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Serbian Young Chemists' Club

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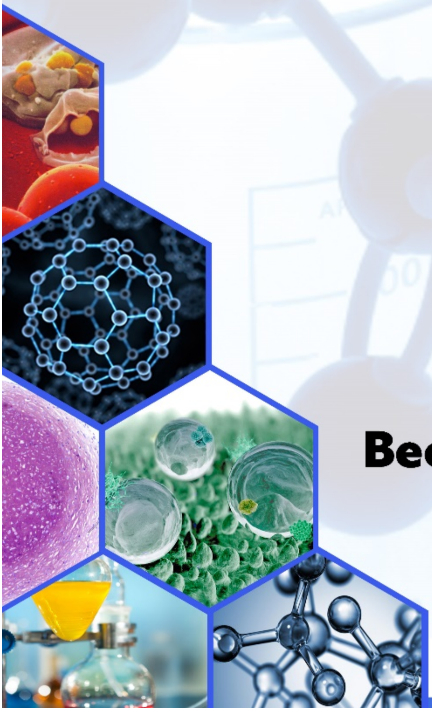
Kratki izvodi radova

Sixth Conference of the Young Chemists of Serbia

Book of Abstracts



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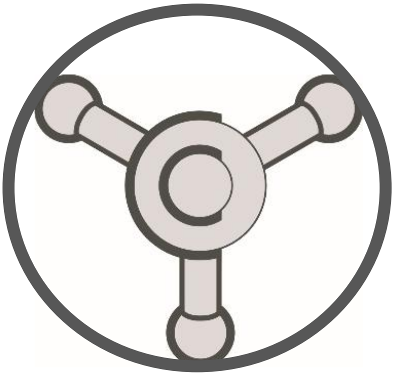

Serbian Young
Chemists' Club

Plenarno predavanje i Predavanja po pozivu

Plenary and Invited Lectures

PP 01

Planar chromatography today: application in natural product and food analysis

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Planar chromatography is a commonly used technique for analysis of food and natural products. Here, it will be presented different aspects concerning to recent development and application in HPTLC research: i) hyphenation of HPTLC with chemometrics, ii) development of bioautography assays and structure elucidation of bioactive compounds, iii) HPTLC-bioautography-chemometrics approach for classification of samples with the most beneficial health effects.

Colorful image-like high-performance thin layer chromatography (HPTLC) chromatograms are excellent input data for the image and multivariate analysis. Pattern recognition techniques were applied to the classification of different samples based on geographical and botanical origin. Constituents responsible for classifications were identified as the main markers.

Simple, low-cost, and high throughput bioautography assays were developed for the identification of compounds with potentially radical scavenging activity, antimicrobial activities as well as enzyme inhibitors from complex natural products. After bio profiling, discovered bioactive zones were online eluted and characterized by high-resolution mass spectrometry (HRMS).

Besides, HPTLC-bioautography-chemometrics approach which combines pharmaceutical activities showed the potential to identify and cluster the samples regarding their health-related activities, and thus, to find samples with the most beneficial application.

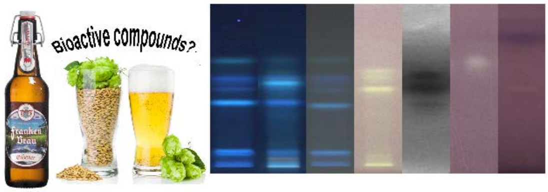

Figure 1. The HPTLC chemical /biological phenolic profile of German beer sample.

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Acknowledgments

This work has been supported by the Ministry of Education and Science of Serbia, Grant No.172017 and DAAD bilateral project No. 451-03-01732/2017-09-11.

PPP 01

Covalent functionalization of black phosphorus

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Since 2014, two-dimensional (2D) Black Phosphorus (BP) has attracted enormous attention throughout the scientific community due to its high p-type charge carrier mobility up to ~6000 $cm^2 V^{-1} s^{-1}$ and its tuneable direct band gap ranging from ~0.3 eV for bulk to ~2 eV for monolayers.[1] However, due to its poor stability under ambient conditions, this material has to be somewhat modified. The first chemical bulk reductive covalent functionalization of thin layer black phosphorus (BP) beginning with BP intercalation compounds has been developed. Through effective reductive activation, covalent functionalization of the charged BP is achieved by organic alkyl halides. Functionalization was extensively demonstrated by means of several spectroscopic techniques, showing higher functionalization degrees than the neutral routes. Moreover, these results were complemented by means of DFT calculations.

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Acknowledgments

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PPP 02

Interaction of human immunoglobulins with metalloporphyrins

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Heme is a coordination complex of an iron cation and a cyclic tetrapyrrole ligand – protoporphyrin IX. Many biologically important metalloproteins contain heme as a prosthetic group that endows them with various functionalities. It was also demonstrated that a fraction of antibodies present in all healthy individuals was able to bind heme and subsequently started to recognize multiple structurally unrelated protein antigens (1). However, molecular mechanisms of heme binding and the induction of polyreactivity of antibodies are not known. Heme molecule is able to form different non-covalent interactions with both polar and non-polar amino acids. Valuable information on the nature of interactions were obtained by following the effect of change in the structure of antibody or metalloporphyrin on the binding. Site-directed mutagenesis of selected heme-sensitive antibody (2) revealed that four tyrosines in CDR3 region were important, but none of the individual mutations was completely detrimental for the binding. When all tyrosines were replaced with alanine or serine, complete loss of binding followed. From the investigation of diverse metalloporphyrins it was concluded that the presence of coordinating metal is essential for the interaction. Small changes in porphyrin ring structure also had an effect on the intensity of binding. Additionally, after treatment with moderate excess of hydrogen peroxide, oxidized heme showed a considerably higher potential for immunoglobulin binding compared to its non-oxidized analogue. This was not observed for any of the other porphyrin molecules.

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Acknowledgments

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Biohemija i biotehnologija
Biochemistry and biotechnology

BB01 PE 1

Heterocyclic guanylhydrazones inhibit heme-induced antibody polyreactivity

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Various *in vitro* studies have demonstrated that exposure of human antibodies to heme can result in the appearance of binding polyreactivity (1). Although the phenomenon has never been directly observed *in vivo*, it is known that hemolytic disorders are often accompanied by the presence of autoantibodies and the deposition of immunoglobulins in kidneys. If these pathologies are a consequence of binding of heme to antibodies, drugs that can prevent the binding would be a useful addition to the therapy of the hemolytic diseases. A series of guanylhydrazones (2) were tested for the inhibition of heme-induced polyreactivity of the selected heme-sensitive antibody. It was demonstrated that compounds were excellent inhibitors of the induced binding to three different antigens, with some of the compounds completely neutralizing the heme-mediated polyreactivity at two times molar excess compared to heme.

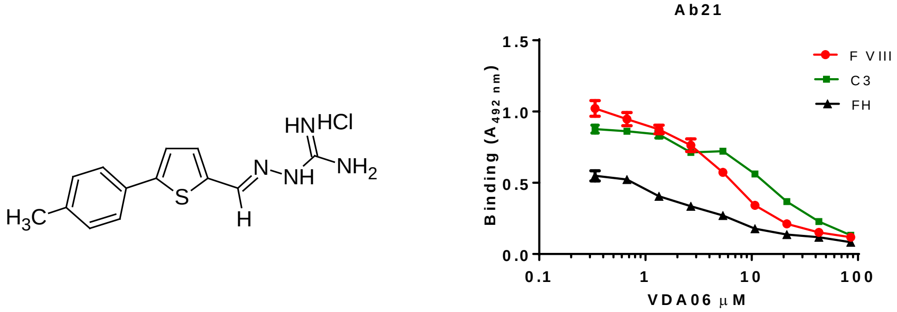

Figure 1. Structure of VDA06 and its inhibitory activity.

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BB02 PE 2

Antioxidant and pro-oxidant properties of catecholamines and their metabolites towards hydroxyl radical

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The hydroxyl radical ($^{\bullet}OH$) in biological systems, due to its high reactivity, can react practically with all biologically important molecules. The main source of the hydroxyl radical in living systems is Fenton reaction (reaction between Fe(II) and H_2O_2)[1]. In the central nervous system (CNS), because of the inability of artificial antioxidants to pass through the blood-brain barrier, neurotransmitters and their metabolites act as the first line of defense against hydroxyl radical. Also, it is shown that catecholamines and their metabolites can form complexes with Fe(III) and promote the Fenton reaction[2] primarily by promoting the availability of Fe(II) to react with H_2O_2. The reaction of dopamine, epinephrine, norepinephrine, 3,4-dihydroxy-L-phenylalanine (L-DOPA), catechol as well as their metabolites (3,4-dihydroxyphenylacetic acid (DOPAC), homovanilic acid (HVA), vanillylmandelic acid (VMA) and 3-methoxytyramine (3-MT)) with hydroxyl radical generated in Fenton reaction were investigated experimentally at different pH values. Electron paramagnetic resonance (EPR) spectroscopy was used to monitor this reaction. At pH 3,3 catecholamines and their metabolites with catechol moiety show strong pro-oxidant activity which results in producing more OH radical, while metabolites without catechol moiety show weak antioxidant properties. This is because the ability of molecules with catechol moiety to form monocomplexes with Fe(III) which leads to the reduction of Fe(III) and promotion of the Fenton reaction. Molecules without catechol moiety can't form this complexes and they show antioxidant properties. At pH 7,8 the investigated molecules did not enhance the production of OH radicals. Molecules with catechol moiety showed strong antioxidant properties, while molecules without it showed again weak antioxidant properties. At this pH, the investigated molecules with catechol moiety are forming bis-complexes through which iron is sequestered from the reaction system and thereby prevented from reacting with other compounds such as H_2O_2.

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BB03 PE 3

Antioxidant potential of R-phycoerythrin, red protein isolated from macroalga *Porphyra* spp.

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Algae have been consumed as food and medicine for centuries. Their benefits are so pronounced, due to high concentrations of vitamins, minerals, antioxidants and proteins, that they are commonly referred to as superfoods. R-phycoerythrin (R-PE) is a red protein-pigment complex from the light-harvesting phycobiliprotein family, present in large quantities in red algae. It contains covalently bound open chain tetrapyrolle pigments: red phycoerythrobilin and yellow-orange phycourobilin. This study aims to evaluate the antioxidant potential of R-PE from commercially available red alga *Porphyra* spp. ("nori"). Two other phycobiliproteins (with dark blue phycocyanobilin pigment): R-phycocyanin (also isolated from *Porphyra* spp.) and C-phycocyanin (from Hawaiian Spirulina Pacifica), were used for comparison purposes. Purified phycobiliproteins were evaluated for antioxidant and metal ion chelating activity by various *in vitro* antioxidant assay systems: DPPH–, ABTS–, hydroxyl radical–, and superoxide anion radical–scavenging activity, ferric ion reducing ability of plasma (FRAP) assay, ferrous ion-chelating activity (FICA), and reducing power (RP) assay. The results showed R-PE exhibit concentration-dependent antioxidant potential similar to, if not better than that found in phycocyanins, confirming the exceptional value of R-PE as a nutraceutical (dietary supplement, functional food and pharmaceutical).

BB04 PE 4

The influence of alkaline environment on ureolytic bacteria *Sporosarcina pasteurii*

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The ureolytic bacteria are one of the most efficient microorganisms able to produce high amount of carbonate that easily react with the free calcium ions from the environment. The controlled use of these bacteria as agent of bioremediation offers a new approach for preservation, protection and restauration of building materials (1). When ureolytic bacteria are used as biohealing agent, it is unavoidably exposed to complex environmental conditions. In order to study the activity of *S. pasteurii* DSM 33 in different conditions, experiment such as strong-alkaline tolerance and presence of urea in nutrient media were conducted (2).

The aim of this study was to identify the influence of the alkaline environment (pH value of 8 to 13) on the production of *S. pasteurii* biomass. In order to achieve a high yield of biomass, the culture was aerobically incubated at 30 °C for 48h on Tripton Soya Broth (with and without addition of urea). The pH value of the TSB medium was increased by two different solutions (non-carbonate solution 1M NaOH and carbonate solution Na-sesquicarbonate). The effect of the pH value was conducted in terms of biomass concentration on Trypton Soya Agar with the addition of 20% urea. Furthermore, the change of pH value was monitored at the start and at the end of the experiment.

The results show that the strong-alkaline environment (>10) is close to the inhibition of ureolytic activity, but it does not strongly affect the bacterial growth. Moreover, bacterial activity is enhanced with the addition of urea, specifically in nutrient media with pH value of 9 and 10. According to the obtained results, *S. pasteurii* biomass can be used in alkaline environment, as a part of the self-healing system for the cementitious materials.

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Acknowledgments

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BB05 PE 5

Microbiological quality of indoor air in university and school rooms

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Air quality of indoor environments is one of the most important factors that directly affect human health. The human health may be corrupted by the presence of airborne and air-transmitted microorganisms including bacteria, fungi and viruses, because people spends about 80-90% of their time in indoor environments by inhaling on average 14 m^3 of air per day (1).

The purpose of this study was to evaluate the concentration and composition of bacteria and fungi of in the most used rooms at Faculty of Technology Novi Sad and in Secondary school Svetozar Marković in Novi Sad.

The air sampling was performed in 5 rooms at the Faculty (laboratory, student's laboratory, reading room, meeting room and the main hall of the faculty) and in 5 rooms of the Secondary school (classroom, assembly hall, meeting room, library and the main hall of the school). In order to determine the concentration of the present bacteria and fungi two methods were employed: the settle plate method and air sampling with MAS-100® Microbiological Air Sampler at air flow of 100 L/min. During sampling procedures, two culture media were used: Plate Count Agar and Potato Dextrose Agar. Isolates were identified according to their macro- and micromorphological characteristics and, in case of fungi isolates, by usage of fungi identification key (2).

The total number of bacteria and fungi was almost the same in rooms at the Faculty and the Secondary school. The highest number of bacteria and fungi was isolated in reading room at Faculty and in classroom in the Secondary school. According to the obtained results the most isolated bacteria were gram-positive and rod-shaped, whereas *Alternaria*, *Penicillium* and *Aspergillus* were predominant among fungi.

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BB06 PE 6

The influence of the extraction technique and the applied solvent on the biological activity of the extracts of *Sambucus nigra* L. flowers

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The European elderberry (*Sambucus nigra* L.) is an attractive shrub, grows in subtropical and temperate areas, and is in addition to Europe widespread in America, Africa, Asia and New Zealand and produces flowers and berries. The elderflowers used to make foodstuffs and also used in folk medicine to the prevention of several degenerative diseases such as cancer, inflammatory and cardiovascular diseases, and diabetes. The elderberry represents an unused biopotential for the production of new phytopreparates [1].

Plant material, collected in June in Montenegro. The extracts were prepared using maceration as an extraction technique, using two solvents (water and 50% ethanol) in ratio 1:30. Antioxidant potential was analyzed using in vitro antioxidant assays: ABTS DPPH and CUPRAC. Total phenolic and total flavonoid content were determined spectrophotometrically. Enzyme inhibitory effects were tested against acetylcholinesterase and glucosidase. The obtained results have shown that samples have strong bilogical activity. Higher antioxidant activity was achieved by using 50% ethanol as a solvent in all three applied assays. Also, the analyzes have determined that the extract of 50% ethanol have a higher content of total phenols and flavonoids in compared with water extract (50% ethanol extract 322.25±8.75 and water extract 187.25±2.09 mg GAE/g extract for total phenols; 50% ethanol extract 95.11±0.70 and water extract 46.50±1.17 mg CE/g dry matter for flavonoids). Stronger inhibition of both analyzed enzymes is caused by 50% ethanol extract. In this way, the flowers of *Sambucus nigra* may be initial material for the future investigation in order to examine them in greater detail and to determine their potential application in food and pharmaceutical preparations.

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Hemija hrane
Food chemistry

HH01 PE 1

Determination of iron and zinc content in organic and conventional spelt seed *(Triticum spelta)*

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Numerous scientific studies around the world have proven the existence of significant differences in the content of macro- and microelements between organically and conventionally produced food [1, 2]. Spelt (*Triticum spelta*) represents commonly grown organic crops due to the ideally balanced ratio of nutrients. Bearing in mind importance of iron (Fe) and zinc (Zn) for the normal functioning of the human organism, the aim of this paper was to examine their content in organically and conventionally produced spelt seeds. Determination was conducted by using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) with previous digestion of samples. The obtained results were expressed as mg/kg of dry weight (DW). Quantity of both elements was higher in conventionally grown spelt seed (Fe: 45.832 mg/kg DW; Zn: 30.932 mg/kg DW) compared to organically grown seed (Fe: 32.595 mg/kg DW; Zn: 26.377 mg/kg DW).

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HH02 PE 2

Quality assessment of geographically different fruit juices by HPTLC bioautography/MS fingerprint combined with chemometrics

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Fruit products are a treasured source of different bioactive compounds such as phenolic acids, flavonoids, and carotenoids. Different pharmaceutical effects such as antioxidative, antimicrobial, and anticancer, have been associated with fruit juice consumption.[1] The aim of the present study was the quality assessment of 36 geographically different apple and grape juices from Serbia and Germany, using high-performance thin-layer chromatography (HPTLC) and bioautography hyphenated with pattern recognition technique. The bioautography assays were performed for the identification of constituents with potential radical scavenging activity, enzymes inhibition, and antimicrobial activity from complex juice extracts. Furthermore, HPTLC-electrospray ionization high-resolution mass spectrometry (ESI-HRMS) was used for characterization of bioactive compounds from investigated extracts. Principal component analysis confirmed the separation between geographically different juice samples and recognized their main markers. Several constituents such as chlorogenic acid, phloridzin, epicatechin were identified as potential bioactive compounds from juices.

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Acknowledgment

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HH03 PS 3

Determination of the content of biometals in various honey samples using inductively coupled plasma optical emission spectroscopy

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Honey is natural substance created by honey-bearing bees. About 95% of dry honey matter are carbohydrates, mostly fructose and glucose. Aside from sugar, honey contains amino-acids, enzymes, vitamins, flavonoids, phenols and minerals in small amounts. [1] Na, K, Ca and Mg are often referred to as to macronutrients. These are necessary for regular function of the entire organism.

The aim of this paper was determination of Na, K, Ca and Mg content in various honey samples by using inductively coupled plasma optical emission spectroscopy (ICP-OES). Twenty honey samples were tested. The samples were prepared by the wet digestion method.

The content of calcium in honey samples was in the range of 23.2 mg kg^{-1} to 143.1 mg kg^{-1}, magnesium content was in the range of 3.5 mg kg^{-1} to 121.5 mg kg^{-1}, potassium content was in the range of 10 mg kg^{-1} to 1370 mg kg^{-1}, while the content of sodium was in a very narrow range of 12.2 mg kg^{-1} to 13.6 mg kg^{-1}. These values correlate with the values obtained by other authors. [2] Higher content of the examined elements was detected in forest and meadow honey samples, while acacia and linden honey samples showed lower content of these elements.

Based on the obtained results in this study, it can be concluded that the content of examined elements is higher in polyfloral types of honey, compared to monofloral ones. In additon, it can be concluded that homemade honey contains higher amount of examined elements, compared to the honey that can be bought in supermarket. Honey is not an essential source of these elements but the use of honey in everyday diet can contribute to total daily intake of those.

