POSTER SESSION I

WEDNESDAY, JUNE 1st, 2016

CHAIRPERSONS:

Anna Bodzoń-Kułakowska

and Ana Protić

1.

Pesticide residues in surface and drainage waters of agriculture intensive area at El-Behira province, Egypt

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The organochlorines OCs) and organophosphorus (OPs) pesticide residues in surface and drainage waters having intensive agriculture activities were determined to evaluate their potential pollution and risks for human health. Pesticide residues were extracted from water samples by solid phase extraction method (SPE) and Chromatographic Separation of the OCs and OPs pesticide residues were achieved using HP-608 fused silica capillary column ,30 m X 0.53 mm i.d., 0.5 um film thickness and HP- 5 MS capillary column, 30m x 250 um ID and 0.25 um film thickness , respectively . The OCs and OPs pesticide residues detection were done by GC-ECD and GC-ITD , respectively . were more than 85 percent at a fortification level of 5 ng/ml . Detection limit of compounds ranged between 10 to 30 ng/ml . The OCs residues detected in both drainage and drinking waters were B-HCH , gamma HCH , heptachlorepoxide , p,p -DDE , p,p -DDD, dieldrin , endrin aldehyde , endosulfan-sulfate and endrin ketone . On the other hand , the OPs residues , ethoprophos , diazinon and fenthion were only found in drainage water . Water samples collected during summer season were more polluted with pesticide residues than that of winter season. Heptachlorepoxide , p,p-DDE , dieldrin and p,p-DDD residues were more higher than the recommended permissible limits in drainage waters . Concentration of OCs residues found in the surface waters were in the acceptable limits of WHO . In conclusion drainage water was more polluted and contains more pesticide residues than the drinking water . This means that the discharging of agricultural wastes in this area of study must be controlled to protect the environment and human health from pollution of these pesticide residues .

Keywords: Organochlorine pesticide (OC) residues in water , Organophosphorus pesticide residues(OP) in water , SPE , GC-ECD , GC- ITD .

2.

Synthesis of deuterium labeled denatonium cation and its application in the quantitative analysis of Bitrex® by liquid chromatography-mass spectrometry

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Denatonium benzoate, known as Bitrex®, is a an extremely bitter compound used commonly to denature industrial alcohols and to make potential harmful household products extremely unpalatable [1]. Several methods of quantitative analysis of Bitrex have been applied to determine its level in different samples [2], however they are time-consuming and may suffer from errors inherent to the extraction process during sample preparation [1]. Recently, liquid chromatography-mass spectrometry (LC-MS) has become a method of choice in the rapid analysis of chemicals, however for the quantitative analysis, application of isotopically labelled standards is required.

Here we present a rapid and cost-efficient method of deuterium labeling of Bitrex via H/D exchange of its hydrogen atoms in CH_2 group directly bounded to quaternary nitrogen atom which occurs during a 60 minutes incubation in 1% *N,N,N*-triethylamine (TEA) solution in D_2O (Fig. 1A). The proposed strategy does not require derivatization reagents nor de-novo synthesis of denatonium benzoate from deuterated substrates.

