični i rastvorni u vodi.

Hofmann rearrangement mediated by N-bromoacetamide

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Hofmann rearrangement presents a useful method for the conversion of carboxamides to amines and their derivatives, with one carbon atom fewer than the reactant. Reaction occurs via formation of isocyanates, useful synthetic intermediates which can be isolated, but often reacts immediately with present nucleophile (water, alcohole).

We found that Hofmann rearrangement of various primary amides is promoted by *N*-bromoacetamide providing methyl and benzyl carbamates in good yields. The reaction requires lithium hydroxide or lithium methoxide as a base for the optimal results. Comparable yields of the aliphatic carbamates are also obtained using *N*-bromosuccinimide with the same bases, however activated aromatic rings are extensively brominated. Five-membered cyclic ureas resulted stereospecifically from β-phenylamino amides. Cinnamide reacted via a novel tandem process involving Hofmann rearrangement and 1,2-dimethoxylation of the double bond. $NBA/LiOH{\cdot}H_2O$ is comparing well to the other reagents in terms of the product yields, purity and the cost-effectiveness. The reagent preparation is simple and inexpensive on any scale. For the less sensitive substrates, $NBS/LiOH{\cdot}H_2O$ has comparable effectiveness. Both reagents often allow for the simple, chromatography-free isolation of the products, while the by-products are non-toxic and water-soluble.

HS P 08

Sinteza i karakterizacija novih tricikličnih pirimidinskih derivata

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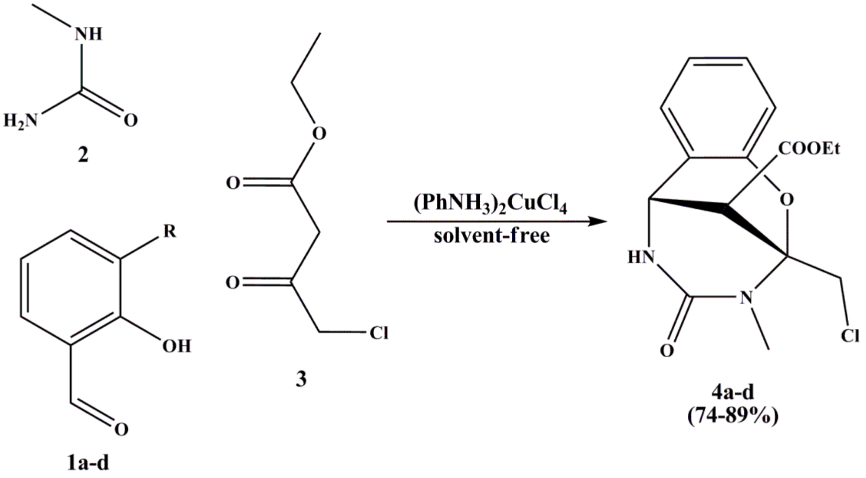
Razvijena je efikasna i zelena reakcija za sintezu novih tricikličnih pirimidinskih derivata sa kiseoničnim mostom (4a-d) iz različitih salicilaldehida (1a-d), uree (2) i 4-hloro-etilacetoacetata (3), a koja je katalizovana po ranije opisanoj proceduri[1] u vrlo dobrim prinosima (Šema 1).



R = OH, OMe, NH_2, NHMe

Šema 1. *Sinteza novih tricikličnih pirimidinskih derivata*
Scheme 1. *Synthesis of novel pyrimidine tricyclic derivatives*

Synthesis and characterization of novel pyrimidine tricyclic derivatives

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An efficient and green reaction has been successfully developed for the synthesis of oxygen-bridged pyrimidine tricyclic derivatives (4a-d) from different salicylaldehydes (1a-d), urea (2) and 4-chloro-ethyl acetoacetate (3) catalyzed by earlier described procedures[1] in very good yields (Scheme 1).

Acknowledgements: The autors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Grant 172011)

1. N. Jankovic *et. al. J. Serb. Chem. Soc.*, **80(5)** (2015) 595.

HS P 09

Sinteza i antifungalna aktivnost tiofenskih guanilhidrazona

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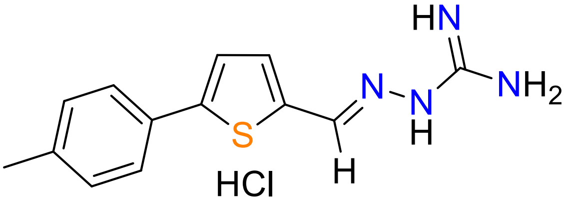
Sintetisali smo seriju novih tiofenskih guanilhidrazona u dva reakciona koraka, koristeći jednostavne procedure. Ispitivanje antifungalne aktivnosti sintetisanih guanilhidrazonskih derivata urađeno je na osam klinički važnih sojeva, a rezultati su prikazani kao MIC (minimalna inhibitorna koncentracija) i upoređeni sa vorikonazolom. Citotoksičnost jedinjenja je određena prema zdravim humanim ćelijama MRC5 (fibroplasti izolovani iz pluća čoveka). U nastavku istraživanja dodatno smo ispitali uticaj najaktivnijeg derivata na inhibiciju formiranja hifa i biofilma.



	MIC (μg/mL)
Candida albicans **CA5**	0,5
Candida albicans **ATCC10231**	0,9

Synthesis and antifungal activity of thiophene-based guanylhydrazones

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A series of new thiophene-based guanylhydrazones (iminoguanidines) were synthesized in high yields using a straightforward two-step procedure. The antifungal activity of compounds was evaluated against a wide range of medically important fungal strains including yeasts, molds, and dermatophytes in comparison to clinically used drug voriconazole. Cytotoxic properties of compounds were also determined using human lung fibroblast cell line. The most active compound was tested as a potential inhibitor of hyphal and biofilm formation.

Acknowledgements: This research was financially supported by the Ministry of Education, Science and Technological Development of Serbia (Grant No. 172008 and 173048) and the Serbian Academy of Sciences and Arts.

HS P 10

Sinteza novih derivata 4-ferocenilhinolina

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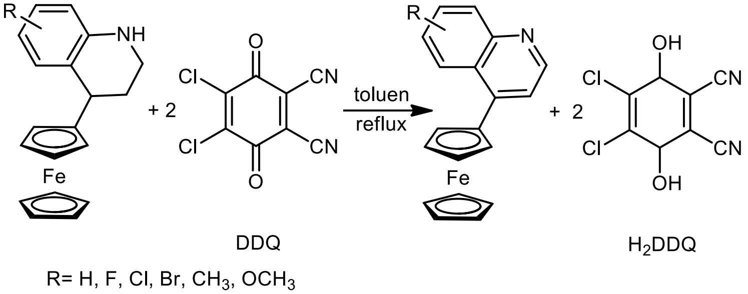
Hinolin i njegovi derivati spadaju u važnu grupu organskih jedinjenja koja, pored izuzetnog sintetičkog značaja, često pokazuju različite oblike biološke aktivnosti.[1] Ferocenski derivati ovog heterocikla sve više privlače pažnju sintetičara zbog njihovog potencijalnog farmakološkog značaja.[2] U ovom radu biće opisana sinteza novih 4-ferocenilhinolina (58-93%) oksidacijom odgovarajućih 4-ferocenil-1,2,3,4-tetrahidrohinolina,[3] pod relativno blagim reakcionim uslovima, pomoću 2,3-dihloro-5,6-dicijano-1,4-benzohinona (DDQ).



Synthesis of novel 4-ferrocenylquinolines

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Quinoline and its derivatives are particularly important organic compounds, since they are known to possess a plethora of biological activities, in addition of their importance in organic synthesis.[1] Ferrocene containing derivatives of this heterocycle have nowadays also attracted much attention due to their high pharmacological potential.[2] The present paper deals with the synthesis of novel 4-ferrocenylquinolines (58-93%) through the oxidation of the corresponding 4-ferrocenyl-1,2,3,4-tetrahydroquinolines,[3] by means of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), under mild reaction conditions.

1. J. A. Joule, K. Mills, *Heterocyclic Chemistry*, 5th ed., A John Wiley & Sons, Ltd., Publication, **2010**, pp. 115-220.
2. a) S. Madapa, Z. Tusi, S. Batra, *Cur. Org. Chem.* **2008**, *12*, 1116-1183; b) S. M. Prajapati, K. D. Patel, R. H. Vekariya, S. N. Panchal, H. D. Patel, *RSC Adv.* **2014**, i, 24463-24476.
3. A. Minić, D. Stevanović, I. Damljanović, A. Pejović, M. Vukićević, G. A. Bogdanović, N. S. Radulović, R. D. Vukićević, *RSC Adv.* **2015**, *5*, 24915-24919.

HS P 11

Meldrumna kiselina kao C_2-sinton

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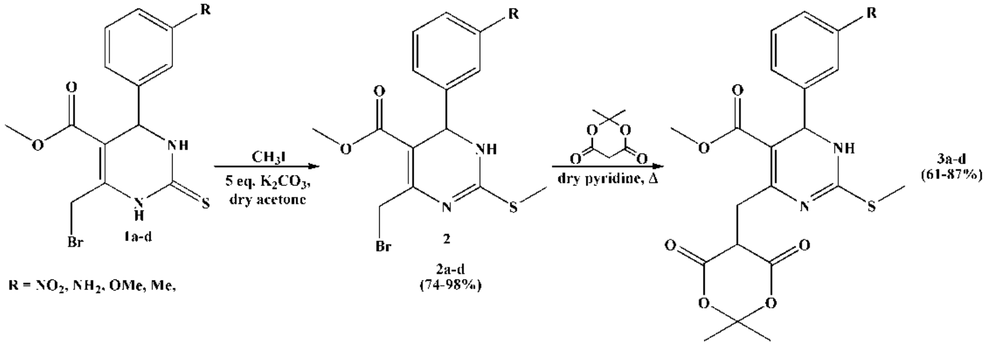
Meldrumna kiselina je veoma elegantan sinton u organskoj sintezi.[1] Mi smo opisali u Šemi 1 odličnu primenu Meldrumne kiselina kao C_2-sintona. Prvo smo alkilovali Biđinelijeve estre (1a-d), koji su prethodno sintetisani po ranije opisanoj metodi.[2] Zatim smo, preko funkcionalizacije proizvoda 2a-d sa Meldrumnom kiselinom sintetisali proizvode 3a-d u odličnim prinosima.



Scheme 1. *Functionalization of Biginelli esters with Meldrum's acid*

Meldrum's acid as a C_2-synthon

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Meldrum's acid is a very elegant synthon in organic synthesis.[1] We describe in Scheme 1 excellent application of Meldrum's acid as a C_2-synthon. First, we are alkylation of Biginelli esters (1a-d), which are synthesized by earlier described method.[2] Then, products 3a-d are synthesized in very good yields through functionalization 2a-d with Meldrum's acid.

Acknowledgements: The autors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Grant 172011)

1. Lipson *et. al. Molec. Divers.* 2009, 13, 399.
2. N. Jankovic *et. al. J. Serb. Chem. Soc.* 2015, 80(5), 595.

HS P 12

Uticaj položaja cijano-grupe u novim aminohinolinskim derivatima benzotiofena na inhibitornu aktivnost prema BoNT/A LC

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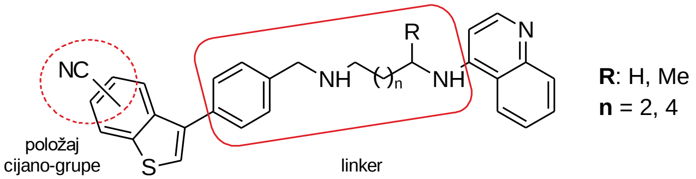
Botulinum neurotoksine (BoNT), najjače poznate biološke toksine, proizvodi bakterija *Clostridium botulinum*. Ovi toksini dovode do blokade neuromišićne transmisije i stanja poznatog kao botulizam. Fokus istraživanja je na malim molekulima kao inhibitorima BoNT/A LC. Izvršena je sinteza novih aminohinolinskih derivata benzotiofena, različite strukture linkera, i ispitana njihova *in vitro* inhibitorna aktivnost prema BoNT/A LC. Sintetisani molekuli pokazuju visok procenat inhibicije – do 84%. U cilju ispitivanja uticaja položaja cijano-grupe benzotiofenskog dela strukture na aktivnost, sintetisani su odgovarajući analozi. Molekulsko modelovanje i *docking* simulacije inhibitora u aktivnom mestu BoNT/A LC su omogućili objašnjenje dobijenih vrednosti inhibitorne aktivnosti i uočenih trendova.



Effect of cyano group position in new aminoquinoline derivatives of benzothiophene on inhibitory activity against BoNT/A LC

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Botulinum neurotoxins (BoNT), the most potent of the biological toxins, are produced by the bacterium *Clostridium botulinum*. These toxins block neuromuscular transmission and cause botulism. Small molecules inhibitors of BoNT/A LC are the focus of research. We carried out the synthesis of new aminoquinoline derivatives of benzothiophene with different linker structures and determined their *in vitro* inhibitory activity against BoNT/A LC. Synthesized molecules show high inhibition percent – up to 84%. In order to examine the effect of cyano group position on benzothiophene moiety on inhibitory efficacy, structural analogs were synthesized. Molecular modeling and docking simulations of inhibitors in BoNT/A LC active site enabled us to explain obtained inhibitory activities and observed trends.

Acknowledgement: This research was supported by the Ministry of Education, Science and Technology Development of Serbia (grant no. 172008) and US *National Institute of Health (1U01AI082051-01).*

HS P 13

Sinteza novih Biđinelijevih analoga sa 1,3-thiazinskim prstenom

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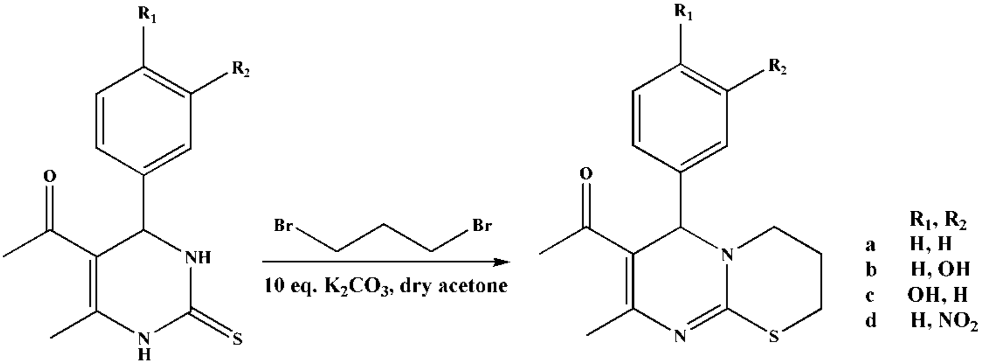
Tetrahidropirimidini i njihovi analozi predstavljaju klasu heterocikličnih molekula koji su privukli veliko interesovanje medicinske hemije.[1] Mala serija 2-tiokso-1,2,3,4-tetrahidropirimidina (1) sintetisana je po ranije opisanoj metodi.[2] Ovi molekuli su polazna jedinjenja za dialkilovanje u jednoj fazi pomoću 1,3-dibrompropana (Šema 1). Nova jedinjenja sa 1,3-thiazinskim jezgrom (2a-d) sintetisana su u dobrim prinosima.



1

2a-d
(65-81%)

Scheme 1. *One-pot dialkylation of 2-thioxo-1,2,3,4-tetrahydropyrimidines*

Synthesis of novel Biginelli analogs with 1,3-thiazine ring

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Tetrahydropyrimidines and their analogs represent a class of heterocyclic molecules that have attracted a considerable interest in medicinal chemistry.[1] The small series of 2-thioxo-1,2,3,4-tetrahydropyrimidines (1) are synthesized by previously described method .[2] This molecules is starting compounds for *one-pot* dialkylation with 1,3-dibromopropane (Scheme 1). Novel compounds with 1,3-thiazine core (2a-d) prepared in good yields.

Acknowledgements: The autors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Grant 172011)

1. O. C. Agbaje *et. al.* Bioorg. *Med. Chem. Lett.* 2011, 21, 989.
2. N. Jankovic *et. al. J. Serb. Chem. Soc.* 2015, 80(5), 595.

HS P 14

Sinteza tiepinskih derivata kao potencijalnih antifungalnih agenasa reakcijom Suzukijevog kuplovanja

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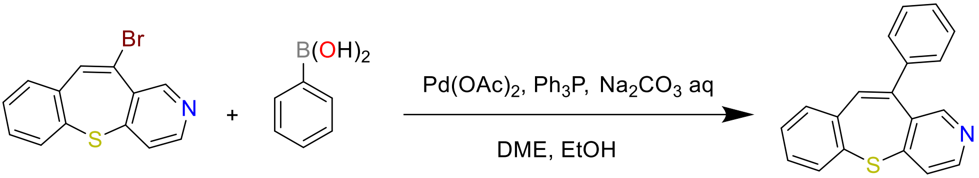
Nedavno, razvili smo novu metodologiju za sintezu 5*H*-diaril[b,f]tiepina iz odgovarajućih *Z*-stilbena, građenjem dve C-S veze uz pomoć paladijuma kao katalizatora.[1] U planarnoj konformaciji sedmočlanog prstena, elektronski par sumpora bi, sa trienskim delom strukture, činio antiaromatični 8π elektronski sistem. Teorijski proračuni pokazali su da sistem odstupa od planarne geometrije, što povećava reaktivnost dvostruke veze. Bromovanjem dvostruke veze, a zatim eliminacijom HBr u baznim uslovima, dobijen je vinil-bromid, koji je zatim podvrgnut reakcijama Suzukijevog kuplovanja sa serijom fenilboronskih kiselina. Dobijeni molekuli pokazali su značajnu antifungalnu aktivnost.



Synthesis of thiepine derivatives with potential antifungal activity via Suzuki coupling

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We recently reported the preparation of 5*H*-diaryl[b,f]thiepines using the palladium-catalyzed sulfonation-cyclization reaction of *ortho*-halogensupstituted *Z*-stilbenes.[1] In the planar conformation, thiepine 4n-π electron rings would be formally anti-aromatic. Distortion from planar geometry causes different bond localisation, which leaves the double bond out of the conjugated system. In order to confirm this theoretical prediction for our system, we performed the simple alkene bromination reaction on a thiepine derivative. Base-promoted HBr-elimination of the vicinal dibromide gave vinyl bromide and the reaction proceeded with good regioselectivity. The obtained vinyl bromide was successfully coupled with a series of arylboronic acids under Suzuki reaction conditions. The *in vitro* antifungal activities of compounds are notable.

Acknowledgment: This research was supported by the Ministry of Education, Science and Technological development of the Republic of Serbia (grant no. 172008).

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HS P 15

Sinteza i karakterizacija (*E*)-2-(2-(piridin-2-ilmetilen)hidrazinil)-4-(4-tolil)-1,3-tiazola i njegovog kompleksa kobalta(III)

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**Poljoprivredni fakultet, Beograd*

U cilju dobijanja biološki aktivnih jedinjenja sintetisan je ligand (*E*)-2-(2-(piridin-2-ilmetilen)hidrazinil)-4-(4-tolil)-1,3-tiazol (HL) i njegov kompleks kobalta(III). Utvrđeno je da reakcioni uslovi Hantschove ciklizacije 2-formilpiridin-tiosemikarbazona i 2-bromo-4'-metilacetofenona diktiraju vrstu dobijenog proizvoda. HL se dobija na sobnoj temperaturi u smeši vode i etanola (zapreminski odnos 1 : 1), dok korišćenjem apsolutnog etanola uz refluks nastaje HL×HBr. Reakcijom HL liganda sa $Co(BF_4)_2 \times 6H_2O$ u metanolu na povišenoj temperaturi sintetisan je kompleks $[CoL_2]BF_4$. Sve supstance su okarakterisane elementalnom analizom, NMR, IC i UV-Vis spektroskopijom, a struktura im je određena rendgenskom strukturnom analizom. Poređenjem kristalnih struktura protonovanog i neutralnog oblika liganda uočavaju se razlike u dužinama i uglovima veza. Razlike u molekulskim strukturama HL i HL×HBr ukazuju na to da je usled protonovanja piridinskog azota došlo do pomeranja elektronske gustine ka piridinskom prstenu. U oktaedarskom kompleksu kobalta(III) ligand je koordinovan tridentatntno, u monoanjonskom obliku, preko piridinskog i iminskog atoma azota i atoma azota iz tiazolskog prstena, pri čemu nastaju dva petočlana helatna prstena. Ispitivanje biološke aktivnosti sintetisanih jedinjenja je u toku.

Synthesis and characterization of (*E*)-2-(2-(pyridin-2-ylmethylene)hydrazinyl)-4-(4-tolyl)-1,3-thiazole and its cobalt(III) complex

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**Faculty of Agriculture, Belgrade*

In order to obtain biologically active compounds, the ligand (E)-2-(2-(pyridin-2-ylmethylene)hydrazinyl)-4-(4-tolyl)-1,3-thiazole (HL) and its cobalt(III) complex have been synthesized. It has been determined that the reaction conditions of Hantsch cyclization of 2-formylpyridine thiosemicarbazone with 2-bromo-4′-methoxyacetophenone dictated the type of derived product. HL was obtained at room temperature in a mixture of water and ethanol (volume ratio of 1 : 1), whereas HCl×HBr was obtained under the reflux when absolute ethanol was used as a solvent. The complex [CoL2]BF4 was synthesized in reaction of HL with Co(BF4)2×6H2O in methanol at elevated temperature. All compounds were characterized by elemental analysis, NMR, IR and UV-Vis spectroscopy, while X-ray structural analysis was used for determination of molecular and crystal structures of the compounds. In the molecular structure of protonated and neutral form of the ligand, there are differences in bond lengths and angles. This implies that protonation of pyridine nitrogen moves electron density towards pyridine ring. In octahedral cobalt(III) complex, the ligand is coordinated tridentately in monoanionic form, through pyridine and imine nitrogen atoms and nitrogen atom of thioazole ring, forming two five-membered chelate rings. Investigation of biological activity of the synthesized compounds is in progress.

HS P 16

Sinteza i karakterizacija pentagonalno bipiramidalnog izotiocijanato kompleksa Zn(II) sa kondenzacionim proizvodom 2,6-diacetilpiridina Žirarovog T reagensa

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Ligand **1** je sintetisan u reakciji 2,6-diacetilpiridina i Žirarovog T reagensa u molarnom odnosu 1:2 u metanolu. U reakciji liganda (**1**), cink(II)-hlorida dihidrata i amonijum-tiocijanata dobijen je Zn(II) kompleks (**2**). U kompleksnom katjonu pentagonalno-bipiramidalne geometrije ligand (**1**) je N_3O_2 koordinovan u ekvatorijalnoj ravni, dok apikalne položaje zauzimaju tiocijanatni anjoni koordinovani preko atoma azota. Kompleksni anjon je tetraedarski izotiocijanato Zn(II) kompleks. Ligand (**1**) i kompleks (**2**) okarakterisani su elementalnom analizom, NMR, IC i UV/Vis spektroskopijom, konduktrometrijom, dok je struktura kompleksa (**2**) određena rendgenskom strukturnom analizom.

Synthesis and characterization of pentagonal bipyramidal isothiocyanato Zn(II) complex with condensation product of 2,6-diacetylpyridine and Girard's T reagent

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The ligand (**1**) was synthetized in the reaction of 2,6-diacetylpyridine and Girard's T reagent in molar ratio 1:2 in methanol. In the reaction of ligand (**1**), zinc(II) chloride dihydrate and ammonium thiocyanate Zn(II) complex (**2**) was obtained. Pentagonal bipyramidal complex cation consists of N_3O_2 coordinated ligand (**1**) in equatorial plane with two isothiocyanates in apical positions. Complex anion is tetrahedral isothiocyanato Zn(II) complex. The ligand (**1**) and the complex (**2**) were characterized by elemental analysis, NMR, IR and UV/Vis spectroscopy, conductometric measurements, and structure of the complex (**2**) was defined by X-ray analysis.