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Acknowledgments

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HH04 PE 4

Development of a novel HPTLC method for the evaluation of the authenticity of apricot and pumpkin juices

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The European Commission requires that fruit products distributed on the market are authentic and of high quality. Since the lower costs, pumpkin juice is used to be added in a certain amount to apricot products, this unauthorized addition must be figured out by establishing criteria [1]. Different carotenoid profiles of apricots and pumpkins could be the key point in this particular case. The main aim of the research was the establishment of criteria for the authenticity evaluation of some apricot juices, which will result in a new analytical method for the detection of adulteration of apricot juice with pumpkin juice. The HPTLC separation of carotenoids of 13 pure juices of apricot and pumpkin and their mixtures from 5 to 50% was performed using RP-18 plates with a mixture of methanol, ethyl acetate and *n*-hexane (85:20:15, *V*/*V*/*V*) as mobile phase. Line profiles of pure apricot, pumpkin, and their mixtures were evaluated using ImageJ software to find a qualitative difference between the investigated samples. Densitometric detection and quantification of *β*-carotene and zeaxanthin were performed (Figure 1). The optimized HPTLC method confirmed differences in the carotenoid profiles between apricot and pumpkin and identified responsible markers.

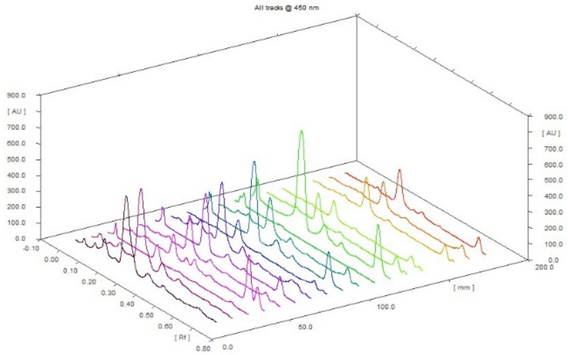

***Figure 1**: HPTLC densitogram of β-carotene and zeaxanthin at 450 nm*

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Hemija makromolekula i nanotehnologije

Chemistry of macromolecules and nanotechnology

MN01 PE 1

NMR analysis of single molecule magnets

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Single Molecule Magnets (SMMs) are paramagnetic complexes with potential applications as memory storage devices or in quantum information processing.[1,2] Since their discovery, SMMs are commonly studied in the solid state, at temperatures close to zero Kelvin. The purpose of this thesis was to study SMMs with solution NMR, utilizing the sensitivity of the chemical shifts to the spin density. Experimental measurements were supplemented with density functional theory calculations. Due to the favorable relaxation in lanthanide and some 3d-complexes, well-resolved 1D and 2D spectra of commonly observed nuclei (^{1}H, ^{13}C, etc.) were obtainable. It was possible to study the solution structure[1], structural changes due to e.g. redox processes or (de)protonation, magnetic exchange couplings, the direction of the magnetic easy axes[2], ion pairing, dynamic processes, dimerization and to screen for potential SMMs by comparing magnetic susceptibility anisotropies.

In summary, it was shown that solution NMR is a useful and widely available addition to the already well-established methods for the characterization of SMMs.

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MN02 PE 2

Synthesis and characterization of novel semi-degradable, pH and temperature sensitive hydrogels based on 2-hydroxyethyl methacrylate and 2-hydroxyethyl acrylate

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Hydrogels represent three-dimensional hydrophilic polymer networks, capable of absorbing large quantities of water[1]. Due to their tissue-like characteristics, hydrogels have been widely used for a variety of biomedical and pharmaceutical applications. The synthesis and characterization of novel semi-degradable, pH and temperature sensitive hydrogels is presented in this work. These new functional hydrogels represent copolymers based on 2-hydroxyethyl methacrylate (HEMA) and 2-hydroxyethyl acrylate (HEA), crosslinked using poly(β-amino ester) (PBAE) degradable macromer. PBAE crosslinker was synthesized by Michael addition reaction of diethylene glycol diacrylate (DEGDA) and piperazine. PBAE chemical structure was confirmed by proton nuclear magnetic resonance (^{1}H NMR) and Fourier transform infrared (FTIR) spectroscopy. HEMA/HEA/PBAE hydrogels were synthesized by free radical copolymerization, by varying the monomer ratio. Structural characterization of hydrogels was carried out using Fourier transform infrared spectroscopy (FTIR). Swelling studies, performed in different pH buffers, ranging from 2.00 to 7.40, and different temperature values, ranging from 20 to 55°C, showed the pH and temperature sensitivity of the hydrogels. From the obtained results it can also be concluded that the swelling and degradation rates of new hydrogels can easily be adjusted by altering the comonomer ratio, making them a class of materials that is particularly suitable for potential drug delivery and tissue engineering applications.

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MN03 PE 3

Mesotrione photodegradation catalyzed by TiO_2 and fullerenol in the presence of electron acceptor $KBrO_3$: Kinetics and factorial design analysis

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Mesotrione [2-(4-methylsulfonyl-2-nitrobenzoyl)cyclohexane-1,3-dione] is a triketone herbicide for pre- and post-emergence control of broadleaf and some grass weeds in maize [1]. Beside the good properties of mesotrione in control of weeds there are harmful and toxic effects on non-target organisms. Moreover, widespread use of mesotrione may cause environmental threat because of its residue in soil and environmental waters [2]. Due to the undesirable presence in the environment there is a need for efficiently removing of mesotrione. Photocatalytic degradation has attracted increased attention because of its efficiency and degradation of organic pollutants to non-toxic substances. There are many operational parameters influencing the efficiency of photocatalytic degradation of organic pollutants. Furthermore, the effect of different operational parameters and interactions must be evaluated in order to decide whether they should be considered for optimization method. In this paper, full factorial experimental design was used to study the influence of main parameter effects and interactions on the photocatalytic degradation of mesotrione using TiO_2 Hombikat (TiO_2) suspension under simulated sunlight. Parameters such as loading of TiO_2, concentration of $KBrO_3$, absence/presence of fullerenol and absence/presence of O_2 purging were investigated at two levels (low and high). Statistical analysis of mesotrione photocatalytic degradation efficiency (%) after 30 min of irradiation was performed. According to statistical analysis, the highest influence on the system showed loading of TiO_2 and concentration of $KBrO_3$. In addition, statistical analysis also revealed four significant interactions between two parameters and one interaction between three parameters.

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MN04 PE 4

Biosynthesis of silver nanoparticles using areal part and root aqueous extracts of purple loosestrife (*Lythrum salicaria* L.)

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Silver nanoparticles (AgNPs) are used in various applications, such as biomedical devices, biosensors, catalysis, electronics, and pharmaceuticals. However, many of chemical and physical processes currently used for the synthesis of metal nanoparticles are expensive and may be destructive to the environment. Employing biological materials, like plant extracts, for synthesizing various metallic nanoparticles proves to be an eco-friendly technology for large-scale production [1]. The aim of this study was to investigate the synthesis of silver nanoparticles using *Lythrum salicaria* L. areal part (LSA) and root aqueous extracts (LSR). *L. salicaria* (purple loosestrife, fam. Lythraceae) is an herbaceous perennial plant containing *C*-glucosidic ellagitannins and *C*-glucosidic flavonoids as dominant polyphenolic compounds [2]. For AgNPs synthesis *L. salicaria* extracts were obtained using extraction with boiling distilled water (10% w/v). The synthesis of AgNPs was induced by treating 200 ml of diluted *L. salicaria* water extracts with the same amount of aqueous solution of $AgNO_3$ and stirring the mixture. Biosynthesis was performed under the following reaction conditions: LSA and LSR were diluted 20 and 10 times, respectively; the used $AgNO_3$ concentrations were 0.02 M for LSA and 0.01 M for LSR; and the reactions proceeded at 25 ^{o}C for LSA and 80 ^{o}C for LSR, under pH 12, during 30 min for both extracts. The bioreduction of Ag^+ was monitored spectrophotometrically in the wavelength range 300-800 nm and peaks were located within 395-415 nm, indicating AgNPs formation. FTIR spectra of synthesized AgNPs and *L. salicaria* extracts were compared for identification functional groups of biomolecules that serve as reducing, capping and stabilizing agents. Based on obtained results, *L. salicaria* polyphenols acted as good reducing and capping agents. Next step in this research will be the detailed characterization of nanoparticles and their biological activities.

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MN05 PE 5

Mechanical properties and morphology of the poly(urethane-siloxane) copolymers and their clay nanocomposites

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In this paper the series of poly(urethane-siloxane) copolymers and their clay nanocomposites were synthesized based on 4,4'-diphenylmethane diisocyanate and 1,4-butanediol as the part of the hard segments (HS) and α,ω-dihydroxy-poly(propylene oxide)-*b*-poly(dimethylsiloxane)-*b*-poly(propylene oxide) as the part of the soft segments (SS). Organomodified montmorillonite clay (Cloisite 30B®) was used as nano-filler in the amount of 1 wt.% within prepared nanocomposites. Mechanical properties and morphology of these polymers were investigated by dynamic mechanical thermal analysis (DMTA) and wide angle X-ray diffraction (XRD) measurements.

Viscoelastic properties of the copolymers and their nanocomposites mostly depended on the content of the HS. The storage shear (G') and loss modulus (G'') were slightly enhanced within prepared nanocomposites, compared to the neat copolymers, due to the addition of the clay nanoreinforcements. Moreover, prepared both series of samples had phase separated morphology due to the existence of the multiple local segmental motions (T_g of the HS and SS). XRD analysis revealed that clay layers were separated into an individual layer without any regular stacking which indicates that exfoliated morphology of the clay nano-fillers was obtained inside prepared nanocomposites [1,2].

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Hemija u nastavi

Educational chemistry

HN01 OS 1

Application of web pages for self-help in teaching subjects on solutions and dissolution

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Due to the abstract nature of chemical terms, various teaching tools are used throughout the teaching process in order to help students to form clear representations of these terms. Information and Communication Technologies (ICT) make the teaching and learning of chemistry easier by enabling those involved in the system of education to prepare and implement digital multimedia teaching materials that make the attainment of learning goals and better learning outcomes possible.

This paper is a research aimed at examining the efficiency of using web pages as a teaching tool to be used by students in order to self-help in understanding and remembering the terms “solutions” and “dissolution”.

The seventh grade elementary school students from two primary schools in Belgrade participated in this study, total of them 249 took tests of which 210 with statistically analyzed results. In addition to the tests, two questionnaires were used as research instruments.

The obtained results showed that students who had accessed information on solutions and dissolution via web pages, compared to pupils who did not use them, had better performance on the tests.

HN02 PS 1

Application of eye-tracking technique for analyzing students' performances in solving systemic questions in organic chemistry

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The problem of this research was perceived in the fact that many organic chemistry concepts are characterized as difficult and abstract for learning and understanding, even for the chemistry students. In addition to performances, variables such as mental effort, time for solving problems, confidence level, also reflect students' difficulties. Henceforth, the aim of this study was to analyze these variables within 15 bachelor chemistry students, in Faculty of Sciences, Novi Sad. The research instrument contained organic chemistry problems, presented as systemic multiple-choice questions. For the purpose of further analysis with eye-tracking technique, two systemic questions were chosen: with the lowest and the highest performances. Obtained results in the form of heat maps and fixations duration highlighted a specific approach for solving systemic multiple-choice questions, as well as differences in students' abilities to perceive relevant and irrelevant parts of the diagrams.

Acknowledgments

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HN03 PS 2

Analysis of the success in solving stereochemistry problems by using eye-tracking technique

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Eye-tracking is a very powerful research tool, and its advantages made it accessible to researchers from various research areas. It found significant application in research studies in the field of education as well. Thanks to the ability to monitor every conscious and unconscious movement of the eye, this technique gives researchers an insight into the students' experience, which no other technique can provide in similar way [1]. The aim of this study was to determine to which extent bachelor chemistry students had mastered the contents of stereochemistry, employing eye-tracking analysis. A set of 5 stereochemistry problems was used in the study which subjected 17 respondents from the Faculty of Sciences, Novi Sad. Students' responses and visual attention were recorded by using the Gaze point device. In addition to analyzing students' responses, the results include the presentation of heat maps and average fixation duration, which allow deeper analysis and evaluation of the conceptual understanding among students.

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Acknowledgments

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Hemijska analiza

Chemical analysis

HA01 OE 1

First electrochemistry of arrow poison tubocurarine. Quantification in blood serum and urine samples

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In the following paper electrochemical behavior and quantitative analysis of tubocurarine has been studied for the first time. Tubocurarine (TUB) is natural plant alkaloid isolated from the plant *Chondrodendron tomentosum* which is a species of the *Menispermaceae* family [1]. *Chondrodendron tomentosum* is a tropical liana widely found in Central and South America region. TUB was used as arrow poison. Later, this compound was used during surgeries as a muscle relaxant. This alkaloid competes with acetylcholine for the nicotinic receptors at the neuromuscular junction of skeletal muscles [2].

The electrochemical behavior of TUB has been tested using several different organic solvents (DMSO, DMF and mixture acetonitrile/methanol) together with aqueous buffer solutions at different pH values (Britton-Robinson buffer solution and HNO_3), as supporting electrolytes. In mixture acetonitrile/methanol (80:20) were observed well-defined and sharp two oxidation peaks of tubocurarine at potentials around 1.15 V and 1.45 V. In 1M nitric acid (pH=1), in anodic potential range, were observed three oxidation peaks. At potential of 0.75 V occurs oxidation of tubocurarine with low current intensity, but at potentials of 1.0 V and 1.5 V well-defined and sharp two oxidation peaks were noticed. Also, it was recorder cathodic electroactivity of tubocurarine at potential of around 0.0 V. Tubocurarine quantitative analysis procedures were developed within an acetonitrile/methanol (80:20) mixture and 1 M nitric acid (pH=0), with the linear ranges from $4 \cdot 10^{-6}$ to $1 \cdot 10^{-4}$ M (LOD = $3.53 \cdot 10^{-6}$ M) and $4 \cdot 10^{-6}$ to $9 \cdot 10^{-5}$ M (LOD = $2.96 \cdot 10^{-6}$ M and $5.50 \cdot 10^{-7}$ M, depending on a selected peak), respectively. Remarkable selectivity and good sensitivity were obtained after the detection method optimization, making it applicable for the quantification of TUB in biological fluids, with excellent reproducibility, accuracy as well as precision.

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HA02 OE 2

Development of amperometric biosensors for ethanol and NADH determination based on RuO_2/graphene nanoribbons composite supported on screen printed electrode

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In the last few decades, significant efforts have been made to develop various electrochemical biosensors for the detection of numerous biological compounds such as ethanol, glucose, amino acids. Accurate and precise analysis of ethanol is of great importance in various applications while the significance of coenzyme nicotinamide adenine dinucleotide (NADH) is related to the cellular respiration redox reaction. Due to that, existence of selective and sensitive method for monitoring of this process is of great importance.

In this work we developed a new sensor for ethanol and NADH quantification. For preparation of electrochemical sensor for NADH we used screen printed carbon electrode (SPCE) enriched with new composite material based on graphene nanoribbons modified with nanoparticles of ruthenium dioxide. Additionally, surface of electrode was modified with alcohol dehydrogenase (ADH) for the preparation of amperometric biosensor for analysis of ethanol.

Synthesized composite material was characterized using microstructural (FE-SEM) and electrochemical (CV) techniques. The electrochemical response of the tested analytes was investigated as a function of important parameters. Under optimal conditions, the working linear range and limit of detection for ethanol sensing was 1–1800 μM and 0.19 μM, respectively. For NADH, the linear range was from 1 to 1600 μM with limit of detection of 0.52 μM. Moreover, effects of some possible interfering compounds were investigated and the developed procedure was applied to commercial alcoholic beverages. The results obtained showed satisfactory precision and accuracy of the developed method and confirm the proposed approach could be a possible replacement for the currently used techniques for ethanol and NADH quantification.

Acknowledgments

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HA03 PE 1

New neryl esters from *Helichrysum italicum* essential oil

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Helichrysum italicum (Roth) G. Don (*Asteraceae*), commonly known as the everlasting or curry plant, is endemic to the Mediterranean region where at least 3 subspecies can be found. The typical subspecies (*italicum*) produces an essential oil rich in the acetate (≥ 30%) and propionate (≥ 5%) of nerol, and the characteristic β-diketones (≥ 10%). It is appreciated by perfumers because of the spicy saffron character well complemented with curry, nutty and celery facets [1]. As esters are an important group of aroma-active volatiles, in this work we aimed to study the composition of the ester fraction of the mentioned everlasting essential-oil chemotype. After chromatographic separations, our attention was focused on the ester fraction that contained numerous minor neryl and angeloyl esters undetectable in the direct GC-MS analyses of the unfractioned oil (series A and B, respectively; Fig. 1). Three esters of nerol and medium-chain *anteiso*-fatty acids (C_7, C_9 and C_{11}) represented new natural products, while several other esters (e.g. neryl decanoate and dodecanote, and phenethyl, heptyl and octyl angelates) have a rather restricted occurrence in the Plant Kingdom. Our study disclosed an extensive diversity of volatile esters present in the studied chemotype, some of which may contribute to the overall aroma-profile of the essential oil.

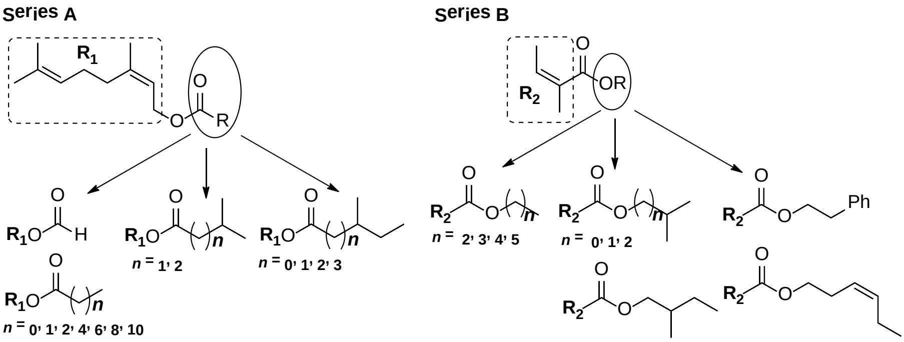

Figure 1. Structures of neryl and angeloyl esters identified in H. italicum essential oil.

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HA04 PE 2

Optimization of solid-phase extraction for analysis of artificial sweeteners in water

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After decades of using artificial sweeteners in the food and pharmaceutical industry, their ubiquitous presence in the environment has been determined [1,2]. These substances are recognized as emerging pollutants due to limited data on their occurrence, environmental fate and ecotoxicity. Prior to analysis of artificial sweeteners at trace levels in water samples, it is necessary to isolate and concentrate analytes and clean-up the obtained extracts. In this paper, the optimization of the preparation method for the determination of saccharin, sucralose and neotame in water by solid-phase extraction (SPE) was performed. The extracts were analyzed by liquid chromatography–tandem mass spectrometry (LC–MS/MS). In the SPE optimization, the following parameters were tested: the sorbent type, the pH value and the volume of water sample and the elution solvent. The suitability of anion-exchange, polymeric, C18 and carbon sorbents for the extraction of selected sweeteners was assessed. The results showed that the highest recoveries were obtained using polymeric Oasis HLB cartridges, with copolymer poly(divinylbenzene-co-N-vinylpyrrolidone). Furthermore, it was determined that the pH value of water sample was crucial for extraction efficiency. For all three artificial sweeteners, the optimal pH value of the sample was 3. Finally, the sample volume of 100 ml ensured a high preconcentration factor without the sorbent breakthrough, and methanol was selected as the elution solvent.

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HA05 PE 3

Chemical composition of hexane extract of Artemisia scoparia Waldst. et Kit.