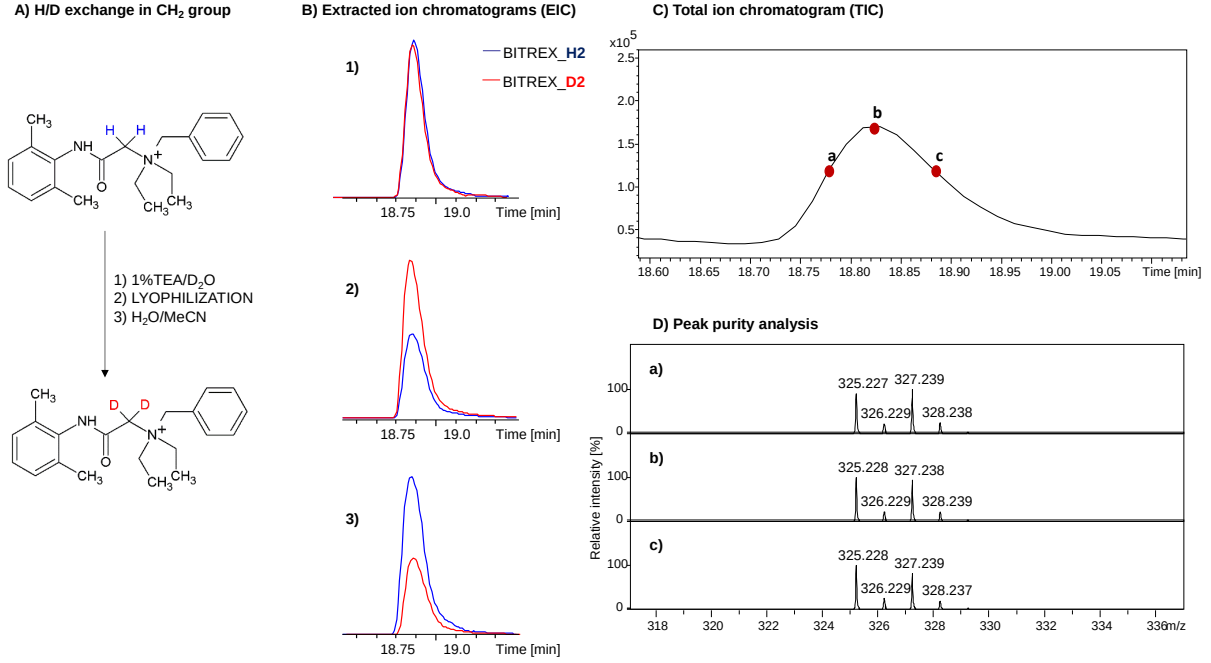

Fig. 1. Schematic presentation of isotopic exchange of the hydrogens in CH_2 group (A), extracted ion chromatograms (B) of deuterated and non-deuterated denatonium benzoate samples mixed in different ratios: 1) 1:1; 2) 2:1 and 3) 1:2. The total ion chromatogram peak at Rt 18.83 min was selected for peak purity analysis (C). The ESI-MS spectra presented for points a-c of the total ion chromatogram (D).

It was found that the introduced deuterons do not undergo back-exchange under acidic aqueous solutions. The co-elution of deuterated and non-deuterated forms on RP column was also confirmed (Fig. 1B-D) [3]. The presented isotopically labeled betaine is proposed as a new internal standard in the quantitative analysis of Bitrex in commercially available household products by LC-ESI-MS.

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3.

Multidimensional (3D/4D-QSAR) probability-guided pharmacophore mapping: Investigation of activity profile for series of drug absorption promoters

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The rational production of the desired compound pharmacological profile is enormously challenging issue that still lacks a general approach. The computer–assisted drug design (CADD) is regarded as the art of specifying molecules of potential therapeutic values working as preliminary stage namely 'pre-synthesis' or 'intuitive roadmap' on the path towards the *the production of properties*. The elementary idea underlying the CADD for the robust identification of hit→lead→drug candidate is the comprehensive projection of the compound topology and/or topography into the chemical property space. A variety of the CADD methodologies, in particular multidimensional quantitative structure–activity relationships (mD–QSAR) procedures employ implicitly or explicitly the similarity principle where *compounds with similar structure are expected to have similar biological activity.*

A number of modern drugs are not available to the patients due to their poor aqueous solubility and permeability. Generally, modification/optimization of poor permeability through membranes can be solved by selection of appropriate excipients to function as transporters (surfactants or pharmaceutical complexing agents, permeability enhancers) being components of a dosage form. These excipients that increase absorption of drugs to blood circulation are known as intestinal absorption promoters in oral drug formulations and transdermal penetration enhancers in transdermal therapeutic systems.

Cholic acid is one of the most important human bile acids. Bile acid derivatives/analogues are an important class of compounds with a range of pharmacological activities. Bile acids could be easily modified by derivatisation of the functional groups on the steroid nucleus. Cholic acid derivatives were studied also as transdermal penetration enhancers.

The principal objective of the current investigation was 2–fold. First of all, it is of interest to compare the impact of the coding molecular systems on the efficiency of structure–activity performance using 3D (CoMFA and CoMSA) and 4D (standard and neural formalism) methods on the ensemble of drug absorption promoters. Additionally, we concentrated on systematic model space inspection with splitting data collection into training/test subsets to monitor statistical estimators performance in the effort for mapping of the *probabilistic* pharmacophore geometry using stochastic model validation (SMV) approach. The automated variable reduction with IVE–PLS procedure represents a sieve for detecting only those descriptors, which have prescribed the greatest individual weighting to the observed cholic acids analogue activity. A 'pseudo–consensus' 4D–QSAR methodology was used to extract an 'avarage' 3D–pharmacophore by exploration of a various data subpopulations which embodies the *quantity for quality argument* to indicate the relevant contributing factors of the cholic acid absorption activity.

