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PLENĀRREFERĀTI ĶĪMIJAS NOZARĒ

ION PAIRING IN IONIC LIQUIDS

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In liquids, a plurality of forces exist that add together and lead to physical properties that can be determined with a single measurement. The understanding of these forces is therefore crucial for allowing a rational molecular design of liquid materials.

Ionic liquids (ILs) are low-melting salts: in the condensed phase, among forces such as dispersion and hydrogen bonding, Coulombic interactions prevail. Amid the numerous demonstrated and industrialized IL contributions to sustainability, these conductive and non-volatile, non-flammable materials are primarily considered for energy storage and conversion [1]. Nevertheless, despite the high ion concentrations in neat ILs, their electrical conductivity rarely outperforms conventional electrolytes. Ion pairing is a process that often is associated with the limited electrical conductivity of ILs, though evidence for the existence of long-lived ion pairs (IPs) in [1+][1-] ILs has not been yet found.

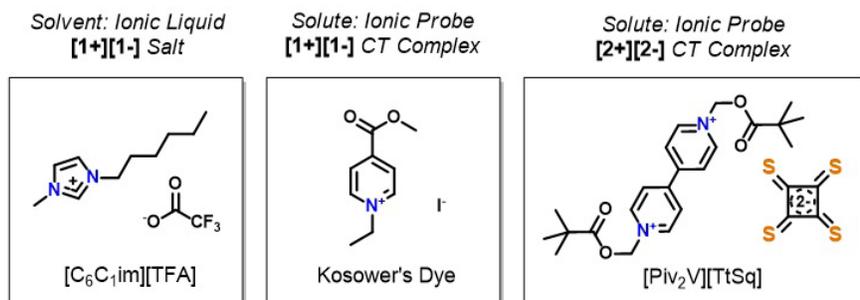


Fig. 1. Chemical structure of an ionic liquid and ion pairing probes

In this study, an experimental evidence for IP formation in ILs was sought by designing strongly interacting functionalized ILs and testing for [1+][1-] ion pairing in these. A UV-Vis-active IP charge transfer complex, Kosower's dye (Fig. 1), was utilized for estimating the extent of ion pairing. Furthermore, a library of novel [2+][2-] charge transfer complexes were systematically devised *via* DFT modelling and iterative syntheses. Their suitability for CT in solution was tested and spectroscopic properties explored.

[Piv₂V][TtSq] (Fig. 1) as a suitable [2+][2-] probe was quantitatively generated *in situ* and revealed that even between doubly charged ions no Coulombic IPs form in an IL. An ideal mixing of ILs with charged solutes was observed in all instances, suggesting that forcing of IP formation in ILs is very difficult, if not impossible. The mechanism of IL electrical conduction likely does not depend on the extent of ion pairing.

References:

- [1] Watanabe et al. *Chem. Rev.*, **2017**, 117(10), 7190–7239.
- [2] Lui et al. *Chem. Sci.*, **2011**, 2, 1491–1496.

ADVANCED ELECTRODES FOR LITHIUM AND SODIUM-ION BATTERIES

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Both Li and Na-ion batteries are based on reversible insertion and extraction of mobile ions into the crystal structure of electrode materials. In a battery, the rate of this reaction depends on both properties of the insertion materials and the supply of electrons and ions, which is a function of electrode porosity and conductivity. Here, we look at the phenomena influencing the rate capability of lithium and sodium-ion batteries: electrical conductivity and porosity enhancing additives.

Carbon additives usually increase the reaction rate and allow access to more particles of the active material. For instance, we prepared $\text{Na}_2\text{FeP}_2\text{O}_7$, a promising two-phase material for Na-ion batteries and found that its capacity is increased from 49 to 71 mAh/g. The rate capability of the $\text{Na}_2\text{FeP}_2\text{O}_7/\text{C}$ composite is shown in fig.1a. This is in accordance with the general tendency of carbon additives increasing rate capability, especially for electrode materials with lower electronic conductivity [1].

Introducing structured carbon conducting networks proves to be of further benefit. We have shown that addition of reduced graphene oxide (rGO) to LiFePO_4 leads to increased rate capability. However, the mixing of the additives and active material are of crucial importance as seen when comparing rate capabilities of composites with different mixing procedures [2], see Fig.1b.

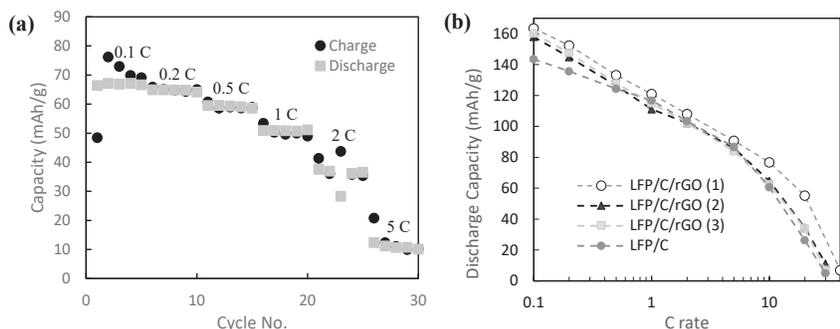


Fig. 1. Gravimetric capacity of (a) $\text{Na}_2\text{FeP}_2\text{O}_7/\text{C}$ with 5% carbon, (b) $\text{LiFePO}_4/\text{rGO}$ composites prepared via various synthesis routes

The authors acknowledge project Advanced Materials for Sodium Ion Batteries, project No. 1.1.1.2/VIAA/1/16/166.

References:

- [1] Park, M., Zhang, X., Chung, M., Less, G. B., Sastry, A. M. A review of conduction phenomena in Li-ion batteries. *J. Power Sources*, **2010**, 195, 7904–7929. <https://doi.org/10.1016/j.jpowsour.2010.06.060>.
- [2] Kucinskis, G., Bajars, G., Bikova, G., Kaprans, K., Kleperis, J. Microstructural Influence on Electrochemical Properties of $\text{LiFePO}_4/\text{C}/\text{Reduced Graphene Oxide}$ Composite Cathode, *Rus. J. Electrochem*, **2019**, 55, 517–523. <https://doi.org/10.1134/S1023193519060120>.

A NON-TARGETED AND TARGETED SCREENING OF HUMAN PHARMACEUTICALS IN WASTEWATER USING ULTRA-HIGH RESOLUTION MASS SPECTROMETRY

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The presence of human pharmaceuticals (PhACs) in the environment still remains an increasingly alarming environmental issue. Recent technological advances in analytical chemistry have increased our understanding, nonetheless, several knowledge gaps remain. The chemical diversity that exists between drug substances is extremely vast, hence state-of-art applications, e.g. high-resolution mass spectrometry (HRMS) based methods, are crucial to identify the true extent of pollution caused by PhACs [1].

In this study, 72 wastewater samples from different locations in Latvia were analyzed in order to identify PhACs that are poorly removed during wastewater treatment. A total of 573 and 26 compounds were screened by un-targeted and targeted approach, respectively. Results showed that diclofenac (194 ng/L – effluent, 569 ng/L influent) was the most frequently detected PhAC via targeted mode. Meanwhile, un-targeted screening revealed high prevalence of telmisartan and numerous psychoactive drugs in both effluents and influents (Fig. 1).

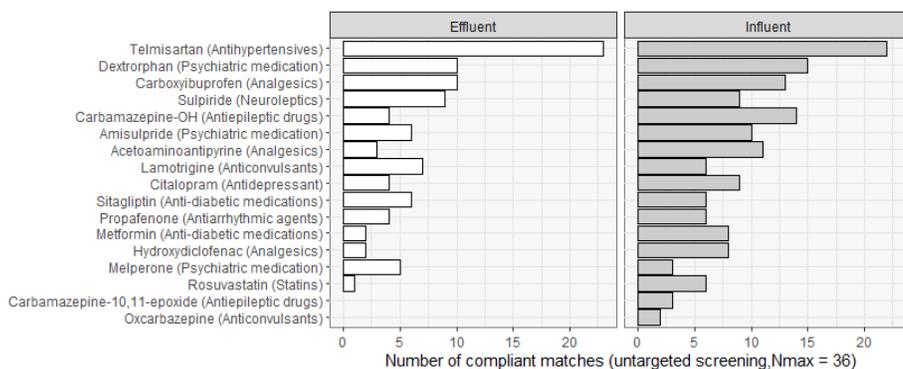


Fig. 1. Un-targeted screening results - detection frequency of selected PhACs

References:

- [1] Casado, J., Brigden, K., Santillo, D., Johnston, P. Screening of Pesticides and Veterinary Drugs in Small Streams in the European Union by Liquid Chromatography High Resolution Mass Spectrometry. *Sci. Total Environ.*, **2019**, *670*, 1204–1225.



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ANALĪTISKĀS UN
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ACADEMIC WORK OF JĀNIS STRADIŅŠ AT THE FACULTY OF CHEMISTRY

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Full Member of Latvian Academy of Sciences, physical chemist and historian Jānis Stradiņš has passed away on November 29, 2019. Prof. Stradiņš has been the President of the Latvian Academy of Sciences from 1998 to 2004, but from 2004 – Chair of the Senate (Latvian Academy of Sciences). His academic knowledge, human values and clear mind won him great popularity. However, his CV and bibliography will be not complete without including his employment with the Faculty of Biology and Chemistry at the Latvian State university (LSU), especially from 1958 to 1964, when the faculty was reopened. The Latvian Soviet Encyclopedia (Vol. 9, p. 200) do not provide any information about teaching and even the data included in the book devoted to the 50th anniversary of Faculty of Chemistry are incorrect [1]. Also, the university archive do not provide any information about J. Stradiņš as a teacher.

In J. Stradiņš biobibliography (published in 2017), it was stated that he was employed as a Professor in Physical chemistry with the Faculty of Chemistry LSU from 1969 to 1976 and as a lecturer already with the “old” faculty from 1956 [2].

In 1958, the “old” Faculty of Chemistry LSU became part of Riga Polytechnical Institute (RPI). In the same year, the Chair of Chemistry was founded at the University of Latvia, the Faculty of Biology. In 1959, first chemistry students were enrolled. The problem was that the staff was transferred to RPI. According to the study program from academic year 1961/1962, the study program for 3rd year chemistry students included physical chemistry. Chemical thermodynamics course has been taught by assistant Uldis Alksnis. As a part-time lecturer (and from 1972, the Professor in Physical chemistry) was invited J. Stradiņš, the Head of the Laboratory of Physical Organic Chemistry at Institute of Organic synthesis (Dr. chem. (Candidate of Science in former USSR, Ph.D. in Western countries), M. Lomonosov Moscow State University, 1960). He presented the Theory of Solutions, Chemical kinetics and Photochemistry.

Students test records at the University of Latvia archive helped to restore the list of courses, which were taught by J. Stradiņš. The courses were following (a-autumn, s-spring): *Physical chemistry* – 1962 (s, a), 1963 (s); *History of Chemistry* –1965 (s), 1974–1976 (a); *Polarography* – 1967–1969 (a), 1974–1975 (a); *Physicochemical analysis of Organic compounds* –1968–1969 (a); *Modern research methods* – 1969 (a), 1971–1975 (a); *Instrumental research methods* – 1970 (a); *Physicochemical analysis methods* – 1964 (s).

Such wide profile of teaching was possible because of being excellent student by themselves (Latvian State University, Faculty of Chemistry, cum laude, 1956) and later postdoctoral research at the N. Zelinsky Institute of Organic Chemistry and the N. Semyonov Institute of Chemical Physics (Academy of Science of USSR, Moscow, 1961), as well as at the Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw (1968).

15 years of teaching by Jānis Stradiņš were crucial to provide professional development and academic excellence for new Faculty of Chemistry (established in 1964).

References:

- [1] Latvijas Universitātes Ķīmijas fakultātei 50. / Redkolēģija: A. Prikulis, A. Prikšāne, U. Alksnis. Rīga: LU Akadēmiskais apgāds, 2014, 404 lpp.
- [2] Latvijas Zinātņu akadēmijas akadēmiķis Jānis Stradiņš. Biobibliogrāfija III (1993. un 2004. gada izdevumu turpinājums un papildinājumi). Rīga: Zinātne, 2017.

STUDY OF HEAT PUMP USE IN TOMATO DRYING PROCESS USING EXCESS HEAT FROM GREENHOUSES

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This study tested the possibilities of using air-to-air type heat pumps in the process of tomato drying as an energy efficient and environmentally friendly method in greenhouse agriculture. Since in Latvia climatic conditions greenhouses used for tomato growing need to be periodically cooled during summer, the excess heat can be effectively removed and used for biomass drying via heat pumps.

An air-to-air heat pump system was tested in a purpose built test greenhouse with parameters identical to regular production greenhouses of the research partner SIA Rītausma. The temperatures in the test facility and the exhaust air temperatures of the heat pump were measured. The measurements showed a predominant cycle of 6–7 hours of heat-pump cooling the test facility and 17–18 hours of inaction in cases of warm sunny weather. The temperature of the hot air dispatched into atmosphere reached up to 40C during the cooling period, the exact temperature depending on the outdoor air temperature in the atmosphere and the sun radiation level.

Several most probable drying cycles were established from the temperature measurements of the heat pump's hot exhaust air. The basic drying cycle was established to be 40 °C air temperature applied for 6 hours during 24 hour period. The experimentally established hot exhaust air temperature modes and time cycles were then applied to tomato drying study in laboratory using a conventional domestic electrically heated hot air fruit dryer. Tomatoes of Roma variety from greenhouses of the SIA Rītausma were used in the study. The tomatoes were divided in 1/8 pieces and dried with a set temperature for a selected period of time and then left in room temperature for the rest of the 24h period. The cycle is repeated until tomatoes lost sufficient amount of water.

It was found that tomatoes can be successfully dried without spoilage in temperatures as low as 40C and drying periods as short as 6 hours in 24 hour cycle. Lower temperatures and shorter drying periods resulted in total drying time (defined as time necessary for loss of 90% of raw tomato mass) of three days. At the lowest temperatures there were several instances of dark discoloration of the tomatoes without any effect on taste or smell of the dried tomatoes.