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Artemisia scoparia Waldst. et Kit., also known as redstem wormwood, is a member of genus *Artemisia*, family Asteraceae. The plant is well known in traditional medicine for its pharmacological properties. The aerial parts of the plant in the full-blooming stage were collected at Niška Banja site, near Niš, Serbia. Hexane extract was prepared using dry, grinded plant material (10 g of the plant was overflowing with 100 mL of hexane). Submerged material was kept for 72 hours in the dark, at room temperature, filtered and evaporated on a rotary vacuum evaporator. The dry extract weight was 0.09 g. The chemical composition of the hexane extract of *A. scoparia* was analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS). The number of identified components was 125, which representing 99.3% of the total GC peak areas. The major class of compounds was straight-chain alkanes, with a share of 60.5% of total extract. The most abundant component was nonacosane (19.4%), which represented about 1/5 of total oil composition. Other compounds present in significant amounts were hentriacontane, heptacosane, capillene and stigmasterol (11.0%, 9.0%, 5.8% and 5.5%, respectively). To the best of our knowledge this was the first time that anyone analyzed hexane extract using GC and GC/MS.

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Ministry of Education, Science and Technological Development of the Republic of Serbia [172047].

HA06 PE 4

Determination of some toxic elements in water samples from Bojana river, Montenegro - preliminary study

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Since the beginning of life on Earth, water is one of the most precious natural resources. A series of inorganic, organic and biological pollutants, such as highly toxic heavy metals threaten the water quality [1, 2]. No matter how enormous available amounts of water in nature are, its usability has been significantly decreased by pollution and only 0.3% of all world's water resources is fresh water which can be used for drinking or industrial purposes.

The aim of this study was to determine content of selected toxic elements (Pb, As and Mn) in water samples from the place where Bojana river (Montenegro) forms a small delta (**S1**), and the other one where it flows into the Adiatic Sea (**S2**). All samples were collected and analysed in August 2017. The contents of elements were determined using ICP analysis and obtained results have shown that the concentrations of As were 1.95 (**S1**) and 2.84 µg/L (**S2**). Furthermore, the content of Pb in **S2** was below the limit of dection (< 0.1 µg/L), while in **S1** was 2.23 µg/L. Additionally, Mn was not detected in **S1**, while the concentration of this element was 2.92 µg/L in sample **S2**.

On a long-term basis, the presence of the mentioned elements is not harmful and does not have a negative effect on human skin. Further research will focus on testing other potentially toxic microelements with the goal to evaluate quality of water from this area.

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HA07 PE 5

Determination of tritium activity: measurement uncertainty

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The analysis of the radioactive isotope tritium in water samples is done after the distillation of the samples and their electrolytic enrichment (because of the very low level of radioactivity) in the set of electrolytic cells of certain volumes or mass. Enriched samples are measured on a liquid scintillation spectrometer in polyethylene plastic bottles of a volume of 20 ml (ratio sample-scintillation cocktail is 8:12). The result of the tritium activity is shown with a certain measurement uncertainty. It is the combined uncertainty multiplied by the chosen coverage factor (k) in order to obtain an interval which may be expected to encompass a large fraction of the distribution of values which could reasonably be attributed to the measuring. The expanded relative combined uncertainty cover relative uncertainty of contributors: sample count rate, efficiency, the activity of standard solution, the enrichment parameter, the enrichment factor, sample weighing (mass/volume), electrolytic cell weighing/normal court and graduated cylinder, electric current, automatic pipette. The aim of this paper is to compare determined combined uncertainty (coverage factor k=2) when mass/volume enter in the final formulae in order to minimize measurement uncertainty. For these results preparation of precipitation and surface waters was explained and results of tritium activity in these samples are presented. Insignificantly higer measurement uncertainties were obtained when the mass is used (approximately 5%).

Acknowledgments

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HA08 PE 6

Degradation of triazine group herbicides by chlorine dioxide

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This study investigates degradation of triazine group herbicides (atrazine, terbuthylazine and prometryn) with chlorine dioxide in deionized water and in real water system (water from river Sava) under optimal conditions. Previously, we investigated in details the influence of various parameters such as concentration of chlorine dioxide, reaction time, pH, light conditions and determined the optimal conditions for the herbicides degradation based on degradation efficiency monitored by HPLC-DAD.[1] Atrazine and terbuthylazine (10 ppm) were completely degraded by 10 ppm chlorine dioxide, at pH 2.00 in a very short time (1 h). The percentage of herbicide degradation in water from river Sava was lower in relation to deionized water, but good value was obtained (degradation efficiency of 100% for atrazine and terbuthylazine after 2 h of initial treatment and degradation efficiency of 73% for prometryn after 24 h of initial treatment under the same conditions for deionized water and water from river Sava). GC-QQQ (gas chromatograph with triple quadrupole mass detector) analysis identified three main atrazine, three main terbuthylazine and four main prometryn degradation products. A simple mechanism of degradation of herbicides was also proposed.

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Acknowledgements

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HA09 PE 7

Nanoparticle enhanced laser-induced breakdown spectroscopy of aluminum alloy samples

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Laser-Induced Breakdown Spectroscopy (LIBS) technique has been recognized as a modern, fast and direct method for multielement material analysis since more than 20 years. Specific advantages of LIBS include very small amount of the sample required for the analysis with little or no sample preparation and no consumable or waste products. [1] In spite of the intrinsic benefits of the LIBS method with respect to other analytical techniques, some fundamental limitation in detectability, precision and reproducibility of the analytical results has limited the developing of this method. We report an approach based on silver nanoparticles deposition on the sample surface for improve the limit of detection of laser-induced breakdown spectroscopy (LIBS) analysis for of minor elements in aluminum alloys.

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HA10 PE 8

Conformation of a ferrocene–dihydrotestosterone hybrid by single-crystal X-ray diffraction and solution NMR

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Preparing ferrocene–steroid hormone hybrids has proven a promising strategy for developing selective antiproliferative agents for hormone-dependent tumors [1]. We have recently reported the synthesis of (*E*)-2-(ferrocenylmethylidene)-17β-hydroxy-5α-androstan-3-one, a hybrid of ferrocene with dihydrotestosterone, the most potent endogenous androgen [2]. Having now determined its crystal structure by single-crystal X-ray diffraction (Figure 1), an analysis of its conformation was performed. A total assignment of the ^{1}H and ^{13}C NMR spectra of this compound enabled a subsequent investigation into its solution conformation, including the interpretation of nOe interactions and the values of observed ^{1}H–^{1}H coupling constants.

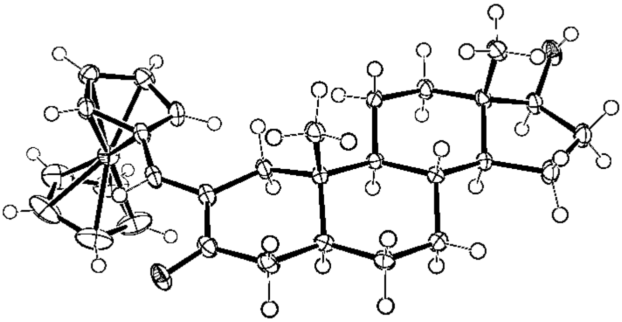

Figure 1. ORTEP diagram of the molecular structure of the hybrid

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HA11 PE 9

Turkey oak wood characterization

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Turkey oak (*Quercus cerris*) is a tree naturally grown in southern Europe and Asia Minor, often planted as an ornamental tree. The leaves, bark and wood are used commercially as a source of tannins (1). However, Turkey oak is inferior in comparison to other oak species because of poorer quality of wood, which is used mainly for temporary buildings and firewood (2). Hence, it has not investigated too thoroughly as other oak species.

In our research, Turkey oak wood from Kuršumlija (Serbia) was characterized. The cellular structure of wood was investigated by scanning electron microscopy (SEM), while elemental analysis was done using inductively coupled plasma-optical emission spectrometry (ICP-OES). The results were compared with those of sessile oak (*Quercus sessiliflora*) wood from the same locality. The most abundant metal in Turkey oak wood was zinc, which was present in sessile oak wood only in traces. The content of calcium, potassium and selenium was high in both wood species. On the other hand, Turkey oak wood contains significantly lower levels of lead and nickel than sessile oak wood.

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HA12 PE 10

Chemical composition of the essential oil of Lavandula angustifolia Mill.

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Lavandula angustifolia Mill., also known as lavender, is one of the most valuable plant in the Lamiaceae family. This plant has been used in traditional medicine as relaxant and insecticide for many years. Flowers of the plant species *L. angustifolia* were collected at the urban area of the city of Niš, Serbia and essential oil was hydrodistillated using Clevenger type apparatus. The chemical composition of the decanted oil (DEO) and the extracted oil (EEO) was analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS). In decanted oil 94 components were identified, which representing 99.5% of the total GC peak areas. In the extracted essential oil 78 components were identified, what makes 99.6% of all. The major class of compounds in those samples was oxygenated monoterpens (DEO 79.6%, EEO 84.8%). The dominant component in both cases was linalool (DEO 34.6%, EEO 36.5%), which accounts nearly 1/3 parts of the essential oil weight. Other compound present in significant amount was 1,8-cineole (DEO 11.9%, EEO 11.3%). There was no significant differences in the composition of those two essential oils of *L. angustifolia*, althought they were prepared for analyzing in different manners.

Acknowledgments

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HA13 PE 11

LIBS as an innovative analytical tool for testing of biosorption efficiency

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Environmental pollution with heavy metals is one of the most important problems. To avoid environmental hazards, it is essential to remove these metals from wastewater before its disposal. For the last few years biosorption has been heralded as a promising cost-effective clean-up biotechnology which is used for the removal of heavy metals.[1] With increasing interest in biosorption, the development of the fast and enviro-friendly reliable methods of quantitative analysis of the biosorption process is required. Nowadays, Laser Induced Breakdown Spectroscopy (LIBS) has been well recognized as a modern, fast and direct analytical tool for different applications.[2] This powerful analytical technique uses the optical emission spectroscopy of the laser generated plasma to determine the elemental composition of the sample. The idea of the present study is to use LIBS as a green analytical method to estimate biosorption efficiency. The biomass generated of sunflower seed husk was used as biosorbent for the removal of Cu and Cd from waste water. In order to verify accuracy of the LIBS elemental analysis, the reference procedure based on well established technique (ICP-OES) was applied. It was demonstrated that proposed LIBS technique can be used to produce quantitative data from biosorption studies.

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HA14 PE 12

Tritium content in Danube and Sava river in Belgrade

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Tritium can be naturally occurring and also be artificially introduced. Naturally, tritium is mainly produced in the atmosphere by the interaction between the neutrons in cosmic radiation and the nitrogen and oxygen, while anthropogenically, it is produced by a variety of activities, including nuclear weapons testing, fuel reprocessing plants, the operation of nuclear power reactors. Due to a series of nuclear power plants on the banks of the Sava and Danube and possible contamination of these rivers with tritium, which can occur through precipitation, it is important to continuously examine the content of this radioisotope. The water sampling site in Belgrade on Sava is Belgrade Port and on the Danube in Zemun. Analysis of the tritium content in surface waters was done in composite monthly samples. The samples were electrolytically enriched and measured on the liquid scintillation spectrometer *Quantulus 1220*. The detector efficiency are 27.5 and 30.8%. Results of the obtained tritium content in the Sava River for period January 2017 - June 2018. were in range from 1.00 Bq/l (April 2018) to 4.22 Bq/l (January 2018), while the content of tritium in the Danube for the same period was 1.53 Bq/l (January 2018) to 5.39 Bq/l (January 2017). Tritium content in Danube is slightly higher than values obtained in Sava, which can indicate that this radioisotope in the Danube reaches less from sources located upstream. Generally, seasonal variations have been obtained with a maximum in spring – summer months and minimum in winter (except for January at both locations), which is probably due to the stratospheric origin of tritium in the investigated rivers.

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HA15 PE 13

Evaluation of commercial bottled water quality from the health aspect

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Center of Ecology and Techno Economics

The term bottled water means water packed in a health-correct packaging and available in the market for human consumption. Consumers still have insufficient knowledge of importance of the certain ingredients and their harmful or beneficial effect on the human organism. There is not enough expert information about the harmfulness of certain ingredients in the water, but many countries in the world have adopted legal regulations in which quality parameters of bottled water are standardized (EEC, WHO[1], EPA, IBWA, FDA). The race for profit and the lack of necessary quantities of bottled waters moved declarations in to the second plan. The declaration on bottled waters should describe also the physiological characteristics, since the consumption of high-mineral water may lead to adverse effects on the health of consumers, primarily children. In such declared water, missing physiological characteristics of water, redox statuses, and possible consequences on the health, are neglected due to excessive consumption of waters with high mineral content. Due to the increased content of mineral substances and high sodium intake, the allowed daily intake should be declared for water loaded with mineral substances. Redox status of water represents a health factor and it is completely defined by the pH value, redox potential and rH_2 factor, parameters which were the subject of this study in this work. The oxide-reduction potential of water, E_{ROX}, represents the mixed potential of all present redox pairs and directly affects the behavior of water relative to the agents to which comes into contact[2]. The results pointed to the necessity of a fuller declaration of bottled water, because in that case bottled water gained in importance and would decrease the consequences of the possible bad effects on health due to excessive consumption of water rich with minerals. Test results demonstrated that our market has a wide range of bottled waters, and that the health aspect can be estimated through the oxidation-reduction properties.

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HA16 PE 14

The isovalerate and 2-methylbutanoate of artemisia alcohol – new compounds from Artemisia annua L. essential oil

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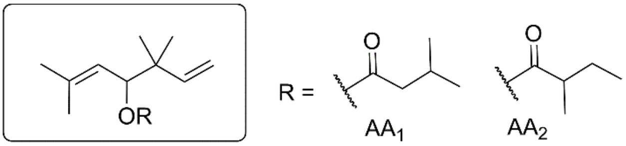
Artemisia annua L. (sweet wormwood) is an essential oil (EO)-rich, medicinally valuable plant species from the Asteraceae family [1]. During the analysis of the biologically active *A. annua* EO sample (hydrodistilled from the dry aboveground parts of the plants; oil yield 0.2%, w/w; the main components (relative abundance): artemisia ketone (35.7%), α-pinene (16.7%), 1,8-cineole (5.5%), artemisyl alcohol (4.8%), and trans-pinocarveol (4.8%) [1]), we have detected two minor compounds, AA1 and AA2 (0.06% and less than 0.05% of the total oil, with RI (DB5-MS) values of 1367 and 1373, respectively) with practically identical mass spectral (MS) fragmentation patterns (EI, 70 eV; m/z (rel. int.)): 169(15), 85(100), 57(38), 41(17). The comparison of GC (≈300 unit higher RI values) and MS data of AA1 and AA2 with those of artemisyl acetate (often present in EOs containing artemisia ketone and artemisia alcohol) suggested these might be esters of artemisia alcohol and (isomers of) pentanoic acids. To confirm this tentative identification, and possibly detect some additional AA1 and AA2 homologs, we prepared esters of artemisia alcohol and valeric, isovaleric, 2-methylbutanoic, butanoic, isobutanoic and propanoic acids (Steglich esterification; the starting alcohol was obtained by LiAlH4 reduction of artemisia ketone isolated from the *A. Alba* Turra EO). Co-injection of the EO sample with synthetic standards confirmed AA1 and AA2 were artemisyl isovalerate and artemisyl 2-methylbutanoate, respectively (Fig. 1). Detailed re-analysis of the EO revealed the presence of initially undetected trace amounts of artemisyl acetate. The results of this work once again confirm the importance of natural product-inspired libraries of synthetic compounds in the analysis of EOs, especially when it comes to the detection and identification of trace constituents

Figure 1. Structures of artemisyl isovalerate (AA1) and artemisyl 2-methylbutanoate (AA2).



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Acknowledgments
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Hemijska sinteza
Chemical Synthesis

HS01 OE 1

Are fulleropyrrolidine alcohols really good building blocks for the synthesis of more complex structures?

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Thanks to the synthetic utility of the hydroxylic group, fulleropyrrolidine alcohols seem to be good precursors for the synthesis of more complex covalent, as well as supramolecular structures. Willing to incorporate the fullerene moiety into natural polymers, such as pullulans, we explored the synthesis of the key intermediate – fulleropyrrolidine alcohol. Considering quite different reactivity of the amino and hydroxyl groups, we applied the synthetic route depicted in Figure 1, starting from the unprotected amino alcohol **1**. Subsequent *N*-alkylation to ester **2**, and hydrogenization afforded an inseparable mixture of diketopiperazine **3a** and the free acid **3**. Due to that, the next step – the Prato reaction of the glycine derivative **3**, formaldehyde and the fullerene C_{60} provided desired products **4** in a significantly lower yields than expected. So, in order to employ the fulleropyrrolidine alcohols as a good building blocks for complex systems, their synthesis should be carefully revised and optimized. However, the performed synthesis afforded diketopiperazine **3a**, which is a good candidate for the preparation of a flexible, tweezer-like bridged difullerenes.

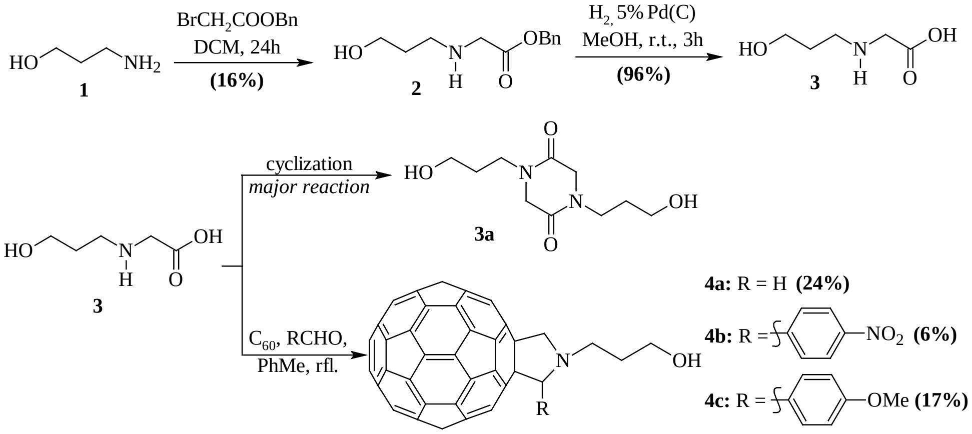

Figure 1. Sheme of the synthetic strategy for preparing fulleropyrrolidine alcohols.

Acknowledgments

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HS02 OE 2

Molecular diversity through $LiAlH_4$ reduction of Biginelli compounds

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The reduction of Biginelli compounds by $LiAlH_4$ was investigated for the first time (Fig.1). The reduction of urea-derived dihydropyrimidinones yielded 80-95% of hydrogenolysis products (4-aryl-5-(m)ethyl-6-methyl-3,4-dihydropyrimidin-2(1*H*)-ones; 11 examples), while the reduction of N-1-methylated Biginelli compounds gave the corresponding alcohols (4-aryl-5-((1-)hydroxy(m)ethyl)-6-methyl-3,4-dihydro-pyrimidin-2(1*H*)-ones; 4 examples) in 70-80% yield. The obtained alcohols could be readily dehydrated to vicinal bis(exo-methylene) derivatives (4-aryl-1-methyl-5-(m)ethylene-6-methylene-tetrahydropyrimidin-2(1*H*)-ones; 4 examples) or isomerized to acyclic compounds (1-methyl-3-(1-aryl-2-methylene-3-oxobutyl)ureas; 2 examples) under mildly acidic conditions. The outcome of the reduction also depended on other structural features and reaction conditions such as: urea/thiourea and the type of 1,3-dicarbonyl compound, order of reagent addition, etc. The $LiAlH_4$-reduction of Biginelli compounds affords a rapid approach to a library of diverse compounds of apparent synthetic utility and possible biological interest. The mechanism of this reduction was discussed and additionally elucidated through deuteration experiments and *p*Ka measurement.