4.

Present state and future perspectives of using countercurrent chromatography (CCC) in phytochemical research

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Introduction: The separation of high purity compounds from complex mixtures is widely used in the pharmaceutical, cosmetic and also food industry. Among various separation techniques countercurrent chromatography (CCC) becoming attractive due to its high resolving power. The method of countercurrent chromatography is based on selective division of separated substances (relative to their partition and solubility coefficients) between two immiscible liquid phases. The stationary phase is maintained in place by simple or complex impact of a centrifugal or gravitational field. In 1940 Craig and Post designated the first apparatus for countercurrent chromatography (CCC) and separated first compounds with similar values of the partition coefficient. In 1960 Yoichiri Ito defined this liquid chromatography as countercurrent.

Thesis aim: The evaluation of countercurrent chromatography in the process of separation of various biologically active substances.

Materials and methods: Overview and analysis of selected research and review papers concerning the use of countercurrent chromatography in the separation of biologically active compounds. The following databases have been used: PubMed, Embase, Web of Science, Medline, Science Direct (Elsevier) available from Main Library of the Medical University of Silesia.

Results: Selected papers regarding the use of countercurrent chromatography in the process of separation of biologically active compounds have been reviewed. Literature review indicates that both HSCCC and HPCCC methods are useful in the resolution of the following bioactive compounds: betanins, anthocyanins, coumarins, terpenoids, and proteins. This allows to obtain highly purified biomolecules in a novel and highly specialized way.

5.

Application of TLC-densitometry in pharmaceutical analysis of finasteride

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Finasteride is a synthetic steroid compound which is used as a surgical alternative for treatment of prostatic hyperplasia.

A new, simple in use and economical TLC-densitometric method in normal and reversed phase system (NP-TLC and RP-TLC) has been developed and validated for the identification and quantitative determination of finasteride in bulk drug and in tablet formulation containing finasteride as an active component. NP-TLC analysis was performed on aluminum plates precoated with silica gel $60F_{254}$ as the stationary phase using chloroform-acetone (40:10, v/v) as mobile phase. In the case of RP-TLC system, a mixture consisted of dioxane-water in volume composition 35:15 (v/v) and silica gel RP-$18F_{254}$ plates were optimal. Densitometric analysis was carried out at λ=212 nm in both cases. The proposed NP-TLC and RP-TLC densitometric methods were validated according to ICH guideline and other validation requirements in terms of its specificity, linearity, precision, accuracy, robustness and sensitivity. All validated parameters are satisfactory including the limit of detection (LOD) and limit of quantification (LOQ). The percent content of finasteride in marketed tablet formulation was found to be 99.0 % of label claim. The developed TLC-densitometric methods can be successfully used in quality control of finasteride in bulk material and also in tablet formulation.

Our study confirms that thin-layer chromatography combined with densitometry is a reliable, precise and cost-effective analytical tool which allows determine the content of biologically active steroid namely finasteride in tablet dosage form.

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6.

TLC-densitometric analysis of clobetasol propionate in pharmaceutical preparation

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Clobetasol propionate is one of the most important bioactive compounds important for treatment of dermatitis. It is widely used in form of cream or as lotion containing 0.5 mg/mL of clobetasol propionate. Medical importance of this substance indicates that there is a need to find a rapid analytical method for the quality control of pharmaceutical preparations containing of clobetasol propionate. Therefore, the main aim of this work was to develop the optimal chromatographic conditions, such as mobile phase composition and proper chromatographic plates enabling TLC-densitometric analysis of clobetasol propionate in form of lotion. Among different chromatographic systems which have been studied in this paper, the best are: acetonitrile-methanol 38:12 (v/v) and silica gel RP-18F_{254} in the case of RP-TLC analysis. For the purpose of adsorption thin-layer chromatography (NP-TLC) a mixture of toluene-methanol in volume composition 40:10 (v/v) and silica gel 60F_{254} can be recommended. Densitometric analysis was carried out at λ=246 nm in both cases.

The results performed in this study confirm that the developed method in NP-TLC and RP-TLC systems in combination with densitometry is a good tool in quality control of pharmaceutical formulation containing clobetasol propionate. Thus, it can be successfully applied in pharmaceutical analysis of this steroid as an alternative method to other required by Pharmacopoeia.

