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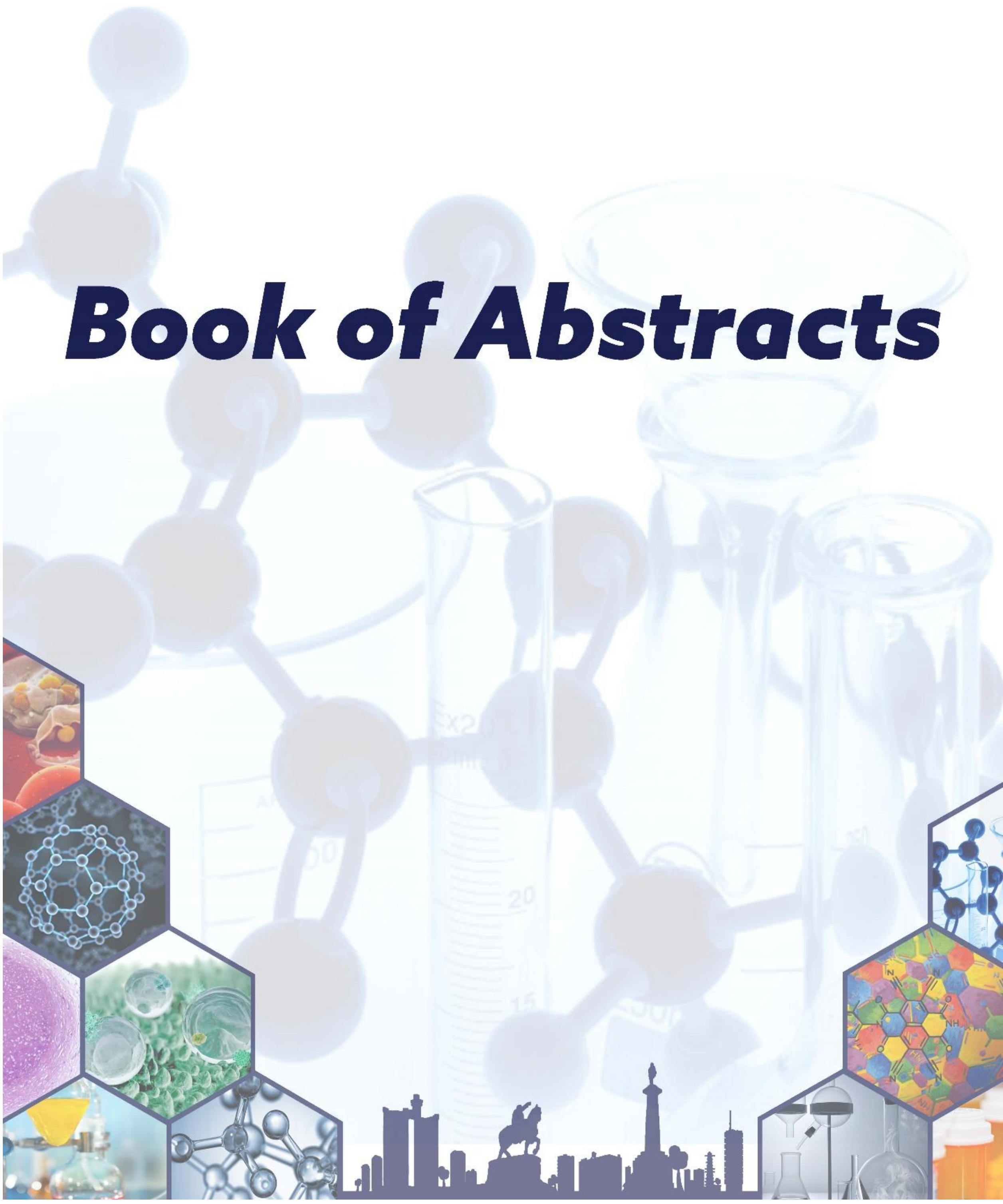
Table of Contents

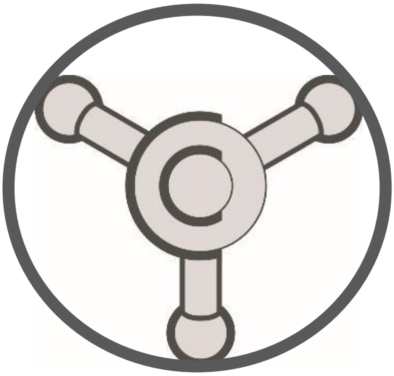
Plenary Lecture

Invited Lectures

Contributions

Book of Abstracts





Serbian Young Chemists' Club

Plenary and Invited Lectures

Belgrade, 2nd November 2019

PP OP 01

The poly(ε-caprolactone) chemistry role in creating new polymer biomaterials

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Over the last decades, widespread use of plastics on daily basis resulted in accumulation of polymer waste and further impact the environment. Great concern about the reduction of waste, mostly coming from plastic packaging, has initiated new research focused on the development of new materials with suitable properties to replace traditional plastics. The use of biodegradable polyesters has great potential in suppression of environmental pollution, but also this type of polymers has been applied in different biomedical fields. Among the polyesters, poly(ε-caprolactone), PCL, biodegradable, aliphatic and hydrophobic polyester is widely utilized for biomedical application, as well as for environmentally sustainable packaging. PCL has been recognized as biomaterial of choice in tissue engineering due to its slow degradation ability, biocompatibility and as suitable substrate for cell growth, as a vehicle for controlled drug delivery because of its good permeability to drugs and non-toxicity[1]. In contrary to all benefits that put PCL apart from other biodegradable polymers, slow degradation rate and relatively high degree of crystallinity remarkably limits its wider application.

Therefore, the present research reveals two different approaches related to the improvement of PCL biodegradability. One of the ways is to introduce the hydrophilic, short segments (such as poly(ethylene oxide), PEO) into PCL chains and accordingly two series of both diblock and triblock PCL copolymers with different PCL blocks length and different amount of PEO were synthesized, characterized and explored in term of degradation under controlled hydrolytic, enzymatic and composting conditions[2,3]. It was shown how the change in polymer structure and composition could be used as powerful tool in controlling degradation behavior of PCL/PEO based block copolymers. Another approach is to decrease the crystallinity by synthesizing star-shaped PCLs because branched structure disrupts well-ordered crystal structure of linear PCL. In a line with this approach, star-shaped PCL with different number of arms (three, four and six) were prepared and susceptibility to hydrolysis at different pH values (7.4 and 1.0) was investigated. The great potential of both PCL/PEO block copolymers and star-shaped PCLs in drug delivery was pointed out by preparation of ibuprofen loaded microspheres. The absence of cytotoxycity of all applied new PCL based materials confirmed that this type of polymers can be proposed for biomedical application.

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PPP OP 01

Novel diazachrysenes and naphthyridines in the fight against Ebola

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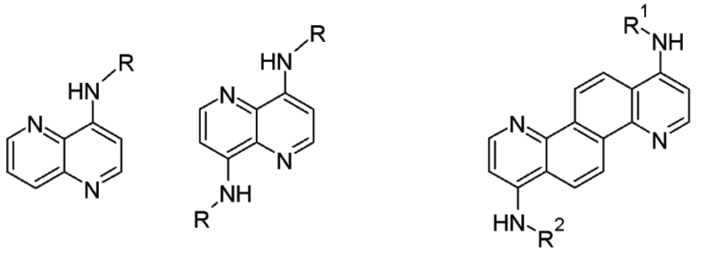
Ebolaviruses are a virus genus of the *Filoviridae* family. Species from this genus, endemic to Sub-Saharan Africa, cause a lethal hemorrhagic fewer in humans and non-human primates. There are still no approved vaccines or other therapeutics to tackle this menacing infection, although several vaccine candidates have reached clinical trials. Grounded on the knowledge previously gained in our research group, we developed two new chemotypes as possible antivirals – derivatives of 4,10-diazachrysene and 1,5-naphthyridine, respectively (Fig. 1). Several small series of compounds were tested, yielding two derivatives with excellent *in vitro* activity. Furthermore, these two compounds protected 90-100% of infected mice from a fatal Ebola challenge (10 mg/kg dose). Additional experiments were performed in order to elucidate the mechanism and mode of action of these compounds. Although it was discovered that the derivatives block viral entry, it was proven that the precise manner differs to a degree from the processes described in literature. The results obtained in this thesis show that the compounds are distinctive and warrant further research.



aminoalkyl derivatives of 1,4-naphthyridine

aminoalkyl derivatives of 4,10-diazachrysene

Figure 1. General structures of our Ebola inhibitors.

Acknowledgments

This research was supported by the Ministry of Education and Science of Serbia (Grant No. 172008).

PPP OP 02

Stacking interactions of aromatic ligands in transition metal complexes

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We have studied stacking interactions of aromatic moieties that coordinate to transition metals through their π-electrons, mostly by analyzing crystal structures deposited in the Cambridge Structural Database (CSD) and by performing quantum chemical calculations. These interactions are important in the areas of materials science, catalysis, crystal engineering, and, most importantly, medicinal chemistry.

The studies showed that both coordinated benzene[1,2] and coordinated cyclopentadienyl (Cp) anion[2] form strongest stacking interactions at small horizontal displacements (about 1.5 Å), but in crystal structures they have the tendency towards large horizontal displacements (> 4.5 Å, Figure 1) in order to achieve more stable supramolecular structures. Stacking geometries between substituted aromatic ligands, such as *p*-cymene (Figure 1), as well as their energies, are determined by additional interactions between substituents and aromatic rings.

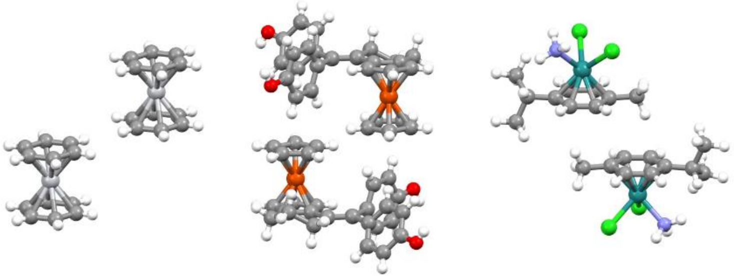

Figure 1. Stacking interactions in CSD crystal structures between coordinated benzenes (left), Cp anions (middle) and p-cymenes (right).

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Biochemistry and biotechnology

Belgrade, 2nd November 2019

BB OP 01

Ectodomain shedding of epidermal growth factor receptor by cysteine cathepsins

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Cysteine cathepsins are lysosomal proteases which are also known to be secreted to the extracellular space. Secreted cysteine cathepsins can cleave ectodomains of membrane proteins including receptors, growth factors, cytokines and adhesion proteins.[1] Among the receptors, epidermal growth factor receptor (EGFR) was identified as cathepsin substrate candidate with high physiological relevance. Epidermal growth factor receptor belongs to the ErbB family of receptor tyrosine kinases, and play an important role in cell differentiation, migration, proliferation, and metabolism. This receptor is found to be overexpressed in a number of cancers. Moreover, cancers overexpressing EGFR showed to be more aggressive and resistant to the chemotherapeutics. Signalling through EGFR is commonly triggered by ligand binding, however, deletions in extracellular region of EGFR can also cause constitutive activation which is ligand independent. Such deletions can influence receptor activation and downstream signalling cascades such as phosphotidylinositol 3 ON (PI3K) pathway. Using mass spectrometry-based proteomics, we have proved that cysteine cathepsin L proteolytically cleaves domain II of EGFR and that this cleavage cause its activation and influences its physiological function. We have shown that ectodomain deletion which emulates cathepsin cleavage affects phosphorylation profile of cellular kinases. However, our findings open new questions about EGFR and could possibly lead to more effective strategies in anticancer therapy.

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BB PP 01

Effects of immortelle essential oil on macrophage NO production

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The essential oil of immortelle, *Helichrysum italicum* (Asteraceae), has a long application for wound healing. Nowadays, it is one of the most popular essential oils in cosmetics as it may stimulate blood circulation and regeneration of the skin, and reduce the appearance of fine lines and wrinkles. However, several chemotypes of *H. italicum*, characterized by distinct essential-oil profiles, were described and it is unlikely that all show the same therapeutic efficacy. Recently, we found that antimicrobial activity and cytotoxicity toward macrophages of immortelle oil strongly depends on its composition. In continuation of our research, we evaluated the effects of 4 commercial immortelle oils (**1**, **2**, **3**, and **4**, respectively) containing differing amounts of nerol esters (23 : 43 : 12 : 21), α-pinene (17 : 2 : 20 : 5), *γ*- and *ar*-curcumenes (19 : 14 : 16 : 15), and β-diketones (3 : 12 : 5 : 7) on LPS-stimulated NO production in macrophages. All oils suppressed NO production at the highest tested concentration (0.1 mg/mL). Oil **1**, rich in mono- and sesquiterpene hydrocarbons, induced the greatest concentration-dependent decrease in NO production ($IC_{50} = 1.5 \times 10^{-4}$ mg/mL), while oil **2**, rich in nerol esters and β-diketones, was two-fold less active ($IC_{50} = 1.6 \times 10^{-2}$ mg/mL). Four chromatographic fractions, enriched in mono- and sesquiterpene hydrocarbons (**f1**), curcumene (**f2**), nerol esters (**f3**), and β-diketones (**f4**), were also tested in order to potentially identify the carriers of the observed activity. The most potent was the curcumene fraction that reduced the production of NO to only 20% at 1×10^{-5} mg/mL. In comparison to the oils, fractions **f1** and **f2** displayed stronger inhibitory effect at all tested concentrations, whereas fractions **f3** and **f4** were less active at the highest tested concentration. Overall, these results imply that the higher content of mono- and sesquiterpene hydrocarbons in immortelle oil had the most prominent positive impact on its activity, whereas the amount of β-diketones had the opposite effect. A statistical (PCA) treatment of the obtained composition-activity data provided further confirmation; strong positive correlations were observed between the activity and the amount of limonene, *trans*-α-bergamotene and *ar*-curcumene, while very strong negative correlations were noted for all β-diketones. Interestingly, in our previous study oils **1** and **3** also showed higher cytotoxicity toward macrophages than oils **2** and **4**, while fractions **f1** and **f2** were more potent than the other two but still inferior to the oils.

Acknowledgments

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BB PP 02

Determination of the antioxidant activity of 20 different pumpkin varieties

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Flesh and seeds of pumpkins are commonly used for culinary and medicinal purposes. In this study, 20 different varieties of pumpkin grown at the Institute of Field and Vegetable Crops in Novi Sad, Serbia were analyzed for their polyphenol and carotenoid content and evaluated for their antioxidant properties. These 20 different varieties belong to two basic species: *Cucurbita maxima* and *Cucurbita moschata*. Carotenoids are the natural plant pigments responsible for the color of pumpkins. The consumption of a diet rich in carotenoids has been epidemiologically correlated with a lower risk for several diseases. The antioxidant activity of carotenoids and biochemical properties influencing signaling pathways have been discussed as basic mechanisms of prevention. Carotenoids are highly present in the fruit of these plants, namely α-carotene, β-carotene, ζ-carotene, neoxanthin, violaxanthin, lutein, zeaxanthin, taraxanthin, luteoxanthin, auroxanthin, neurosporene, flavaxanthin, 5,6,5′,6′-diepoxy-β-carotene, phytofluene, α-cryptoxanthin and β-cryptoxanthin. The extracts of these 20 different varieties of pumpkins were investigated for their antioxidant properties using ABTS radical scavenging capacity assay and ferric reducing antioxidant potential (FRAP) assays. Total phenolic content was also determined by the Folin−Ciocalteu method. Antioxidant properties and total phenolic content differed significantly among the selected plants. The results of antioxidant capacity detected by ABTS assay are expressed as mM Trolox equivalent (TxE) of extract. ABTS assay showed that pumpkins from *Cucurbita maxima* marked as **Max 118-1** (0,204 mM TxE/g) and **Max 117** (0,175 mM TxE, (both have an orange color flesh, round shape) and *Cucurubita moschata* marked as **Mo 29-2** (0,174 mM TxE; orange color flesh, bell shape) possessed the highest antioxidant capacities (all these pumpkins are originally from Serbia). The highest phenolic content (the results are expressed as mM galic acid equivalent (GAE) of extract) was found in pumpkins species *Cucurbita moschata* marked as **Mo 38** (0,182 mM GAE/g) and **Mo 39** (0,176 mM GAE) (both have an orange color flesh, bell shape). When the FRAP assay was used, the highest antioxidant capacities were found in the following pumpkins: *Cucurbita maxima* marked as **Max 1** (16,89 μg/ml AAE; orange color flesh, round shape) and *Cucurbita maxima* “Hokkaido” type (14,15 μg/ml AAE; orange color flesh, round shape). The results of antioxidant capacity detected by FRAP assay are expressed as μg Ascorbic acid equivalent in one ml of extract (μg/ml AAE). A significant correlation between antioxidant capacity and total phenolic content was found, indicating that phenolic compounds are the major contributors to the antioxidant properties of these plants.

BB PP 03

Screening of new alkalophilic bacterial strains from soil

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In the recent decades, biodiversity of microorganisms in extreme environments have been extensively studied because of the microorganisms that can grow in these conditions have great potential in biotechnological applications (1). In this study, screening of new alkalophilic sporogenic strains from alkaline soil samples were performed.

Calcified and leached soil samples were collected from four different sites: (I) leached soil from the river Danube near Novi Sad, (II) cement factory waste water near the Dunavac bayou, (III) deposit of limestone near the Bešenovo lake and (IV) the Beli Majdan cave in the Fruška gora mountain. The homogenized soil samples were subjected to thermal treatment (80 °C, 10 min). After an incubation period of 24h on 22 °C, series dilutions were made and aliquots were streaked onto pH modified R2A agar following by the incubation period at 30 °C for 48h. After the selection of targeted isolates, the growth tolerance and the optimal temperature for bacterial growth were detected by monitoring of growth intensity on pH modified R2A slant agar during the 5 days incubation at different temperatures (20, 30, 37 and 44 °C), while the influence of pH value (5, 7, 9 and 11) was monitored in R2A broth.

The results obtained indicate that 75% of the total of 43 isolated strains belong to Gram-positive bacteria, while oxidase and catalase are 50 and 98% positive, respectively. More than half of the selected strains (62%) belong to the group of alkalophilic or alkali resistant bacteria, and for 19% of the strains the pH value 11 represents the optimum growth. The optimal growth temperature for most strains is between 30 and 37 °C, while temperatures of 20 and 44 °C are not outside the biokinetic zone for 97% of isolates.

In this study, a total of 43 alkalophilic bacterial strains have been successfully isolated from soil samples. The most of the isolated bacteria have potential to grow at temperatures between 30 and 37 °C in media with pH value between 9 and 11. The obtained results indicate the examined soils are habitats rich in alkaline microbiota.

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BB PP 04

Microencapsulation of peach pomace extract in *Saccharomyces cerevisiae* cells

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Peach pomace, as an industrial by-product, is rich in antioxidants such as carotenoids, and polyphenols, etc. (1). Preserving these substances can be provided by microencapsulation, which prolongs the shelf life ensuring stability of bioactive compounds and prevents deleterious reactions caused by its surroundings (2). The aim of this study was to evaluate the feasibility of differently prepared cells of *Saccharomyces cerevisiae* as an encapsulation carrier for polyphenols and carotenoids present in peach pomace extract.

The yeast *Saccharomyces cerevisiae* ATCC 9763 is used as a carrier of peach pomace extract as: (I) non-plasmolyzed lyophilized cells, (II) plasmolyzed (with 10% NaCl) lyophilized cells and fresh yeast (non-plasmolyzed and lyophilized). Freeze-dried extract was mixed with yeast carriers on UltraTurrax at 11000 rpm (3 min), then lyophilized. The content of polyphenols and carotenoids were spectrophotometrically determinated in the microcapsules and the efficiency of microencapsulation of above-mentioned substances was calculated.

The number of living yeast cells in microcapsules I and III was reduced to 6.9 and 5.5 log CFU/ml compared to the number of cells in carriers (9.62 and 9.3), caused by lyophilization. In carrier II cells number was significantly lower than in carriers I and III as a result of plasmolysis. The highest content of bound polyphenols was found in microcapsule I (4.21 mg GAE/g), therefore this capsule has the highest microencapsulation efficiency of polyphenols (66.26%). Microencapsulation efficiency polyphenols in capsules II and III was 24.59 and 46.82 mg GAE/g. The biggest content of carotenoids compared to the content with added extract was determined in sample I. Microencapsulation efficiency of carotenoids for samples I, II and III was 86.59, 63.17 and 26.97%.

According to the obtained results, all of the three yeast samples could be used as carriers of peach pomace extract. Non-plasmolyzed lyophilized yeast cells have shown the highest microencapsulation efficiency.

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BB PP 05

Influence of pesticides thiacloprid and clothianidin on phenol oxidase and prophenol oxidase activity in honey bee (*Apis mellifera* L.)

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Honey bee (*Apis mellifera* L.) is one of the most important pollinators in the world, but the number of colonies has been decreasing for the last few decades. Pesticides, as well as parasites and pathogens, affect colony survival. It has been shown that pesticides thiacloprid and clothianidin are highly toxic to bees and weaken their immune response. In honey bees individual immunity consists of cellular and humoral immunity. Melanization, as innate humoral immune defense in insects, plays important roles in diverse physiological processes including wound healing, chorion hardening, cuticle tanning and defense reactions. Phenol oxidase (POx) and prophenol oxidase (PPOx) are key enzymes in the synthesis of melanin and indicators of individual immunity.

In this experiment, the bees were treated by thiacloprid and clothianidin for 48h with three sublethal doses of pesticides. Seven different groups were formed with three biological replicates (control, and six experimental groups). Results showed that treatment with pesticides caused significant decrease in POx and PPOx activity in all experimental groups except in the group treated with the lowest dose of thiacloprid. The results showed that sublethal doses of pesticides disturb immune response and therefore conservation measures should be taken.

Acknowledgements
This study was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, grant no. 173014, project entitled “Molecular mechanisms of redox signaling in homeostasis: adaptation and pathology”.

BB PP 06

Antimicrobial profile of *Maclura pomifera* dry extracts

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Maclura pomifera is a deciduous tree native to North America, which parts contain phytochemical compounds with antimicrobial properties. The aim of this study was to investigate the antimicrobial profile of dry leaf 30, 50 and 70% ethanol and methylene-chloride extracts of the *Maclura pomifera* plant, as well as to determine the minimum inhibitory concentration (MIC) of the extracts against selected microorganisms.

The plant material was collected on the surrounding area of Zrenjanin (Autonomous Province of Vojvodina, Republic of Serbia) in August 2018. The dried plant material was grounded in a domestic blender and the particle size of ground material was determined using sieve sets (MAIG Braunschweig, Germany). Antimicrobial properties of the prepared *Maclura pomifera* extracts were individually determined against *Escherichia coli* ATCC 25922, *Pseudomonas aeruginosa* ATCC 27853, *Bacillus cereus* ATCC 11778, *Staphylococcus aureus* ATCC 25923, *Enterococcus faecalis* ATCC 19433, *Listeria monocytogenes* ATCC 35152, *Saccharomyces cerevisiae* ATCC 9763 and *Candida albicans* ATCC 10231, *Aspergillus brasiliensis* ATCC 16404. The estimation of the antimicrobial activity was conducted by implementation of two different methods: disk diffusion method and assessment of minimal inhibitory concentration (MIC) by the method of serial dilutions in microtiter plates (1).

According to the obtained results, Gram-negative bacteria, yeast and fungus were found to be resistant to the effects of *Maclura pomifera* extracts by the disk diffusion method. In contrast, Gram-positive bacteria have been shown to be sensitive to all ethanol extracts and resistant to methylene-chloride extract. The highest antimicrobial activity of ethanol extracts was observed in the case of *E. faecalis*. When determining MIC of the extracts, it was found that 70% ethanol extract had the highest activity against *L. monocytogenes* and *S. aureus* (10 mg / mL).

Based on the results, it can be concluded that 70% of the ethanolic extract of *Maclura pomifera* has great potential for use as a preservative in the food industry or as an ingredient of moderate antimicrobial pharmaceuticals.

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BB PP 07

Phenolic profile of *F. fomentarius* extracts from Bosnia and Herzegovina

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Fomes fomentarius (L.) Fr. commonly known as the thinder fungus is a saprophytic, perennial fungal species with wood structure found in Europe, Asia, Africa and North America[1]. Fungal species *F. fomentarius* are used for medicinal purposes: diarrhea, cauterization of the wound, as painkiller, for hepatoprotective effect, neuroprotective and nephroprotective effect etc.

This fungal species is a important source of phenolic compounds, therefore, the aim of this study was to exemine phenolic profile by LC/MS-MS method.

Fruiting bodies of were collected in October 2018, from Vrelo Bosne (Sarajevo, Republic of Bosnia and Herzegovina). Ethanol (70% EtOH) and chloroform ($CHCl_3$) extracts were prepared in the same way by incubation, double filtration and vacuum evaporation. Hot water (H_2O) extracts were prepared by imitating making tea and methanol extracts (80% MeOH) were prepared by several steps: maceration, centrifugation, double filtration and vacuum evaporation. Detail examination of phenolic profile included quantitative analysis of 45 phenolic compounds by highly sensitive and specific LC-MS/MS tehnique[2].

LC-MS/MS analysis of selected phenolic compounds resulted in quantitative determination of 7 among 45 examined compounds. From 7 detected compound, 6 were detected in MeOH extract. The most dominant are phenolic acids, as well as quinic acid in MeOH and EtOH extracts (996,78 and 414,18 ng/mL d.w., respectively). In addition to these compounds, coumarins (esculetin and scopoletin) were detected for the first time in analyzed fungal species.

In conclusion, presented results highlight phenolic profile of analyzed extracts, especially MeOH. Based on this results, phenolic profile is a potential indicator of antioxidant activity of *F. fomentarius* which may have the potential to substantially neutralize free radicals and keep the cells safe.