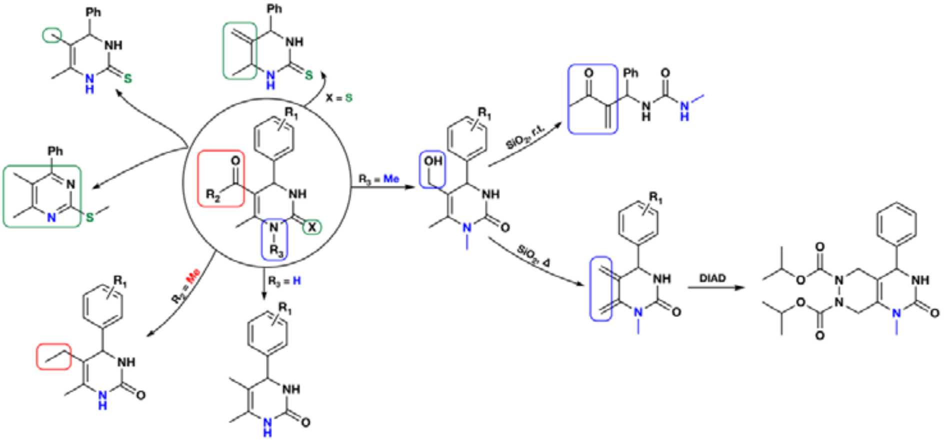

Figure 1. Access to structurally diverse products by a $LiAlH_4$ reduction of Biginelli compounds.

Acknowledgments

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HS03 PE 1

Synthesis, structural characterization and antimicrobial activity of silver(I) complexes with aromatic nitrogen-containing heterocycles

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An attractive class of the ligands for the synthesis of silver(I) complexes as potential antimicrobial agents comprises aromatic nitrogen-containing heterocycles.[1,2] Herein, we report the synthesis, structural characteristics and antimicrobial activity of new polynuclear silver(I) complexes, $\{[Ag(bpe)_2]CF_3SO_3{\cdot}H_2O\}_n$ and $\{[Ag(dpe)]CF_3SO_3\}_n$, where bpe is 1,2-di(4-pyridyl)ethane and dpe is 1,2-di(4-pyridyl)ethylene. These complexes were obtained in the reactions of $AgCF_3SO_3$ with the corresponding aromatic *N*-heterocycle in 2 : 1 mole ratio, respectively, in ethanol at room temperature and characterized by NMR, IR and UV-Vis spectroscopy and single-crystal X-ray diffraction analysis. The antimicrobial potential of $\{[Ag(bpe)_2]CF_3SO_3{\cdot}H_2O\}_n$ and $\{[Ag(dpe)]CF_3SO_3\}_n$ complexes was evaluated against the broad panel of Gram-positive and Gram-negative bacteria and fungi. These complexes showed selectivity towards *Candida spp*. and Gram-negative *Escherichia coli* in comparison to the other investigated bacterial strains, effectively inhibiting the growth of four different *Candida* species with minimal inhibitory concentrations (MIC) between 2.5 and 25 µg/mL and the growth of *E. coli*, with MIC values being 1.6 and 12.5 µg/mL, respectively.

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Acknowledgments

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HS04 PE 2

Synthesis and crystal structure of Cu(II) complex with condensation product of 2,6-diacetylpyridine and Girard's T reagent

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The complex [Cu**L**(H_2O)](BF_4)$_2$·H_2O was obtained in the reaction of **H_2L**Cl_2·4H_2O(2,2′-[2,6-pyridinediylbis(ethylidyne-1-hydrazinyl-2-ylidene)]bis[N,N,N--trimethyl-2-oxoethanaminium] dichloride tetrahydrate)with Cu(BF_4)$_2$ · 6H_2O and NaN_3 in molar ratio 1:1:4 in CH_3CN/H_2O. The structure of complex is determined by elemental analysis, IR spectroscopy and X-ray diffraction analysis. The geometry of complex is distorted square pyramidal with double deprotonated bishydrazone ligand coordinated in base plane of pyramide through N_3O set of donor atoms and aqua ligand in apical position.

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HS05 PE 3

Synthesis and characterization of copper(II) complex with 4-(diethylamino)salicylaldehyde and 2,2'-bipyridine

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In this work we are presenting the synthesis and characterization of a new mononuclear copper(II) complex with 4-(diethylamino)salicylaldehyde (H**L**) and 2,2'-bipyridine (bipy), [Cu(bipy)(**L**)]$BF_4 \cdot H_2O$. The synthesis was done in methanol as a solvent, and the complex was obtained in the reaction of 4-(diethylamino)salicylaldehyde, $Cu(BF_4)_2 \cdot 6H_2O$ and 2,2'-bipyridine in molar ratio 2:1:1. Characterization was achieved by elemental analysis, spectroscopic methods (FT-IR, UV-Vis) and magnetic measurements. Crystal structure of the complex was determined by X-ray crystallography. In the complex cation the Cu(II) ion is placed in a slightly distorted square-planar coordination environment, formed by the phenolate and carbonyl O donors of 4-(diethylamino)salicylaldehyde ligand, and two N donors of the bipyridine ligand (Fig. 1).

*Figure 1. Structure of the complex [Cu(bipy)(**L**)]$BF_4 \cdot H_2O$, obtained by X-ray crystallography*

Acknowledgement

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HS06 PE 4

Synthesis and spectral characterization of natural and related synthetic iodinated tyramides

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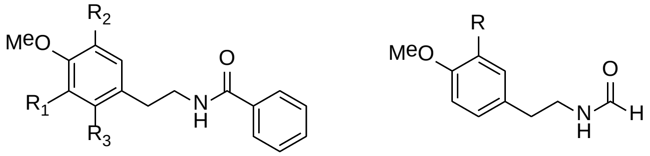
Ascidians (Tunicates; Ascidiacea), also known as tunicates, the most frequently investigated groups of marine organisms, represent an unusually rich source of bioactive secondary metabolites. Solano and co-workers (2009) isolated and structurally elucidated seven iodinated tyramine derivatives from an ascidian, *Didemnum rubeum*. Having only minute quantities of the isolated compounds in their hands, the researchers had to use spectral data from HSQC and HMBC experiments to extract ^{13}C NMR resonances. With an aim to provide a definitive proof of the structures of some of these *Didemnum* metabolites, and to allow access to larger amounts of these compounds, we set ourselves to a synthetic endeavor to prepare compounds **1-7**, that either represent a natural compound (**1**) identified in this tunicate, or are isomers (**2**), or closely related compounds to the ones naturally occurring (**3**, **4** and **7** are related to benzamides, **5** and **6** are related to formamide). One should note that the structures of these metabolites (for example compound **1**, Fig. 1) contain an iodinated methoxyaryl group reminiscent of thyroxine. To the best of our knowledge, compounds **2**, **3**, **5** and **7** represented new compounds. Also, complete experimental data (NMR spectra, IR and MS) of **6** do not exist in the literature. A complete assignment of ^1H and ^{13}C NMR resonances was accomplished by a detailed analysis of 1D and 2D NMR spectra (a series of selective homonuclear ^1H decoupling, and HSQC, HMBC, ^1H-^1H COSY and NOESY).



1 R_1=I, R_2=I, R_3=H
2 R_1=H, R_2=I, R_3=I
3 R_1=H, R_2=I, R_3=H
4 R_1=H, R_2=H, R_3=H
7 R_1=H, R_2=H, R_3=I
5 R=I
6 R=H

Figure 1. Structures of compounds 1-7.

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Acknowledgments

This work was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project 172061).

HS07 PE 5

Polynuclear silver(I) complex with 2,2'-biquinoline: synthesis and structural properties

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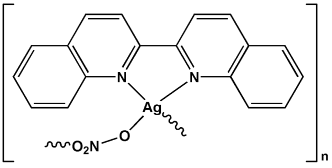
Silver(I) complexes with aromatic nitrogen-containing heterocycles are of special interest in the field of medicinal chemistry and polymer design.[1,2] New silver(I) complex with 2,2'-biquinoline, $[Ag(NO_3\text{-}O)(2,2'\text{-bq-}N,N')]_n$, was synthesized by the reaction of $AgNO_3$ with an equimolar amount of 2,2'-biquinoline (2,2'-bq) in ethanol at room temperature. This complex was characterized by elemental microanalysis, IR, NMR (^1H and ^{13}C) and UV-Vis spectroscopy, while its crystal structure was determined by single-crystal X-ray diffraction analysis. The spectroscopic and crystallographic results revealed that in $[Ag(NO_3\text{-}O)(2,2'\text{-bq-}N,N')]_n$ complex, the Ag(I) ion is bidentately coordinated by 2,2'-biquinoline and two oxygen atoms of the nitrate ions, resulting in distorted tetrahedral geometry. Two Ag(I) ions are connected by nitrate to form coordination polymer in the solid state.



$[Ag(NO_3\text{-}O)(2,2'\text{-bq-}N,N')]_n$

Figure 1. Structural formula of polynuclear silver(I) complex with 2,2'-biquinoline.

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Acknowledgments

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HS08 PE 6

Hydrolysis of the amide bond in *N*-acetylated L-methionylglycine catalyzed by new dinuclear palladium(II) complexes

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During the last decades, hydrolytic reactions between various palladium(II) complexes with L-methionine or L-histidine-containing peptides have been extensively investigated. It was found that Pd(II) complexes spontaneously bind to the side chains of the peptide and effect selective cleavage of the amide bond involving the carboxylic group of the anchoring amino acid. Recently, we have investigated the reactions of dinuclear $[\{Pd(en)(H_2O)\}_2(\mu\text{-pz})]^{4+}$ and $[\{Pd(en)(H_2O)\}_2(\mu\text{-pydz})]^{4+}$ complexes (en is ethylenediamine, pz is pyrazine and pydz is pyridazine) with L-methionine- and L-histidine-containing peptides. [1] As continuation of this study, two new dinuclear palladium(II) complexes, $[\{Pd(en)Cl\}_2(\mu\text{-1,5-nphe})](NO_3)_2$ and $[\{Pd(1,2\text{-pn})Cl\}_2(\mu\text{-1,5-nphe})](NO_3)_2$ (1,2-pn is (±)-1,2-propylenediamine and 1,5-nphe is 1,5-naphthyridine) have been synthesized and characterized by elemental microanalysis, NMR (^{1}H and ^{13}C), IR and UV-vis spectroscopy. These complexes were converted into the corresponding aqua derivatives, $[\{Pd(en)(H_2O)\}_2(\mu\text{-1,5-nphe})]^{4+}$ and $[\{Pd(1,2\text{-pn})(H_2O)\}_2(\mu\text{-1,5-nphe})]^{4+}$, and their reactions with Ac-L-Met-Gly were studied by ^{1}H NMR spectroscopy. All reactions were performed at $2.0 < pH < 2.5$ in D_2O and 37 °C. It was found that both $[\{Pd(en)(H_2O)\}_2(\mu\text{-1,5-nphe})]^{4+}$ and $[\{Pd(1,2\text{-pn})(H_2O)\}_2(\mu\text{-1,5-nphe})]^{4+}$ complexes promote the regioselective cleavage of the Met-Gly amide bond in the investigated Ac-L-Met-Gly dipeptide. The catalytic activities of the investigated Pd(II) complexes were compared with those for $[\{Pd(en)(H_2O)\}_2(\mu\text{-pz})]^{4+}$ complex. We have found that the rate of the hydrolysis in the presently investigated reactions strongly depends on the steric bulk of bidentate coordinated diamine ligand in the dinuclear palladium(II) complexes.

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Financial support by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172036) is gratefully acknowledged.

HS09 PE 7

Optimized synthesis of 4-anilidopiperidine / *N*-arylpiperazine conjugates as potential bivalent ligands for opioid and dopamine receptors

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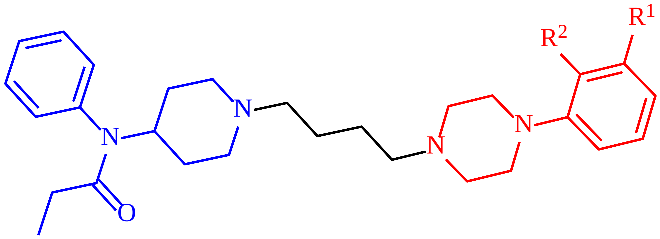
Three novel structures **1a-b** (Figure 1), were synthesized, that contain 4-anilido piperidine moiety as μ-opioid and *N*-aryl piperazine moiety as D_2/D_3 receptors pharmacophores, linked by four methylene group chain. Optimized synthetic route provided the final products in high overall yields after four steps namely: formation of γ-halogen butyril carboxamide via *N*-acylation of *N*-aryl piperazine, subsequent alkylation of 4-anilinopiperidine, reduction of carboxamide to methylene group, and *N*-propionylation of anilino piperidine moiety.

These compounds may potentially serve as bivalent ligands for μ-opioid and D_2/D_3 dopamine receptors, and will be pharmacologically tested as a part of our ongoing work. Hopefully the results will help in further understanding of interaction between dopaminergic and opioid signal pathways. In addition, new insights may be gained into the tolerance and dependence phenomena associated with opioid intake.



1a, $R^1=R^2=H$
1b, $R^1=OMe$, $R^2=H$
1c, $R^1=R^2=Cl$

Figure 1. Novel, potentially bivalent ligands that contain 4-anilido piperidine (colored blue) as μ-opioid and N-aryl piperazine moiety (colored red) as D_2/D_3 receptors pharmacophores

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HS10 PE 8

Synthesis and characterization of 1-(4-substitutedbenzyl)-3’,4’-dihydro-2’H-spiro[imidazolidine-4,1’-naphtalene]-2,5-dione derivatives as potential anticonvulsant agents

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Among the diverse pharmacological activity reported for spirohydantoin and the closely related spirosuccinimides, their anticonvulsant and antiproliferative activities are commonly encountered. Of all cyclic ureide derivatives, Phenytoin (5,5-diphenylhydantoin) is one of the well-known commercially available anticonvulsants, which is also widely used as an antiarrhythmic agent. However, the clinical use of 5,5-diphenylhydantoin is limited by its central nervous adverse effects in addition to a wide variety of drug interactions [1]. With the aim of developing new analogs with a more efficient therapeutic effect, a series of 1-(4-substitutedbenzyl)-3’,4’-dihydro-2’H-spiro[imidazolidine-4,1’-naphtalene]-2,5-diones, have been synthesized, characterized by melting points, FT-IR, ^{1}H and ^{13}C NMR spectroscopic techniques, and evaluated for anticonvulsant activity. The objective of the present investigation is to identify the pharmacological impact of the spirocyclic attachment of a semi-rigid tetralin residue at C-5 of the imidazolidine-2,4-dione ring and to explore the effect of substitution at N-3 on anticonvulsant activity.

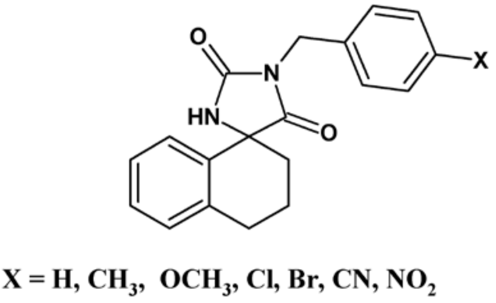

Figure 1. Structure of the investigated spirohydantoin derivatives

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HS11 PE 9

Influence of azo dye structure on photovoltaic characteristics of dye sensitized solar cells

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Dye-sensitized solar cells (DSSC), as a main competitor to a silicon solar cells, present a new technology which has been in constant development for two decades. In this paper, six azo dyes based on benzoic and cinnammic acid moiety, which represent a generators of charge carriers, have been synthesized. Compounds were characterized by melting point, UV-Vis, FT-IR, ^{1}H i ^{13}C NMR spectroscopy. Current density-voltage curves were recorded in order to determine basic DSSC operating parameters, *i.e.* short-circuit current density (Jsc) and open-circuit voltage (Voc). Based on the obtained resultes, 4-(2-hydroxynaphthalenazo)cinnamic acid and 4-[4’-(*N*,*N*-dimethylamino)phenylazo)--cinnamic acid have shown the most significant energy conversion efficiency (η) [1,2].

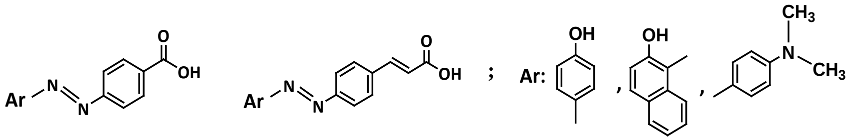

Figure 1. *Molecular structures of synthesized dyes*

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Acknowledments

This work was supported by the Ministry of Education, Science and Technological Development, of the Republic of Serbia (Project no. OI 172013).

HS12 PE 10

Studies towards mechanism elucidation of Pd/γ-Fe_2O_3 catalyzed decarbonylation of aryl carbaldehydes

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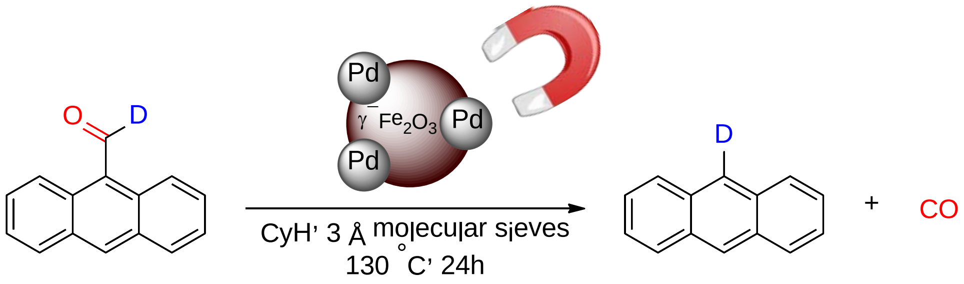
Transfer of carbon monoxide via transition metal catalysis belongs to the heart of the organometallic chemistry. Maghemite supported palladium catalyst, a magnetically active catalyst recently reported by our group [1], was successfully used for this purpose. In this work, mechanism for decarbonylation of aryl carbaldehydes using Pd/γ-Fe_2O_3 was investigated. Utilizing different approaches, which include H/D exchange, radical clock experiment and carbon monoxide trapping, we propose a Pd^0/Pd^{II} catalytic cycle mechanism.



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HS13 PE 11

Synthesis and characterization of new Schiff base for application in biology and medicine

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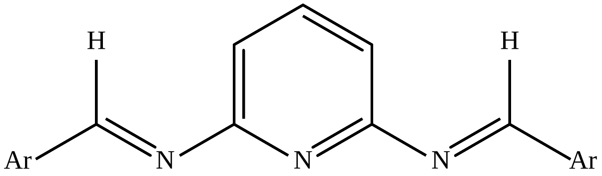
Schiff bases, obtained by condensation of aromatic aldehydes and 2,6-diaminopyridine, are interesting compounds due to their potential biological, antibacterial, antiproliferative and antioxidant activity. The structure of synthesized compounds (Figure 1.) was confirmed using ATR-FTIR, UV/Vis and NMR techniques. Solvent influences on UV absorption peaks changes was correlated using Linear Solvation Energy relationship (LSER), by using Kamlet-Taft equations, and discussed in relation to the contribution of solvent polarity and hydrogen bond donor capabilities. Synthesized compounds were also investigated in relation to their antioxidant potential using DPPH and ABTS methods.