HS P 17

Sinteza i karakterizacija pentagonalno bipiramidalnih izotiocijanato kompleksa Co(II) i Ni(II) sa kondenzacionim proizvodom 2,6-diacetilpiridina i Žirarovog T reagensa

Gabrijela Brađan, Milica Milenković, Božidar Čobeljić, Katarina Anđelković
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Ligand (**1**) je sintetisan u reakciji 2,6-diacetilpiridina i Žirarovog T reagensa u molarnom odnosu 1:2 u metanolu. Pentagonalno-bipiramidalni izotiocijanato kompleksi Co(II) (**2**) i (**3**), kao i Ni(II) (**4**) dobijeni su direktnom i templatnom sintezom. Reakcioni proizvodi u direktnoj i templatnoj sintezi Co(II) kompleksa su dva kompleksa Co(II) koji imaju isti kompleksni katjon, ali različite anjone, tiocijanat u kompleksu **2**, odnosno tetraedarski izotiocijanato Co(II) kompleks u kompleksu **3**. Kompleks Ni(II) (**4**) pentagonalno-bipiramidalne geometrije, izostrukturan sa kompleksom **3**, izolovan je samo u direktnoj reakciji, dok u slučaju templatne sinteze dolazi do raspadanja nestabilnog kompleksa. Ligand i kompleksi okarakterisani su elementalnom analizom, IC i UV/Vis spektroskopijom, konduktrometrijom, magnetnim merenjima, dok su strukture kompleksa (**2**), (**3**) i (**4**) određene rendgenskom strukturnom analizom.

Synthesis and characterization of pentagonal bipyramidal isothiocyanato Co(II) and Ni(II) complexes with condensation product of 2,6-diacetylpyridine and Girard's T reagent

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The ligand (**1**) was synthetized in the reaction of 2,6-diacetylpyridine and Girard's T reagent in molar ratio 1:2 in methanol. Pentagonal bipyramidal isothiocyanato complexes of Co(II) (**2**) and (**3**), as well as Ni(II) (**4**) were synthetized performing direct and template methods of synthesis. Both template and direct synthesis of Co(II) complexes resulted in formation of two complexes with the same complex cation, but different anions i.e. thiocyanate anions (**2**) and tetrahedral Co(II) complex anion (**3**), respectively. Pentagonal bipyramidal isothiocyanato complex of Ni(II) (**4**), isostructural with **3**, was isolated only in direct reaction, while template synthesis resulted in decomposition of unstable complex to the starting compounds. The ligand and the complexes were characterized by elemental analysis, IR and UV/Vis spectroscopy, conductometric measurements, and structures of the complexes (**2**), (**3**) and (**4**) were determined by X-ray analysis.

HS P 18

Синтеза и карактеризација комплекса [Ru(η^6-*p*-cimen)Cl(N-PrIm)$_2$][Ru(η^6-*p*-cimen)]

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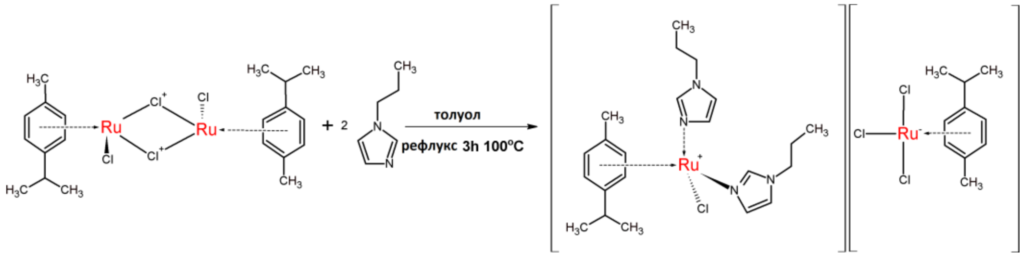
У овом раду приказана је синтеза комплекса Ru(II)-*p*-цимена и *N*-пропилимидазола као лиганда. Смеша [Ru-(η^6-*p*-cimen)Cl$_2$]$_2$ (0.199 g, 0.326 mmol) и *N*- пропилимидазола (75.6 μL, 0.652 mmol, 2.0 еквив.) је растворена у 30 ml толуола на собној температури. Добијена смеша је рефлуктована 3 сата на 100 °C. Након рефлуктовања, раствор је охлађен и процеђен, при чему се издваја наранџаст пудераст талог. Карактеризација синтетисаног комплекса [Ru(η^6-*p*-cimen)Cl(*N*-PrIm)$_2$][Ru(η^6-*p*-cimen)] извршена је анализом IR и NMR спектара, микроанализом и одређивањем тачке топљења. Испитиван је степен интеракције синтетисаног комплекса са молекулом ЦТ-ДНК-а као и његова биолошка активност на одређеним ћелијским линијама.



Synthesis and characterization of [Ru(η^6-*p*-cimen)Cl(N-PrIm)$_2$][Ru(η^6-*p*-cimen)]complex

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In this report we have synthesized complex of Ru(II)-*p*-cymene and *N*-propylimidazole ligand. To a suspension of [Ru-(η6-*p*-cymene)Cl$_2$]$_2$ (0.199 g, 0.326 mmol) in toluene (30 mL), *N*-propylimidazole (75.6 μL, 0.652 mmol, 2.0 equiv) was added at room temperature. The resulting mixture was heated to reflux for 3 h on 100 °C. After the mixture was cooled, the precipitate was filtered, affording an orange powdery residue. Characterization of the synthesized complex [Ru(η^6-*p*-cymene)Cl(*N*-PrIm)$_2$][Ru(η^6-*p*-cymene)] was performed by using IR and NMR spectroscopy, microanalysis and melting point determination. The interaction of the complex with a molecule of CT-DNA as well as its biological activity was examined on certain cell lines.

HS P 19

Синтеза и карактеризација платина(II) комплекса са етил естром етилендиамин-*N*,*N*'-ди-*S*,*S*-(2,2'-ди-(4-хидрокси)-бензил) сирћетне киселине

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У овом раду приказана је синтеза комплекса $K_2[PtCl_4]$ са етил естром етилендиамин-*N*,*N*'-ди-*S*,*S*-(2,2'-ди-(4-хидрокси)-бензил) сирћетне киселине (det-*S*,*S*-ed-dtyr 2HCl $2H_2O$).

У раствор добијен растварањем 0,050 г (0,121 ммол) $K_2[PtCl_4]$ у 10 мл воде, додато је 0,067 g (0,121 mmol) лиганда, етил естра етилендиамин-*N*,*N*'-ди-*S*,*S*-(2,2'-ди-(4-хидрокси)-бензил) сирћетне киселине. Реакциона смеша се меша два сата. Током тог периода у малим порцијама додаје се водени раствор литијум-хидроксида (0,0058 g, 0,242 mmol у 10 ml воде).

Комплекс [Pt(edtyr-etil)Cl_2], талог светло жуте боје, је филтриран, испран водом и сушен на ваздуху. Принос је 0,023 g(27,05%).

Састав комплекса је утврђен на основу резултата елементалне микроанализе, а структура комплекса је предвиђена на основу инфрацрвених и нуклеарно-магнетно-резонанционих спектара.

Synthesis and characterization of platinum(II) complex with ethyl ester of (*S*,*S*)-ethylenediamine-*N*,*N*'-di-(2,2'-di(4-hydroxy)-benzyl-acetic acid

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The complex of $K_2[PtCl_4]$ with ethyl ester of (*S*,*S*)-ethylenediamine-*N*,*N*'-di-(2,2'-di(4-hydroxy)-benzyl-acetic acid have been synthesized. $K_2[PtCl_4]$ (0.050 g, 0.121 mmol) was dissolved in 10 mL of water and *O*,*O*'-diethyl-(*S*,*S*)-ethylenediamine-*N*,*N*'-di-(2,2'-di(4-hydroxy)-benzyl-acetate dihydrochloride dihydrate, det-*S*,*S*-eddtyr·2HCl·$2H_2O$ (0.067 g, 0.121 mmol) was added. The mixture was stirred for 2 h and during this period water solution of LiOH (0.0058 g, 0.242 mmol) was introduced.

The complex, [$PtCl_2$(det-*S*,*S*-eddtyr)] as a light yelow precipitate was filtered, washed with water and air-dried. Yield: 0.023 g (27.05%).

The obtained complex have been characterized by elemental microanalysis, infrared, ^{1}H and ^{13}C NMR spectroscopy.

HS P 20

Neočekivani proizvod reakcije oksidativnog kuplovanja eugenola

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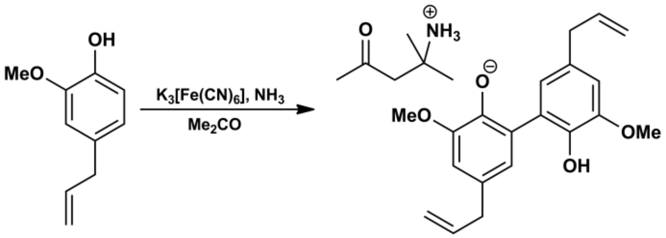
U reakciji eugenola i kalijum-heksacijanoferata(III) u acetonskom rastvoru amonijaka (po proceduri za dobijanje neolignana dehidrodieugenola [1]) dobijeno je mikrokristalno jedinjenje nerastvorno u vodi, ali rastvorno u hloroformu. ^{1}H NMR spektar proizvoda se razlikovao od očekivanog spektra dehidrodieugenola – primećena su tri dodatna singleta (koja predstavljaju tri CH_3- i jednu -CH_2- grupu). ^{13}C NMR spektar je takođe sadržao signale (četiri alifatična i jedan karbonilni) koji nisu mogli da potiču od očekivanog proizvoda. Detaljnom analizom 1D i 2D NMR spektara utvrđeno je da izolovani proizvod predstavlja so 4-amino-4-metil-2-pentanona i dehidrodieugenola. Katjon je nastao u reakciji enolata acetona i imina acetona ili konjugovane Michael-ove adicije amonijaka na proizvod aldolne kondenzacije dva molekula acetona.



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An unexpected product from the oxidative coupling of eugenol

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The reaction of eugenol and potassium hexacyanoferrate(III) in an acetone solution of ammonia was performed following the procedure described by Dias [1] with an aim to prepare the known neolignane dehydrodieugenol. A microcrystalline product was obtained which was insoluble in water, but soluble in chloroform. Its ^{1}H NMR spectrum differed from the expected spectrum of dehydrodieugenol–three additional singlets (corresponding to three CH_3- and one -CH_2- group) were observed. ^{13}C NMR spectrum also contained signals (four aliphatic and one carbonyl carbon) which could not be connected to the structure of the expected product. Detailed analyses od 1D and 2D NMR spectra revealed that the isolated product represented the salt of 4-amino-4-methylpentan-2-one and dehydrodieugenol. The cation could have formed in the reaction between the enolate of acetone and the imine of acetone or in the Michael addition of ammonia to the product of aldol condensation of two molecules of acetone.

This work was supported by the Ministry of Education, Science and Technological Development of Serbia [Project No. 172061].

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HS P 21

Diamindihalogenidoplatina(II) kompleksi: sinteza, karakterizacija i antitumorska aktivnost

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Dugi niz godina glavni motiv za sintezu diamindihalogenidoplatina(II) kompleksa jeste da se napravi još efikasniji lek od cisplatine, sa što manje neželjenih sporednih efekata. Tako su sintetisani dihlorido i dijodido kompleksi platine(II) sa diaminskim ligandom - *O,O'*-dietil-(*S,S*)-etilendiamin-*N,N'*-di-2-amino-(3-cikloheksil)propanoat dihidrohloridom. Ligand je sintetisan polazeći od neesencijalne aminokiseline nizom uobičajenih reakcija alkilovanja i esterifikacije. Kompleks dihlorido-platine(II) je sintetisan direktnom reakcijom vodenog rastvora kalijum-tetrahloridoplatinata(II) i metanolnog rastvora dehidrohlorovanog liganda. Dijodido-platina(II) kompleks dobijen je u analognoj sintezi, u kojoj je polazni kompleks bio kalijum-tetrajodidoplatinat(II), dobijen *in situ* iz kalijum-tetrahloridoplatinata(II) i viška kalijum-jodida.

Strukture sintetisanih liganda i kompleksa utvrđene su standardnim spektroskopskim metodama: infracrvenom spektroskopijom, NMR spektroskopijom, masenom spektrometrijom dok je pretpostavljena molekulska formula potvrđena elementalnom analizom. Rezultati *in vitro* biološke aktivnosti, na ćelijskoj liniji humanih promijelotskih leukemičnih ćelija, pokazali su snažniju aktivnost liganda i kompleksa u odnosu na cisplatinu, kao i nešto bolju aktivnost dijodidoplatina(II) kompleksa u odnosu na dihlorido analoge.

Diaminedihalogenidoplatinum(II)-complexes: synthesis, characterization and antitumor activity

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For many years, the main motiv for synthesis diaminedihalogenidoplatinum(II) complexes is to make more effective antitumor agent than cisplatin, with less unwanted side effects. So, one of this attempts was synthesis of dichlorido and diiodido platinum(II) complexes with *O,O'*-diethyl-(*S,S*)-ethylendiamine-*N,N'*-di-2-amino-(3-cyclohexyl)propanoate dihydrochloride. This ligand was prepared starting from unessential aminoacid folowed by standard reaction of alkylation and esterification. Complex dichloride-platinum(II) was synthesized directly from aqueos solution of potassium-tetrachloridoplatinum(II) and methanol solution of neutralized ligand. Diiodido-platinum(II) complex was obtained in similar synthesis starting from potassium-tetraiodido-platinum(II) complex formed *in situ* from potassium-tetrachloridoplatinum(II) and the excess of potassium-iodide.

Structures of synthesized ligand and complexes were confirmed by standard spectroscopic methods: infrared spectroscopy, NMR spectroscopy, mass spectrometry and molecular formulas were confirmed by elemental analysis. Results of *in vitro* cytotoxicity analyses, on the human promyelocytic cell line showed better activity of ligand and synthesized complexes than cisplatin, and a litle better activity of diiodido than analogue dichlorido platinum(II) complexes.

HS P 22

Sinteza ugaono-kondenzovanih hidantoina (homo)trikvinanskog tipa kao prekursora bicikličnih α-prolina

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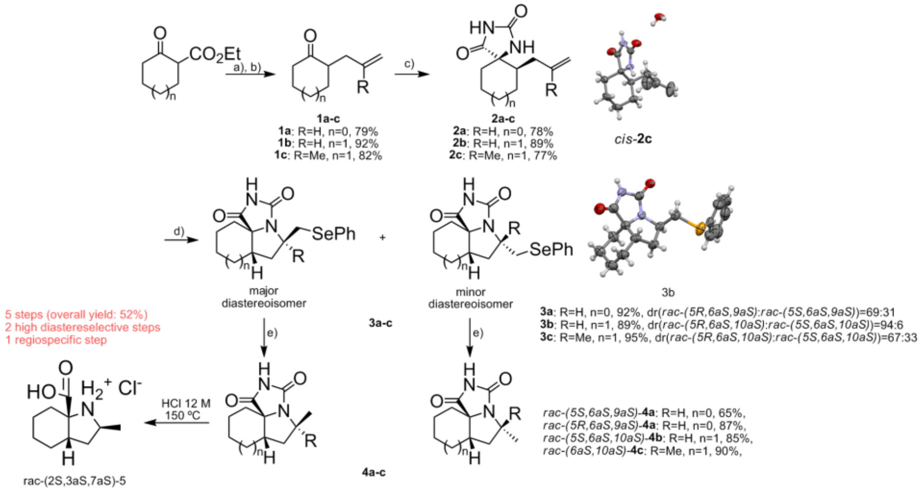
Razvijena je strategija za sintezu prekursora bicikličnih *cis*-kondenzovanih α-aminokiselina koja uključuje visoko diastereoselektivnu Bucherer-Bergs-ovu reakciju 2-alkenilcikloalkanona i regiospecifično zatvaranje pirolidinskog prstena elektrofilnom selenociklizacijom. Primenom ove metodologije u pet faza dobijen je jedan derivat bicikloprolina u ukupnom prinosu od 52%.



a) EtOH, EtONa (1 equiv), allyl or methallyl chloride (1 equiv), r.t. to reflux (3-5 h); b) NaOH (3 equiv), H_2O, reflux 2 h; c) NaCN (2 equiv), $(NH_4)_2CO_3$ (4 equiv), EtOH/H_2O (1:1), reflux 24 h; d) PhSeCl (1.1 equiv), SiO_2 (5 equiv), dry MeCN, r.t. 24 h; e) Raney-Ni, THF, H_2 balloon pressure, r.t. 1h;

Synthesis of angularly fused (homo)triquinane type hydantoins as precursors of bicyclic α-prolines

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The strategy for four-step synthesis of angularly fused tricyclic hydantoins as suitable precursors of *cis*-fused bicyclic α-amino acids is developed by combining highly diastereoselective Bucherer-Bergs reaction of 2-alkenylcycloalkanones and regiospecific selenium-induced closure of pyrrolidine ring. This methodology was applied in five-step synthesis of bicycloproline derivative in 52% overall yield.

HS P 23

Fulerosteroidni i disteroidni [2]rotaksani uređeni vodoničnim vezivanjem: Translacija i/ili disocijacija indukovana rastvaračima

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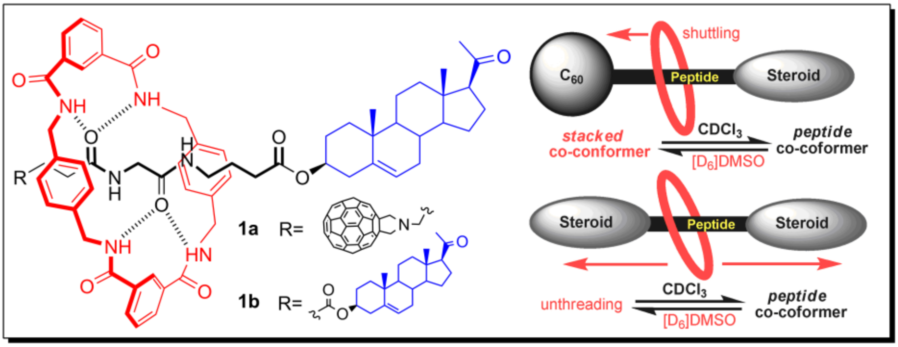
Fulerosteroidni i disteroidni [2]rotaksani uređeni vodoničnim vezivanjem (**1a**,**b**) koji sadrže peptidne jedinice (GABA-Gly-GABA and GABA-Gly-Succ) sintetisani su i okarakterisani. Za određivanje translatornog kretanja karike duž ose u rastvaračima različite polarnosti primenjena je NMR spektroskopija. Oba rotaksana su stabilna i zauzimaju *peptidnu* ko-konformaciju u $CDCl_3$. Ispitivanjem ponašanja rotaksana u $[D_6]$DMSO, ustanovljeno je da se karika fulerosteroidnog rotaksana prvenstveno pomera ka fulerenu i uspostavljajući π-π interakcije sa njim zauzima drugu stabilnu ko-konformaciju, dok disteroidni rotaksan kvantitativno disosuje.



Hydrogen bond-assembled fullerosteroidal and disteroidal [2]rotaxanes: Solvent-induced shuttling and/or dissociation

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Hydrogen bond-assembled fullerosteroidal and disteroidal [2]rotaxanes **1a**,**b** containing peptide units (GABA-Gly-GABA and GABA-Gly-Succ) in the thread are synthesized and characterized. ^1H NMR spectroscopy was used to investigate macrocycle shuttling along the axis in solvents of different polarity. An NMR study shows that both rotaxanes are stable and occur in a *peptide* co-conformation in $CDCl_3$. DMSO-induced macrocycle translocation in fullerosteroidal rotaxane **1a** is a predominant process due to presence of a voluminous C_{60} moiety which provides π-π interactions with the aromatic rings of macrocycle enabling the formation of the second stable *stacked* co-conformer, while disteroidal rotaxane **1b** completely dissociates.

HS P 24

Kristalografska analiza (2-(piridin-2-il)-1H-indol-3-il)(3,4,5-trimetoksifenil)-metanona (HL) i njegovih kompleksa sa Cu(II) i Pd(II)

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Novi kompleksi Cu(II) i Pd(II) sa 2-(2’-piridil)-indolskim ligandom HL, modifikovanim dodatkom 3,4,5-trimetoksibenzoil grupe, sintetisani su sa ciljem dobijanja biološki aktivnih kompleksa prelaznih metala. Kompleksi su sintetisani reakcijom HL sa $CuCl_2 \cdot 2H_2O$, odnosno $[PdCl_2(CH_3CN)_2]$, a prekristalisani difuzijom etanolnih para u DMSO rastvor sirovih proizvoda. HL i kompleksi $[Cu_2Cl_2L_2(DMSO)_2]$ i [PdClL(HL)] su dobijeni u vidu monokristala i njihova struktura je određena rendgenskom strukturnom analizom. Kompleks Cu(II) je centrosimetrični dimer kvadratno-piramidalne geometrije. Jedan molekul HL je u monoanjonskom obliku bidentatno koordinovan preko indolskog i piridinskog atoma azota za jedan Cu(II) jon, formirajući petočlani helatni prsten, dok je kiseonikov atom karbonilne grupe liganda koordinovan za drugi jon Cu(II). Ostala dva bazalna koordinaciona mesta zauzimaju hloridni jon i molekul DMSO-a. Kompleks [PdClL(HL)] je kvadratno-planarne geometrije. Sadrži dva molekula liganda, od kojih je jedan vezan u monoanjonskom obliku bidentatno, preko indolskog i piridinskog atoma azota formirajući petočlani helatni prsten. Drugi molekul liganda je vezan monodentatno u neutralnom obliku preko piridinskog azota, a četvrto koordinaciono mesto zazima hloridni jon. Kristalno pakovanje HL i njegovih kompleksa je zasnovano na vodoničnim vezama i π–π steking interakcijama.

Crystallographic analysis of (2-(pyridin-2-yl)-1H-indol-3-yl)(3,4,5-trimetoxiphenyl)-methanone (HL) and its complexes with Cu(II) and Pd(II)

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New Cu(II) and Pd(II) complexes with 2-(2’-pyridyl)-indole ligand HL, modified with 3,4,5-trimetoxybenzoyl group, were synthesized with aim of getting biologically active transition metal complexes. The complexes were obtained by the reaction of HL with $CuCl_2 \cdot 2H_2O$ or $[PdCl_2(CH_3CN)_2]$, and recrystalized by diffusion of ethanol vapor into DMSO solution of the crude products. Single crystals of HL and complexes $[Cu_2Cl_2L_2(DMSO)_2]$ and [PdClL(HL)] were obtained and their structures were determined by X-ray diffraction analysis. Cu(II) complex is a centrosymmetric dimer with square-pyramidal geometry. One molecule of HL in anionic form is coordinated bidentately *via* pyridine and indole nitrogen atoms to Cu(II) ion, forming five-membered chelate ring, while oxygen atom from carbonyl group is coordinated to another Cu(II) ion. Remaining two coordination sites are occupied by a chloride ion and a DMSO molecule. Complex [PdClL(HL)] has square-planar geometry. It contains two molecules of HL. One of them is coordinated bidentately in monoanionic form *via* pyridine and indole nitrogen atoms, forming five-membered chelate ring, while other one is coordinated monodentately in neutral form *via* pyridine nitrogen atom. Fourth coordination site is occupied by chloride ion. Crystal packings of HL and its Pd(II) and Cu(II) complexes are based on hydrogen bonds and π–π stacking interactions.

HS P 25

Sinteza i rendgenska strukturna analiza kompleksa kobalta sa 8-hinolinkarboksaldehid-(halkogen)semikarbazonima

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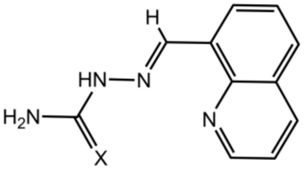
U cilju praćenja uticaja vrste halkogenog donorskog atoma na strukturu, geometriju i biološku aktivnost, u ovom radu su sintetisana i okarakterisana tri kompleksa kobalta sa (halkogen)semikarbazonima 8-hinolinkarboksaldehida (H8qaSC, H8qaTSC i H8qaSeSC). Sva tri kompleksa, $[Co(H8qaSC)_2]Cl_2 \times 2H_2O$ (**1**), $[Co(8qaTSC)_2]ClO_4 \times DMSO$ (**2**) i $[Co(8qaSeSC)_2]ClO_4 \times DMSO$ (**3**), su dobijena templatnom reakcijom sinteze u etanolnom rastvoru. Struktura liganda H8qaTSC i H8qaSeSC i kompleksa **1–3** određena je rendgenskom strukturnom analizom. Sva tri kompleksa su oktaedarske geometrije sa dva tridentatno koordinovana halkogensemikarbazonska liganda. Kordinacija liganada se ostvaruje preko hinolinskog i iminskog atoma azota i atoma halkogena, pri čemu svaki od liganada sa metalnim jonom gradi po jedan petočlani i jedan šestočlani helatni prsten. Za razliku od liganda H8qaSC koji je u kompleksu **1** koordinovan u neutralnom obliku za Co(II) jon, u izostrukturnim kompleksima **2** i **3** ligandi su koordinovani u monoanjonskom obliku za Co(III) jon. Svi kompleksi su pokazali značajno veću antimikrobnu aktivnost u odnosu na ligande.