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BB PP 08

Buffer Composition and Nonionic Surfactants Could Influence Cold Stability of Trypsin Enzyme

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Trypsin, as a serine protease, has a variety of applications (protein sequencing, tissue dissociation). It was previously shown that the storage of trypsin in acidic conditions can reduce the activity recovery by more than 40% after 7 freeze-thaw cycles and that cold storage in ammonium-bicarbonate buffer with the addition of glycerol or lysine, can lead to the protein stabilization and high activity recovery[1]. In present study, potassium-phosphate and ammonium-phosphate buffers were used with high activity recovery rate (up to 90 %) after 7 freeze-thaw cycles. For sodium-phosphate buffer, during 7 freeze-thaw cycles, there was as an incise in binding of the hydrophobic fluorescent probe, 1-anilino-naphthalene-8-sulfonate (ANS). This is due to forming of molten globule state of trypsin protein. Nonionic surfactants (NS) Tween 20, Tween 80 and Triton X-100 were used with high activity recovery rate (up to 94 %). There were no significant changes of bands maxima corresponding to specific secondary structures, in the Fourier transform infrared (FT-IR) spectrum. This is indicative of no freezing-induced damage to the trypsin protein. As denaturation of trypsin occurs when the protein adsorbs to the ice crystal surface during the crystallization process, the NS's can protect trypsin by competing with the protein for sites on the ice surface. Furthermore, trypsin that was stored in this fashion, was used for digestion in the conventional method for preparing *Listeria monocytogenes* suspension from meat products. This significantly improved the recovery yield and it was evidenced by an increase in the number of *L. monocytogenes* colony forming units (CFUs).

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Food chemistry

Belgrade, 2nd November 2019

FC OP 01

Supercritical fluid extraction of grape seed: Effects of process parameters on target compounds

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Wine production is one of the biggest agricultural activities worldwide. This industry each year generates significant amounts of waste, which has to be treated to minimize the impact on the environment. In the last few years, the attention has been paid to recycling these by-products with a view of recovering valuable bioactive compounds. The promising alternative to conventional solvent extraction processes is supercritical fluid extraction (SFE) that could provide equal oil yield with better product characteristics. The main goal of this study is to investigate how the parameters of SFE, for instance, pressure, temperature, CO_2 flow rate and particle size influence the quantitative and qualitative characteristics of obtained grape seed oils. Grape seed oils were compared in terms of yield, fatty acid profile, tocopherol content and antioxidative activity. Results showed that the highest yield was obtained when SFE conditions were 350 bar, 60 °C and 0.4 kg CO_2/h. Grape seed oils are rich in α- and γ-tocopherols. Fatty acid profile consisted mostly of polyunsaturated fatty acids (>69%) where the most dominant one was linoleic acid. Modern extraction technique gave possibility to valorize winery by-product as raw material and recover high-value grape seed oils that could find application in food, pharmaceutical and cosmetic products.

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FC PP 01

Igg - Marker For Food Tolerance

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There are various reasons why a food can cause problems, among them a classic IgE food allergy (type I) and a delayed IgG food allergy (type III), later is also referred as food intolerance. What both allergies have in common is that the immune system is involved. However, there are some differences in the way it responses. A type III food allergy is when the immune system (B cells and plasma cells) produces specific **IgG antibodies** (immune globulins of the subclass G) against usually harmless foodstuffs. Our interest is to find out which type of food often gives an increase or high titre of antibodies to random patients from our country.

Foodscreen analyse is works on the ChemWell, ELISA method (Enzyme immunoassay for the detection of specific IgG antibodies against food antigens in human serum). Ig G titre (marker of food tolerance) can be quantified in several groups (negative, low, increased and high). Our foodscreen analyses IgG antibody reactions to 90 possible triggers of chronic diseases. We analyzed 160 randomized patients aged 18 to 65 years. Of all 90 type of foods, our patients are usually intolerant of cow's milk (increased 10.6% high 44.4%), cow sour milk (increased 11.9% high 41.9%), goat cheese (increased 16.3% high 23.1%), sheep cheese (15.0% high 25.6%), eggs (increased 18.1% high 45.5%), wheat (increased 26.3% high 36.3%), gluten (increased 22.5% high 48,8%), nuts - almond (increased 15.0% high 21,9%), black pepper (increased 37.5% high 29.4%) and vanilla (increased 11.3% high 32.5%). Gluten (71.3% increased and high titre of antibodies) is one of the most common causes of food intolerance.

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FC PP 02

Effect of different extraction methods on fatty acid composition of lipid extracts from rosehip seeds

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Rosehip is a pseudo-fruit of the wild rose, one of the most widespread wild species of the genus *Rosa* in Serbia. Due to its nutritional value and sensory properties, rosehip takes a significant place in the human nutrition. Rosehip seeds are by-product in the industrial production of marmalade, jam, beverages, jelly, syrup, tea etc. In the recent years, rosehip seeds have been used in the pharmaceutical and cosmetic industries, due to their specific fatty acid composition [1].

In this study two different methods for the extraction of fatty acids from the wild rosehip seeds have been used; ultrasound and extraction with solvent. Both procedures were performed at room temperature using n-heptane for the extraction of fatty acids (FA) from plant material. Different solvent volumes and seeds weights were used. The identification and content of fatty acids were analyzed by gas chromatography with a flame ionization detector (GC/FID). Extracts were filtered through a filter paper and the filtrate was evaporated in a stream of nitrogen. The lipid extract was dissolved in 1 mL of n-heptane and converted to fatty acid methyl esters (FAME's) by using 1 ml of 14% BF_3/MeOH reagent [2]. Fatty acid content was expressed in relative quantities as mass % of total fatty acids.

Obtained results indicated that applied methods, as well as the ratio of solvent volume and seeds weight had influence on the composition of fatty acids and their amount (%). Extraction of the lipid fraction by ultrasound and GC-FID analysis resulted in unsaturated fatty acids, while saturated and unsaturated fatty acids were obtained by solvent extraction.

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FC PP 03

DPPH and ABTS assays of some culinary herbs extracts

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Culinary herbs are often used in traditional gastronomy and folk medicine. Those herbs are now even more popular in consumer's baskets because of their antioxidative activity [1] that positively affects human health. The aim of this study was to determine antioxidative capacity in methanolic extracts of five different culinary herbs (Breckland Thyme, Basil, Bay Laurel, Parsley and Oregano) purchased from local markets in Belgrade. Antioxidative capacity was determined in reactions with two stable radicals: 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) and expressed as IC_{50} values. This is the concentration of the examined extracts that is required for 50% reduction of initial concentration of DPPH/ABTS radicals. According to obtained results the highest IC_{50} value is determined in Parsley (*Petroselinum crispum*) extract (26.3951 mg/ml (DPPH method); 17.8852 mg/ml (ABTS method)), while the lowest IC_{50} value had Oregano (*Origanum vulgare*) extract (5.5898 mg/ml (DPPH method); 6.5184 mg/ml (ABTS method)). The obtained results show that the highest antioxidative activity possess Oregano and Bay Laurel, while the lowest is observed in case of Parsley.

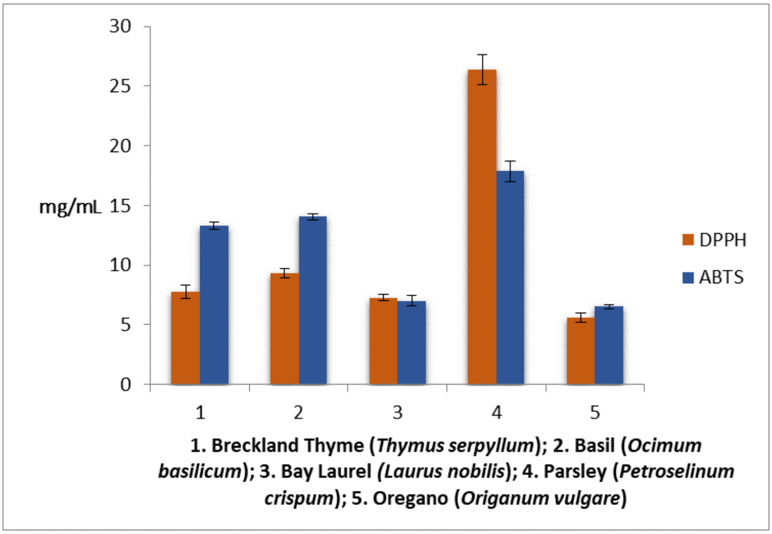

Figure 1. IC_{50} values of plant extracts for DPPH and ABTS assay

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FC PP 04

Mineral profile of berry of table grape varieties (*Vitis vinifera* L.)

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Grapevine (*Vitis vinifera* L.) is considered as the most important fruit crop in the world, and includes a large number of varieties of different use values. Table grapes are widely grown and consumed around the world due to its economic importance and beneficial effects on human health [1]. In addition, the interest to use grape seed oil in culinary preparations has increased.

In this work 27 elements were studied in seeds and mesocarp of six table grape varieties: Muscat Italy, Muscat Hamburg, Victoria, Michele palieri, Afuz-ali and Moldova in order to evaluate their mineral profiles. For the analysis inductively coupled plasma - optical emission spectrometry (ICP–OES) using US EPA Method 200.7 was employed [2].

Toxic and potentially toxic elements Ag, As, Cd, Co, Cr, Hg, Sb, Se, Tl and V were not detected in studied grape samples. Al, Fe and Ni were detected only in mesocarp of Moldavia, seeds of Muscat Italia and mesocarp of Afuz-ali grapes, respectively. Na was detected in Victora seeds and Afuz-ali seeds and mesocarp. Among essential elements Ca was measured in the highest concentrations in seeds of all studied grape varieties (2145.842-5536.409 mg/kg). Concentrations of K ranged from 747.533 mg/kg (Afuz-ali) to 1424.929 mg/kg (Victoria), Mg from 44.105 mg/kg (Michele palieri) to 996.044 mg/kg (Muscat Hamburg) and Zn from 0.212 mg/kg (Muscat Italia) to 5.638 mg/kg (Muscat Hamburg). Obtained results indicate that detected elements were found in higher concentrations in seeds compared to mesocarp of studied grapes, with exception of B in Moldavia, Bi in Victoria, K in Muscat Italia and Moldavia, Mo in Moldavia, Na in Muscat Italia and Afuz-ali, and Sn in Muscat Hamburg.

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FC PP 05

Utilization of plant species *Sambucus nigra* L. in order to obtain potential functional products with therapeutic effects

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Sambucus nigra (elderberry) is one of the most widespread plants in the Balkan Peninsula. The healing properties of this plant have been known since ancient times, while its use in the human diet is very rarely. Due to the increasing correlation between diet and health, this study was based on the utilization of the natural potential of the plant species *S. nigra* for the purpose of obtaining wine, as a potential functional product not yet recognized on the market.

For the purpose of the research, two types of wine were prepared, which were exposed to the influence of temperature, in order to monitor certain parameters of wine quality, as well as the influence of temperature on the biological activity of the wines. One type of wine was exposed to a temperature of 60 °C for 10 minutes and the other 70 °C for 5 minutes. To determine the quality of the prepared wines, pH value, alcohol content, methanol content, volatile acids, and mineral content were determined. The antioxidant capacity, neuroprotective and antidiabetic activity were analyzed using *in vitro* assays.

The content of ethanol as the main product of alcoholic fermentation was in the range 2.17-2.35% v/v. Methanol content was in the range of concentrations characteristic of fruit wines, while the content of volatile acid was 0.58-0.73 g/mL. The presence of volatile acids did not influence negatively on the taste of wine. The presence of minerals in wines is of particular importance because of their functionality. Wine exposed to the temperature of 70 °C for 5 minutes had proven to be a better source of minerals, especial K, Mg, and Fe. Both types of wine showed very good biological activity. Also, wine treated at a temperature of 70 °C for 5 minutes had a better antioxidant capacity and antidiabetic activity, then wine treated at temperature 60 °C for 10 minutes. When it comes to neuroprotective activity, wine treated with a temperature of 60 °C for 10 minutes has stood out as a stronger neuroprotective agent.

The investigated elderberry wine on the based chemical composition and great biological activity could be considered as a potential new functional product.

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FC PP 06

Response surface methodology: optimization of microwave-assisted extraction (MAE) of defatted wheat germ phenolic antioxidants

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Defatted wheat germ (DWG) represents main by-product in the process of the wheat germ oil extraction and it can be considered as valuable source of polyphenols [1]. In following research oil was recovered from wheat germ using supercritical CO_2 extraction. Afterwards, DWG was utilized as a material for isolation of polyphenols using microwave-assisted extraction (MAE). The aim of this work was to evaluate influence of the extraction parameters on the investigated responses and to optimize MAE. In order to accomplish that, three level and four variables face-centered central composite design with response surface methodology (RSM) was applied. As input variables following parameters were observed: ethanol concentration of solution (50, 70 and 90%), extraction time (5, 10 and 15 min), liquid-solid ratio (5, 15 and 25 mL/g) and irradiation power (400, 600 and 800 W). Output variables were total extraction yield (Y), total polyphenols content (TPC), and antioxidant activity of extracts, determined by DPPH, ABTS and FRAP assay. Extracts with highest Y (36.8%) and TPC (705.86 mg GAE/100gDW) were obtained at the same experimental conditions (50% ethanol, 15 min, 25 mL/g and 800 W). High positive correlation of TP and antioxidant activity parameters (DPPH, FRAP and ABTS) was observed. Generally, influence analysis suggested that ethanol concentration most dominantly influenced all observed responses. Multi-response optimization was performed and optimized MAE conditions determined by RSM were: ethanol concentration of 58.03%, extraction time of 14.48 min, liquid-solid ratio of 25 mL/g and irradiation power of 800 W.

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FC PP 07

Efficiency of different solvent systems for the conventional solid/liquid extraction of *Thymus serpyllum* polyphenols

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The main goal of this study was to valorize the by-product of processed *Thymus serpyllum* filter-tea, in terms of obtaining potent extracts with high antioxidant capacity by conventional solid-liquid extraction. The conventional solid/liquid extraction was performed for 24 hours at the 150 rpm shaking speed, whereas the solid/liquid ratio was 1:10 (m/v). Responses that gave us complete and useful information were total extraction yield (Y) and yields of total phenolics (TP) and flavonoids (TF) contents, as well as antioxidant activity parameters obtained by DPPH assay. In order to maximize yields of target responses and improve antioxidant potential of *T. serpyllum* liquid extracts, different concentrations of ethanol (0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 96%), as a solvent, were examined. The values obtained of the Y, TP, TF and DPPH were 13,10 g/100 g DW, 17,35 mg GAE/g DW, 15,91 mg CE/g DW and 34,37 mg TE/g DW, respectively, which determined the most adequate concentration of solvent was 60% of ethanol. It could be concluded that *T. serpyllum* herbal dust could be used as raw material for production of antioxidant-rich extracts.

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FC PP 08

Development of extraction method of phenolic compounds from grape seeds

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Food industry, including wine industry, has a need for rapid, simple and cheap techniques for the objective evaluation the quality of grapes and wines. Analysis of phenolic compounds of grapes and wines is affected by several factors such as extraction technique, method assay, selection standards, *etc.* The aim of this study was to optimize ultrasound assisted extraction (UAE) by response surface methodology (RSM) to maximize extraction yield, total phenols and phenolic compounds such as (+)-catechin, (-)-epicatechin and proanthocyanidins obtained from Vranac (*Vitis vinifera* L.) grape seeds [1]. Analysis of the experimental design data and calculations of predicted responses were carried out using Design Expert software (Version 7.1.6., Minneapolis, USA). The predicted values of model are in accordance with experimental data obtained under these optimal conditions for this extraction. The predicted values of the model were in accordance with experimental data under the same conditions (RSD was 0.74%). Experimental data also confirmed that UAE gives a better yield of phenolics than conventional solvent extraction (23.76% increase). The UAE under optimal extraction conditions predicted by central composite design is suitable for obtaining seed extracts that are rich in phenolic compounds.

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FC PP 09

The content of total flavonoids in the samples of dark chocolates on the Serbian market

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Many studies have shown that polyphenols play an important role in preserving health due to their antioxidant properties [1]. Cocoa and cocoa-based products, such as dark chocolate, contain a range of different biologically active compounds which include polyphenols (phenolic acids and flavonoids).

The aim of this study was to investigate the content of total free flavonoids depending on the amount of cocoa percentage in the sample of dark chocolates from the Serbian market. After defatting with petrolethar, ten samples of dark chocolates were extracted with acetone-water-hydrochloric acid (80 : 19.5 : 0.5, *v*/*v*/*v*), and content of total flavonoids was determined using standard aluminum chloride method [2]. The results of the measurement are expressed as mg of catechin equivalents (CE) per gram of dried weight (dw) of samples.

The results have shown that the content of total flavonoids was in the range from 10.15 to 39.70 mg/g dw CE. The obtained results exhibit that the sample with the highest amount of cocoa mass demonstrates the greatest content of total flavonoids. Furthermore, the samples which contain dried pieces of fruits (orange or raspberries) show a higher quantity of free flavonoids in comparison to chocolate without the addition of fruits with the same percentage of cocoa mass.

It can be concluded that the percentage of cocoa mass influence on the content of total free flavonoids in different dark chocolate samples. Additionally, the investigation showed that the presence of dried fruit pieces also affects the flavonoid content of the samples. Based on the obtained results, it can be assumed that the consumption of dark chocolate may potentially have a positive effect on human health, especially those with a high percentage of cocoa mass.

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This research was done at Faculty of Agriculture, University of Belgrade, Department of Chemistry and Biochemistry.

Chemistry of macromolecules and nanotechnology

CMN PP 01

Nanoclay reinforcement of poly(urethane-siloxane) copolymers

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Series of poly(urethane-siloxane) nanocomposites (PUNC) was prepared with the *in situ* polymerization, based on 4,4′-diphenylmethane diisocyanate and 1,4-butanediol as the comonomers of the hard segments (HS) and α,ω–dihydroxy ethoxy poly(dimethylsiloxane) (EO-PDMS) as the part of the soft segments (SS). PUNC series was composed of five samples of different HS contents (from 10 to 50 wt.%). Organomodified montmorillonite clay (Cloisite 30B®) was used as nanofiller in the amount of 1 wt.% (relative to the total weight of reactants), within prepared PUNCs. The effect of the addition of nanoclay on structure, surface properties and morphology of these PUNCs was investigated.

The obtained FTIR spectra confirm successful preparation and incorporation of nanoclay particles inside of PUNC samples with different compositions i.e HS/SS ratio. Incorporation of the EO-PDMS segments and nanoclay particles i.e. enrichment of the surface of these PUNC films with Si and O atoms allows highly hydrophobic surface of the PUNCs. Samples with the highest content of SS had the best hydrophobicity and the highest contact angle values with water, formamide and diiodomethane. According to the SEM images PUNCs exhibited two-phase morphology that was more pronounced in samples with higher HS content due to the higher level of microphase separation. Moreover, the addition of nanoclay particles has led to the appearance of more prominent cross-sectional morphology [1,2].

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CMN PP 02

Efficiency of horseradish peroxidase-catalyzed phenol removal from water

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Horseradish peroxidase (HRP) is one of the most recently used enzymes in the process of enzymatic phenol removal [1]. In water treatments, peroxidases could be used in free or immobilized form. Magnetite nanoparticles (Fe_3O_4) represent a suitable support for enzyme binding due to their specific properties. The aim of this work was to investigate the efficiency of immobilized and free form of HRP for phenol removal from aqueous solution in the presence of polyethylene glycol. The efficiencies of the raw (extracted from horseradish roots) and pure (commercial EC 1.11.1.7) peroxidase were also compared in the same process.

The phenol solution (2 mM) was treated by peroxidase (free and immobilized form) with the concentration in the reaction mixture of 110 U and hydrogen peroxide solution (2.5 mM). The low molecular polyethylene glycol (PEG 300) was used for enzyme stabilization. The reaction was carried out at room temperature (30°C) and in phosphate buffer solution pH 7.2 during 2h. The activities of free forms of raw and pure HRP were similar (approximately 35 U/ml). Raw enzyme was successfully immobilized on magnetite nanoparticles by physical adsorption and showed activity of 17.8 U/g. Both free forms, as well as raw immobilized peroxidase, were successfully employed to remove the phenol from buffer solution. The efficiency of pure enzyme in phenol degradation was 40% after one hour duration of the reaction. Raw and immobilized HRP showed similar efficiency for phenol removal after one hour (around 60%). In both situations, prolonging the reaction time did not have any significant effect on the process efficiency. The results of this work show that peroxidase extracted from horseradish root can be successfully immobilized on magnetite nanoparticles and used in environmental applications. Other advantages of using the immobilized form of enzyme will be the subject of further investigation.

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CMN PP 03

Synthesis and characterization of novel polymer networks based on star-shaped PCL with different number and length of arms

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In the past decades, great efforts have been made to create new biodegradable polymeric materials which would successfully replace non-degradable polymers. In the group of biodegradable polymers, poly(ε-caprolactone), PCL, an aliphatic polyester has been recognized as synthetic biomaterial of choice due to its biocompatibility, non-toxicity and as environmentally friendly material. Relatively high degree of crystallinity and hydrophobic nature of PCL are responsible for its slow degradation rate which in turn restricts its wider application. One of the ways to overcome this problem is to synthesize star-shaped PCL based polyesters and to create PCL network structures by crosslinking in order to prevent crystallization and improve degradation ability [1].

Therefore, the present study was related to synthesis of star-shaped poly(ε-caprolactones) with different number of arms (three, four and six) and different PCL arms length, as well as preparing their networks by using hexamethylene diisocyanate as crosslinking agent. Star-shaped PCLs were synthesized through the ring-opening polymerization by using multifunctional alcohols as initiators (trimethylolpropane (TMP), pentaerythritol (PERT), and dipentaerythritol (diPERT)). In the series with varying number of arms from three to six, PCL length was fixed to 1000 g/mol. In the second series of star-shaped PCLs with three arms, the length of an arm was targeted to 500, 1000 and 2000 g/mol. The structure of obtained star-shaped polyesters was confirmed by NMR analysis. FTIR spectroscopy confirmed successful formation of networks through the urethane bonds. In order to estimate the quality of obtained PCL networks and crosslinking density, swelling degree and gel fraction were determined in two solvents of different polarity (chloroform and DMF). It was shown that with decrease in arm length and increase in number of arms higher crosslinking density was achieved. DSC analysis showed that with the increase of number of arms and decrease in the arm length, degree of crystallinity decrease due to the higher crosslink density. Therefore, it was shown that by changing the molecular architecture of starting star-shaped PCL, degree of crystallinity of final PCL network can be tailored.

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CMN PP 04

Properties of nanocomposites based on polyurethanes and mesoporous silica nanoparticles

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A series of three polyurethane nanocomposites using mesoporous silica nanoparticles (PU-MSNs) was prepared from Boltorn® hydroxy-functional hyperbranched polyesterof the second pseudo generation as a cross-linking agent, α,ω-dihydroxy-ethoxypropyl- poly(dimethylsiloxane) and 4,4'-methylenediphenyl diisocyanate, by *in situ* two-step polymerization in solution. Each sample of the prepared PU-MSNs had different type of mesoporous silica nanoparticles. For comparison purposes, PU without mesoporous silica nanoparticles was also synthesized. The chemical structure of the PU-MSNs and pure PU as well as the influence of the type of MSN on the hydrogen bonding formation and phase separation were analyzed by FTIR spectroscopy. The effect of the type of the MSNs on the swelling behavior and water absorption was also investigated. The uniform distribution of MSN particles within PU matrix, achieved in PU-MSN nanocomposites, allowed the formation of additional hydrogen bonding and caused enhanced hydrogen bonding compared to the pure PU network. Prepared PU-MSN nanocomposites showed better phase separation, higher swelling degree, lower crosslinking density and better hydrophobicity as compared to pure PU network.

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CMN PP 05

Indirect photolysis of fumonisin B_1 in aqueous medium

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Abstract Photochemical methods can be used for removing toxic organic pollutants in aqueous medium. These processes also include photolysis, where oxidation occurs through the use of UV or solar radiation, and can be in combination with some of the compounds: hydrogen peroxide (H_2O_2), ammonium persulfate $(NH_4)_2S_2O_8$, and potassium bromate ($KBrO_3$). These processes are reactions of indirect photolysis. Generally, the effectiveness of homogeneous light-driven oxidation processes is associated with very reactive species, such as hydroxyl radicals ($^{\cdot}OH$), which can lead to complete mineralization of pollutants. The UV/H_2O_2 process is able to oxidize a wide variety of organic pollutants in aqueous solutions [1], but also the processes of persufate oxidation are receiving increasing attention in the treatment of pollutants in water [2].

In this paper, we have investigated efficiency of indirect photolysis of fumonisin B_1 (FB_1) in ultrapure water using UV and simulated solar radiation in the presence of H_2O_2 as well as $(NH_4)_2S_2O_8$. The effect of pH on the degradation efficiency was also examined. Degradation kinetics was monitored by high performance liquid chromatography with fluorescence detector technique using o-phthaldialdehyde 2-mercaptoethanol for derivatization of FB_1. It was found that efficiency of degradation was the highest using of UV radiation in the presence of 1.36×10^{5} mol/dm^3 $(NH_4)_2S_2O_8$ at pH ~ 4. Namely, after 60 min of irradiation, the degradation of the FB_1 was complete.

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Educational chemistry

EC OP 01

Teaching chemistry with online labs by using Go Lab platform

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Nowadays, in 21st Century, a transformation of the educational system is needed more than ever. The current state of the different educational systems is based on pedagogical theory dated from 19th Century, the teachers are trained in 20th Century and the students are capable of dealing with modern digital technologies.

Therefore, we as teachers have seen this chance and opportunity to modify the way of transferring the knowledge to our students and to motivate them for getting new knowledge through experience. Especially, having in mind Science and Chemistry, the experiments and inquiry based learning are the best way to keep the students' attention [1]. The Go Lab platform is based on inquiry learning and follows the scientific steps containing online laboratories for virtual experiments. Moreover, creating the ILS (Inquiry Learning Spaces) is really simple and enables students to collaborate and communicate during the tasks. Also, the platform offers different tools to teachers for easy tracking of the students' improvement. ILS can be used as flipped classroom, allowing more time for discussion and critical thinking during the class. Since students are tech savvy, they embrace this method of learning. The ILSs [2] that we have created so far have significantly helped students in achieving their intended goals, far more than they would have been able to through the traditional way of teaching.