Comp.	Ar
1	Phenyl
2	4-methylphenyl
3	2- hydroxyphenyl
4	2-quinoline
5	4-chlorophenyl
6	4-fluorophenyl
7	4- methoxyphenyl

Figure 1. Structures of synthetized compounds

Acknowledgments
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HS14 PE 12

Synthesis, characterization and biological activity in melanoma cells of novel ruthenium(II)-arene complexes containing intercalating ligands

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Ruthenium(II)-arene complexes with planar polyaromatic ligands, have attracted significant attention because of the possibility to bind DNA both by metal coordination or through intercalation of an attached aromatic ligand.[1] Three new ruthenium(II)-arene complexes have been synthesized: **C1** ([(η^6-toluene)Ru(ppf)Cl]PF_6), **C2** ([(η^6-*p*-cymene)Ru(ppf)Cl]PF_6) and **C3** ([(η^6-benzene)Ru(ppf)Cl]PF_6; ppf = pyrido[2',3':5,6]--pyrazino[2,3-f][1,10]phenanthroline) The structures of complexes were determined with elemental analysis, IR, ESI-MS, ^{1}H and ^{13}C NMR spectroscopy. Complexes are soluble and stable in DMSO solution. Biological activity have been evaluated for *in vitro* cytotoxic activity on three human neoplastic cell lines (A549, A375, LS 174T) and on one human non-tumor cell line (MRC-5), by the MTT assay, in comparison to cisplatin as a referent compound. Complexes **C1-C3** showed IC_{50} values in the micromolar range below 100 µM on all tested cell lines. Complex **C2** displayed cytoselectivity against melanoma A375 cells (IC_{50}=15.78 µM), observed in four times lower activity in MRC-5 cells and two times lower cytotoxicity than cisplatin, and it has been selected for further analyses of its biological effects. Flow cytometry analyses revealed that complex **C2** induce neither substantial alterations in cell cycle phase distribution nor triggers apoptosis or necrosis in A375 cells, indicating distinguish and more specific type of action. Drug-accumulation study performed by ICP-MS showed that after 24 h of treatment with equimolar concentrations (10 µM), complex **C2** entered the cells less efficiently (1.55 ng Ru/10^6 cells) in comparison to cisplatin (28.58 ng Pt/10^6 cells). Investigations in the 3D model of A375 cells, disclosed different effects of complex **C2** and cisplatin on growth of multicellular tumor spheroids (MCTSs). While the size of cisplatin-treated MCTSs decreased with time, MCTSs treated with **C2** continued to growth. These results pointed out completely different mechanism of action of this type of ruthenium(II)-arene complexes *versus* cisplatin in A375 malignant melanoma cells, and necessity for additional biological studies for its potential application as anti-cancer drug candidate.

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Ministry of Education, Science and Technological Development of the Republic of Serbia, grant numbers 172035 and III 41026.

HS15 PS 13

Synthesis and characterization butyl ester of (*S*,*S*)-ethylenediamine-*N*,*N'*-di-(2,2'-di(4-hydroxy-benzyl))-acetic acid and corresponding palladium(II)-complex

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(*S,S*)-Ethylenediamine-*N,N'*-di-(2,2'-di(4-hydroxy-benzyl))-acetic acid dihydro-chloride, [(H_2-(*S,S*)-eddtyr)]Cl_2 was prepared using similar methods described earlier [1]. *O,O'*-Dibutyl-(*S,S*)-ethylenediamine-*N,N'*-di-(2,2'-di(4-hydroxy)-benzyl-acetic acid dihydrochloride dihydrate, dbu-S,S-eddtyr·2HCl·$2H_2O$ was synthesized in such a way: in 40 mL of dry alcohol 1-butanol saturated with gas HCl, 1.50 g (3.25 mmol) of H_2-(*S,S*)-eddtyr was added and the mixture was refluxed for 12h. The mixture was filtered off and the filtrate was left for a few days in the refrigerator. The ester was recrystallized from hot 1-butanol and used for synthesis of the corresponding palladium(II)-complex. The ligand was obtained in yield of 0.87 g (44.13%).

The complex was synthesized in the following way: 0.05 g (0.153 mmol) $K_2[PdCl_4]$ was dissolved in 10 mL of water on a steam bath and 0.0932 g (0.153 mmol) (*O,O'*-dibuthyl--(*S,S*)-ethylenediamine-*N,N'*-di-(2,2'-di(4-hydroxy-benzyl))acetate dihydrochloride dihydrate was added. The mixture was stirred for 2h and during this period water solution of LiOH (0.0073 g, 0.306 mmol) was introduced. The complex, [$PdCl_2$(dbu-*S,S*-eddtyr)] was a light yellow precipitate was filtered, washed with water and air-dried. The complex was obtained in yield of 0.066 g (64.12%).

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

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Acknowledgments

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HS16 PE 14

Pt(II) and Pd(II) complexes with thiomorpholine-4-carbonitrile

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Of the binding modes potentially available for unsubstituted thiomorpholine (TM), monodentate N-coordination, bidentate N,S-chelation and tridentate bridging have been established [1]. Only monodenate S-coordination remains unobserved. However, in N-substituted thiomorpholines, when N atom is a part of delocalized system its coordination ability is reduced. In order to study possibility for monodentate coordination *via* S atom, thiomorpholine-4-carbonitrile (TM-CN) was used as a ligand for preparation of Pd(II) and Pt(II) complexes of general formula [M(TM-CN)$_2$Cl$_2$]. The obtained complexes are centrosymmetric, with metal ions residing on a special position with site symmetry –1. Thus, asymmetric units of *trans* isomers consist of a metal center, one TM-CN ligand coordinated *via* S atom and one chloride ion (Fig. 1). In both complexes thiomorpholine rings are in a chair conformation, but with different position of M–S bonds: axial in Pt-complex and equatorial in Pd-complex. Due to the absence of classical proton donors crystal packings are based on weak non-covalent interactions. The topology of intermolecular interactions is revealed by energy frameworks where separate frameworks for the electrostatic and dispersion components provide insight into the nature of different interactions.

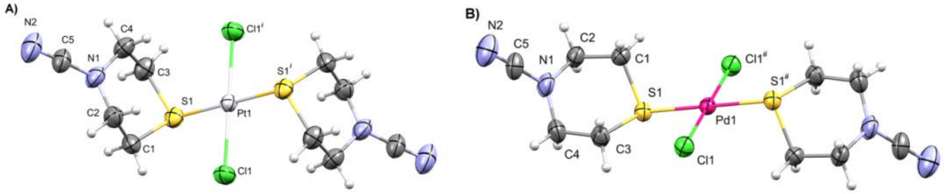

Figure 1. ORTEP drawing of molecular structure of: (A) Pt(II) complex and (B) Pd(II) complex. i =1 – x, 1 – y, 1 – z; ii =1 – x, – y, 1 – z. Displacement ellipsoids are drawn at 50% probability level.

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This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant 172055).

HS17 PE 15

Structure of Zn(II) complex with condensation product of 2,6-diacetylpyridine and Girard's T reagent in solid state and solution

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The ligand $\mathbf{H_2LCl_2{\cdot}4H_2O}$ (2,2′-[2,6-pyridinediylbis(ethylidyne-1-hydrazinyl-2-ylidene)]bis[N,N,N-trimethyl-2-oxoethanaminium] dichloride tetrahydrate) was synthesized in reaction between 2,6-diacetylpyridine and Girard's T reagent. The complex $[Zn\mathbf{L}(H_2O)_2](BF_4)_2$ was obtained in the reaction of $\mathbf{H_2LCl_2{\cdot}4H_2O}$ with $Zn(BF_4)_2 \cdot 6H_2O$ and NaOCN in molar ratio 1:1:4 in H_2O. The structure of complex is determined by elemental analysis, IR and NMR spectroscopy and X-ray diffraction analysis. The geometry of complex is pentagonal-bipyramidal with double deprotonated bishydrazone ligand coordinated in equatorial plane as pentadentate through azomethine nitrogens, pyridine nitrogen and carbonyl oxygen atoms. The apical positions in Zn(II) complex are occupied with aqua ligands. NMR spectra of Zn(II) complex recorded in DMSO-d^6 confirmed the same coordination pattern of bishydrazone ligand as in the solid state.

Acknowledgments

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HS18 PE 16

Crystal structures of pentagonal-bipyramidal Co(II) and Fe(III) complexes with condensation product of 2,6-diacetylpyridine and Girard's T reagent

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The ligand $\mathbf{H_2L}Cl_2 \cdot 4H_2O$ (2,2′-[2,6-pyridinediylbis(ethylidyne-1-hydrazinyl-2-ylidene)]bis[N,N,N-trimethyl-2-oxoethanaminium] dichloride tetrahydrate) was synthesized in reaction between 2,6-diacetylpyridine and Girard's T reagent. The complex $[Co\mathbf{L}(H_2O)_2](BF_4)_2$ was obtained in the reaction of $\mathbf{H_2L}Cl_2 \cdot 4H_2O$ with $Co(BF_4)_2 \cdot 6H_2O$ and NaOCN in molar ratio 1:1:4 in H_2O. The complex $[Fe\mathbf{L}(N_3)_2]BF_4$ was synthesized in the reaction of $\mathbf{H_2L}Cl_2 \cdot 4H_2O$ with $Fe(BF_4)_2 \cdot 6H_2O$ and NaN_3 in molar ratio 1:1:4 in mixture CH_3CN/H_2O. The structures of complexes were determined by elemental analysis, IR spectroscopy and X-ray diffraction analysis. The geometry of both complexes is pentagonal-bipyramidal with double deprotonated bishydrazone ligand coordinated in equatorial plane through azomethine nitrogens, pyridine nitrogen and carbonyl oxygen atoms. The apical positions in Co(II) complex are occupied with aqua ligands. In Fe(III) complex azido ligands are in apical positions.

Acknowledgments
This work was supported by the Ministry of Education, Science and Technological development of the Republic of Serbia (Grant OI 172055).

HS19 PE 17

Synthesis, structure and solvatochromic properties of novel 4-((4-(1H-benzo[d]imidazol-2-yl)phenyl)diazenyl)-2-(((2-hydroxyphenyl)imino)methyl)phenol

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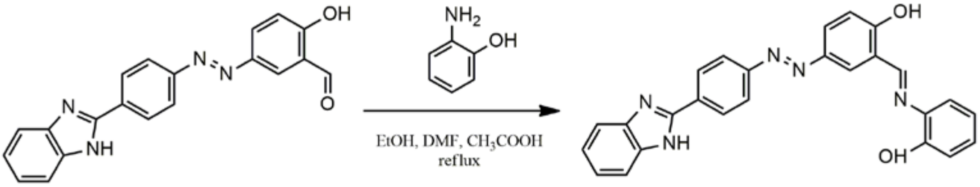
The azo dyes are used in textile industry, printing systems and electro-optical devices [1]. Also, azo–Schiff bases and their metal complexes are known to have a broad range of antibacterial, antifungal, antitumor and antioxidant activities [2]. New azo-azomethine dye, 4-((4-(1H-benzo[d]imidazol-2-yl)phenyl)diazenyl)-2-(((2-hydroxyphenyl)-imino)methyl)-phenol (**2**), have been synthesized in condensation reaction of 5-{[4-(1H-benzimidazol-2-yl)phenyl]diazenyl}-2-hydroxybenzaldehyde (**1**) with 2-aminophenol. The compounds **1** and **2** have been characterized by melting points, FT-IR, UV–Vis and ^{1}H NMR data. The solvatochromic behavior and tautomerism of dyes were studied in various solvents of different polarity. Furthermore, the ability of **1** and **2** to form metal complexes, with different cations, was examined.



1 **2**

Figure 1. Synthesis of 4-((4-(1H-benzo[d]imidazol-2-yl)phenyl)diazenyl)-2-(((2-hydroxyphenyl)imino)methyl)phenol

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HS20 PE 18

Comparative study of two methods for decarbonylation of aromatic and aliphatic aldehydes

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Transition-metal-promoted decarbonylation reaction has been drawing the attention of researchers for many years for it plays an important role in both synthetic organic chemistry and pharmaceutical industry. Therefore, we have described and compared two palladium-catalysed decarbonylation reactions of aromatic and aliphatic aldehydes which showed significant conversion (Fig. 1). One of them is utilizing previously developed method based on palladium immobilized on maghemite support giving it magnetic properties and enabling efficient recovery and reusability of the catalyst.(1) The latter reaction is an example of methodology which uses a commercially available Pd/C catalyst exhibiting good functional-group tolerance.(2)

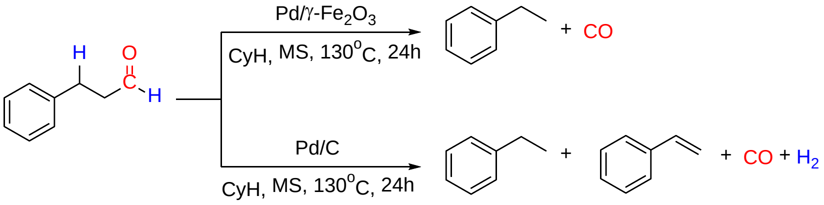

Figure 1. Two methods for decarbonylation of 3-phenylpropanal

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Industrijska i primenjena hemija

Industrial and applied chemistry

IP01 OE 1

The effect of the use of iron and aluminum electrodes on the process of removing arsenic from water by electrocoagulation

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One of the greatest problems of the 21st century is to provide a sufficient quantity of water for various purposes to the growing world population. Water resources on the Earth are limited, and the quality of water is constantly endangered primarily due to pollution caused by anthropogenic activity, but also by various natural processes. Because of its high toxicity, arsenic is a subject of many concerns and presence of arsenic in drinking water present a major problem. Electrocoagulation is an advanced treatment of water treatment, which contains arsenic, toxic heavy metals and organic ions, and is based on the generation of a coagulation agent in situ, by applying an electric current to metal electrodes. [1]

This study was intended to evaluate the performance of electrocoagulation process using iron or aluminum electrodes for arsenic removal in raw groundwater from Vojvodina, northern part of Serbia. Initial concentration of arsenic in the raw water was around 36,34 ± 3,95 µg/l, pH value was 8,20 ± 0,21 and electrical conductivity was 799 ± 5,58 µS/cm, based on 15 measurements. The EC reactor with different number of plate electrodes (two or four) was operated in the horizontal continuous flow mode, with flow rate 9 l/h. Four electrodes were at a inter electrode distance of 1,2 cm and two electrodes were at a distance of 2,4 cm or 4,4 cm. Different type of voltage (7,5, 10 or 15 V) was applied in the system. Concentration of As, Al and Fe in raw and treated water was determined with ICP-MS, EPA method 200.8.

This method is found to be very effective for arsenic removal, with efficiency up to 95%. When iron electrodes were being used better results were being obtained than when aluminum electrodes were used. It is determined that large amount of coagulants remains in the treated water, so it would be necessary for some additional treatment to be used after the electrocoagulation process.

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IP02 PE 1

The antioxidant properties of tobacco waste

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Tobacco contains significant concentration of phenolic compounds that are important naturally occurring antioxidants. Phenolic compounds are secondary metabolites in tobacco plant, and they have impact on quality of tobacco leaves due to their contribution to sensory properties-flavor, color, bitterness, and antioxidant properties. The aim of this work was to investigate the influence of different ultrasound extraction condition on antioxidant activity of tobacco waste extracts. Tobacco waste: fraction 1 (leaf waste and mid-rib) and fraction 2 (dust) were obtained from tobacco factory Hrvatski duhani, Virovitica.

Ultrasound-assisted extraction of tobacco waste was performed. The influence of extraction temperature (30, 50, 70 °C), time (15, 30, 45 min), ethanol: water ratio (40%, 60%, 80% v/v) and solvent-solid ratio (10, 30 and 50 mL/g) on the antioxidant activity was monitored.

Antioxidant activity was performed by DPPH (1,1-diphenyl-2-picrylhydrazyl) radical scavenging method, which showed that extracts with lower ethanol concentration possess better antioxidant activity. The strongest antioxidant activity showed fraction 1 extract obtained under following condition: temperature: 50 °C, time: 30 min, solvent/solid ratio: 10 mL/g and ethanol: water ratio 40% v/v.

Acknowledgment
This work has been supported by Croatian Science Foundation under the project “Application of innovative techniques of the extraction of bioactive components from by-products of plant origin” (UIP-2017-05-9909)

IP03 PE 2

Potential application of pharmaceutical waste: oxaprozin as corrosion inhibitor on aluminium alloy AA2024

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Oxaprozin, 3-(4,5-diphenyl-1,3-oxazole-2yl)-propanoic acid, belongs to the class of non-steroidal anti-inflammatory drugs (NSAIDs) with analgesic and antipyretic properties. Since it was observed that it formes complex compounds with various metals, the goal of this research was to investigate its potential adsorption on aluminium surface hence providing corrosion inhibition properties. Oxaprozin as active component of Duraprox® tablets, was adsorbed on AA 2024 surface in molecular or ionic forms (obtained by neutralization of carboxyl group). Influence of different drug concentrations and temperatures on its corrosion inhibition properties were tested. Corrosion of aluminium alloy AA2024 in 3 wt. % NaCl solution was investigated using electrochemical impedance spectroscopy and linear sweep voltammetry. Electrochemical impedance spectrosopy measurements showed that oxaprozin was adsorbed on aluminium surface therefore providing protection from electrolyte. Tafel polarization technique revealed that oxaprozin behaves as anodic inhibitor, since no change in cathodic current was observed.

IP04 PE 3

Influence of reaction parameters on the FAME yield in transesterification reaction

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Biodiesel as non-petroleum derived fuel is a mixture of fatty acid methyl or rarely ethyl esters (FAME, FAEE) obtained by catalytic transesterification of vegetable oils/fats with the two short chain alcohols. In our case, transesterification is done using sunflower oil and methanol. Product of reaction is mixture of fatty acid methyl esters (FAMEs). As catalyst we used heterogeneous calcium-oxide based catalyst. Catalyst is thermally activated before usage. Reaction parameters are crucial for conversion of triglycerides to FAMEs. In this paper, influence of reaction parameters to conversion rate is investigated. Influence of methanol to oil ratio, reaction temperature and time was determined. For all reactions, CaO calcined at 900°C is used because previous researches show that it is the most active. Reaction temperature was varied in the range between 60°C and 120°C. It is shown that reaction rate rise with temperature, also FAME yield up to 100°C. At 120°C reaction rate and yield is lower than at 100°. To determine optimal molar ratio oil to methanol, reaction are done with ratios 6:1, 9:1 and 12:1. Oil to methanol molar ratio is crucial to FAME yield. It is shown that reaction rate and yield rise with rise of molar ratio. Reaction is relatively fast and after 2 h almost maximum yield is obtained. Results show that the best yield is obtained for 12:1 methanol to oil ratio at 100°C in 5 h.

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IP05 PE 4

Experimental determination and modeling of the sunflower oil ozonization process

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Ozonization is a significant reaction in vegetable oil chemistry since the ozonization products are involved in therapeutical applications because of its antimicrobial effect[1]. Information about standard preparation procedures of ozonized sunflower oil is limited. The development of an adequate technology for the effective production of ozonized oil was carried out on the laboratory level.

The purpose of this study was to establish an experimental procedure using two different types of apparatus in order to optimize the ozonization process. Within the first procedure, the reaction was carried out inside a bubble reactor, while following the second procedure, the reaction was performed inside an absorption column. The second procedure gave better results regarding the content of ozonized products in the final sample. It was concluded that the ozonization process should be carried out in a packed-bed absorption column. The model of the chosen process was created using software *Design II* and though simulations carried out within the model, optimal working conditions for the ozonization process were determined.

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IP06 PS 5

Investigation of antifungal activity of newly synthesized ionic liquids on fungi of the genus *Alternaria*

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Plant diseases caused by fungal pathogens can lead to major economic losses in agriculture, still may be controlled through the use of fungicides. However, intensive application of synthetic fungicides in combat against phytopathogenic fungi has recently caused considerable concern due to toxic and carcinogenic chemical compounds existed in the environment. A modern sustainable approach in agricultural practice should be a replacement of synthetic and toxic substances in the treatment of crop with biocontrol agents of natural origin or environmentally friendly alternatives. Since *Alternaria* includes one of the most frequent pathogenic species that may cause various plant diseases, the objective of this study was to examine *in vitro* antifungal activity of ten newly synthesized ionic liquids (IL) against three phytopathogenic strains *Alternaria padwickii*, *A. dauci* and *A. linicola* isolated from rice, carrot and linseed, respectively. All ionic liquids showed strain specificity, but good antifungal activity on *Alternaria* strains with MIC and MFC detected at the range from 0,03 mol/dm^3 to 0,73 mol/dm^3. Obtained results indicate the possibility of usage of the most effective ILs as potential biocontrol agents of plant diseases caused by *Alternaria* strains.