X = O, H8qaSC
X = S, H8qaTSC
X = Se, H8qaSeSC

Synthesis and X-ray structural analysis of cobalt complexes with 8-quinolinecarboxaldehyde (chalcogen)semicarbazones

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In order to elucidate the chalcogen donor identity on the structure, geometry and biological activity, three cobalt complexes with 8-quinolinecarboxaldehyde (chalcogen)semicarbazones (H8qaSC, H8qaTSC and H8qaSeSC) have been synthesized and characterized. The complexes $[Co(H8qaSC)_2]Cl_2 \times 2H_2O$ (**1**), $[Co(8qaTSC)_2]ClO_4 \times DMSO$ (**2**) and $[Co(8qaSeSC)_2]ClO_4 \times DMSO$ (**3**) were obtained by the template reactions in etanolic solution. The structures of the ligands H8qaTSC and H8qaSeSC, as well as complexes **1–3** were determined by X-ray structural analysis. The geometry of all complexes is octahedral, where the ligands are tridentately coordinated *via* the quinoline and imine nitrogen atoms and chalcogen donor atoms, forming one five-membered and one six-membered chelate ring around the central metal ion. Unlike the ligand H8qaSC which is coordinated in the neutral form to Co(II) in **1**, the other two ligands are coordinated in monoanionic form to Co(III) in isostructural complexes **2** and **3**. All the complexes showed significantly higher antimicrobial activity compared to the activity of the corresponding ligands.

HS P 26

Eksperimentalna, biološka i kvantnohemijska proučavanja 3-(4-supstituisanih benzil)-1,3-diazaspiro[4.5]dekan-2,4-diona i 3-(2-(4-supstituisanih fenil)-2-oksoetil)-1,3-diazaspiro[4.5]dekan-2,4-diona

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U radu su sintetizovane dve nove serije jedinjenja koje poseduju antitumorsku aktivnost. Hemijska struktura i čistoća 3-(4-supstituisanih benzil)-1,3-diazaspiro[4.5]dekan-2,4-diona i 3-(2-(4-supstituisanih fenil)-2-oksoetil)-1,3-diazaspiro[4.5]dekan-2,4-diona, potvrđene su primenom ^{1}H i ^{13}C NMR, FT-IR i UV/Vis spektroskopskih metoda. Uticaj supstituenata na apsorpcione spektre cikloalkanspiro-5-hidantoina, u različitim rastvaračima kao i smešama rastvarača, proučavan je primenom Hametove jednačine. Korišćenjem Kamlet-Taftovih parametara analiziran je efekat polarnosti i polarizabilnosti rastvarača na pomeranje UV/Vis apsorpcionih maksimuma. Eksperimentalni rezultati su pokazali zadovoljavajuću saglasnost sa rezultatima kvantnohemijskih proračuna dobijenih primenom DFT metode. Pokazano je da supstituenti značajno utiču na intramolekulski transfer naelektrisanja (ICT) kao i na aktivnost proučavanih jedinjenja.

Experimental, biological and quantum chemical studies of 3-(4-substituted benzyl)-1,3-diazaspiro[4.5]decane-2,4-diones and 3-(2-(4-substituted phenyl)-2-oxoethyl)-1,3-diazaspiro[4.5]decane-2,4-diones

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In this work two new series of compounds which possess antitumor activity were synthesized. Chemical structure and purity of 3-(4-substitutedbenzyl)-1,3 diazaspiro[4.5] decane-2,4-diones and 3-(2-(4-substituted phenyl)-2-oxoethyl)-1,3-diazaspiro[4.5]decane-2,4-diones, were confirmed by ^{1}H and ^{13}C NMR, FT-IR and UV/ Vis spectroscopic methods. The effect of substituents on the absorption spectra of cycloalkanespiro-5-hydantoins in different solvents and solvent mixtures, was studied by Hammett equation. The effects of solvent polarity and polarizability on the UV/Vis absorption maximum were analyzed using Kamlet-Taft solvent parameters. The experimental results showed a satisfactory agreement with quantum chemical calculations obtained using DFT method. It was shown that substituents change the extent of conjugation, affect intramolecular charge transfer (ICT) character and significantly influence the activity of the studied compounds.

HS P 27

Sinteza hidrazida iz derivata holne kiseline

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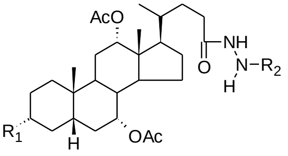
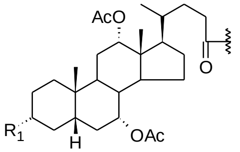
Steroidni hidrazidi i njihovi derivati, hidrazoni ili kompleksi sa prelaznim metalima pokazuju izraženu antimikrobnu aktivnost. Bez obzira na veliki biološki potencijal, vrlo malo hidrazida izvedenih iz supstituisanih derivata holne kiseline je opisano. U ovom radu opisana je sinteza sedam novih hidrazida derivata holne kiseline, od kojih su tri bis-steroidna. Sinteza je vršena polazeći od 3,7,12-triacetoksiholanske kiseline **DO-3**, preko mešovitog anhidrida **JD10** pomoću hidrazina ili njegovih derivata. Pojedini hidrazidi su dalje transformisani selektivnom baznom ili kiselom hidrolizom do 3-hidroksi derivata. Potvrda strukture sintetisanih jedinjenja je izvršena pomoću spektralnih (^{1}H-NMR, ^{13}C-NMR, IR (ATR), i (+)TOF HRMS) i analitičkih (mikroanaliza) metoda.



R_1 = OAc ili OH

R_2 = H, Ph ili



Zahvalnica: Ova istraživanja su podržana od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije (projekat br. ON172008).

Synthesis of hydrazides from cholic acid derivatives

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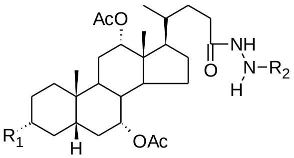
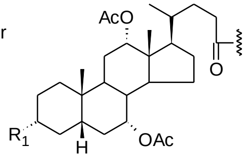
Steroidal hydrazides and their derivatives, hydrazones and transition metal complexes, showed high antimicrobial activities. In spite of high biological potential very few hidrazydes obtained with substituted cholic acid derivatives were obtained. Here in we described synthesis of seven hydrazides of cholic acid derivatives, three of which are bis-steroids. The synthesis was carried out starting from the 3,7,12-triacetyloxy- 5β-cholic acid **DO-3**, via the mixed anhydride **JD10** by means of hydrazine or its derivatives. Some of hydrazides were further transformed applying of basic or acidic hydrolysis to 3-hydroxy derivatives. Structures of the synthesized compounds were confirmed by spectral (^{1}H-NMR, ^{13}C-NMR, IR (ATR), and (+)TOF HRMS) methods and combustion analysis.



R_1 = OAc or OH

R_2 = H, Ph or



Acknowledgements: These researches were supported by the Ministry of education, science and technological development of the Republic of Serbia (project ON172008).

HS P 28

Uticaj rastvarača i supstituenata na solvatohromizam N-supstituisanih-5-ariliden-2,4-tiazolidindiona

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Tiazolidin-2,4-dion (TZD) predstavlja interesantnu strukturnu jedinicu u medicinskoj hemiji koja je odgovorna za brojna farmakološka svojstva i biološke aktivnosti. TZD derivati privlače značajnu pažnju istraživača zbog različitih sintetičkih mogućnosti i terapeutskog značaja. Raznim hemijskim modifikacijama ovog heterocikla dobijena su jedinjenja sa širokim spektrom biološke aktivnosti kao na primer, antidijabetska, antireumatska, antimikrobna, antifugalna, anti-inflamatorna, antikonvulzivna i antioksidativna aktivnost. U cilju istraživanja solvatohromnog ponašanja TZD derivata, sintetisane su dve serije derivata, N-metil- i N-fenil-5-ariliden-2,4-tiazolidindiona sa različitim supstituentima u arilidenskom jezgru i njihovi UV spektri su snimljeni u rastvaračima različite polarnosti u opsegu od 200-600 nm. Uticaj specifičnih i nespecifičnih interakcija rastvorak-rastvarač na pomeranje apsorpcionih maksimuma procenjen je pomoću Catalán-ovog modela linearne solvatacione energije (LSER). Uticaj supstituenata na solvatohromizam ovih derivata je proučavan i pomoću principa korelacija linearne slobodne energije (LFER) korišćenjem SSP i DSP modela koji su dalje primenjeni na apsorpcione maksimume.

Solvent and substituent effect on solvatochromism of N-substituted-5-arylidene-2,4-thiazolidinediones

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Thiazolidine-2,4-dione (TZD) represents an interesting scaffold in medicinal chemistry responsible for numerous pharmacological properties and biological activities. TZD derivatives have attracted a significant research interest because of their synthetic diversity and therapeutic relevance. Diverse chemical modifications of this heterocycle have resulted in compounds with a wide spectrum of biological activities *e.g.*, antidiabetic, antiarthritic, antimicrobial, antifungal, antiinflamatory, anticonvulsant and antioxidant activity. In order to investigate solvatochromic behaviour of TZD derivatives, two series of N-methyl- and N-phenyl-5-arylidene-2,4-thiazolidinediones were synthesized with different substituents at aryl moiety, and their UV absorption spectra have been recorded over the range of 200-600 nm in organic solvents of different polarity. The effect of specific and non-specific solvent–solute interactions on the absorption maxima shifts were evaluated by means of the linear solvatation energy relationship (LSER) model proposed by Catalán. Linear free energy relationship (LFER) has been further applied to absorption maxima. The study of substituent effect on solvatochromism of these derivatives has been performed using SSP (single substituent parameter) and DSP (dual substituent parameter) model.

HS P 29

Sinteza i karakterizacija novih rutenijum(II) polipiridil kompleksa

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U cilju daljeg istraživanja odnosa između strukture i aktivnosti, serija Ru(II) polipiridil kompleksa opšte formule [Ru(Cl-tpy)(*N*-*N*)Cl]$^+$ prethodno razvijena u našoj grupi (gde Cl-tpy = 4'-hloro-2,2':6',2''-terpiridin, *N*-*N* = 1,2-diaminoetan (en), 1,2-diaminocikloheksan (dach) or 2,2'-bipiridin (bpy))[1] proširena je sintezom novih kompleksa sa neutralnim tridentatnim ligandom, 4'-(4-Hlorofenil)-2,2':6',2''-terpiridin (Ph-Cl-tpy). Novosintetisani kompleksi su okarakterisani pomoću NMR i IR spektroskopije, UV-Vis spektrofotometrije i elementalne analize. Hemijsko ponašanje ovih kompleksa u vodenom rastvoru, kao i interakcije sa derivatima guanina 9EtG (9-etilguanin) i 5'-GMP (guanozin-5'-monofosfat) ispitivane su pomoću NMR i UV-Vis spektroskopije. Kinetika reakcije hidrolize i interakcije sa derivatima guanina i amino kiselinama ispitivana je kvantitativno pomoću UV-Vis spektrofotometrije. Citotoksičnost Ru(II) terpiridin kompleksa je u toku ispitivanja.

Synthesis and characterization of new water-soluble ruthenium(II) polypyridyl complexes

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With the aim of expanding the structure-avtivity relationship investigation, the series of Ru(II) polypyridyl complexes of the type [Ru(Cl-tpy)(*N*-*N*)Cl]$^+$ previously described by us (where Cl-tpy = 4'-chloro-2,2':6',2''-terpyridine, *N*-*N* = 1,2-diaminoethane (en), 1,2-diaminocyclohexane (dach) or 2,2'-bipyridine (bpy))[1] was extended to 4'-(4-Chlorophenyl)-2,2':6',2''-terpyridine (Ph-Cl-tpy). All new terpyridine complexes were fully characterized by NMR and IR spectroscopy, UV-Vis spectrophotometry and elemental analysis. The chemical behavior in aqueous solution of the new complexes and their binding properties towards the guanine derivatives 9EtG (9-ethylguanine) and 5'-GMP (guanosine-5'-monophosphate), as model DNA bases, were investigated by NMR and UV-Vis spectroscopy. The kinetics of the aquation of selected complexes and of the subsequent interaction with guanine derivatives and amino acids were established quantitatively by UV-Vis spectroscopy. The cytotoxic properties of these complexes are under investigation.

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HS P 30

Sinteza 3β,5α,6β-trihidroksi-17-oksa-D-homoandrost-16-ona

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Sintetisan je potencijalni inhibitor enzimskog kompleksa aromataze i antitumorski agens, 3β,5α,6β-trihidroksi-17-oksa-D-homoandrost-16-on (**5**). Kao polazno jedinjenje upotrebljen je dehidroepiandrosteron (**1**), a sinteza se sastojala iz četiri faze. U prvoj fazi izvršeno je oksiminovanje dehidroepiandrosterona sa izoamilnitritom, u prisustvu kalijum-*terc*-butoksida u *terc*-butanolu, a dobijen je 3β-hidroksiandrost-5-en-16,17-dion 16-oksim (**2**). Zatim je izvršena redukcija keto grupe natrijum-borhidridom, pri čemu je dobijen 16-hidroksimino-androst-5-en-3β,17β-diol (**3**). Laktonizacija jedinjenja **3** sprovedena je zagrevanjem sa kalijum-hidroksidom u etilen-glikolu, pri čemu je dobijen 3β-hidroksi-17-oksa-D-homoandrost-5-en-16-on (**4**). Konačno, stereospecifična dihidroksilacija dvostruke veze jedinjenja **4** izvedena je sa vodonik-peroksidom, u prisustvu kalijum-jodida i sumporne kiseline kao katalizatora.

Autori se zahvaljuju Ministarstvu prosvete, nauke i tehnološkog razvoja Republike Srbije (br. projekta 172021) na finansijskoj podršci.

Synthesis of 3β,5α,6β-trihydroxy-17-oxa-D-homoandrost-16-one

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A potential inhibitor of the aromatase enzyme complex and antitumor agent, 3β,5α,6β-trihydroxy-17-oxa-D-homoandrost-16-one (**5**), was synthesised. Starting from dehydroepiandrosterone (**1**), the synthesis encompassed four phases. In the first phase, oximination of dehydroepiandrosterone with isoamyl nitrite in the presence of potassium *tert*-butoxide was performed, which yielded 3β-hydroxyandrost-5-en-16,17-dione 16-oxime (**2**). Subsequently a reduction of the keto group by sodium borohydride was carried out, and 16-hydroxyimino-androst-5-en-3β,17β-diol (**3**) was obtained. Compound **3** was lactonised by heating in a mixture of potassium hydroxide in ethylene glycol, which produced 3β-hydroxy-17-oxa-D-homoandrost-5-en-16-one (**4**). Finally, stereospecific dihydroxylation of the double bond of compound **4** was performed using hydrogen peroxide with potassium iodide and sulphuric acid as catalysts.

Authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 172021) for financial support.

HS P 31

Sinteza i karakterizacija dinuklearnih kompleksa zlata(III) sa nekim aromatičnim heterocikličnim jedinjenjima koja sadrže azot

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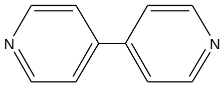
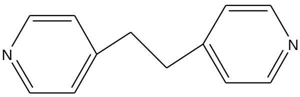


4,4'-bipy



4,4'-bpe

U ovom radu, sintetisana su dva nova dinuklearna kompleksa zlata(III) opšte formule $\{[AuCl_3]_2(\mu\text{-L})\}$, L je mostni *N*-heterociklični ligand 4,4’-bipiridin (4,4’-bipy) i 1,2-bis(4-piridil)etan (4,4’-bpe), u reakciji između $K[AuCl_4]$ i odgovarajućeg *N*-heterocikličnog liganda u 2:1 molskom odnosu. Dobijeni zlato(III) kompleksi su okarakterisani primenom elementarne mikroanalize, NMR (^{1}H i ^{13}C) i IR spektroskopije, kao i UV-vis spektrofotometrije. Primenom teorije funkcionalne gustine (DFT) optimizovane su geometrije ovih kompleksa u vakuumu. Pored toga, hemijski sastav $\{[AuCl_3]_2(\mu\text{-4,4'-bipy})\}$ kompleksa je potvrđen metodom difrakcije X-zraka sa kristala od strane Hemijskog fakulteta, „Adam Mickijevič“ Univerziteta iz Poznanja, Poljska. Dobijeni rezultati su pokazali da je formiranje dinuklearnih $\{[AuCl_3]_2(\mu\text{-L})\}$ kompleksa u reakcijama Au(III) jona sa 4,4’-bipy i 4,4’-bpe ligandima u suprotnosti sa ranije ispitivanim reakcijama ovog jona sa drugim *N*-heterocikličnim ligandima, gde isključivo dolazi do građenja mononuklearnih $[AuCl_3(N\text{-heterocikl})]$ kompleksa [1].

Synthesis and characterization of dinuclear gold(III) complexes with some aromatic nitrogen-containing heterocycles

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In the present study, we have synthesized two new dinuclear gold(III) complexes of the general formula $\{[AuCl_3]_2(\mu\text{-L})\}$, L is bridging *N*-heterocyclic ligand, 4,4’-bipyridine (4,4’-bipy) and 1,2-bis(4-pyridyl)ethane (4,4’-bpe), in the reactions between $K[AuCl_4]$ and the corresponding *N*-heterocycle in 2:1 molar ratio, respectively. The obtained gold(III) complexes were characterized by elemental microanalysis, NMR (^{1}H and ^{13}C) and IR spectroscopy, and UV-vis spectrofotometry. The geometry of these complexes in vacuo was optimized by using DFT method. Moreover, the chemical constitution of the 4,4’-bipyridine complex with gold(III) has been confirmed by X-ray diffraction carried out at the Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland. The obtained results showed that the formation of dinuclear $\{[AuCl_3]_2(\mu\text{-L})\}$ complexes in the reactions of Au(III) ion with 4,4’-bipy and 4,4’-bpe ligands is in contrast with the previously investigated reactions of this ion with some other *N*-heterocyclic ligands, which resulted only in formation of the mononuclear $[AuCl_3(N\text{-heterocycle})]$ complexes [1].

Acknowledgements: This work was funded in part by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172036) and was also supported by the Polish Grid Infrastructure PL-Grid.

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HS P 32

„Zelena” sinteza i potpuna asignacija ^{1}H- i ^{13}C-NMR spektara svih stereoizomernih oksima 3,7-dimetil-2,6-oktadienalâ

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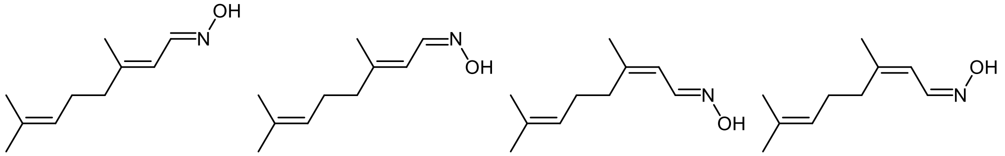
Sinteza bez prisustva rastvarača smeše svih stereoizomernih oksima 3,7-dimetil-2,6-oktadienalâ ostvarena je iz citrala, jeftine komercijalne smeše nerala i geranijala ((*Z*)-, odnosno (*E*)-dijastereoizomer), jednostavnom homogenizacijom sa viškom hidroksilamin-hidrohlorida i natrijum-hidroksida, u tarioniku pistilom na sobnoj temperaturi. Stereoizomerni oksimi ((*1E,2E*)-, (*1Z,2E*)- (*1E,2Z*)- i (*1Z,2Z*)-) su razdvojeni izokratskom hromatografijom (heksan/etar = 4:1, *v*/*v*) na koloni silika-gela. Po prvi put, oksimi su okarakterisani 1D- (^{1}H i ^{13}C) i 2D-NMR spektroskopijom u dva rastvarača ($CDCl_3$ i CD_3SOCD_3). Izvršena je potpuna asignacija spektara i njihovo međusobno poređenje. Utvrđeno je da tokom reakcije nije došlo do promene konfiguracije C=C veze, a da oksimi grade vodonično vezane asocijate u $CDCl_3$, dok njih nema u CD_3SOCD_3.



Green synthesis and complete assignation of ^{1}H- and ^{13}C-NMR spectra of all stereoisomeric oximes of 3,7-dimethylocta-2,6-dienal

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A solvent-free synthesis of a mixture of all stereoisomeric oximes of 3,7-dimetylocta-2,6-dienal was performed starting from citral, a cheap commercially available mixture of neral and geranial ((*Z*)- and (*E*)-, respectively). This was achieved by grinding citral with an excess of hydroxylamine hydrochloride and sodium hydroxide in a mortar with a pestle at room temperature. The stereoisomeric oximes ((*1E,2E*)-, (*1Z,2E*)-, (*1E,2Z*)- and (*1Z,2Z*)-) were isolated in pure state by silica gel column chromatography (isocratic elution with hexane/ether = 4:1, *v*/*v*). For the first time, the oximes were characterized by 1D- (^{1}H and ^{13}C) and 2D-NMR spectroscopy in two solvents ($CDCl_3$ and CD_3SOCD_3). Their spectra were fully assigned and mutually compared. Under the reaction conditions, the configuration of C=C bond did not change; the oximes were found to form hydrogen-bonded adducts in $CDCl_3$, whereas these adducts were absent in CD_3SOCD_3.

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Biohemija i biotehnologija - Biochemistry and Biotechnology

BB P 01

Prevazilaženje industrijskih ograničenja hidrolize koncentrovane suspenzije sirovog kukuruznog skroba

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Skrob predstavlja jeftin izvor sirovine za dobijanje glukoznih, fruktoznih i maltoznih sirupa koji su široko rasprostranjeni u prehrambenoj industriji. U pogledu cene energenata, efekasnije upotrebe prirodnih resursa i problema viskoznosti, poželjna je direktna hidroliza sirovog skroba na temperaturi nižoj od geliranja upotrebom enzima kao što je α-amilaza. α-amilaza iz soja *Bacillus licheniformis* 9945a (*Bli*Amy) se pokazala kao veoma efikasna amilaza u hidrolizi visoko koncentrovanih suspenzija sirovog skroba. Metoda odgovornih površina korišćena je za optimizaciju količine *Bli*Amy, koncentracije skroba i vremena za dobijanje maksimalno efikasnog procesa.

Overcoming hydrolysis of raw corn starch under industrial conditions

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Starch represents an inexpensive source for production of glucose, fructose and maltose syrups which are widely used in food industries. Regarding energy costs, effective utilization of natural resources and viscosity problems, direct hydrolysis of raw starch below the gelatinization temperature by using raw-starch-digesting enzymes, such as α-amylase is desirable. *Bacillus licheniformis* 9945a α-amylase (*Bli*Amy) has the ability to hydrolyze high concentration raw starch suspensions effectively. Response Surface Methodology was used to optimize *Bli*Amy doses, starch concentration and incubation times to achieve the maximal efficiency of the process.

BB P 02

Difuzija kofeina iz sistema lipozomi-alginat

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Da bi se omogućilo kontrolisano otpuštanje aktivnih komponenti jedan od načina je inkapsuliranje aktivne supstance unutar polimera. Cilj ovog rada je istraživanje prenosa mase kofeina iz različitih polimernih nosača. Prolipozomnom metodom su pripremani lipozomi u koje je inkapsuliran kofein u koncentracijama; 5, 10, 15, 20, 25 mg/ml. Lipozomi su inkapsulirani u čestice alginata i čestice alginat-hitozan koristeći tehniku elektrostatičke ekstruzije. Brzina otpuštanja kofeina iz ovih čestica praćena je eksperimentalno upotrebom standardne Franz-ove difuzione ćelije. Na osnovu eksperimentalnih rezultata određeni su koeficijenti difuzije kofeina iz rastvora (5 mg/ml), lipozoma (5 mg/ml), lipozoma inkapsuliranih u alginatne čestice (7.5 mg/ml) i lipozoma inkapsuliranih u čestice alginat-hitozan (7.5 mg/ml), a sve u cilju određivanja difuzionih otpora pomenutih polimera. Takođe je izvršena karakterizacija i određivana stabilnost lipozoma sa različitim koncentracijama kofeina u periodu od tri nedelje. Rezultati su pokazali da je difuzioni otpor lipozoma za red veličine veći od otpora gela i sloja hitozana, pa se može zaključiti da su u ovim sistemima lipozomi kao nosači leka najviše zaslužni za produženo otpuštanje, a da alginat i hitozan dodatno doprinose otporu difuziji kofeina. Analize stabilnosti lipozoma su pokazale da lipozomi u kojima su koncentracije kofeina 10 i 15 mg/ml imaju najuniformniju raspodelu i očuvanu stabilnost u ispitanom periodu.