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7.

LC-MS, GC-MS and NMR based untargeted metabolomics in searching for urine biomarkers of bladder cancer

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Bladder cancer (BCa) constitutes ninth type of cancer in terms of cancer incidences worldwide. The diagnosis of BCa is based either on cystoscopy, ultrasound scan, computed tomography (CT) urogram, magnetic resonance imaging (MRI) scan, intravenous urogram (IVU) or histopathologic evaluation of biopsy sample. All of mentioned diagnostic methods requires the use of specialist equipment operated by a professional, may cause patients' discomfort and most of all – are adopted when disease symptoms are observed, mostly at the late stage of the disease. Therefore, specific and non-invasive diagnostic method for early diagnosis of BCa is needed. Among possible approaches, metabolomics seems to be a great tool in searching for new potential biomarkers of BCa and explanation of its pathomechanisms on molecular level. Therefore, urine metabolic fingerprinting was utilized in order to determine metabolites that could become potential biomarkers of BCa.

Urine samples obtained from BCa patients (muscle invasive, high grade BCa, n=24) and healthy volunteers (n=24) were analyzed with the use of 3 complementary analytical techniques: high performance liquid chromatography (in RP and HILIC mode) coupled with time of flight mass spectrometry detection (HPLC-TOF/MS) in positive and negative ionization modes, gas chromatography hyphenated with triple quadruple mass spectrometry detection (GC-QqQ/MS) in a scan mode and nuclear magnetic resonance spectroscopy (^{1}H NMR). Applied analytical methods were previously optimized at the Department of Biopharmaceutics and Pharmacodynamics at MUG (in case of HPLC/MS and GC/MS) and at Groupe de RMN Biomédicale, Université Paul Sabatier in case of ^{1}H NMR. After data treatment (deconvolution, filtration and normalization) statistical analysis was applied to select metabolites that represented statistically significant differences between compared groups. Finally, the identification of selected metabolites was performed with the use of publicly available databases allowing for creation of a list of putative biomarkers. The selected metabolites (e.g. uric acid, hippuric acid, glutamine, phenylacetylglutamine, pipecolic acid, acetylspermidine, tyrosine, dodecanamide or hydroxytryptophan) can play crucial role in pathogenesis of BCa.

The obtained results suggest that urine metabolic fingerprinting could be a powerful tool for biomarkers' investigation. Differences in metabolism, specific for BCa, may provide non-invasive diagnosis of the disease. Nevertheless, it should be emphasized that obtained results are preliminary and require validation on larger set of samples in order to confirm diagnostic value of selected metabolites.

Acknowledgements

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8.

The hydrogen-deuterium exchange in betaine moiety does not affect chromatographic behaviour of peptides labeled with quaternary ammonium derivatives

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The isotopically labeled standards for mass spectrometry are expected to present the same retention during chromatographic analysis as regular analytes. Therefore there is a preference for stable heavier atoms (^{13}C, ^{15}N, ^{18}O) exchange, as there is practically no isotopic effect and such isotopologues co-elute during HPLC analysis. Despite the retention time differences, the application of deuterated standards is an attractive option [1] due to low cost and relatively simple synthesis, even if additional operations are needed in proteomics studies [2].

We developed a simple procedure for hydrogen-deuterium exchange (HDX) of α-C hydrogens in *N,N,N*-trialkylglycine residues in peptides [3]. The process occurs in 1% aqueous triethylamine and the modification is not reversible under acidic conditions.

As the chromatographic separation of native and deuterium-labeled peptides depends on localization of deuterons [4], a series of model peptides containing modified betaine was subjected to HDX in methylene group (Fig.1) and the precision of co-elution in LC-MS was analyzed. We examined the modified peptides using on-line reversed phase (RP) and hydrophilic interaction (HILIC) LC-MS (Table 1).