Acknowledgments

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Medicinska hemija
Medicinal chemistry

MH01 OE 1

Synthesis and anti-virulence activity of *N'*-benzyl-4--aminoquinolines against *Serratia marcescens*

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Increased number of difficult-to-treat nosocomial infections and complications of other diseases in immunocompromised patients due to the presence of multidrug-resistant bacteria create a high pressure for a new strategy for treatment and prevention of bacterial infections. Quorum sensing (QS) is a complex mechanism of cell-density-dependent communication, through which many bacteria control the production and secretion of their virulence factors, motility, and biofilm formation. *Serratia marcescens* has become a serious healthcare problem due to multiple antibiotic resistances. Virulence of *S. marcescens* is regulated by QS, and disruption of these signalling pathways may be a novel, promising approach in the treatment of this infection. Anti-virulence agents do not target vital functions, therefore selective pressure is reduced.

Long-chained 4-aminoquinolines were reported as first quinoline derivatives with anti-biofilm formation activity in *S. marcescens*.[1] Ten new derivatives of 7-Cl and 7-CF_3-substituted *N*-alkylamino-4-aminoquinolines were synthesized by introducing different *N'*-benzyl substituents, and by changing the length of the aminoalkyl chain. The tested derivatives showed low antibacterial activity, thus resulting as candidates for anti-virulence agents. The anti-QS activity of the synthesized compounds in *S. marcescens* was tested by measuring the inhibition of prodigiosin biosynthesis and biofilm formation. From obtained activities, it could be seen that the modification of the terminal amino-group affects these processes. The presence of benzyl-substituents significantly increases the ability of biofilm formation inhibition, and the most potent derivatives show 55–65% inhibition at 10 and 50 μM. It was shown that small structural modifications enabled further optimization of 4-aminoalkylquinoline anti-QS activity making them promising anti-virulence agents against *S. marcescens*.

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MH02 OS 2

3-D QSAR-driven design of novel coumarin ERα antagonists

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The estrogen receptor α (ERα) represents the 17β-estradiol (E_2)-inducible transcriptional regulator that initiates the RNAP II-dependent transcriptional machinery, accountable for the breast cancer development *via* the tethered pathway. Thus, ERα appears as a promising target for developing pharmaceuticals potentially useful to treat this vicious disease. To contribute to the development of tethered pathway antagonists, herein, an *in silico* procedure is enclosed, including: (1) definition of optimized and validated structure-based (SB) 3-D QSAR models, by means of 3-DQSAutogrid/R protocol[1], derived from co-crystallized antagonist-ERα complexes; (2) elaboration of SAR features for ERα antagonists; (3) definition of structure-based (SB) alignment rules assessments for the evaluation of untested ERα antagonist; (4) predictive ability validation of the best, N probe-derived, SB 3-D QSAR model ($r^2 = 0.984$, $q^2_{\mathrm{LOO}} = 0.877$, $q^2_{\mathrm{K5FCV}} = 0.864$) through SB modeling of selected external test sets. Based on the generated N probe-derived 3-D QSAR model, ten novel coumarin based ERα antagonists were rationally designed and validated by subjecting to the SB alignment (by means of AutoDock Vina[2]) are topic of design and biochemical evaluation.

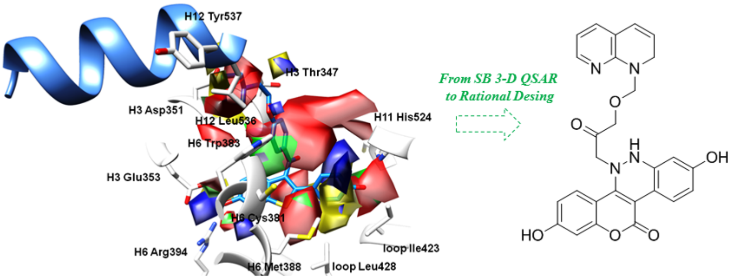

Figure 1. Rational design of novel ERα antagonists

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MH03 PE 1

Cu-MOF compounds as strong inhibitors of acetylcholinesterase

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Inhibition of acetylcholinesterase (AChE) represents a promising strategy in the treatment of Alzheimer disease (1) providing inspiration for new discoveries and investigations towards less toxic and more effective potential anti Alzheimer drugs. The aim of our study was to evaluate the effect of newly synthesized three copper(II) MOF derivatives based on different types of Cu4 units, namely a discrete 0D macrocyclic complex $[O\subset Cu_4\{N(CH_2CH_2O)_3\}_4(BOH)_4][BF_4]_2$, a 1D coordination polymer based on Cu4 cubane-like units $[Cu_4(\mu_4\text{-}H_2edte)(\mu_5\text{-}H_2edte)(sal)_2]_n \times 7nH_2O$ and a 3D metal-organic framework $[\{Cu_4(Hbes)_4(hba)\}K(H_2O)_4] \times 2H_2O$ on the activity of AChE and to examine possible binding modes of our three compounds to AChE using kinetics measurements and molecular docking approach. We found that investigated MOFs are capable to effectively inhibit the activity of AChE, in a concentration-dependent manner while $[O\subset Cu_4\{N(CH_2CH_2O)_3\}_4(BOH)_4][BF_4]_2$ has been found to be the most promising agent with IC50 values in low μM range. Kinetic measurements revealed reversible and uncompetitive type of inhibition while docking studies pointed out presence of two binding sites.

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Acknowledgments

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MH04 PE 2

Synthesis and antiproliferative activity of two new analogues of goniofufurone

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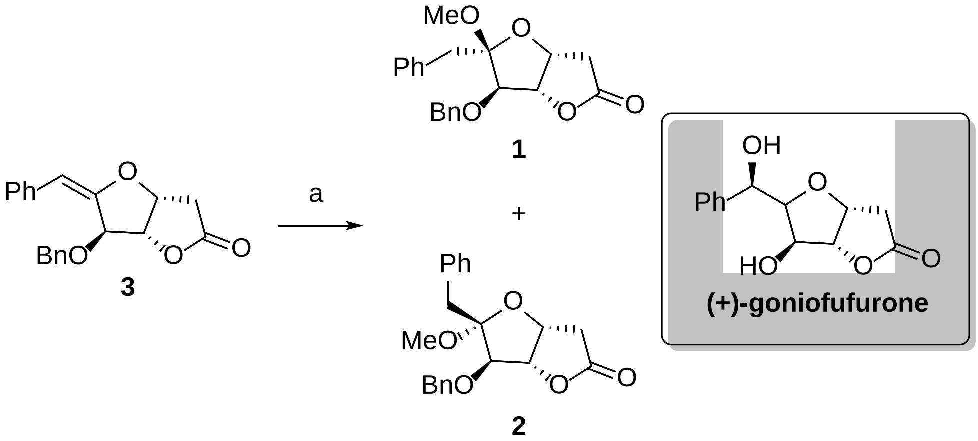
Herein, we want to report a synthesis of two new analogues (**1** and **2**) of naturally occurring styryl lactone (+)-goniofufurone (*Scheme 1*). These compounds were evaluated for their *in vitro* cytotoxicity against a panel of human tumor cell lines and also against a single normal cell line, foetal lung fibroblasts (MRC-5). Both synthesized analogues and natural product goniofufurone showed a significant antiproliferative activity against evaluated tumor cell lines. Also, analogues **1** and **2** was more active against several tumor cell lines than (+)-goniofufurone.



Scheme 1. Reagents and conditions: (a) H_2, PtO_2, MeOH, 26% of ***1*** *and 14% of* ***2****.*

Acknowledgments

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MH05 PE 3

Evaluation of antibacterial activity of *Sedum* species methanol extracts and their hydrolysates by TLC bioassay

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As edible and curative, many members of the genus *Sedum* (Crassulaceae) are used in nutrition and ethnopharmacology. This study tends to display results of antibacterial activity of methanol extracts and their hydrolysates of four *Sedum* species: *Sedum acre* L., *Sedum sarmentosum* Bunge, *Sedum hispanicum* L. and *Sedum rupestre* subsp. *rupestre*. Among them, *S. acre* and *S. sarmentosum* are representatives which are the most known in phytotherapy and for that reason they have been investigated from different aspects [1, 2]. On the contrary, *S. hispanicum* and *S. rupestre* are less investigated species. However, this is the first report on antibacterial activity of methanol extracts and their hydrolysates of above mentioned species by TLC bioassay. The samples were tested against panel of bacterial strains: Gram-positive bacteria *Bacillus subtilis* and *Staphylococcus aureus*, and Gram-negative bacteria *Escherichia coli*, *Pseudomonas aeruginosa* and *Salmonella typhimurium*. It was observed that investigated hydrolysates showed certain antibacterial activity against tested panel of bacterial strains, while methanol extract did not showed any antibacterial potential.

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Acknowledgments

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MH06 PE 4

Nickel(II) complex with (*E*)-4-(4-methoxyphenyl)-2-(2-(2-pyridylmethylidene) hydrazinyl)thiazole: synthesis, characterization and antiproliferative activity

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(1,3-Thiazol-2-yl)hydrazones are known to have significant biological activity [1]. This property can be enhanced if these compounds are used as ligands in transition metal complexes. A complex of Ni(II) with (*E*)-4-(4-methoxyphenyl)-2-(2-(2-pyridylmethylidene)hydrazinyl)thiazole (HL) was synthesized from $Ni(ClO_4)_2 \times 6H_2O$ and methanol solution of the ligand. Its crystal structure was determined by X-ray structural analysis. The complex was characterized by IR and UV/Vis spectroscopy, magnetic and conductivity measurements. It was found that the complex has the general formula $[Ni(HL)_2](ClO_4)_2$ and a distorted octahedral geometry, with the ligands tridentately coordinated through the imine, pyridine and thiazole nitrogen atoms in neutral form (Fig. 1). *In vitro* antiproliferative activity of the ligand and Ni(II) complex was evaluated against six human solid tumor cell lines. The activity of the complex was comparable or even better than that of the positive control 5-fluorouracil, the blockbuster anticancer drug.

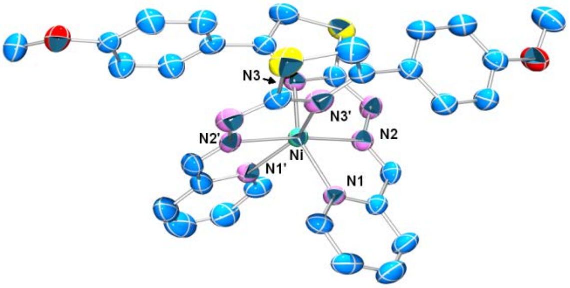

Figure 1. ORTEP drawing of the complex cation $[Ni(HL)_2]^{2+}$. Displacement ellipsoids are drawn at 50% probability level. For clarity, hydrogen atoms and perchlorate anions have been omitted.

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MH07 PE 5

Synthesis and antitumor potential of 3β-acetoxy-5α-bromo-6β,19-epoxy-16,17-secoandrostan-16,17-dioic acid

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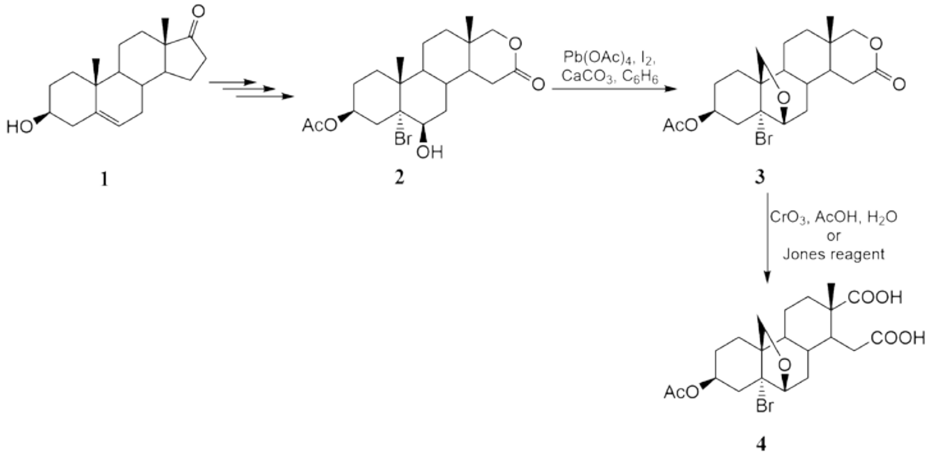
In order to obtain good antitumor compounds, 5α-bromo-6β,19-epoxide **3** was synthesised from bromohydrin **2** (Scheme 1).[1] Starting 5α-bromo-6β-hydroxy derivative **2** was previously obtained from dehydroepiandrosterone (**1**) in five synthetic steps.[2] Furthermore, oxidation of synthesized compound **3** was conducted using two oxidation methods and 16,17-seco dicarboxylic acid **4** was obtained. Finally, investigation of antitumor potential of novel compounds **3** and **4** was conducted. Their compliance with the Veber, Oprea and Lipinski rules was tested in order to investigate possible drug-like behavior, while antiproliferative activity against selected human cancer cells was measured *in vitro* using MTT assay.



Scheme 1.

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Acknowledgments

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MH08 PE 6

Interaction of synthetic guanylhydrazones with heme-sensitive human antibody

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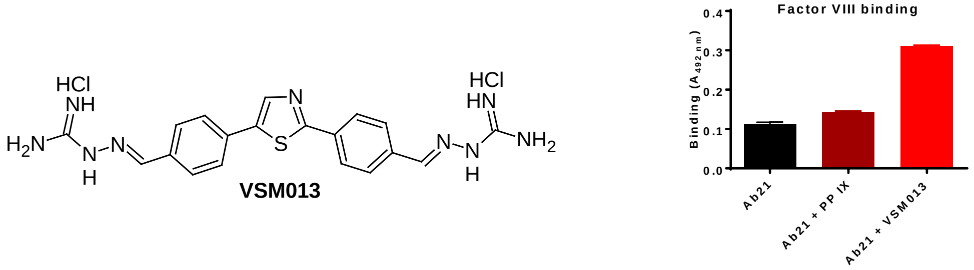
The goal of this work was to identify iminoguanidine-based antifungal agents with the potential for dual mechanism of action: direct, affecting the fungal cell, and indirect, by diversification of host antibodies (Abs) specificity. Binding of metalloporphyrins such as heme can endow a fraction of Abs with an ability to recognize numerous unrelated protein antigens (polyreactivity), which can lead to the neutralization of pathogens *in vitro* (1). Out of eleven tested guanilhydrazones, previously shown to exhibit excellent antifungal properties (2), one was found to induce polyreactivity of a selected heme-sensitive Ab. Polyreactivity-inducing potential of our compound was lower than that of heme, but considerably higher than that of protoporphyrin IX. It is the only non-metal containing compound that has been found to exhibit such an effect on IgG. Thus, we believe that this molecule can serve as a lead for the development of a novel generation of dual-acting antifungal agents.



VSM013

Figure 1. Structure and activity of VSM013

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MH09 PE 7

In vitro anticancer activity of a novel organotin(IV) complex with oxiprozin

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Many organotin(IV) complexes [1], especially carboxylate derivatives [2], have shown stimulating antitumor activities. The aim of synthesis is to minimize the well-known side effects of currently used platinum-based drugs. A novel organotin(IV) complex with is obtained by combining a water solution of the oxiprozin salt with methanolic solution of $(C_6H_5)_3SnCl$, in 1:1 molar ratio to form a white precipitate.

The structure is confirmed by elemental analysis, IR and NMR spectroscopy as well as mass spectrometry. Cytotoxicity was determined against tumor cell lines: human prostate (PC-3), human colorectal adenocarcinoma (HT-29), breast cancer (MCF-7) and human liver cancer (Hep G2) using MTT assay. The results have shown that synthesized complex exhibits high antiproliferative activity versus all four malignant cell lines with the IC_{50} values (in µM): 0.67±0.03 (PC-3), 0.50±0.09 (HT-29), 0.52±0.01 (MCF-7) and 0.47±0.08 (Hep G2). Novel organotin(IV) compound is 15 to 44 folds more active than the reference compound cisplatin. The effects of this complex towards cancer cells indicate the necessity for further studies with *in vitro* and/or presumably *in vivo* tests.

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MH10 PE 8

Investigation of the type of interactions between novel platinum(II) and palladium(II) complexes and DNA

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Platinum-based drugs are widely used anticancer agents with a broad range of antitumor activities. Although, cisplatin, cis-[$PtCl_2(NH_3)_2$], is one of the most common chemotherapy drugs, the acquired toxicity and resistance limit its clinical use.[1] Antitumor activity of platinum drugs is based on their interaction with DNA molecule, therefore, understanding the type of their interactions with DNA under physiological conditions can improve our knowledge of the biochemical processes that occur in the body during the application of metal complexes as antitumor drugs. In addition, studies of the interactions of palladium complexes, as model compounds, are very common.

Hydrodynamic properties and especially viscosity can give better indications on the binding mode of a small molecule toward DNA. Classical intercalation results in lengthening of DNA, due to the separation of base pairs at the intercalation site, which produces a concomitant increase in the relative specific viscosity of such solutions. Thus, such studies offer the least ambiguous test of intercalation.[2]

The principal objective of our study was to investigate the type of interaction between four new Pt(II) and Pd(II) complexes, $[Pd(H_2L^{tBu})Cl]Cl$, $[Pt(H_2L^{tBu})Cl]Cl$, $[Pd(Me_2L^{tBu})Cl]Cl$ and $[Pt(Me_2L^{tBu})Cl]Cl$ (where H_2L^{tBu} = 2,6-*bis*(5-(*tert*-butyl)-1H-pyrazol-3-yl)pyridine and Me_2L^{tBu} = 2,6-*bis*(5-(*tert*-butyl)-1-methyl-1H-pyrazol-3-yl)pyridine) with DNA by measuring the change of viscosity of CT-DNA solution in the presence and absence of above mentioned complexes, respectively.

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Acknowledgments

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MH11 PE 9

Synthesis and characterization of biologically active zinc(II) complex with (*E*)-4-phenyl-2-(2-(pyridin-2-ylmethylene)hydrazinyl)thiazole

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In order to obtain biologically active complexes with biometals, zinc(II) complex with the ligand (*E*)-4-phenyl-2-(2-(pyridin-2-ylmethylene)hydrazinyl)thiazole (HL) was synthesized and characterized. The complex was obtained as a single crystal and the structure was solved by X-ray diffraction analysis (Fig. 1). Complex was characterized by IR and NMR spectroscopy. Molar conductivity measurements showed that the complex is nonelectrolyte. Antitumor effect of the ligand and complex was examined against various human cancer cell lines. The complex showed higher antitumor activity than the ligand, comparable to the activity of positive control 5-fluorouracil. Antimicrobial activity of the complex was tested against five strains of Gram-positive bacteria and three strains of Gram-negative bacteria using disc-diffusion method. Antioxidant activity was evaluated using DPPH assay.