This project is supported by EAFRD – The European agricultural fund for rural development, project Nr. 17-00-A01620-000013.

FTIR STUDIES OF RADIATION STABILITY OF SINGLE-LAYERED AND MULTI-LAYERED Si_3N_4 NANOFILMS

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Silicon nitride (Si_3N_4), due to its high dielectric constant and low leakage current, is a perspective material for the fabrication of dielectric nanolayers in nanocapacitors. It is proposed to use Si_3N_4 in nanocapacitors operating in harsh conditions, for example, in environments where the action of ionizing radiation is possible.

To eliminate the pinhole defects that facilitate dielectric breakdowns in nanolayers, Si_3N_4 was fabricated as a stack of several Si_3N_4 nanolayers where each subsequent nanolayer covered the pinholes of the previous one.

In this study we compared radiation stability of 60 nm thick single-layered and multi-layered Si_3N_4 nanofilms which were deposited on SiO_2 and polySi substrates. The nanofilms were irradiated with 1 kGy of 5 MeV *Bremstrahlung* rays produced by a linear electron accelerator ELU-4 (Salaspils, Latvia) and the effect of radiation on chemical bonds of Si_3N_4 was analysed using a Bruker Vertex 70v Fourier transform infrared (FTIR) spectrometer.

Three groups of signals were observed in both types of the nanofilms. The signal at $430\text{--}480\text{ cm}^{-1}$ could be attributed to Si-O bending, the signal at $1015\text{--}1135\text{ cm}^{-1}$ comes from Si-O-Si and Si-O bonds. The band at $490\text{--}530\text{ cm}^{-1}$ is due to Si-N breathing [1] and Si-N stretching. The signal at 840 cm^{-1} is due to Si-N bonds, while at $1000\text{--}1100\text{ cm}^{-1}$ Si-N stretching occurs [2]. The main bonds remained unchanged after irradiation. Variations in the IR intensity were attributed to inhomogeneity of the deposited Si_3N_4 layers and not to the influence of radiation. The results show that Si_3N_4 multilayers are stable after exposure to 1 kGy dose of *Bremstrahlung* rays and can be used in nanocapacitors exploited in harsh radiation conditions.

The research was supported by the ERDF project No. 1.1.1.1/16/A/203 "Multilayer Silicon Nanocapacitor with Improved Dielectric Layers".

References:

- [1] Cianci, E., Schina, A., Minotti, A., Quaresima, S., Foglietti, V. *Sensors and Actuators A*, **2006**, 127, 80–87.
- [2] Walsh, L. A., Mohammed, Sh., Sampat, S. C., Chabal, Y. J., Malko, A. V., Hinkle, Ch. L., *Thin Solid Films*, **2017**, 636, 267–272.

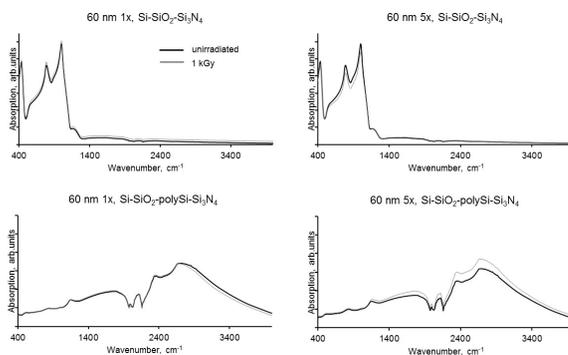


Fig. 1. FT-IR spectra of the unirradiated and irradiated 60 nm thick Si_3N_4 nanofilms on SiO_2 and polySi

EVALUATING OF THE CHEMICAL COMPOSITION OF LINGONBERRIES (*VACCINIUM VITIS-IDAEA* L.) BY THEIR GROWTH SITES

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The geographic distribution of lingonberries in the world extends from Eurasia (mainly Scandinavia) to North America (USA, Canada). The first lingonberry plantation was created in Sweden in 1962 for cultivation and berry study. The climatic conditions in Latvia are favourable for the growth of these plants. The chemical composition of lingonberries is characterized by a diverse content of macro- and trace elements.

The use of various berries, both wild and cultivated, in medicine, food production, pharmacology, and cosmetology are becoming increasingly popular. In recent years, the use of lingonberries in the production of medicinal products and nutritional supplements has been actively researched, not only lingonberry berries but also their components (leaves and roots) are being analysed.

The aim of our research was to evaluate the chemical composition on lingonberries (*Vaccinium vitis-idaea* L.) depending on their growth places and soil. The roots of lingonberry have also been collected to study the flow of metallic elements from soil to plants. Lingonberry and soil samples at the depth of the root zone (~ 10 cm) were collected in September 2019 in two areas:

- 1) Garkalne (pine forest, a favourite spot for many berry and mushroom pickers with busy traffic nearby). Rīga-Lugaži railway is crossing the Garkalne forest and it runs passenger trains and cargo transportation;
- 2) Vecumu forest in Žiguri parish. From 1916 to 1993 was located railway line Rīga-Pskov. The territory is located ~ 8 km from the Latvian-Russian border.

The unwashed lingonberry samples were dried at 50 °C for 7 days and ashed in the muffle at 550 °C. The soil samples were extracted with 1 M HNO₃.

The forest soil is very acidic (pH 3.4–4.0) at the lingonberry growth sites. The low content of Zn and Cu in the soil indicates the mobility and leaching of these elements to the deeper layers of the soil [1].

Zinc and copper contents were determined by flame atomic absorption spectrometry (FAAS). The iron content in the soil and lingonberry samples was determined both photometrically and by FAAS. For the determination of other trace elements, the ICP-MS method was used.

The content of Fe in the soil samples in the Garkalne and Vecumu forests varies substantially (from 8 mg·kg⁻¹ to 1247 mg·kg⁻¹), but Fe content in lingonberries are similar (10,3 mg·kg⁻¹). The content of Cu and Zn in lingonberries are independent of their growth site. Lingonberry samples from the Garkalne and Vecumu forests contains 4,2 mg·kg⁻¹ and 9,9 mg·kg⁻¹ of Cu and Zn respectively.

References:

- [1] Rutkowska, B., Szulc, W., Bomze, K., D. Gozdowski, D., Spychaj-Fabisiak, E. Soil factors affecting solubility and mobility of zinc in contaminated soils. *Int. J. Environ. Sci. Technol.*, **2015**, *12*, 1687–1694.

USE OF $\delta^{15}\text{N}$ VALUES IN STUDIES OF INTRODUCED MINERAL NITROGEN CIRCULATION IN FERTILIZED FOREST AREAS

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Each forest ecosystem can be divided into three basic components – plants, growing conditions and living organisms. Carbon, hydrogen, oxygen and nitrogen are forming the bulk of the plant's dry matter. Nitrogen is one of the most important and most abundant nutrients in the plant. The amount of nutrients is ascending in following order – N, K, Ca, P, Mg, or comparatively more or less when changing between these plants. Nitrogen is a constituent of all plant and animal proteins. Nitrogen is generally highly up taken by plants in the form of nitrates and less in the form of ammonium and free nitrogen.

Light Stable Elemental Isotope Ratio Mass Spectrometry (IRMS) is a method, which allows to determine ratio of nitrogen isotopes in different plants and its parts and from its value it is possible to make conclusions about the source of nitrogen – does it comes from soil, fertilizer or air. Nitrogen content in the mineral part of the soil is very low that's why fertilization is often used to improve growing conditions. In other words, IRMS is method which can be used to evaluate effect of fertilization on plant and efficiency of fertilization.

Since the development of the manufacturing industry, human influence has increased rapidly on nitrogen cycle in nature, urban areas and in the forest ecosystem. Various production processes, chemical waste discharges, the use of mineral fertilizers, as well as various other human factors influence the nitrogen cycle balance in nature, in result which affects the nitrogen isotope ratio of various plants, including trees.

When studying the nitrogen isotope ratio in trees, the leaves and trunk rings are usually used for the samples to be analyzed. The $\delta^{15}\text{N}$ value in different trees is measured by measuring nitrogen cycle changes in undisturbed forests, in forests using fertilizers, as well as in deforestation impacts and other management practices in adjacent areas.

In the research were analysed pine needle spines and blueberry and lingonberry plant samples from differently fertilized and non-fertilized forest sample fields. The analyses were carried out with Nu Horizon IRMS at the University of Latvia, using certified inorganic reference materials USGS-40 and USGS-41 (L-Glutamic acid). The $\delta^{15}\text{N}$ values are expressed relative to air.

The first results show that the value of $\delta^{15}\text{N}$ was more positive in pine needles from fertilized sample fields which indicates the influence from nitrate and ammonia nitrogen forms in used fertilizers.

BIOGENIC AMINES IN MOULD CHEESES FROM THE LATVIAN MARKET

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Nowadays blue-veined cheeses have become more popular in the market due to the increased varieties of the product, whereas the quality and safety of different mould cheeses continue to rise awareness.

Biogenic amines (BA) are low-molecular-weight nitrogenous compounds, that are mainly produced through amino acid decarboxylation, which exists in most fermented foods such as cheese, sausage, wine and fish. [1] In Europe, permitted levels for histamine (His) in fish and fish products have been established at 100–400 mg kg⁻¹, while there are not regulations set for dairy products. [2]

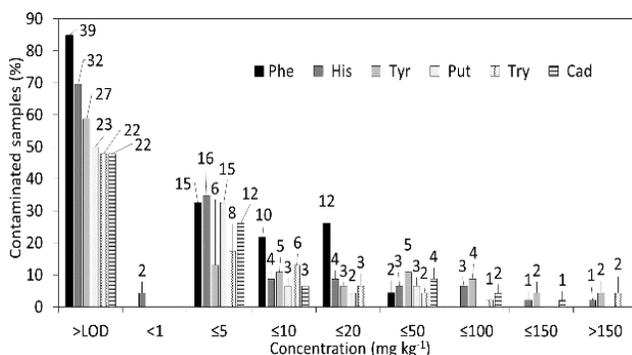


Fig. 1.
Histograms of biogenic amines in 46 blue mold cheese samples from the Latvian market

A sensitive UHPLC-PAD method for determination of 6 BAs (Figure 1) was optimized and applied to analyze 46 blue-veined cheese samples representative of most brands and varieties in local supermarkets in Latvia.

Tested cheese samples were positive for one to six BAs, with the individual concentrations ranging from just above the reporting level (< 1 mg kg⁻¹) up to 719 mg kg⁻¹, while the total content of BAs ranged from 5.5 to 824 mg kg⁻¹. Almost a quarter ($n = 12$) of the tested cheese samples contained under 10 mg kg⁻¹ of BAs (Figure 1).

With respect to scientific risk assessment, high acute hazard indexes were obtained for histamine and tyramine according to the worst-case scenario based on high consumption and 95th percentile occurrence, whereas other BAs were present at insignificant levels, thus the analysed cheeses can be considered as safe for healthy adults.

References:

- [1] Benkerroum, N. Biogenic amines in dairy products: origin, incidence, and control means. *Compr. Rev. Food Sci. Food Saf.*, **2016**, *15*, 801–826.
- [2] European Commission. Commission Regulation (EC) No. 2073/2005 of 15 November 2005 on microbiological criteria for foodstuffs. *Off. J. Eur. Union*, **2005**, *338*, 1–26.

CONTENT OF METALLIC ELEMENTS IN THE SOIL IN THE TERRITORY OF LIEPAJA NORTHERN FORTS

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The northern forts are only a small part of the remaining buildings of the Karosta Military Complex in Liepaja. Karosta occupies approximately 1/3 in the northern part of Liepaja territory, it is the largest historical military territory in the Baltic States and now also one of the most popular tourist destinations.

In 1994, when the Soviet army left Latvia, there was no survey of the Karosta territory and an assessment of the level of pollution. During the Soviet occupation, Karosta was a secret military facility for USSR military base with ships and submarines, it was a closed area for visitors.

The northern forts are located in the immediate vicinity of the sea, and there is a possibility that metallic contamination can be transmitted to both soil and water and also have an adverse effect on groundwater quality [1]. The main chemical elements most directly related to the use of military techniques and munitions are Fe, Zn, Cu, Al, Cd, Pb, Cr and Ni.

Soil samples in the Karosta area were taken at different sites and at 3 different depths: upper layer (0–5 cm), middle layer (20–30 cm) and boundary layer between black earth and sand (25–35 cm). The content of 10 metallic elements (Al, Fe, Mn, Zn, Cu, Cd, Cr, Ni, Co, Pb) in the soil samples was determined by ICP-MS. The results showed a tendency that the highest content of metallic elements in soil are in the medium layer. The soil pollution of the northern fort area with metallic elements has only been identified in separate sites (the largest pollution on the island of Lutene). The concentrations of metallic elements increase depending on the soil sampling place: Shkedes forest → Redan island → Old forts → Lutene island.

The concentrations of Ni, Cr, Cu, Pb, Zn and Cd in soil on Lutene island exceed the target values for mould soils specified in MK Regulation No. 804 up to 2.4 times. The results of the research show that the concentrations of Cr, Cd and Zn in soil on Lutene island are approximately 2 times higher compared to the same content of the same elements in soil samples from the smoke field area of the Adage military landfill.

At the same time, in other places of the Northern Forrest area (Shkedes forest, Redan island, Old Forts), the concentration of metallic elements in soil is at such a layer that they do not adversely affect soil and soil quality.

References:

- [1] Nikodemus, O., Kārklīņš, A., Kļaviņš, M., Melecis, V. *Augsnes ilgtspējīga izmantošana un aizsardzība*. Riga: LU Akadēmiskais apgāds, 2008, 265 lpp.

HYBRID ZINC OXIDE – POROUS ANODIC ALUMINIUM OXIDE NANOSTRUCTURE OPTICAL PROPERTIES

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Zinc oxide is known as a biocompatible, chemically stable, semiconducting material, with strong photoluminescence in the ultraviolet and visible spectral range [1]. In nanostructured form, e.g., nanowires, the surface effects are more expressed and sensitive to chemical environment changes, which makes ZnO nanostructures a perspective active element for optical sensing devices. A possible route to overcome the difficulties of lithographic production is use of self-organized porous anodized aluminum oxide (PAAO) as a template for nanostructure fabrication with well-established synthesis protocols and easily tunable parameters [2].

