POSTER SESSION II

THURSDAY, MAY 28th, 2015

CHAIRPERSONS: Andrzej Bąk and Andrzej Swinarew

1.

Synthesis and physicochemical properties of terephthalamides

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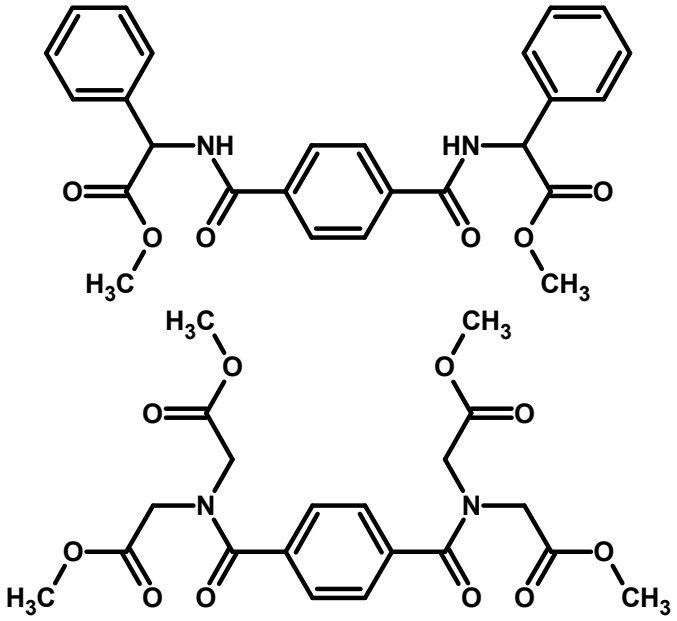
Key words: terephthalamides, spectroscopy, crystallographic

Abstract:

The aim of this study was to obtain new diamide of terephthalic acid and derivatives of phenylglycine and iminodiacetic acid. In the first step of the synthesis, the methyl ester hydrochlorides of these amino acids were obtained by reaction with methanol and thionyl chloride. Then, the hydrochlorides were carried out into diamides by reaction with terephthalic acid chloride and triethylamine in chloroform solution. After purification diamides were examinated, the melting point and the solubility were determined. Their chemical structure was confirmed by defining their crystallographic structure and by using spectroscopic methods: ^{1}H, ^{13}C NMR, ESI-MS and IR.



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2.

Top 100 drug bestsellers are getting older

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Drug design and development is an extremely complex technological and economic problem. The complications are clear when we explore recent controversy in pharmaceutical R&D. There are sufficient arguments and evidence to support a hypothesis that R&D productivity is steadily declining [1]. This decline is so important that new designs for Phase II trials were suggested to increase the productivity gap [2]. On the other hand, other arguments are based on evidence of no productivity crisis [3] or that "productivity rides again" [4].

We analyzed the top 100 bestselling drug list as a struggling market for FDA approvals. Our analysis showed that the time from drug (FDA) approval, if used as a measure of drug age for probing the data of the top drugs, indicated a clear increasing effect. In our opinion, this reflects the stalled launch of new drugs into the market in recent years. We probed drug-likeness MW, log P and topological polar surface (TPSA). Interestingly, the lowest MW central nervous system drugs also appeared to be the winners on the list.

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3.

Synthesis of a new nanographene model containing seven-membered ring

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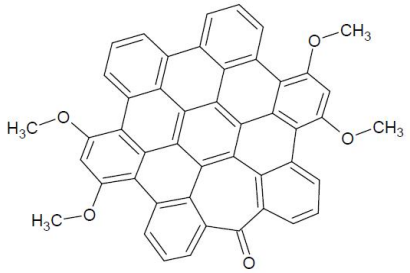
One of the interesting feature of our new nanographene model is that forced into nonplanar structure may lead to changes in the optical and electrical properties. Nanographene containing in its structure a five- or seven-membered rings is more soluble than the hexagonal counterparts[1].

The aim of this study was obtaining a new model of nanographene, in which one of the six-membered rings has been replaced by the seven membered ring[2]. The distorted nanographene was synthesized by Sonogashira coupling, cyclotrimerization with cobalt complex $Co_2(CO)_8$, Scholl oxidation[3] and the ring closure was performed using iron chloride (III)[4].

The chemical structure of the obtained compounds was confirmed using ^1H and ^{13}C NMR. Attempts have been made to obtain a crystal structure.