Diffusion of caffeine from liposome-alginate systems

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The primary method of accomplishing controlled release of drugs is through incorporating the active compound within polymers. The aim of this paper is determination of mass transfer of caffeine from polymer matrix. Liposomes, in which caffeine was incorporated in, with concentrations of: 5, 10, 15, 20, 25 mg/ml, were prepared using the proliposome method. Liposomes were then encapsulated into alginate and alginate-chitosan micro-beads using electrostatic extrusion technique. The release experiments were conducted for caffeine solution (5 mg/ml), liposomes with caffeine (5 mg/ml), alginate beads with liposomes (7.5 mg/ml) and alginate-chitosan beads with liposomes (7.5 mg/ml) using Franz diffusion cell. Diffusion coefficients were determined using experimental results, and further processed to determine resistance factors the polymers. The stability of liposomes with incorporated caffeine of different concentrations was also determined during period of 3 weeks. Results showed that diffusion resistance of liposomes is an order of magnitude stronger than resistance made by alginate and chitosan layers. Therefore, it can be concluded that in this systems controlled release is in most part accomplished by liposomes, but the alginate and chitosan matrix also contribute to diffusion resistance of caffeine. Results gained in these experiments showed that with proper choice of encapsulation system, the release of active compound can be controlled. Stability analysis showed that liposomes with caffeine concentration of 10 and 15 mg/ml had most uniform particle size distribution and were most stable during the monitoring period.

BB P 03

Antinociceptivna aktivnost etarskog ulja biljne vrste *Amorpha fruticosa* L. (Fabaceae)

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Detaljna analiza (GC i GC/MS) uzorka etarskog ulja dobijenog hidrodestilacijom iz zrelih suvih plodova biljne vrste *Amorpha fruticosa* L. omogućila je identifikaciju velikog broja jedinjenja, koja su sačinjavala 92,8% ulja. Glavni sastojci su bili germakren D (24,5%), δ-amorfen (11,4%), α-pinen (10,6%), (*E*)-kariofilen (9,6%), γ-murolen (7,3%), α-kopaen (3,9%), γ-kadinen (3,1%) i α-humulen (3,1%). U cilju utvrđivanja potencijalne antinociceptivne aktivnosti ovog ulja *A. fruticosa*, BALB/c miševi (n=6), *i.p.* tretirani etarskim uljem u dozama od 400, 200 i 100 mg/kg, kao i aspirinom u dozi od 200 mg/kg (pozitivna kontrola), odnosno maslinovim uljem (negativna kontrola), podvrgnuti su testu abdominalnog grčenja izazvanog sirćetnom kiselinom. Sve testirane doze etarskog ulja su smanjivale broj grčeva kod miševa: procenat inhibicije za dozu ulja od 400 mg/kg (54,4%) je bio skoro duplo manji od dejstva aspirina (90,2% inhibicije), koji je primenjen u dozi od 200 mg/kg.

Antinociceptive activity of *Amorpha fruticosa* L. (Fabaceae) essential oil

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A sample of *Amorpha fruticosa* L. essential oil (hydrodistilled from ripe dry fruits) was analyzed (GC and GC/MS) in detail. These analyses led to the identification of more than 100 oil constituents (representing 92.8% of the oil composition). The main constituents of the oil were: germacrene D (24.5%), δ-amorphene (11.4%), α-pinene (10.6%), (*E*)-caryophyllene (9.6%), γ-muurolene (7.3%), α-copaene (3.9%), γ-cadinene (3.1%), α-humulene (3.1%). The essential oil of *A. fruticosa* L. (Fabaceae) was evaluated, at the doses of 400, 200 and 100 mg/kg, for its antinociceptive activity using the acetic acid-induced abdominal writhings test in BALB/c mice (n=6), alongside aspirin (200 mg/kg; positive control) and olive oil (negative control). All tested essential-oil doses reduced the number of writhings induced by an *i.p.* injection of acetic acid. The calculated percent of inhibition for the 400 mg/kg dose of the oil (54.4%) was almost two times less effective that the positive control, aspirin (90.2% of inhibition), applied at the dose of 200 mg/kg.

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BB P 04

Razvoj nove visoko specifične i neradioaktivne metode za identifikaciju i skrining liganada estrogenog receptora β

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Karcinom dojke je najčešći oblik kancera kod žena širom sveta. Estrogeni hormoni promovišu rast estrogen-pozitivnog karcinoma dojke vezivanjem za estrogene receptore (ER). Stoga, estrogeni receptori predstavljaju terapeutsku metu koja najviše obećava. Naš cilj je bio razvijanje novog visoko specifičnog i neradioaktivnog testa koji može biti koristan u detekciji liganada ERβ. Konstruisali smo fluorescentni ćelijski biosenzor ekspresijom žutog fluorescentnog proteina (YFP) spojenog sa ligand-vezujućim domenom (LBD) ERβ u *Saccharomyces cerevisiae.* Vezivanje liganda indukuje dimerizaciju estrogenog receptora, što uzrokuje povećanu fluorescenciju YFP-a usled fluorescentnog rezonantnog transfera energije (FRET). Intenzitet fluorescencije proporcionalan je afinitetu vezivanja liganda. Naš fluorescentni ćelijski biosenzor se može primeniti za identifikaciju i skrining jedinjenja koja menjaju aktivnost ERβ, kao što su potencijalni lekovi u terapiji kancera, ali i za endokrine disruptore iz životne sredine koji pokazuju estrogena svojstva. Ovaj rad finansiralo je Ministarstvo prosvete, nauke i tehnološkog razvoja Republike Srbije (ON 172021).

Development of a novel highly specific and nonradioactive method for identification and screening of estrogen receptor β ligands

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Breast cancer is the most common cancer among women worldwide. Estrogen hormone promotes the growth of estrogen-positive breast cancer by binding to estrogen receptors (ERs). Hence, ERs represent one of the most promising therapeutic drug targets. Our aim was to develop a novel, highly specific and nonradioactive assay that could be useful for the detection of ER β ligands. We constructed fluorescent cellular biosensor by expressing yellow fluorescent protein (YFP) fused to the ligand binding domain (LBD) of ERβ in *Saccharomyces cerevisiae.* Ligand binding induces estrogen receptor dimerization causing increased YFP fluorescence due to fluorescence resonance energy transfer (FRET). The intensity of fluorescence correlates with ligand binding affinity. Our fluorescent cell-based biosensor could be applied for the identification and screening of compounds that alter ERβ activity such as potential anticancer drugs, but also for possible endocrine disrupting chemicals from the environment that exhibit estrogenic properties.

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BB P 05

Aktivnost acetilholin-esteraze kod medonosnih pčela (*Apis mellifera* L.) uticaj selećeg tipa gajenja pčela

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Medonosne pčele (*Apis mellifera* L.) kao glavni oprašivači brojnih biljnih vrsta doprinose održivom razvoju poljoprivrede i održanju biodiverziteta. Kao posledica uticaja brojnih patogena i parazita, kao i raznih zagađujućih jedinjenja zapažen je značajan pad brojnosti pčelinjih zajednica. Tome doprinosi i savremeni pristup gajenju pčela koji obuhvata pčela šećernim sirupom, gajenje pčela u selećim pčelinjacima, veštačku oplodnju i hemijske tretmane pčelinjih zajednica. Jedan od načina procene uticaja zagađenja iz spoljašnje sredine na živi organizam je analiza specifičnih biomarkera. Acetilholin-esteraza (AChE), enzim zastupljen u holinergičkim sinapsama, osetljiv na brojne ksenobiotike, predstavlja pouzdan biomarker intoksikacije organizma. Cilj našeg rada je procena uticaja selećeg tipa gajenja pčela, u odnosu na stacionarni, na intoksikaciju pčela merenjem aktivnosti AChE u letnjem, aktivnom periodu pčela. Zapaženo je signifikantno smanjenje aktivnosti AChE u pčelinjim zajednicama selećih pčelinjaka (7,7 nmol/min/mg proteina; 4,4 nmol/min/mg proteina) u odnosu na kontrolnu grupu iz stacionalrnog pčelinjaka (14,9 nmol/min/mg proteina). Seleći tip gajenja pčela, iako ekonomski isplativiji u poređenju sa stacionarnim tipom, praćen je povećanom intoksikacijom i smanjenom otpornošću pčela.

Acetylcholinesterase activity in honey bees (*Apis mellifera* L.) correlation with migratory beekeeping practice

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Honey bees (*Apis mellifera* L.) as the main pollinators for numerous plants contribute to sustainable development in agriculture and have an irreplaceable role in the maintenance of biodiversity. Unfortunately, honey bees are challenged by natural enemies (i.e. pathogens and parasites) and different pollutants and, as a result, decline in their number is observed throughout the world. Also, modern beekeeping practices including unnatural feed, migratory beekeeping, artificial insemination and chemical treatments put severe stress on honeybees. One possible method to assess the exposure and potential impact of environmental pollutants on living organisms is biological monitoring using biomarkers. Acetylcholinesterase (AChE), a crucial enzyme in the nervous system of vertebrates and invertebrates, is the functional target of several xenobiotics including drugs, pesticides and heavy elements. Therefore, inhibition of this enzyme is commonly used as biomarker for intoxication. The focus of this study is assessment of migratory beekeeping impact on honey bees in terms of acetylcholinesterase activity during the active honey bee foraging period. We observed significant decrease in AChE activity in migratory honey bee populations (7.7 nmol/min/mg of protein; 4.4 nmol/min/mg of protein) compared with the control hives in stationary apiary (14.9 nmol/min/mg of protein). The migratory beekeeping is more economical than stationary beekeeping but on the other side causes stress, increased intoxication and reduced resistance of honey bees.

BB P 06

Alkalni uslovi čuvanja tripsina na hladno sprečavaju denaturaciju ovog proteina na niskim temperaturama

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Tripsin je serin proteaza sa raznovrsnim aplikacijama uključiv i sekvenciranje proteina. U ovom radu je pokazano da čuvanje tripsina u kiselim uslovima na hladno dovodi do očuvanja aktivnosti od svega 40% posle 7 ciklusa zamrzavanja i odmrzavanja, Takođe, pokazano je da se tripsin čuvan u kiselim uslovima denaturiše na hladno što je praćeno gubitkom nativne strukture uz povećanje sadržaja β-pločica od 10% (maksimum trake na 1634 cm^{-1} u infracrvenoj spektroskopiji sa *Fourier*-ovom transformacijom). Sa druge strane, čuvanje tripsina na hladno u amonijum-bikarbonatnom puferu (pH 8.2) sa dodatkom krioprotektanata (glicerol ili lizin) rezultira stabilizacijom proteina. Pokazano je da je preko 90 % aktivnosti očuvano sa umerenom autolizom (<10%) uz kompletno očuvanje sadržaja sekundarnih struktura. Rezultati ovog rada ukazuju da čuvanje tripsina na hladno u baznim uslovima sa dodatkom krioprotektanata može dovesti do produžavanja njegovog roka trajanja.

Cold storage of trypsin in alkaline conditions prevent protein cold denaturation

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Trypsin is a serine protease with widespread applications, including protein sequencing and trypsin mass fingerprinting. In the present study, the storage of trypsin in acidic conditions significantly affected the recovery of activity (40%) after 7 freeze-thaw cycles. Further, trypsin lost parts of its native secondary structure elements, which resulted in a 10% increase in β-sheet content (band maximum detected at a frequency of 1634 cm^{-1} in the Fourier transform infrared (FT-IR) spectrum) indicative of freezing-induced denaturation of the protein. The cold storage of trypsin in ammonium bicarbonate (pH 8.2) with the addition of cryoprotectants, such as glycerol or lysine, led to protein stabilization (complete secondary structure content preservation was detected by FT-IR), higher activity recovery (>90%) and modest autolysis (<10%). Results of the present study suggest that the cold storage of trypsin in slightly alkaline conditions with the addition of cryoprotectants could prolong its shelf life.

BB P 07

Citotoksični efekat nanočestica CeO_2 na kancerskim ćelijama kolona (HT-29)

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Terapija zračenjem se uobičajeno koristi za tretman kancera kolona. Dodatno se razna antioksidativna sredstva, kao što su nanočestice cerijum-oksida (nanoCeO_2), istražuju kao pomoćna terapija. CeO_2 pokazuje aktivnost superoksid-dismutaze (SOD) i mimetičku aktivnost katalaze, koje su zaslužne za njegovo antioksidativno ponašanje. Međutim, dugotrajno izlaganje ćelija većim koncentracijama nanoCeO_2 dovodi do disfunkcije antioksidativnog sistema, indukovanja unutarćelijskog oksidativnog stresa i naknadne citotoksičnosti u ćelijama. Cilj ovog istraživanja je bio ispitivanje citotoksičnog efekta nanočestica CeO_2 na kancerskim ćelijama kolona HT-29 i razvoj odgovarajuće metode za praćenje ovog efekta. MTT test je pokazao nižu citotoksičnu aktivnost u odnosu na standard cisplatin (korišćene koncentracije 0 do 100 μM). EPR detekcija ukupnih radikala spinskom probom TEMPONE i detekcija OH radikala fluorescentnom spektroskopijom su pokazale da su ćelijski mehanizmi za uklanjanje slobodnih radikala manje efikasni kod ćelija tretiranih sa CeO_2, čime se objašnjava citotoksičnost ovih nanočestica na kancerskim ćelijama kolona.

Cytotoxic effect of nanoceria on colon cancer cells (HT-29)

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Radiotherapy is commonly used for the treatment of colon cancer. Additionally, various antioxidant agents, such as nanoparticles of cerium oxide (nanoceria, nanoCeO_2), are being investigated as the adjunctive therapy. CeO_2 shows the activity of superoxide dismutase (SOD) and catalase mimetic activity, which are responsible for its antioxidant behavior. However, prolonged exposure to higher concentrations of nanoceria cells leads to the dysfunction of the antioxidant system, induction of intracellular oxidative stress and subsequent cytotoxicity in cells. The aim of this study was to investigate the cytotoxic effect of nanoparticles of CeO_2 in colon cancer cells (HT-29) and the development of appropriate methods to monitor this effect. MTT test showed a lower cytotoxic activity than the standard cisplatin (concentrations used between 0-100 μM). EPR detection of total radicals using a spin probe TEMPONE and detection of OH radicals by fluorescence spectroscopy have shown that cellular mechanisms for the removal of free radicals are less efficient in cells treated with nanoceria, which explains the cytotoxicity of these nanoparticles on colon cancer cells.

BB P 08

Antitumorski potencijal novih steroidnih tiosemikarbazona i tijadiazolina

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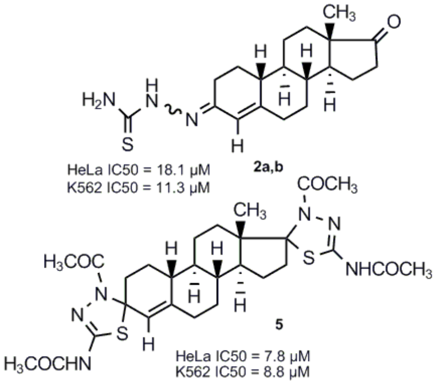
Cilj ovog rada je bio da se detaljno ispita *in vitro* citotoksična aktivnost četiri nova steroidna derivata, tiosemikabazona **2a,b** i **3a,b** dobijena iz 19-norandrost-4-en-3,17-diona i odgovarajućih 1,3,4-tijadiazolina **4** i **5**. Aktivnost ovih jedinjenja ispitivana je na šest tumorskih ćelijskih linija (HeLa, K562, MDA-MB-361, MDA-MB-453, LS174 i A549) i dve normalne humane ćelijske linije (MRC-5 i PBMC). Najbolju aktivnost pokazala su jedinjenja **2a,b** i **5**. Ispitivanje mehanizma citotoksične aktivnosti prema ćelijama adenokarcinoma grlića materice je pokazalo da ova dva jedinjenja izazivaju apoptozu ćelija karcinoma. Takođe, ova jedinjenja su pokazala mogućnost smanjenja angiogeneze *in vitro*.

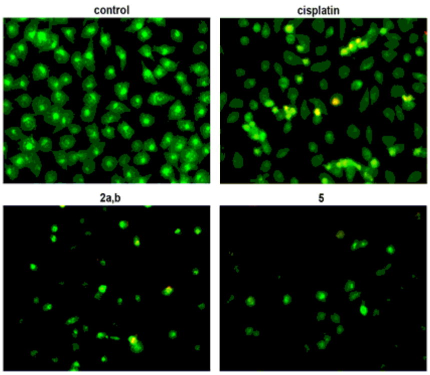


2a,b

HeLa IC50 = 18.1 μM
K562 IC50 = 11.3 μM

5

HeLa IC50 = 7.8 μM
K562 IC50 = 8.8 μM



Anti-cancer potential of new steroidal thiosemicarbazones and thiadiazolines

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The aim of this study was to perform extensive investigation of *in vitro* cytotoxic activity of four novel steroid derivatives (thiosemicarbazones **2a,b** and **3a,b** prepared from 19-norandrost-4-ene-3,17-dione, and corresponding 1,3,4-thiadiazolines **4** and **5**). These compounds were tested against six tumor cell lines (HeLa, K562, MDA-MB-361, MDA-MB-453, LS174 and A549), normal human cell line MRC-5 and PBMC cells isolated from healthy donors. The best activity was exhibited by compounds **2a,b** and **5**. Examination of the mechanisms of cytotoxicity on cervix adenocarcinoma HeLa cells revealed pro-apoptotic action of these two compounds. Also, these compounds showed the ability to decrease angiogenesis *in vitro*.

BB P 09

Optimizacija proizvodnje i analitika biodizela dobijenog katalitičkom aktivnošću lipaze B *Candidae antarcticae*

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Tokom protekle dve decenije pozamašan intelektualni napor uložen je u istraživanje biodizela s ciljem pomeranja proizvodnje od tradicionalnih ka ekonomski-isplativim enzimski-katalizovanim pristupima. Polazeći od kanole i upotrebom metanola kao acil-akceptora i metodologije odzivnih površina kao optimizacione tehnike, ustanovili smo da su optimalni parametri reakcije katalizovane hidroksiapatitnim imobilizatom CAL B sledeći: 65 °C, 5% enzimskog imobilizata u odnosu na masu ulja, molarni odnos ulje/metanol 1:3 uz postupno dodavanje metanola. Najveći prinosi su dobijeni iz 48-časovnih procesa i sadržaj vode u sistemu nije od presudnog značaja za reakciju. Biodizel dobijen na ovaj način je zadovoljio određene standarde koje su propisale vodeće svetske agencije za kontrolu kvaliteta u pogledu elementalnog sastava.

Production optimisation and analysis of biodiesel obtained through catalitical activity of *Candida antarctica* lipase B

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Over the course of the past two decades considerable intellectual effort has been invested in biodiesel research, with the goal of shifting its production from traditional to economically feasible enzyme-catalised approaches. Starting with canola oil and using methanol as an acyl acceptor and the response surface methodology as an optimisation technique, we have established the optimal parameters of hydroxyapatite-immobilised CAL B-catalised reaction as follows: 65 °C, 5% of enzyme immobilisate in regards to oil weight, 1:3 oil to methanol molar ratio with gradual methanol introduction. The highest yields were obtained from a 48-hour-long process and water content in the system isn't critical to the reaction. Biodiesel produced in such fashion satisfied certain standards demanded by world's leading agencies for quality control.

BB P 010

Lipaze iz *Candida rugosa* imobilizovane na hidroksiapatitu: stabilan biokatalizator sa velikim industrijskim potencijalom

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Zahvaljujući proboju biokatalizatora, današnji proizvodni procesi su tehnološki i ekonomski efikasniji, a savremena industrija je napravila veliki zaokret u smeru očuvanja životne sredine. Vanćelijske lipaze, poreklom iz *Candida rugosa* (CRL) su visoko cenjene u industrijskim krugovima zbog izuzetne efikasnosti u reakcionim sredinama sa različitim sadržajem vode. Ipak, za njihovu uspešnu primenu je neophodna dodatna stabilizacija. Naša grupa je osmislila jednostavan, ekonomičan i visokoefikasan protokol za imobilizaciju ovih značajnih biokatalizatora na hidroksiapatit (HAP) – biomaterijal poznat po visokom kapacitetu za vezivanje proteina. Imobilizovani preparat CRL (CRL-HAP) je dobijen u visokom prinosu (≥ 98%) nakon samo 30 min inkubacije na sobnoj temperaturi. Ispitivanje stabilnosti u uslovima povišene temperature (60 i 65 °C) i prisustvu različitih 95 % polarnih i nepolarnih organskih rastvarača, tokom tročasovne inkubacije, je jasno pokazalo superiornost dobijenog imobilizata u odnosu na slobodan enzim. Naši rezultati pokazuju da dobijeni imobilizat ima odlične mogućnosti za industrijsku primenu, pre svega u reakcionim uslovima koji iziskuju visoku operativnu stabilnost katalizatora.

Candida rugosa lipase immobilized on hydroxyapatite: stable biocatalyst with great industrial potential

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Due to biocatalysts breakthrough, today's manufacturing processes are significantly efficient, cost-effective and seriously shifted towards environmental protection[1]. Extracellular lipase originating from Candida rugosa (CRL) are highly valued in industry circles because of its exceptional efficiency in reaction environments with different water content. However, for their successful application requires additional stabilizacija2. Our group has developed a simple, economical and highly effective protocol for the immobilization of these important biocatalyst to hydroxyapatite (HAP) - biomaterial known for its high capacity for binding protein. The immobilized preparation of the CRL (CRL-HAP) was obtained in high yield (≥ 98%) after only 30 min incubation at room temperature. Stability studies in conditions of elevated temperature (60 and 65 ° C) and the presence of various 95% polar and nonpolar organic solvents after 3h tretment, have clearly demonstrated the superiority of the immobilizate obtained as compared to the free enzyme. These results strongly support the possibility of industrial applications, primarily under reaction conditions, where high operational stability of the catalyst is required.

BB P 11

Inaktivacija papaina tokom skladištenja na niskoj temperaturi prouzrokovana je promenama u tercijarnoj strukturi i agregacijom

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Papain je komercijalno važna cistein-proteaza. Stabilan je na visokim temperaturama, ali stabilnost na niskim temperaturama još uvek nije ispitana. Poslednjih decenija pretpostavlja se da proteaze tokom skladištenja na niskim temperaturama gube aktivnost usled autoproteolize. Cilj ove studije bilo je ispitivanje stabilnosti primarne i tercijarne strukture papaina tokom skladištenja na niskoj temperaturi, praćene agregacijom, kao potencijalnih uzroka gubitka aktivnosti. Potvrdili smo da je papain stabilan na povišenim temperaturama (ΔG^{o}_{321}=13,9 ± 0,3 kJ/mol, Tm=84 ± 1°C). Usled ograničenja spektroskopskih metoda za praćenje strukturnih promena proteina za uzorke u zamrznutom stanju, za ispitivanje stabilnosti papaina na niskim temperaturama koristili smo pristup uzastopnog zamrzavanja/odmrzavanja. Detektovali smo dramatičan gubitak aktivnosti nakon 6 ciklusa zamrzavanja (75%). Nakon 6 ciklusa papain je izgubio elemente nativne sekundarne strukture, uz porast od 40% intermolekulske β-pločice nagoveštavajući prisustvo struktura neophodnih za agregiranje. Prisustvo agregata dokazano je gel-filtracijom. Nakon 6 ciklusa zamrzavanja manje od 8% primarne strukture je narušeno usled autolize, što će reći da se inaktivacija od 75% ne može pripisati autolizi. Zaključak je da je inaktiviranje papaina tokom skladištenja na niskoj temperaturi prouzrokovano promenama tercijarne strukture (denaturacijom na hladno i agregiranjem).

Papain inactivation during cold storage is caused by tertiary structure changes and aggregation

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Papain is a cysteine protease of commercial importance. Papain is stabile at elevated temperatures, but cold stability of papain has never been investigated. Further, there is a common belief that during storage proteases undergo inactivation due to autoproteolysis. Aim of our study was to investigate primary and tertiary structure stability of papain upon cold storage followed by aggregation and their influence on papain inactivation. We confirmed that papain is stable at elevated temperatures (ΔG^{o}_{321}=13.9 ± 0.3 kJ/mol, Tm=84 ± 1°C). Due to the limitations of spectroscopy methods for samples in frozen state, we employed approach of repeated freeze-thaw cycles for investigation of cold stability of papain. We detected dramatic activity loss after 6 freeze-thaw cycles (75%). After cold storage, we observed that papain lost parts of its native secondary structure elements which gave an increase of 40% of intermolecular β-sheet content indicating the presence of secondary structures necessary for aggregation. The presence of protein aggregates after cold storage was proven by size exclusion chromatography. After six freeze-thaw cycles, less than 8% of protein was lost due to autolysis, which suggests that dramatic inactivation of 75% can not be attributed to papain autolysis. It can be concluded that papain inactivation during cold storage is influenced by tertiary structure changes, i.e. cold denaturation and aggregation of misfolded protein.