In this study, thin PAAO membranes with variable layer thickness (60–800 nm, pore diameter 40–50 nm) on Al substrate [3] and PAAO membranes with constant layer thickness (300 nm, pore diameter 40–50 nm) were used as a template for 35 nm thin ZnO layer synthesis by atomic layer deposition. The room temperature photoluminescence of nanostructures and spectral components of scattered light were identified by fitting to three Gaussian constituents. Luminescence intensity dissimilarity and peak position shift were observed. We used light reflectance simulation model to determine layer thickness of nanostructured multilayers [4]. Obtained data was validated using scanning electron microscopy.

Correlation between hybrid nanostructure luminescence and nanostructure layer thickness was observed.

Moreover, freestanding ZnO nanorods were produced by selective aluminium oxide dissolution. Red shift of photoluminescence and decrease of intensity were observed.

References:

- [1] Graniel, O., Fedorenko, V., Viter, V., Iatsunskyi, I., Nowaczyk, G., Weber, M., Załęski, K., Jurga, S., Smyntyna, V., Miele, P., Ramanavicius, A., Balme, S., Bechelany, M. Optical properties of ZnO deposited by atomic layer deposition (ALD) on Si nanowires. *Materials Science & Engineering B*, **2018**, 236–237, 139–146.
- [2] Malinovskis, U., Popļausks, R., Erts, D., Ramser, K., Tamulvičius, S., Tamulevičiene, A., Gu, Y., Prikulis, J. High-Density Plasmonic Nanoparticle Arrays Deposited on Nanoporous Anodic Alumina Templates for Optical Sensor Applications. *Nanomaterials*, **2019**, 9(4), 531.
- [3] Popļausks, R., Jevdokimovs, D., Malinovskis, U., Erts, D., Prikulis, J. Variable Thickness Porous Anodic Alumina/Metal Film Bilayers for Optimization of Plasmonic Scattering by Nanoholes on Mirror. *ACS Omega*, **2018**, 3(5), 5783–5788.
- [4] Prikulis, J., Tamulevičius, T., Popļausks, R., Bergs, G., Apsite, I., Malinovskis, U., Actins, A., Erts, D. Optical properties of thin metal films with nanohole arrays on porous alumina-aluminum structures. *RSC Advances*, **2015**, 5(83), 68143–68150.

DETERMINATION OF VITAMIN B12 REFERENCE INTERVALS FROM LARGE NUMBER OF GENERAL PATIENT DATA ACCUMULATED IN E. GULBIS LABORATORY IN LATVIA

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Introduction. Reference intervals (RIs) plays a crucial role in the interpretation of any clinical laboratory analysis and in the decision making in clinical medical practice. International Federation of Clinical Chemistry's (IFCC) and Clinical and Laboratory Standards Institute's (CLSI) defined C28-A3 guidelines [1] with 3 different methods which describe how reliable RIs should be established. Determination of RI via special research is time consuming and costly process involving recruitment of many reference individuals, alternative methods of calculating RIs from existing patient data can play important role in medical development and adaption of RI to special patient groups.

Aim of this paper is to study the possibility of using all Egils Gulbis laboratory (EGL) accumulated B12 test results for the determination of RI.

Materials and methods. In this study B12 RI, mean value and distribution function were determined using 201 127 B12 values from 125 119 patients that have performed B12 tests at EGL from year 2004 to year 2019. Standard EGL clinical laboratory technique and procedures were used. For patients who have taken multiple B12 tests over years their B12 value was used as a single date point, thus each patient was represented with one data point. The results were plotted as patient density distribution over the logarithm of B12 value. Meta-analysis for B12 RIs reported in literature was done for comparing with the results acquired in this study.

Results. The resulting distribution was well approximated with Gaussian distribution. Parameters of Gaussian distribution were determined by fitting to the high B12 value part of the distribution, as it was deemed that there was overrepresentation of patients with B12 deficit. The RI determined in this study corresponds with RI obtained in our meta-analysis study of B12 reference values reported in literature. The method developed in this work provides significant cost and efficiency advantages as compared to the classical methods of establishing RI.

Conclusion. Local RI for B12 level can be established using large number of patient data without preselecting "healthy" individuals. This method can be used in cases where material from predominantly healthy individuals is analyzed.

References:

- [1] Gary, L., Horowitz, M. D., Soutan Altaie, James C. Boyd. EP28-A3c: Defining, Establishing, and Verifying Reference Intervals in the Clinical Laboratory; Approved Guideline – Third Edition. *Clinical and Laboratory Standards Institute*, 2010, 28, 12.

BIOMASS BASED CARBOHYDRATES SEPARATION USING AN ON-LINE SPE-HPLC SYSTEM

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Fast pyrolysis of biomass is one of the possible routes of wood biomass valorization that can be utilized in integrated biorefinery processing [1]. Although it allows to obtain various high value chemicals from biomass such as monomeric and oligomeric carbohydrates, levoglucosan, levoglucosenone, furfural, vanillin and other high potential chemicals [2, 3], the main drawback of fast pyrolysis is that all obtained compounds still need to be separated from the obtained pyrolysis liquor, which in many cases can be quite challenging and work intensive [4]. In this study a method for separating monomeric and oligomeric carbohydrates from this pyrolysis liquor is being developed utilizing an on-line SPE-HPLC-RI system.

The main object of this study is the biomass pyrolysis liquid obtained by performing fast pyrolysis of birch wood chips. This liquid was condensed to decrease the amount of water and various volatiles. After that this pyrolysis liquid was further processed by performing crystallization with acetone to separate levoglucosan. The separated acetone soluble fraction was used in the further experiments.

SPE cartridges were filled with ion-exchange resins *Levatit* to separate phenolics and furan derivatives from the carbohydrate fraction. SPE system was operated together with HPLC-RI system using *Shodex sugar SP0810* analytical column. Separations were performed by filling the cartridge with the resin in a water suspension and then pumping a separated acetone soluble fraction through the system with flow rate 30 mL·min⁻¹. Analysis of the separated fraction was performed every 25 minutes with a changeable switch valve that changes flow from fraction collection to the analytical system. Mobile phase for HPLC analysis was deionized water with flow rate 0.5 mL·min⁻¹. Column temperature was 80 °C, but the temperature of the RI cell was 55 °C. Injection volume was 20 µL. To test this method in more controlled conditions, an artificially created sample was used. This sample was prepared by combining various available standards of carbohydrates, furan and its derivatives, and phenol derivatives in a single deionized water solution.

The first obtained results have shown that the on-line SPE-HPLC method can be successfully used for analysis of carbohydrates from the separated acetone soluble fraction.

References:

- [1] Ed de Jong, A. H., Patrick Walsh, M. W. Bio-Based Chemicals. Value Added Products from Biorefineries. *IEA Bioenergy Task 42 Biorefinery* 33, **2012**, 1–36.
- [2] Brownsort, P. A. Biomass Pyrolysis Processes: Performance Parameters and Their Influence on Biochar System Benefits, **2009**, 1–93.
- [3] Balat, M. Mechanisms of Thermochemical Biomass Conversion Processes. Part 1: Reactions of Pyrolysis. *Energy Sources, Part A Recover. Util. Environ. Eff.*, **2008**, 30(7), 620–635.
- [4] Rover, M. R. Analysis of sugars and phenolic compounds in bio-oil. Iowa State University, **2013**, 134.

SYNTHESIS AND CHARACTERIZATION OF CARBONATED AMORPHOUS CALCIUM PHOSPHATES WITH VARIABLE REAGENT MOLAR RATIOS

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Hydroxyapatites (HAP) and other synthetic amorphous calcium phosphates (ACP) nowadays are widely used biomaterials in implantology and biomedicine due to their high similarity to the chemical structure of human bone tissue inorganic fraction and such indispensable properties as biocompatibility, bioactivity, osteoconductivity, osteointegration and non-toxicity [1].

Although different chemical composition and stoichiometry HAP have been synthesized and introduced into industrial production over the last century, the development, refinement and optimization of synthesis methods to achieve better implant qualities still remain relevant. Studies of carbonate-containing HAP synthesis aspects are of special importance because of presence of relatively large amounts of carbonates in native bones [2, 3].

The aim of current study was to investigate correlations between the molar ratios of the reagents used during the synthesis of ACP in the reaction mixture and various physical and chemical characteristics of the products obtained. A series of ACP syntheses by wet precipitation method has been performed with different molar ratios of ammonium carbonate, calcium nitrate and ammonium phosphate. Samples obtained were characterized using X-ray powder diffractometry to assess the crystallinity of products, ICP-OES to determine calcium and phosphorus mass fractions, CHN elemental analysis to quantify carbonate content as well as FTIR and Evolved Gas Analysis to get additional information on synthesized sample qualitative composition.

Table 1. Expected characteristics of the synthesized ACP products

Ca/P theor.	Product formula	Molar mass, g·mol ⁻¹	wCa, %	wP, %	Ca/P exper.	wCO ₃ ²⁻ , %
1.5	Ca ₁₀ (PO ₄) ₆ (OH) ₂	1004.62	39.89	18.50	1.67	0
1.6	Ca _{9,6} (PO ₄) _{5,6} (CO ₃) _{0,4} (OH) _{1,6}	967.80	39.75	17.92	1.71	2.48
1.7	Ca _{9,2} (PO ₄) _{5,2} (CO ₃) _{0,8} (OH) _{1,2}	930.98	39.61	17.30	1.77	5.16
1.8	Ca _{8,8} (PO ₄) _{4,8} (CO ₃) _{1,2} (OH) _{0,8}	894.17	39.44	16.63	1.83	8.05
1.9	Ca _{8,4} (PO ₄) _{4,4} (CO ₃) _{1,6} (OH) _{0,4}	857.35	39.27	15.90	1.91	11.20
2.0	Ca ₈ (PO ₄) ₄ (CO ₃) ₂	820.53	39.08	15.10	2.00	14.63

References:

- [1] Combes, C., Rey, C. Amorphous calcium phosphates: Synthesis, properties and uses in biomaterials. *Acta Biomaterialia*, **2010**, 6, 3362–3378.
- [2] Tadic, D., Peters, F., Epple, M. Continuous synthesis of amorphous apatites. *Biomaterials*, **2002**, 23 2553–2559.
- [3] Gibson, I. R., Bonfield, W. Novel synthesis and characterization of an AB-type carbonate-substituted hydroxyapatite. *J. Biomed. Mater. Res.*, **2001**, 59, 697–708.

DIRECT-INJECTION FOURIER-TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRIC METHOD FOR ULTRA-FAST QUANTIFICATION OF QUINOLONES IN POULTRY

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Many recent studies have shown high detection frequencies of quinolone antibiotics in poultry, as well as an increasing trend of antimicrobial resistance development [1].

The main purpose of the research was to develop a fast and reliable analytical method for the detection of quinolones in poultry meat. In order to develop a rapid quantitative confirmation method, ion cyclotron resonance mass spectrometer was utilized. Firstly, the sample preparation procedure was simplified by reducing the procedure to extraction and freezing out steps. Secondly, the chromatographic separation step was excluded and mass spectrometric parameters were optimized. Thirdly, the method was validated by fortifying blank matrix at four levels (0.5, 1, 1.5 and 2 times the maximum residue limit (MRL) or level of interest, where no MRL was established). As a result, the overall analysis time was reduced to less than an hour. The validation study revealed that the method is capable of detection and confirmation of ten quinolone compounds in poultry above CC β levels. Finally, the developed method was applied to 19 commercially available chicken meat samples. None of the samples contained quinolones above the method's limit of quantification.

The developed method could be one of the fastest quantitative confirmatory methods for the analysis of quinolones available so far.



Fig. 1. Method overview

References:

- [1] World Health Organization. Tackling antibiotic resistance from a food safety perspective in Europe. 2011.

SEPARATION AND CHARACTERISATION OF THE BY-PRODUCTS OF LEVOGLUCOSENONE PRODUCTION FROM LIGNOCELLULOSE

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It is believed that the depletion of fossil resources and the increase in environmental pollution promotes the idea of developing and moving towards more sustainable strategies to use natural carbon sources [1, 2]. One such natural source of carbon is lignocellulosic biomass, which, after fast pyrolysis, allows the production of bio-oil, which is rich with various chemicals. It mainly consists of carbohydrates, phenols, furans and the like.

It is considered economically advantageous to obtain levoglucosenone (LGO) from biomass rather than synthetically. Sugar itself is well suited for organic synthesis [3]. However, the removal of LGO from biomass yields a relatively high residual condensable by-product. Therefore, in order to increase the economic feasibility of the production of levoglucosenone from biomass, it is valuable to develop a strategy for valorisation of the remaining by-products, not just the removal of LGO itself.

The study analyzes the condensable residues remaining after the distillation of LGO, which mainly consists of phenol and furan derivatives.

The analyzed by-product fraction is split with liquid-liquid and SPE extractions with water, methanol, acetone and hexane, where in SPE case there is using SP850 synthetic adsorbent resin (P.R. 45 angstrom). The obtained fractions are analyzed by UHPLC system with CSH Phenyl-Hexyl column, FTIR, analytical pyrolysis, UV/VIS.

The combination of different analytical techniques has shown significant qualitative differences in the by-product fractions obtained by solid phase extraction, allowing a comprehensive characterization of the pyrolysis products.

References:

- [1] Talebi Amiri, M., Dick, G. R., Questell-Santiago, Y. M. et al. Fractionation of lignocellulosic biomass to produce uncondensed aldehyde-stabilized lignin. *Nat. Protoc.*, **2019**, 14, 921–954.
- [2] Forberg, D, Schwob, T., Kempe, R. Catalytic condensation for the formation of polycyclic heteroaromatic compounds. *Nat. Commun.*, **2018**, 9, 1751.
- [3] Comba, M. B., Tsai, Y. H., Sarotti, A. M., Mangione, M. I., Suárez, A. G., Spanevello, R. A. Levoglucosenone and Its New Applications: Valorization of Cellulose Residues. *European J. Org. Chem.*, **2018**, 5, 590–604.