Synthesized compounds have potential application in electrochemistry as organic semiconductors, in molecular electronics and in nanotechnology.



Scheme 1. The obtained model of nanographene.

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4.

Mercapto-modified graphene oxide for determination of divalent metal ions and arsenic species

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Direct determination of trace and ultratrace amounts of heavy metal ions in samples with complex composition is a difficult task. Therefore, the application of an additional separation and/or preconcentration step before the measurement is necessary. Solid phase extraction (SPE) is one of the most commonly applied sample preparation technique due to its rapid phase extraction and low consumption of organic solvents. Another advantage of this technique is its easiness in combining with different spectroscopic techniques, both online and offline mode. The selection of the proper sorbent material is an essential step allowing to obtain high enrichment factor values and good selectivity of the procedure. The most popular solid sorbents used in SPE are silica gel, cellulose, chelating resins and, most of all, carbon nanomaterials, such as carbon nanotubes, graphene and graphene oxide (GO).

The aim of this study was to apply mercapto-modified graphene oxide (GO-SH) as solid sorbent in dispersive micro-solid phase extraction (DMSPE) for the determination of heavy metal ions and arsenic species with the use of total-reflection X-ray fluorescence spectrometry (TXRF) [1]. GO-SH was prepared by grafting 3-mercaptopropyl trimethoxysilane on a graphene oxide surface [2]. The sorption of Co(II), Ni(II), Cu(II), Cd(II), Pb(II), As(III) and As(V) ions on GO-SH was investigated. The parameters affecting the extraction process like pH, sample volume, or contact time between the analytes and sorbent were thoroughly evaluated. Proposed procedure allows obtaining high recoveries, detection limits and enrichment factors. The proposed methodology was successfully applied for determination of ultratrace amounts of metal ions in water samples. It is also noteworthy, that proposed DMSPE/TXRF procedure meets all requirements of green analytical chemistry [3].

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5.

Synthesis, properties and applications of thioterephthalamides

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One of the characteristics of symmetric thioamides is a self-assembly process, due to secondary effects. Forming a supramolecular structure of the nano-chair is used for the preparation of nanomaterials.[1,2] The study of crystal structures is an important contribution to the understanding of the interaction of NH···O hydrogen type, appearing in diamides terephthalic acid.[3,4,5] Presence of sulfur atoms deepens the characteristic effects of the electron, compared with the spectral properties of their oxygen counterparts.[6,7] Of particular note are thioamides forming hydrogen bonds type NH···S.

The studies relate to the synthesis of new sulfur derivatives of terephthalic acid substituted methyl esters of selected amino acids. Acquiring of target compounds consists of synthesis with the use methyl ester hydrochlorides of chosen amino acids, terephthalic acid chloride, phosphorus pentasulfide supported on Al_2O_3 as a thionation agent.[8]

The chemical structure of the obtained compounds was confirmed using ^{1}H and ^{13}C spectra, and ESI-MS spectra. For each of the thioamide was examined physico-chemical properties, and attempts have been made to obtain crystal structures.

Presented class of compounds can be used as a precursor for the synthesis dithiazolidines which can be used as pharmaceuticals and orexin receptor antagonists.[9]

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6.

Investigation of alcohols and polyols oxidation products over Au_{NPs} and Pd_{NPs} catalysts using ^{1}H, ^{13}C NMR and 2D techniques

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Interest in the production of commodity chemicals from biomass feedstocks continues to grow as the biological and chemical transformations of carbohydrates becomes more economical. Conventional resources, mainly fossil fuels, are becoming limited for the rapid increase in energy demand. Biomass is one of renewable resources and can be used to produce various chemicals and fuels. Using renewable biomass for the synthesis of chemicals is greatly highlighted in chemical research field. Among the most promising of these processes is the aqueous-phase oxidation of alcohols and polyols, which utilizes environmentally friendly reagents and can be occured under mild conditions [1–4]. The resulting ketone, ester, aldehyde, and acid products are highly valued intermediates in the fine chemical, pharmaceutical, and agrochemical sectors [5].

Understanding the way of alcohols and polyols oxidation and modification of reaction conditions allows to control of the process towards the required products with high selectivity. The reaction mechanism research and formed mixture of products were performed by spectroscopic techniques ^{1}H, ^{13}C NMR spectra, in the alternative the two-dimensional correlation COSY and HMQC techniques.