BB P 12

Uticaj mešovitih 1,2,4,5-tetraoksana na rast klijanaca kukuruza

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Steroidni i cikloheksilidenski mešoviti 1,2,4,5-tetraoksani su jedinjenja poznata po antimalarijskoj, antimikobakterijskoj i antiproliferativnoj aktivnosti. Struktura ovih derivata slična je brasosteroidima, biljnim hormonima, koji utiču na rast. Cilj ovog rada je bio ispitivanje uticaja serije mešovitih tetraoksana na klijanje semena kukuruza (samoplodna linija SSV-1422). Nakon potapanja u rastvore različitih koncentracija (10^{-6}, 10^{-9} i 10^{-12} M) 11 ispitivanih jedinjenja, i u vodi kao kontroli, semena su stavljena na filter papir tokom 7 dana u klijalište. Normalnih 25, uniformnih klijanaca podeljeno je na koren, izdanak i semeni ostatak. Preko sveže i suve mase izračunati su koeficijenti hidrolize, biosinteze, konverzije i sadržaj vode. Jedinjenja **MD07**, **DO205** i **JR01** utiču na povećanje vrednosti koeficijenta biosinteze i konverzije u poređenju sa kontrolom. Derivati **MD07, MD015** i **DO205**, sa slobodnim hidroksilnim grupama, pokazala su bolji uticaj na rast klijanaca u odnosu na jedinjenja sa estarskim i baznim amino grupama. Izuzetak je derivat **JR01**. Komercijalni 24-epibrasinolid ima slobodne hidroksilne grupe, kao i **MD07, MD015** i **DO205**, pa se može smatrati da je taj strukturni aspekt odgovoran za povoljan uticaj na rast klijanaca kukuruza.

Zahvalnica: Ova istraživanja su podržana od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije (projekti br. TR 31068 i ON172008).

Influence of mixed 1,2,4,5-tetraoxanes on maize seedlings growth

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Steroid and cyclohexylidene mixed 1,2,4,5 tetraoxanes are known as compounds with an antimalarial, antimycobacterial and antiproliferative activities. The structure of these derivates is similar to brassinosteroids, plant hormones, which promote growth. The aim of this study was to examine the effect of a series of mixed tetraoxanes on growth of the maize seedlings (inbred line SSV-1422). After soaking in solutions with different concentrations (10^{-6}; 10^{-9} and 10^{-12} M) of all 11 tested compounds, as well as a water control seeds were placed 7 days on filter paper towels, in germination room. Normal 25, uniformly grown seedlings were fractionated into root, shoot and seed rest. Based on fresh and dry weight, coefficient of hydrolysis, biosynthesis, conversion and water content were calculated. Compounds **MD07**, **DO205** and **JR01** increased values for biosynthesis and coefficient of conversion, compared to the control. Derivates **MD07**, **MD015** and **DO205**, with the free hydroxyl groups, showed a better effect on seedling growth, than the compounds with ester and basic amino groups. The exception is derivative **JR01**. Commercial 24-epibrassinolide have free hydroxyl groups, as a **MD07**, **MD015** and **DO205**, so it can be regarded that this structural aspect is liable for favourable impact on growth of the maize seedlings.

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BB P 13

Molecular dynamics simulations of ovalbumin: solvent exposed surface area of positively charged amino acid residues

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In order to find the most probable sites for covalent ovalbumin derivatization, molecular dynamics (MD) simulations were used. To make a valid approximation of real ovalbumin behaviour in water solution, we performed several MD simulations in explicit solvent model (TIP3P), using different versions of CHARMM force field (22 and 36), on different temperatures (25, 50 and 70 °C), and with or without restraint applied to protein backbone. NAMD 2.9 was used for MD simulations, while MD trajectories were analyzed in VEGA ZZ 3.0.5. Based on values of solvent exposed surface area of positively charged amino acid residues (Arg and Lys), possible salt bridges, visual inspection of trajectories, and estimated pK_a values of side chain ionizable groups, we anticipated which Arg and Lys residues would most probably be modified covalently. Observing the position of those residues in protein, and having knowledge on experimentally characterized ovalbumin epitopes, we proposed potential changes in ovalbumin IgE immunoreactivity due to covalent derivatization.

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Simulacija molekulske dinamike ovalbumina: ispitivanje dostupnosti rastvaraču pozitivno naelektrisanih aminokiselinskih ostataka

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Ispitali smo najverovatnija mesta kovalentne derivatizacije ovalbumina korišćenjem rezultata simulacija molekulske dinamike (MD) ovalbumina. Zbog najbolje aproksimacije realne dinamike ovalbumina u vodenom rastvoru, uradili smo više simulacija MD u eksplicitnom modelu rastvarača (TIP3P), korišćenjem različitih verzija CHARMM polja sila (22 i 36), na različitim temperaturama (25, 50 i 70 °C) i sa i bez ograničenja pokretljivosti osnovnog aminokiselinskog niza proteina. Simulacije MD su urađene u programu NAMD2.9, a rezultati analizirani programom VEGA ZZ 3.0.5. Na osnovu podataka o površini dostupnoj rastvaraču pozitivno naelektrisanih aminokiselinskih ostataka (Arg i Lys), mogućih jonskih mostova, vizuelnog pregleda trajektorija i procenjenih pK_a vrednosti jonizabilnih grupa u bočnim nizovima Arg i Lys, utvrdili smo koji aminokiselinski ostaci Arg i Lys će najverovatnije biti kovalentno modifikovani. Na osnovu njihovog položaja u proteinu i ekspermentalno okarakterisanih epitopa ovalbumina, pretpostavili smo potencijalne promene u IgE reaktivnosti ovalbumina nakon kovalentne derivatizacije.

Hemija makromolekula i nanotehnologije
Macromolecular Chemistry and Nanotechnology

MN P 01

Molekulski obeleženi polimeri za karvedilol

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Molekulsko obeležavanje predstavlja tehnologiju usmerenu ka stvaranju selektivnih vezivnih mesta u polimernom matriksu polimerizacijom u prisustvu željenog molekula - templata [1]. Nakon polimerizacije i uklanjanja templata, u polimeru ostaju vezivna mesta po veličini i naelektrisanju komplementarna templatu. Molekulski obeleženi polimeri (MOPi) imaju univerzalnu primenu u analitici, koriste se kao sorbenti za hromatografiju, ekstrakciju, ali i kao senzori, katalizatori, za kontrolisano oslobađanje lekova itd [2]. Karvedilol predstavlja neselektivni beta-blokator. U literaturi je opisano nekoliko MOPa koji se koriste pri određivanju karvedilola[3]. Naše istraživanje je usmereno ka pripremi novih MOPa, selektivnijih i sa većom sorptivnom moći za karvedilol. Pri sintezi polimera, sem uobičajeno upotrebljavanih umreživača (divinilbenzen, etilenglikol-dimetakrilat), ispitana je mogućnost primene dialil-estara dikarboksilnih kiselina (malonske, maleinske, ćilibarne, adipinske i ftalne kiseline). Sintetisani polimeri ukazuju na mogućnost obeležavanja polimera karvedilolom. Dobijeni polimeri se međusobno razlikuju po količini karvedilola koju mogu vezati, kao i po faktoru obeležavanja (razlika u količinama templata koju mogu vezati MOP i polimer pri čijoj polimerizaciji nije korišćen templat). Daljim istraživanjima biće ispitana mogućnost primene MOPa pri koncentrovanju karvedilola iz realnih uzoraka.

Molecularly imprinted polymers for carvedilol

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Molecular imprinting is a technology for creating selective binding sites in a polymeric matrix by polymerization in the presence of the target compound - the template [1]. The template can be washed out from the polymer and the resulting molecularly imprinted polymer (MIP) is capable of selectively rebinding the target compound from a sample matrix. These polymers have versatile applications ranging from chromatographic and SPE sorbents, sensors and catalysts to drug delivery systems [2]. Carvedilol is a nonselective beta blocker. Various MIPs that can be used for the determination of carvedilol were described in the literature[3]. Main goal of this work was the preparation of new MIPs with higher selectivity and sorptive power for carvedilol binding. Beside usually used crosslinkers (divinylbenzene and ethylene glycol dimethacrylate), the possibility of using diallyl esters of dicarboxylic acids (maleic, malonic, succinic, adipic and phthalic) as crosslinkers was investigated. Newly prepared MIPs showed efficient carvedilol binding, differing in the amount of bound carvedilol and the imprinting factor. Future goal is the investigation of the possibility to use MIPs in pre-concentration of carvedilol from real samples.

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3. J. Appl. Polym. Sci. 2014, 131, 41209

MN P 02

Dobijanje hibridnih termoplastičnih poliuretanskih materijala

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Poslednjih godina predmet sve većeg interesovanja naučne i stručne javnosti je razvoj novih hibridnih materijala. Jedan od glavnih razloga za razvoja ovih materijala su značajno poboljšana svojstva, u odnosu na tradicionalne materijale, i mogućnost dobijanja materijala željenih svojstava. Posebnu klasu predstavljaju poliuretanski hibridni materijali, na osnovu obnovljivih sirovina, koji su označeni kao “zeleni”. U ovom radu je vršena sinteza poliuretanskih termoplastičnih elastomera na osnovu poli(propilenglikola) i dva tipa izocijanata, izoforondiizocijanat i heksametilendiizocijanat. Analiziran je uticaj zamene tradicinalnog produživača lanca, butandiola, sa izosorbidom, kao obnovljivom sirovinom. U cilju poboljšanja svojstava dobijenih materijala, vršena je sinteza nanokompozitnih poliuretanskih materijal dodatkom hidrofilnih i hidrofobnih nanočestica silicijum (IV)oksida. Molekulska struktura dobijenih materijala je potvrđena FT-IC spektroskopijom. Analizom toplotnih svojstava dobijenih materijala potvrđen je uticaj dodatka izosorbida na povećanje vrednosti $T_{g,}$ što omogućava dobijanje termoplastičnih poliuretanskih elastomera željenih svojstava. Dodatkom nanopunila povećana je stabilnost termoplastičnog poliuretana, što je potvrđeno TGA metodom.

Synthesis of thermoplastic polyurethane materials

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In recent years, the subject of increasing interest to the scientific and professional public is research and development of new hybrid materials. The main reason for the development of hybrid materials is their superior properties, compared to traditional materials, and the possibility to tailoring the properties of these materials. Special classes of hybrid materials are polyurethanes based on renewable raw materials, which are recognised as "green". In this paper a series of polyurethane thermoplastic elastomers, based on a poly (propylene glycol) and two types of isocyanates, isophoronediisocyanate and hexamethylenediisocyanate, were synthesised. The influence of substitution the traditional chain extender, butanediol, with isosorbide, as a renewable raw material was also investigated. In order to improve the properties of the obtained elastomers, the polyurethane nanocomposite with hydrophilic and hydrophobic silicon (IV) oxide nanofillers were synthesised. The molecular structures of the resulting materials were confirmed by FT-IR spectroscopy analysis. DSC analysis confirmed that by using isosorbide as chain extender, glass transition temperatures of thermoplastic polyurethane elastomer increase, which enabling fine tuning of thermal properties of obtained hybrid materials. Addition of nanofillers increased thermal stability of thermoplastic polyurethane, which was confirmed by TGA method.

MN P 03

Kontrolisano otpuštanje ibuprofena iz polimernih PCL/PEO/PCL mikrosfera

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Alifatski poliestar, poli(ε-kaprolakton), PCL, biokompatibilan i biodegradabilan materijal je pogodan za izradu sistema za transport i kontrolisano otpuštanje lekova. Iburpofen spada u grupu antiinflamatornih steroida, koji se koristi za oslobađanje od simptoma artritisa, kao antipiretik i kao analgetik. Mikrosfere homopolimera PCL i triblok kopolimera PCL/PEO/PCL sa različitim sastavom su pripremljene postupkom otparavanja lako isparljivog rastvarača iz emulzije. Ispitan je uticaj prisustva hidrofilnog, hemijski vezanog centralnog PEO segmenta u polimernom lancu na efikasnost inkapsulacije i kontrolisano otpuštanje leka. Koncentracija inkapsuliranog ibuprofena je iznosila 10, 20 i 30 mas.%. Prinos pripremljenih mikrosfera je bio iznad 90 mas.% dok je efikasnost inkapsulacije ibuprofena u polimernoj matrici iznosila 70 - 92%. Efikasnost inkapsulacije aktivnog jedinjenja određena je pomoću UV/Vis spektrofotometrije direktnom i indirektnom metodom. Dobijene mikrosfere su karakterisane optičkom mikroskopijom i procenjena je raspodela veličine čestica. Kontolisano otpuštanje leka je ispitivano u fosfatnom puferu (pH = 7,2) na 37 °C tokom 72 h i praćeno UV/Vis spektrofotometrijski na talasnoj dužini λ = 221 nm. Potvrđeno je da se profil otpuštanja leka iz mikrosfera može modifikovati uvođenjem hidrofilnog PEO u polimerne lance kao i količinom unetog leka u mikrosfere. Takođe, uočeno je sporije otpuštanje ibuprofena iz mikrosfera sa većim sadržajima leka.

Controlled release of ibuprofene from polymer PCL/PEO/PCL microspheres

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Aliphatic polyester, poly(ε-caprolactone), PCL, a biodegradable and biocompatible polyester has a great potential in controlled drug delivery/release systems. Ibuprofen is an anti-inflammatory steroid. It is used to relieve symptoms of arthritis, fever, and as an analgesic. Microspheres of homopolymer PCL and PCL/PEO/PCL triblock copolymers with different composition were prepared by classical oil-in-water emulsion solvent evaporation technique. The influence of hydrophilic PEO central segment in copolymer structure on incapsulation efficiency and controlled release of drug was investigated. The concentration of incapsulated ibuprofene in microspheres was 10, 20 and 30 wt.%. The yield of prepared microspheres was more than 90 % and the encapsulation efficiencies were obtained in the range from 70 to 92 %. Encapsulation efficiency of active compound in microspheres was determined by UV/Vis spectrophotometry by using both direct and indirect method. The obtained microspheres were characterized by optical microscopy and particle size distribution was estimated. Drug release was investigated in phosphate buffer solution (pH = 7.2) at 37 °C during 72 h and followed by UV/Vis specrophotometry at a wavelength λ = 221 nm. It was presented that the release profile of ibuprofen could be modified with the PEO content and drug loading of microspheres. It was also observed that the drug release is slower for higher contents of ibuprofen in the microspheres.

MN P 04

Hemijska modifikacija nanokristalne celuloze za primenu u visoko ojačanim nanokompozitima

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Nanokristalna celuloza (CNC) predstavlja predmet opsežnih istraživanja u oblasti nanotehnologije u poslednjoj dekadi, s obzirom na činjenicu da je najdostupniji i najzastupljeniji biopolimer u prirodi. Poseduje odlična mehanička i toplotna svojstva, malu gustinu i visok stepen biorazgradvosti i kao takva predstavlja veliki potencijal kao ojačavajuća komponenta u polimernim nanokompozitima. U cilju pripreme CNC za primenu u kompozitnim materijalima, površina CNC koja je izolovana kiselom hidrolizom upotrebom sumporne kiseline, modifikovana je oleinskom kiselinom i masnim kiselinama ili metil estarima masnih kiselina izolovanih iz sojinog, lanenog i suncokretovog ulja. Ispitivan je uticaj površinskih modifikatora na morfologiju CNC. Modifikovane čestice CNC su okarakterisane primenom FT-IR spektroskopske analize i određena im je vrednost kiselinskog broja. Mikroskopskom analizom CNC potvrđen je uticaj hemijske modifikacije na morfologiju CNC.

Chemical modification of cellulose nanocrystals for high-performance reinforced composites

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Cellulose nanocrystals (CNCs) have been the subject of extensive research in nanotechnology according to the fact that is the most plentiful biopolymer. The impressive mechanical properties, reinforcing capabilities, abundance, low density, and biodegradability of CNCs make them ideal candidates for the processing of polymer nanocomposites. In order to prepare cellulose for composite production the surface of the CNCs, isolated by acid hydrolysis using sulphuric acid, was modified with oleic acid and fatty acids or methyl esters of fatty acids of soyabeen, linseed and sunflower oil by esterification reaction. Influence of the different types of the surface modification on the CNCs morphology was studied. CNCs were characterized using FT-IR spectroscopic analysis and acid values. The microstructural analysis of the CNCs, performed by using scanning electron microscopy (SEM), confirmed that surface modification of CNCs has influence on their morphology.

MN P 05

Elektrohemijsko dobijanje i karakterizacija hidrogelova na bazi polivinil alkohola sa nanočesticama srebra

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U ovom radu se pažnja poklanja sintezi nanokompozitnih materijala na bazi hidrogelova polivinil alkohola (PVA) koji imaju svojstvo imobilizacije nanočestica srebra (poznatog kao odličan antimikrobni agens), kao i njihovog postepenog otpuštanja, što je poželjno za medicinske zavoje i obloge nove generacije. Hidrogelovi PVA su dobijeni umrežavanjem metodom cikličnog zamrzavanja i odmrzavanja vodenog rastvora 10 mas.% PVA. Takođe su, u cilju poboljšanja mehaničkih svojstava PVA gelova, sintetisani kompoziti PVA sa grafenom (PVA/Gr). Inkorporacija nanočestica srebra u hidrogelne matrice postignuta je *in situ* elektrohemijskom redukcijom jona srebra u hidrogelovima koji su bubrili 48 h u rastvoru prekursora $AgNO_3$. Karakterizacija dobijenih nanokompozita izvršena je ispitivanjem njihove citotoksičnosti, kao i metodama atomske apsorpcione spektroskopije (AAS) i ciklične voltametrije (CV). Ciklični voltamogrami nanokompozita Ag/PVA i Ag/PVA/Gr koncentracija 0,25 mM i 1,0 mM Ag, potvrdili su postojanje nanočestica srebra u umreženim matricama gelova. Dvadesetosmodnevni profili otpuštanja srebra, dobijeni merenjem koncentracija otpuštenog srebra metodom AAS, ukazuju na zadržavanje oko 35% početne koncentracije srebra u Ag/PVA hidrogelu, kao i 20% polazne koncentracije u Ag/PVA/Gr, po završetku eksperimenta. Testovi citotoksičnosti su pokazali dobru biokompatibilnost 0,25 mM Ag/PVA i Ag/PVA/Gr nanokompozita (preživljavanje mononuklearnih ćelija periferne krvi, PBMC, je u proseku 75,97%).

Electrochemical synthesis and characterization of polyvinyl alcohol based hydrogels with silver nanoparticles

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This paper focuses on synthesis of poly(vinyl alcohol) hydrogel (PVA) based nano-composite materials with ability for immobilization of silver nanoparticles (known and excellent antimicrobial agent), and their progressive release, i.e. properties which are desirable for new generation of medical wound dressings. PVA hydrogels were obtained by physical cross-linking (freezing-thawing method) of 10 wt.% PVA aqueous solution. PVA composites with graphene (PVA/Gr) were also synthesized in order to improve gels' mechanical properties. Incorporation of silver nanoparticles into hydrogel matrices was achieved by *in situ* electrochemical reduction of Ag ions in hydrogels, previously swollen for 48 h in $AgNO_3$ precursor solution. Obtained nanocomposites were characterized by cytotoxicity tests, atomic absorption spectrometry (AAS) and cyclic voltammetry (CV). Cyclic voltammograms of 0.25 mM and 1.0 mM Ag/PVA and Ag/PVA/Gr nanocomposites confirmed the existence of silver nanoparticles in cross-linked hydrogel matrices. The 28-day silver release profiles, obtained by silver release measurements using AAS, pointed to retention of silver at the end of experiment of around 35% in Ag/PVA, i.e. 20% in Ag/PVA/Gr nanocomposites. Biocompatibility of 0.25 mM Ag/PVA and Ag/PVA/Gr was proved (survival of periferal blood mononuclear cells, PBMC, was 75.97% on average).

Nauka o materijalima - Materials Science

NM P 01

DFT ispitivanje tankih slojeva legura tipa $M_{i3}M_j$ (M_i=Pd i Pt, M_j=Au, Ag i Cu) na WC kao nosaču

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Legure prelaznih metala su pri eksperimentalnim i teorijskim ispitivanjima pokazale dobre karakteristike u mnogim katalitičkim procesima, kako u oblicima tankoslojnih katalizatora ili omotač-jezgro sistema. Istraživanja su pokazala mogućnost uticaja na parametre bitne za katalitičku aktivnost, poput energije centara d-traka, energije segregacije i rastvaranja, što se postiže biranjem sastava legure, odabirom nosača i debljine filma.

U ovom radu prikazani su rezultati DFT proračuna svojstava tankih filmofa u vidu mono-, dvo- i trosloja na WC kao nosaču, kao i napregnutih čistih legura. Odabrane su legure Pt i Pd, kao osnovnog metala, legiranog sa Cu, Ag i Au u odnosu 3:1. Navedene legure su izložene naprezanju povećanjem osnovne ćelije, dok su mono, dvo i trosloji napregnuti zbog razlike između konstanti rešetaka nosača i legure. Pokazano je da postoji značajna korelacija u osobinama čistih napregnutih legura i filmova na nosaču, u zavisnosti od stepena naprezanja. Odnosno, za neke analizirane primere razlika u konstantama rešetki je jedini parametar koji diktira osobine. Ovakva korelacija potencijalno može pružiti smernice za predviđanje osobina katalizatora i podešavanje istih, u njihovoj sintezi.

DFT study of alloy overlayers $M_{i3}M_j$ (M_i=Pd or Pt, M_j=Au, Ag or Cu) on WC as a support

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Transition metal alloys have been proven both by experimental and theoretical examination to have characteristics favorable in many catalytic processes, may it be in the form of thin film, or core-shell catalysts. Studies have shown that it is possible to influence parameters that affect the catalytic activity, such as on the segregation, dissolution energy and the d-band centre, by choosing the right alloy composition, film thickness, and support.

In this study the properties of mono-, bi- and trilayer alloys on WC as a support, as well as pure strained alloys were analyzed by DFT calculations, and the results are presented. The chosen alloys had Pt or Pd as a parent metal and were alloyed with ether Cu, Ag or Au, in the ratio 3:1. The pure alloys were submitted to tensile strain by the increase of the elementary cell size, whereas films were strained due to the difference between the lattice constants of the alloy and support. It was found that significant correlation exists between the properties of pure strained alloys and thin films strained on a support versus the amount of strain, starting at a certain film thickness. More specifically, in certain systems the only parameter determining its properties is the difference of the lattice constants of the support and alloy. This correlation can potentially provide guidelines for synthesis of catalysts with predictable and tunable behavior.

NM P 02

Koroziono ponašanje čistog titana i Ti-13Nb-13Zr legure u rastvoru veštačke pljuvačke

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Komercijalno čist titan (cpTi) i njegove legure su najčešće korišćeni metalni biomaterijali za izradu zubnih implanata, proteza, šrafova i ploča za fiksiranje polomljenih kosti, uređaja za veštačko srce, itd. CpTi i Ti-legure pokazuju dobru mehaničku čvrstoću, niski modul elastičnosti, odličnu biokompatibilnost i otpornost na koroziju. Cilj ovog istraživanja je bio da se proceni elektrohemijsko ponašanje cpTi i savremene Ti-13Nb-13Zr (TNZ) legure. Elektrohemijska merenja su izvedena u rastvoru veštačke pljuvačke pH vrednosti 4,0 na 37^0C u cilju simuliranja oralnog okruženja, jer je materijal prvenstveno razvijen za stomatologiju tj. za primenu kod zubnih implanata. CpTi i TNZ legura su ispitivani spektroskopijom elektrohemijske impedanse (SEI) i potenciodinamičkom polarizacijom. Oba istraživana materijala su pokazala dobru otpornost na koroziju u navedenom rastvoru. Dobijeni rezultati pokazuju da su unutrašnji barijerni i spoljašnji porozni sloj velike otpornosti i kapacitivnosti, ali tanak i uniforman pasivni film koji se formira na površini cpTi daje veću zaštitu.