RELIABLE LC-MS/MS DETERMINATION OF DANSYL CHLORIDE DERIVATIZED GLYPHOSATE, AMPA AND GLUFOSINATE

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In the past decade, glyphosate, its degradation product aminomethylphosphonic acid (AMPA) and some related pesticides, including glufosinate, have been particularly studied due to concerns over their globally wide and intensive use. Applications of such pesticides have resulted in frequent detection and maximum residue limit exceedances in food of plant origin, as well as detection in food of animal origin. Due to the chemical properties of some pesticides (high polarity, low solubility in organic solvents, strong acidity, complex formation, poor electrospray ionization), special methods are usually required to ensure reliable determination.

In this study we report, for the first time to the best of our knowledge, a LC-MS/MS based determination of dansyl chloride (5-(dimethylamino)naphthalene-1-sulfonyl chloride) derivatised glyphosate, AMPA and glufosinate. Large excesses of needed reagents and byproducts thereof may interfere with detection of desired analytes and contaminate analytical columns and mass spectrometers [1]. The present method has been developed to prevent this.

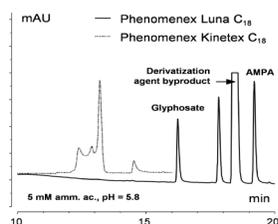


Fig. 1. Separation of analytes from byproducts on different octadecyl bonded silica phases

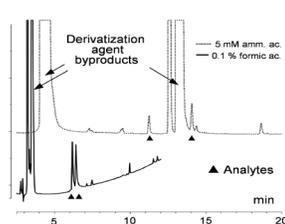


Fig. 2. Separation of analytes from byproducts with different mobile phase additives

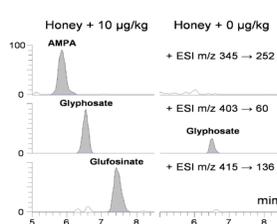


Fig. 3. Detection of analytes in a honey sample and the sample spiked with 10 µg/kg

Honeybees are known to prefer drinking from agricultural and urban runoff, therefore pesticides such as glyphosate may occur in honey [2]. The present method was applied to samples of honey. The LOQ was 10 µg/kg. Linearity was achieved ($R^2 > 0.99$) both with and without use of internal standards. Matrix effect in the LC-MS/MS stage was estimated $< 5\%$.

References:

- [1] Zelenkova, N. F., Vinokurova, N. G., Leontievskii A. A. Determination of amine-containing phosphonic acids and amino acids as dansyl derivatives. *J. Anal. Chem.*, **2010**, 65, 1143–1147.
- [2] Lau, P. W., Nieh, J. C. Salt preferences of honey bee water foragers. *J. Exp. Biol.*, **2016**, 219, 790–796.

TOTAL ANTIOXIDANT STATUS IN SAPROPEL EXTRACTS IN DIFFERENT SEDIMENT DEPTH IN LAKES IN LATVIA

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Freshwater sapropel is sediment in lakes and has unique structure containing more than 10% of unevenly distributed organic matter as well as residues of microscopic aquatic organisms with small content of inorganic components of biogenic origin and mixture of mineral ingredients. The characteristics of sapropel are determined by organic, mineral and biological compounds and it has been traditionally used in skincare and healthcare in external applications. Sapropel extract is a mixture of chemical elements, hormones, various organic acids and vitamins and is also used for therapeutic applications and skincare.

In this study the total antioxidant status (TAS) and fulvic acids in sapropel extract from different layers of sapropel sediments from 5 lakes in Latgale, Latvia, were determined and compared with other characteristics of the sapropel like fulvic and humic acids concentration.

For each sapropel layer the total antioxidant status was measured. There was no significant difference in TAS between different sapropel sediment layers. Median concentration of TAS was calculated to for each individual lake. The total antioxidant status was from 1.25 ± 0.23 to 0.34 ± 0.15 mmol Trolox/L ($M \pm SD$), it was found that TAS is considerably higher in organic sapropel extracts (ash content < 30%) ($p < 0.02$). Currently, the reasons for so large differences in TAS between different lakes are not fully understood. Antioxidant level in each of the lakes does not correlate with the concentration of fulvic acids. Lake with the highest fulvic acid concentration 40.9 ± 4.7 mg/g has the lowest level of antioxidant status 0.34 ± 0.15 mmol trolox/L.

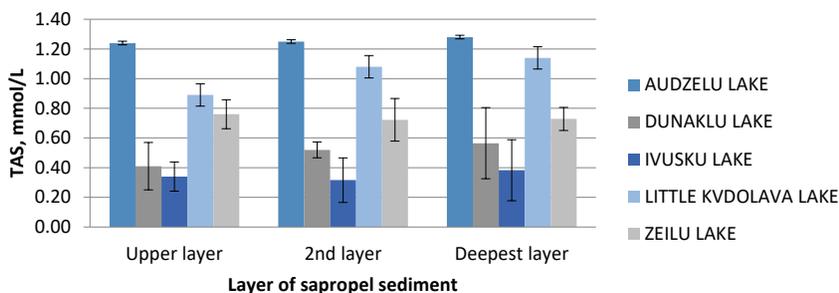


Fig. 1. Total antioxidant status in sapropel extract in different sediment layer and in different lakes

Acknowledgements: This research was supported by “Analysis of characteristics of medical sapropel and its usage for medical purposes and elaboration of industrial extraction methods”, project No. 1.1.1.1/16/A/165.

PHYTOCHEMICAL EVALUATION OF *BIDENS TRIPARTITA*

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The demand for natural ingredients in cosmetic and pharmaceutical industry is growing. Therefore, it is necessary to isolate biologically active compounds and to characterize their chemical, physical and biological properties in order to create new products. The phytochemical evaluation of *Bidens tripartita* is relatively poorly studied, a plant is mainly used as tea. Based on high content of flavonoids and other biological active compounds, its usage could be expanded [1].

The analyses were performed with HPLC/DAD and HPLC/MS methods to identify and quantify chemical compounds in extracts of *Bidens tripartita*. The content of flavonoids (TFC) in the plant was about 27 mg mL⁻¹, the content of chlorogenic acid was approximately 90 µg mL⁻¹ (see Figure 1). 27 compounds (derivatives of luteolin, kaempferol, quercetin) from various classes of organic compounds were identified.

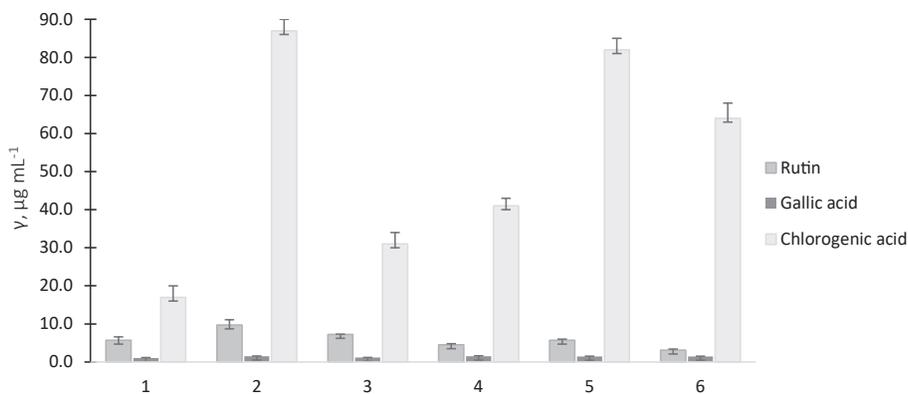


Fig. 1. Content of rutin, gallic acid and chlorogenic acid in different extracts of *Bidens tripartita* (1–10 mg mL⁻¹ in 50% EtOH, 2–50 mg mL⁻¹ in 50% EtOH, 3–10 mg mL⁻¹ in 70% EtOH, 4–50 mg mL⁻¹ in 70% EtOH, 5, 6 – infusion of *Bidens tripartita* tea)

The antibacterial activity of *Bidens tripartita* tea against Gram-positive bacteria *Bacillus subtilis* was determined using dilution and disc diffusion methods. *Bidens tripartita* can be extensively used in pharmacy due to its high antiradical activity, antibacterial activity against widespread Gram-positive bacteria, as well as an isolation of biologically active compounds.

References:

- [1] Uysal, S., Ugurulu, A., Zengin, G., Cengiz, M., Mollica, A., Custodio, L., Nogueira, J. M. F., Mahomoodally, M. *Food Chem. Toxicol.*, **2018**, *11*, 525–536.

DECAMORPHISM OF R-ENCENICLINE HYDROCHLORIDE

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R-encenicline (R)-7-chloro-N-quinuclidin-3-ylbenzo[b]thiophene-2-carboxamide hydrochloride (Enc-HCl) is a partial, selective agonist of the α -7 nicotinic acetylcholine receptor which was developed for the treatment of cognitive deficits in schizophrenia and Alzheimer's disease. Here, we report an experimental, structural and computational study of neat polymorphs of Enc-HCl.

In solid form screening numerous solvates including hydrates have been obtained, and their desolvation produced twelve neat polymorphs. For ten of these polymorphs crystal structures were determined. The crystal structures of precursor solvates/hydrates were found to be relatively structurally similar and related to those of desolvated phases, which was consistent with the observed phase transitions among the related pairs. In addition, a comparison of the thermodynamic stability of polymorphs were performed using differential scanning calorimetry data and solvent mediated slurry-bridging experiments. The energy ranking of ten polymorphs were obtained by DFT calculations with different functionals and/or dispersion correction methods.

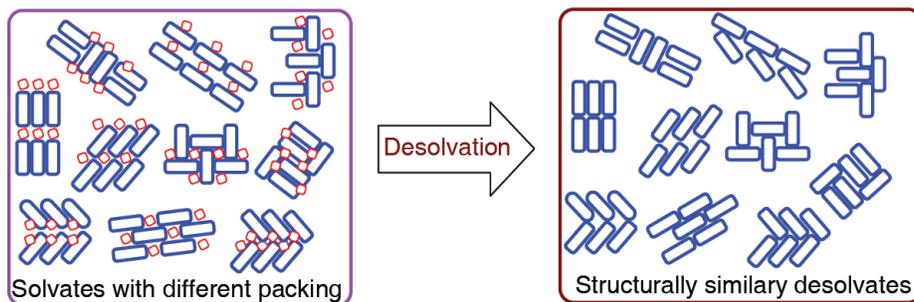


Fig. 1. Schematic representation of accessing structurally similar polymorphs through desolvation of various Enc-HCl solvates by keeping the main packing features

STUDY ON THE CHEMICAL ELEMENT COMPOSITION OF THE LICHENS (*XANTHORIA PARIETINA*) IN RIGA CITY

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Lichens are symbiotic organisms which consist of fungi and algae or cyanobacteria. They are one of the slowest growing plants, which can grow only about 1 to 30 mm in one year. Lichens can grow even in the most unfavourable conditions, where other plant species could not survive or develop.

Lichens absorb water and nutrients directly from the air, and it makes them highly sensitive to air purity. They accumulate substances in the air including heavy metals. The more polluted the air is, the higher concentration of chemical elements will be found in the lichens. Lichens are widely used as bioindicators for monitoring the status of the environment, especially air quality as they grow in a wide geographical area.

Sulphur dioxide is to be one of the most dangerous air pollutants affecting lichens. The higher the air pollution, the less the diversity of lichen species. Lichens (*Xanthoria parietina*) often spotted on tree branches and bark belong to one of the durable lichen species whose growth is affected only by high air pollution

The aim of our research was to evaluate the chemical element composition in lichens (*Xanthoria parietina*) in different parts of Riga. Lichens samples were collected in September of 2019 on different tree species with similar bark structure ~ 1–2 m above the ground in three different locations:

- 1) Freeport of Riga, Kundziņsala (the companies in the territory are engaged in transshipment and transportation of coal and other bulk cargoes);
- 2) Residential area, Sarkandaugava;
- 3) Mežaparks (green area of the city).

Unwashed lichens dried at 90 °C 24 h, homogenized and digested in the mixture $\text{HNO}_3:\text{H}_2\text{O}_2$ using the closed microwave digestion. Metallic element content in lichens was determined by ICP-MS. Sulphur content was determined as sulphate ions by turbidimetry.

Obtained results show that the sulphur content in lichens in the territory of the Freeport of Riga is 5–7 times higher than residential area and Mežaparks. Determined Ca, Mn, Fe and Cu content in lichens from the Freeport of Riga is ~ 2 times higher than in other areas.

Comparing sulphur and iron content in lichens that were sampled from the Freeport of Riga and Mežaparks, that the content of these elements in the territory of Freeport varies over a wide range but in the territory of Mežaparks it is quite similar.

The tendency is observed, that As and Pb content in the analysed lichens decreases in the following order: Freeport of Riga → residential area, Sarkandaugava → Mežaparks.

DETERMINATION OF $\delta^{13}\text{C}$ VALUES IN HONEY SAMPLES OF DIFFERENT FLORAL ORIGIN

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Monofloral honey derived from one particular source plant may be more valuable than honey derived from many types of plants. The price of honey also varies according to the type of plants. Melissopalynology is the main method to distinguish honey by its floral type. Stable isotope ratio mass spectrometry (SIRMS) and liquid chromatography high resolution mass spectrometry is offered as an alternative method [1].

In the research various monofloral and polyfloral honey samples were analysed. The honey samples were collected and information about floral type was inquired from local manufacturers. The analyses were carried out with Nu Horizon SIRMS at the University of Latvia, using certified inorganic reference materials USGS-40 and USGS-41 (L-Glutamic acid). The $\delta^{13}\text{C}$ values are expressed relative to VPDB. Thermo Scientific UltiMate3000 LC system with high resolution mass spectrometer Q Exactive and Kinetex PFP column (3,00 × 100 mm, 1,7 μm , 100Å) were used to determine amount of 7 flavanoids and 11 phenolic acids.