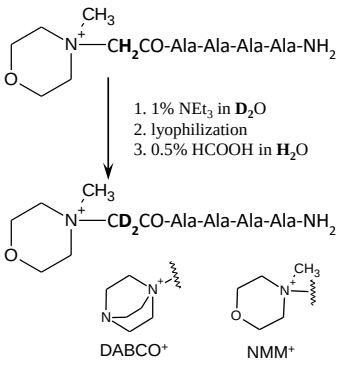

Figure 1. Triethylamine-induced HDX in betaine moiety

Table 1. Experimental conditions for LC-MS analysis of labeled peptides

	Mobile phase A	Mobile phase B
	gradient 0 – 25% B in A in 20 min, 0.1 ml/min	
RP-HPLC (C18)	0.1% HCOOH in H_2O	0.1% HCOOH in ACN
	5 mM $HCOONH_4$ in H_2O (pH 3.2)	acetonitrile (ACN)
	5 mM $HCOONH_4$ in H_2O (pH 6.3)	acetonitrile (ACN)
	5 mM NH_4HCO_3 in H_2O (pH 8.4)	acetonitrile (ACN)
	gradient 5 – 50% B in A in 20 min, 0.1 ml/min	
HILIC (cross-linked diol)	5 mM $HCOONH_4$ in ACN:H_2O (95:5)	5 mM $HCOONH_4$ in H_2O (pH 3.2)
	5 mM $HCOONH_4$ in ACN:H_2O (95:5)	5 mM $HCOONH_4$ in H_2O (pH 6.3)
	ESI-MS Bruker micrOTOF-Q mass spectrometer operated in positive ion mode	

In all experiments we observed identical retention times for native and deuterated peptides as well as the preservation of isotopic distribution through chromatographic peak. In our case, there is no difference in isotopic effect in analyzed pH range, contrary to results of Di Palma *et al.* [5]. It is worth noting that although the order of elution of the peptides labeled with quaternary ammonium group is in most cases reversed on HILIC phase as compared to RP-HPLC, in both systems peptides elute at relatively low concentration of stronger solvent, allowing for short analysis time.

According to our results, the betaine moiety not only introduces permanent positive charge, thus facilitating MS analysis of traces of peptides [6], and allows for mild HDX conditions, but also provides the deuterons with hydrophilic environment, which may be responsible for reduction of isotopic effect.

Acknowledgements:
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9.

Untargeted metabolomics with the use of LC-TOF/MS and GC-MS for selection of tentative markers of renal cell carcinoma

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Kidney cancer is one of the 10 most common cancer types. Among all kidney cancer subtypes, renal cell carcinoma (RCC) is responsible for approximately 90% of cases. Due to the lack of specific symptoms and diagnostic methods, RCC is frequently diagnosed at the late stage of the disease. Therefore, development and application of new high-throughput and specific diagnostic methods is essential for early detection of RCC. In the present study urine metabolic fingerprinting was performed for understanding and explanation of RCC pathomechanisms.

Urine samples collected from RCC patients and healthy volunteers were analyzed with the use of HPLC-TOF/MS in positive and negative ionization modes, as well as GC-QqQ/MS in scan mode. The obtained datasets were processed using deconvolution, alignment, normalization and filtration steps. Afterwards, uni- and multivariate statistical analyses were performed. Statistically significant metabolites were selected according to adjusted p value (FDR p value < 0.05) and variable importance into projection (VIP) value > 1. The identification of selected metabolites using NIST, HMDB, METLIN, KEGG and CEU Mass Mediator databases allowed for creation of a list of putative markers and related biochemical pathways which they are involved in. Selected altered metabolites were found to be involved in amino acid, purine, lipid and glucose metabolism as well as TCA cycle.

The obtained results suggest that urine metabolic fingerprinting is a powerful tool which might be useful in research for RCC diagnosis and eventual further explanation of its molecular pathomechanisms..

Acknowledgements

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10.

Determination of antioxidant properties of selected cruciferous plants

Violetta Kozik, Andrzej Bąk, Krystyna Jarzembek, Marcin Rojkiewicz, Katarzyna Pytlakowska, Aleksandra Łangiewka, Patrycja Glenc, Marta Skorek

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Cruciferous plants is the family to which they belong among other cruciferous vegetables, leafy and oilseeds and spices, for example. broccoli, Brussels sprouts, cabbage, radish, rapeseed, kale, mustard, watercress, arugula and horseradish. As used in the diet of cruciferous vegetables can prevent the occurrence of cancers, due to the high content of antioxidants.

Antioxidants have anti-viral, anti-bacterial, anti-cancer, slow down the action of enzymes[1-3] An important role in preventing cancer and play polyphenols glukobrassycyna glucoraphanin and, in particular, their decomposition products successively, sulforaphane and indole-3-carbinol.

In some cruciferous plants was marked antioxidant capacity and contents poifenoli techniques using UV-Vis spectrophotometry methods based on a radical reaction with DPPH and ABTS• •, and utilizing oxidation and reduction reactions: FRAP and CUPRAK.