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7.

Application of microextraction procedures in determination of trace elements by spectroscopy techniques

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Miniaturisation in its broad sense and development of environmental friendly methodologies reflect current trends in the modern analytical chemistry [1]. Reduction of the amount of toxic solvents and reagents results, inter alia, in the development of new sample pre-treatment techniques as well as measurement automation. According to the aims of green analytical chemistry (GAC), one of the most universally applied enrichment/separation techniques, i.e. liquid-liquid extraction (LLE) and solid-phase extraction (SPE) have been increasingly replaced with microextraction techniques, that are their miniaturised equivalents [2,3]. Application of both liquid phase microextraction (LPME), and solid phase microextraction (SPME) enables to overcome inherent drawbacks of conventional extraction techniques, i.e. lengthy duration, labour intensity, abundant consumption of reagents and production of large amounts of wastes.

Spectroscopic techniques are considered as a sensitive, reproducible and accurate analytical methods, offering great opportunities for the detection and identification of substances in samples of complex composition. Nevertheless, meeting the requirements imposed on the routine analysis, which are especially demanding when it comes to determination of trace and ultratrace amounts of elements, requires an additional separation and/or preconcentration step prior to the measurement. This work covers recently applied approaches aiming at the development of an effective and efficient sample introduction systems, which do not require extract dilution prior the measurement.

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8.

Synthesis of building blocks in the quasi-heterogeneous reactions with nano-Pd/Cu catalyst- monitoring the progress of reaction by TLC

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In our investigations, we revealed that the heterogeneous catalyst composed of active catalytic Pd species on the copper support was active enough to perform the Sonogashira reaction under mild conditions. Further studies were focused on the development of more efficient, less expensive and simply formulated catalyst for the chemistry of alkynes. In these studies, TLC was used to monitor the progress of chemical reaction. Chromatographic purification of the final products was not required. Composition of novel solid phase supports, namely monolithic materials with pore dimensions of several micrometers and Pd nanoclusters with improved solubility in organic media, presumably affected reduction of reaction time and facilitated separation of the catalyst.

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9.

Investigation of antioxidant activity of pomegranate juices by means of electron paramagnetic resonance (EPR) spectroscopy and UV-VIS spectrophotometry

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Pomegranate fruit (*Punica granatum* L.) is a source of numerous phenolic compounds and it contains flavonoids such, as anthocyanins, anthocyanidins, cyanidins, catechins and other complexes of flavonoids, ellagitannins and hydrolyzed tannins. Pomegranate juice shows antioxidant, antiproliferative and antiatherosclerotic properties.

The antioxidant capacity (TEAC) of the pomegranate juices was measured using the EPR spectroscopy method and 1,1-diphenyl-2-picrylhydrazyl (DPPH•) as a source of free radicals, and the total phenolics content (TP) was measured using the UV-Vis spectroscopy. The results obtained are presented in this study.

All the examined pomegranate juices exhibited relatively high antioxidant properties. The TEAC values determined by means of EPR (using trolox, TE, as a free radical scavenger) were in the range of 463.12÷1911.91 μmol TE per 100 mL juice. The total phenolics content (TP) measured by the Folin–Ciocalteu method (using gallic acid, GA, as a free radical scavenger) widely varied in the investigated pomegranate juice samples and ranged from 1673.62 to 5263.87 mg GA per 1 L juice. The strongest antioxidant properties were observed with the fresh pomegranate juices obtained from the fruits originating from Israel, Lebanon and Azerbaijan. Correlation analysis of numerical data obtained by means of EPR (TEAC) and UV/Vis (TP) characterizes with the correlation coefficient $r^2 = 0.81$ ($p<0.05$).

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10.

Bio-corrrosion in biopuryfication of air from VOC's mixture

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Continuous biodegradation of poisonous, volatile organic compounds (VOC's), which are released to the atmosphere during many industrial operations, is one of the fastest-growing areas of bio-processes. Biological degradation of VOC's provides a cost-effective and highly-efficient alternative to most of popular air-purification technologies like absorption or high temperature, catalytic oxidation. Considering that growth of bacteria colonies and sustaining of theirs activity are essential for proper operation of any bio-process, it is clear, that such elements like bio-reactors, piping/tubing, pumps etc. which are constructed from popular metallic materials like carbon steels or stainless steels series 300, will operate under high threat of microbiologically influenced corrosion (MIC).