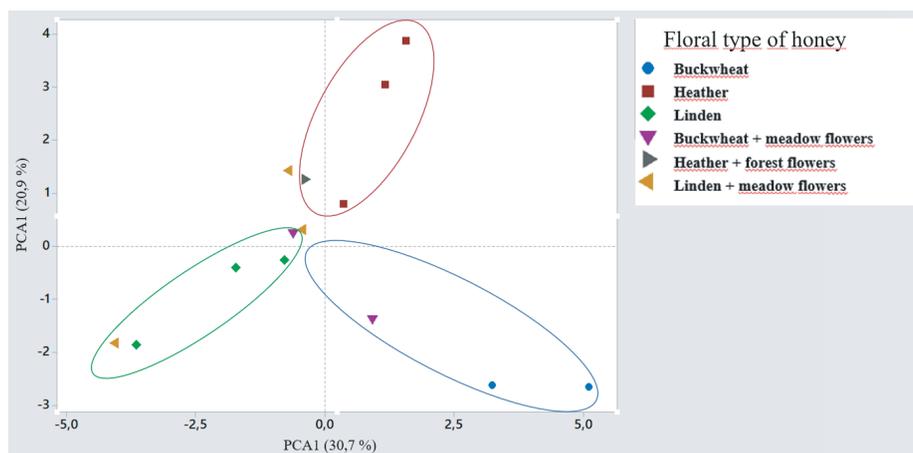


Fig. 1. Score plot of principal component analysis using $\delta^{13}\text{C}$ values and quantitative data of flavonoids and phenolic acids of monofloral and polyfloral honey

The preliminary results show that certain monofloral honey types can be distinguished from each other using particular principal component analysis. Most of polyfloral honey in score plot is closer to its center than monofloral honeys. It shows potential to use this method to distinguish certain types of polyfloral honey.

References:

[1] Geana, E. I., Cuicure, C. T., Costinel, D., Ionete, R. E. *Food Control*, **2020**, 109, article 106919.

USE OF WOOD ASH IN THE FOREST AND ITS EFFECT ON THE MICRO- AND RARE EARTH ELEMENT FLOW IN BLUEBERRIES (*VACCINIUM MYRTILLUS* L.)

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Wood ash is a biological residue produced by the combustion of wood or their products (chips, sawdust, etc). They are rich in macro- and trace elements but have relatively low nitrogen content. During combustion processes, two different ash fractions are produced: fly ash and bottom ash. Using wood ash as a fertilizer allows to solve three important problems: ensures efficient utilization and disposal of wood ash from industrial areas, improves tree growth conditions in the forests and prevents valuable nutrients from being wasted.

Some studies have showed that wood ash affects only the topsoil. Wood ash contains not only macro nutrients, but also heavy metallic elements which can cause poisoning of a plant. For example, wood ash may contain increased amounts of Cd or As.

The wild-growing blueberry (*Vaccinium myrtillus* L.) is one of most popular berries which are common throughout Europe. They are deciduous species as they shed leaves during fall seasons preparing for winter. Blueberries can serve as a model species in the forest due to their place in the ecological system. That's why it is important to study blueberries and they response to any changes (including fertilization), especially in terms of macro- and trace element content.

The aim of our research was to analyse the flow of micro- and rare earth elements in blueberries (berries and roots) in the forest areas which was fertilized with wood ash.

For this research were selected two forests areas which was fertilized with wood ash approximately 3 tons per hectare. Forests are dominated by pine species (*Pinus sylvestris* L.). Two different types of sampling plots were set up in each area – fertilized plots and control plots.

Blueberry samples were collected in August 2019, for analysis were sampled roots and berries. During sample preparation the berries was unwashed, but the roots were washed with deionized water. Samples were dried at 50 °C temperature and digested in the mixture HNO₃:H₂O₂ (6:2) using the closed microwave digestion system. Micro – and rare earth element concentration was determined by ICP-MS.

The research results show that in the area which was fertilized with fly ash are observable trend that in fertilized sampling plots rare earth element content are 2 times higher than in the plant root system of control plots.

This work was supported by Short term scientific mission organized in scope of project "research program on improvement of forest growth conditions 2016–2021" No 5-5.5_000z_101_16_31.

TARGETED ORGANOSOLV DELIGNIFICATION OF RESIDUAL BARK, AFTER SEPARATION OF SECONDARY METABOLITES

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There are two main steps of bark processing for benefit utilization of all constituents of bark biomass including sequential extraction of bark with organic solvents of increased polarity to separate secondary metabolites, predominantly lipophilic and polyphenolics of non-lignin origination (diarylheptanoids, tannins). The next step includes *Organosolv* delignification of extractives free bark and separation of lignin fraction. The solids remaining after delignification can be further used as a substrate for obtaining monomeric sugars or/and as a raw material for fuel pellets production. The main task of this study is to explore possibilities of incorporation green organosolv delignification into biorefinery chain of wood bark processing and optimize organosolv parameters for efficient lignin separation, which can be further used as a source of various added value products. In this context ethanol (ETH) as a solvent obviously will be most suitable. Such parameters as H₂O/ETH ratio, temperature of processing (80–140 °C), duration of process (5–16 h), catalyst (HCl) content could be variable parameters under study for both pine and willow barks. Alternatively, butanol can be an alternative to ETH to give higher extraction efficiency and lignins with improved solubility. Acquired lignins were analysed using novel instrumental analytical methods such as ³¹P NMR for comprehensive analysing of functional groups in these lignins (the origination of OH groups and their occurrence) as well as size exclusion chromatography (SEC) for analysing molecular mass and its dispersity of acquired lignins. Besides that, the characteristics of separated lignins in terms of their structural characteristics such as linkage content and monomer distribution as well as purity was determined by 2D-HSQC NMR.

DETERMINATION OF PHTHALATES IN INDOOR DUST USING GAS CHROMATOGRAPHY COUPLED WITH Q-EXACTIVE MASS SPECTROMETRY

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Phthalate additives are typically used as plasticizers in polymer materials such as cellulose esters, PVC, and vinyl chloride copolymers to make polymeric materials softer and increase their flexibility. Phthalates are esters of phthalic acid with high boiling point and $\log K_{ow}$ value, which results in their low degradability and high persistence in different environmental sites.

Phthalates are not chemically bonded to the original material, hence they can easily enter the environment through leaching, evaporation and abrasion combined with sorption on airborne particles. The widespread use of synthetic materials, which may contain up to 40% of phthalates, results in their presence as pollutants in air and dust in indoor environment [1].

In the present study 18 phthalates and their alternatives were analysed in 34 household dust samples by GC-Orbitrap-HRMS. All samples were collected in Latvia combining dust from all living areas to gain an overall profile of investigated households.

The results show high levels of phthalates in indoor dust (Fig. 1). The total concentration of phthalates ranged from 7020 to 833500 ng/g. As modern people tend to spend up to 85% of time indoors, further investigations concerning uptake and health hazards are in high demand.

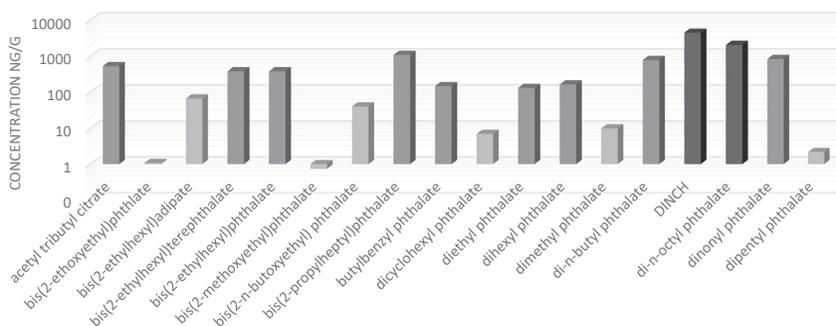


Fig. 1. Median concentrations (ng/g) of phthalates in household dust

References:

- [1] Abb, M., Heinrich, T., Sorkau, E., Lorenz, W. Phthalates in house dust. *Environ. Int.* **2009**, *35*, 965–970.

CRYSTALLIZATION OF AMORPHOUS CALCIUM COMPOUNDS UNDERPINS FURTHER GROWTH OF CRYSTALLINITY CONTROLLED BIOMATERIALS

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Biology has taken advantage of amorphous precursor phases to produce structures with remarkable properties. Also the amorphous state is highly moldable, which is beneficial for the construction of biomaterials [1]. Calcium phosphate-based biomaterials can be used for teeth or bone replacement, bone repair, augmentation, or regeneration because of their similarity to bone mineral [2]. Herein, we study the nature of crystallization of amorphous phase nanopowders – amorphous calcium carbonate (ACC), amorphous tricalcium phosphate (ATCP) and amorphous hydroxyapatite (AHAp). While previous work has shown individual ACC, ATCP and AHAp crystallization studies, here we shall show the crystallization comparison of all three amorphous compounds with the intention to design biomaterials with controlled and improved properties.

Thermal analysis was carried out under non-isothermal conditions by heating all samples up to 800 °C using thermogravimetry (TGA), differential thermal analysis (DTA) and evolved gas analysis (EGA). Heated powders were characterized by X-ray diffraction, ultra small angle X-ray scattering (USAXS), small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) to determine structural changes during heating. As a complementary method for characterizing chemical phases and functional groups Fourier transform infra-red spectroscopy (FTIR) was performed.

Results show significant differences in phase transition rate, temperature range and heat of transition. The fastest phase change occurs with ATCP followed by ACC and AHAp. All powders evolved adsorbed molecules before a subsequent phase change. It was interesting to note a shrinkage for AHAp before crystallization. In further research densification will be explored to exploit the plastic deformation of amorphous phase before returning to crystallization for microstructural design.

Acknowledgements: The Latvian Science Council project “Freedom-to-Move”, Nr. LZP-2018/1-0432, the US Navy and the Advanced Photon Source supported this study.

References:

- [1] Ibsen, C. J. S., Chernyshov, D., & Birkedal, H. Apatite Formation from Amorphous Calcium Phosphate and Mixed Amorphous Calcium Phosphate/Amorphous Calcium Carbonate. *Chemistry – A European Journal*, **2016**. 22(35), 12347–12357. doi:10.1002/chem.201601280
- [2] LeGeros, R. Z. Calcium Phosphate-Based Osteoinductive Materials. *Chemical Reviews*, **2008**, 108(11), 4742–4753. doi:10.1021/cr800427g

THE IDENTIFICATION OF TALL OIL BASED RIGID POLYURETHANE FOAM PYROLYTIC DESTRUCTION GASEOUS PRODUCTS BY PY-GC/MS METHOD

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Polyurethane is widely used, with its two major applications, soft furnishings and insulation, having low thermal inertia, and hence enhanced flammability. In addition to their flammability, polyurethanes (PU) and polyisocyanurates (PIR) form carbon monoxide, hydrogen cyanide and other toxic products on decomposition and combustion [1]. To properly identify the main gaseous products generated during the rigid PU-PIR foam thermal degradation highly sensitive and selective analytical methods must be employed. One analytical method that fits the presented criteria in particular is the pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), often used in different polymer and biomolecular system chemical analysis.

In this research rigid PU-PIR foam samples made from renewable material (tall oil) based polyols were analysed by the Py-GC/MS. The relative amount of gaseous waste products produced during the thermal degradation were evaluated between two samples, differenced by their assigned isocyanate (NCO) index value – 150 and 300.

The analyses were carried out with Frontier Lab (Japan) Micro Double-shot Pyrolyser Py-2020iD and Shimadzu (Japan) GC/MS-QP 2010 apparatuses at the Latvian State Institute of Wood Chemistry. Substance identification was done using the Library MS NIST 147.LI13. The relative areas of the peaks were calculated by the Shimadzu software and, if necessary, corrected or integrated manually on the basis of the GC/MS data. The relative error of measurements was 1–3%. The results were from triplicate experiments.

The results show that the main thermal degradation components originate from the decomposition of the isocyanate moiety part of the rigid PU-PIR foam, i.e., 4,4'-diphenylmethane diisocyanate, primarily forming 4,4'-methylenedianiline, 3,3'-diaminodiphenylmethane, N-methylaniline, aniline, 4-benzylaniline and phenyl isocyanate, the relative amount of the chemical components increasing up to 29% when measured between the samples (NCO 150–300). Though CO₂ and CO, H₂O and nitrogen oxides are present, the observed trend for the relative amount of the generated inorganic gases and the NCO values is inversely proportional. This indicates that the added thermal stability to the rigid PU-PIR foam from the isocyanurate structures within the matrix are responsible for the complication in the thermal decomposition processes by preventing the material to fully decompose under a high-temperature influence.

References:

[1] McKenna, S. T., Hull, T. R., The fire toxicity of polyurethane foams. *Fire Sci. Rev.*, **2016**, 5(1), 27.

SWELLING CHARACTERISTICS OF SULFONATED POLYETHERETHERKETONE MEMBRANES IN ELECTROLYTES

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Sulfonated polyetheretherketone (SPEEK) was synthesized from polyetheretherketone (PEEK), obtained from Sigma Aldrich (average molecular weight $M_n \sim 10300$, weight average molecular weight $M_w \sim 20800$) using advanced sulfonation method [1]. Degree of sulfonation = 0.70. Polymer membranes prepared by using a solvent cast method. Polymer solutions were poured into Petri dishes and dried for 48 h at 80 °C.

Water uptake and swelling degree were determined for each of the prepared membranes. Dry membranes weighted and measured length and thickness. After that, membranes immersed in deionised water for 24 h, weighted and measured again. Alternatively, membranes immersed in a 1 M KHCO_3 solution. Metrohm Autolab potentiostat/galvanostat PGSTAT204 was used for impedance/ conductivity measurements, and measuring parameters were: frequency range was 50 kHz to 100 Hz; 10 frequencies per decade; signal amplitude 10 mV. Potassium content after ion-exchange obtained using XRF element analysis (Bruker S8 Tiger).

Table 1. SPEEK and NAFION membrane characteristics after immersion in 1M KHCO_3

	Mass change, %	Thickness change, %	XRF (K content), %	Conductivity before immersion, mS/cm	Conductivity after immersion, mS/cm
SPEEK	20%	17%	11.1%	5.8	5.1
NAFION	-10%	-13%	6.4%	25.2	5.6

The preliminary results show (Table 1) that the swelling properties for SPEEK and NAFION are different during ion-exchange with potassium.

Acknowledgments: Authors of this work acknowledge funding from European Union's Horizon 2020 Research and Innovation Program project under grant agreement No. 768789.