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11.

Corrosion in continuous bio-degradation of sulfur-containing, volatile organic compounds

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Environmental regulations are continuously pushing industry for emission reduction of NOx, CO, H_2S and other poisonous low-molecular weight gases. Volatile organic compounds (VOC) represented by carbon-based chemicals like vinyl acetate, ethyl acetate, styrene or dimethylsulphide (DMS), however less known to public, play significant role in air poisoning. Industrial emission of those substances is much lower in comparison to gases like NO_x, but their high toxicity, reactivity and consequent severe interference with living organisms puts them at the top of a list of industrial pollutants. Effective removal of VOC from off-gases is a challenging process due to very low concentration of these toxic compounds.

The VOC mixture (as a liquid) was injected to the flow of air and introduced to the reactor co-currently with circulating water phase (see Table 1 for water composition). The VOC mass load varied between 0.07 g/m^3 and 1.2 g/m^3 which translates to concentration of DMS in the inlet gas in range of 3-8 ppm_{mol} which is typical for low polluted gas streams. Biodegradation was carried out at a temperature of 27±2ºC and a pH of 7.0±0.5. The pH was controlled and adjusted automatically by addition of 10% KOH and 10% KH_2PO_4.

Results demonstrate the efficacy of utilizing an industrial-grade, on-line corrosion monitoring technique, integrating multiple electrochemical techniques such as Harmonic Distortion Analysis (HDA), Low Frequency Impedance (LFI) and Electrochemical Noise (ECN). Results also demonstrated that the real-time monitoring described herein provided excellent measurement accuracy even under conditions of very low corrosion rates, as evidenced by the close agreement in general corrosion rate values between online measurements and those obtained through the traditional mass loss technique. Furthermore, these online corrosion measurements could be used to determine the effects of process variables on the severity of corrosion. This result suggests that real-time corrosion measurement can be used to control and minimize corrosion in the bio-processing of VOCs.

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12.

Synthesis and physico-chemical properties of derivatives of graphene oxide as a potential drug carriers

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Synthesis of GO-X is based on the nucleophilic substitution ofaminoacids to graphene oxide nanoparticles. In the frst step, aminoacid compaunds was transformed into methyl ester hydrochloridein order to protect the C-terminal end and the N-terminal end ofthe amino acid. The obtained product, activated in situ, wasused for the formation of amido binding between aminoacids and GO.

The synthesized GO-X was characterized by Fourier transforminfrared spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy.

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13.

Lipophilicity of isomeric *N*-methylquinolinesulfonamides

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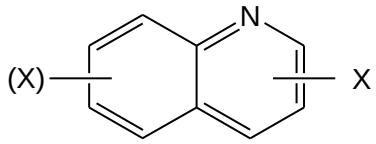
Sulfonamide group containing azine derivatives are of interestfor their biological activity. Several of them are potential diuretic agents.

Lipophilicity is an important factor determinating the biological activity of drugs. RP TLC is very useful method for determination of lipophilicity. We used this method in our study of seven isomers of N-methylquinolinesulfonamide:



X = 2-,3-,4-,5-,6-,7- or 8-$SO_2NH(CH_3)$

TLC was performed on silica gel RP-18 F_{254} plates (Merck #115389), activated by heating at 100 °C for 1 h. Mixtures of methanol-water solutions were used as mobile phases. Relationship between R_M values obtained from chromatography and partition coefficients is described by the equation $R_M = a \log P + b$, where a and b are constants for a particular system and P is the partition coefficient.

Coefficients a and b were found in experiments for compounds with known log P values. Log P values obtained for the compounds investigated were correlated with values calculated by several theoretical methods. Lipophilicity of *N*-methylquinolinesulfonamide isomers were compared with lipophilicity of quinolinesulfonamide and *N*,*N*-dimethylquinolinesulfonamide analogs.

14.