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EC OP 02

Associate programme OPCW: experience and perspectives

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The Chemical Weapons Convention (CWC) has a number of stipulations with implications for the chemical industry (1). The Convention not only mandates the destruction and prohibition of chemical weapons and related facilities, but also provides for restrictions on international trade in toxic chemicals and precursors that could be used for weapons purposes. Article XI of CWC covers issues related to the economic and technological development. With the aim to support of the full implementation of Article XI among state parties, the Organisation for the Prohibition of Chemical Weapons (OPCW) International Cooperation Branch (ICB) has developed Associate Programme (AP), designed to support: national capacity building; skills development (in areas related to the peaceful use of chemistry); the implementation of the Convention; strengthening ties among national capacity building; networking across the scientific community. Each year, AP is conducted over nine weeks and is comprised of practical and theoretical modules, those involves induction, university, intermediate, industry and final segments. Comprehensively, which is at the core of this programme and what makes it most powerful is love - love towards knowledge, science, chemistry, engineering, management, communications, respect among colleagues and different cultures. Since the existence of the Associate Programme, the OPCW has created a strong network of ambassadors in chemistry well-being.

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EC OP 03

Effectiveness of computer-based laboratory work

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The development of Information and Communication Technologies (ICT) and their use in chemistry classes could improve the quality of the teaching and learning process. The incorporation of appropriate multimedia materials into teaching and their educative role have the potential to provide instructional improvement and new learning experience. [1] Computer animations and simulations have been used in a variety of teaching situations, to represent phenomena at the atomic and molecular level, as well as to simulate the laboratory procedures. [2]

This study investigated the effectiveness of using the Multimedia Educational Interactive System (MEDIS), applied in the laboratory class "The effect of temperature on the solubility of substances". Students' attitudes towards this type of learning were also examined.

This study involved 60 seventh grade students and results were statistically processed for 48 of them. These students attended the laboratory class, did two tests (pre-test and post-test) and completed the questionnaire.

Quantitative data were generated from the pre-test and post-test about the solubility concept and from the questionnaire. A paired sample t-test that was used showed that mean differences were not statistically significant, although the mean post-test achievement score (*M* = 7.52, *SD* = 3.64) was higher than the pre-test achievement score (*M* = 6.96, *SD* = 3.12). After analyzing the students' answers obtained by processing the data from the questionnaire, it was concluded that the students liked this way of studying and would like to use MEDIS or similar computer systems in chemistry laboratory classes in the future.

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EC PP 01

Inferring students' cognitive structures in organic chemistry with the use of a word association test

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The aim of this study was to identify students' cognitive structures in organic chemistry domain using word association test instrument with nine stimulus words. The sample of this study included 23 chemistry students from Faculty of Sciences, University of Novi Sad. Each student received a booklet with nine stimulus words in the following order: alcohol, alcoholate, ethanol, acid, substitution, oxidation, dehydration, ester, water. The participants were restricted by time when they were required to write chemical terms associated with the provided stimulus word. During data analysis, frequency mapping method was used as suggested by Derman and Eilks [1] and the strength of the relationships between stimulus word and response words were analysed. The results showed that students provided the greatest number of different responses to the acid stimulus (N=188) and the least to the alcoholate stimulus (N=59). The stimuli alcohol, water and substitution occurred in the group of highest frequency range. Therefore, the strong relationships between these stimuli and response words were found and represented in the map that reflected students' cognitive structures. On the other hand, finding revealed that chemistry students had difficulties to incorporate the concept of alcoholate into their cognitive structures.

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EC PP 02

Analysis of items at the republic chemistry competition test for eighth-grade students

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Item analysis is a very useful tool that employs various statistics in order to assess the quality of individual test items and test as a whole. This work was aimed at studying examination items at the republic chemistry competition test using various psychometric analyses. The method used comprised calculations of descriptive statistical parameters, test reliability, item difficulty and discrimination indices as well as test difficulty and discrimination indices. Item classification was performed based on the parameters described in [1]. A research sample included 69 eight grade students from 59 primary schools in Serbia (56.5% males, 43.5% females). For these students, the republic competition was the 4th round of competition, preceded by a school, municipal and regional competitions. The results of this study showed that the analysed competition test largely meets the criteria of reliability and validity and most items were found to have appropriate difficulty and discrimination indices; however, a few had values that may warrant further evaluation and corrections.

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EC PP 03

Experimental determination of Avogadro's constant in high school chemistry teaching

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Laboratory work helps students to learn abstract concepts, to increase their interest and motivation, to develop their practical skills and abilities but also to understand science and relate it to everyday life. By curricula analysis, it was found that physicochemical constants are represented in a minimal extent in grammar school education, and it was also found that their experimental determination is not defined by curricula. This can raise students' difficulties in understanding physicochemical constants during their studies.

In this paper, the experimental determination of the Avogadro's constant was performed by the method of determining the area of a monolayer [1,2], using two organic fatty acids and different powdered substances: sulfur, activated charcoal, talc and cork powder. For calculation of the volume of one molecule, an approximation was taken that the molecules have a shape of a cube or a ball. The surface area of the monolayer was calculated based on the measured mass and the surface area of the paper cutout, as well as by measuring the 'stain' on the water surface with approximation that the 'stain' is in the form of a circle.

It has been experimentally proven that for high school chemistry teaching in determining Avogadro's constant, it would be best to use oleic acid, activated charcoal as the powdered substance, approximation that the molecule is in the form of a ball and for the surface area to be calculated based on the mass of paper cutout. This method is suitable for high school chemistry teaching because, in addition to a small amount of required chemicals, it does not require a large amount of laboratory glassware. In addition, it is time economical, which is one of the important factors when choosing chemistry teaching experiments.

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EC PP 04

Education using museum instruments and apparatus in The Great Serbian Chemists' Collection

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Scientific instruments and apparatus are noteworthy exhibits in museums. Other than showing evolution of technology in achieving lower limits of detection, these pieces are useful educational resources. Development of specific instrument rarely drastically changes the principles of operation. Showing parts and techniques on old or broken pieces can help students to engage and understand newer scientific instruments.

During exhibition on Science Festival 2018, a set of key pieces were showed. Visitors found that the most interesting one were apparatus for continual bidistillation of water (1961, Glass Factory Pula, Croatia) and pH meter (1940ties, O.M.A.P., Ottica Mecc. App. Di Precisione, Italy). [1]

The distillation apparatus was attractive to visitors and then used to explain the hydrological cycle in nature. pH meter wasn't as visually attractive as distillation apparatus. The most curious visitors had chance to learn about pH values in body and different house chemicals. This seemed to be very important, because some visitors were convicted that human bodies are basic, according to pH scale.

These exhibits are relevant educational resources for education of elementary, high school and faculty students. Science Festival exhibition showed that educating adults is also important. Adult visitors seemed not to be enough critically oriented towards magazine articles that claimed that human body pH was overall above 7.

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EC PP 05

Determination of water content in various materials by Karl Fischer method: a laboratory exercise for undergraduate students

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Water present as impurity in various materials, may significantly influence their characteristics. In spite of the fact that materials are storage in dry conditions, some small amount of water enters into materials (for example powders, organic liquid and solid substances, etc.), due to the constant presence of moisture in the air. The Karl Fisher method is widely accepted method for fast and reliable analysis of water content in materials, and one of the standards which explain the Karl Fischer procedure is [1].
The scope of this work is development and description of a laboratory exercise where the Karl Fischer titration is applied for water analysis in different materials. The exercise is primarily intended for undergraduate students who practice the materials chemical analysis. Theoretical part of the exercise includes the description of the titration with Karl Fischer reagent, description of the instrument, the measurement procedure, and safety measures. Practical part includes the setup installation and the measurement of water in different materials, by students' choice. This work presents the results obtained in one laboratory exercise.

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Chemical analysis

CA OP 01

Bi_2O_3/graphene nanoribbon composite supported on screen printed electrode with enhanced electrocatalytic performances toward glucose biosensing

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In present work we report application of bismuth (III) oxide (Bi_2O_3) decorated graphene nanoribbons (GNR) composite for modification of screen printed electrode, and use of resulting modified screen-printed electrode (SPCE/GNR/Bi_2O_3) as a disposable glucose biosensor. The composite was synthesized by use of co-precipitation method followed by ultra-sonication [1]. After characterization, the material was applied on the surface of the screen-printed electrode in a '*drop casting*' fashion. Glucose oxidase (GO_x) was added to the modified surface and finally covered by Nafion film. Resulting biosensor electrode (SPCE/GNR/Bi_2O_3/GO_x/Naf) shows excellent performance toward glucose detection, with working linear range from 0.28 to 1.70 mmol L^{-1} and detection limit of 0.07 mmol L^{-1}. Prepared biosensor was applied for the estimation of glucose level in standard honey samples with declared glucose level, in order to validate the methods (PT scheme). Proposed biosensor construction shows promising results and can be considered as stabile and reproducible tool for detection and quantification of glucose in investigated samples.

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CA OP 02

The applicability of nomograph of iso-eluotropic binary solvent mixtures to octadecyl column using 16,17-secoestrone derivatives

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The retention behavior of 16,17-secoestrone derivatives was studied by HPLC on octadecyl silica gel column (C18). Methanol-water (MeOH-W) and acetonitrile-water (ACN-W) solutions were used as mobile phases in proportions according to nomograph of iso-eluotropic binary solvent mixtures (Fig. 1), suggested by reference [1] for these eluents. The retention constants log *k* for mobile phases MeOH-W and ACN-W, have been compared by applying Student's paired *t*-test and Fisher's *F*-test to determine the applicability of the nomograph to this column. Namely, in author's paper [2] with the same compounds, the same statistical tests were applied for pentafluorophenyl-propyl (F5) stationary phase with mobile phases MeOH-W and ACN-W. It was found that the nomograph is not appropriate for F5 column, so an experimental check of the applicability of nomograph to C18 column was also needed. Using the above statistical tests (α=0.02), it was concluded that the nomogram is applicable to the C18 column for 16,17-secoestrone derivatives.

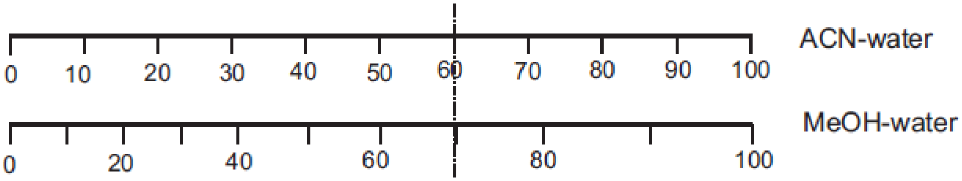

Figure 1. Nomograph of iso-eluotropic binary solvent mixtures.

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CA OP 03

Elemental bioimaging by laser ablation inductively coupled plasma mass spectrometry

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Bioimaging is a term for acquiring, processing and visualizing data (information) of a biological sample or a living object and forming it into an image. With the rapid development of relevant analytical instruments and methods, new possibilities for bioimaging have developed. Among them, laser ablation connected to inductively coupled plasma mass spectrometry (LA-ICP-MS) is frequently used. It is a sensitive microanalytical elemental imaging technique applied to determine the quantitative distribution of elements with high lateral resolution (up to 1µm) and low limit of detection. The main advantage of LA-ICP-MS compared to other mass spectrometry methods it that it offers solid sample elemental mapping with very little interferences compared to conventional ICP-MS analysis, thus being able to measure concentrations down to femtograms per pixel. This method was originally created for analysis of geological samples, but due to its capabilities, it is being developed for other fields. As a new method for determining elemental distribution in cells and tissues, the method itself has a long way to go for development of standards and reference material in order to provide precise quantification. Due to those limitations, this method is not a commercial technique. Besides geological and biological samples, LA-ICP-MS (triple quadrupole) can measure almost every element on any solid sample. Currently, we are developing several analytical methods for biological (tissues, tumorous spheroids[1] and cells[2]) samples that comprise of quantification by matrix matched standards and isotope dilution technique. So far, the most precise quantification method is isotope dilution, as it also serves as an internal standard for instrumental drift correction. Elemental speciation of plant tissues is in the focus of our research.

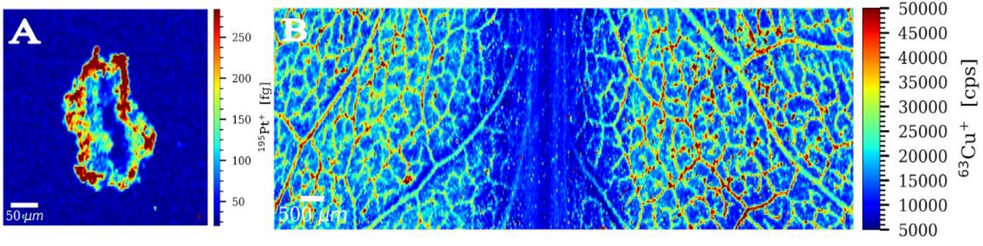

Figure 1. A) Platinum quantification via isotope dilution of a tumorous spheroid treated with cisplatin. B) Copper distribution in a dandelion leaf.

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CA OP 04

Pharmacokinetic studies of Ru-based chemotherapeutics by HPLC-ICP-MS and LA-ICP-QQQ-MS

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Cancer is one of the leading causes of death in Europe, so the development and improvement of its diagnosis and treatment are in the research spotlight. For cancer treatment, Pt-based chemotherapeutics have been commonly used for almost forty years. Their usage is causing many severe side effects and increased drug resistance. In order to overcome these drawbacks, Ru-based chemotherapeutics are synthesized. Among them, two were selected for this study: [(η6-p-Cymene)Ru(1-hydroxypyridine-2(1H)-thionato)Cl] and [(η6-p-Cymene)Ru(1-hydroxypyridine-2(1H)-thionato)pta]PF6. As one of the important segments during preclinical and clinical trials, pharmacokinetic studies were performed. Human serum was spiked with Ru-complexes and analysed by HPLC coupled to ICP-MS. Ru-species bounded to proteins in human serum (transferrin-Tf, albumin-HSA and Immunoglobulin-IgG) were separated from unbound Ru-species by monolithic columns, constructed of CIM Protein G disk (affinity disk for selective separation of IgG) and CIM DEAE disk (weak anion-exchange disk for the separation of unbound Ru from Tf and HSA). Elution profile of proteins was followed by UV detector at 278 nm, while the signal of Ru was quantified by post column isotope dilution ID-ICP-MS technique at *m/z* 101 and 99. [1]

Moreover, spatial distribution of Ru-complexes was analysed in human blood by laser ablation ICP-QQQ-MS in order to follow drug distribution between plasma, erythrocytes and leukocytes. Red blood and white blood cells were differentiated on the basis of their diameter (ranged from 6.2-8.2 µm, and 12-15 µm respectively). Laser ablation was used for the introduction of dried blood sample smeared on glass to the ICP-QQQ-MS, monitoring the signals of Ru at *m/z* 101 and Fe (for the confirmation of erythrocytes) at *m/z* 56.

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CA PP 01

Mechanism of reaction between quercetin and Au (III) in acidic media

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The interest for the investigation of reactions of Au (III) salts with antioxidants arises come from its applicability in the therapy of various diseases and the vide abundance of quercetin and related flavonoids in dietary products. The aim of the present paper was to determine mechanism and identify the products of quercetin oxidation by $[AuCl_4]^-$ ion at pH ~ 2 using UV/Vis spectrophotometry and HPLC coupled with DAD and LC-MS analysis[1]. The spectrophotometric data point out to the formation of the products with absorption maximum at 295 nm in all cases, characteristic for the oxidized forms of quercetin. HPLC coupled with DAD and LC-MS analysis of the reaction products suggest that the oxidation of quercetin results in the generation of similar metabolites including quinone and various oxidized quercetin - solvent adducts. Firstly, two-electron oxidation of hydroxyl groups at ring B of quercetin by Au (III) takes place giving the quinone structure as a mixture of four tautomeric. The formed $[AuCl_2]^-$ ion by reduction Au(III) undergoes disproportionation to give Au(0) and $[AuCl_4]^-$ while the formed quinone easily undergoes nucleophilic attack by solvent molecules. The newly formed Au (III) ions oxidized 3',4'-dihydroxy groups of quercetin adducts obtained after first 2e- oxidation, giving the final reaction products. There is no stable complex formation between Au and quercetin species present in the solution at any time. The reduction of Au (III) to Au(0) takes place followed by the formation of colloidal particles of Au. The only reduction species in the reaction mixture are Au (III) ions and not the Au(I) which is upon formation from Au(III) disproportionated back to Au(III) and Au(0).

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CA PP 02

Elemental composition of non-oak wood extracts commonly used in Balkan cooperage

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In the production of some alcoholic beverages one of the most important practices is the ageing process in a presence of wood. This process contributes to improved sensory characteristics such as aroma, color, taste and astringency. Although oak heartwood is the most used material in cooperage, other species such as chestnut, cherry, and mulberry can be also considered. Currently, limited published data are available on the mineral content of the wood extract from cooperage industry, although some research was done to investigate the content of heavy metals in alcoholic beverages[1], especially in wine[2]. Daily consumption of the wine and brandy with an elevated content of heavy metals might cause chronical poisoning. To avoid this issue, the maximum allowable concentration (MAC, mg L–1) in fruit brandies were established for lead, zinc, arsenium, and copper.[1]

The aim of this research was to investigate elemental composition of ethanolic extracts, obtained from alternative wood species used in Balkan cooperage, such as mulberry (*Morus alba L.*), Myrobalan plum (*Prunus cerasifera Ehrh.*), black locust (*Robinia pseudoacacia L.*), and wild cherry *(Prunus avium (L.) L.*). Elements were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Results indicated that the elemental composition of wild cherry extract was much lower than in other non-oak wood extracts, and all investigated wood extracts have lower content of trace elements than maximum allowable concentration in fruit brandies.

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CA PP 03

The effect of chlorine dioxide on organophosphorous pesticide degradation

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This study investigates degradation of organophosphorus pesticide, such as fenitrothion, with chlorine dioxide in deionized water and in real water system (water from River Sava). We investigated in detail the influence of various parameters such as concentration of chlorine dioxide, reaction time, pH and determined the optimal conditions for the pesticide degradation based on degradation efficiency monitored by HPLC-DAD. After 24 h of degradation at condition of pH 2.00 at light conditions, fenitrothion (20 mg/L) was degraded 82%. The percentage of pesticide degradation in water from River Sava was lower in relation to deionized water, but good value was obtained (degradation efficiency of 72% under the same conditions as in deionized water). GC/MS/MS (gas chromatograph with triple quadrupole mass detector) analysis identified three main degradation products and degradation mechanism was proposed.

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CA PP 04

Properties of nanocomposites based on polyurethanes and mesoporous silica nanoparticles

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A series of three polyurethane nanocomposites using mesoporous silica nanoparticles (PU-MSNs) was prepared from Boltorn® hydroxy-functional hyperbranched polyester of the second pseudo generation as a cross-linking agent, α,ω-dihydroxy-ethoxypropyl-poly(dimethylsiloxane) and 4,4'-methylenediphenyl diisocyanate, by *in situ* two-step polymerization in solution. Each sample of the prepared PU-MSNs had different type of mesoporous silica nanoparticles. For comparison purposes, PU without mesoporous silica nanoparticles was also synthesized. The chemical structure of the PU-MSNs and pure PU as well as the influence of the type of MSN on the hydrogen bonding formation and phase separation were analyzed by FTIR spectroscopy. The effect of the type of the MSNs on the swelling behavior and water absorption was also investigated. The uniform distribution of MSN particles within PU matrix, achieved in PU-MSN nanocomposites, allowed the formation of additional hydrogen bonding and caused enhanced hydrogen bonding compared to the pure PU network. Prepared PU-MSN nanocomposites showed better phase separation, higher swelling degree, lower crosslinking density and better hydrophobicity as compared to pure PU network.

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CA PP 05

New 3-phenylpropyl ester from the essential oil of *Pleurospermum austriacum* (L.) Hoffm. (Apiaceae)

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Pleurospermum Hoffm. (Apiaceae) is a widespread, heterogeneous genus with 110 different taxa [1]. Although several biologically interesting natural products were isolated from some *Pleurospermum* species (e.g. coumarins, phenylpropanoids, etc.), the genus is still poorly phytochemically investigated, especially in terms of the essential oil analysis [1]. According to the SciFinder literature search, essential oil composition was analyzed only for four *Pleurospermum* taxa, including *P. austriacum*.

One of our primary goals was to determine the exact structure of (new) secondary metabolite previously detected in the *P. austriacum* essential oil [1]. The available literature data at that time allowed us to tentatively identify this essential oil constituent as an ester of rarely naturally occurring 3-phenylpropanol and some of the isomeric hexanoic acid (hexanoic, 2-methylpentanoic, 3-methylpentanoic, 4-methylpentanoic, 2,2-dimethylbutanoic, 3,3-dimethylbutanoic, 2,3-dimethylbutanoic or 2-ethylbutanoic acid). Unfortunately, the spectral and GC retention data on the mentioned esters are quite limited (in the literature are present only data for 3-phenylpropyl hexanoate). An additional problem connected to the GC/MS identification of correct isomer is that they have similar MS fragmentation patterns and very close RI values. For that reason, the final structural confirmation could not be done based on MS and RI data.

To resolve that issue, we create a small combinatorial library with 48 isomeric hexanoates (23 completely new compounds). GC/MS in combination with NMR, IR and UV-Vis analyses of the synthesized compounds provided data that led to an identification of the mentioned essential oil constituent as 3-phenylpropyl 4-methylpentanoate (new natural product). We hope that spectral and chromatographical data provided in this study would make the identification of these potentially biologically and pharmacologically significant compounds much easier.

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CA PP 06

Comparison of two cleanup methods of aliphatic hydrocarbons removal for the determination of PAHs in sludge

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Polycyclic aromatic hydrocarbons (PAHs) are classified as priority micropollutants by most environmental authorities around the world. They are produced during all types of incomplete combustion of organic matter. PAHs shows the characteristic POPs effects: persistence, bio-accumulation, potential for long-range environmental transportation.
The purpose of this work was comparison between different methods of-purification of aliphatic hydrocarbons removal from high contaminated sludge samples (more than 20 wt.% content of aliphatic hydrocarbons) and analyze the PAHs by using liquid chromatography with PDA detection. In addition, this method was used to determine the concentration of 16 PAHs in the sludge from industrial plant and to evaluate the PAHs level, composition and potential toxicity in the sludge.
Analytes were extracted from sludge samples using solid-liquid extraction with n-hexane/acetone mixture. They were separated and fractionated on a florisil and silica columns for observation. Florisil was heated for 14h at 140°C, silica 16h at 160ºC for activation [1,2]. Columns were filled with florisil/silica and anhydrated sodium sulphate immediately before use. They were washed with methylene chloride. The extract was loaded on the columns and eluated with n-hexane.
As a controle, samples were spiked for a final concentration of 0.1 mg/kg. Results have shown that florisil recovery assay is extensively higher than those observed with silica. The outcome of this examination is that silica is not suitable for cleanup of PAHs because of its elevated adsorption affinity.

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Acknowledgments

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CA PP 07

TiO_2/APTES core-shell bonded to carboxylic graphene for achieving direct electron shuttle. A single drop impedimetric glucose biosensor

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In this research TiO_2 nanoparticles were functionalized using silane coupling agent 3-aminopropyltriethoxysilane (APTES) in order to achieve direct bonding to carboxylic graphene (CGR). Morphology of composite material (TiO2/APTES@CGR) was investigated using FTIR, XRD and FESEM. Obtained material was used for modification of screen-printed carbon electrode (SPCE) and with addition of glucose oxidase for construction of second generation of glucose biosensor. Electrochemical properties of constructed sensors were studied using cyclic voltammetry (CV) and electrical impedance spectroscopy (EIS). EIS was used as detection technique. After optimization of the method parameters, it was found that developed procedure possesses low detection limit of 24 µM and wide operating linear range, from 50 µM to 1000 µM, with negligible effect of potential interfering compounds. Obtained results indicate that proposed approach proofs the concept of possibility of the electrochemical methods in single drop detection and application of methods for construction of "Point-of-Care" devices.

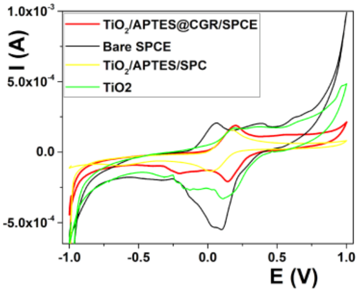

Figure 1. CV voltammograms of different electrodes during modification process in solution containing $Fe^{2+/3+}$ in 0.1 M KCl. Scan rate 100 mV/s

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CA PP 08

Traces of aspartame in river sediments

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Artificial sweeteners are used as sugar substitutes in food and beverages which are regulated by national guidelines on food additives (Regulation No. 53/2018).[1] After decades of application, their widespread occurrence in environment has been confirmed.[2] Furthermore, artificial sweeteners are recognized as emerging pollutants due to their ecotoxicity and limited knowledge on environmental fate. Some sweeteners, like aspartame, possess a high sorption affinity and partition to sediment in the water-sediment system.

In this paper, the presence of aspartame was investigated in sediments of four rivers in Serbia – the Tisza, the Morava, the Sava and the Danube. Analysis of sediment samples was performed by using an ultrasonic extraction as preparation method. The obtained extracts were analyzed by liquid chromatography with tandem mass spectrometry (LC–MS/MS). Aspartame was found in all investigated river sediments in the concentration range from 117 to 568 ng g^{-1}. Data on the contamination levels of sediments in Serbia indicate potentially harmful effects of aspartame on benthic organisms.