References:

[1] Luo, H., Vaivars, G., Mathe, M. *Int. J. Hydrogen Energy*, **2012**, 37(7), 6148–6152.

DETERMINATION OF THE EFFECTIVENESS OF THE LEGUME- RHIZOBIA- SYMBIOTIC SYSTEM

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Biological N₂ fixation is an important aspect of sustainable and environmentally friendly food production and long-term crop productivity. Binding of biological nitrogen is inconceivable without the development of an efficient symbiotic system between legume and rhizobia bacteria.

Experiments were carried out with soya and faba beans. Seeds of soya were inoculated with commercial preparation of rhizobia, control without inoculation just before sowing. Plants were analysed during flowering stage (roots, stems and leaves) and after harvest (seeds). Due to absence of indigenous rhizobia in the soils of Latvia, no nodules were observed on the roots of control plant during plant growth. Soya plants developed from treated seeds had nodules on their roots and it is an evidence of the development of symbiotic system between nitrogen fixing bacteria and plant.

Seeds of faba beans before sowing were inoculated 1) with an effective rhizobia strain from the Rhizobia Collection of Latvia University of Life Sciences and Technologies, 2) with commercial mycorrhiza fungi preparation, 3) with rhizobia and mycorrhiza fungi. Control – without additional microorganisms. Plants were sampled during flowering stage (shoots) and during harvest (seeds). Nodules were found on the roots of all plants, amount and size of nodules differs.

Light Stable Elemental Isotope Ratio Mass Spectrometry (IRMS) is a method, which allows to determine ratio of nitrogen isotopes in different plants and its parts and from its value it is possible to make conclusions about the source of nitrogen. The analyses were carried out with Nu Horizon IRMS at the University of Latvia, using certified inorganic reference materials USGS-40 and USGS-41 (L-Glutamic acid). The $\delta^{15}\text{N}$ values are expressed relative to air.

Obtained results show that the $\delta^{15}\text{N}$ value in faba beans from control plots is approximately 3 ‰ while in samples that was inoculated with rhizobia bacteria these values are in interval from 2–3 ‰ what indicates that for these plants more nitrogen is bonded from air (results tends closer to 0). The same situation was observed with seed of soya – $\delta^{15}\text{N}$ values in control plots were ~ 7 ‰ while in samples inoculated with rhizobia ~ 6 ‰.

INVESTIGATING THE AUTHENTICAL FINGERPRINT OF REGIONAL HONEYS: A NON-TARGET METABOLOMICS APPROACH

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The discrimination of organic, local and conventional production has been a critical topic of public discussion and constitutes a scientific issue. It remains a challenge to establish a correlation between the manufacturing practices and their effects on the composition of honey, especially the phenolic composition, since it defines the sensory and nutritional aspects. Polyphenols are a broad class of plant secondary metabolites which carry out several biological functions for plant growth and protection and are of great interest as nutraceuticals for their antioxidant properties. However, due to their structural variability and complexity, the mass-spectrometric analysis of polyphenol content in plant and food matrices is still an issue.

Thus, a liquid chromatography-electrospray ionization-quadrupole Orbitrap tandem mass spectrometric method was developed and used for target and suspect screening workflows, coupled with chemometrics for the identification of phenolic compounds and the discrimination between honeys of various floral origins and biotopes. For this study a pool of more than 300 authentic honey samples were collected from local producers from various regions of Latvia. Additionally, information was gathered directly from the producers about the geographical and floral origin of the samples, as well as the date of production and the biotope of origin.

The analysis method was initially optimized and evaluated for robustness to allow for generic sample preparation and reproducible analysis followed by high coverage of features in mass-spectrometric detection. The targeted quantification methodology was validated for 30 compounds and a semi-quantification strategy, based on chemical similarities, was introduced for the non-target suspects. Mass-spectrometric parameters were optimized in order to obtain a large set of diagnostic product ions for their high-confidence identification.

Following the optimization of analytical method and selection of appropriate standards for semi-quantification purposes, robust supervised models will be developed to discriminate between the floral honey types and the geographical locals. For example, partial least squares-discriminant analysis (PLS-DA) can score the MS features and select markers, however, the interpretation of results could be complex when the explained variances are too low giving little discriminative power to the PLS-DA model. In this case other supervised models will be applied, until satisfactory discrimination will be found. Models will be inspected by cross-validation analysis and external test sets to verify the correct class assignments.

For the use in prior workflow, customized local and online spectra databases will be allocated for unequivocal identification of mass-spectrometric features responsible for highest variances in the test data. The local databases will include flavonoids, phenolic acids, phenolic aldehydes, ellagitannins and proanthocyanidins and will be based on previous research [1].

References:

- [1] Cerrato, A., Cannazza, G., Capriotti, A. L., Citti, C., La Barbera, G., Laganà, A., ... & Cavaliere, C. A new software-assisted analytical workflow based on high-resolution mass spectrometry for the systematic study of phenolic compounds in complex matrices. *Talanta*, **2019**, 120573.

PREDICTION OF SOLID SOLUTION FORMATION AMONG CHEMICALLY SIMILAR MOLECULES USING CALCULATION OF LATTICE AND INTERMOLECULAR INTERACTION ENERGY

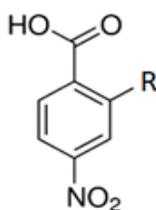
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Organic solids are able to form very wide range of crystalline structures of different compositions – including polymorphs, solvates, co-crystals and solid solutions (SS). In last decade, research of solid solutions has increased significantly and has become common in crystal engineering. While analysing solid solutions and their molecular packing, more attention is paid to structural aspects that promote and are responsible for the formation of solid solutions in two-component systems [1]. Both geometric and chemical aspects, such as molecule dimensions, symmetry, and intermolecular interactions, are important in understanding solid-state properties of all these phases [1, 2].

Several 2-substituted 4-nitrobenzoic acid (NBA) derivatives (Fig. 1) were selected as model compounds because of their availability and chemically similar structures, in which the different group/atom (R) does not significantly affect the dominant intermolecular interactions [2].



R = halogen atom (-Cl), hydroxyl group (-OH) or methyl group (-CH₃)

Fig. 1. Molecular structure of 2-substituted 4-nitrobenzoic acid

Quantum chemical calculations for lattice and intermolecular interaction energy were carried out to identify possible factors, which could be used in prediction of the formation of solid solutions in binary systems of chemically similar molecules, in this case – various nitrobenzoic acid derivatives [2, 3]. Meanwhile crystallization experiments were used to determine the experimental information about formation of solid solutions. Obtained crystalline phases were characterized by combined use of powder X-ray diffraction (PXRD) and differential scanning calorimetry (DSC) [3].

References:

- [1] Lusi, M. *Crystal Growth & Design*, **2018**, *18*(6), 3704–3712.
- [2] Corpinot, M. K., Guo, R., Tocher, D. A., Buanz, A. B. M., Gaisford, S., Price, S. L., Bučar, D. K. *Cryst. Growth Des.*, **2017**, *17*, 827–833.
- [3] Romasanta, A. K. S., Braga, D., Duarte, M. T., Grepioni, F. *CrystEngComm.*, **2017**, *19*, 653–660.

EFFECT OF CONDITIONS AND ADDITIVES ON THE POLYMORPH OBTAINED IN THE CRYSTALLIZATION OF 2-METHYL-4-NITROBENZOIC ACID

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The discovery and preparation of polymorphic forms are important steps in pharmaceutical manufacturing. Although often easier to prepare and handle, the more stable forms tend to have drawbacks, such as low bioavailability [1, 2]. In this case the drug should be taken in higher doses. However, the physical properties of a drug substance can be optimized by changing the crystalline structure. No general mechanism has been discovered to control crystallization of a particular polymorphic form if more than one polymorph can be obtained under similar or even identical conditions. The use of additives (templates) is one of promising approaches being investigated to allow such control by providing selective crystallization of one of known forms or even new polymorphs not obtained in the absence of additives [3, 4].

In this study 2-methyl-4-nitrobenzoic acid (2CH₃4NBA) was used as a model substance for study of crystallization control with additives, as it forms several polymorphic forms during the crystallization.

Firstly, 2CH₃4NBA was crystallized under different conditions by performing evaporation crystallization from different solvents in containers of different materials and size, and cooling crystallization with different temperature change rate. Secondly, crystallization in presence of several selected solid insets of different material, soluble and insoluble polymers as well as soluble molecular templates was tested. The resulting solid forms were described with powder X-ray diffraction and thermal analysis.

The most common outcome of the crystallization is mixture of different polymorphs. Crystallization in the presence of polyethylene glycol (PEG) from tetrahydrofuran, methanol and toluene resulted in formation of PEG inclusion complex. In the presence of solid insets formation of a mixture of polymorphs was observed less frequently than without them, but complete crystallization control was not achieved. Galvanized steel screw and copper rod insets did not function as templates but reacted chemically with 2CH₃4NBA. The studied templates mostly did not affect the resulting polymorphic form. The obtained results are in accordance with Ostwald's rule of stages, because faster crystallization gives a mixture of metastable forms, but slower crystallization gives the thermodynamically more stable forms.

Overall the results show that outcome of 2CH₃4NBA polymorphic form cannot be selectively controlled using the studied templates. This at least partly can be explained by the very high similarity of intermolecular interactions present in the crystal structures of both most frequently obtained polymorphs.

References:

- [1] Bauer, J., Spanton, S., Henry, R., Quick, J., Dziki, W., Porter, W., Morris, J. *Pharm. Res.*, **2001**, 18(6), 859–866
- [2] Barsky, I., Bernstein, J., Stephens, P. W., Stone, K. H. *New J. Chem.*, **2008**, 32(10), 1747–1753.
- [3] Kulkarni, S. A., Weber, C. C., Myerson, A. S., Host, J. H. *ter. Langmuir*, **2014**, 30(41), 12368–12375.
- [4] Srirambhatla, V. K., Guo, R., Price, S. L., Florence, A. J. *ChemComm.*, **2016**, 52(46), 7384–7386.

GEOCHEMICAL AND PHYLOGENETIC FACTORS AFFECTING ACCUMULATION OF MACRO AND TRACE ELEMENTS IN SEVERAL NATURAL PLANT SPECIES

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Until nowadays it is widely believed that plants require not more than 17 elements to fulfill their life cycles. Most of the elements are acquired from the soil. It is assumed that plants can also accumulate nonessential elements in smaller quantities. The biological significance of these elements is still unknown, although it may be assumed that all the elements that at this time is considered as nonessential have a certain role in some biological processes.

Nevertheless, the relative needs of many plant species in different trace elements are poorly understood yet. The effect of soil parameters in the rhizosphere zone of plants on the element accumulation in the plants are also not investigated well enough. The most important factors controlling concentrations of elements in plants are soil where the plants grow and taxonomical group of each plant. On the first look, it seems that bioavailability of one or another macro or trace element presented in the rhizosphere zone of a plant have a decisive role in the process of the element uptake by roots. However, the demand for the elements of one plant may differ in comparison with another plant species. In result, plants growing in the same soil and under the same conditions can differ slightly by the means of element concentrations.

During last years, researchers have studied the ability of different plant species to accumulate various metals and metalloids in the hope to find suitable ways to phytoextract toxic trace elements from contaminated soils. These experimental studies confirm the observation that different taxonomic groups and, moreover, even the plant species that are very close in the botanical classification can accumulate different amounts of nutrients or trace elements even if they grow in the same place. Differences become even more noticeable if we compare plants growing in the soils that differ by the concentration of various elements. It has been speculated that each plant species has developed a specific element composition, and that it reflects plant nutrient requirements rather than nutrient availability in the soil. This means that plants were able to elaborate an optimal range of nutrients typical for one or another plant species. This suggestion, however, has some unclear moments that should be explained.

In the conducted series of experiments, it was found out that different plant species differ widely in the ability to uptake various macro and trace elements even if they grow in the same place in same type of soil. Elemental composition of plants is typical for a plant species and can serve as an indicator of the plant taxon. The concentrations of different elements in the plant roots and leaves also depends on the soil type where the plant grow. The influence of both these factors on the elemental composition of a plant is probably almost the same. The contribution of soil to the accumulation process of different elements in the plant roots is more evident than in comparison to the elemental composition of the plant leaves.

STUDY OF MACRO AND TRACE ELEMENT FLOWS IN THE LEGUME- RHIZOBIA- SYMBIOTIC SYSTEM

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There is about 78% of nitrogen in Earths' atmosphere, but it is not available for most of the plants directly from atmosphere. Nitrogen is one of the crucial elements in every living form and most of all if not all nitrogen compounds are physiologically active. One of the ways to convert atmospheric nitrogen to form in which it is available for plants is by use of different legume and Rhizobia bacteria symbiosis. The aim of this study was to compare how the change in the nitrogen source impacts on the other element content in studied soya and faba beans.

Experiments were carried out with soybeans and faba beans. Seeds of soy were inoculated with commercial preparation of Rhizobia, control without inoculation just before sowing. Plants were analysed during flowering stage (stems and leaves) and after the harvest (seeds).

Seeds of faba beans before sowing were inoculated with an effective Rhizobia strain from the Rhizobia Collection of Latvia University of Life Sciences and Technologies, with commercial mycorrhizal fungi preparation, with rhizobia and mycorrhizal fungi, Control – without additional microorganisms.

Plants were sampled during flowering stage (shoots) and during harvest (seeds). Nodules were found on the roots of all plants, tough amount and size of nodules differs. Samples of seeds were air dried, but shoots were dried at 55 °C, and analyzed with inductively coupled plasma mass Spectrometry (ICP-MS). Microwave assisted acid digestion using trace grade nitric acid and hydrogen peroxide was applied for sample preparation. Total nitrogen content was determined using Kjeldahl distillation method (LVS EN ISO 5983-2:2009). Content of nitrogen and carbon in studied samples were also determined by using EuroVector EA3000 element analyzer.

Obtained results show that inoculating legume plants with Rhizobia strains not only change nitrogen uptake by plants but also changes other element content. Treatment of legume plants with Rhizobia causes decrease of P in seeds, also there is seen changes in elements (Fe, Mn) that are involved in nitrogen metabolism enzymes (cytochromes, nitrate reductase). Ca/Mg an K/Na ratios is also affected.