Application of UHPLC-PDA-ESI-MS^n for phytochemical profiling of antioxidant active extracts from selected *Sorbus* species

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Genus *Sorbus sensu lato* is a broad taxon comprising over 250 species widespread in cool to temperate regions of northern hemisphere [1]. Many of *Sorbus* representatives have been sources of ethnomedicinally used plant materials with diuretic, anti-inflammatory and vasoprotective properties. As rich sources of natural polyphenols, the *Sorbus*-derived extracts have been pointed to as a potential material for development of dietary supplements effective in prevention of many oxidative-stress related diseases [2]. In our previous studies we found out that leaves and inflorescences of species representing the subgenus *Sorbus* are distinguished by the exceptional abundance of polyphenolic compounds [3,4]. We then demonstrated that the polyphenols could be further concentrated by fractionation of hydromethanolic extracts and established that the thus obtained ethyl acetate fractions exhibit the highest antioxidant potential [4]. Preliminary HPLC-PDA analyses of the active fractions revealed the considerable complexity of their composition [4] and prompted us to conduct more detailed investigation into the subject.

Therefore, the aim of the study was thorough phytochemical profiling of the most antioxidant active fractions of selected *Sorbus* species with the use of UHPLC-PDA-ESI-MS^n. The ethyl acetate fractions of hydromethanolic extracts from eight species representing the subgenus *Sorbus* were investigated. The analyses were performed on an UHPLC system (Dionex, Germany) with PDA detector and an ion trap mass spectrometer with ESI interface (Bruker Daltonik, Germany). Separations were carried out on a Zorbax SB C18 column (150 × 2.1 mm, 1.9 μm, Agilent, USA). The compounds were identified based on the comparison of their chromatographic and spectral (UV and MS^n) data with authentic standards (obtained previously in isolation studies) and/or with literature. The extracts exhibited a complex and diverse composition, containing polyphenols classified as flavonoids, phenolic acid derivatives and proanthocyanidins. Eventually, about 40 compounds were identified including kaempferol, quercetin and sexangularetin glycosides, caffeoylquinic acid isomers as well as dimeric and trimeric proanthocyanidins.

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15.

Thin-layer chromatographic identification of phenolic acids in cosmetic raw materials

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An increased interest in bioactive compounds is due to a possibility of using them as additives to cosmetics, alimentary products, and pharmaceuticals. As bioactive compounds, these substances of herbal origin are understood which appear in low quantities in the plants. A particularly interesting group of bioactive compounds are antioxidants. In cosmetics, particularly useful are phenolic acids, which are widespread in the kingdom of plants (e.g., gallic acid appears in strawberried, raspberries, or grapes, etc.).

Antioxidant properties of phenolic acids consist in eliminating reactive forms of oxygen, blocking free radicals, inhibiting the oxidase enzymes but also supporting action of the enzymes with an antioxidant action, and on chelating metal ions (e.g., iron or copper). Such properties of bioactive compounds added to the cosmetics result in preventing human skin from ageing and in extending the shelf life of cosmetics.[1,2]

In our study, we selected a simple and cost-friendly thin-layer chromatographic technique to identify the following phenolic acids: caffeic, ferulic, gallic, and coumaric acid in the commercially available cosmetic raw materials (such, as extracts derived from red wine, grape skins, pomegranate peels and juice, green tea, etc). Moreover, caffeic acids was quantified in the scrutinized samples.[3,4]

In the course of this study, it was established that the highest contents of phenolic acids are in the cosmetic raw material obtained from green tea.

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16.

Functionalization of quinoline derivatives by Reimer-Tiemann reaction; the GC-MS and TLC investigation

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Aldehydes are the main precursor of very important chemical reactions. There are a lot of synthetic routes that allow to obtain aldehydes. They can be obtained by the electrophilic aromatic substitution (S_EAr) route such as Reimer-Tiemann reaction. This is a three steps reaction. The first step consists of generation of electrophilic carbenes: CX_2 (X = halogen). During second step is formation of C_{Ar}-C_{carben} bond based on S_EAr substitution. The final third step leading to aldehydes is the hydrolysis of C-X (X = halogen) bond of C_{carben} fragment [1, 2]. This type of reaction has been used to transformed variety of phenols, and many electron rich aromatic or heteroaromatic compounds [3].

However, quinoline was firstly isolated by F.F. Runge in 1834 during the extraction of coal tar [4]. Currently, quinoline and their derivatives have found a wide range of applications. They are a valuable material for the preparation of dyes and pharmaceuticals. Quinoline derivatives exhibit biological activity against malaria and possess antifungal, antibacterial, anti-asthmatic and anti-inflammatory properties. They also reduce blood pressure [5, 6].