Corrosion behavior of pure titanium and Ti-13Nb-13Zr alloy in artificial saliva solution

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Commercially pure titanium (cpTi) and its alloys are the most commonly used metallic biomaterials for dental implant and prostheses manufacturing, structural applications such as screws and plates for broken bones fixing, in devices for artificial hearts, etc. CpTi and Ti-alloys have demonstrated high mechanical strength, low elastic modulus, excellent biocompatibility and corrosion resistance. The aim of this study was to estimate electrochemical behavior of cpTi and contemporary Ti-13Nb-13Zr (TNZ) alloy. Electrochemical measurements were performed in artificial saliva solution with pH value of 4.0 at 37°C in order to simulate oral environment, because these materials are primarily developing for dentistry, *i.e.* dental implant applications. cpTi and TNZ were investigated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. Both investigated materials showed high corrosion resistance in mentioned solution. The obtained results show that inner barrier and outer porous layer were highly resistant and capacitive, but the thin and uniform passive film on the cpTi surface was more protective.

NM P 03

Elektronska i magnetna svojstva dopiranih MgO nanotuba

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Oksidni materijali koriste u mnogim bitnim tehnološkim disciplinama. Oksidi pokazuju veliku raznovrsnost u kristalnoj i elektronskoj strukturi, tako su neki pokazuju izolatorska svojstva, drugi su poluprovodnici, dok su za neke karakteristične provodne osobine svojstvene metalima. MgO je jedan od oksida čija se svojstva u poslednje vreme intenzivno proučavaju. Zbog njegove dostupnosti, lakoće pripreme, stabilnosti i hemijske inertnosti, moguća je njegova primena u proučavanju adsorpcije, kao podloga za različite katalizatore, ili funkcionalizacija uvođenjem defekata ili nečistoća u strukturu.

U ovom radu su prikazani rezultati DFT proračuna svojstava heksagonalnih MgO nanotuba različite veličine. Osobine nanotuba menjane su uvođenjem vakancija u strukturu na mestu kiseonika ili zamenom kiseonika dopantom X (X = B, C ili N) na različitim položajima duž nanotube. Pokazuje se da se osobine nanotuba sa povećanjem dužine približavaju osobinama MgO na makroskopskoj skali. Promena elektronske strukture i pojava magnetizacije na mestu dopanta ukazuju na moguću primenu ovakvih sistema kao adsorbenasa i katalizatora, ili novih vrsta magnetnih materijala.

Electronic and magnetic properties of doped MgO nanotubes

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Oxide materials have a wide range of application in various fields of technology. Oxides exibit diverse electronic and crystalline structures, so some can behave as insulators, others as semiconductors, while some have the conductive properties similar to those of metals. MgO is on of the oxides whose properties are being intensively studied. Due to its availabity, ease of preparation, stability and chemical inertness, it can be used in investigating adsorption, as a catalyst support, or it can be functionalized by introducing defects or impurities into its structure.

Shown in this paper are the results of DFT calculations of the properties of MgO nanotubes of varying size. Properties of the nanotubes were altered by introducing an oxygen vaccancy or by replacing the oxygen with a dopant X (X = B, C, or N) at different sites along the nanotube. It is demonstrated that with increasing size, the properties of nanotubes converge to those of bulk MgO. Change of electronic structure and the induction of magnetization at the dopant site points towards the possible use of these systems as adsorbents or catalysts, or as new types of magnetic materials.

NM P 04

Dimenzionalna stabilnost pletenina na bazi konoplje

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Relaksacioni procesi koji se neminovno dešavaju tokom prerade i upotrebe tekstilnih materijala, dovode do promene dimenzija materijala. Sklonost ka skupljanju posebno je izražena kod pletenina, pre svega zbog specifičnog položaja koji pređa zauzima u strukturi pletenine. Fenomen promene dimenzija pletenine javlja se kao rezultat kombinovanog dejstva čitavog niza faktora kao što su svojstva vlakana i pređa i tehnološki parametri mašina. U okviru ovog istraživanja ispitivane su 100% pletenina od konoplje, 100% poliakrilonitrilna (PAC) pletenina i mešavina 50% / 50% konoplja/PAC pletenina. Eksperimentalno ili računski su određeni strukturni parametri pređa (debljina, gustina), primarni strukturni parametri (debljina, dužina petlje, površinska gustina, površinska masa) i sekundarni strukturni parametri (gustina, poroznost, površina petlje, pokrivni faktor, strukturni pokrivni faktor, površinski i zapreminski modul petlje) delimično relaksiranih (suva relaksacija) i potpuno relaksiranih pletenina (mokra relaksacija), kao i pletenina koje su bile podvrgnute testu nege i nošenja. Vrednosti sekundarnih strukturnih parametara ispitivanih pletenina pokazali su da, uz povećanje vrednosti gustine i strukturnog pokrivnog faktora konoplja/PAC i pletenine od konoplje, poroznost, veličina površine petlje, površinski i zapreminski modul petlje opadaju u procesima mokre relaksacije i prilikom nege i nošenja.

Dimensional stability of hemp based knitted fabrics

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Relaxation processes inevitably occurring during processing and usage of textile materials, changes their structural characteristics. Knitted fabrics are particularly susceptible to relaxation due to specific yarn configuration in the structure of a knit. Dimensional changes in knitted fabrics occur as a result of complex interaction between fibre and yarn properties, and technological parameters of the production process. Three variants of plain knitted fabrics were investigated in this study: 100% hemp, 100% acrylic (PAC), and blended hemp/PAC (50%/50%). The range of the structural parameters of yarns (thickness, bulk density), and knitted fabrics – primary (thickness, loop length, stitch density, surface density) and secondary (bulk density, porosity, stitch area, cover factor, structural cover factor, planar stitch modulus, and volume stitch modulus) were determined experimentally or by calculation. All the procedures were conducted on the dry and wet relaxed knitted fabrics, as well as after wear trial tests. The values of the secondary structural parameters of the knitted fabrics indicated a reduction in porosity, area of a stitch, and planar and volume stitch moduli, whereas the bulk density and structural cover factor of the hemp/PAC and pure hemp knitted fabrics were increased after wet relaxation and wear and care cycles.

NM P 05

Nov materijal za medicinsku upotrebu zasnovan na kompozitu srebro-modifikovan zeolit / polivinil-hlorid

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Polivinil-hlorid (PVC) koji se koristi za proizvodnju endotrahijalnih tubusa često predstavlja podlogu za razvoj bakterija koje izazivaju ozbiljne bolničke infekcije. U ovom radu prikazano je dobijanje kompozita srebro-modifikovan zeolit/PVC (Ag-NZ/PVC) i njegova antibakterijska aktivnost prema kliničkom izolatu *Acinetobacter baumannii* (soj ST145, izolovan u Splitskoj Univerzitetskoj bolnici) koja spada u red multirezistentnih bakterija. Kompoziti su pripremljeni tako što je u 5 mas.% rastvor PVC u tetrahirofuranu (THF) dodavan u različitim koncentracijama (0, 5, 10 i 15 mas.%) prirodni zeolit – klinoptilolit (NZ) prethodno modifikovan srebro-jonima. Modifikacija NZ izvršena je jonskom izmenom na sobnoj temperaturi, pomoću vodenog rastvora $AgNO_3$. Suspenzije su najpre homogenizovane na magnetnoj mešalici (2 h na 500 rpm) a zatim, Ultra Turrax mešalicom na 8000 rpm tokom 10 min. Iz suspenzija su dobijeni kompoziti izlivanjam u Petri šolje i sušenjem na sobnoj temperaturi i u vakuum sušnici. Ispitivanja reoloških svojstava kompozita pokazala su da modifikacija ne narušava procesabilnost PVC-a ni pri najvećim koncentracijama Ag-NZ. Antibakterijska aktivnost kompozita prema ispitivanoj bakteriji dobra je i pri malim koncentracijama Ag-NZ što upućuje na zaključak da bi kompoziti mogli da nađu primenu kao nov medicinski materijal.

Novel material for medical use based on Ag-zeolite/poly(vinyl chloride) composite

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Poly(vinyl chloride) (PVC) used for the production of endotracheal tubes usually acts as a reservoir for bacteria causing nosocomial infections. In this study, the preparation of Ag-exchanged zeolite / PVC composites (Ag-NZ/PVC) and its antibacterial activity toward clinical isolate of *Acinetobacter baumannii* (strain ST145, isolated from the Split University Hospital) were investigated. The composites were prepared by the following procedure. natural zeolite – clinoptilolite (NZ) was firstly converted into Ag-NZ by an ion-exchange at the room temperature, using $AgNO_3$ solution. Then, Ag-NZ was added into 5 wt.% PVC solution in tetrahydrofuran (THF) at different concentration (0, 5, 10 and 15 wt.%) and the suspensions were homogenized by a magnetic stirrer (2 h, 500 rpm) and by an Ultra Turax at 8000 rpm for 10 min. Finally, the suspensions were poured in Petri dishes and left to dry on the air and in a vacuum oven. Reological properties of the obtained composites showed that procesability of PVC is not influenced by Ag-NZ even at its high concentration. The composites exhibit good antibacterial activity toward examined bacteria at low Ag-NZ which indicates that they be promising material for medical application.

NM P 06

Grafen-oksid kao elektrodni materijal za Na-jonske baterije teorijska studija

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Grafen poseduje niz izuzetnih svojstava koja ga kvalifikuju za veliki broj praktičnih primena. Pored toga, prisustvo različitih defekata i funkcionalnih grupa na površini grafena modifikuje elektronsku strukturu i reaktivnost ovog materijala. U cilju ispitivanja mogućnosti korišćenja oksidovanog grafena kao elektrodnog materijala u natrijum-jonskim baterijama, primenom Teorije funkcionala gustine pokazali smo kako prisustvo epoksi i hidroksilnih grupa na bazalnoj ravni utiče na interakciju grafena sa natrijumom. Grafen interaguje slabo sa natrijumom, sa energijom adsorpcije od približno −0,4 eV, pri čemu postoji značajan doprinos disperzionih interakcija. U prisustvu kiseoničnih grupa uočena je jonska interakcija sa Na koja je mnogo jača nego u slučaju idealnog grafena i koja sprečava precipitaciju metalne faze u toku rada baterije. S druge strane, prisustvo hidroksilnih grupa na bazalnoj ravni može izazvati ireverzibilno formiranje NaOH. Vrsta, koncentracija i raspored kiseoničnih grupa imaju presudan uticaj na performanse oksidovanog grafena u Na-jonskim baterijama. Koncentracija kiseonika mora biti pažljivo optimizovana. Neophodno je naći koncentraciju koja je dovoljno visoka da obezbeđuje željeni kapacitet za skladištenje Na^+ jona i onemogućava izdvajanje hidroksidne faze, a istovremeno dovoljno niska da bi se izbegli gubici usled smanjene provodljivosti materijala.

Graphene-oxide as an electrode material for Na-ion batteries theoretical study

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Graphene possesses a number of extraordinary properties which qualify it for numerous practical applications. Besides that, the presence of different defects on graphene basal plane modifies its electronic structure and reactivity. In order to investigate the possibility of using oxidized graphene as an electrode material in sodium-ion batteries, we have conducted Density Functional Theory calculations and revealed the effects of epoxy and hydroxyl groups located on the basal plane on the graphene-sodium interactions. Pristine graphene interacts weakly with sodium, with the adsorption energy amounting to approx. −0.4 eV and significant contribution of dispersion interactions. The presence of oxygen-containing groups gives rise to strong ionic interactions which are able to prevent precipitation of metallic Na phase during battery operation cycle. On the other hand, presence of hydroxyl groups on the basal plane may result with irreversible formation of NaOH phase. The groups' type, content and distribution have crucial influence on the performance of oxidized graphene in Na-ion batteries. Oxygen concentration should be carefully optimized. It must be high enough to provide good Na^+ storage capability and prevent hydroxide phase separation, and yet low enough to avoid performance losses due to reduced conductivity.

NM P 07

Aktivni biopolimerni filmovi na bazi amidovanog pektina za očuvanje kvaliteta hrane

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U ovom radu su ispitivani sinteza i strukturna i fizička svojstva bioaktivnih filmova na bazi amidovanog pektina koji sadrže 0.02, 0.1, 0.2, 0.6, 2 i 4% (w/v) esencijalnog ulja origana. FTIR rezultati su potvrdili da je došlo do interakcija između polimerne matrice i etarskog ulja. Dodatak esencijalnog ulja u matricu amidovanog pektina izazvao je smanjenje propustljivosti vodene pare, dok su mehanička svojstva neznatno pogoršana. Ispitivana je antimikrobna aktivnost filmova na sledeće patogene: *Escherichia coli*, *Staphilococcus aureus* i *Candida albicans*. Rezultati su pokazali da je najjače antimikrobno dejstvo filmova na gram-pozitivne bakterije. Minimalna koncentracija esencijalnog ulja od 0.2% (w/v) je neophodna da se osigura antibakterijska efikasnost filmova. Preliminarni rezultati su pokazali da ovi filmovi produžavaju vek trajanja ribljih fileta.

Active biobased films from amidated pectin for food preservation

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In this work the synthesis and structural and physial properties of active biobased films from amidated pectin containing 0.02, 0.1, 0.2, 0.6, 2 and 4% (wt/v) of Oreganoessential oil (OEO) were investigated. FTIR results confirmed that an interaction between polymer matrix and essential oil occurred. The incorporation of the tested oil provoked a remarkable reduction in the water vapor permeability properties, while mechanical properties showed to be slightly worsened. The antimicrobial activity of the films against the pathogenic microorganisms *Escherichia coli*, *Staphylococcus aureus* and *Candida albicans* was investigated. The bioactive films exhibited the most pronounced effect for Gram-positive bacteria. A minimum concentration of 0.2% (wt/v) of OEO was necessary to ensure their antibacterial efficacy. The preliminary results showed that these films ensured the extension of shelf-life of fish fillets.

NM P 08

Sinteza i karakterizacija adsorbenta na bazi prirodnog zeolita za uklanjanje fosfata iz vodene sredine

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U ovom radu je zeolitski tuf bogat klinoptilolitom modifikovan gvožđe(II)-oksidom u cilju dobijanja adsorbenta za uklanjanje fosfat-jona iz vodene sredine. Modifikacija tufa (Z) izvršena je u rastvoru $Fe_2(SO_4)_3$ u puferu, pri pH=3,6. Sušenjem Fe-modifikovanog zeolita (FeZ) na 90 °C dobijen je FeO-Z koji je zatim okarakterisan različitim instrumentalnim metodama: rendgenskom difrakcijom praha (PXRD, APD2000 Ital Structure) u cilju ispitivanja kristaliničnosti, transmisionom elektronskom mikroskopijom (TEM, JEM-2100) u cilju ispitivanja detalja površine, simultanom TG/DTG/DTA analizom (SDT Q600, TA Instruments) radi analize termičkih svojstava i N_2-BET adsorpcijom (ASAP 2020, Micromeritics) u cilju određivanja specifične površine. PXRD-analiza je pokazala da modifikacija ne narušava kristalnu strukturu klinoptilolita. Specifična površina FeO-Z je u odnosu na Z povećana pet puta što je, na osnovu rezultata TEM-analize, pripisano obrazovanju sekundarne porozne strukture na površini Z, tj. nano-česticama FeO sa strukturom vuestita. Adsorpcija fosfat-jona za FeO-Z proučavana je na 25 °C pri različitim početnim koncetracijama fosfat-jona. Utvrđeno je da se adsorpcija fosfata na FeO-Z odigrava prema kinetici pseudo-drugog reda i da je adsorpciona izoterma u skladu sa Lengmirovim modelom.

Synthesis and characterization of adsorbent based on natural zeolite for phosphate removal from water media

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In this work a clinoptilolite-rich zeolitic tuff was modified by iron(II) oxide in order to obtain an adsorbent for removal of phosphate ions from water media. Zeolitic tuff (Z) was modified using a solution of $Fe_2(SO_4)_3$ in buffer at pH=3.6. Fe-modified zeolite (FeZ) was dried at 90 °C to give FeO-Z wich is than characterized by different techniques: powder X-ray diffraction method (PXRD, APD2000 Ital Structure) was used to check the crystallinity of the zeolite, transition electron microscopy (TEM, JEM-2100) was performed to analyze the texture, a simultaneous TG/DTG/DTA (SDT Q600, TA Instruments) was applied to study thermal behaviour and N_2-BET adsorption method (ASAP 2020, Micromeritics) was used to measure specific surface area. PXRD analysis showed that the modification does not affect the zeolite crystallinity. Specific surface area was increased five times which is explained by formation of a secondary porous structure (SPS) at the Z surface. TEM showed that SPS belongs to nano-oxide particles of wuestite FeO. The adsorption kinetics studied at 25 °C using different initial concentrations follows the pseudo-second order equation and the adsorption isotherm is in accordance with the Langmuir model.

NM P 09

Elektrohemijsko taloženje niobijuma iz hloroalumonatnog rastopa kome je dodat Nb_2O_5

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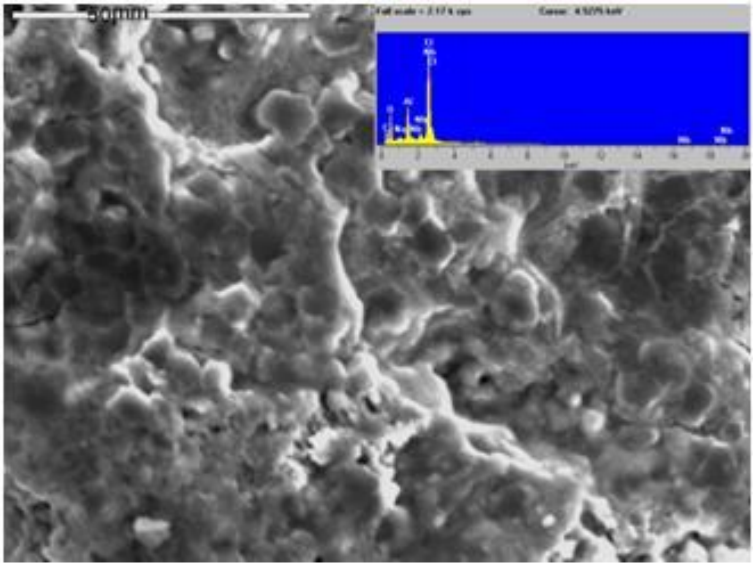
Ispitivano je elektrohemijsko taloženje i rastvaranje niobijuma iz ekvimolarnog rastopa $AlCl_3$+NaCl na staklastom ugljeniku na temperatuti od 200^0C. Niobijum jon obezbeđen je rastvaranjem Nb_2O_5. Elektrohemijske tehnike linearne ciklične voltametrije i hronoamperometrije korišćene su za analizu ovih procesa. Karakterizacija dobijenog depozita vršena je skenirajućom elektronskom mikroskopijom (SEM) i energetsko disperzivnom spektroskopijom (EDS). Utvrđeno je da dolazi do kotaloženja niobijuma i aluminijuma pri čemu dolazi i do formiranja Al-Nb legura (vidi sliku).



The electrochemical deposition of niobium from chloroaluminate melts with Nb_2O_5

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The electrochemical deposition and dissolution of niobium on glassy carbon in $AlCl_3$+NaCl equimolar melts at temperatures of 200^0C have been investigated. Nb_2O_5 was used as niobium source. As electrochemical techniques the linear sweep voltammetry and potential step were applied. Deposits were studied by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). It was found that niobium can be electrodeposited from this melts followed by aluminium deposition, when codeposited leads to the formation of Al-Nb alloys (see figure).

NM P 10

Uticaj visoko-temperaturnog starenja na svojstva aluminijumskih legura iz serije 6000

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Predmet istraživanja u ovom radu je bio da se ispita uticaj termičke obrade na strukturu, fizička i mehanička svojstva aluminijumskih legura 6060 i 6082. Termička obrada je sadržala žarenje radi uklanjanja polazne strukture ispitivanih legura i dobijanja strukture homogenog čvrstog rastvora, dobijanje presićenog čvrstog rastvora (α_{ssss}) rastvornim žarenjem i kaljenjem i nakon toga starenje na temperaturama od 230 °C i 280 °C u trajanju od 30 minuta, 1 sata, 1 sata i 30 minuta i 2 sata. Mehanička svojstva su ispitivana merenjem tvrdoće, dok je elektroprovodljivost merena kako bi se iskazala promena u fizičkim svojstvima. Rezultati pokazuju da se mehanička i fizička svojstva kao i mikrostruktura menjaju sa promenom temperature i vremena starenja. Promenom ovih parametra menja se i precipitaciono ojačavanje koje predstavlja ključ dobijanja različitih mehaničkih i fizičkih osobina ispitivanih legura. Efekat precipitacionog ojačavanja je zapažen i zabeležen i uz pomoć optičke mikroskopije na optičkim mikrofotografijama.

Influence of high-temperature ageing on properties of 6xxx aluminium alloys

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The key aspect of this work was to study the effect of heat treatment, on structure, physical and mechanical properties of 6060 and 6082 Al alloys. Heat treatment included annealing, in order to remove as received structure and obtain homogenized structure, solution heat treatment followed by quenching for acquiring supersaturated solid solution (α_{ssss}), after that, ageing at 230 °C and 280 °C was done for a period of 30 minutes, 1 hour, 1 hour and 30 minutes and 2 hours. In this paper, mechanical properties were investigated by hardness measurement and for studying physical properties electroconductivity was measured, respectively. The results show that mechanical and physical properties as well as the microstructure change with temperature and time of ageing. Changing these parameters causes change in precipitation hardening which is the key in obtaining the wide range of mechanical and physical properties of mentioned alloys. The effect of precipitation hardening was observed and recorded by optical microscopy on obtained microphotographs.

Teorijska hemija - Theoretical Chemistry

TH P 01

Steking helata nikla(II) – energije interakcija na visokom računarskom nivou i potraga za manje zahtevnim metodama

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Helatni prstenovi metala i njihove steking interakcije su od velikog značaja za proces dizajna provodnih i magnetnih materijala, kao i u oblastima linearne optike, katalize i inženjeringa kristala. U ovom radu, energije steking interakcija između dva helatna prstena nikla(II) procenjivane su na CCSD(T)/CBS nivou, koji se smatra zlatnim standardom kvantne hemije. Ove energije su potom upoređivane sa rezultatima dobijenim pomoću nekoliko disperzno korigovanih DFT metoda uz korišćenje šest različitih bazisa, kako bi se pronašle manje zahtevne metode koje mogu uspešno da izvrše ove proračune. Statistička studija je pokazala da M06-D3, ωB97xD, B3LYP-D3BJ, a posebno LC-ωPBE-D3BJ funkcional gustine, mogu da reprodukuju CCSD(T)/CBS energije sa većinom bazisa, te stoga mogu da se koriste za računanje površina potencijalne energije za helate nikla(II).

Stacking of chelates of nickel(II) – interaction energies at high computational level and search for less demanding methods

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Metal-chelate rings and their stacking interactions are of great importance for the designing process of conducting and magnetic materials and in the areas of linear optics, catalysis and crystal engineering. In this work, energies of stacking interactions between two chelate rings of nickel(II) were estimated at CCSD(T)/CBS level, which is considered to be the gold standard of quantum chemistry. These energies were then compared to the results obtained with several dispersion corrected DFT methods by using six different basis sets, in order to find less demanding methods that can successfully perform these calculations. The statistical study showed that M06-D3, ωB97xD, B3LYP-D3BJ, and particularly LC-ωPBE-D3BJ density functional, can reproduce CCSD(T)/CBS energies with most of the basis sets, and therefore can be used for calculations of potential energy surfaces of chelates of nickel(II).

TH P 02

Улога спинских стања у каталитичком механизму интра- и екстрадиолног раскидања катехоловог прстена са O_2

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Раскидање прстена код инетртних ароматичних једињења може бити катализовано Fe-зависним ензимима и биомиметичким комплексима гвожђа. Механизам ових транс-формација и фактори који доводе до ектрадиолног или интрадиолног раскидања нису у потпуности разјашњени. Коришћењем теорије функционала густине разјаснили смо механизам каталитичког циклуса за два биомиметичка комплекса, и објаснили разлике у добијеним производима.
Такође, показано је да, иако је основно стање комплекса гвожђа на почетку и на самом крају каталитичког циклуса секстет, квартетно стање одређује реакциони ток и расподелу производа .

The role of spin states in catalytic mechanism of the intra- and extradiol cleavage of catechols by O_2

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The ring cleavage of very inert and aromatic compounds can be catalyzed by iron-dependent enzymes and biomimetic iron complexes. The mechanism of these transformations and the factors leading to extradiol or intradiol cleavage are not fully understood. Using density functional theory we have elucidated the mechanism of the catalytic cycle for two biomimetic complexes, and explained the difference in the experimentally obtained products.
Also, it is shown that, although the sextet state is the ground state of iron complex at the beginning and at the very end of the catalytic cycle, the quartet state governs the reaction and determinates the product distribution.