COMPUTATIONAL STUDY OF ASSOCIATION IN SOLUTION OF DIHYDROXYBENZOIC ACIDS: USE OF SELF-ASSOCIATION COMPUTATIONAL METHODOLOGY FOR FORMATION OF BINARY SYSTEMS

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Dihydroxybenzoic acids (diOHBA) are small organic molecules that have the ability to form a variety of polymorphic forms, hydrates, and solvates [1–5]. In this study all six diOHBA isomers and three salicylic acids (SA; benzoic acids with ortho-OH group) were studied – 2,3-diOHBA, 2,4-diOHBA, 2,5-diOHBA, 2,6-diOHBA, 3,4-diOHBA and 3,5-diOHBA, 5-nitroSA, 3-nitroSA, 3-methoxySA.

Crystal structures of anhydrate forms, hydrates and solvates of diOHBA found in Cambridge Structural Database (CSD) make it evident that dimeric motif is present in most cases and is the main motif of hydrogen bonding. Nevertheless, few other motifs that include COOH group were also found in structures of SA – heterotetramers with 2 diOHBA and two water molecules forming $R_4^4(12)$ as found in monohydrate of 3MeOSA (DIWNON01[6]) and associate with solvent molecule as found in 5-nitrosalicylic acid 1,4-dioxane (DXN) solvate (GUTNOY[7]). In order to evaluate the likelihood of existence of such motifs in solutions of diOHBA and studied SA, association energies of these associates and dimers in multiple mediums were compared. Used computational approach is already validated for molecular self-association and dimerization in solution [8, 9]. This study also allows to test if application of given methodology is possible in other situations than dimerization.

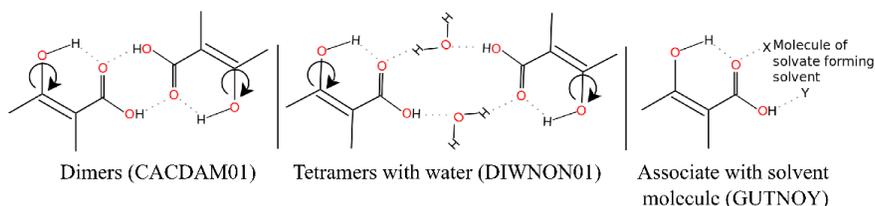


Fig. 1. Hydrogen bond motifs, CSD recodes and identification of flexible torsion angles

References:

- [1] Sarma, B., Sanphui, P., Nangia, A. *Cryst. Growth Des.*, **2010**, *10*(5), 2388–2399.
- [2] Adam, M. S., Gutmann, M. J., Leech, C. L., Middlemiss, D. S., Parkin, A., Thomas, L. H., Wilson, C. C. *New J. Chem.*, **2010**, *34*, 85–91.
- [3] Varughes, S., Desiraju, G. R. *Cryst. Growth Des.*, **2010**, *10*(9), 4184–4196.
- [4] Braun, D. E., Karamertzanis, P. G., Price, S. L. *Chem. Commun.*, **2011**, *47*, 5443–5445.
- [5] Braun, D. E., Karamertzanis, P. G., Arlin, J., Florence, A. J., Kahlenberg, V., Tocher, D. A., Griesser, U. J., Price, S. L. *Cryst. Growth Des.*, **2011**, *11*(1), 210–220.
- [6] Montis, R., Hursthouse, M. B. *CrystEngComm.*, **2012**, *14*, 5242.
- [7] Kumar, V. S. S., Nangia, A., Kirchner, M. T., Boesegutnoy, R. *New J. Chem.*, **2003**, *27*, 224.
- [8] Di Tommaso, D. *CrystEngComm.*, **2013**, *15*, 6564–6577.
- [9] Redivo, L., Anastasiadi, R. M., Pividori, M., Berti, F., Peressi, M., Di Tommaso, D. Resimini, M. *Phys. Chem. Chem. Phys.*, **2019**, *21*, 4258–4267.

HPLC STUDY OF TETRAPEPTIDE ENANTIOMERIC SEPARATION ON CROWN ETHER BASED CHIRAL STATIONARY PHASE

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Over the past decade, peptide drug discovery has experienced a revival of interest as the pharmaceutical industry has come to appreciate how this class of compounds can be an excellent complement or even a preferable alternative to small molecule drugs [1]. The essential biological functions of peptides depend on peptide stereochemistry. Amino acids exist in D and L forms and as a result the peptide can exist as several stereoisomers with different biological properties. Therefore, chiral separation of peptides is an important challenge in the biological and medical sciences and necessary for enantiomeric purity control for the pharmaceutical industry.

Among the numerous commercially available chiral stationary phases (CSPs), crown ether-based CSPs have been proven to be very effective for the resolution of chiral analytes containing primary amino groups [2]. However, a search of literature indicates that there are only a few articles containing dipeptide resolution on crown ether-based CSPs. In order to clarify the prospects of using crown ether-based CSPs for enantioseparation in more complex systems, e.g. tetrapeptide, Tyr-Arg-Phe-Lys-NH₂ (LDLL isomer also known as μ -opioid receptor agonist DALDA) was chosen as a model structure and all 16 stereoisomers were synthesized during this study.

Chromatographic behaviour of each Tyr-Arg-Phe-Lys-NH₂ stereoisomer was studied on crown ether CSP based on (R)-(3,3'-diphenyl-1,1'-binaphthyl)-20-crown-6 as chiral selector (*CROWNPAK CR-1 (+)*). Different chromatographic conditions, e.g. organic and acidic modifier content in aqueous mobile phase, as well as column temperature were tested in order to improve enantioselectivity. As a result, baseline separation of all 8 tetrapeptide enantiomer pairs was achieved under isocratic elution mode. The retention factors formed "U-shaped" plots against MeCN content in MP with an increased analyte retention at high MeCN content. These results indicate that multiple separation mechanisms can be possible based on MeCN concentration in mobile phase.

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References:

- [1] Henninot, A., Collins, J. C., Nuss, J. M. *J. Med. Chem.*, **2018**, 61(4), 1382–1414.
- [2] Hyun, M. H. *J. Chromatogr. A*, **2016**, 1467, 19–32.

EFFECT OF ACIDS ON THE EXTRACTION OF NATURAL PIGMENTS FROM DYED WOOL

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Natural dyes of plant or animal origin have been used until the mid-nineteenth century. Identification of pigments and dyes is a useful source of knowledge on the cultural history and technology of textile craft. The most commonly used method for natural dyes analysis is HPLC with UV-Vis and MS detection [1]. The HPLC analysis requires the extraction of the dyes from textile fibres. The traditional extraction method is hydrolysis with 37% HCl/MeOH/H₂O/ (2:1:1, v/v/v). The disadvantage of method is decomposition of flavonoids (aglycon + sugar derivatives), the most widespread used as source of yellow colour [2]. For this reason, a method with milder extraction conditions is required.

The object of this study is wool that was dyed with crushed apple-tree leaves, as mordant was used potassium aluminium sulphate. In the research a traditional method was modified changing extraction conditions. Concentrated hydrochloric acid (37%) was replaced by weak organic acids: formic acid ($pK_a = 3.75$) and acetic acid ($pK_a = 4.756$). Diluted hydrochloric acid ($c = 1M$) was used to compare effect of concentration of acid on extraction process. Extraction was performed at 100 °C temperature or using ultrasound treatment (25 °C). The analyses were performed with UHPLC/MS method to identify chemical compounds in extracts of dyed wool.

References:

- [1] Ahmed, H. E., Tahoun, I. F., Elkhloy, I., Shehata, A. B., Ziddan, Y. *Dyes Pigm.*, **2017**, 145, 486–492.
- [2] Valianou, L., Karapanagiotis, I., Chryssoulakis, Y. *Anal. Bioanal. Chem.*, **2009**, 395, 2175–2189.

BERYLLIUM OXIDATION IN AIR AT ELEVATED TEMPERATURES DEPENDING ON THE RELATIVE HUMIDITY OF AIR

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Beryllium is an important material of the environmentally friendly nuclear fusion; it is present in the vacuum vessel and has direct contact with isotope plasma as well as is proposed for the water-cooled pebble bed blanket as neutron multiplier [1]. In the case of loss of vacuum accidents [1], interaction between beryllium and hot and/or humid air could be possible (e.g., beryllium oxidation) [2].

In the research oxidation processes of beryllium depending on the relative air humidity have been studied with means of thermogravimetric / differential thermal analysis. The oxide layer was analysed with scanning electron microscopy.

The analyses were carried out with TG/DTA SEIKO Exstar 6300, heating rate 10 °C/min, up to 1200 °C and SEM-EDX Hitachi S-480. Beryllium pebbles (1 mm in diameter, mass ~ 1 mg) produced by rotating electrode process [2] were heated in air flows of different relative humidity (RH), dry air flow 2–6%, air flow 40–50%, humid air flow 94–96% RH, as well as in air without flow (38–57% RH).

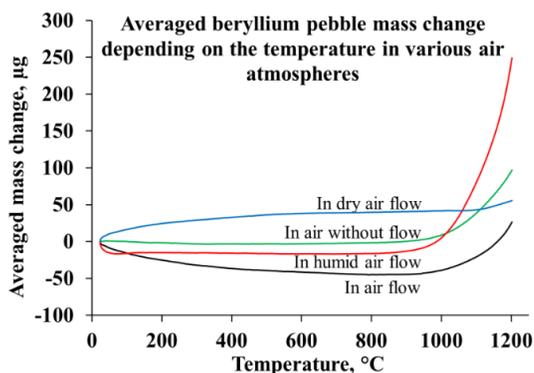


Fig. 1. Averaged mass changes of beryllium pebbles

Heating beryllium in RH < 50% the average mass increases by no more than 100 µg (< 20% of the initial mass) whereas increasing the level of humidity above 50%, the mass of the beryllium increases by 250 µg (28 ± 7%). The mass increase corresponds to the formation of the BeO layer during reactions with O₂ and H₂O present in the air. The elevated humidity speeds up the oxidation process which should be taken into account for further studies.

References:

- [1] Nakamura, M. M., Kim, J.-H., Nakamichi, M., Someya, Y., Tobita, K., Sakamoto, Y., Hiwatari, R. *Fusion Engineering and Design*, **2018**, 136, B, 1484–1488.
- [2] Pajuste, E., Kizane G., Avotiņa L., Zariņš A. *Journal of Nuclear Materials*, **2015**, 465, 293–300.



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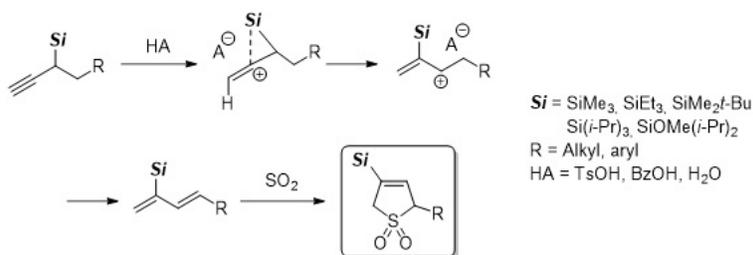
ORGANISKĀS ĶĪMIJAS SEKCIJA

SYNTHESIS OF SILYL SULFOLENES IN TANDEM TRANSFORMATION FROM PROPARGYL SILANES IN LIQUID SO₂

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It is known that silicon can stabilize reactions of vinyl, allyl, allenyl and propargyl silanes, that proceeds *via* β -silyl carbenium ion and is more recognized as β -silicon effect. Several studies on the possible mode of stabilization from silicon shows two distinct pathways that may occur through vertically (e.g. hyperconjugation) or non-vertically (e.g. formation of silylium ion) stabilized carbocations [1]. Therefore, formation of cyclic silylium ion in combination with other stabilizing effects explains, possibility of 1,2-silyl migration.



Previously we have reported the use of propargylsilanes in the synthesis of silyl dienes and indenes by the catalytic amounts of strong Brønsted acids (TfOH, Tf₂NH, Tf₃CH) that involves 1,2-silyl shift [2]. Herein we report the use of liquid sulfur dioxide for this transformation as highly polar and Lewis acidic reaction media which offers possibility to use weaker acids (e.g. BzOH, TsOH). Moreover, in a tandem cheletropic addition process silyl sulfolenes are obtained from the *in situ* formed dienes.

Supervisor: Dr. chem. M. Turks

References:

- [1] Labert, J. B., Zhao, Y., Emblidge, R. W., Salvador, L. A., Liu, X., So, J.-H., Chelius, E. C. *Acc. Chem. Res.*, **1999**, 32, 183.
- [2] Puriņš, M., Mishnev, A., Turks, M. *J. Org. Chem.*, **2019**, 84, 3595.

SYNTHESIS OF ENANTIOENRICHED CYANOHYDRINS

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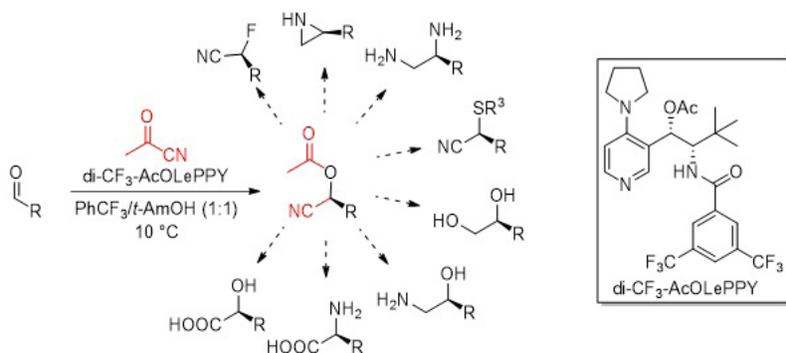
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Cyanohydrins are bifunctional compounds containing nitrile and alcohol groups at the same carbon atom. Both cyanohydrin functional groups can be easily modified giving access to many different valuable organic compounds, for example amino acids, hydroxy acids, aziridines, amino alcohols, diamines and diols [1].