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CA PP 09

Analysis of microplastics in landfill leachate

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In recent years, microplastics have become a subject of interest to the scientific and professional public, due to their harmful impact on the environment. Research carried out so far indicates the presence of microplastics in all environmental media. Globally, including in our country, one particular problem is the disposal of packaging waste in municipal landfills, as under current regulations, such waste should be recycled. Plastics represent one of the biggest problems because of their diverse polymer structure, widespread use and resistance to degradation processes (*Auta et al., 2017*). A literature review indicates that very little is known about the impact of these types of pollutants on freshwater ecosystems, soil and groundwater. Hence there is a clear need to monitor microplastics in all environmental media, especially near landfills, not just as a group of pollutants which must be prioritized due to their physical presence, but also because of their ability to adsorb, concentrate and transport different pollutants. To date, there is no information on the quantities and type of microplastics found in the environment in Serbia.

The aim of this paper was to identify and characterize microplastics in the leachate of a municipal landfill in Novi Sad. Microplastics were isolated by membrane filtration (0.45 µm), with prior destruction of the organic matter present using H_2O_2. Visual identification of the microplastics was performed using a light microscope, and structural confirmation was performed by FTIR analysis. The identification confirmed the presence of microplastics in the landfill leachate, with polyethylene and polypropylene present the most. The obtained results indicate the passage of pollution from the landfill into surface waters around the landfill, from where they may then pass into the soil and groundwater (*Nuelle et al., 2014*).

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CA PP 10

Effects of hydroquinone on dynamics of Bray-Liebhafsky oscillatory reaction

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The Bray-Liebhafsky (BL) reaction is an oldest known oscillatory reaction conducted in water solution. It includes only three reactants: hydrogen peroxide (H_2O_2), sulfuric acid (H_2SO_4) and potassium iodate (KIO_3). In this work, the hydroquinone (1, 4-benzendiol) effects on BL reaction dynamics is investigated. Hydroquinone is primarily used as a stabilizer in colorants and different types of adhesives. Also, the hydroquinone finds it purpose in pharmaceutical industry, mostly as an ingredient in skin whitening products. The addition of different hydroquinone concentration after fifth oscillation has consequences on obtained system parameters: i) inter-oscillatory period of fifth and sixth oscillation and ii) the amplitude of the sixth oscillation. However, another phenomenon was noticed. Addition of hydroquinone after fifth oscillation caused an appearance of the new oscillation immediately after addition. The small concentration of hydroquinone ($4.00 \cdot 10^{-4}$ mol/dm^3) in the BL system inducted oscillation, allowing the potential application of BL reaction in analytical purpose for determination of unknown hydroquinone concentration. Potential mechanism of hydroquinone acting in BL reaction was also considered.

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CA PP 11

Isolation and structure elucidation of jatrophane diterpenes from the root of *Euphorbia nicaeensis* All.

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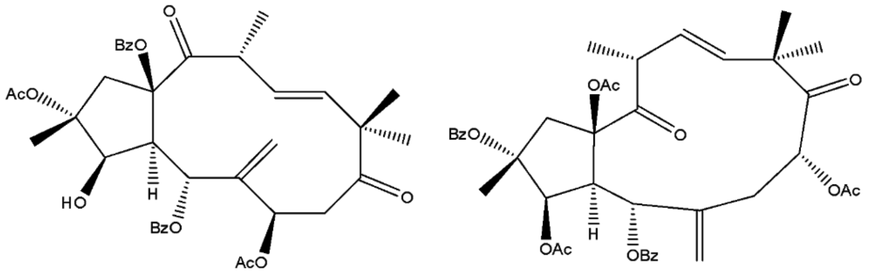
This research represents a continuation of the chemical investigation of *Euphorbia nicaeensis* All. In the previous research, from the latex of *E. nicaeensis*, fifteen jatrophanes were isolated.[1] Analyzing the root of this species two novel jatrofane derivatives were isolated using chromatographic methods: 2α,7β-diacetyloxy-5α,15β-dibenzoyloxy-3β-hydroxyjatropha-6(17),11*E*-diene-9,14-dione (**1**) and 3β,8α,15β-triacetyloxy-2α,5α-dibenzoyloxyjatropha-6(17),11*E*-diene-9,14-dione (**2**). The root was firstly grounded and extracted with 95% ethanol with heating for 2 hours and then extraction was continued overnight at room temperature. The extract was first fractionated by silica gel flash column chromatography. The selected fraction was once again fractionated by flash column chromatography and then the selected sub-fractions were finally purified by normal phase HPLC. Compounds **1** and **2** were isolated as amorphous substances. Structures of the isolated compounds were determined by means of the 1D and 2D NMR spectra, and the proposed molecular formulas were confirmed by HRESIMS.



1 **2**

Figure 1. The structures of the isolated compounds from root of E. nicaeensis

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CA PP 12

Determination of Pb and Cd in the territory of Kosovo in the soil and water using ICP-OES

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Heavy metals as pollutants in the workplace and environment are a serious health and environmental problem because they are toxic, not biodegradable, accumulate in living systems and have a long half-life in soil. [1]

The study is based on analyzing the presence of Pb and Cd in soil and water using the ICP-OES method. This method is based on the introduction of samples into the plasma source, where it evaporates and decomposes into free atoms and ions, which are then detected and determined. The permissible concentrations of Pb and Cd in soil and water are for Pb (10-700 mg/kg and 0.01 mg/l), and for Cd (0.01-2 mg/kg and 0.003 mg/l). [2] Based on the analysis, the results obtained from the territory of Kosovo, location Gracanica, for Pb and Cd are for Pb (14.00±0.08 mg/kg and 0.00082±0.0004 mg/l) and are for Cd (0.069±0.004 mg/kg and $4 \cdot 10^{-5} \pm 0.0001$ mg/l) . The permissible concentration of the analyzed heavy metals is higher than that obtained, so that the results obtained do not pose a risk. A large number of samples were analyzed to obtain these results. Based on the numerous advantages of the ICP-OES method, it has found great use in the determination of trace elements for a wide range of samples. The further direction of this research is determination of correlation between the contents of Pb and Cd in water and soil and the proximity of their source of pollution.

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CA PP 13

Identification of pigments from objects of the cultural-historical heritage of Bosnia and Herzegovina using FTIR spectroscopy

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An important part of the cultural heritage are various cultural monuments, and among them, great importance belongs to religious monuments. Main elements of religious monuments as an immovable cultural property are stone as constructive material and paint pigments which are used for ornamentation. Investigating this element gives important informations about usage and availability of different materials and knowledge about techniques used by certain nation in specific time in past. In this research, samples were taken from the Ćejvan-Ćehaja's Mosque from Mostar, Bosnia and Herzegovina and investigated using FTIR spectroscopy. KBr pellet method was used for the preparation and analysis of the samples. In this research, the substrate below the paint layers and samples of paint pigments of green, purple-brown and golden color were analyzed. The interpretation of the IR spectra led to the following results: Main components of the substrate below the paint layers are minerals calcite and gypsum; the sample of green pigment contains an inorganic synthetic *viridian* pigment and traces of linseed oil as a binder; purple-brown pigment is a natural mixed pigment made of mineral components which are metal oxides - iron (III) oxide (mineral hematite) and manganese dioxide (mineral pyrolusite) which also contained traces of oil; microscopic examination of the "golden pigment" and "no-band" informations in IR spectrum indicate that this pigment is actually gold in the form of very thin sheets which are applied to a layer of green pigment by organic adhesive. This research provided information whose importance is indisputable in performing restoration and conservation procedures and also in obtaining information on the materials used in order to learn about the cultural and historical background of the immovable cultural property.

CA PP 14

LIBS as powerful technique for rapid elemental analysis and surface hardness estimation of metal samples

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Laser-Induced Breakdown Spectroscopy (LIBS) is an innovative analytical technique based on optical emission spectroscopy. Compared to other standard and well established techniques (ICP, AAS, XRF) LIBS has numerous advantages. This laser-based technique is suitable for rapid multielement analysis of all chemical elements in any types of samples, without prior preparation and chemical waste. We developed a unique LIBS setup based on TEA CO_2 laser and non-gated detection system[1]. Rapid and sensitive analysis of metals is one of the most major LIBS application[2]. On the other hand, metal surface hardness is one of the most important mechanical characteristics and it is defined as a resistance to permanent deformation. It was found that the ratio between ionic and atomic LIBS emission lines may be used for surface hardness estimation[3]. From this point of view, this paper reported on LIBS application for simultaneous elemental analysis and determination of surface hardness of aluminum and cast iron samples.

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CA PP 15

Study of interactions between quercetine and 4-vinylpyridine by UV Vis and NMR spectroscopy

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Investigation of quercetine-vinylpyridine interactions is important in the light of using quercetine (Q) as a template for molecular imprinting of polymers made with 4-vinylpyridine (4VP) as a functional monomer [1]. The study of the type and the strength of interactions between template and functional monomer in the prepolymerization mixture is the key step of preparing selective polymers with high capacity towards template molecule [2]. UV Vis and ^{1}H NMR spectroscopy were used to study these interactions. No interactions were seen in UV Vis spectra when water/methanol/tetrahydrofurane and acetonitrile/buffer (pH 5.5, 7.3 and 10.0) mixtures were used as solvent systems. Obtained spectra showed no differences when compared to theoretically obtained sum of pure compound spectra. Thus, interactions were further studied by ^{1}H NMR spectroscopy in two different solvents, DMSO-d6 and acetonitrile-d3. When 4VP was added to quercetine solution in DMSO-d6, signals of quercetine OH groups disappeared, except 5OH signal which is bound into intramolecular bond with keto group. In ACN-d3, signals of OH groups changed even after addition of 1 4VP equivalent. Hydrogen bonding between Q and 4VP in ACN is more favored because of its lower polarity. As DMSO can form hydrogen bonds with quercetine, it is better to use ACN as a porogen during molecular imprinting process.

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CA PP 16

Molecularly imprinted polymers for diosgenin

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Diosgenin is steroid sapogenin used in therapies of many diseases such as breast cancer, cervix cancer, prostate cancer, certain forms of leukemia and in infertility therapy. Diosgenin is a precursor for production of other significant steroidal compounds such as dehydroepiandrosterone [1]. Molecularly imprinted polymers can be used as selective sorbents for solid phase extraction (SPE) [2]. In this study, several imprinted polymer were prepared, with the aim to investigate their potential use in SPE. Several functional monomers, crosslinkers and porogenic solvents were used. Some polymers were prepared without functional monomers other than crosslinking monomer. Functional monomers during synthesis were methacrylic acid, styrene, 4-vinylpyridine, or diethylaminoethyl methacrylate. Crosslinkers during synthesis were ethylene glycol dimethacrylate (EDMA), 1,4-butanediol dimethacrylate (BDMA), 1,6-hexanediol dimethacrylate (HDMA) or divinylbenzene. As a porogen acetonitrile and 2-propanol were used. For rebinding assays, mixture of methanol and water in 9/1 and 8/2 solvent ratios showed best results. Even though for divinylbenzene polymers no obvious imprinting effect was noticed, non-imprinted polymers showed high affinity for diosgenin binding. On the other hand, series of methacrylate polymers were prepared using crosslinker analogs – EDMA, BDMA, and HDMA, where imprinting can be seen, and the capacity for diosgenin binding was increasing with increasing hydrophobicity of the polymer. Diosgenin binding sorbents could potentially be used in extraction of diosgenin from different plant species containing diosgenin.

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CA PP 17

Phenylalaninol as a dummy template for molecularly imprinted polymers for beta blockers

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Potential use of *N,O*-bismethacryloyl ethanolamine (NOBE) molecularly imprinted polymers (MIPs) for extraction of beta blockers was studied. A simple method of a dummy-template molecular imprinting is presented that uses a single cross-linking monomer NOBE, initiator, and solvent. This formulation eliminates the need for additional functional monomers and empirical optimization of relative ratios of functional monomers, cross-linkers, and template [1]. Previous studies showed that amide functionality of NOBE interacts very well with most templates with the exception of amines [2]. This paper focuses on beta blockers as among others, they have an amino functional group. Dummy-template approach was taken so that same polymer could be used for various beta blockers. Effectiveness of NOBE MIPs was tested for the following beta blockers: propranolol, metoprolol, and carvedilol. Phenylalaninol was used as a dummy-template as it is commercially available, and has similar functionality to beta blockers. Binding of beta blockers was tested by batch binding experiments. Binding to NOBE MIPs was compared to traditionally used methacrylic acid(MAA)/ethylene glycol dimethacrylate MIPs, as well as MAA/NOBE MIPs. MIPs with a single cross-linking monomer showed higher affinity to beta blockers than other tested polymers. Furthermore, number of active sites and constant of binding of propanol and phenylalaninol to all mentioned polymers were determined. All polymers had two zones of affinity based on different concentration of propranolol and phenylalaninol solutions. NOBE MIPs had the highest values for the binding constant which again justifies the use of dummy-template NOBE MIPs for extraction of beta blockers.

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Acknowledgments

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CA PP 18

Ultrasound-assisted extraction of heavy metals from different particle size fractions of soil

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Determination the content of elements in samples from different origins in nature is important, among other things, in assessing their positive and negative effects on plants and animals. Conventional methods used to determine the heavy metal content of soils are generally time consuming. The use of ultrasound-assisted extraction (UAE) for digestion of samples offers a great reduction in time and solvent consumption, as well as the opportunity to perform multiple extractions.

As the biological productivity of soils associated with heavy metals has a significant correlation with the size and composition of particle fractions, it is of great importance to understand the distribution characteristics of heavy metals in soils. Therefore, in this research, the possibility of using UAE of Cd, Co, Cr, Cu and Pb from different particle sizes of samples was investigated. Metal concentrations were determined using atomic absorption spectrometry. Additionally, the efficiency of ultrasound on the solubility of metals, due to the presence of clay minerals, organic matter, and Fe/Mn/Al oxides in different soil fractions, was compared to conventional extraction method using aqua regia. For this reason, soil samples were fractionated into six particle size fractions: F1 (1-2 mm), F2 (0.5-1 mm), F3 (0.25-0.5 mm), F4 (0.125-0.25 mm), F5 (0.063-0.125 mm) and F6 (< 0.063 mm). The results showed that the efficiency of UAE was quite dependent on the particle size fraction of the soil as well as the type of metal. The highest *recovery* values were obtained for Cd in F1, F2 and F6 fractions (101%, 107% and 94%, respectively). In the case of Cu, for all investigated particle size fractions recovery values are in the range of 82.5 ± 6%. Furthermore, the results showed a high influence of the particle size of soil on the UAE of Pb, whereas cobalt and chromium were not extracted efficiently using ultrasound.

The research showed that the UAE of metals from soil can be used as a simple procedure for sample preparation alternative to conventional sample preparation method with aqua regia, but it is necessary to optimize the parameters that affect the efficiency of the extraction.

Chemical Synthesis

CS OP 01

Synthesis and characterization of new cadmium(II) complexes with 2-acethylpyridine-aminoguanidine

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Two new cadmium(II) complexes with 2-acetylpyridine-aminoguanidine, were synthesized, physicochemically and structurally characterized and their antioxidant activity was determined. The obtained complexes have the coordination formulas $[H_2L][CdBr_4]$ (**1**) and $[H_2L][CdI_4]$ (**2**), and they are characterized by elemental analysis data, IR spectra, conductometric measurements and for the latter the X-ray structural analysis.

In these complexes, the Schiff base is not coordinated to the central atom and in its dicationic form acts as a counter ion for tetrahalogenidocadmiate(II) ions. Since complex **2** is monocrystalline, it was possible to determine its composition and structure by X-ray structural analysis, which confirmed the previous conclusions. It was found that the asymmetric unit of the complex contains the dication of ligand, with a protonated nitrogen atom of the pyridine group (N5) as well as nitrogen atom (N1) of the aminoguanidine fragment, and $[CdI_4]^{2-}$ anion, in which the cadmium(II) ion is located in tetrahedral environment four iodide ions (Fig. 1).

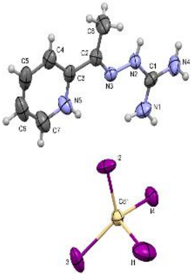

Figure 1. Molecular structure of complex ***2***

Finally, the antioxidant activity of these complexes was investigated by a DPPH test, where complex **2** showed more pronounced antioxidant activity in comparison to complex **1**. Both complexes showed higher antioxidant activity in comparison to the standard compound, trolox.

Acknowledgments

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 172014).

CS OP 02

Palladium catalyzed synthesis of *N*-arylated 1-substituted-1*H*-tetrazol-5-amines

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Nitrogen containing heterocyclic compounds are one of the most abundant motifs in pharmaceuticals. [1] As such, 5-aminotetrazoles have versatile application in the industry of materials, pharmaceuticals and coordination chemistry. The synthesis of the compounds containing 5-aminotetrazole moiety has been investigated in depth, however the methodology is particularly based on the formation of the tetrazole ring from *N*-substituted acyclic precursors.

Herein, we report the first example of palladium catalyzed *N*-arylation of 1*H*-tetrazol-5-amines. [2] The desired compounds are obtained in good to excellent yields with vast functional group tolerance. The use of 1-benzyl-1*H*-tetrazol-5-amine as a precursor provides a regioselective approach for the functionalization of N5 as well as a convenient strategy for the synthesis of N1 unsubstituted tetrazole scaffolds (after the hydrogenolysis of benzyl group) which represent the bioisostere for the carboxyl functional group (Figure 1).

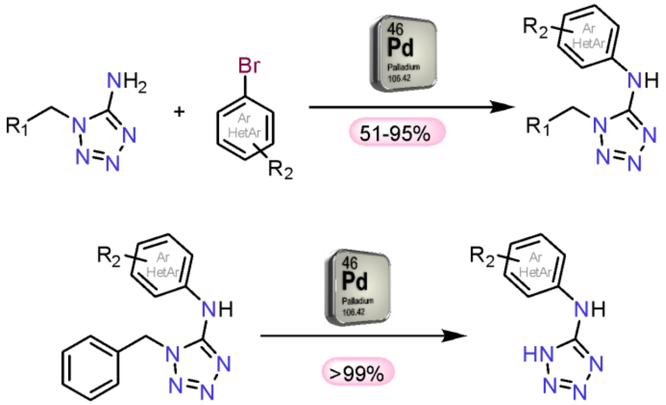

Figure 1. Buchwald-Hartwig reaction of 1-substituted-1H-tetrazol-5-amines and the subsequent hydrogenolysis of benzyl group

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Acknowledgments

This research was financially supported by the Ministry of Education, Science and Technological Development of Serbia (Grant No. 172008).

CS PP 01

Design, synthesis and spectral characterization of novel 4-ferrocenyl-8-(phenylthio)-1,2,3,4-tetrahydroquinoline

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Herein, we report the design, synthesis and spectral characterization of a novel 4-ferrocenyl-8-(phenylthio)-1,2,3,4-tetrahydroquinoline. [1] Desired synthesis was achieved in a three-step reaction, with a good overall yield (67%) (Fig. 1). First step included aza-Michael addition of 2-(phenylthio)aniline to 1-ferrocenyl-propenone (synthesized from commercially available ferrocene). Subsequently, the obtained ketone was smoothly reduced to the corresponding 1,3-amino alcohol. The final step was an intramolecular cyclization prompted by acetic acid, proceeding *via* corresponding α-ferrocenyl carbocation. The synthesized compounds have been isolated pure, and their structure have been undoubtedly confirmed by standard spectral techniques (^{1}H NMR, ^{13}C NMR, IR and elemental analyses).

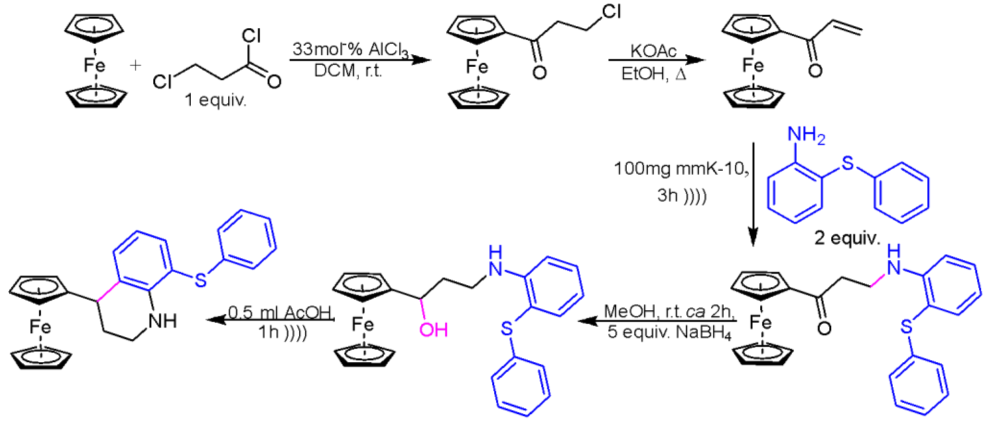

Figure 1. The synthesis of 4-ferrocenyl-8-(phenylthio)-1,2,3,4-tetrahydroquinoline starting from ferrocene

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Acknowledgments

This work was financially supported by the Ministry of Education, Science and Technological Development of Serbia [“*Novel electrochemical and chemical methods in synthesis of organic compounds of interest for medicine and material chemistry*” - **Project No. 172034**; project leader dr Ivan Damljanović].

CS PP 02

More efficient synthesis and *in silico* ADME properties of 3-benzyloxy-17-oxa-17a-homoestra-1,3,5(10)-trien-16-one

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There is large number of estrogen dependent diseases in women. Finding new potent agonists or antagonists of estrogens for these diseases treatment is one of fundamental goals of modern medicinal chemistry. Furthermore, estrogen production by enzyme aromatase controls estrogen blood levels. With this in mind, synthesis of 3-benzyloxy-17-oxa-17a-homoestra-1,3,5(10)-trien-16-one was performed and published [1, 2]. This compound has shown antiaromatase activity in high doses, while in lower doses activates aromatase [2]. In order to obtain this compound in more efficient way we have synthesised it in four synthetic steps starting from estrone as opposed to six previously reported. Last but not least, in silico ADME profile were evaluated by comparing physicochemical properties calculated by SwissADME web tool with five different sets of criteria, as well as using the BOILED-Egg model to analyse possibility of the gastrointestinal absorption and brain penetration.

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Acknowledgments

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CS PP 03

Electrochemical evaluation of the DNA-binding capacity of a series of new ferrocene-containing pyrrolidines

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We report the synthesis and electrochemical evaluation of the fourteen novel ferrocene-containing pyrrolidines by [3+2] dipolar cycloaddition of azomethine ylides to acryloylferrocene. The rapid procedure was carried out under mild conditions, resulting in a moderate to high yields (up to 86%). Electrochemical studies (cyclic voltammetry – CV and differential pulse voltammetry – DPV) revealed that all compounds exhibit the quasi-reversible, diffusion-controlled one-electron oxidation process that originates from ferrocene moiety.

Anticancer, antioxidant and/or anti-inflammatory activities generally are properties of compounds that can be correlated with DNA-binding. To assess the medicinal potential of synthesized pyrrolidines, we considered examining their interaction with calf thymus DNA (CT DNA) employing CV and DPV. DNA-binding study showed significant interactions with pyrrolidines, mostly of the electrostatic type, between positive ferrocenium ion and negatively charged phosphates of DNA. The presence of the interactions was confirmed by calculations of the diffusion coefficients, binding constants and the size of the binding sites. *In vitro* behavior of synthesized compounds expressed toward CT DNA may be considered promising for further biological studies and their potential application as pharmaceutical agents.

Acknowledgments

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CS PP 04

Ultrasound-assisted solvent free [3+2] cycloaddition of enones with azomethine imines for easy access to tetrahydropyrazolopyrazolones

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The synthesis of pyrazolidinone derivatives such as *N*,*N*-bicyclic tetrahydropyrazolo[1,2-a]pyrazolones attracted great attention in the past decades due to their interesting bioactivities.[1] One of the most efficient strategies for the construction of such fused skeletons relies on the 1,3-dipolar cycloaddition reactions of azomethine imines.[2] Since we noticed there is limited number of studies about the usage of enones in this type of reactions in general and especially with the azomethine imines we devoted ourselves to the exploration of the cycloaddition reactions of this class of compounds. According to our research, vinyl enones proved to be excellent precursors for synthesis of novel pyrazolopyrazolones.

The ultrasound-assisted solvent free reaction of various enones that contain vinyl group and different *N*,*N′*-cyclic azomethine imines in the presence of acetic acid as the catalyst proved to be an excellent way to synthesize series of tetrahydro-pyrazolopyrazolones in moderate to excellent chemical yield (up to 99%). Products are easily separable what allows isolation of pure diastereoisomers that would be interesting in the studies of bioactivities. All synthesized compounds are characterized by spectroscopic techniques (^{1}H NMR, ^{13}C NMR and IR) and this new procedure is experimentally simple and feasible with cheap and commercially available catalyst.

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Acknowledgments

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CS PP 05

Synthesis of bromopyrrole alkaloids longamide B and stylisine D and their derivatives via metal-catalyzed cyclizations of allenes

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Longamide B and stylisine D are members of a large family of bromopyrrole alkaloids featuring pyrroloketopiperazine moiety. To access this structural motif and to control the substitution pattern of the products, two processes, Pd- and Ag-catalyzed cyclizations have been employed complementary. The investigated methodologies provided a novel synthetic route for preparation of the above-mentioned alkaloids and also for their derivatives. This offers potential for wider exploration of the chemical and biological space defined by these natural products.

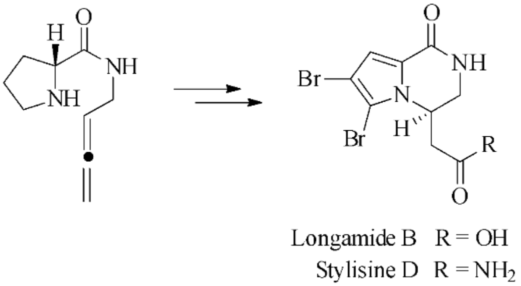

Figure 1. Annulations of allene-substituted proline derivatives promoted by transition metals provide access to bromopyrrole alkaloids.