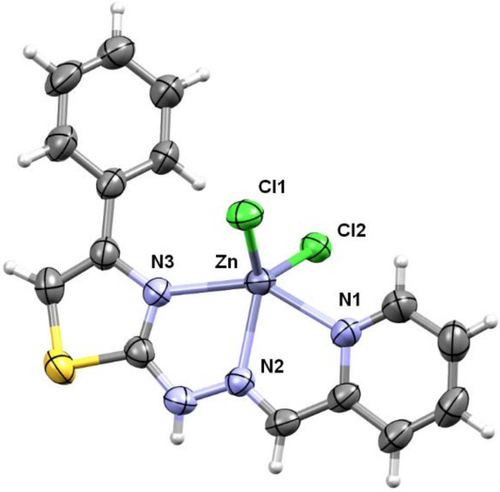

Figure 1. ORTEP drawing of the complex [Zn(HL)Cl_2]. Displacement ellipsoids are drawn at 50% probability level.

Acknowledgments

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MH12 PE 10

Synthesis, characterization and antimicrobial activity of cobalt(III) complex with the condensation product of 2-formylpyridine selenosemicarbazone and 2-bromoacetophenone

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New Co(III) complex with the condensation product of 2-formylpyridine selenosemicarbazone and 2-bromoacetophenone (HL), was synthesized and characterized. The complex was obtained by reaction of the ligand with $Co(BF_4)_2 \times 6H_2O$ in methanol. The composition of the complex was obtaind by elemental analysis, while molar conductivity measurements showed that the complex is 1 : 1 electrolyte type. The structure of the complex was solved by X-ray structural analysis and confirmed by ^1H and ^{13}C NMR spectroscopy. Two ligands in monoionic form are tridentately coordinated to Co(III) *via* pyridine, imine, and selenazole nitrogen atoms, while in outher sphere there is one tetrafluoroborate ion (Fig. 1). The complex showed good antimicrobial activity on different strains of bacteria and fungi.

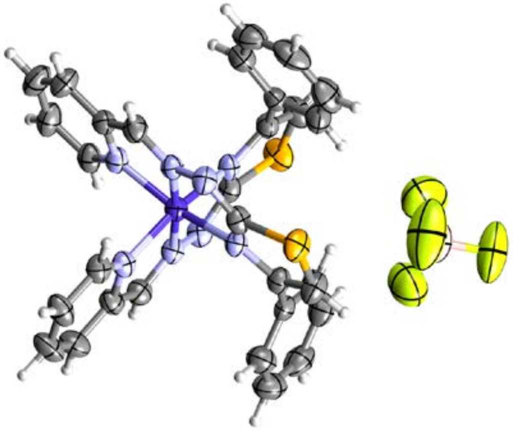

Figure 1. ORTEP drawing of $[CoL_2]BF_4$. Displacement ellipsoids are drawn at 50% probability level.

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MH13 PE 11

Interactions of copper(II) complexes of some Schiff base ligands with calf thymus DNA and bovine serum albumin

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Transition metal ions in combination with different ligands offer a large number of possibilities for testing potential bioactivities. Among transition metal ions copper is known as an endogenous metal for humans, with characteristic biological redox activities and relatively strong affinity for nucleobases. Copper complexes exhibit their antitumor activity on few different ways, they generate a high amount of reactive oxygen species, which causes oxidative damage to mitochondria and biomacromolecules. Copper(II) complexes have been reported to have moderate to good binding affinity with DNA, mostly via intercalation [1].

The interaction of a few copper(II)-complexes of Schiff base ligands to calf thymus DNA (CT-DNA) and bovine serum albumin (BSA) was further examined. Overall, the studied complex exhibited good DNA and BSA interaction ability. All obtained results in this study indicate that the introduction of S-alkyl derivatives of thiosalicylic acid as ligand can be used to improve the stability and reactivity of copper(II) complexes.

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MH14 PE 12

Antimicrobial activities of two copper(II) complexes with 4-(diethylamino)salicylaldehyde and α-diimine

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Two novel copper(II) complexes (Fig. 1) with 4-(diethylamino)salicylaldehyde as ligand (H**L**) and α-diimine - 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) with potentially antimicrobial activity are described. Complex **1** is a mononuclear copper(II) complex, [Cu(bipy)(**L**)]$BF_4 \cdot H_2O$, whereas complex **2** is a binuclear [Cu(phen)(**L**)]$_2(BF_4)_2$. Antimicrobial activities of those complexes, corresponding Cu(II) salt, α-diimines (phen and bipy) and ligand H**L** were studied by examining the minimum inhibitory concentration (MIC) on four Gram-positive and four Gram-negative bacterial species and three fungal strains. Amikacin and fluconazole were used as the standard drugs for the comparison of the MIC values. Cu(II) complexes **1** and **2** demonstrated significantly stronger antibacterial activities than parent ligands (*α*-diimines and H**L**) or starting Cu(II) salt. Complex **2** is the most active of all examined compounds. The activity of this complex against *E. coli* is comparable to the activity of the standard antibiotic amikacin. Unlike increasing antibacterial activity of complexes **1** and **2** in regard to all coordinated ligands, antifungal activities showed the opposite trend.

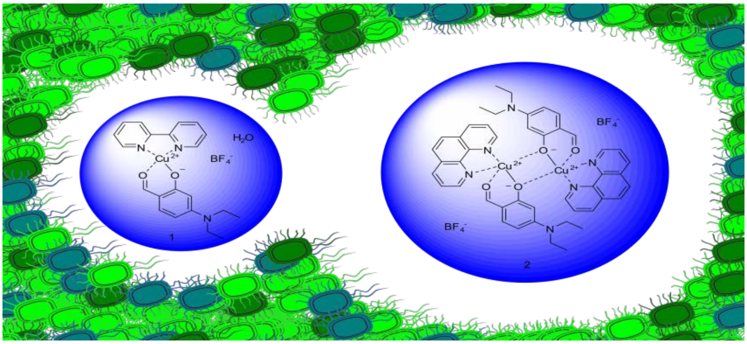

*Figure 1. Complexes [Cu(bipy)(**L**)]$BF_4 \cdot H_2O$ (left) and [Cu(phen)(**L**)]$_2(BF_4)_2$ (right)*

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MH15 PE 13

*h*DHFR inhibitors: Molecular determinants seen through the structure-based 3-D QSAR

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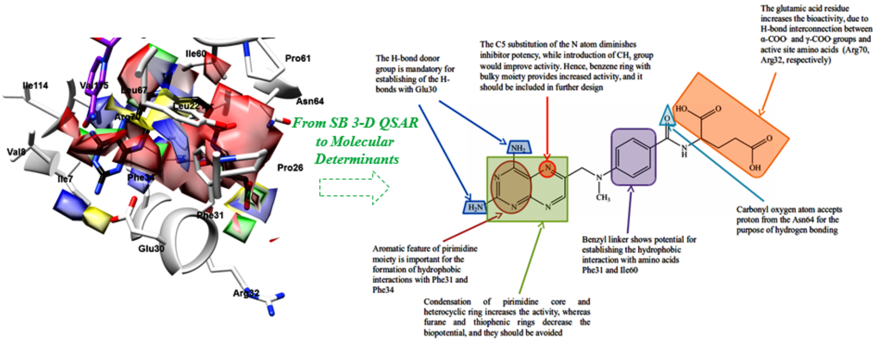
Human Dihydrofolate reductase (*h*DHFR) is a NADPH-dependent oxidoreductase which disfunction may lead to acute lymphoblast leukemia (ALL) development. Thus, *h*DHFR appears as a promising target for developing pharmaceuticals potentially useful to treat this vicious disease. To provide new guidelines for the evolution of *h*DHFR inhibitors, herein, an *in silico* procedure is confined, including: (1) generation of optimized and validated structure-based (SB) 3-D QSAR models, by means of 3-DQSAutogrid/R protocol[1], derived from co-crystallized inhibitor-*h*DHFR complexes; (2) establishment of structure-based (SB) alignment rules assessments for the evaluation of untested *h*DHFR inhibitors; (3) predictive ability validation of the best, HD probe-derived, SB 3-D QSAR model (Fig. 1, $r^2 = 0.985$, $q^2_{\mathrm{LOO}} = 0.939$, $q^2_{\mathrm{K5FCV}} = 0.892$) through SB modeling of selected external test sets. Based on the generated HD probe-derived 3-D QSAR model, the *PLS-coefficients*/Actual Activity Contribution-based biophysical rationale was transposed into the unique SAR model (Fig. 1), unequivocally applicable in future design of novel *h*DHFR inhibitors.



The H-bond donor group is mandatory for establishing of the H-bonds with Glu30

The C5 substitution of the N atom diminishes inhibitor potency, while introduction of CH$_3$ group would improve activity. Hence, benzene ring with bulky moiety provides increased activity, and it should be included in further design

The glutamic acid residue increases the bioactivity, due to H-bond interconnection between α-COO- and γ-COO- groups and active site amino acids (Arg70, Arg32, respectively)

Carbonyl oxygen atom accepts proton from the Asn64 for the purpose of hydrogen bonding

Benzyl linker shows potential for establishing the hydrophobic interaction with amino acids Phe31 and Ile60

Aromatic feature of pirimidine moiety is important for the formation of hydrophobic interactions with Phe31 and Phe34

Condensation of pirimidine core and heterocyclic ring increases the activity, whereas furane and thiophenic rings decrease the biopotential, and they should be avoided

Figure 1. Transposing the 3-D QSAR rationale into the hDHFR inhibitors SAR model

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MH16 PE 14

Synthesis, characterization and antimicrobial activity of cobalt(III) complex with (*E*)-4-(4-methoxyphenyl)-2-(2-(pyridin-2-ylmethylene)hydrazinyl)-1,3-selenazole

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New cobalt complex with (*E*)-4-(4-methoxyphenyl)-2-(2-(pyridin-2-ylmethylene)hydrazinyl)-1,3-selenazole (HL) was synthesized and characterized in order to obtain biologically active compound. The complex was synthesized by the reaction of HL with cobalt(II) tetrafluoroborate. The complex was characterized by conductivity measurements, elemental analysis, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, while X-ray structural analysis (XRD) was used for molecular and crystal structure determination. XRD data elucidated that the complex has octahedral geometry with two ligands coordinated to cobalt(III) as tridentates, both in monoionic form, through pyridine, imine and selenazole nitrogen atoms (Fig. 1). In the outer sphere of the complex there is one tetrafluoroborate ion. The complex crystallizes as monohydrate. Antimicrobial activity of the ligand and complex was evaluated against eleven strains of bacteria and fungi. The complex showed better antibacterial than antifungal activity.

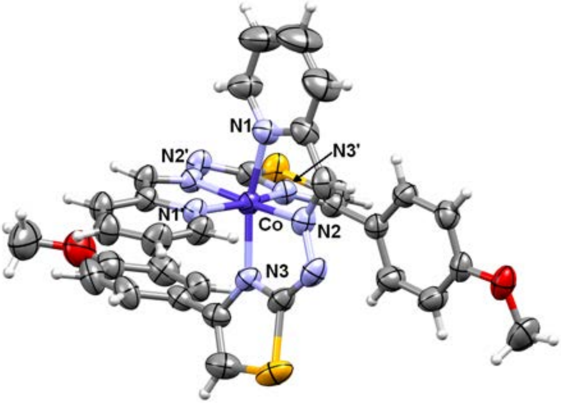

Figure 1. ORTEP drawing of the complex cation [Co(L)$_2$]$^+$. Displacement ellipsoids are drawn at 50% probability level. For clarity, tetrafluoroborate anion and crystalline water molecule have been omitted.

Acknowledgments
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Nauka o materijalima
Materials science

NM01 OE 1

Influence of the alkali treatment conditions on the chemical composition and capillarity of the jute woven fabrics

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Jute fibers have been subjected to various types of chemical modifications to improve their suitability as textile materials. Among them, the alkali treatments have been widely used as the most direct and ecological chemical treatments to remove the hemicelluloses from the jute fibers. The content of hemicelluloses has impact on the various sorption properties, such as capillarity, moisture sorption, water retention power, etc. Capillarity, defined as macroscopic motion of the fluid system under the influence of its own surface and interfacial forces, is a desirable quality in textile materials, because it allows the fiber to absorb moisture, liquids, oils etc. [1].

In this investigation, the influence of the alkali treatment conditions on the chemical composition (content of hemicelluloses) and capillarity of the jute woven fabrics was studied. In order to partially remove hemicelluloses, the jute fabric was alkali treated with NaOH solution of different concentrations (5%, 10% and 17.5%) during 5 min at room temperature, while the capillarity rise method was applied to evaluate the capillarity of the jute fabrics with different content of hemicelluloses. The capillarity rise height of untreated jute woven fabric is 1.0, 4.0, 10.0, 16.0, 36.0 and 55.0 mm after 1 min, 5 min, 15 min, 30 min, 45 min and 1 h respectively. With increasing the NaOH concentration, the content of hemicelluloses decreased. The untreated jute woven fabric has 21.76% hemicelluloses, while after the alkali treatments, the content of hemicelluloses decreased down to 13.79%. When the hemicelluloses were reduced progressively, the capillarity of the jute woven fabrics was improved, i.e. the capillarity rise height increased up to 11.0, 43.5, 68.5, 77.0, 97.0, and 124.5 mm after 1 min, 5 min, 15 min, 30 min, 45 min, and 1 h, respectively.

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Acknowledgement

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NM02 OE 2

Novel luminescent tetrakis lanthanide β-diketonate complexes: structural study and temperature sensing

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Lanthanide β-diketonate complexes have been extensively investigated in the past, as they are cheap, easy to synthesize and they tend to form highly stable complexes with lanthanide ions. Lanthanide β-diketonate complexes have been used as NMR shift reagents, also they are good precursors for further synthesis in some more complex matrixes (such as sol-gels, polymers…), used as OLEDs and as temperature probes because of their distinct luminescence properties.[1] Optical thermometry based on luminescence is an expanding field of research because non-contact temperature sensing can have different applications, such as in bioimaging, anti-counterfeiting or in an industry where it is necessary to have good sensing properties in precisely defined temperature ranges.[2] Here, we report novel structures of different homonuclear (Ln^{3+} = Pr, Nd, Sm, Eu, Tb, Dy, Er and Yb) complexes and four heteronuclear complexes: two Eu-Tb and two Tb-Sm complexes with different ratios of the two ions. The 1,1,1-trifluoroacetylacetonate (tfac) has been chosen for the synthesis because it is well known and widely used in complexation chemistry. The complexes crystallize in the orthorhombic system with the Pna2 space group with four molecules per unit cell. The structure consists of a $[Ln(tfac)_4]^-$ salt with a sodium cation, where the Ln ion is coordinated with eight O atoms from the $tfac^-$ ligands. The homonuclear complexes show luminescent properties in both the visible and NIR region. The Dy complex shows good temperature sensing properties in the region 280-380 K, with a maximum value Sr = 3.45 % K^{-1} at 280 K; Tb-Sm heteronuclear complexes with different ion ratios show good temperature sensing in the same region with maximum Sr = 2.30 % K^{-1} at 360 K. The Eu-Tb complexes show temperature sensing properties in different regions which are influenced by different ion ratios in the complexes. For the complex with Tb^{3+} ions the region of temperature sensing is 10-335 K with max Sr = 1.65 % K^{-1} at 285 K, and for the complex with higher Eu^{3+} ions content the region of temperature sensing is the physiological range with max Sr = 2.70 % K^{-1} at 353 K.

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NM03 OS 3

TEMPO oxidation as pre-treatment for improving antibacterial activity of viscose functionalized by chitosan

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The main objective of this study was to obtain viscose fabric functionalized by chitosan with effective antibacterial activity and good durability to washing. In this regard, viscose fabric was pre-treated, i.e. TEMPO oxidized in system containing 50 mL phosphate buffer solution/20 mg TEMPO/50 mg $NaClO_2$/5 mmol NaClO/g viscose fabric under neutral pH condition at 60°C during 5 min, to introduce carboxyl and aldehyde groups for irreversible binding of chitosan. Pristine and TEMPO oxidized viscose fabrics were functionalized with 0.5% solution of chitosan (pH 5.5) during 30 min at room temperature using a material–liquid bath ratio of 1:50, with a wet pickup of 100%. Carboxyl and aldehyde groups content of pristine and TEMPO oxidized viscose fabrics were determined by calcium acetate method [1]. Zeta potential measurements were carried out to monitor influence of acidic groups' quantity on surface charge of pristine and TEMPO oxidized viscose fabrics, as well as stability of chitosan bound onto fabrics. Antibacterial activity against Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacterial strains was evaluated before and after 1, 3 and 5 washing cycles. Washing of functionalized viscose fabrics was performed according to standard ISO 105-C01. Zeta potential measurements showed release of chitosan during washing. Pristine viscose fabric functionalized by chitosan provided effective bacterial reduction against *S. aureus* after 1 washing cycle and *E. coli* before washing, while TEMPO oxidized viscose fabric functionalized by chitosan provided effective bacterial reduction against *S. aureus* after 5 washing cycles and *E. coli* after 3 washing cycles.

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NM04 PE 1

B-doped graphene as an electrode material in novel metal-ion batteries: the role of dopant concentration

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Graphene, a 2D hexagonal sp^2-carbon structure, is extensively studied for electrochemical energy conversion and storage applications. Pristine graphene is chemically very inert and interacts weakly with species of electrochemical interest, restricting its use as an electrode material in metal-ion batteries, fuel cells and electrochemical capacitors. However, an improvement in that sense can be achieved by altering the electronic structure of carbon atoms in graphene, by introducing defects into its basal plane. The defects can be in the form of dopant atoms, vacancies, surface functional groups, or distortion (corrugation) of the graphene sheet. When it comes to metal-ion batteries, the material's interaction with the chosen metal ions is of crucial importance for its performance. Due to the difficulties that Li-ion batteries are facing, the attention of the electrochemical community is turning towards sodium and some multivalent metal-ion batteries. Many studies, both experimental and theoretical, have proposed boron-doped graphene as a promising electrode material for sodium-ion batteries. Using Density Functional Theory (DFT) calculations, we demonstrate how substitutional doping of graphene with boron affects its electronic structure, charge distribution, and the interaction with the metals of electrochemical interest: Na, Mg, Al and Zn. The influence of the oxygen-containing groups, which are often present on such surfaces, is discussed. We investigate the role of B concentration and the changes that it induces in graphene's electronic structure and the studied interactions.

NM05 PE 2

Synthesis of 3-hydroxyalkanoic acids, their spectral characterization and thermal properties

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Phase change materials (PCM's) are substances that absorb and release thermal energy during the process of melting and freezing at a nearly constant temperature. They are used to store energy for a broad range of applications. The aim of our research was to investigate the thermal properties of tree different 3-hydroxyalkanoic acids and their binary mixtures.

3-Hydroxyalkanoic acids were obtained by hydrolysis of their ethyl or methyl esters in almost quantitative yields (92-99%). Ethyl 3-hydroxyalkanoates were synthesized by Reformatsky reaction in 55-60% yields.[1] Methyl 3-hydroxyalkanoates were obtained by depolymerization of biopolymers, namely polyhydroxyalkanoates (PHA's) in high yield (95%).[2] Using the differential scanning analysis method, the thermal properties of individual 3-hydroxyalkanoic acids as well as their binary mixtures were studied. Tested 3-hydroxyalkanoic acids showed great potential for application as new PCM's in latent heat thermal energy storage (LHTES) systems. Thermal properties and behavior of eutectic mixture of 3-hydroxydecanoic and 3-hydroxydodecanoic acid (60/40 w/w%) showed significant application potential as PCM in LHTES systems.

Considering that 3-hydroxyalkanoic acids are relatively inexpensive and easily available from naturally occurring biopolymers, their application as PCM would be significant improvement in development of new materials.