High dynamics of bio-processes that includes several operational cycles like bacterial growth, immobilization and reaction, accompanied by typical operating fluctuations of process parameters like pH, oxygen concentration or fluid composition (chlorides) can significantly alter the general corrosion rate as well as potential for localized corrosion. Additionally, bio-degradation of sulphur-containing VOC's usually involves formation of additional corrosive by-products like H_2SO_4 or H_2S which may significantly accelerate corrosion processes. From such perspective, the on-line, real-time insight on the process fluid corrosivity plays a vital role in the proper corrosion management cycle and further in asset's integrity assessment.

11.

Synthesis of phthalamides obtained from methyl esters of amino acids

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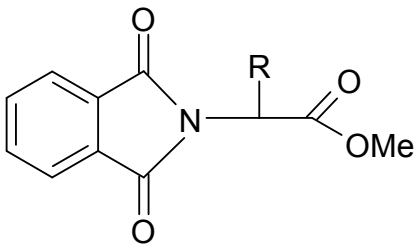
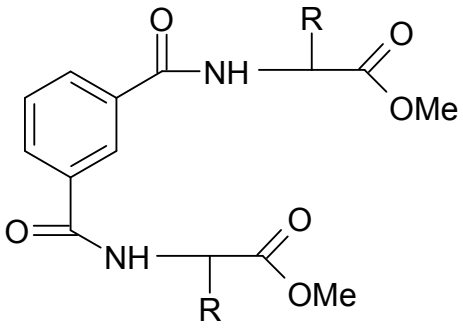
The aim of this study was to obtain new derivatives from the reaction isophthaloyl or phthaloyl chloride with hydrochlorides of selected amino acids.

Diamides of isophthalic acid and phthalimides of phthalic acid were produced with the selected aminoacids in two steps of the synthesis. In the first step of the synthesis the methyl ester hydrochlorides of chosen amino acids were obtained by reaction with methanol and thionyl chloride. Then, the obtained compounds were carried out into diamides with acid chloride and triethylamine in chloroform solution.





The usage of isophthalic acid dichloride and methyl ester with one of the selected aminoacids allows to obtain amides disubstituted. In case, when the isomer ortho of phthaloyl dichloride is used the cyclic monoamides of phthalic acid might be received corresponding to the selected methyl ester aminoacids.

The chemical structures of the obtained compounds was confirmed using ^{1}H NMR, ^{13}C NMR and ESI-MS spectra.

12.

Chromatographic and spectroscopic methods for the identification of two new psychoactive substances contained in "designer drugs"

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„Designer drugs" are groups of substances which are from the structure and mechanism of action point of view similar to illegal psychotropic substances or narcotics like amphetamine, phencyclidine, cannabis. As a result of the closure "legal highs shops" in the last two years, designer drugs are sold on the market as "bath salt", "freshener for toilets", "kindling for the stove", "talisman smile" etc. Lots of these substances are prohibited but some of them still not. The manufactures of these specifics constantly introduced to the market new derivatives. Moreover, these substances are not under consideration of any pharmacological and toxicological studies so we observe rapidly emerging cases of poisoning by unknown substances.

Among these compounds are derivatives of cathinone. It's alkaloide contained in *Catha edulis* – flowering plant native from the Horn Africa and the Arabian Peninsula. Cathinone affect on the central nervous system like amphetamine – stimulating and empatogenic. Selection of appropriate chromatographic and spectroscopic techniques allow to develope rapid methods for identification of psychoactive cathinone's derivatives contained in sold on the market powders or pills.

In this study, we presented method for powdered samples preparation of two new cathinone derivatives and its identification by high performance liquid chromatography coupled with mass spectrometer and by mass spectroscopy MS^n with electrospray ionization.

13.