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Acknowledgments

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CS PP 06

Green synthesis of bicyclic thiazolo-pyrimidines

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For the first time, green, selective and high-yields approach to 40 novel 5,6-dihydropyrimidin-4(3H)-ones (**1**) by one-pot reaction of aldehydes, Meldrum's acid and isothioureas under solvent-free conditions, in the presence of water is presented. In the majority of cases, introduced methodology gave an unprecedented tautomer-selective fashion toward targeted compounds with the excellent tautomeric purity (>99.9%).[1]
In the next step, thiazolo-pyrimidines (**2**) were obtained via phenylseleno-induced cyclization of **1** (**Figure 1**).

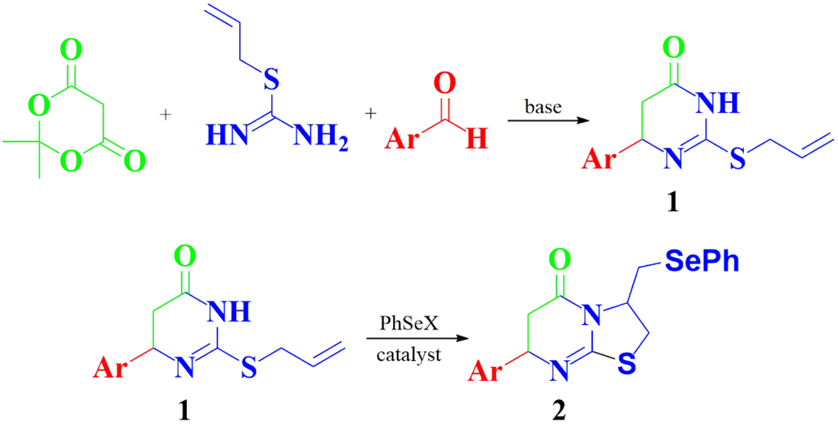

Figure 1. *Synthesis of Biginelli hybrids (**1**) and thiazolo-pyrimidines (**2**).*

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Acknowledgments

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CS PP 07

Synthesis, characterization and biological activity of square pyramidal isothiocyanato Zn(II) complex with condensation product of 2-quinolinecarboxaldehyde and Girard's P reagent

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The ligand (**1**) was synthetized in the reaction of 2-quinolinecarboxaldehyde and Girard's P reagent in molar ratio 1:1 in ethanol. In the reaction of ligand (**1**), zinc(II) tetrafluoroborate hexahydrate and ammonium thiocyanate Zn(II) complex (**2**) was obtained. The Zn(II) ion has distorted square based pyramidal coordination geometry. The tridentate ligand **(1)** is coordinated to the zinc ion with a NNO set of donor atoms forming two five-membered chelate rings and the other two coordination sites are supplemented by thiocyanate ligands. The ligand (**1**) and the complex (**2**) were characterized by elemental analysis, NMR and IR spectroscopy and structure of the complex (**2**) was defined by X-ray analysis. Complex **2** exhibited excellent antibacterial and moderate antifungal activity.

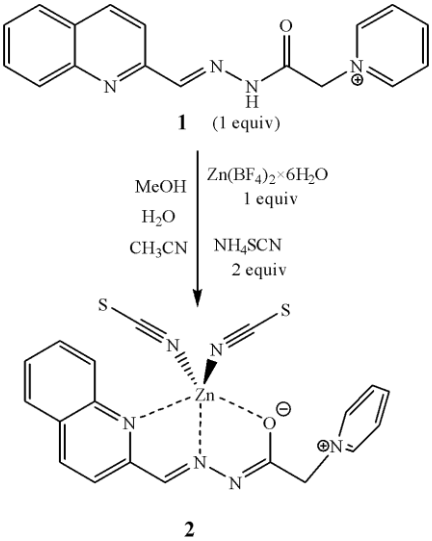

*Figure 1. Synthesis of complex (**2**)*

CS PP 08

Kinetic modeling of the cherry seed kernel (*Prunus cerasus L.*) oil methanolysis using CaO as a catalyst

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The biodiesel production process is mainly limited by the oily feedstock cost. Due to many advantages of biodiesel over fossil diesel, it is important to use low-cost oily raw materials, such as non-edible and waste oils, in the biodiesel production process. The fruit processing industry is a promising source for cheap oily feedstocks for the biodiesel production. Cherry cultivation and its use in the production of juices, jams and marmalades are widely widespread in south Serbia, so cherry kernels as a by-product from this industry can be used as an oily source for biodiesel production. The present paper deals with the synthesis of fatty acid methyl esters (FAME) from cherry kernel oil (CKO). The goals of the paper are the development of the biodiesel production process and the kinetic modeling of the CKO methanolysis.

The oil was obtained from the kernels by the Soxhlet extraction using n-hexane as an extraction solvent. Because of the high free fatty acids (FFA) content (14.63%) in the CKO, the synthesis of FAME was performed in two steps: the H_2SO_4-catalyzed esterification of FFAs present in the CKO followed by the CaO-catalyzed methanolysis of the esterified CKO. The CKO esterification was performed at the methanol:oil molar ratio of 8:1, the H_2SO_4 amount of 2 wt% (to the oil) and the temperature of 45 °C. The oily phase was separated and washed with cold distilled water to remove the traces of the acid. The methanolysis of the esterified CKO was carried out in a batch reactor, equipped with a reflux condenser and a magnetic stirrer (900 rpm), at the methanol:oil molar ratio of 9:1, the CaO loading of 9 wt% (to the oil), the temperatures of 40, 50 and 60 °C, under the atmospheric pressure. The kinetics of the CKO methanolysis was modeled by the simplified model combining the changing reaction mechanism and the first-order-rate law with respect to triacylglycerols. The reaction rate constant depended on the reaction temperature according to the Arrhenius equation. The activation energy and the pre-exponential factor were calculated to be 80.61 $kJ\cdot mol^{-1}$ and $3.04\cdot 10^{11}$ min^{-1}, respectively. The used model described reliably the progress of the methanolysis reaction, which was supported by a low mean relative percentage deviation between the calculated and experimental triacylglycerol conversion degree (±7.8%, based on 40 data).

CS PP 09

Synthesis and structural characterization of novel Cd(II) complex with Schiff base derivative of 1,3-thiazole

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Due to the fact that thiazole derivatives show significant biological activity [1], the aim of this work is synthesis and structural characterization of novel Cd(II) complex with Schiff base derivative of 1,3-thiazole (HL1). The complex was obtained by the reaction of HL1 with $Cd(ClO_4)_2 \times 6H_2O$ in methanol. The product was characterized by FTIR, ^1H and ^{13}C NMR spectroscopy and single crystal X-ray diffraction analysis. The coordination geometry around Cd(II) is distorted octahedral. The ligand is tridentatly coordinated to Cd(II), through pyridine, imine and thiazole nitrogen atoms (Fig. 1). Crystal packing of the complex is based on classical and non-classical hydrogen interactions and π-π stacking interactions. Powder X-ray diffraction experiment confirmed the presence of a single phase in the bulk sample. The stability of the complex was monitored by UV-Vis spectroscopy during 24 h. The results showed that the complex is stable, so the future research will be directed towards evaluation of biological activity of the complex.

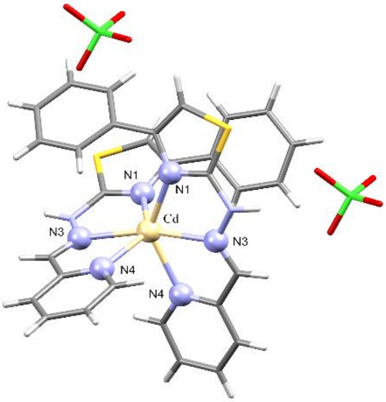

Figure 1. Molecular structure of the complex $[Cd(HL1)_2](ClO_4)_2$

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Acknowledgments

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CS PP 10

Nickel(II) complex with hydrazinyl-thiazole: structural charactacterization, antiproliferative and photocatalytic activity

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New nickel(II) complex with (*E*)-4-(4-tolylphenyl)-2-(2-(2-pyridylmethyilidene)--hydrazinyl)thiazole (HL) was synthesized and characterized. The complex was synthesized by the reaction of the ligand with nickel(II) perchlorate hexahydrate and obtained in a single crystal form. The structure of the complex, with general formula $[NiL_2](ClO_4)_2$, was solved by a single crystal X-ray diffraction analysis (Fig. 1). HL is tridentately coordinated to nickel(II) *via* pyridine, imine and thiazole nitrogen atoms with two perchlorate anions in the outer sphere. Besides electrostatic interactions, hydrogen interactions are also present in the crystal packing of the complex. Magnetic moment and conductivity measurements showed that the complex is paramagnetic and 2 : 1 type of electrolyte.

Antiproliferative activity of the complex was evaluated against several human tumour cell lines. The complex showed better activity than positive control 5-fluorouracil. The complex was shown to highly efficiently catalyze photodegradation of reactive Orange 16 dye.

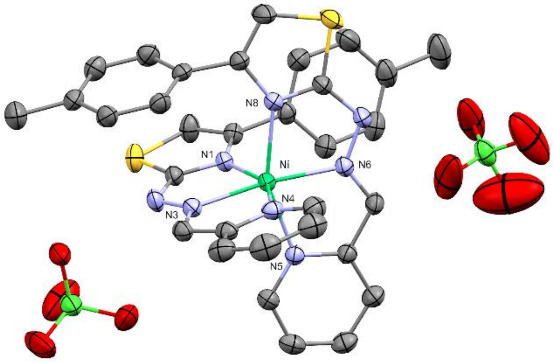

Figure 1. ORTEP drawing of $[NiL_2](ClO_4)_2$ with thermal ellipsoids given at the 30 % probability level. Hydrogen atoms are omitted for clarity.

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

CS PP 11

Synthesis and characterization of Fe(III) and Mn(II) complexes with 2- acetylthiazolethiosemicarbazone

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The ligand **HL** was synthesized in the reaction of thiosemicarbazide and 2-acetylthiazole in molar ratio 1 : 1 in water (pH = 2). The ligand was characterized by elemental analysis, IR and NMR spectroscopy. Cationic complex **1** was prepared by dissolving ligand **HL** in methanol and direct addition of $Fe(BF_4)_2·6H_2O$ in molar ratio 1 : 1. Neutral complex **2** was formed by dissolving ligand **HL** in methanol followed by adding solid $MnCl_2·4H_2O$ and methanolic solution of NaN_3 in molar ratio 1 : 1 : 4. Complexes were characterized by elemental analysis, IR spectroscopy and single crystal X-ray analysis. In both cases the **HL** ligand is coordinated through a NNS donor atoms set in deprotonated form. Geometry surrounding metal centres is distorted octahedral.

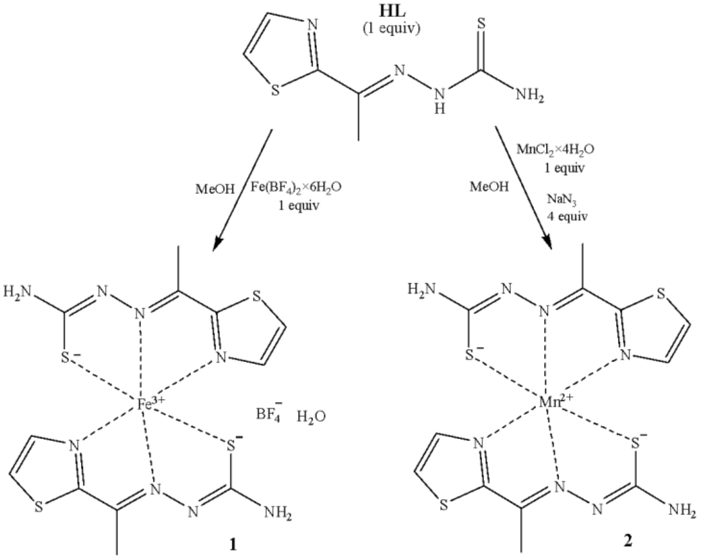

*Figure 1. Synthesis of complexes **1** and **2**.*

CS PP 12

A crystallographic and theoretical study of intermolecular interactions of newly synthesized spirohydantoins

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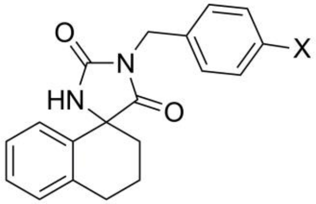
A series of spirohydantoins derived from α-tetralone (Figure 1) was synthesized and the compounds were characterized using the melting point measurements, FTIR, ^{1}H and ^{13}C NMR spectroscopic methods. The molecular conformation, crystal packing properties and intermolecular interactions of 1-(4-methoxybenzyl)-3',4'-dihydro-2H-spiro[imidazolidine-4,1'-naphtalene]-2,5-dione were analyzed by single crystal X-ray diffraction and quantum chemical calculations. The crystal packing of this compound (monoclinic, $P2_1/c$, a = 12.682(3), b = 6.4568(13), c = 20.826(4) Å, β = 98.61(3) °, R = 4.3%) contains centrosymmetric dimmers linked by N–H···O hydrogen bonds, which are further connected *via* C–H···O, C–H···π and parallel interactions of the phenyl rings at a large offset (PILO) to form infinite pseudo-layers. As a result, the pseudo-layers are associated into highly ordered three-dimensional framework along the b-axis. By combination of the crystal packing analysis and quantum chemical calculations, it was concluded that the structural motif formed by N–H···O hydrogen bonds between hydantoin rings is the most stable in the crystal structure. It was shown that the introduction of an electron-donating substituent into the benzyl moiety leads to strengthening of N–H···O hydrogen bonds, while an electron-accepting substituent has the opposite effect. The introduction of substituents enhances the stacking, C–H···π and PILO interactions, so it is expected that PILO interactions are the most represented in the crystal structures, as shown by statistical analysis of crystal structures of benzene molecules from Cambridge Structural Database.[1]



X = H, CH_3, OCH_3, Cl, Br, CN, NO_2

Figure 1. The chemical structure of the investigated compounds.

CS PP 13

Synthesis and characterization of new pyridones containing pyridinium scaffold

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Considering that 2-pyridones and their derivatives are found to have wide range of physiological activities, they are significant products of the pharmaceutical industry. Large group of 2-pyridone based disperse azo dyes, represent a considerable number of commercially used dyes, and find their application traditionally in textile industry [1]. On the other hand, pyridinium salts are known surfactants and cleaning agents as well as a part of biologically active compounds [2].

The aim of this research is to merge two heterocyclic scaffolds in order to ameliorate the properties and application of synthetized molecules. This paper contains synthesis and characterization of some new 6-hydroxy-4-methyl-3-pyridinium-2-pyridones. Molecules differ in the substituent on the pyridinium scaffold. Obtained pyridones have been analyzed by NMR, FTIR and UV-Vis spectroscopy. Moreover, acid/base equilibrium has been investigated in order to examine possible tautomeric forms of 6-hydroxy-4-methyl-3-pyridinium-2-pyridones.

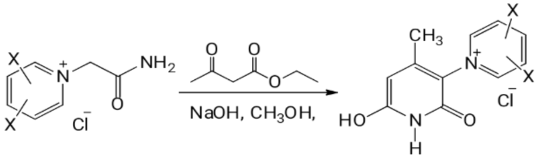

Figure 1. Synthesis of substituted 6-hydroxy-4-methyl-3-pyridinium-2-pyridones, X= H, Me, CN

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Acknowledgments

Financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. OI172013) is gratefully acknowledged.

CS PP 14

Optimization of Microwave-Assisted synthesis of 5-hydroxymethyl-2-furfural

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Heterocyclic furan-based compounds are interesting bio-renewable materials used as intermediate for pharmaceuticals, biodegradable resins, biofuels and fine chemicals syntheses. In this work, optimization procedure of HMF microwave-assisted D-fructose dehydration in hydrochloric acid and ionic liquid (1-butyl-3-methylimidazolinium bromide) was performed. In order to obtain highest yield and purity of the product optimization of HMF synthesis was performed with respect to pH, temperature, irradiation power and time of reaction. The structure and purity of HMF (Figure 1.) was confirmed according to results from elemental analysis, ATR-FTIR and NMR spectroscopy. HMF was further subjected to oxidation and reduction processes to obtain 2,5-furandicarboxyic acid and furan-2,5-diyldimethanol, respectively, useful reactants in a biorenewable based polyester resins synthesis.

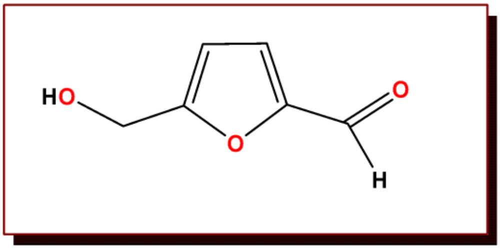

Figure 1. Structure of 5-hydroxymethyl-2-furfural (HMF)

Acknowledgments

The authors acknowledge financial support from Ministry of Education, Science and Technological development of Serbia, Project Nos. TR 34028, OI 172013 and OI 176018.

CS PP 15

Microwave-Assisted of synthesis and characterizations of levulinic acid (LA)

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Levulinic acid (4-oxopentanoic acid) (LA) is a two-functional γ-keto acids widely used in a production of pharmaceuticals, ethyl levulinate, substance which is widely used in the cream and perfume industry, polymers, plasticizers, biofuel, resins and various other additives. In this work LA was synthesized by the dehydration of fructose in a strongly acidic aqueous medium, using diluted hydrochloric acid, and subjected to microwave irradiation at different operational conditions. The structure of the synthesized compound (Figure 1.) was confirmed by elemental analysis, ATR-FTIR and NMR spectroscopy. LA was further used in a two subsequent steps of peroxidation and dehydration to obtain 3-hydroxypropanoic acid and acrylic acid, respectively, which could be used for acrylic ester synthesis which could be used as monomer in a polyacrylate production.

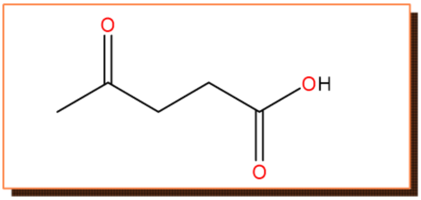

Figure 1. Levulinic acid (LA)

Acknowledgments

The authors acknowledge financial support from Ministry of Education, Science and Technological development of Serbia, Project Nos. TR 34028, OI 172013 and OI 176018.

CS PP 16

Geometric isomers of a ferrocene–steroid hybrid form in a Claisen-Schmidt condensation reaction of testosterone

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It was previously reported [1] that the Claisen-Schmidt reaction of testosterone with ferrocenecarboxaldehyde in ethanol yields 2-(ferrocenylmethylidene)-17β-hydroxyandrost-4-en-3-one (**1**, Figure 1), but the configuration of the newly formed double bond was not specified. Interesting to us as a means to potentially obtain selective antiproliferative agents acting upon hormone-dependent cancers, we revisited this reaction. Surprisingly, two reaction products formed in nearly equal amounts were isolated, and were determined to be geometric isomers of **1** by 1D and 2D NMR techniques.

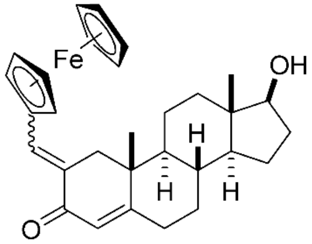

*Figure 1. Structure of compound **1***

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Acknowledgments

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CS PP 17

Claisen–Schmidt reaction of ferrocenecarboxaldehyde with 16-dehydropregnenolone in ethanol

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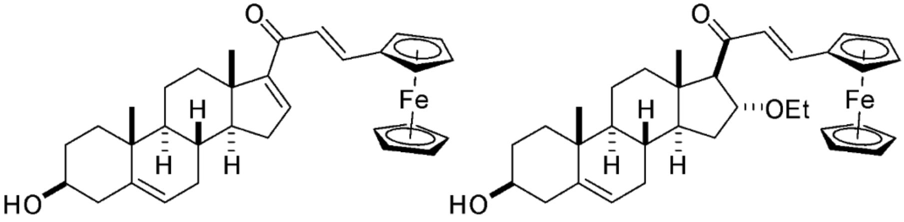
Some ferrocene–steroid conjugates prepared by the Claisen-Schmidt reaction of steroidal ketones and ferrocenecarboxaldehyde in ethanol were previously investigated for antitumor activity [1]. Expanding upon this work, we aimed to prepare the pregnane-type conjugate **1** by applying an identical synthetic methodology. However, compound **1** was found to form only as a minor product, while the main reaction product was compound **2**, a result of the conjugate addition of ethoxide to the Δ^{16} double bond; this is a known side reaction in the pregnan-16-en-20-one series [2]. The conjugate addition reaction was stereospecific, affording the 16α-ethoxy derivative **2** as confirmed by ^{1}H–^{1}H NOESY. Structures of the obtained compounds were determined by one- and two-dimensional NMR spectroscopy and IR spectroscopy.



1 **2**

Figure 1. Structures of compounds **1** *and* **2**

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Acknowledgments

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

CS PP 18

Novel silver-based 3D coordination polymer with piperazine-1,4-dicarbonitrile

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3D coordination polymer of silver(I) with piperazine-1,4-dicarbonitrile was prepared and characterized by single crystal X-ray diffraction analysis (SCXRD) (Figure 1). The obtained polymer crystallizes in triclinic crystal system, in *P*-1 space group. In the complex, each silver(I) is in a tetrahedral environment coordinated to four nitrogen atoms from four different ligands, with 1,4-piperazine ring in a chair conformation. Results obtained from FTIR spectroscopy, elemental and thermogravimetric analysis are in agreement with SCXRD results. Phase analysis was performed by powder XRD. The overlapping of the experimental and theoretical powder XRD patterns of the bulk sample clearly shows that the polymer represents a single-phase system. In order to increase porosity, further study will be focused on synthesis of silver(I) coordination polymers with similar organic linkers and potential application in heterogeneous catalysis.

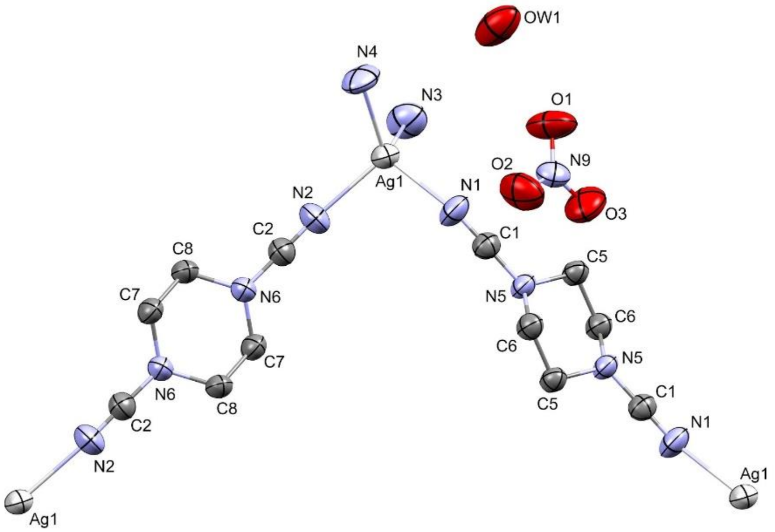

Figure 1. ORTEP drawing of a part of the structure of silver(I) coordination polymer. Thermal ellipsoids are shown with 50% probability and hydrogen atoms are omitted for clarity.

Acknowledgments
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CS PP 19

Synthesis and characterisation of Marchantin's A esters

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Marchantin A is a natural product isolated as a major component from liverwort *Marchantia polymorpha*. Only one total synthesis has been reported in literature ever since. This molecule is a member of cyclic bis(bibenzyls) as it contains two asymmetrically substituted bibenzyls connected by two ether bonds. [1] (Figure 1)

In this work we have analysed the reactivity of this natural product, which is mostly based on three phenolic hydroxyl groups and successfully carried out triple esterification. The complete esterification of Marchantin A has been conducted both under acidic and basic reaction conditions and the corresponding products have been thoroughly characterized.

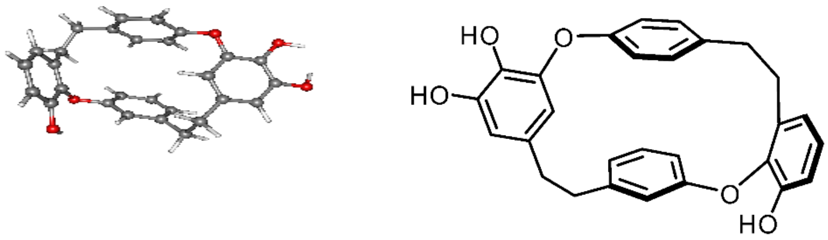

Figure 1. 3D structure and the structural formula of Marchantin A

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Industrial and applied chemistry

IAP PP 01

Biodiesel synthesis over green catalyst: The effect of thermal treatment of CaO/Zeolite precursor on catalytic activity

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The green CaO/Zeolite catalyst for methanolysis of fatty oils was synthesized entirely from the waste materials. CaO derived from chicken eggshell was loaded onto fly ash-based zeolite catalyst carrier by the wet impregnation method using an alcohol solution [1]. The effect of thermal activation at different temperatures ranging from 450 to 600 °C on catalytic activity was studied. The precursor and catalyst samples were characterized by XRD, FTIR, SEM, and Hg-porosimetry techniques. The catalytic tests were performed in a stirred batch reactor at the following reaction conditions: 60 °C - reaction temperature, 12:1 - methanol/oil molar ratio, and 4 wt% - catalyst concentration. The obtained results showed that the synthesized CaO/Zeolite catalyst has preserved alumosilicate framework-cancrinite type [1], with uniformly distributed calcium oxide (CaO) on its surface (Fig. 1c). It is shown that the catalyst sample calcinated at 550 °C exhibited the highest FAME content of 96.46%, which was achieved in 2 h (Fig. 2). Increasing temperature of calcination above 550 °C led to the formation of inactive calcium alumosilicate forms causing a decrease in the FAME content [2].