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NM06 PE 3

Removal of Pb^{2+}, Cd^{2+}, and Ni^{2+} from aqueous solution using structurally modified three-dimensionally ordered (3DOM) alumina

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The adsorption of iron oxide doped alumina, $FeAl_2O_3$, was investigated for Pb^{2+}, Cd^{2+} and Ni^{2+} removal. The impact of parameters on adsorption of selected cations, such as, contact time, adsorbent dosage, temperatures, was examined. The obtained adsorbent was characterized by ATR FT-IR spectroscopy, TG, XRD, S_{BET} and SEM analysis. Concentrations of the examined cations, before and after adsorption experiments, were determined by using Atomic Absorption Spectroscopy (AAS). For determination of the adsorption capacities the best fit was obtained using Freundlich model of the adsorption isotherm for all three cations.

Acknowledgments
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NM07 PE 4

Antibacterial silver/poly(vinyl alcohol)/chitosan hydrogels for wound dressing applications

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This study presents the electrochemical synthesis of silver nanoparticles (Ag-NPs) in the physically cross linked poly(vinyl alcohol) (PVA) and chitosan (CHI) hydrogel matrices. The obtained silver/poly(vinyl alcohol)/chitosan (Ag/PVA/CHI) nanocomposite hydrogels were prepared with two different chitosan concentrations, in order to investigate the influence of chitosan on physicochemical and biological properties. The UV-visible (UV-vis) spectroscopy confirmed the presence of nano-sized silver particles inside the hydrogel matrices, and the silver release kinetics was monitored over 28 days in order to determine the release mechanism. The swelling of the hydrogels was investigated in phosphate buffer (PB) which imitates physiological environment, and it was found that the hydrogels with higher chitosan content exhibited better swelling ability and reached higher equilibrium swelling degree. The antibacterial properties were confirmed by disc-diffusion and test in suspension against *Staphylococcus aureus* and *Escherichia coli* bacterial strains.

The obtained results indicated the potential for the use of Ag/PVA/CHI hydrogels in biomedical applications, as they meet the requirements for hydrogel wound dressings, such as strong antibacterial properties, time-dependent controlled silver release profiles and good sorption and swelling properties.

Acknowledgments

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NM08 PE 5

Preparation of zeolite from coal fly ash as waste raw material

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The zeolite from F class coal fly ash (FA) was prepared from alkali fused fly ash followed by hydrothermal treatment. Sodium water glass obtained from the calcined and acid activated FA and sodium aluminate were used in zeolitization. Hydrothermal reaction was performed at 90°C for 4h. The prepared zeolitic material was characterized by EDX, XRD, FT-IR and Hg-porosimetry. The concentrations of the main components SiO_2, Al_2O_3, and Na_2O in the synthesized material are: 51.45%, 30.01%, and 16.64%, respectively. The diffraction patterns show that the characteristics lines are at 14.4°, 20.5°, 25.5°, 32.7°, 39°, and 44.5° that are typical for Na-X zeolite. The FT-IR spectra show that the strongest vibration is at 960 cm^{-1} (T-O stretch), whereas the vibrations in the region between 600 and 750 cm^{-1} are related to tetrahedral atoms in zeolite structure [1, 2]. The Hg porsimetry measurements show that the porosity of obtained material is around 62% and the total pore volume is 1,10 cm^3/g. Such characteristics of the prepared zeolitic material allow its use in various catalytic chemical processes for converting vegetable oil to biofuel including transesterification, deoxygenation, thermal cracking, catalytic cracking, and hydroprocessing.

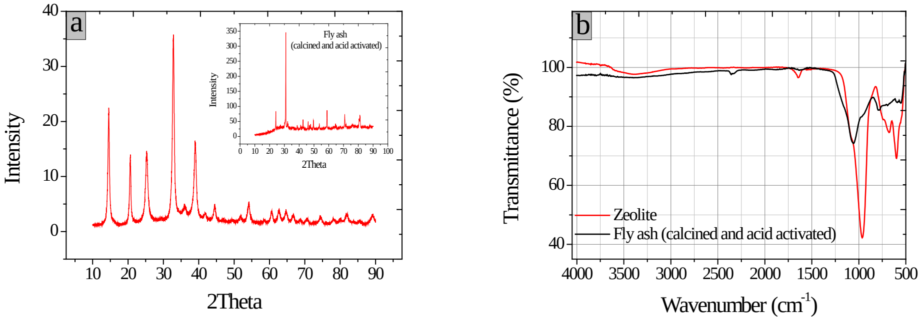

Figure 1. XRD pattern (a) and FT-IR spectra (b) of the prepared zeolite material and activated FA

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NM09 PE 6

Application of branched aminated waste polyacrylonitrile fibers for Pb^{2+} and Cd^{2+} removal

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Adsorbent, based on waste polyacrylonitrile (PAN) fibres, was obtained in three addition/amidation successive steps to produce amino terminal functionalities. Characterization was performed using FTIR and SEM techniques. Adsorption results have been showed that synthesized adsorbent could be efficiently used for Pb^{2+} and Cd^{2+} removal. The influence of different parameters, such as initial pH, contact time, adsorbent mass and concentration, before and after adsorption experiments, was determined using Atomic Absorption Spectroscopy (AAS). The best fitting of adsorption data was obtained using Langmuir isotherm model.

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NM10 PE 7

Innovative aproach for wireless electrochemical remediation of cyanotoxins based on bipolar electrochemistry

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Bipolar electrochemistry (BPE) is an unconventional method to address conducting and semiconducting particles in a wireless manner. Unique features of BPE when compared to conventional electrochemical setup where electrochemical reactions take place at the surface of two different electrodes both connected to a potentiostat, allow us to address bipolar electrode electrochemically in a wireless fashion because there is no direct connection with the power supply (see Figure 1.). Herein, we used the concept of BPE as a straightforward way for the site selective deposition of materials on bipolar electrodes. Furthermore, we use these materials for the electrochemical remediation of cyanotoxins, a potential global health problem, exploiting the versatility of bipolar electrochemistry. Due to the high toxicity of cyanotoxins, highly efficient remediation methods have been under development in recent years, with advanced oxidation processes focused on mineralization as major target. Electrochemical remediation arose as an interesting alternative with few reported protocols to date.

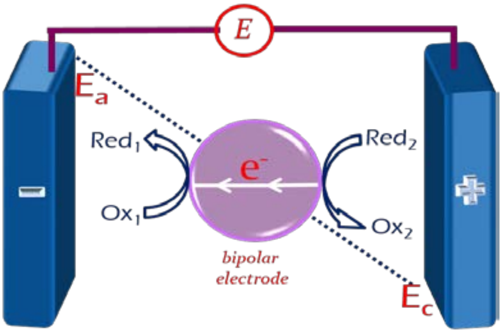

Figure 1. Schematic illustration of the principle of bipolar electrochemistry based on the polarization potential established alongside a conducting object immersed in an electrolyte and exposed to an electric field.

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NM11 PE 8

Antibacterial activity and biocompatibility of novel composite hydroxyapatite/chitosan/gentamicin coating

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Novel composite coating based on hydroxyapatite, chitosan and gentamicin (HAP/CS/Gent) was successfully obtained by single-step electrophoretic deposition process from aqueous suspension. In order to investigate the potential application of composite HAP/CS/Gent coating, biological properties were examined. The antibacterial activity of composite coating was tested using an agar diffusion method and test in suspension against two bacteria strains- *Staphylococcus aureus* and *Escherichia coli*. Biocompatibility was evaluated by cytotoxicity testing, towards MRC-5 and L929 cell lines using MTT and DET tests. The ability of biomineralization was tested by ALP assay towards MRC-5 and L929 cell lines as model cells. Excellent antibacterial properties were observed for HAP/CS/Gent coating, especially in case of *S. aureus*. DET and MTT assays indicated low cytotoxicity against MRC-5 and L929 tested cell lines, indicating good biocompatibility. High ALP level in the cell extract implicates the good bioactivity of HAP/CS/Gent coating. Due to the compatibility of the cells, MRC-5 cell line responded better in ALP assay.

Due to good antibacterial and anti-biofilm efficacy, good biocompatibility and ability to promote biomineralization, composite HAP/CS/Gent coating can be can be considered for future medical application as hard tissue implant.

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NM12 PE 9

Comparative study of degradation efficiency of ceftriaxone in ultrapure and natural water using different types of irradiation

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A large amount of pharmaceutical products, especially antibiotics is used in the world reaching to an estimation of 100.000 to 200.000 tons per year. Despite their vital importance in our daily life, antibiotics seem to raise a concern as a persistent water contaminant [1]. Ceftriaxone (third-generation cephalosporin antibiotic) is extensively applied to treat respiratory tract infection, urinary system infection and gonorrhea. It poses potential risks to aquatic ecosystem and human health due to recalcitrant molecular structure, as its chemical structure [2]. In this comparative study, degradation efficiency of ceftriaxone using different types of commercial nanopowders (TiO_2 Degussa P25, TiO_2 Hombikat, TiO_2 Wackherr, and ZnO) were studied in ultrapure and in natural water (Danube river). Also effect of type of irradiation (simulated sunlight and UV) was studied. The obtained results were also compared to results of direct photolysis. The kinetics of degradation was monitored by ultra fast high performance liquid chromatography with diode array detector.

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Teorijska hemija

Theoretical chemistry

TH01 OE 1

Density functional theory calculation of lipophilicity - bridging the gap between experiment and theory

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Density functional method with continuum solvation model is used for calculation of partition coefficient logK_{OW} and determination of lipophilicity of 22 most frequently used organophosphate type pesticides. Excellent agreement with experimental data is obtained using three different density functional approximations (one local, one general gradient and one hybrid), and our result highlights DFT as a reliable and trustworthy method for calculation and of lipophilicity for this important class of molecules. Lipophilicity represents the affinity of a molecule or moiety to dissolve in fats, oils, lipids, and non-polar solvents, it affects important biological processes that follow chemical intake such as absorption, distribution, passage through biological membranes, receptor interactions, toxicity and metabolism. According to original "shake-flask" method based on liquid-liquid partitioning, the partition coefficient K_{OW} is defined as a concentration ratio of compound distributed between n-octanol and aqueous phase, but is frequently obtained by methods based on solid-liquid partitioning (retention on reversed-phase high-performance liquid chromatography (RP-HPLC) or thin-layer chromatography (TLC) system), what makes it an important means in analytical chemistry in general. In present work, our calculated lipophilicity results are associated with experimentally determined LD_{50} and LC_{50} values, showing that the most toxic pesticides are these with transient characteristics (medium lipophilicity), although this concussion must be taken with a caution due to the many factors influencing the ingestion and action of a certain substance in the body beside lipophilicity.

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TH02 PE 1

Modelling of cholesterol and ethanol cumulative effect on hypothalamic-pituitary-adrenal axis

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This study deals with the mathematical modelling of the acute cholesterol and ethanol perturbations of the hypothalamic-pituitary-adrenal (HPA) axis stoichiometric network model. The cumulative effect was investigated in order to improve this model of HPA axis activity to more acurately describe realistic conditions of ethanol consumption. Already developed model for regulating the role of cholesterol on HPA activity [1], extended by Čupić et al [2] in order to examine the influence of ethanol, was used.

Results suggest that both ethanol and cholesterol alters the dynamics regulation of HPA axis activity by affecting the amplitudes of hormonal ultradian oscillations. Moreover, different responses of the HPA axis to the cumulative effect of cholesterol and ethanol from the response to the ethanol perturbation only were observed. Response of the HPA axis model is shown to be proportional to the initial concentrations of ethanol. Furthermore, perturbations of the system with all tested concentrations of ethanol annul the effects of lowering the amplitudes of ultradian oscillations by cholesterol and return the system to the dynamics it possessed before perturbation. Finally, results of this study can be a useful tool in further understanding and investigation of the mechanism of the alcohol effects on neuroendocrine system.

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TH03 PE 2

Valence bond study of intramolecular hydrogen bonding in malondialdehyde

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Intramolecular hydrogen bonding plays a fundamental role in many fields of chemistry. In this work the resonance assisted hydrogen bonding in malondialdehyde was examined. The energy of hydrogen bonding was calculated with different methods: *cis-trans* comparative analysis method, isodesmic reaction, analysis of electron density topology (AIM method) and valence bond method. The contribution of resonance was calculated by comparison of the energy of selected valence structures of malondialdehyde at VBSCF level of theory. Our results indicate that the effect of π-electrons delocalization to hydrogen bonding is approximately 13% of the total energy.

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TH04 PE 3

Automatic generation of 3D-MMPs from PDB and ChEMBL

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Matched Molecular Pairs (MMPs) are an established local QSAR method. Their usefulness has been showcased in a number of settings including prediction of ADME, bioisosterism, solubility, logD and other [1]. As for QSAR methods in general, the idea of MMPs is based on the assumption that the effect of a substitution can be generalized. This assumption holds true as long as the environment is homogenous. Scenarios like trans-target binding affinity prediction are usually not coverable with an MMP approach.

For proper predictive power of such models three-dimensional (3D) information can be included. 3D methods allow for the inclusion of the binding site surrounding. This includes spatial boundaries as well as amino acid composition. With proper descriptors valuable additional information can be extracted from 3D representations of protein-ligand complexes. Patterns and interaction networks obtained from such an analysis can then be used to rationalize activity cliffs or unexpected results of substitutions [2].

Here, we present a novel workflow for generating 3D-MMPs. With the Protein Data Bank (PDB) and the ChEMBL database as basis, related structural data and binding affinity values are connected and saved in a database. Matching of the macro-molecules that are stored in the PDB and those used in biochemical assays is achieved via an approach utilizing residue sequences. Ligands for which affinity values could be found are pooled and 2D-MMPs are extracted. PDB structures that are part of a 3D-MMP are superimposed and the RMSD of the common core of both ligands is calculated. Based on the RMSD and the difference in affinity values MMPs can be classified as standard MMP or activity cliff. Cases with small transformations, e.g. exchange of a few atoms, and a significant change of pose associated are of special interest (pose cliffs).

The workflow presented is going to be structured into three parts. First, affinity values have to be found for PDB structures. Second, 2D-MMPs have to be extracted from the resulting dataset. And last, active sites have to be aligned and the RMSD of the common core has to be calculated. The presentation will focus on the compilation and combination of structural and activity data. Furthermore, an analysis of the current status of 3D-MMPs will be featured.

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TH05 PE 4

Discussing aqueous uracil aggregation with first principle molecular dynamics simulations

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It is well known that nucleobases in water solution spontaneously aggregate to form stacked dimers and multimers. Hydrophobic and base−base dispersion interactions are assumed to be main forces to govern this process. Employing density functional based molecular dynamics simulation of uracil monomer and dimer in bulk water (Fig 1.) we withdraw conclusions that stacking leads to polarization of monomer units in the dimer and therefore modifies uracil−water interactions [1]. This has been concluded on the basis of increased hydrogen bonding strength between water molecules and the uracil polar sites which modifies radial distribution functions and infrared absorption spectrum. Water interaction with π electron cloud is also modified. These results are showing that monomer's dipole interactions in the dimer contribute with less than 0.1 kcal/mol for the dimer stabilization. Excluded solvent volume and monomer's dipole interactions are not the main driving thermodynamic forces in dimerization process, whereas stacking primary occurs due to dispersion interaction between bases and changes in the hydration structure with an estimate that this process changes stacking free energy by approximately -1.3 kcal/mol.

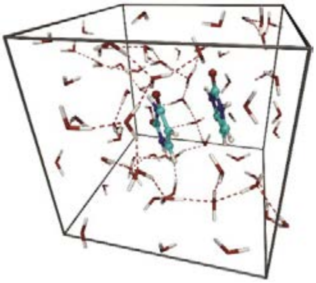

Figure 1. Instantaneous configuration of uracil and water molecules in simulation box sampled from the ab initio molecular dynamics simulation.

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TH06 PE 5

Dependence of ΔH_f of ketones on structural properties – computational modeling

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Enthalpy of formation of acyclic saturated ketones was examined while molecular structural properties such as number of carbon atoms, position of the carbonyl group, and branching of a molecule were variables. In order to pursue this investigation we developed a simple computational model based on spectral graph theory. Experimental gas-phase ΔH_f data of 27 acyclic saturated ketones were used to model the heat of formation. The results pointed out that the major part of enthalpy of formation depends on the size of molecules. Position of the carbonyl group and branching of a molecule have less influence on ΔH_f of ketones. Our computational model showed good performance, with the average relative error of 0.7%. In addition, the model predicts a unique ΔH_f value of a certain ketone, independently on the number of its conformers.

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TH07 PE 6

Theoretical and spectral analysis of 6-hydroxydopamine

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Density functional theory calculations, with B3LYP, B3LYP-D3, APFD, M05-2X, M06-2X functionals and 6-311G++(d,p) basis set, are performed with the aim to support the molecular structure and the spectroscopic characteristics of 6-hydroxydopamine [1]. The optimization results of molecular geometry, obtained using different functionals, were compared with experimental data for the crystallographic structure [2]. The highest degree of agreement between experimental and theoretical values was obtained using B3LYP-D3 functional for bond distances and M06-2X functional for interbond angles. The correlation coefficients were 0.997 for B3LYP-D3 and 0.915 for M06-2X functional. The theoretical spectra are predicted based on the structure optimized at M06-2X/6-311++G(d,p) level of theory. Three stable conformers are obtained from the conformational analysis. The most stable conformer is stabilized by the intramolecular hydrogen bond between amino group and hydroxyl group attached to aromatic ring. The cation→π interaction is present in second conformer. The last conformer resembles the crystalographic structure, and has relative Gibbs energy that is 28 kJ/mol higher than for the first conformer. 6-Hydroxydopamine has been characterized by several spectroscopic techniques (IR, Raman and NMR). The experimentally obtained and theoretically calculated IR and Raman spectra of 6-hydroxydopamine were compared. Most of the modes are present in both spectra, although the relative intensities are different. The broad bands which appear in 3860-3200 cm^{-1} region are assigned to the *m*-OH, *p*-OH and *o*-OH stretching vibrations, while the stretching modes of the NH_2 group appear at about 3500 cm^{-1}. The broadness of this modes is possibly due to the formation of the hydrogen bond within the condensed sample. There are also differences in the experimental and theoretical ^1H NMR spectra. The chemical shifts are in good agreement for the H atoms bonded to the C atoms in the ring, while the values for the H atoms in the OH and NH_2 groups are significantly different. The correlation coefficient (R) and mean absolute error (MAE) are 0.999 and 0.07 ppm for ^1H spectrum. A higher level of agreement was achieved in ^{13}C NMR spectra, with R and MAE being 0.998 and 1.9, respectively. This result is expected due to the rigidity of molecule.

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The interaction of bipyridyl gold(III) complexes with Au(111) surface – a DFT study

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Adsorption of selected Au(III) complexes $[Au(OH)_2(bipy)]^+$, $[Au(CH_3COO)_2(py^{dmb-H})]$ and $[Au(bipy^{dmb-H})(OH)]^+$ (1) on periodic Au(111) surface slab was investigated using density functional theory (DFT) within GGA-PBE approximation. Optimization of adsorption geometries resulted in minimal equilibrium complex – surface distances in the range 2.13 – 3.27 Å. In case of charged complexes $[Au(OH)_2(bipy)]^+$ and $[Au(bipy^{dmb-H})(OH)]^+$, adsorption energies larger than -7 eV per molecule are obtained. Charges calculated from Bader analysis confirm that a significant transfer of electrons (about 0.11 e^- per molecule) occurs from the surface to the positively charged complexes. In case of neutral $[Au(CH_3COO)_2(py^{dmb-H})]$, calculated adsorption energy is -0.36 eV per molecule and charge transfer from the surface to the molecule achieves 0.016 e^- per molecule. Obtained results represent a new approach to the investigation of interaction between Au(III) complexes and metal surfaces, provide a model to predict and/or explain the behavior of Au(III) complexes on similar supports (in particular Au nanoparticles), and set up a basis for further investigations.

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