Differences in polyphenolic and elemental composition of red and white Serbian wines

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The analysis of wine is very important since this beverage has a great economic and social significance. Fingerprint techniques based on chemical composition and multivariate statistical analysis can be used for classifying wine according to origin, quality, and type. In this study, 40 red wine samples and 17 white wine samples were characterised by elemental composition and polyphenolic profile. Samples were collected from different regions in Serbia: Belgrade, Central Serbia, Vojvodina, East Serbia, South Serbia and Kosovo. The measurements of major elements (calcium, sodium, potasium, magnesium, rubidium, and iron) were carried out in a Inductively Coupled Atomic Emission Spectrometer, ICP-OES (Thermo Scientific, United Kingdom), model 6500 Duo. The other elements were determined using an inductively coupled plasma mass spectrometer (ICP-MS iCAP Q, Thermo Scientific Xseries 2, UK). Quantification of phenolics was done using UHPLC coupled with a diode array detector (DAD) and connected to a triple-quadrupole mass spectrometer. PCA was performed to establish the relationship between the element composition and quantifed phenolics of wines and wine types (black and white). The PCA correlation plots showed clustering of the wines not only according to their types (red and white), but also according to geographical origin. The most influential variables responsible for the clustering were identified using the loading plots.

14.

Elemental composition and antioxidant activity of selected juices

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The progressive degradation of the environment has an important impact on human health causing development of many civilization diseases, including different types of cancer, cardiovascular and neurological diseases, and aging-related disorders. In order to prevent these pathologies more and more attention has been paid to watch properly balanced diet. In the nutritional pyramid fruit and vegetable juices play a vital role as good sources of many valuable components, including various types of minerals and organic compounds. Among other chemical constituents they contain antioxidants such as vitamins A, C, and E, carotenoids and phenolic compounds such as flavonoids (anthocyanins, flavonols, catechins, etc.) which display antiradical, antiviral and antimicrobial activity. Moreover, they can also chelate iron, inhibit enzymes (matrix metalloproteinases), regulate gene expression, and significantly improve endothelial function.

The aim of this work was to:

- estimate the antioxidant capacity of selected fruit and vegetable juices (obtained from pomegranates, oranges, apples, pears, pineapple, mandarin, white and red grapefruits, beets, tomatoes and aloe). For this purpose four different methods: DPPH, TEAC, FRAP and CUPRAC were applied. Moreover, total phenolic content was determined using Folin-Ciocalteu reagent;
- determine elemental composition of juices by ICP-OES technique. Prior to analysis samples were mineralized using HNO_3 and H_2O_2.

15.

Analytical techniques used in the synthesis of novel thiosemicarbazones based on 5-bromosalicylaldehyde

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Thiosemicarbazones (TSC) are a class of organic compounds of great pharmaceutical value - they exhibit anticancer, antimicrobial and antiviral activity. TSCs are a versatile ligands due to the potential donor atoms that they possess, among sulfur and nitrogen are of paramount importance in the metal - ligand linkage (especially for transition metal ions). Considering all of these properties, it is important to be able to synthesize new series of thiosemicarbazones which shows biological activity without any side effects.

Microwave – assisted synthesis of TSC allows to obtained pure products in high yields, minimize to use of organic solvents and shorter reaction times [1-3].

During our work, twelve thiosemicarbazides were prepared using a reflux method (2h under reflux in ethanol) and the same quantity of thiosemicarbazones were synthesized using a microwave – assisted methodology, all of them are novel compounds.

For the preparing thiosemicarbazones we used thiosemicarbazides and 5-bromosalicylaldehyde. The reaction mixtures were irradiated in a scientific microwave reactor at 83˚C for 20 minutes at 50W. As the environment of the reaction we used 5 ml of ethanol, and the two drops of acetic acid act as a catalyst.

This method permit to obtain products in high-purity and satisfactory yields after a short time. The thiosemicarbazides and thiosemicarbazones were fully characterized by Liquid Chromatography - Mass Spectrometry, ^{1}H- and ^{13}C-NMR spectroscopy. The progress of the reaction was checked by using TLC – technique.

Acknowledgments:

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16.

One-pot synthesis of 1,4-disubstituted-1,2,3-triazoles using nano-Pd/Cu catalyst

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Triazoles are useful building blocks in chemistry and pharmacy. The 1,2,3-triazole heterocycles are recognized as biological active (e.g. anti-HIV theraupetics), antiallergic, antifungal and antimicrobial agents. Disubstituted 1,2,3-triazoles are synthesized in 1,3-dipolar Huisgen cycloaddition between organic azides and substituted alkynes. However, this synthesis requires elevated temperature and often produces mixture of the two regioisomers when asymmetric alkynes are used (fig 1.). In addition, separation of these regioisomers by chromatographic method is not straightforward and encounters difficulties. 1,4-Disubstituted-1,2,3-triazoles can be obtained via copper-catalyzed reactions. In our studies, nano-Pd/Cu system exhibited high catalytic activity in the azide-alkyne cycloaddition reaction. Bi-metallic nanocatalysts provided several advantages over the homogeneous catalysts, i.e. they featured easier separation, recovery and recycling or/and improved stability (longer lifetimes).