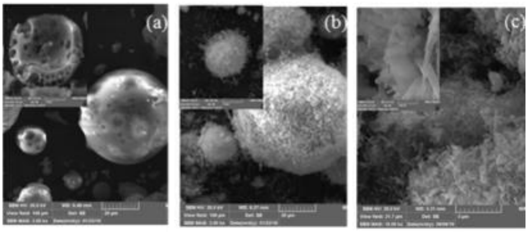

Figure 1. SEM microphages of (a) fly ash (b) Zeolite and (c) CaO/Zeolite-550 catalyst

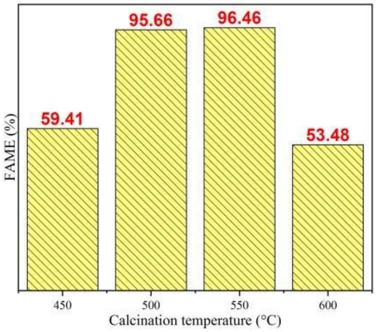

Figure 2. The FAME content after 2 h with catalyst calcined at different temperatures.

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Acknowledgments

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IAP PP 02

Study of solid deposits from Turija oil field wells (SE Pannonian Basin, Serbia)

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Formation of wax deposits in oil wells is one of the most challenging flow assurance issues in oil production processes [1]. With a decrease in temperature and pressure during oil exploitation and transportation, waxes dissolved in crude oil crystallize, adsorb and precipitate on the inner walls of production equipment. This process leads to a decrease of well flow rates and eventually causes total blockage, thus generating unfavorable economic and operational consequences. In order to understand this problem better, physicochemical properties, chemical composition and distribution of different classes of chemical compounds in deposits were studied in this paper. Four crude oils and four corresponding deposits were collected from Turija oil field, Serbia. Three of four investigated deposits have very low contents of water and mechanical impurities and mainly consist of extractable organic matter. Group composition analysis indicated that paraffin component is dominant in all four deposits. According to the values of P/(A+S) parameter (P = paraffins, A = asphaltenes, S = resins), all investigated deposits are classified as paraffinic (i.e. wax deposits). High-temperature chromatographic analysis showed that wax deposits are substantially enriched in C_{28}-C_{40} hydrocarbons; hence, the calculated average chain length shifts from approx. 22-23 C-atoms in oils to 30-31 C-atoms in wax deposits. Furthermore, a number of specific organic geochemical parameters was calculated based on gas chromatography – mass spectrometry (GC-MS) analysis of aliphatic and aromatic fractions. Excluding the parameters based on the distribution of *n*-alkanes, wax deposits and oils from three of four investigated wells show almost identical values for set of 11 calculated parameters; using linear regression, R^2 values of 0.9395-0.9984 were obtained. This is highly indicative of common genetic origin of oil and wax deposit, as well as of their similar maturity, whereas the precipitation of long-chain *n*-alkanes initiated the formation of wax deposits. The only exception is a well with biodegraded oil from the NE part of Turija oil field, where significant differences in the values of organic geochemical parameters were obtained for oil and wax deposit. Detailed GC-MS analysis revealed possible mixing of two oil types: very mature oil in the late "oil window" (which migrated from the greater depths or from the easternmost part of the Turija oil field) and autochthonous oil in the early stage of "oil window".

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IAP PP 03

The kinetic of *Cannabis sativa* L. extraction by supercritical carbon dioxide

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Hemp (*Cannabis Sativa* L.) has multiple applications in the industry for the production of fabrics, paper and construction materials. Today, there is an increasing interest in its application for medical purposes, as opposed to its opiate activity. Hemp has more than 480 compounds: cannabinoids, terpenoids, flavonoids, noncannabinoid phenols, hydrocarbons, nitrogen-containing compounds, carbohydrates [1].

The influence of pressure (100 - 300 bar) and temperature (40°C - 60°C) on supercritical carbon dioxide extraction of aerial parts of hemp in terms of extraction yield was examined. Total extraction yields were in the range from 0.25 to 1.37, from 4.28 to 4.68, and from 4.85 to 6.14 g/100 DW for extract on different pressures and at temperature 40, 50 and 60°C, respectively. The highest yield was obtained with pressure 300 bar and temperature 60°C.

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IAP PP 04

Nickel removal from water by ion-exchange

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The presence of nickel in the water resources, used for drinking water supply is serious issues since long term consumption of nickel polluted drinking water can affects human health [1]. The World Health Organization (WHO) recommends a maximum allowable concentration (MAC) for nickel in drinking water of 20 µg/l [2]. Different conventional techniques such as coagulation and flocculation, adsorption, membrane and ion-exchange processes are applied for nickel removal from water. Among these processes, adsorption and ion exchange are mostly in used since adsorbents as well ion exchange resins can be easily recovered and reused by regeneration operation. The aim of this study was to examine the efficiency of macroporous cation-exchange resin (Levatit® MonoPlus TP 207) for nickel removal from surface water. Kinetic and equilibrium experiments were performed with nickel contaminated surface water (C_0(Ni)=32 µg/l) using standard JAR test (JAR-FC6S VELP scientifika). Nickel concentration in the samples were determined by ICP/MS. The results of kinetic experiments showed that nickel concentration in surface water can be easily reduced below the MAC after 30 minutes using 2ml/l Levatit® MonoPlus TP 207. The maximum adsorption capacity, q_{max}, of resin obtained by Langmuir model, was 0.7 mg/g. Based on these results and taking into account techno-economic aspects of the ion-exchange process it can be assumed that the application of macroporous cation-exchange resin, Levatit® MonoPlus TP 207, could be an effective solution for nickel removal from investigated water resource.

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Acknowledgments

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IAP PP 05

Influence of the ionic liquids based electrolytes on the tomato growth, development and oxidative stress

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One of the current aspirations of today's, modern society is the continuous increase in the production of energy from renewable, „green“ sources in order to reduce dependence on the use of fossil fuels. The use of batteries as a technology where energy is stored directly where it is produced, not only contributing to the „green“ way of producing energy, but also facilitating the distribution of energy in the electricity grid. Due to the increasing use of lithium-ion batteries, their continuous improvement is needed in terms of capacity, electrical density and stability. One of the most promising ideas for improving batteries today is thought to be the use of ionic liquids (ILs) as electrolytes in lithium-ion batteries. However, their potential environmental toxicity also needs to be examined. In this work, the effect on tomato (*Solanum lycopersicum* L.) growth and development of four different electrolytes from lithium-ion batteries based on mixtures of propylene carbonate, lithium salts and ionic liquids, namely: 1-butyl-1-methylpyrrolidinium dicyanamide, [bmpyrr][DCA]; 1-butyl-3-methylimidazolium dicyanamide, [bmim][DCA]; 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6]; and 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide, [bmim][NTf_2], together with commercial electrolyte from *VARTA*® (Dischingen, Germany), were examined. The influence of anion on the reduction of the ionic liquid’s toxicity and lithium salts’ toxicity were investigated. For all investigated plants, significant reduction of biomass was noted, with the incoherent influence of the electrolytes concentration. The total inhibition of development was shown at the highest used concentration for some of the used electrolytes. Higher concentrations of photosynthetic pigments (such as chlorophyll *a*, chlorophyll *b* and carotenoids) may be explained by their potential antioxidant role. On the other hand, the content of the stress indicator, malonildialdehyde (MDA), was low, which may be explained by the increased activity of antioxidants in tomato leaves. The data collected in this study indicate that ionic liquids used in the electrolytes of lithium-ion batteries contribute to their pronounced toxicity.

Acknowledgments

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IAP PP 06

Influence of the electrolytes from lithium-ion batteries on the cucumber (*Cucumis sativus* L.)

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Batteries are an essential part of our lives. We have grown so dependent on them for almost everything – from mobile phones, cars, remote controls, watches, laptops, and anything else in between. Each year consumers dispose of billions of batteries, all containing toxic or corrosive materials. Some batteries contain toxic metals such as cadmium and mercury, lead and lithium, which become hazardous waste and pose threats to health and the environment if they are improperly disposed. The objective of this study was to examine the impact of electrolytes leaching into the soil on which the cucumber is grown. In this work, the effect on cucumber (*Cucumis sativus* L.) growth and development of four different electrolytes from lithium-ion batteries based on mixtures of propylene carbonate, lithium salts and ionic liquids (ILs), namely 1-butyl-1-methylpyrrolidinium dicyanamide, [bmpyrr][DCA]; 1-butyl-3-methylimidazolium dicyanamide, [bmim][DCA]; 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6]; and 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide, [bmim][NTf_2], together with commercial electrolyte from VARTA® (Dischingen, Germany), were examined. Some of the questions we wanted to know the answers are: will the plant absorb some of the chemicals, or perhaps the electrolyte will prevent the absorption of some of the essential substances that the plant adopts under normal conditions. Also, the subject of the study was the influence on the growth and development of the aboveground part and / or cucumber fruits, and the influence on the content of metabolites involved in antioxidant protection of the plant under stress conditions, such as malonildialdehyde (MDA) and photosynthetic pigments, chlorophyll *a*, chlorophyll *b* and carotenoids. Most of the investigated electrolytes affected aboveground part length growth of cucumber, as well as on the mass and appearance of the cucumber fruitage. Also, almost all treated plants had an increase in the concentration of stress marker MDA and, on the other hand, decreased levels of photosynthetic pigments, which indicates that the plants survived stress.

Acknowledgments

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IAP PP 07

Hydrogen peroxide production in water treated by non-thermal plasma in different atmospheres

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Chemical properties of distilled water treated by non-thermal plasma reactor were studied. Hydrogen-peroxide production, pH value and conductivity in distilled water were measured after plasma-treatment in air, argon and argon-oxygen mixture as working gases. Water falling film dielectric barrier discharge (DBD) reactor [1] was used for water treatment. Direct contact of water film with plasma in this reactor enables efficient transfer of reactive species generated in plasma to liquid phase. For optimization of reactive species production frequency and amplitude of the applied voltage were varied.

Chemical characterization of water treated by DBD generated in different gases shows that hydrogen peroxide production in argon reaches yield of 0.78 g/kWh, while in air it was 0.19 g/kWh. Both measurements were made with 35 W of power dissipated in plasma. Moreover, significant influence of gas atmosphere was observed in measurements of pH value and conductivity which imply that production of ions is about 15 times greater in water treated with plasma generated in air than in argon.
Advanced oxidation using this type of non-thermal plasma reactor enables production of active species *in situ*, while working in ambient conditions.[1] Effectiveness of plasma treatment was already confirmed with degradation of some waterborne pharmaceuticals.[2] This opens opportunities for new studies of plasma oxidation of pharmaceuticals in aquatic environments.

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This study was supported by the Ministry of Education, Science and Technological development of the Republic of Serbia through projects 172030 and 171034.

IAP PP 08

Determination of bioaccessible fraction of elements in soil and the concentration of elements in tap and well water; risk assessment for children and people

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Children can be exposed to the elements in the soil while playing in parks, orally, dermal and through inhalation of soil particles. The aim of this paper is to assess risk of children's health, using pseudo total element concentrations in the soil samples from the parks, and assess the health risk for people who consume investigated tap and use well water. For determining concentration of elements in soil extracts and water samples, ICP-OES instrumental technique was used. Non-cancerogenic and cancerogenic risks for children are increased and their greatest contributors are Fe, Al, Cr, Co and As. The concentration of As in drinking water is three times higher than maximum allowed concentration prescribed by the Council Directive 98/83/EC[1]. Also, in this paper three procedures of soil extraction are being compared for determination of bioaccessible fraction of elements in the soil. These procedures are gastro *in vitro* extraction (GE), gastro-intestinal *in vitro* extraction (GIE) and extraction with 0,4M solution of glycine (Gly). For the majority of established elements, GE and Gly proved to be more efficient than GIE in obtaining the bioaccessible fraction of analyzed elements[2], which described that the higher bioaccessibility of the investigated elements is provided in the stomach than in the small intestine.

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Medicinal chemistry

MC OP 01

Synthesis and biological evaluation of a thiazole bioisostere of goniofufurone

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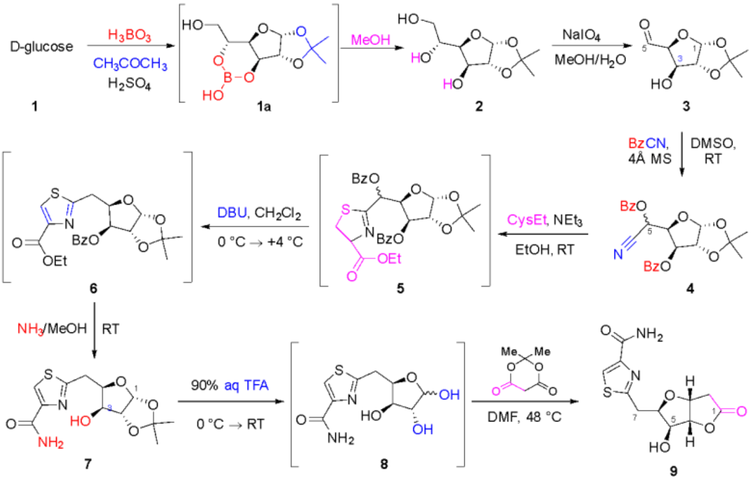
In this work, a multistep synthesis of compound **9**, which is a hybrid of the synthetic *C*-nucleoside thiazofurine and the natural product goniofufurone, was achieved (*Scheme 1.*). This compound was tested for its *in vitro* antiproliferative activity against a panel of tumor cell lines, as well as against a single normal cell line (MRC-5).[1] Also, the *in vivo* toxicity of synthesized compound on a zebrafish embryos (*Danio rerio*), was evaluated.[2] Compound **9** exhibited significant antitumor activity on several tumor cell lines. Additionally, this compound did not show toxicity in *in vivo* experiments on a zebrafish model.[1]



Scheme 1. Synthetic route of compound ***9****.*

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This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 172006), and (in part) by the Serbian Academy of Sciences and Arts (Grant No. F-130).

MC OP 02

Optimization of reaction pathways toward the key chiral intermediate for cleistanolate analogues synthesis

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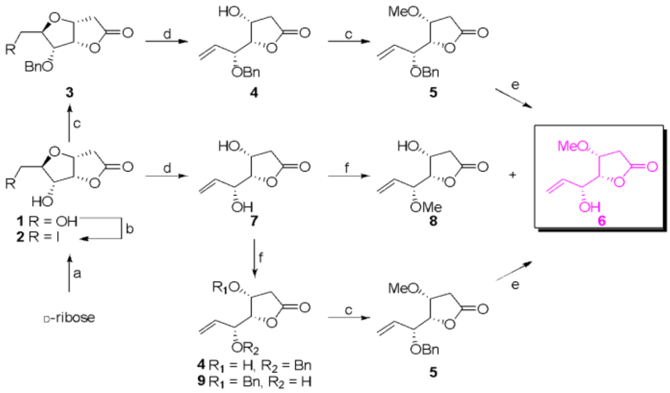
(−)-Cleistanolate is a natural butanolide[1] isolated from the leaves of *Cleistochlamys kirkii* (Benth.) Oliv., Annonaceae. Herein, we present the optimization of synthetic sequence toward the key chiral intermediate **6** for the novel synthesis of cleistanolate analogues (*Scheme 1.*).[2]



Ag_2O, AgOTf, Et_2O; (d) Zn dust, 4:1 THF/H_2O; (e) $TiCl_4$, CH_2Cl_2 (f) BnBr or MeI, $PhB(OH)_2$, Ag_2O, AgOTf, CH_3CN.

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The work was supported by a grant from Ministry of Education, Science and Technological Development (Project 172006), and (in part) by a research project from the Serbian Academy of Sciences and Arts (Grant No. F-130).

MC OP 03

Synthesis, cytotoxicity and *in silico* ADME properties of steroidal 19-hydroxy D-homo lactones

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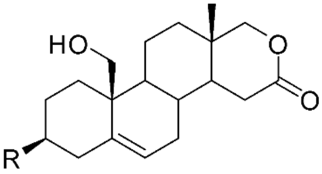
Cytochrome P450 aromatase is enzyme involved in biosynthesis estrogens from androgens. This makes its inhibition one of leading means for treatment of estrogen positive breast cancer. Hem is involved in aromatisation and it is located in the active center of this enzyme. It was also proved that C19 methyl group of androgen is very close to hem. Taking into account this facts we have synthesised new compounds **1** and **2** with hydroxyl group on C19 in order to obtain good inhibitors of aromatase and potential therapeutics for breast cancer (Fig. 1). This compounds were synthesised from 3βacetoxy17oxa-17a-homoandrost-5-en-16-one through multistep synthesis involving halohydrins [1, 2], 5,6-epoxide and 6,19-epoxy derivatives. Furthermore, *in silico* ADME properties were calculated using SwissADME web tool and compared with five different sets of criteria. Preliminary biological investigation included *in vitro* cytotoxicity testing. Cytotoxicity of novel compounds was measured using MTT assay on panel of human cancer and one normal cell line. ER+ and ER- breast cancer cell lines were included in testing.



1, R = OAc
2, R = OH

Figure 1. Novel C19 modified steroids.

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MC OP 04

Synthesis, characterization and pro-apoptotic activity of quinoline-based thiosemicarbazones and their Pt(II) complexes

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The World Health Organization recognizes cancer as the second leading cause of death worldwide, responsible for 9.6 million deaths in 2018. The main challenge of clinical cancer research is to find a therapeutic approach that specifically inhibits the reproduction of malignant cells, while limiting side effects on normal tissues. In recent years, there is an increasing interest in multi-targeting cancer therapy involving metal-chelating agents.[1] Biological evaluations and mechanisms studies of thiosemicarbazones showed that these compounds target several pathways in cancer cells.[2]

In the current study we used 2- and 8-quinolinecarboxaldehyde-based thiosemicarbazones as ligands (Fig. 1), providing detailed spectroscopic and structural characterization of the novel Pt(II) complexes. Evaluation of the anticancer potency of the ligands and their Pt(II) complexes was carried out in order to investigate their ability to trigger apoptotic death in the human pancreatic adenocarcinoma (AsPC-1) and acute monocytic leukemia (THP-1) cell lines.

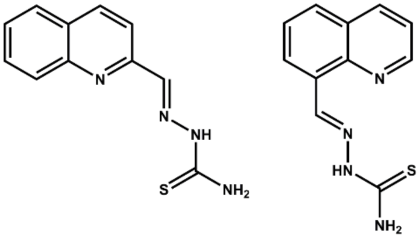

Figure 1. Structures of quinoline-based thiosemicarbazones

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Acknowledgments

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

MC PP 01

Antioxidant activity of β-diketonates and effects of coordination to copper(II) ion on their activity

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In order to make some progress in discovering the more effective way to eliminate ROS which cause the oxidative stress in organism in humans and bearing in mind the fact that *β*-diketonates belong to a class of biologically active molecules, potential drugs, and precursors in the synthesis of many natural products,[1,2] series of *β*-diketonates were synthesized, characterized, and tested to evaluate there antioxidant activity. Further, to investigate how coordination to copper(II) ion affects the activity of *β*-diketonates, appropriate complexes were synthesized and characterized. Scavenging activity on DPPH radical revealed that three compounds possess good free radical scavenging, comparable to standard while results of superoxide anion scavenging activities of tested samples showed that one compound, shown in Fig. 1., exbited very similar activity to the standard ascorbic acid with IC_{50} of 168.92 µg/mL. Furthermore, all *β*-diketonates exibited better scavenging activities than their corresponding copper complexes.

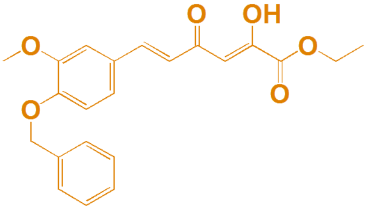

Figure 1. Structure of the most active compound.

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

MC PP 02

DNA and BSA binding study of polynuclear silver(I) complexes with 1,2-bis(4-pyridyl)ethane/ethene

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Silver(I) complexes with aromatic nitrogen-containing heterocycles have shown an effective and wide-spectrum biological activity.[1] The activity of this type of silver(I) complexes is related to the presence of a weak Ag–N bond, which can be easily cleaved in their interaction with different biomolecules.[2] Herein, we used 1,2-bis(4-pyridyl)ethane (bpa) and 1,2-bis(4-pyridyl)ethene (bpe) for the synthesis of polynuclear silver(I) complexes, $\{[Ag(bpa)]NO_3\}_n$ (**1**), $\{[Ag(bpa)_2]CF_3SO_3{\cdot}H_2O\}_n$ (**2**) and $\{[Ag(bpe)]CF_3SO_3\}_n$ (**3**). In the synthesized complexes, the corresponding nitrogen-containing heterocycle acts as a bridging ligand between two Ag(I) ions. The interactions of these complexes with calf thymus DNA (ctDNA) and bovine serum albumin (BSA) were studied to evaluate their binding affinities towards these biomolecules for possible insights on their mode of action.

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MC PP 03

Effect of ionic liquid on the kinetic reactions of Rh(III) complexes with biologically important ligands

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Interactions between transition metals and biomolecules play a very important role in medicine. In recent years, Rh(III) complexes attract increasing attention as potential pharmacological agents despite the fact that they are very inert and stable.[1] Within this study, we examined the kinetics of the substitution reaction for different Rh(III) complexes with 5'-GMP, as a biologically important ligand. Reactions were recorded in HEPES buffer and in 1-ethyl-3-methylimidazolium ethyl sulfate (ionic liquid). To show if the presence of ionic liquid effected the kinetic of these reactions, the results obtained in HEPES buffer and in ionic liquid were compared.

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MC PP 04

QSRR prediction of the chromatographic retention behaviour of spirohydantoin derivatives

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Spirohidantoins represent a pharmacologically important class of compounds. Many of them display activities against a wide range of biological targets[1]. A recent study shows that a wide range of biological activities of spirohydantoin derivatives strongly depends upon their structure. Hence it is important to understand their properties, particularly the properties of newly synthesized derivatives. One of the most important properties for biological activity is lipophilicity. Lipophilicity is responsible for pharmacokinetics, and hence important for further development of potentially active compounds. The aim of this study is to determine the chromatographic retention parameter of the new synthesized spirohydantoin derivatives as a measure of their lipophilicity. Chromatographic retention parameters of investigated compounds have been determined by reversed-phase thin-layer chromatography on C-18 modified silica gel. Mobile phases were two-component mixtures of water and aprotic organic solvents (i.e. acetonitrile, acetone, dioxane, and tetrahydrofuran).

Quantitative structure-retention relationship[2] (QSRR) was used for assessment of relationships between chromatographic retention parameters, R_M^0, and calculated partition coefficients of the molecule, log P. For the calculation of log P and additional molecular descriptors were used several software packages (Dragon and ChemDraw) in addition to online internet modules Molinspiration (https://www.molinspiration.com/) and ADMETlab (http://admet.scbdd.com/).

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MC PP 05

Rational drug design of novel 5-HT$_{2A}$ antagonists

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Serotonin 5-HT$_{2A}$ receptors are widely distributed in the central nervous system where they plays an important role in many physiological functions.[1] Certain imbalances in 5-HT neurotransmission are mainly associated with various neurological and psychiatric disorders.[2] Therefore, antagonists of these receptors can be used in treatment of depression, schizophrenia, anxiety as well as Parkinson disease. In our study, we have used the data set that contains three structurally diverse compounds clusters: clozapine, ziprasidone, and ChEMBL240876 derivatives. Combined ligand and structure based approaches were used to identify differences in the binding mode of structurally diverse antagonists as well as conformational changes they provoke. Three separate molecular dynamics simulations, for each cluster representative, were performed in order to identify virtually bioactive conformations of the examined ligands. Subsequently, conformers of all studied 5-HT$_{2A}$ antagonists selected by molecular docking method were used for 3D-Quantitative Structure Activity Relationship (3D-QSAR) study. Statistically significant variables were used for clarifying the most important structural features required for 5-HT$_{2A}$ antagonistic activity and to propose structural modifications for novel antagonists of serotonin 5-HT$_{2A}$ receptors. Considering the importance of hydrophobic and hydrogen bonding interactions in the binding site of this receptor, we have designed new compounds with better antagonistic activity.

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Acknowledgments

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MC PP 06

Synthesis and biological evaluation of novel benzylated analogues of (–)-goniofufurone

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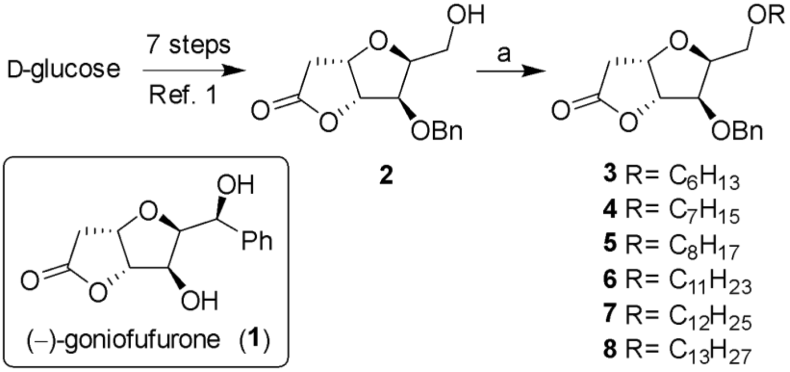
(–)-Goniofufurone (**1**) is the opposite enantiomer of naturally occurring cytotoxic styryl lactone (+)-goniofufurone. A series of new (–)-goniofufurone mimics bearing an alkoxymethyl group as the side chain on the position C-7 and benzyl group on C-5 has been synthesized from D-glucose (Scheme 1).[1] Herein we want to present results of antitumor activity for six novel benzylated analogues, evaluated by *in vitro* experiments against ten tumour cell lines, as well as against normal foetal lung fibroblasts. Structure-activity relationship (SAR) of **1** and its benzylated mimics (**3**–**8**), as well as related oxa analogues will be presented in details.