TH P 03

Struktura 4-metoksidibenzoilmetan-a u osnovnom i pobuđenim elektronskim stanjima

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4-metoksidibenzoilmetan (MDBM) je β-dikarbonil jedinjenje koje je podložno keto-enol tautomerizaciji i jedan od molekula koji se najviše koristi u zaštiti od štetnog UVA zračenja. Pored enol i keto tautomera MDBM može postojati i kao enolni izomer (rotamer) koji se javlja kao prelazni oblik prilikom relaksacije pobuđenog singletnog elektronskog stanja. Osnovno (S_0), prvo pobuđeno singletno (S_1) i prvo pobuđeno tripletno (T_1) elektronsko stanje enol, keto i rotamer oblika MDBM-a su ispitivana korišćenjem metode teorije funkcionala gustine (DFT). Optimizovane su strukture sva tri molekula i izračunati vertikalni i vibracioni spektri za svaku optimizovanu molekulsku strukturu.

Structure of 4-methoxydibenzoylmethane at the ground and excited electronic states

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4-methoxydibenzoylmethane (MDBM) is a β-dicarbonyl compound that is liable to keto-enol tautomerization and one of the most widely used molecule which provide protection from harmful UVA radiation. Beside two tautomeric forms, MDBM can exist as a short-lived enol isomer (rotamer). This isomer is formed during the relaxation of excited singlet electronic state. The ground (S_0), first excited singlet (S_1) and first excited triplet (T_1) electronic states of keto, enol, and rotamer form of MDBM have been characterized using density functional theory (DFT) method. We optimized nuclear arrangements of these three molecules and calculated vertical excitation and vibrational spectrum of all optimized molecular structures.

TH P 04

Ispitivanje uticaja molekula rastvarača na elektronske prelaze molekulskog prekidača HAPI

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Strukture deprotonovanog E izomera N'-[1-(2-hidroksifenil)etiliden]izonikotinoil-hidrazida (HAPI) sa jednim (1W) i pet molekula vode (5W) su optizovane na CAM-B3LYP/cc-PVTZ nivou programskim paketom *Gaussian*. Četiri 1W i jedna 5W struktura su analizirane kako bi se ispitao uticaj rastvarača na elektronski spektar HAPI-ja. TD-DFT pristup je korišćen za izračunavanje elektronskih prelaza. Detaljna analiza najviših popunjenih i najnižih nepopunjenih orbitala je objasnila spektralne promene do kojih dolazi dodatkom jednog molekula vode. Na osnovu NBO analize i analize izračunatih elektronskih spektara sa različitim brojem i položajem molekula rastvarača, identifikovane su hromofore na koje rastvarač ima najveć uticaj – fenolatni O, karboksilni O i N-N. Dobijeno je odlično slaganje položaja pikova izračunatog spektra 5W strukture i eksperimentalnog spektra vodenog rastvora HAPI. Neophodna su dodatna istraživanja kako bi se dobio odnos intenziteta pikova koji je uporediv sa eksperimentalnim vrednostima.

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Investigation of the influence of solvent molecules on the electronic transitions of the molecular switch HAPI

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Structures of deprotonated E isomer of N'-[1-(2-hydroxyphenil)ethyliden] isonicotinoyl-hydrazide (HAPI) with one (1W) and five water molecules (5W) are optimized at CAM-B3LYP/cc-PVTZ level using the *Gaussian* program package. Four 1W structures and a 5W structure are analyzed in order to investigate solvent effects on HAPI electronic transitions. TD-DFT method is used for the calculation of electronic transitions. A detailed analysis of frontier orbitals explains spectral changes that arise upon inclusion of a single water molecule. Based on Natural Bond Orbital (NBO) analysis and analysis of computed electronic spectra with different number and position of solvent molecules, chromophores that are most affected by the solvent are identified – phenolate O, carboxyl O and N-N groups. Excellent agreement between peak positions in the computed spectrum of the 5W structure and the experimental spectrum of the aqueous solution of HAPI is obtained. Further investigation is needed in order to obtain relative peak intensities comparable with the experimental values.

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TH P 05

Kompjuterske (konformaciona i doking) analize ciljanih pesticida

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Kristalne strukture nekih pesticida su poznate, i mogu se koristiti kao polazne tačke u konformacionoj analizi. Skoro sintetisani pesticidi nisu dovoljno istraženi. Obratili smo posebnu pažnju na neonikotinoidne i organofosfatne insekticide (imidakloprid, tiametoksam, i dimetoat) i koristili njihove kristalne strukture kao polazne tačke za istraživanje konformacija korišćenjem Avogadro i CONFLEX softvera. Rezultati dobijeni u dvofaznoj membranskoj ekstrakciji su bili u saglasnosti sa konformacionim analizama i kompjuterski predviđenim logD vrednostima, tako da su se kompjuterske metode pokazale kao pouzdani alati. Tako, znajući energiju određenog pesticida i njegovu logD vrednost („standardni pesticid"), možemo predvideti ekstrakciono ponašanje pesticida znajući samo njihove strukture (izračunavanjem energije u besplatnom softveru kao sto je Avogadro). Molekulska doking proučavanja daju nam mogućnost da teorijski predvidimo potencijalno raspoložive džepove za molekule ligande (pesticide) u metama (proteinskim receptorima).

Computational (conformational and docking) analyses of targeted pesticides

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Crystal structures of some pesticides are known, and can be used as starting points for conformational analysis. Recently synthesized pesticides are not investigated enough. We paid particular attention to neonicotinoid and organophosphate insecticides (imidacloprid, thiamethoxam, and dimethoate) and used their crystal structures as starting points for the investigation of the conformations using Avogadro and CONFLEX softwares. Results obtained in two-phase membrane extraction were in accordance to conformational analyses and computationally predicted logD values, so computational methods were proved as reliable tools. Thus knowing the energy of particular pesticide and its logD value ("standard pesticide"), we can predict the extraction behaviour of pesticides knowing only their structures (by calculating energy in free software, like Avogadro). Molecular docking studies give us the possibility to theoretically predict the potential available pockets for ligand molecules (pesticides) in targets (protein receptors).

TH P 06

Ispitivanje kružnih struja u fluoro derivatima fulvena

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U prethodnim istraživanjima pokazano je kako fluor, kao najelektronegativniji element, može značajno da utiče na aromatičnost nekog molekula. U ovom radu ispitivan je uticaj supstitucije atoma fluora na aromatičnost fulvenovog prstena. Fulven je izabran kao tipičan nearomatičan molekul. U cilju ispitivanja aromatičnosti fulvenovih fluoro-derivata korišćene su mape kružnih struja. Mape indukovahih gustina elektronskih struja izračunate su pomoću CTOCD-DZ/HF/def2-TZVP metode polazeći od B3LYP/def2-TZVP optimizovanih geometrija. Analizom mapa kružnih struja pokazano je da prisustvo fluora povećava aromatičnost fulvenovog petočlanog prstena.

Ring currents in flourinated fulvene derivatives

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In a series of recent papers it has been shown that the presence of fluorine, the most electronegative atom, can significantly affect aromaticity of a given molecule. In this work, it was examined how fluorine substitution influence the aromaticity of the fulvene five-membered ring. It is well known that fulvene is a typical nonaromatic system. The current density maps were used to rationalize the aromaticity of flourinated fulvene derivatives. The current density maps were computed by means of the CTOCD-DZ/HF/def2-TZVP method, starting from the B3LYP/def2-TZVP optimized geometries. The current density maps showed that the aromatic character of the fulvene five-membered ring is increased by fluorine substitution.

TH P 07

Mehanizmi antioksidativne aktivnosti hlorogenske kiseline: termodinamički pristup

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Sva izračunavanja su izvršena u programu Gaussian 09, pomoću teorijskog modela B3LYP-D2/6-311++G(d,p) i solvatacionog modela CPCM. Izračunati su termodinamički parametri za hlorogensku i kafeinsku kiselinu u benzenu, metanolu i vodi. Ove vrednosti su iskorišćene za razmatranje glavnih antioksidativnih mehanizama: transfer vodonikovog atoma (Hydrogen Atom Transfer) - HAT, gubitak protona praćen transferom elektrona (Sequential Proton-Loss Electron-Transfer) - SPLET, i transfer jednog elektrona i transfer protona (Single Electron Transfer – Proton Transfer) - SET-PT. Pronađeno je da obe kiseline imaju slične vrednosti za svaki termodinamički parametar. Na osnovu toga se može pretpostaviti da oba polifenola pokazuju sličnu antioksidativnu aktivnost. U nepolarnim rastvaračima preovladava HAT mehanizam, dok su u polarnim rastvaračima HAT i SPLET kompetitivni.

Antioxidative mechanisms of chlorogenic acid: a thermodynamic approach

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All calculations were performed by means of the Gaussian 09 program package, using the B3LYP-D2/6-311++G(d,p) theoretical model and CPCM solvation model. The thermodynamic paramethers for chlorogenic acid and caffeic acid in benzene, methanol, and water were calculated. These values were used for thermodynamic consideration of the major antioxidative mechanisms: HAT (Hydrogen Atom Transfer), SPLET (Sequential Proton-Loss Electron-Transfer), and SET-PT (Single Electron Transfer – Proton Transfer). It was found that both compounds are characterised with very similar values of each thermodynamic parameter. Thus, one can suppose that both polyphenols will exhibit very similar antioxidative activities. In nonpolar solvents HAT mechanisam may be predominant, while in polar solvents HAT and SPLET are competitive mechanistic pathways.

TH P 08

Rener-Telerov efekat u četvoroatomskim molekulima: izračunavanje neadijabatskih matričnih elemenata i vibronskog spektra $C_2H_2^+$ u $X\ ^2\Pi_u$ elektronskom stanju

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Rener-Telerov (R-T) efekat predstavlja jedan od najbolje proučenih primera narušavanja Born-Openhajmerove aproksimacije. R-T efekat se javlja kada se potencijalna površ nekog elektronskog stanja prostorno degenerisanog pri linearnoj geometriji (Π, Δ, . . .), usled savijanja molekula, cepa na dve površi. R-T efekat može prouzrokovati komplikovanu strukturu molekulskih spektara i određivati ponašanje molekula u hemijskim reakcijama. Veliki broj slobodnih radikala koji su od intersa za astrofiziku i astrohemiju i/ili pojavljuju se kao reakcioni intermedijeri u različitim važnim hemijskim procesima, imaju prostorno degenerisano elektronsko stanje i ispoljavaju R-T efekat.

U ovom radu, putem *ab initio* računa elektronskih potencijalnih površi i neadijabatskih matričnih elemenata $C_2H_2^+$ u $X\ ^2\Pi_u$ elektronskom stanju, potvrdili smo plauzabilnost jednostavnog modela za tretiranje R-T efekta u četvoroatomskim molekulima sa linearnom ravnotežnom geometrijom. Samo četri parametra (plus spin-orbitna konstanta, ako su spinski efekti uzeti u obzir), koja se mogu dobiti iz nekoliko *ab initio* računa, su dovoljna za konstrukciju matrice hamiltonijana, čijom dijagonalizacijom se dobija kompletan nisko-energetski vibronski spektar.

Renner-Teller effect in tetra-atomic molecules: Calculation of non-adiabatic matrix elements and the vibronic spectrum of $X\ ^2\Pi_u$ electronic state of $C_2H_2^+$

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The Renner-Teller (R-T) represents one of the best studied examples for the breakdown of the Born-Oppenheimer approximation. It appears when the potential energysurfaces of an spatially degenerate electronic state at the linear molecular geometry (Π, Δ, . . .) splits upon bending into two surfaces. The R-T effect can cause complicated structure of molecular spectra and determine behavior of molecule in chemical reactions. A great part of radicals being of crucial interest from astrophysical and astrochemical point of view and/or playing as reaction intermediates as important role in various chemical processes have spatially degenerate ground states and exhibit R-T effect.

In this work, we prove the plausibility of a simple model for the R-T effect in tetra-atomic molecules with linear equilibrium geometry, by *ab initio* calculations of the electronic energy surfaces and non-adiabatic matrix elements for the $X\ ^2\Pi_u$ state of $C_2H_2^+$. Only four parameters (plus the spin-orbit constant, if the spin effects are taken into account), derivable from few single-point *ab initio* calculations, are sufficient for building up the Hamiltonian matrix whose diagonalization results in the complete low-energy (bending) vibronic spectrum.

TH P 09

Stability 4-phenyl-2,4-dioxobutanoic acid tautomeric forms in vacuum, implicit, and explicit solvent model

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Aryldiketo acids (ADKs) are promising leads for the development of antibacterials. Compounds can exist in three tautomeric forms: two enol (**I** and **III**) and one diketo form (**II**), **Figure 1**.

In crystal structures of ADK complexes with various bacterial enzymes, both diketo and enol forms are found.[1, 2] *Ab initio* calculations (MP2/6-31G**) of the stability of tautomeric forms in vacuum, water solvation model (PCM), and considering the single explicit water molecule interacting with ADK, showed that only results obtained accounting explicit water are in agreement with the experiments. The enol **I** was 2.82 and 9.67 kJ/mol more stable than enol **III** and diketo form **II**, respectively. Such results suggest that enol form **I** is the most abundant one in biologically relevant environments. These observations should be taken into account in future efforts to develop drug-like molecules based on ADK scaffolds.

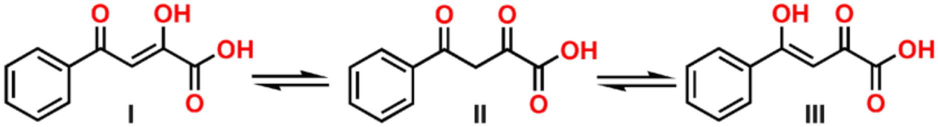

***Figure 1**. Tautomeric forms of 4-phenyl-2,4-dioxobutanoic acid.*

Stabilnost tautomera 4-fenil-2,4-dioksobutanske kiseline u vakuumu, impicitnom i eksplicitnom modelu rastvarača

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Arildiketo kiseline (ADK) su potencijalni antibakterijski agensi. Mogu postojati u tri tautomerna oblika, dva enolna (**I** i **III**) i diketo obliku (**II**), **Slika 1**. U kristalnim strukturama kompleksa derivata ADK sa različitim bakterijskim enzimima nađeni su i enolni i diketo tautomerni oblici. *Ab initio* izračunavanja stabilnosti tautomera u vakuumu, implicitnom (PCM model) i eksplicitnom modelu vode kao rastvarača pokazala su da se jedino rezultati dobijeni izračunavanjima sa eksplicitnim molekulima vode slažu sa eksperimentalno dobijenim rezultatima. Enol **I** je stabilniji od enola **III** i diketo oblika **II** za 2,82, odnosno 9,67 kJ/mol i može se smatrati za najverovatniji oblik koji ova klasa jedinjenja zauzima u biološki važnim sredinama.

References:
1. I. V. Krieger et al., *Chemistry & biology*, 2012, **19**, 1556-1567.
2. W. Zhu *et al.*, *PNAS* 2013, **110**, 123-128.

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IP P 01

Verifikacija McCabe-Thiele-ove metode i određivanje osnovnih parametara destilacije softverskim paketima MATLAB i ChemCAD za razdvajanje smjese n-heptan-n-oktan

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U radu je izvršena provjera grafičke McCabe-Thiele-ove metode za razdvajanje smjese n-heptan-n-oktan. Provjera McCabe-Thiele-ove metode vršena je analitičkim proračunima sistema za destilaciju, kao i primjenom SHORTCUT metode za proračune destilacije u ChemCAD-u, kao i programom koji je osmišljen u MATLAB-u koji omogućava izračunavanje veoma važnih parametara u destilaciji poput minimalnog refluksnog odnosa, radnog reflusknog odnosa, broja teorijskih podova, mjesta napojnog poda, određenih veličina koje u velikoj mjeri zavise od refluksa i broja teorijskih podova potrebnih za razdvajanje. U radu su prikazane i grafičke zavisnosti navedenih parametara od udjela lako isparljive komponente, u ovom slučaju n-heptana, u napojnoj smjesi. Pri tome, provedena su dva postupka razdvajanja, prvi je rigorozni postupak razdvajanja, koji zahtjeva razdvajanje od 99 %, a drugi je manje rigorozan i zahtjeva razdvajanje navedene smjese od 95 %.

Verification of McCabe-Thiele's method and determination of basic parameters of distillation by using software package MATLAB and ChemCAD for separating of mixture n-heptane-n-octane

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This paper shows the verification of the graphic McCabe-Thiele's method for separating of mixture n-heptane-n-octane. Verification of McCabe-Thiele's method was performed by analytical calculations system for distilling and applying SHORTCUT methods for calculation of distillation in ChemCAD as well as a program that is designed in MATLAB that allows calculation of important parameters such as the minimum reflux distillation relations, working reflux relationships, the number of theoretical plates, the supply of the floor, certain values, which depend largely on the reflux and the number of theoretical plates required for the separation. The paper describes the graphic dependence of parameters of interest volatile components, in this case n-heptane, in the supply of the mixture. At the same time, conducted two of the separation, the first rigorous process of separation, which requires a separation of 99 %, the other less rigorous and requires separation of mixture of 95 %.

IP P 02

Primena biodizela u cilju smanjenja emisije štetnih izduvnih gasova

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Biodizel je alternativno gorivo čije poreklo ne potiče iz nafte. Predstavlja mešavinu estara masnih kiselina i alifatičnih alkohola kratkog lanca. Dobija se reakcijom transesterifikacije triglicerida u prisustvu katalizatora. Biodizel predstavlja obnovljivo alternativno gorivo, pa stoga privlači dosta pažnje istraživača. Pored toga, smatra se da primena biodizela ima dosta pozitivnih efekata. Smatra se da biodizel ima bolje mehaničke karakteristike koje utiču na rad motora. Takođe, biodizel predstavlja ekološki prihvatljivo gorivo jer se smatra da se njegovom upotrebom smanjuje količina štetnih „gasova staklene bašte“ u izduvnim gasovima. Ispitivali smo sadržaj CO_x i NO_x gasova u izduvnim gasovima motora sa unutrašnjim sagorevanjem pri radu motora koji je koristio biodizel kao gorivo. Koristili smo čist biodizel i smeše biodizela sa komercijalnim dizel gorivom sa niskim sadržajem sumpora. Korišćeni biodizel je dobijen reakcijom transesterifikacije uz primenu CaO kao katalizatora. Korišćene su smeše sa sadržajem biodizela od 25, 50 i 75%. Rezultati su pokazali da primenom biodizela, tj porastom njegovog udela u smeši dolazi do smanjenja emisije CO i CO_2, dok emisija NO_x gasova neznatno raste. Ovim rezultatima je potvrđeno mišljenje da se primenom biodizela može smanjiti uticaj motornih vozila na emisiju „gasova staklene bašte“.

The application of biodiesel in order to reduce harmfull emissions

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Biodiesel is non-petroleum alternative fuel. Represents a mixture of fatty acid esters of short-chain aliphatic alcohols. It is obtained by a transesterification reaction of triglycerides in the presence of a catalyst. Biodiesel is a renewable alternative fuel, and therefore attracts a lot of attention of researchers. In addition, it is considered that the application of biodiesel has many positive effects. It is believed that biodiesel has better mechanical characteristics that affect engine operation. Also, biodiesel, an environmentally friendly fuel because it is considered that its use reduces the amount of harmful "greenhouse gases" in the exhaust gases. We examined the contents of COx and NOx emissions in the exhaust gases of internal combustion engines with the engine, which is used as biodiesel fuel. We used pure biodiesel and mixtures of biodiesel with commercial diesel fuel with low sulfur content. Used biodiesel is obtained by a transesterification reaction with the use of CaO as a catalyst. Used as a mixture with the content of biodiesel of 25, 50 and 75%. The results showed that using biodiesel, ie increase its share in the mixture comes to the reduction of CO and CO2 emissions while NOx emissions slightly growing. These results confirmed the view that the application of biodiesel can reduce the impact of motor vehicles on the emission of "greenhouse gases".

IP P 03

The friction theory (f-theory) for viscosity modeling of pure substances - esters and alcohols

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The presented theory for viscosity modeling is based on friction concept of classical mechanics and the Van der Waals theory of fluids. The fundamental difference between this theory and other available theories is the fact that the viscosity of dense fluids, which characterizes pure shear flow, is approached as a mechanical, rather than as a transport, property. Thus, theory separates the total viscosity into a dilute gas term and a friction term which is then, using temperature-dependent friction coefficients, linked to the Van der Waals repulsive and attractive pressure terms. As a result, a rather simple cubic equation of state can be used as a basis for obtaining highly accurate modeling of the viscosity of fluids from low to extreme high pressures.

In this case, the f-theory for viscosity modeling is used in conjunction with the PR and SRK cubic equations of state in order to develop general models for viscosity prediction.

The measured viscosities and densities, on atmospheric pressure and in temperature range 288.15-323.15 K, of four esters (ethyl butyrate, ethyl octanoate, diethyl succinate and diethyl tartrate) and five alcohols (propanol, butanol, hexanol, isoamyl and isobutyl alcohol), are used to evaluate this theory on pure substances. In most cases, absolute average deviations are within 1%.

Primena frikcione teorije (f-teorije) za modelovanje viskoznosti čistih supstanci – estara i alkohola

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Predstavljena je teorija za modelovanje viskoznosti koja se zaniva na konceptu trenja klasične mehanike i Van der Valsovoj teoriji. Glavna razlika između ove teorije i ostalih dostupnih modela je činjenica da se na viskoznost gleda kao na mehaničku više nego transportnu veličinu. Tako da teorija razdvaja viskoznost na član koji se odnosi na razređeni gas i član trenja, koji je, koristeći temperaturno zavisne parametre, povezan sa Van der Valsovim privlačnim i odbojnim članovima pritiska. Kao rezultat, prilično jednostavne kubne jednačine stanja mogu se koristiti kao osnova za veoma tačno modelovanje viskoznosti pri različitim vrednostima pritiska.

U ovom slučaju, frikciona teorija je korišćena zajedno sa PR i SRK jednačinama stanja da bi se dobili modeli za predviđanje viskoznosti.

Model je testiran na merenim vrednostima viskoznosti i gustine, na atmosferskom pritisku i temperaturnom opsegu od 288.15-323.15 K, četiri estara (etil butirat, etil oktanoat, dietil sukcinat i dietil tartarat) i pet alkohola (propanol, butanol, heksanol, izoamil i izobutil alkohol). U većini slučajeva, apsolutne srednje procentualne greske su manje od 1%.

IP P 04

Gustine smeša biodizela i dizel goriva na višim pritiscima

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Zbog opštepoznatih posledica do kojih dovodi upotreba fosilnih goriva, kao i ograničenosti njihovih resursa, intenzivno se radi na pronalaženju i unapređenju alternativnih izvora energije. Jedno od rešenja za smanjenje emisije štetnih gasova jeste upotreba biogoriva, a posebno biodizela. Biodizeli su smeše alkil estara viših masnih kiselina koje zadovoljavaju uslove propisane odgovarajućim standardima. Oni su posebno zanimljivi zato što se pomešani sa dizel gorivom, u odnosu do 20% biodizela, mogu koristiti kao goriva u postojećim dizel motorima bez dodatnih ispravki na motorima. Za potrebe procene rada motora i povećanja njegove efikasnosti potrebno je poznavanje osnovnih karakteristika goriva pri različitim radnim uslovima, od kojih su među najvažnijima gustina i viskoznost. Stoga će ovde biti predstavljene gustine čistog dizel goriva, kao i njegovih smeša sa etil estrima suncokretovog ulja u odnosu 10% i 20% biodizela, na temperaturama 293.15-413.15 K i na pritiscima 0.1-60 MPa. Merenja su vršena na Anton Paar DMA HP gustinomeru, a pri kalibraciji uređaja je primenjena klasična kalibraciona metoda sa jednim refrentnim fluidom. Takođe, za iste uzorke su merene i viskoznosti na temperaturama 288.15-373.15 K i na atmosferskom pritisku, kao i indeksi refrakcije na istom pritisku i temperaturama 288.15-343.15 K.