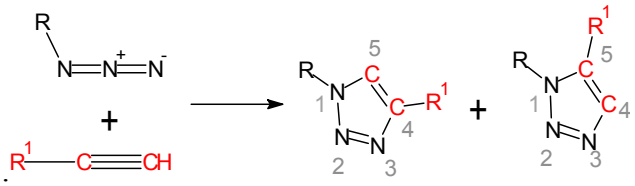

Fig. 1. Two regioisomers 1,2,3-triazole

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17.

Studies on the Cadiot - Chodkiewicz coupling reaction in heterogeneous system using chromatographic techniques

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The Cadiot–Chodkiewicz reaction and other related methods including coupling of haloalkynes with terminal alkynes (Fig.1.) are the most efficient and widely used synthetic routes to variety unsymmetric diynes.

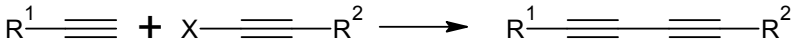

Fig.1. The Cadiot-Chodkiewicz coupling

These coupling reactions have several advantages including relatively high yield, low cost of catalyst, wide substrate scope and mild conditions. To improve the efficiency of the Cadiot–Chodkiewicz coupling, palladium catalysts with Cu(I) salts were employed.

In our investigations, we aimed to study the possibility of using the new catalysts in the Cadiot – Chodkiewicz coupling reaction. In addition, our research was focused on the synthesis of unsymmetrical and symmetrical diynes which were analyzed qualitatively and quantitatively using chromatographic methods: TLC and HPLC.

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18.

Determination of lipid concentration in liposomal drug formulation

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The use of liposomes as drug carriers has been widely investigated due to their abilities to improve pharmacokinetic and reduce toxicity. Active loading of drug in the liposomes interior is one of the most efficient methods to encapsulate drug molecule. In the method an electrochemical gradient is used to drive the active molecule through the lipid bilayer. The process of liposomes manufacturing require several steps. Briefly, liposomes are extruded in solutions with high salt concentration and then the external part of the salt is substituted by a second isotonic solution, e.g. sucrose. Concentration of lipids on each step has to be precisely controlled because of the potent losses associated with complicated nature of the processes and thermal instability of some lipids. Sample preparation for HPLC is complicated due to high salt content which precipitate in organic solvents. In the presented study we investigated the use of ultrafiltration on MicroKros columns (SpectrumLabs) and Chromabond RP SPE columns (Macherey-Nagel) as a desalting method during sample preparation. Lipids were analyzed on C8-HPLC-ELSD method with the gradient of ammonium acetate in water and methanol. Obtained results shown that both method have good recovery and could be used during sample preparation process.

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19.

An analysis of fragmental drug-likeness topology.

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Data mining methods have potential advantages for structural chemical data and have significant impact in chemistry and drug development. Knowledge Discovery in databases allows to find interesting patterns in databases.

In contrast to the traditional drug design methods, polypharmacology is focused on the fact that one drug can interact with multiple targets. Identification of compounds that interact with multiple targets could provide information about potential side effects and improve better results for drug discovery.

Structure-Activity Relationship is an approach designed to find relations between chemical structure and biological activity of studied compounds. It is the concept of linking chemical structure to a chemical property or biological activity. Lipinski's rule of five is used as a filter and a guideline for bioavailability estimation, it defines cutoffs for molecular mass, lipophilicity, number of hydrogen bond donors and acceptors. The concept of drug-likeness has gained wide acceptance as an approach to reduce attrition in discovery and development.

Thiosemicarbazones are a class of compounds exhibiting a broad range of biological activity such as: anticancer, antibacterial, antiviral and antiparasitic. An increasing number of publications devoted to TSCs indicated the growing interest in this group of compounds. In this study we performed a query of chemical databases in a search for (Q)SAR that could explain the molecular basis of the TSC activity. The partial charge, Tanimoto and ADMET properties was used as molecular descriptors in our analyses.

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20.