Scheme 1. Reagents and conditions: (a) RBr, Ag_2O, AgOTf, Et_2O, reflux.

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MC PP 07

Pd(II) complexes with quinoline-based thiosemicarbazones: synthesis, characterization and pro-apoptotic activity

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In most developed countries, cancer is the second largest cause of death after cardiovascular disease and one of the primary targets in therapeutic chemistry. Very important class of anticancer drugs is metal-based compounds which have been introduced in 1978 when the U.S. Food and Drug Administration approved cisplatin for use in the treatment of testicular and ovarian cancers.[1] Pd(II) complexes have been explored as an alternative to Pt-based compounds owing to structural and thermodynamic analogy between Pt(II) and Pd(II) species. Pd(II) complexes have been shown reduced crossed resistance to cisplatin, decreased toxicity, and high specificity.[2]

In the current study, spectroscopic and structural characterization of the novel Pd(II) complexes (Fig. 1) with 2- and 8-quinolinecarboxaldehyde thiosemicarbazones was done. The anticancer activity of the complexes was evaluated on human pancreatic adenocarcinoma (AsPC-1) and acute monocytic leukemia (THP-1) cell lines and compared to the activity of corresponding ligands and cisplatin. The pro-apoptotic activity of the compounds was evaluated on both cell lines.

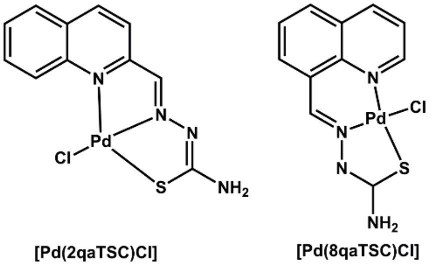

Figure 1. Structures of Pd(II) complexes

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Acknowledgments

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

MC PP 08

Antioxidant activity of copper(II) complexes with salicylaldehyde derivatives and *α*-diimines

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In this work are presented the antioxidant activities of four copper(II) complexes. Our complexes contain a combination of two types of ligands – salicylaldehyde derivatives (methyl 3-formyl-4-hydroxybenzoate (H**L1**) or 4-(diethylamino)salicylaldehyde (H**L2**)) and *α*-diimines (bipyridine (bipy) or phenanthroline (phen)). Complex **1** is a dinuclear Cu^{2+} complex containing **L1** and bipy ligands, complex **2** is dinuclear and contains **L1** and phen ligands, complex **3** is a mononuclear Cu^{2+} complex containing **L2** and bipy ligands, whereas complex **4** is dinuclear and contains **L2** and phen ligands. Based on IC_{50} values, it was established that complex **4** exhibits an excellent antioxidant activity, which is at the same time the highest among all four complexes (Table 1). Complex **3** exhibits moderate activity, whereas complexes **1** and **2** show the lowest antioxidant activity. All four complexes have better antioxidant activity than starting compounds.

Table 1. Antioxidant activity of Cu(II) complexes and starting compounds

Compound	**IC_{50} (mM)**
2,2'-Bipyridine	/
1,10-Phenanthroline chloride monohydrate	15.630
Methyl 3-formyl-4-hydroxybenzoate	/
4-(Diethylamino)salicylaldehyde	54.642
$Cu(BF_4)_2{\cdot}6H_2O$	18.061
1	3.330
2	3.202
3	2.179
4	0.339
Ascorbic acid	0.079

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

MC PP 09

Synthesis of (−)-cleistenolide and its 4-*O*-cinnamoyl analogues from diacetonide of D-glucose

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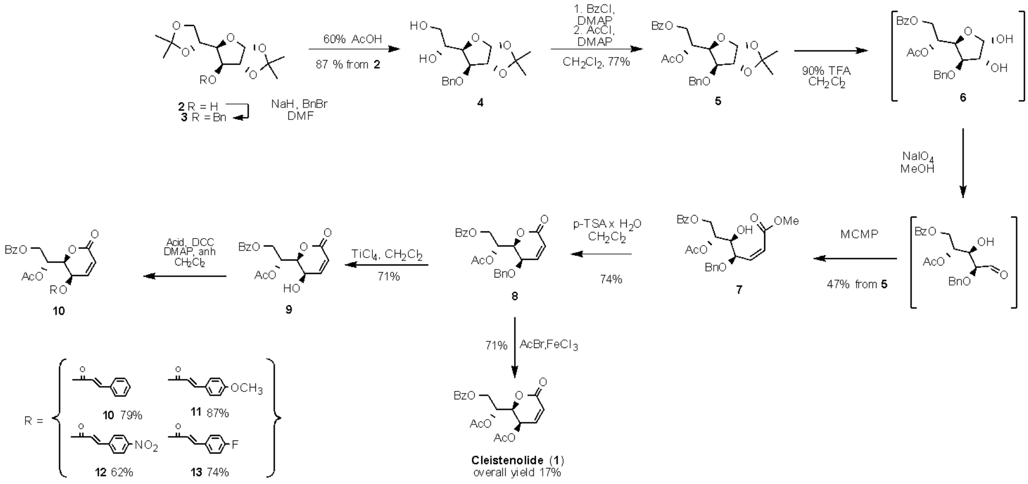
In this work, we wish to present the synthesis of (−)-cleistenolide[1,2] and four novel 4-*O*-cinnamoyl derivatives, as presented in *Scheme 1*. Diacetonide of D-glucose has been used as a convenient starting material for the preparation of the natural product and analogues.



Scheme 1. Synthesis of 4-O-cinnamoyl (−)-cleistenolide analogues

References

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MC PP 10

Spectrophotometric determination of the composition and stability constants of the complex of gadolinium(III)-ion and kaempherol

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Flavonoids (or bioflavonoids) represent the largest group of plant polyphenols. They are plant pigments and their name comes from the latin word *flavus*, meaning yellow. So far, over 8000 compounds belonging to this group have been isolated. Most flavonoids are found in fruits, vegetables and beverages (tea, coffee, beer, wine etc.) derived from fruits and vegetables [1]. Flavonoid kaempherol is a low molecular weight yellow substance, commonly found in food of plant origin, as well as in plants used in traditional medicine. Since the enzymes used in kaempherol biosynthesis are relatively common in the plant kingdom, it is not surprising that this flavonoid is widespread in various plants. There is plenty of kaempherol in: apples, grapes, ginkgo, onions, leeks, citrus, red wine, tea, as well as in some edible berries. Many preclinical studies have confirmed that kaempherol and some kaempherol glycosides exhibit great pharmacological activity, including antioxidant properties, anti-inflammatory, anticancer, antimicrobial, cardioprotective, neuroprotective, antidiabetic, antiosteoporotic. Gadolinium belongs to the lanthanide (Ln) group. Gadolinium is a silvery white metal, it is soft and easy to process. It reacts very violently with dilute mineral acids, but is almost inert to strong bases and water. In this research study the reaction of making complex compound between gadolinium(III)-ion and kaempherol was observed by spectrophotometric method. Investigation of equilibrial reactions of kaempherol in the presence of gadolinium(III)-ion was made in Tris buffer pH 7.4 at the temperature of 298 K. Composition and stability constants of the complex of kaempherol and gadolinium in solution were determined. The obtained results would help to better understand the reactions between kaempherol and medicines that contain gadolinium.

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MC PP 11

3D-QSAR studies and design of selective PI3K-α kinase inhibitors as potential antineoplastics

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Recent studies have shown that PIK3CA, gene that codes p110 catalytic subunit of PI3K-α enzyme is mutated, and the enzyme has increased activity in various types of cancer cells[1]. Since PI3K has an important role in cell growth and formation, specifically inhibiting PI3K-α represents a promising strategy for developing safer antiproliferative agents[2]. In total 92 selective PI3Kα inhibitors, which were taken from ChEMBL database, were used for 3D-QSAR studies (3D quantitative structure-activity relationship), whose experimentally determined inhibitory activities were collected from literature. Pentacle 1.07 program was used for creating the model by using PLS regression analysis. The model has passed both internal (R^2=0.84; Q^2=0.67; RMSEE=0.442) and external (R^2_{pred}=0.681; r^2_m=0.594; Δr^2_m=0.00039; RMSEP=0.567) validation which indicates its good reliability and predictive power. Optained variables were used for determining pharmacophore structure which includes: presence of hydrogen bond donor and hydrogen bond acceptor at a distance of 18-18.4Å or 12-12.4Å, the optimal distance of 15.2-15.6Å between hydrophobic domain and hydrogen bond donor at a distance of 15.2-15.6Å, presence of steric hotspot at a distance of 1.6 - 2Å from hydrogen bond donor and acceptor, and presence of hydrogen bond acceptor and steric hot spot at a distance of 14.4 – 14.8Å. The defined pharmacophore was used as a guideline to modify lead structures from the dataset in order to design new ligands with potentially stronger PI3K-α inhibitory activity.

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Materials science

MS OP 01

Theoretical and experimental study of multiferroics $BiFeO_3$ and $Bi_{(1-x)}Ho_xFeO_3$

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The magnetoelectric materials have been studied due to the scientific chalenges and the very promising possibility of applications in electronic devices. Bismuth ferrite (BFO) is one of the few room temperature magneto-electric multiferroics. Bismuth ferrite ($BiFeO_3$) is one of the most studied multiferroic system with a large number of published articles. This is mainly because $BiFeO_3$ material possesses both ferromagnetic and ferroelectric properties observed at room temperature, which opens great possibility for industrial and technological applications. The influence of Ho doping on the crystal structure and magnetic properties of bismuth ferrite (BFO) nanopowders was investigated. $BiFeO_3$ and $Bi_{1-x}Ho_xFeO_3$ ultrafine nanopowders were synthesized by the hydrothermal method. Here we use simple, low-cost and energy-saving hydrothermal method, which has advantages over the conventional methods. The diffraction pattern was recorded at room temperature and atmospheric pressure in the absence of any re-heating of the sample. A fitting refinement procedure using the Rietveld method was performed which showed the incorporation of Ho^{3+} ions in the $BiFeO_3$ crystal lattice, where they substitute Bi^{3+} ions. All the samples belong to $R3c$ space group. In addition, theoretical investigation using bond valence calculations have been performed in order to mimic pure and Ho doped $BiFeO_3$ compounds produced in the experiment. Various BFO polymorphs were investigated as function of holmium concentration and final optimization of crystal structures has been performed on *ab initio* level using Density Functional Theory (DFT). Furthermore, electronic and magnetic properties of $BiFeO_3$ were investigated using combination of experimental and theoretical methods. Magnetic behavior of synthesized materials was investigated by SQUID. Magnetometer in wide temperature interval (2-800 K). Splitting between the zero-field-cooled and field-cooled magnetization curves becomes more pronounced as the Ho concentration is increased, pointing to the development of weak ferromagnetic moment, which is usually connected with uncompensated spins or spin canting. Hysteresis loops show the same fact, attaining higher magnetization with more Ho included, and becoming wider, i.e. magnetically harder.

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MS OP 02

A new kinetic model for optimization of rubber curing process

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The rubber industry is a huge consumer of energy and determining the optimal curing time and temperature is an important challenge. This research work is devoted to the development of an advanced kinetic model of the rubber curing process in order to simulate and optimize vulcanization process. Commercially available rubber gum was used. Vulcanization kinetic is investigated using oscillating disc rheometer at six temperatures in the range from 130 to 180°C and obtained rheograms were fitted with new proposed kinetic model that include curing and degradation. The proposed model was solved together with the heat transfer equation and numerical solutions were obtained for the rubber spheres (1, 2, 5 and 10 cm in diameter). Proposed model was used in order to calculate curing time and temperature range where, for sphere of 10 cm in diameter, temperature range was estimated from 136°C to 151.9°C with corresponding curing time from 147.2 to 100.6 min. The optimal parameters for vulcanization of sphere is determined as the mean value of the temperature range and corresponding values are 144.05°C, 117.7 min and degree of cure that is achieved is 0.95. In this way, new developed procedure for optimization of rubber curing process can contribute towards reducing of energy consumption.

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MS OP 03

Brushite-metakaolin-based geopolymer materials

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In a field of green chemistry there are ways to come up with new and more advanced materials using on the one hand natural, recyceled or waste materials and on the other hand syntethic materials obtained by using pure synthesis processes. The aim of this paper is to synthesize and characterize brushite-metakaolin- based geopolymer materials (Fig. 1) and to examine the possibility of using these materials in the fields of construction, cement industry, as well as in environmental protection as submersible filters and adsorbents. Materials which was used for geopolymer synthesis was brushite which is obtained by solution-precipitation reaction form acetate solutions [1] and metakaolin clay [2] from Rudovci deposit (Serbia). The obtained mixture powders were dissolved in a strong alcaline solution with addiction of water glass. Produced geopolymers was cast into mods and preserved for 30 days. The starting materials and the synthesized geopolymer material were examined in a field of: XRPD, FTIR and SEM-EDS methods.

Figure 1. Brushite-metakaolin-geopolymer material.

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MS OP 04

Genipin crosslinked chitosan hydrogels for drug delivery of methylene blue

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Controlled drug release from hydrogels is a method of drug delivery that could help mitigate problems that ensue during the standard methods of administering drugs.

In this paper, the chitosan-genipin hydrogel as an agent for controlled delivery of methylene blue as a model drug was investigated. Series of chitosan-genipin hydrogels of different compositions, loaded with methylene blue, were prepared. Since the application of such system in a biological medium is desired, all of the experiments were conducted in simulated body fluid.

Using measurements obtained from an optical reactor[1], the swelling behavior of chitosan-genipin hydrogels of different compositions was investigated, as well as the effects methylene blue has on their swelling. Employing the methods of UV-VIS spectroscopy, the drug release from the aforementioned hydrogels was examined. Our results show that the increase in the concentration of genipin within hydrogel resulted in an increased rate of swelling. It is shown that there are differences in the rate of drug release with the increase of genipin concentration, most noticeable in the first hour of the drug release.

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MS OP 05

Modified eggshell catalyst for transesterification of sunflower oil: The effects of catalyst loading on FAMEs content

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Modified highly active CaO catalyst (ESCHC-600) derived from waste chicken eggshells were prepared and used in the transesterification of sunflower oil. Eggshells were subjected to calcination-hydration-calcination (CHC) cycles described in detail previously [1]. After CHC treatments, highly active CaO was obtained, which indicates its great potential for biodiesel synthesis. The transesterification reaction was carried out in a batch reactor at 60 ºC, methanol to oil molar ratio of 12:1, and different catalyst concentrations ranging from 2 to 8 wt%. Fatty acid methyl esters (FAMEs) content was determined by the HPLC analytical technique. The highest triacylglycerols (TAGs) conversion to FAMEs was achieved at a catalyst loading of 4 wt% (Fig. 1a). A further increase in catalyst loading (> 4 wt%) led to a decrease in TAGs conversion. The higher catalyst loadings (6 and 8 wt%) limited mass transfer of the TAGs and reaction products (FAMEs, DAGs and MAGs) due to the higher reaction mixture density and viscosity of the complex multiphase system. Compared to raw eggshell calcined at 900 ºC (ES-900) (Fig. 1b), the synthesized ESCHC-600 catalyst showed a higher activity, which could be attributed to a more favourable pore structure of CHC treated catalyst and better availability of the active sites.

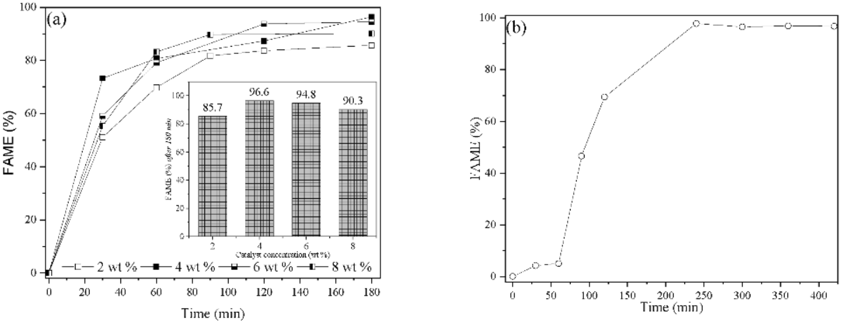

Figure 1. Variations of FAME content with time (a) at different concentration of ESHC-600 and (b) for reaction with ES-900

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MS PP 01

Three dimensional polymeric networks based on poly(methacrylic acid) and protein for targeted delivery of poorly water-soluble drugs

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Three dimensional polymer networks, hydrogels, have shown a great potential in controlled release and targeted delivery of active substances. pH sensitive hydrogels based on poly(methacrylic acid) have attracted significant attention due to their biocompatibility, non-toxicity and the possession of the huge number of ionogenic carboxylic groups. On the other hand, the usage of these hydrogels for controlled release and targeted delivery of poorly water-soluble drugs is limited by their highly hydrophilic nature. We overcame this limitation by modifying PMAA with amphiphilic substance - casein. The addition of this natural protein enabled the encapsulation, targeted delivery and controlled release of poorly water-soluble model drug - caffeine. Three carriers with different neutralization degree of methacrylic acid were synthesized via free radical polymerization. The FTIR spectra revealed that two types of interactions were established between casein and caffeine: hydrophobic interactions and hydrogen bonds. The SEM micrographs showed that the structure of the carriers depended on the change of neutralization degree of the methacrylic acid. The swelling of synthesized carriers and the caffeine *in vitro* release were monitored in two environments at 37°C: 0.1M HCl pH=1.2 (simulation of environment in human stomach) and phosphate buffer pH=6.8 (simulation of environment in human intestines). The synthesized carriers had higher swelling degree and the higher release rate of caffeine in the phosphate buffer pH=6.8 than in 0.1M HCl. The increase in neutralization degree of methacrylic acid caused the increase in swelling degree of the carriers and the increase in release rate of caffeine. Presented results showed that synthesized carriers are promising candidates for targeted delivery of poorly water-soluble drugs.

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MS PP 02

Nickel modified titanate semiconductors for photocatalytic hydrogen production

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Today's global energy supply mainly relies on fossil fuels, which are depleting rapidly, consequently increasing demand for renewable and CO_2-free energy sources. Hydrogen has been considered as efficient and clean alternative to fossil fuels, that enables 100% decarbonisation across the global economy. Solar-driven photocatalytic water splitting is a sustainable way to store and convert solar energy into clean hydrogen fuel. However, the main challenge in photocatalytic hydrogen production is to develop highly efficient, visible light active photocatalyst with potential to be economically viable.[1,2]

Owing to their unique morphology, large specific surface area, as well as excellent ion-exchange/intercalation activities, charge separation, lower recombination, 1-D titanate materials have found application in photocatalytic reactions. The aim of this work is to investigate photocatalytic activity of synthesized Ni modified titanate/titania photocatalyst towards hydrogen production. The series of catalysts were synthesized by deposition of nickel ions on hydrothermally prepared titanate support, followed by hydrogen-temperature programmed reduction. Final catalysts were characterized using different techniques, such as N_2 physisorption, XRD, TPR-temperature programed reduction. Photocatalytic tests were performed under simulated sun light irradiation using isopropanol as sacrificial agent. Results of this study have demonstrated how activity and stability of prepared catalysts towards hydrogen production can be improved by changing the textural, morphological and structural properties of the synthesized catalysts. It was concluded that catalyst phase structure was the dominant factor for photocatalytic hydrogen production activity. The research also showed that proper selection of synthesis parameters had considerable impact on catalyst activity and stability.

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MS PP 03

Photocatalysis of third generation cephalosporin antibiotics ceftriaxone as model compound using newly synthesized TiO_2, ZnO and MgO nanopowders

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Occurrence of pharmaceutically active compounds in aquatic systems and drinking water has emerged as one of the major issues of water and wastewater treatment plants. The main factors contributing to this problem are the substantial increase in the consumption of drugs over the past years and prevalence of improper medication disposal procedures [1]. Ceftriaxone belongs to a third generation cephalosporin antibiotics which is effective for the treatment of pneumonia, bacteremia, spontaneous bacterial peritonitis, urinary infections, etc. It has been found in hospital effluents in India, in collected samples from a wastewater treatment plant in Romania and in river or drinking water and river sediments [2]. Within this study, we investigated the performance of newly synthesized TiO_2, ZnO, and MgO in photodegradation process using ceftriaxone as model compound for photodegradation. Also, the influence of different concentrations of $(NH_4)_2S_2O_8$ (0.5 and 0.125 mmol/dm^3) as electron acceptor was examined. As well, the effect of type of irradiation (simulated sunlight and UV light) was studied.

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MS PP 04

Alkali activation of fly ash as a waste product of coal combustion process

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Fly ashes are glassy and fine powders with a smooth surface and particles of spherical shape that are obtained as a by-product of coal combustion. They consist of substantial amounts of different oxide: calcium, aluminum, and iron oxide, silicon dioxide, and have appropriate composition for the fabrication of new materials known as a geopolymer [1, 2]. Presented study deals with researching of structure and radiological properties of different samples of fly ashes and fly ash-based geopolymers. Synthesis of the geopolymers was conducted by mixing determined ratio of solid (fly-ash) and liquide phase (sodium silicate solution, sodium hydroxide and water). The samples were cured at 60°C for two days after staying at room temperature in covering mold for 24 h. X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR), and SEM-EDS analysis were used for structural analysis of geopolymer samples after 28 days process of geopolymerization. X-ray diffraction measurements one of the samples of fly ashes shows anhidrite as the main constituent. Fourier transform infra-red (FTIR) spectroscopy was applied for determination a polymeric Si-O-Al framework while microstructure of investigated samples was investigated by using SEM analysis. Activity concentration of ^{40}K and radionuclides from the ^{238}U and ^{232}Th decay series in fly-ash samples and fly ash-based geopolymers were determined by means of gamma ray spectrometry.

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MS PP 05

Cavitation of refractory samples based on talc and domestic zeolite from Igros

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Domestic zeolite from Igroš as raw material for ceramic samples for application in condition of cavitation erosion was used. Samples based on talc with 15% of zeolite, from Igroš sintered at 1200ºC were used in this investigation[1]. The ultrasonic vibratory cavitation set up with stacionary specimen was used. Mass loss was measured as well as the degradation level of the samples using image analysis and Young modulus of elasticity. Obtained resultes showed good resistance of the sample to the cavitation erosion, which gives the possibility for viable future application of ceramic samples based on talc and zeolite in different conditions, where cavitation erosion is expected[2].

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MS PP 06

In vitro investigation of hydogel wound dressing materials with electrochemically incorporated silver nanoparticles

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Many shortcomings of traditionally-used, cotton-based wound dressings dictate the ever-increasing need for research and development of novel dressing materials with improved properties. These new materials should be biocompatible and should act as an active barrier against bacterial infection, but they should also address many other drawbacks of commonly-used dressings, e.g. by improving absorption and moisture regulation, elasticity, oxygen permeability, etc. [1]. Hydrophilic gels based on synthetic polymer poly(vinyl alcohol) (PVA) and natural polysaccharide chitosan (CHI) are an excellent choice for such purpose, as they combine elasticity and biocompatibility of PVA hydrogel with intrinsic antibacterial properties of CHI, while they also represent suitable matrices for incorporation of an active antimicrobial component, such as silver nanoparticles (AgNPs) [2]. In this work, we present new materials for wound dressing applications, obtained by electrochemical reduction of silver ions in PVA/CHI hydrogel matrices. Hydrogels were obtained by green physical cross linking method, and chitosan content was varied in order to elucidate its effect on physico-chemical and biological properties. The obtained materials were characterized by UV-visible spectroscopy, scanning and transmission electron microscopy, to confirm the incorporation of AgNPs and to evaluate hydrogels' structural properties. Kinetics of swelling and silver release were monitored in the phosphate buffer solution (pH 7.4), and subsequently, the obtained profiles were fitted to several models in order to calculate the kinetic parameters. Non-cytotoxicity of the obtained hydrogels was confirmed using MTT assay and dye-exclusion test, which confirmed their potential for wound dressing applications.

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MS PP 07

Graphene-reinforced composite hydroxyapatite/chitosan and hydroxyapatite/chitosan/gentamicin coatings

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Graphene (Gr) is a superior material with favorable mechanical and thermal properties, predominately utilized as a component of exceptional composites [1]. In this work graphene-reinforced composite coatings based on hydroxyapatite (HAP) and chitosan (CS), with and without antibiotic gentamicin (Gent) were investigated.

Composite HAP/CS/Gr and HAP/CS/Gr/Gent coatings were electrophoretically deposited in a single step process from aqueous suspension on pure titanium foils. Detailed physico-chemical and biological characterization analyses were performed in order to evaluate the influence of graphene on the properties of newly formed composites. The formation of HAP/CS/Gr and HAP/CS/Gr/Gent composite coatings was confirmed by X-ray diffraction, field emission scanning electron microscopy and Fourier transform infrared spectroscopy. On micro level, composite coatings exhibited porous, homogenous surfaces suggesting strong interfacial interactions between HAP, CS and Gr.

Agar diffusion testing was performed against *Staphylococcus aureus* and *Escherichia coli* in order to evaluate the antibacterial potential and possible medical applications of obtained composite coatings. The results indicated excellent antibacterial properties of the gentamicin-containing coating (HAP/CS/Gr/Gent) with a slightly more pronounced effect against *S. aureus* compared to *E. coli*. Composite coatings were also subjected to cytotoxicity MTT assay to prove the biocompatibility and non-cytotoxic effect towards MRC-5 and L292 cell lines. Obtained results indicated the high potential of HAP/CS/Gr/Gent coating for use in medicine as a part of bone implants.