Densities of biodiesel and petro-diesel mixtures at high pressures

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Due to the generally known consequences of the use of fossil fuels and also to the limitations of their sources, one intensively works on finding and promoting of alternative energy sources. One of the solutions for reducing greenhouse gas emissions is the use of biofuels, especially biodiesel. Biodiesels are mixtures of alkyl esters of lond-chain fatty acids which satisfy the conditions prescribed by the relevant standards. They are especially interesting because their mixtures with petro-diesel, containing up to 20% of biodiesel, can be used as fuel in existing diesel engines without additional corrections in engines design. In order to estimate engine performance and increase its efficiency, it is necessary to know the basic properties of fuels under different operating conditions, and among the most important ones are density and viscosity. Therefore, the densities of pure petro-diesel, as well as densities of its mixtures with sunflower oil ethyl esters, in the ratio of 10% vol. and 20% vol. of the biodiesel, at temperatures 293.15-413.15 K and at pressures of 0.1-60 MPa, will be presented here. Measurements were taken at an Anton Paar DMA HP densimeter and for the calibration of the device the classical calibration methods with one reference fluid was applied. Also, for the same samples, the viscosities at temperatures 288.15-373.15 K and at atmospheric pressure and the refractive indices at the same pressure and at temperatures 288.15-343.15 K were measured.

IP P 05

Solid-liquid equilibria measurements and modeling for three binary systems of aniline and N,N-dimethylaniline with poly (ethylene glycol) 2050 and 35000

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Solid-liquid equilibria of two solid poly (ethylene glycols), with average molar mass of 2050 and 35000, with aniline and N,N-dimethylaniline, organic aromatic solvents of common interest, in temperature range T = (298.15 to 350.15) K and at ambient pressure of 0.1 MPa, was studied. This study is investigating the possibility to use solid PEGs - average molecular mass 2050 (PEG2050) and 35000 (PEG35000) – as co-solvents for aniline and N,N-dimethylaniline. Poly (ethylene glycol) 2050 exibited slightly higher solubility in aniline compared to that in N,N-dimethylaniline, due to higher hydrogen bond acidity of aniline which provided stronger hydrogen bonding with polymer chain. On the other hand, longer polymer chain provoked dramatically lower solubility in both studied organic solvents. Result of those measurements are presented on temperature-molar fraction phase diagram.

The experimental solid-liquid equilibrium data have been correlated by the Non-Random Two-Liquid (NRTL) model with two different temperature dependant parameters Δg_{12} and Δg_{21}, and the correlation results are in accordance with the experimental results.

Eksperimentalno merenje i modelovanje ravnoteže čvrsto-tečno tri binarna sistema anilin i N,N-dimetilanilin sa polietilen glikolom 2050 i 35000

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U ovom radu eksperimentalno je određivana ravnoteža čvrsto-tečno dva čvrsta poli (etilen glikola), srednjih molarnih masa 2050 i 35000, u kombinaciji sa anilinom i N,N-dimetil-anilinom, organskim aromatičnim rastvaračima od opšteg značaja, u temperaturnom opsegu T = (298.15 do 350.15) K i pri atmosferskom pritisku od 0.1 MPa. Ispitivana je mogućnost upotrebe čvrstih PEG-ova – srednjih molarnih masa 2050 (PEG2050) i 35000 (PEG35000) – kao ko-rastvarača za anilin i N,N-dimetilanilin. Polietilen glikol 2050 pokazao je znatno veću rastvorljivost u anilinu u poređenju sa N,N-dimetilanilinom, usled veće kiselosti vodoničnih veza anilina, što dovodi do jačih veza sa polimernim lancem. Sa druge strane, duži polimerni lanac izaziva dramatično nižu rastvorljivost u oba razmatrana organska rastvarača. Rezultati ovih merenja prikazani su na faznom dijagramu temperatura-molski udeo.

Eksperimentalni podaci ravnoteže čvrsto-tečno korelisani su sa NRTL modelom sa dva različita temperaturno zavisna parametara Δg_{12} i Δg_{21}, a rezultati korelacije u dobrom su slaganju sa ekperimentalno dobijenim rezultatima.

IP P 06

Termodinamička i spektroskopska analiza molekulskih interakcija binarnih smeša nikotin+1,2-propandiol i nikotin+1,3-propandiol

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Eksperimentalna merenja gustine ρ, viskoznosti η i indeksa refrakcije n_D dve binarne smeše nikotin+1,2-propandiol i nikotin+1,3-propandiol su izvršena u temperaturnom opsegu T = (293.15 to 323.15) K sa korakom 5 K i na atmosferskom pritisku. Dopunska molarna zapremina V^E, promena viskoznosti $\Delta\eta$ i promena indeksa refrakcije Δn_D su izračunati iz eksperimentalnih podataka i fitovani Redlich-Kister polinomom. Usled polarne prirode ispitivanih komponenata i njihove sposobnosti građenja vodoničnih veza pretpostavljeno je da može doći do formiranja vodoničnih veza između raličitih molekula. Tehnika infracrvene spektroskopije sa Furijeovom transformacijom (FTIR) je primenjena na ispitivane binarne smeše i odgovarajuće čiste komponente na temperaturi 298.15 K da bi se stekao uvid u molekulsku strukturu smeša i moguće intermolekulske interakcije. Primenjena infracrvena analiza je potvrdila prisustvo vodoničnih veza između komponenata smeše što je u skladu sa negativnim V^E vrednostima i pozitivnim $\Delta\eta$ vrednostima u oblasti u kojoj je odrađena FTIR analiza. Uzrok negativnih $\Delta\eta$ vrednosti mogu biti disperzione sile ili geometrijski efekti.

Thermodynamic and spectroscopic interpretation of molecular interactions of nicotine+1,2-propanediol and nicotine+1,3-propanediol binary mixtures

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Density ρ, viscosity η and refractive index n_D have been experimentally measured for two binary mixtures nicotine+1,2-propanediol and nicotine+1,3-propanediol in the temperature range T = (293.15 to 323.15) K with temperature step 5 K and at atmospheric pressure. Excess molar volumes V^E, viscosity deviations $\Delta\eta$ and deviations in refractive index Δn_D were calculated from experimental data and fitted using Redlich-Kister polynomial. Due to polar nature of the components and their ability to form hydrogen bonds it was assumed that intermolecular hydrogen bonds between unlike molecules are possible. Fourier-transform infrared analysis (FTIR) of binary mixtures and corresponding pure components was performed at 298.15 K in order to gain insight into the molecular structure of mixtures and possible intermolecular interactions. Performed infra-red analysis confirms the presence of hydrogen bonding between unlike compounds which is in accordance with negative V^E values and positive $\Delta\eta$ values in the region where FTIR is performed. In the case of negative $\Delta\eta$ values dispersion forces or geometrical effects are possible cause.

IP P 07

Proizvodnja suvog ekstrakta divlje jabuke (*Malus sylvestris*) primenom spray drying tehnike

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Prilikom proizvodnje mešavine filter čaja koji kao jednu od komponenata sadrži divlju jabuku, proizvede se oko 20-30% sprednog proizvoda/otpada od divlje jabuke, tzv. „herbalne ili voćne prašine“. Primenom ultrazvučne ekstrakcije sa 50% etanolom kao ekstragensom, na optimalnim uslovima, od ovakvog sporednog proizvoda pripremljen je tečni ekstrakt divlje jabuke. Upotrebom spray drying tehnike dobijeni tečni ekstrakt je osušen odnosno preveden u formu suvog ekstrakta. U procesu sušenja ispitan je uticaj koncentracije dodatog agensa za sušenje-maltodekstrina, na efikasnost sušenja, na fizičke karakteristike suvog ekstrakta, kao i na sadržaj farmakoloških aktivnih komponenti u dobijenom suvom ekstraktu. Sušenje je rađeno na ulaznoj temperaturi od 120 °C i izlaznoj temperaturi od 80 °C. Koncentracije maltodekstrina koje su korišćene u procesu sušenja iznosile su 30%, 70% i 100%, računato na masu suvog ostatka tečnog ekstrakta. Efikasnost ovakvog sušenja tečnog ekstrakta divlje jabuke kretala se od potpuno neefikasnog procesa, preko procesa okarakterisanog slabom efikasnošću od 26.05% i na kraju veoma efikasnog procesa okaratekrisanog efikasnošću od 65.74%. U dobijenim suvim ekstraktima sadržaj vlage se kretao od 4.13% do 4.39%, higroskopnost se kretala se od 18.61% do 20.39%, a rastvorljivost od 96s do 183s. Za dobijene suve ekstrakte određen je i sadržaj fenola, flavonoida i antocijana, kao i antioksidativna aktivnost.

Production of dry extract of wild apple (*Malus sylvetris*) using spray drying techniques

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During the production of a tea filter mixture that contains wild apple, 20 to 30% of waste/by-product is produced, so-called „herbal powder“ or „fruit powder“. By applying ultrasonic extraction at optimal conditions, with 50% ethanol as extraction solvent, this by-product was turned into wild apple liquid extract. Using the spray drying technique obtained liquid extract was converted to a dry extract. During drying process the influence of concentration of added drying agent (maltodextrine) on drying efficiency, physical characteristics of the dry extract, and the content of pharmacologically active components in the dry extract, was observed. The drying was done on inlet temperature of 120 °C and outlet temperature of 80 °C. The concentrations of maltodextrine used in the drying process were 30%, 70% and 100%, based on the mass of the liquid extract's dry residue. The efficiency of wild apple liquid extract drying ranged from completely ineffiecient, less than efficient (with an efficiency of 26.05%), to very efficient (with an efficiency of 65.74%). In the obtained dry extracts, moisture content ranged from 4.13% to 4.39%, hygroscopicity from 18.61% to 20.39%, and the solubility from 96s to 183s. Also, the total phenol, total flavonoid and anthocyanin content, as well as the antioxidant activity in the dry extracts, were determined.

IP P 06

Ekstrakcija sporednog proizvoda iz proizvodnje filter čaja od uve ekstrakcionim sistemom superkritični ugljen-dioksid i smeša voda/etanol

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Prilikom proizvodnje jednokomponentnog ili mešavine čajeva u filter vrećice koje sadrže uvu, proizvede se oko 10-20% sporednog proizvoda/otpada od uve tzv. „herbalne prašine“. Herbalna prašina predstavlja materijal čije su čestice manjeg prečnika od prečnika pora na filter vrećici. S obzirom na visok sadržaj fenola i fenolnih jedinjenja u nativnom materijalu, pretpostavlja se da se odgovarajućim metoda čvrsto-tečne ekstrakcije iz ovakvog materijala može dobiti visokokvalitetan proizvod u formi tečnog ekstrakta. Kao metoda „reciklaže“ ovakvog biljnog materijala korišćena je ekstrakcija sistemom superkritični ugljen-dioksid i smeša etanol/voda (70% etanol). Sve ekstrakcije su rađene na pritisku od 100 bar, a temperatura je varirana u opsegu od 40 do 80 ˚C. U ekstraktima je određen sadržaj ukupnih fenola i flavonoida. Ispitivana je i antioksidativna aktivnost, primenom DPPH testa, kao i reduktivni kapacitet. U dobijenim ekstraktima sadržaj suvog ostatka se kreće od 6,924-8,106 g/100 ml ekstrakta, sadržaj ukupnih fenola od 26,310 do 30,730 mg EGK/ml, a sadržaj flavonoida od 4,902 do 5,982 mg EK/ml. Zbog visokog sadržaja fenola ispitivani ekstrakti su pokazali visoke antioksidativne aktivnosti (IC50 od 0,0225 do 0,0141 µl/ml test smeše) i redukcione kapacitete (EC50 od 0,070 do 0,044 µl/ml test smeše).

Extraction of uva by-product from filter tea factory by aplication of extraction system supercritical carbon dioxide and water/ethanol mixture

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During the production of uva filter tea, or a uva containing herbal mixture in filter bags, around 10-20% of uva by-product/waste, so-called „uva herbal dust“, is produced. Herbal dust is a material of particles lower than diameter of the pore of the filter bag. Due to the high content of phenols and phenolic compounds in native material, it is assumed that the appropriate method of solid-liquid extraction of such materials could enable production of a high quality product in the form of liquid extract. As a metod of „recycling“ of such a plant material extraction by system supercritical carbon dioxide and a mixture of ethanol/water (70% ethanol) was used. Extraction was carried out at pressure of 100 bar, while temperature was varied in the range from 40 to 80 ˚C. In extract content of total phenols and flavonoids was determined. The antioxidant activity, using DPPH test, and reductive capacity were determined. In the obtained extract content of dry metter was from 6,924 to 8,106 g/100 ml, the content of total phenols from 26,310 to 30,730 mg GAE/ml, and a flavonoid content from 4,902 to 5,982 mg CE/ml. Due to the high content of phenols test extract showed high antioxidant activity (IC50 from 0,0225 to 0,0141 µl/ml of the test mixture) and reducing capacity (EC50 from 0,070 to 0,044 µl/ml of the test mixture).

IP P 09

Mikrotalasna ekstrakcija lišća vinove loze i modelovanje proces

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Rezidbeni otpad od vinove loze spada u sekundarne biljne sirovine, koje zbog značajne količine bioaktivnih materija, u prvom redu polifenola, ima veliku mogućnost primene u farmaceutskoj tehnologiji. Ekstrakcija polifenolnih jedninjenja rezidbenog otpada od vinove loze vršena je mikrotalasnom ekstrakcijom. Uticaj različitih parametara ekstrakcije (koncentracije etanola (40-80%), vremena ekstrakcije (15-35 min) i snage mikrotalasa (400-800 W)) na prinos ekstrakcije, sadržaj ukupnih fenola, sadržaj flavonoida i antioksidativnu aktivnost, određenu DPPH testom, i reduktivni kapacitet, određen metodom Reducing power, ispitani su primenom metode odzivne površine. Kao eksperimentalni dizajn odabran Box-Behnken-ov dizajn. U dobijenim ekstraktima sadržaj ukupnih fenola iznosio je od 1,3764 do 2,8228 mg EGK/ml, sadržaj ukupnih flavnooida od 0,6768 do 1,3063 mg EK/ml. Antioksidativna aktivnost dobijenih ekstrakata iznosila je od 0,000321 do 0,000730 ml ekstrakta/ml. Eksperimentalno dobijeni rezultati su opisani modelom polinoma drugog reda koji je ocenjen analizom varijansi (ANOVA). Uticaj pojedinih nezavisnih promenljivih sagledan je na trodimenzionalnim graficima koji su dobijeni pomoću modela polinoma drugog reda. Zatim je izvršena optimizacija procesa za svaki parametar posebno, kao i za sve parametre istovremeno, kako bi se dobio maksimalan prinos polifenolih jedinjenja i antioksidativna aktivnost.

Microwave-assisted extraction of green vineprunings and modeling the process

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Green vineprunings is the secondary plant material which contains significant amounts of bioactive substances, primarily polyphenols, and therefore it have great potential for pharmaceutical technology. Extraction of polyphenols from green vinepruning was done by microwave assisted extraction. The effects of different extraction parameters (ethanol concentration (40-80%), extraction time (15-25 min) and microwave power (400-800 W)) on the extraction yield, total phenol, total flavonoid content, antioxidant activity, determinate by DPPH method, and reductive capacity, were investigated using a response surface method. For experimental design was chosen Box-Behnken's design. In obtained extracts content of total phenols was in the range from 1,3764 to 2,8228 mg EGK/ml, content of total flavonoids was in the range from 0,6768 to 1,3063 mg KE/ml. Antioxidant activity was from 0,000321 to 0,000730 ml ekstrakta/ml. Experimental results are described by the second order polynomial model. Model was estimated using analysis of variance (ANOVA). The effect of some independent variables was presented by three-dimensional plots obtained by using a second order polynomial model. Then the optimization process carried out for each parameter separately, as well as for all parameters at the same time, in order to obtain maximum yields of polyphenols compounds and antioxidant activity.

IP P 10

Sinteza i karakterizacija katalizatora na bazi zeolita za dobijanje industrijski značajnih hemikalija depolimerizacijom lignina

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Katalizatori na bazi zeolita pripremljeni su i okarakterisani u cilju primene u procesu mikrotalasne depolimerizacije lignina, za dobijanje industrijski značajnih hemikalija. Zeoliti H-ZSM-5, H-Y, H-BETA i H-Mordenit, impregnirani su nano-česticama NiO mehanohemijskim postupkom (MCDM). Smeša zeolita i čvrstog nikal(II)-hlorida tretirana je u Retsch PM-100 planetarnom kugličnom mlinu tokom 10 min na 350 rpm. Proizvodi su zatim kalcinisani na 400 °C u struji vazduha tokom 4 h. Dobijeni katalizatori su okarakterisani različitim instrumentalnim tehnikama: rendgenskom difrakcijom praha (PXRD, Bruker D8 Discover), merenjem specifične površine - adsorpcijom N_2 (ASAP 2010, Micrometrics), kao i transmisionom elektronskom mikroskopijom (TEM, FEI Tecnai G2 20 S-TWIN Scanning Transmission Electron Microscope System). Kod svih dobijenih proizvoda, primenjeni postupak nije doveo do narušavanja kristalne strukture zeolita, a specifična površina delimično je smanjena usled nastanka nikal(II)-oksida. TEM-analizom je utvrđeno da su oksidne čestice nanometarskih dimenzija (oko 60 nm) sa strukturom bunsenita. Aktivnost dobijenih katalizatora ispitana je u depolimerizaciji Biolignin^{TM} u CEM Discover mikrotalasnom reaktoru (300 W, 1 h) u prisustvu mravlje kiseline kao proton-donora. Najveći prinos bio-ulja dobijen je u prisustvu NiO/H-ZSM-5.

Synthesis and characterization of zeolite-based catalysts for obtaining of industrial important chemicals from lignin depolymerisation

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Zeolite-based catalysts were prepared and characterized in order to be used in a microwave-assisted depolymerisation of lignin, for obtaining industrial chemicals. Zeolites H-ZSM-5, H-Y, H-BETA and H-Mordenite were impregnated with nano-NiO particles by mechanochemical dry milling (MCDM) method. The mixture of zeolite and nickel(II) chloride was treated in a Retsch PM-100 planetary ball mill during 10 min at 350 rpm. The products were then calcined at 400 °C under air for 4 h. The obtained catalysts were characterized by different characterization techniques: powder X-ray Diffraction (Bruker D8 Discover), N_2 physisorption (ASAP 2010, Micrometrics) and Transmission Electron Microscopy (TEM, FEI Tecnai G2 20 S-TWIN Scanning Transmission Electron Microscope System). The applied procedure did not affect crystal structure of the zeolites but slightly decreased specific surface area due to the formation of nickel(II) oxide. TEM analysis showed that the oxide particles of nanometer size (about 60 nm) have structure of bunsenite. Activity of the obtained catalysts was tested in the depolymerisation of Biolignin^{TM} which was performed using CEM Discover microwave reactor (300 W, 1 h) in the presence of formic acid as a proton-donor. The highest bio-yield was obtained in the presence of NiO/H-ZSM-5.

IP P 11

Mogućnost uklanjanja fenola iz otpadne vode drvne industrije elektrohemijski sintetisanim feratom(VI)

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Tretman otpadne vode (OV) iz drvne industrije je od velikog značaja zbog velike koncentracije i toksičnosti fenola i njegovih derivata. Visoke koncentracije fenola u OV iz drvne industrije potiču od pentahlorofenola (PCP) koji se koristi za konzervaciju drveta. Prema Pravilniku o opasnim materijama u vodama (Službeni glasnik SRS, br. 31/82) dozvoljena koncentracija fenola u vodama III i IV kategorije je 300 μg/L. Konvencionalne metode za uklanjanje fenola iz OV kao što su adsorpcija, biološka ili hemijska oksidacija, koagulacija, ekstrakcija i podesavanje pH su ili ekološki ili ekonomski neprihvatljive. Tretman feratom(VI) ima značajne prednosti u odnosu na konvencionalne postupke: korišćenje jedne hemikalije, jednog sistema za doziranje i mešanje, manja proizvodnja mulja i izbegavanje formiranja toksičnih sporednih proizvoda koji mogu nastati primenom hlora i njegovih jedinjenja kao sredstava za oksidaciju. Predmet ovog rada je tretman uzoraka OV iz drvne industije, iz termo sušare i parione, elektrohemijski sintetisanim feratom(VI), korišćenjem Jar postupka. Početna koncentracija fenola u uzorku iz termo sušare je bila 27 mg/l a u uzorku iz parione 30 mg/l. Ova voda ima i visok sadržaj prirodnih organskih materija (HPK uzorka iz termo sušare je bila 3233,1 mgO_2/l a uzorka iz parione 4692,1 mgO_2/l). Efikasnost uklanjanja fenola feratom(VI) je bila 74,85% i 72,67% za uzorke iz termo sušare i parione, respektivno.

Possibility of phenol removal from wood industry wastewater by electrochemically synthesized ferrate(VI)

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Treatment of wastewater (WW) from the wood industry is of great importance due to high concentration and toxicity of phenol and its derivatives. High concentration of phenol in WW of the wood industry originates from pentachlorophenol (PCP), which is used for wood conservation. According to the Regulations on Hazardous Substances in Water (Službeni glasnik SRS, br. 31/82) allowed phenol concentration in waters of the III and IV class is 300 mg/l. Conventional methods for removal of phenol from WW, such as adsorption, biological or chemical oxidation, coagulation, extraction and adjustment of pH are either environmentally or economically unacceptable. The use of ferrate(VI) as a multifunctional chemical reagents has significant advantages over conventional methods: use of one chemical, one system for dosing and mixing, reduced sludge production and avoiding the formation of toxic by-products that may be incurred by using chlorine and its compounds as oxidizing agents. The subject of this paper is treatment of samples of WW from the wood industry, from the thermal dryer and steam chamber, by electrochemically synthesized ferrate(VI) using the Jar procedure. The initial concentration of phenol in the sample from the thermal dryer was 27 mg/l and in the sample from the steam chamber 30 mg/l. This wastewater also has a high content of natural organic matter (COD of the sample from the thermal dryer was 3233.1 mgO_2/l and COD of the sample from the steam chamber was 4692.1 mgO_2/l). The efficiency of removal of phenol by ferrate(VI) was 74.85% and 72.67% for samples from the thermal dryer and the steam chamber, respectively.

IP P 12

Complex formation and liquid-liquid extraction in the niobium (V) – 2,4-dihydroxythiophenol– hydrophobic amines system

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The real work is devoted to studying of reaction of a complex formation of Niobium (V) with 2,4-dihydroxythiophenol (DHTP), and hydrophobic amines (Aм). As hydrophobic amine aniline (An), N-methylaniline (mAn) and N, N-dimetilaniline (dAn) were used.
Chloroform was found to be the most effective. At the optimum conditions this solvent provides degrees of extraction R=98.3-98.6%. Extractable ternary complexes are formed in acidic and weakly acidic medium (pH 3.1-6.2; pH_{opt} 4.3-5.0). Maximum and constant Nb(V) extraction can be achieved at DHTF and HAs concentrations not lower than $(0.95\text{-}1.28)\times10^{-3}$ mol L^{-1} and $(1.0\text{-}1.2)\times10^{-3}$ mol L^{-1}, respectively. The extraction equilibria establish within 5-10 minutes. The absorbance of the extracts is stable for at least 72 hours. The absorption bands in the visible range of the ternary Nb(V)-DHTF-Am complexes are symmetrical and relatively narrow (λ_{max}=420-430 nm). The Komar-Tolmachev method also allows to calculate the true molar absorptivity of the complex: $\varepsilon = (3.5\text{-}3.9)\times10^4$ L mol^{-1} cm^{-1}. The molar ratios between the components of the ternary complex were found by several methods: straight line method, equilibrium shift method and crossed lines method (Nb:DHTP:Am=1:2:2). Nazarenko method that Nb(V) in the complexes was present in the form of $Nb(OH)_3^{2+}$. Nb(V) may be determined in the range 0.44-20 μg/ml.
The results showed that great excesses of alkali, alkali earth, and rare earth elements, as well as NO_3^-,ClO_4^-, $SO_4{}^{2-}$ and CH_3COO^- do not interfere determination of niobium with DHTP and Am. Interference of most cations masked by the addition of complexone III. Tartrate mask the milligram quantities of Ta, Ti, W and Mo. Zr fluorides should mask, and copper-thiourea.
The proposed method under the already established optimum conditions was applied for the determination of Nb (V) in steels of different brands.

Conclusions

Mixed-ligand complexes of Nb (V) with 2,4-dihydroxythiophenol and hydrofob amins have been studied by spectrophotometry. Extraction of mixed ligand complexes is maximal at pH 3.1-6.0. The molar absorptivities belong to the interval $(3.75\text{-}3.9)\times10^4$ L mol^{-1} cm^{-1} for the complexes of Nb(V). A procedure has been developed for extraction-spectrophotometric determination Nb in steels of different brands.

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