Despite their potential value, their synthetic protocols are poorly characterized according to literature data. Some characterizations are not clear or contained mistakes. Some authors announced quinoline aldehyde structures with newly formed $C_{quinoline}$-C_{carben} bond in 7 position (phenol ring), instead of 5 (prefer activated position on phenol ring). We obtained and characterized both regioisomers of 8-hydroxyquinoline derivatives by the combination of NMR, GC-MS and TLC and electronic absorption spectroscopy.

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17.

Chemometric analysis of some histamine H_1- and H_2-receptor antagonists on the basis of chromatographic data and molecular descriptors

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Chemometric analysis was performed on 18 compounds with histamine H_1- and H_2-receptor affinity. Thin layer chromatographic data and physicochemical parameters of the examined compounds were applied in this study.

Glass TLC silica gel 60 F_{254} plates (20×20 cm, Merck, Darmstadt, Germany) were used in two developing solvents as H_1-, H_2-antihistaminic interaction models:

a) acetonitrile:water (80:20, v/v)

b) acetonitrile:methanol:water (40:40:20, v/v/v).

Additionally, the stationary and mobile phase were modified with a solution of aspartic acid (L-Asp) and a solution of an analogue of aspartic acid (propionic acid).

The plates were scanned densitometrically at 254 nm by means of a Desaga CD 60 densitometer with Windows-compatible ProQuant software (Desaga, Germany).

The semiempirical method AM1 (HyperChem v. 7.0 program) and ACD/Labs v. 8.0 program were employed to calculate a set of physicochemical parameters for the investigated compounds. The pK_i values of H_1- and H_2-receptor ligands were collected from the literature and used for generating QSAR models. The correlations obtained for the compounds studied represent their interactions with the proposed chromatographic models. The good multivariate relationships obtained by means of regression analysis can be used for predicting the quantitative effect of biological activity of different compounds with histamine H_1- and H_2-receptor affinity. Leave-one-out (LOO) and leave-N-out (LNO) crossvalidation methods were used to judge the predictive power of final regression equations.

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18.

Chemometric analysis of some dopamine receptor agonists and antagonists on the basis of chromatographic data and molecular descriptors

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Chemometric analysis was performed on 23 drugs with affinity for dopamine receptors. A set of physicochemical parameters calculated by HyperChem 7.0 and ACDLabs 8.0 programs and thin layer chromatographic data were applied in (Q)SAR analysis. Chromatography was performed on glass TLC silica gel 60 F_{254} plates (20×20 cm, Merck, Darmstadt, Germany) impregnated with a solution of L-aspartic acid and a solution of an analogue of aspartic acid (propionic acid) with two mobile phases: a) acetonitrile:water (80:20, v/v) and b) acetonitrile:methanol:water (40:40:20, v/v/v). The systems were chosen as models of drug-dopamine receptor interaction. The pK_i values of dopamine receptor ligands, including agonists and antagonists, were collected from the literature and used for generating these models. Relationships between chromatographic data, molecular descriptors and biological activity data were found by means of stepwise multiple linear regression (MLR) and stepwise discriminant analysis (SDA).

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19.

Determination of acrylamide in real samples

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Frying or baking of food products improves their taste, but decrease their nutritional value. This is a result of thermal processing of food due to decomposition of some substances (e.g. ascorbic acid), or the formation of new compounds that may affect our body. The second group includes acrylamide (AA) among others, which has neurotoxic, mutagenic and carcinogenic properties - AA binds to hemoglobin and DNA [1]. It is formed as a product of the Maillard reaction between amino acids (mainly asparagine) and reducing sugars such as glucose or fructose. The Maillard reaction is triggered in when food is heated above 120 °C [2].

Acrylamide due to the harmful properties must be monitored. Usually it is done using different chromatographic techniques including high performance liquid chromatography, gas chromatography and liquid chromatography coupled with mass spectrometry or tandem mass spectrometry detection [3]. However, these techniques are in general expensive, time-consuming and laborious.

It is known that AA has quenching properties. It is interesting, that two mechanisms of quenching occurs which can be distinguished by means of fluorescence spectroscopy with liquid nitrogen. This method is simple, cost-effective and very sensitive technique compared with chromatography methods. In static quenching non-fluorescent complex is formed. In second mechanism, quenching occurs as a result of the collision of quencher with fluorescent probe (dynamic/collisional quenching) [4]. If we freeze the sample, we can eliminate a collisional quenching. This property will be used for the construction of advanced chemometric calibration models enabling quantification of analyte under the presence of additional fluorescence interferents [5].

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