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MS PP 08

Improving sodium bonding to graphene by phosphorus doping: the role of oxidation from a DFT point of view

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Nowadays, there is a great need for different energy conversion and storage devices, especially commonly used metal-ion batteries. Due to many problems related to lithium-ion batteries, sodium-ion batteries are now widely considered. Graphene-based materials are proposed as good candidates for many applications, including the one as electrode materials in novel metal-ion batteries. Graphene is a planar, one atom thick material consisting of sp^2 hybridized carbon atoms arranged in a hexagonal crystal lattice. It is a zero-gap semimetal, which makes it a good electrical conductor. Pristine graphene is chemically inert, due to the presence of delocalized π electronic cloud. It interacts rather weakly with sodium (adsorption energy −0.36 eV). Deviation from perfection, *i.e.* defects on graphene induce changes in its electronic structure and reactivity. Defects can be introduced through different dopant atoms and functional groups. Using the Quantum ESPRESSO[1,2] package for Density Functional Theory (DFT) calculations, we have investigated the effects of substitutional doping of graphene with phosphorus (P) and its oxidation on sodium binding. We demonstrate that P-doping induces significant topology and reactivity changes in graphene, enhancing Na binding. Additionally, oxidation further tunes Na binding properties: P-doped graphene in the presence of an epoxy group binds sodium about 6.4 more strongly compared to pristine graphene. We discuss this, and other aspects of doping/oxidation relevant for the possible application of such materials in sodium-ion batteries.

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MS PP 09

Synthesis of active biodegradable starch-based plastic and migration of vitamin B3

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A new method for starch-based biodegradable plastic film synthesis was studied. Two types of plastic films were formed: one, in which the starch source was dried purple sweet potato powder, and the other, in which the starch source was cornflower. Anthocyanins are a pH-sensitive group of pigments, which can be found in dried purple sweet potato powder. It was determined that the plastic films made of purple sweet potato powder also change color upon the change in pH. This feature of plastic films could be used in food packaging, for food products that release compounds that change the original pH when spoiled. The color transition in different pH values matches the anthocyanin color transition. Vitamin B3 was incorporated into the polymer blend, with the intention of extending food shelf-life. Migration of vitamin B3 was observed in four different food simulants. By HPLC analysis of antioxidant migration samples, it was determined that the migration is most suitable for 90% ethanol solution, which represents food products with a high content of fatty acids.

MS PP 10

Thermal treatment of metakaolin based geopolymer

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Metakaolin based geopolymer samples were prepared using metakaolin as solid precursor. Metakaolin was activated by NaOH solution of different concentrations and sodium silicate solution. Geopolymer samples were calcined at 900°C which was found as a key transition temperature. During the calcined at 900°C the geopolymer began to melt partly and coagulate locally, and considerable interspaces existed and separated the partly melted geopolymer [1]. Fourier transformation infrared spectroscopy (FTIR), X-ray diffraction (XRD) and SEM-EDS analysis were used for structural analysis of geopolymer samples before and after the thermal treatment. The thermal treatment at 900°C leads to a considerable reduction of oxygen and particularly sodium, followed by formation of a complex porous structure. Additionally, new semicrystaline phases were appeared. XRD results imply that one of these new phases is nepheline and it is possible that this phase starts to nucleate at temperatures below 900 °C.

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MS PP 11

Preparation and characterization of oxidized wheat starch with hydrogen peroxide as an environmentally friendly oxidant

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The starch oxidation involves oxidation of primary or secondary hydroxyl to carbonyl or carboxyl groups, whereas the number of these groups indicates the level of oxidation. Oxidized starch is used as surface sizing agent and coating binder in the paper industry, or as polymeric filler that increases the polymer degradability. The main objective of the presented study is to investigate the effects of various parameters on the oxidation process of the wheat starch, using dry method (Fig. 1). These parameters include oxidizer concentration, catalyst type (iron(II) sulphate, copper(II) sulphate and copper(II) citrate), presence of plasticizers/modifiers (ricinoleic acid, (R-(*Z*))-12-hydroxy-9-octadecenoic acid, RA) and diizopropyl tartarate ((dipropan-2-yl 2,3-dihydroxybutanedioate, DIPT) and reaction temperature (20 and 80 °C). The obtained results suggest that higher values of carbonyl and carboxyl groups lead to an increase of swelling capacity and solubility, while viscosity decreases, compared to the native wheat starch. The analysis of FTIR spectra, especially region of carbonyl/carboxyl groups absorption, reveals high impact of process parameters on the oxidation degree and band structure. The morphology of native and oxidized starches, investigated by the SEM method, shows that after oxidation the surface of the starch particles becomes smoother then for the native starch, with aggregation of small and large-sized granules.

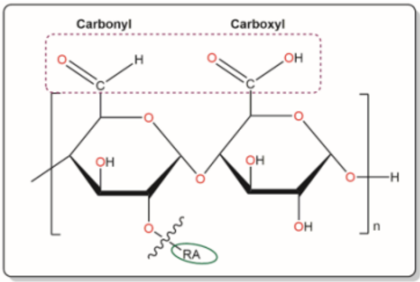

Figure 1. Modified/oxidized starch

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MS PP 12

Efficient removal of Pb^{2+} from aqueous solution using hybrid material based on chitin and hydroxyapatite

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A macrofungi species, mosaic puffball (*Handkea utriformis*-HU) goes through the process of autodigestion during maturation of the fruiting bodies, which turns their inside-gleba, into a spore-bearing powder and the lower portion of the fruiting bodies-subgleba, into a dry, spongy mass, consisting mainly of polysaccharides and proteins. The subgleba was modified via embedding of hydroxyapatite (HAp) by successive ionic layer adsorption and reaction (SILAR) method for removal of Pb^{2+} from aqueous solution. Experimental data obtained at three different temperatures for the adsorption of Pb^{2+} by HU-HAp were applied in a batch system at a constant initial concentration of adsorbate and pH and different concentrations of the adsorbent. The material was characterized by ATR FT-IR spectroscopy, SEM and EDAX analysis in order to reveal their composition and surface morphology. Concentrations of Pb^{2+}, before and after adsorption, were determined by using Atomic Absorption Spectroscopy (AAS). Different models of the adsorption isotherms are evaluated to determine adsorption capacities. The best fit was obtained using Freundlich adsorption isotherm model.

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MS PP 13

Removal of hexavalent chromium Cr(VI) from aqueous solutions using cellulose-magnetite membrane CelMag- M

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The industries of leather-tanning, mining and textile dyeing, generate large amounts of chromium-containing wastewater. Hexavalent Cr(VI) is highly poisonous and extremely mobile in the surface-water and groundwater in a broad pH range and therefore it has been identified as a potentially carcinogenic substance. The aim of the presented work was to develop cellulose-based membrane functionalized with magnetite, which could be used as an efficient adsorbent for the removal of hexavalent chromium Cr(VI) ions from aqueous solutions. Cellulose-based filter (CF) was functionalized with magnetite in three-step process. In the first and second step CF surface was modified using an ethanolic solution of (3-aminopropyl)triethoxysilane (APTES), and diethylenetriaminepentaacetic acid dianhydride, respectively. The introduction of amino and carboxylic groups provided successful precipitation of magnetite in the third step. The obtained cellulose-magnetite membrane (CelMag-M) was characterized by FTIR and SEM analysis. Adsorption of Cr(VI) onto CelMag-M was studied using batch-adsorption test. Under optimum pH conditions, the maximum experimental adsorption capacity of CelMag-M for Cr(VI) was found to be 111.2 mg g^{-1}. The adsorption process was endothermic, the equilibrium adsorption data could be best fitted to the Langmuir adsorption isotherm model and kinetics was in agreement with the pseudo-second-order rate equation.

Acknowledgments

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MS PP 14

Novel pH-sensitive hydrogels based on poly(β-amino esters)

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Hydrogels are crosslinked hydrophilic polymer networks, able to swell and absorb large amount of water and fluids, without dissolving. Because of their stimuli-responsive characteristics, hydrogels have been thoroughly explored in past years, and show great potential for various biomedical applications.[1] In this work we present the synthesis and characterization of novel poly(β-amino ester) (PBAE) macromers obtained by Michael addition reaction of a natural compound, γ-aminobutyric acid (GABA), and a combination of synthetic diacrylates, diethylene glycol diacrylate (DEGDA) and polyethylene glycol diacrylate (PEGDA). By varying the ratio of DEGDA/PEGDA, and keeping the amount of GABA constant, we were able to produce four different PBAE macromers with tailored functional properties.[2] PBAE macromers were used in a free-radical polymerization reaction to obtain novel semi-degradable, pH sensitive zwitterionic hydrogels. Chemical structure of the PBAE macromers and hydrogels was determined by Fourier transform infrared (FTIR) spectroscopy. Swelling studies, performed in phosphate buffers, (physiological pHs 2.20, 5.45 and 7.40), showed pH-sensitive behavior. Properties of the synthetized hydrogels, including swelling and degradation rates, depended significantly on their chemical structure, which can be easily adjusted by changing the diacrylate ratio. The obtained results suggest that the synthesized hydrogels display a great potential for a range of biomedical applications, such as intelligent drug delivery systems and tissue regeneration.

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MS PP 15

Study of biological properties of Ag+/poly(2-hydroxyethyl acrylate/itaconic acid) hydrogels

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For several decades antibiotics were successfully used in treatment of bacterial infections, but the persistent application led to the development of bacterial resistance. The resistance is now developed to every major class of antibiotics, where infections caused by resistant microorganisms often fail to respond to the usual treatment, resulting in prolonged illness, increased health care costs and risk of death. The discovery of novel antimicrobials became necessity, as alternatives to traditional antibiotic treatment. Herein, we developed the series of hydrogels based on 2-hydroxyethyl acrylate (HEA) and itaconic acid (IA) with silver(I) ions embedded in polymeric network. Physico-chemical characteristics were examined by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). Swelling study was conducted in wide range of physiological pHs at 37 °C. The *in vitro* release study revealed suitability of these pH sensitive hydrogels as the systems for topical delivery of silver(I) ions. For the purpose of potential application as antibacterial biomaterials, in particular in wound management, the biological studies were performed. MTT test revealed good biocompatibility of the hydrogels. According to results obtained from Comet assay, the hydrogels did not exhibit any genotoxic effect on human fibroblast cells (MRC-5 cell line). Microbiological tests showed antibacterial activity of the hydrogels against methicillin sensitive *Staphylococcus aureus* (MSSA) and methicillin resistant *Staphylococcus aureus* (MRSA). The obtained results indicated the great potential of the hydrogels as novel antibacterial biomaterials.

Acknowledgments

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Theoretical chemistry

TC PP 01

Experimental and computational analysis (DFT method) of some quinoxalinones and benzoxazinones

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The selected quinoxalinones and benzoxazinones derivatives (Fig. 1), synthesized in our laboratory earlier[1], were explored by spectroscopic techniques (UV-Vis, IR, Raman and NMR) and theoretical study (DFT calculations). In order to understand the electronic properties of these compounds the theoretical UV spectra have been investigated by TDDFT/B3LYP method with 6-311+G(d,p) basis set in ethanol as a solvent. The frontiers molecular orbitals are calculated and contributions of the electronic transitions are determined. Also, we did quantum chemical calculations to investigate the corrosion inhibition properties of these molecules. The vibrational analysis was performed and obtained results are in very good agreement with experimental data. The calculated ^{13}C NMR shifts in all cases are in good-to-excellent agreement. Also, ^{1}H NMR predicted shifts are comparable with experimental results, but there are some deviations (for N-H shifts) probably as a consequence of intramolecular interactions. Computational techniques are useful for solution of the problems confronted in the experimental chemistry.

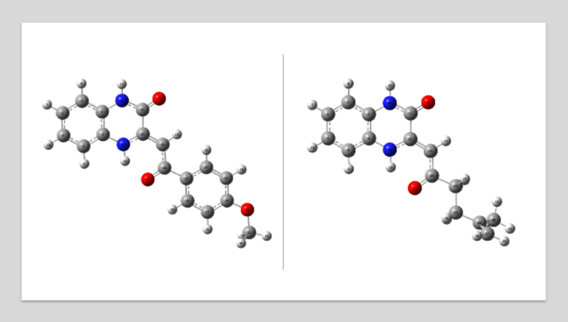

Figure 1. Optimized structures of some investigated quinoxalinones.

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TC PP 02

Amyloid PDB structure set

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Amyloids are insoluble proteins of a cross-β structure found as deposits in many diseases. They are largely examined structurally, but there is a lack of a unique structural database for amyloid proteins resolved with atomic resolution. Here, we present a constructed set of amyloid structures found in the Protein Data Bank based on keyword criterion as well as structural features of amyloids described in literature (Fig. 1). An amyloid consists of parallel self-assembled β-sheets or coils [1,2]. The searching filter was performed by python programming. The total number of structures is 109 and it keeps increasing. This database can help further structural general and statistical analysis of amyloids.

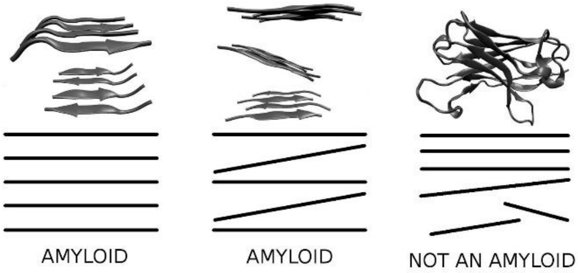

Figure 1. Criterion for distinguishing amyloid structures from other non-helical structures: an amyloid consists of parallel self-assembled β-sheets or coils.

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TC PP 03

Influence of the metal ions on the charge transfer states in the G-octet-metal ion complexes

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The telomeric, guanine (G) rich, region at the end of the linear chromosomal DNA strand have the ability to form highly organized biologically relevant nanostructures called G-quadruplexes [1]. These structures can accommodate various metal ions into the central cavity to further improve their stability. G-quadruplexes can be potentially useful systems for the application in molecular electronics and optoelectronics, since they can be easily integrated in nanodevices. Although their ground state properties are now largely understood, little is known about their exited states. In this work, we study G-octet-metal ion complexes (M-G$_8$, Fig 1a) which act as models for the G-quadruplex supramolecular arrangement within DNA. We used DFT based molecular dynamics (BLYP-D3/DZVP+PW+GTH) for configuration sampling purposes and calculated electronic excitations to initially populated (Franck-Condon) states. To capture charge transfer content of the excited states, we used descriptors who rely on the analysis of the one-electron transition density matrix acquired from the TDDFT calculation (CAM-B3LYP/6-31G(d)). Our results indicate that the M-G$_8$ (M=Li$^+$, Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}) systems absorption spectrum is slightly modulated by introducing alkali metal ions compared to the empty scaffold while earth-alkali metal ions have somewhat larger impact on the red tail of the spectrum (Fig 1b). On the other hand, charge transfer content is highly modulated and shifted towards lower energies for the Mg^{2+}-G$_8$ and Ca^{2+}-G$_8$ systems (Fig 1c) indicating that earth-alkali templated G$_8$ structures are more suitable for potential technological applications.

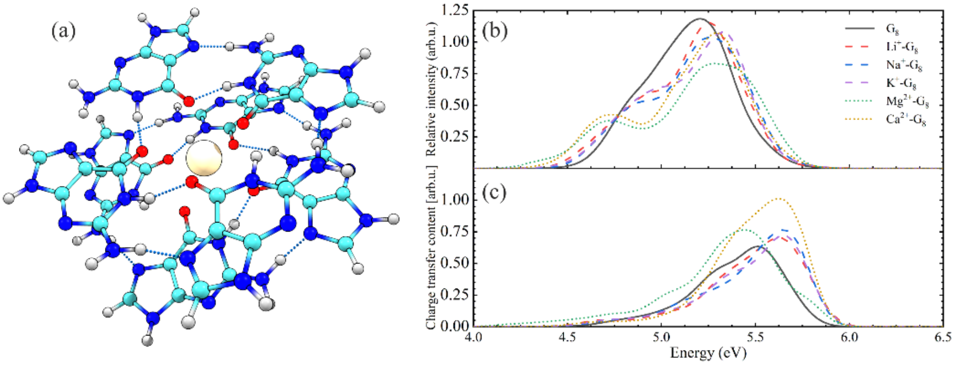

Figure 1.(a) M-G$_8$ structure; (b) M-G$_8$ electronic absorption spectrum; (c) Charge transfer content.

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TC PP 04

Study of phenol and toluene stacking interactions, including interactions at large horizontal displacements, in crystal structures and calculated potential energy surfaces

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Importance of aromatic interactions has been widely documented. The arrangements of molecules in solids, liquid crystals and solution are influenced by aromatic stacking interactions. In biological systems, the role of aromatic residues has been identified as very important in protein-protein, protein-folding, protein function, protein-ligand, protein-lipid, protein-nucleic acids interactions and protein structure stability.

Here, we searched the Cambridge Structural Database to find interactions of stacking benzene, *p*-phenol and toluene dimers. Beside this, we calculated interaction energies of phenol and toluene dimers and compared with benzene dimers previously calculated. The results have shown that stacking p-phenol/p-phenol dimer tends to be orientated in parallel and antiparallel fashion while stacking toluene/toluene dimers have almost exclusively antiparallel orientation of two rings. As for benzene molecules, number of interactions for stacking p-phenol/p-phenol and toluene/toluene dimers is increasing at the large offsets (4.0 - 6.0 Å). Additionally, interactions of p-phenol/p-phenol and toluene/toluene dimers show peak at offset 1.5 Å.

The potential surfaces of stacking interactions of phenol-phenol and toluene-toluene were investigated, including interactions at large offsets. Three different geometries of parallel and antiparallel phenol-phenol and toluene-toluene dimers were considered. The DFT calculations have shown that the interaction energies for phenol/phenol and toluene/toluene dimers have similar trends. For parallel orientations at negative and positive offsets for toluene/toluene, the strongest interaction energy is –3.98 kcal/mol. For antiparallel orientations, at negative offsets, the strongest interaction energy is –5.39 kcal/mol, while at positive offset the strongest interaction has energy of –2.83 kcal/mol. Both systems phenol/phenol and toluene/toluene, in crystal structures show preference for large offsets (4.0 - 6.0 Å) and have significant calculated interaction energy similar to benzene dimer.

TC PP 05

Barbituric acid derivatives as push-pull electronic systems. A Quantum Chemical study

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Benzylidene barbituric acids are used for synthesizing merocyanine dyes and, designing PPAR$_\gamma$ ligands. They can act as antibacterial agents, tyrosinase inhibitors and have attracted great attention as nonlinear optical materials. In order to interpret their different solvatochromic behavior, 5-arylidene barbituric acid derivatives were synthesized with different chromophores, and their UV-Vis absorption spectra have been recorded in organic solvents of different polarity. All calculation for the studied isomers were carried out using Gaussian 09 software. Elements of the optimized geometries of 5-arylidene barbituric acid derivatives were obtained by *ab initio* MP2/6-311G(d,p) method. UV-Vis spectra of all synthetized molecules were calculated using TD-DFT method, more specifically B3LYP functional with 6-311G(d,p) basis set in different solvent using the Self-Consistent Reaction Field (SCRF) theory with Polarized Continuum Model (PCM). From obtained ground and excited state electron densities, charge-transfer distances (D_{CT}) between charged barycenters, amount of transferred charge (Q_{CT}) and associated dipole moments (μ_{CT}) were evaluated.[1] Maps of molecular electrostatic potentials (MEP) were calculated for all molecules in their ground state. The intramolecular charge transfers of the investigated molecules were interpreted using natural localized molecular orbital (NLMO) analysis.

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TC PP 06

Comparison of strength of metal-hydrogen interaction energies between cisplatin and transplatin molecules and different hydrogen donors

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Early experimental and theoretical evidences of the existence of platinum-hydrogen interactions emerged more than four decades ago [1]. Although metal atoms are not usually seen as hydrogen atom acceptors, many crystallographic studies as well as our recent quantum chemical study, showed that they can be involved in very strong hydrogen bonding [2].

In this work, energies and geometries of X-H/Pt interactions involving cisplatin and transplatin molecules as hydrogen atom acceptors and different hydrogen atom donors were evaluated. Interaction energies and optimal geometries were calculated using MP2/aug-cc-PVDZ level of theory. Cambridge Structural Database search was performed and all structures containing cisplatin and transplatin molecules involved in X-H/Pt interactions were extracted. Geometrical parameters important for the analysis of X-H/Pt interactions were statistically analysed.

Results indicated that there are significant differences in metal-hydrogen bonding between cisplatin and transplatin molecules. The energy of the strongest X-H/Pt interactions involving cisplatin molecule are calculated to be $E_{O\text{-}H/cis\text{-}Pt} = -5.97$ kcal/mol while interaction energy of the strongest X-H/Pt interactions involving transplatin molecule was calculated to be $E_{O\text{-}H/trans\text{-}Pt} = -4.43$ kcal/mol. Electrostatic potential maps were calculated for both cisplatin and transplatin molecules and used to explain trends in interaction energies. Results of interaction energies calculations were in excellent agreement with the results of statistical analysis of crystallographic data.

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TC PP 07

Binding of uranyl cation to peptides: a combined quantum chemical and crystallographic study

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Interactions of uranyl cation with peptides are drawing attention of the researchers mostly because of the importance of these interactions for understanding of uranium toxicity but also because of the possible application of uranyl-peptide binding for extraction of uranium from the seawater [1]. Although structure of many complexes containing uranyl cation attached to amino acids and proteins were determined and analysed, a systematic theoretical study related to binding of uranyl cation to peptides was not performed yet [2].

Here we present theoretical study of stability of complexes containing uranyl cation and different dipeptides and tripeptides. The study was based on Density Functional Theory calculation as well as very precise CCSD(T) calculations. In the frame of this study, different bonding patterns between uranyl cation and selected peptides were proposed and analysed. Stability of structures in which uranyl cation is bonded to carboxyl group were compared to the stability of structures in which uranyl cation was bonded to atoms involved in peptide bond. In addition, crystal structures of proteins containing uranyl cation were extracted from Protein database and analysed.

Results of theoretical calculations were compared to the results of analysis of crystal structures archived in Protein databank.

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TC PP 08

How disulfide bond interacts with sulfur atom? Quantum chemical and crystallographic study.

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Sulfur-sulfur interactions have been recognized in crystal structures containing cysteine residues [1] as well as in well-known organic conductors [2], where they are important for molecular structure and function.

Interactions between sulfur and disulfide bond represent the special case of sulfur-sulfur interactions. These contacts have been investigated by analysing data obtained from crystal structures archived in Cambridge Structural Database and by very accurate CCSD(T)/CBS quantum chemical calculations. Analysis of crystallographic data showed that bifurcated S-S···S interactions are predominantly present in crystal structures. An example is a crystal structure containing a bifurcated S-S···S interaction (Fig. 1). Results of quantum chemical calculations showed that interaction energy calculated for bifurcated geometry is quite strong, –2.83 kcal/mol. The SAPT decomposition energy analysis indicates that dispersion is main attractive force in bifurcated geometries, while electrostatics significantly contributes to the strength of bifurcated S-S···S interactions.

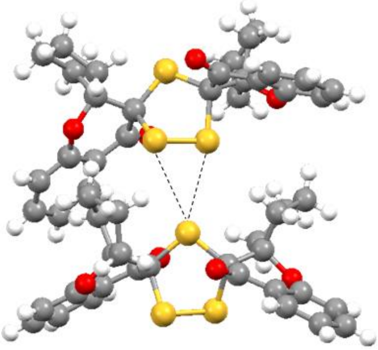

Figure 1. Crystal structure BAHBOB containing bifurcated S-S···S interaction.

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TC PP 09

Crystallographic and quantum-chemical study of stacking interactions of resonance-assisted hydrogen-bridged rings

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Mutual contacts between resonance-assisted hydrogen-bridged (RAHB) rings,[1] as well as contacts between RAHB rings and C_6-aromatic rings[2] are systematically analyzed by searching Cambridge Structural Database (CSD) (Fig. 1). It is observed that the tendency of forming stacking interactions is very high in RAHB/RAHB contacts, since 91% of them corresponds to stacked arrangement. At the other side, the tendency of forming stacked contacts is not so pronounced in RAHB/C_6-aromatic contacts, although the majority of them (59%) correspond also to stacking. The high level quantum-chemical calculations (CCSD(T)/CBS) are performed on model systems that are based on abundance in CSD. The energies of the strongest calculated RAHB/RAHB stacking interactions can reach –4.7 kcal/mol. The strongest calculated RAHB/benzene stacking interactions are weaker (–3.7 kcal/mol), but they can be also stronger than the corresponding RAHB/RAHB stacking interactions, depending on the RAHB system considered.

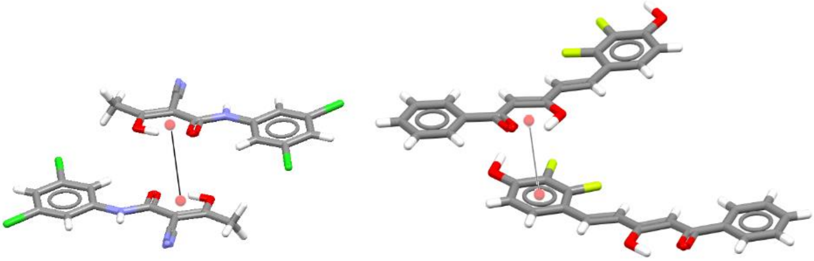

Figure 1. Fragments found in CSD RAHB/RAHB contacts; (left); RAHB/C_6-aromatic contacts (right).

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TC PP 10

Thermochemistry of organometallic reactions in solution: joint ITC and DFT study

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The understanding of certain, still unknown, aspects of the chemical bond is made possible by new theoretical tools, particularly static DFT-D or DFT methods corrected for dispersion. These methods allow accounting for, in a physically relevant way, the effects of dispersion at medium and long distance [1]. For the further assessing the accuracy of static DFT-D calculations the providing of referential experimental data was found to be essential. It has been shown that Isothermal titration calorimetry (ITC) techniques can provide reliable thermodynamic parameters of reaction (enthalpy ΔHr, Gibbs free energy ΔGr and entropy ΔSr) [2], while some recent studies showed good agreement between experimental and theoretical results [2].

The study presented here sheds some light on the thermochemistry of reactions in solution by preforming ITC experiments in chlorobenzene and static DFT-D calculations. The study points out that, in cases where solvent molecules can interact significantly with molecules of reactants, an accounting for the explicit solvation is of crucial importance for agreement between experiment and theory. The results of various kinds of organometallic reactions will be presented in some details.

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Author Index