Application of high-performance counter-current chromatography for the isolation of coumarins from the non-polar extract of *Mutellina purpurea* L.

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In the study, high-performance counter-current chromatography (HPCCC) has been successfully used for the semi-preparative isolation and purification of coumarin derivatives from non-polar extract from the fruits of *Mutellina purpurea* L.

Mutellina purpurea L. is a plant commonly growing on pastures, alpine grasslands halls and greenswards. It is typically seen in the Polish Tatra and Carpathian mountains and is easy to grow. Despite the large accessibility, the literature data contain a small amount of information concerning the detailed phytochemical researches. Previously experiments demonstrated the antibacterial, antifungal, anti-inflammatory, anti-tumor and antioxidant efficacy. As the part of our researches, the modern and innovative method - a high-performance counter-current chromatography (HPCCC) was used. The method allowed to carry out the isolation and purification of 2 simple coumarins (including osthole and its derivative) as well as an angular pyranocoumarin, named hyuganin C, in a short time. For the proper isolation a series of the two-phase systems was tested, which are the mixture of n-hexane, ethyl acetate, methanol and water. Based on the results of the selected partition coefficients, finally the mixture of n-hexane - ethyl acetate - methanol - water (5: 2: 5: 2, v/v/v/v) was chosen. The isolation was performed in the reversed phase system. As a result, in one single, isocratic run 1,7mg osthol and 1,3mg of its derivative, and 2,1mg of hyuganin C from 300 mg of the crude extract in less than 40 minutes were obtained. All compounds were separated with purity in a range between 95-99%. Identification of pure compounds was performed by using of HPLC-DAD, LC/HRMS and 1D and 2D NMR method.

21.

A new similarity measure for comparative analysis of two-way chromatographic fingerprints

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Hyphenated techniques, such as liquid chromatography with diode array detection, are frequently used to characterize complex samples (drugs, biological fluids, etc.). However, there are two major difficulties in handling chromatographic fingerprints obtained from hyphenated techniques. Usually, they provide a huge amount of data that require advanced chemometric treatment [1], since sample is characterized by a two-way chromatographic fingerprint with elements corresponding to signal intensities measured at a given wavelength channel and certain elution time. Moreover, the retention process in a given chromatographic system is amenable to small changes of experimental conditions and/or is affected by column ageing. These result in considerable shifts of corresponding peaks in collected signals that make their further chemometric analysis impossible. In the literature different alignment methods have been proposed to compensate peak shifts, but they are rather time consuming and require optimization of various input parameters [2]. Therefore, a real challenge is to enable comparative analysis of two-way chromatographic fingerprints without their prior alignment [3]. We have developed a new similarity measure, based on the correlation coefficient in order to score similarity between two two-way chromatographic fingerprints. Its performance is demonstrated using a simulated HPLC-DAD chromatographic fingerprints that take into account different chemical composition of samples, different level of peaks co-elution and different degree of peaks shifting.

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22.

Chromatographic separation of products of 4-bromotoluene nitration

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Nitroarenes are a class of compounds frequently used in organic synthesis because they can be easily converted into many other derivatives through reduction of nitro group into amine, and subsequent forming of diazonium salts and further displacement of N_2 group. 2-nitrobenzaldehyde can be used for synthesis of indigo, thus 2-nitro-4-bromobenzaldehyde can give tyrian purple (6,6'-dibromoindigo) in analogous way. Electron withdrawing groups such as nitro group in halogenoarenes are advantageus in such reactions as Sonogashira coupling. Our attempt to synthesize 6,6'-substituted indigo derivatives consists of nitration of 4-bromotoluene, oxidation into 2-nitro-4-bromoaldehyde, Sonogashira coupling with terminal alkynes, and synthesis of indigo derivatives by Baeyer-Drewson procedure.

Nitration of 4-bromotoluene in mixture of nitric and sulfuric acid does not lead to the formation of simple mixture of two isomers. During the nitration reaction also the mixture of dinitro derivatives of 4-bromotoluene is formed, thus the resulting mixture consists of six different compounds. Besides the two mononitro derivatives there are four dinitro derivatives formed in the reaction. The column chromatography allowed the identification of each compound on ^{1}H-NMR spectrum of crude product sample. Identification of isolated individual products also allowed to find rapid method to control progress of chromatographic separation of reaction mixture by thin layer chromatography.

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