Synthesis of chiral cyanohydrins is usually achieved using chiral Tisalen complexes as catalysts [1]. However, Ti-salen catalysts feature high molecular mass, which makes them less attractive for the large scale applications. To address this issue, we plan to develop the asymmetric synthesis of enantiomerically pure cyanohydrins using chiral DMAP-catalysed dynamic kinetic resolution approach. To this end a variety of chiral DMAP catalysts have been screened. The best enantioselectivity (30% ee) was achieved using di- CF_3 -AcOLePPY catalyst at 10 °C in $\text{PhCF}_3/t\text{AmOH}$ (1:1) mixture.



Supervisor: Dr. chem. Artis Kinēns^{1,2}

References:

[1] North, M., Usanov, D. L., Young, C. *Chem. Rev.*, **2008**, 108, 5146.

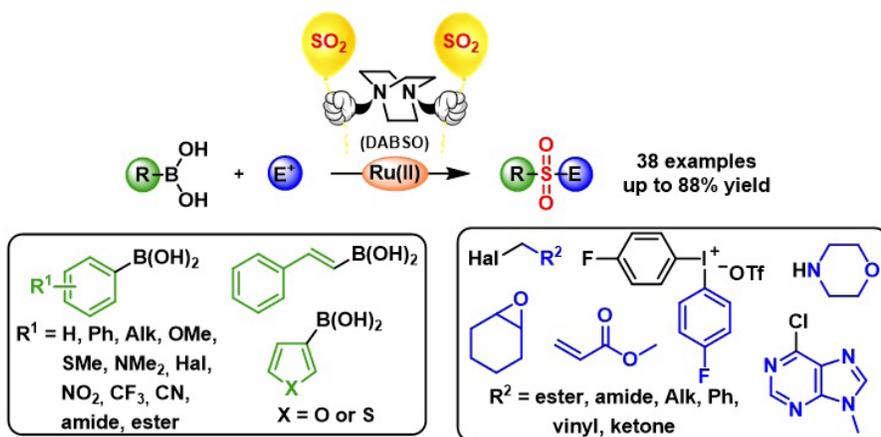
RU(II)-CATALYZED SULFINATION OF BORONIC ACIDS: NOVEL MULTI-COMPONENT PROCEDURE TOWARDS SULFONES

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Sulfones are valuable intermediates and building blocks in organic synthesis applied to obtain biological active molecules, as well as functional materials. During the last decades, great attention has been paid to the synthesis of sulfones *via* one-pot multi-component procedures that employ a simple sulfonyl source (SO_2 , DABSO, MSO_3 or $\text{M}_2\text{S}_2\text{O}_5$) and two sulfur free reactants. So far, application of transition metal catalysis for this type of reactions has been demonstrated by employing Pd(II), Au(I), Cu(I), Co(II) and Ni(II) catalytic systems [1–3].

We have developed the first Ru(II)-catalyzed sulfonylative cross-coupling reaction starting from (het)aryl- or alkenyl boronic acids and DABSO as a SO_2 surrogate. Initial transmetalation-sulfination steps proceed in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ (5 mol%) and Et_3N in methanol at 100 °C. Next, generated sulfinate salt intermediate can be easily quenched by various types of electrophiles such as alkyl halides, epoxides, Michael acceptors and λ^3 -iodanes in moderate to good yields.



Supervisor: prof. Dr. chem. Māris Turks

References:

[1] Emmett, E. J., Willis, M. C. *Asian J. Org. Chem.*, 2015, 4, 602.

AZIDE-TETRAZOLE EQUILIBRIUM MEDIATED S_NAr REACTIONS OF ARYLTHIOPURINE DERIVATIVES

Andris Jeminejs

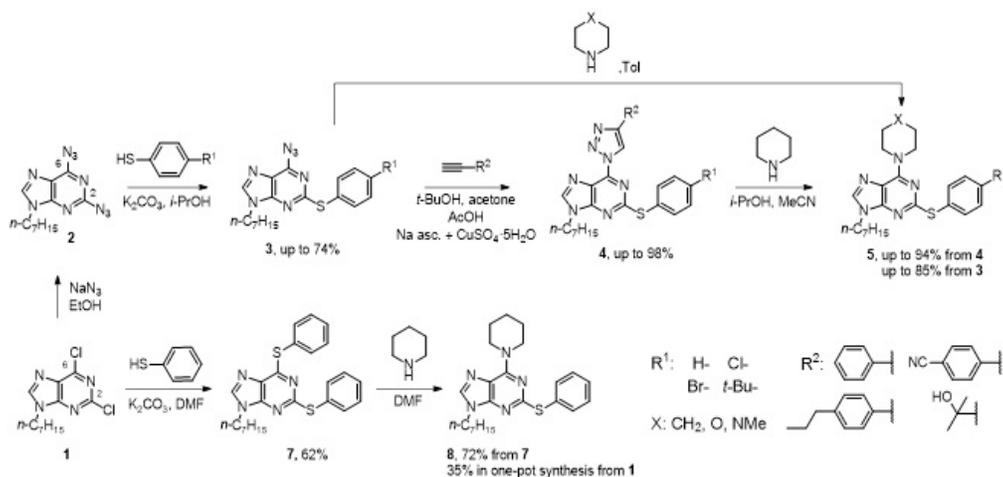
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Several purine based compounds that contain both arylthio and amino moieties have been established as potential medicine in the treatment of adenocarcinoma, chronic lymphocytic leukemia and other carcinogenic disorders [1, 2]. Till now purine derivatives with arylthio and amino groups at C(2) and C(6) positions were not synthesized.

Several synthetic approaches for the synthesis of 6-amino-2-arylthiopurine derivatives **5** and **8** were developed. 2,6-Diazidopurine derivative **2** was proven to be a valuable starting material for introduction of arylthio group at C(2) position of purine. Both triazoles and thiophenolates can be used as good leaving groups in nucleophilic aromatic substitution reactions with amines giving products in yields up to 94% and 85%, respectively.



Compound **3** exists in a broad, easily shifted azide-tetrazole equilibrium that affects the regioselectivity of S_NAr reaction with amines, providing the target products **5** with good yields up to 85%.

This work was supported by the Latvian Council of Science grant No. LZP-2018/2-0037.

Supervisor: Dr. chem. Ē. Bizardēna, Dr. chem. I. Novosjolova

References:

- [1] Speranza, G. et al. *Invest. New Drugs*, **2018**, 36(2), 230–239.
- [2] Hei, Y. et al. *Bioorg. Med. Chem.*, **2018**, 26(8), 2173–2185.

SYNTHESIS OF NOVEL ASPARTIC-PROTEASE INHIBITORS FOR TREATMENT OF MALARIA

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Malaria is a life threatening infectious disease, which is widespread in tropical and subtropical regions. Malaria parasite is becoming more resistant against almost every known anti malarial drug, so there is a growing need for new and effective drugs.

Previous results show that compound **1** is a potent inhibitor of haemoglobin-degrading enzymes (aspartic proteases, plasmepsins, Plm) [1]. Computer docking of the enzyme and the inhibitor **1** gave information about possible interactions and bioactive conformations. Based on this information, macrocyclic analogs **2–7** were synthesised using new scheme, which was designed specifically for the synthesis of these analogs.

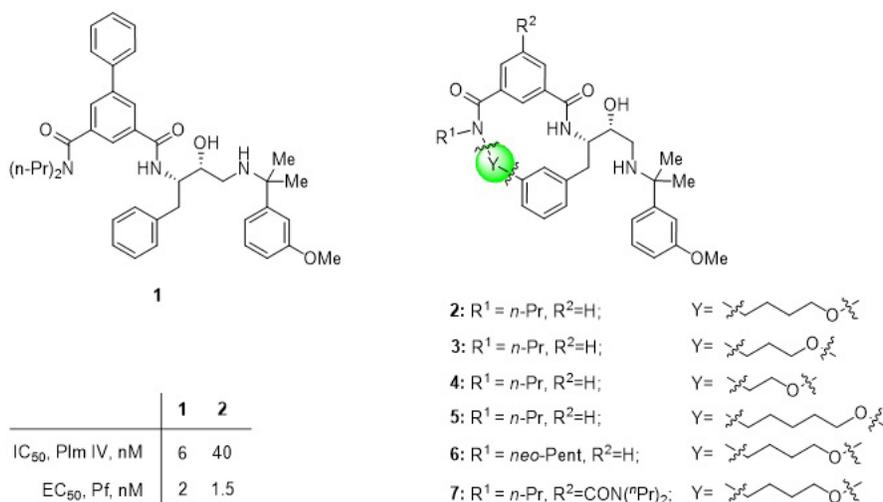


Fig. 1. Known inhibitor **1** and macrocyclic analogs **2–7**

According to the results of bioassays for inhibitory activity (IC₅₀, LIOS) and potency (EC₅₀, *P. falciparum*, Francis Crick Institute), macrocyclic analogs have comparable biological activity to the non-macrocyclic inhibitor **1**.

Supervisor: Dr. chem. E. Suna^{1,2}

Reference:

- [1] Zogota, R., Kinena, L., Withers-Martinez, C., Blackman, M. J., Bobrovs, R., Pantelejevs, T., Kanepe-Lapsa, I., Ozola, V., Jaudzems, K., Suna, E., Jirgensons, A. *Eur. J. Med. Chem.*, **2019**, 163, 344–352.

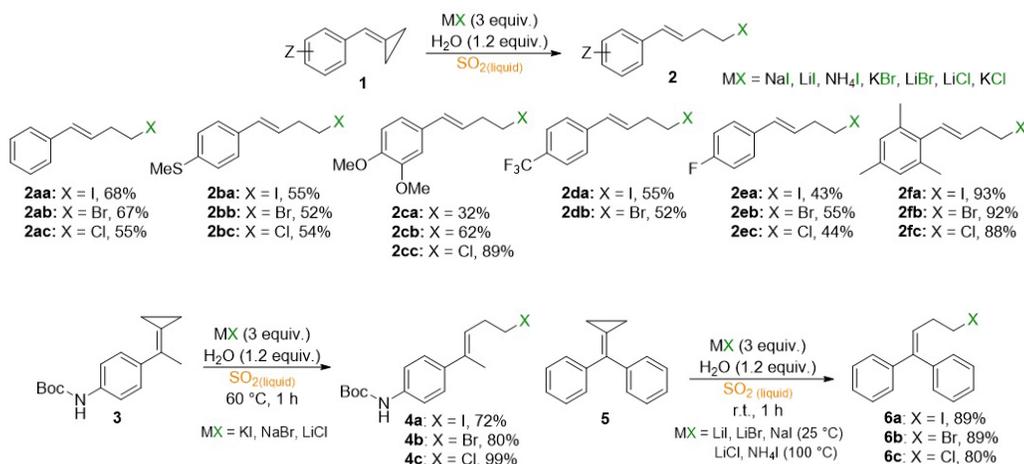
HOMOALLYLHALIDE SYNTHESIS FROM CYCLOPROPYLIDENES IN LIQUID SO₂ MEDIUM

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Methylenecyclopropanes (MCPs) are easily accessible yet highly strained and reactive building blocks.¹ MCP can be readily opened under transition metal or Lewis acid catalyzed conditions.² We have hypothesized that a highly polar and Lewis acidic reaction medium could facilitate the ring opening of MCPs with simple nucleophiles. We have recently shown that liquid sulfur dioxide perfectly fulfils the aforementioned solvent requirements.³ Additionally, it dissolves well inorganic salts.⁴ Here we report ring opening of MCPs in liquid SO₂ with I and II group metal halides.

For scope of group I metal catalysts we chose benzyldenecyclopropane **1** as model substrate. From results we found cation activity order: Li⁺ > Mg²⁺ > Cs⁺ > K⁺ > Na⁺ > NH₄⁺ and anion activity order: I⁻ > Br⁻ > Cl⁻. Various substituted MCP opening products **2a–2f** were obtained in good yields. The developed method is sufficiently mild against acid labile protecting groups and *N*-Boc protected products **4a–c** were obtained in excellent yields.



Supervisor: Dr. chem. M. Turks

References:

- [1] a) Shi, M., Shao, L.-X., Lu, J.-M., Wei, Y., Mizuno, K., Maeda, H. *Chem. Rev.*, **2010**, *110*, 5883; b) Brandi, A., Cicchi, S., Cordero, F. M., Goti, A. *Chem. Rev.*, **2014**, *114*, 7317.
- [2] Shi, M., Lu, J.-M., Wei, Y., Shao, L.-X. *Acc. Chem. Res.*, **2012**, *45*, 641.
- [3] a) Suta, K., Turks, M. *ACS Omega*, **2018**, *3*, 18065; b) Posevins, D., Suta, K., Turks, M. *Eur. J. Org. Chem.*, **2016**, 1414.
- [4] a) Lugiņina, J., Turks, M. *Synlett*, **2017**, *28*, 939; b) Lugiņina, J., Uzuleņa, J., Posevins, D., Turks, M. *Eur. J. Org. Chem.*, **2016**, 1760.

LINKER DESIGN ENABLES ULTRA-LONG PHOSPHORESCENCE

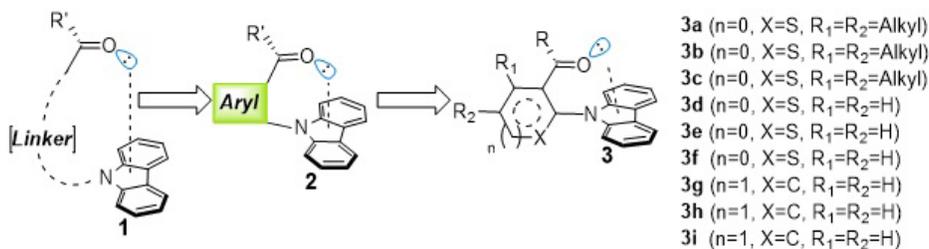
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Metal containing compounds commonly exhibit phosphorescence, however their high manufacturing costs, toxicity and relatively low stability limits their practical applications. In light of these limitations purely organic phosphorescent materials have acquired large interest due to their low toxicity, relatively cheap production and almost infinite design possibilities [1]. Phosphorescence in purely organic compounds is a rare phenomenon because of the lack of spin-orbit coupling. Spin-orbit coupling can indirectly lead to a more efficient formation of excited triplet states. Excited triplet states are characterized by relatively long lifetimes which in turn results in a long emission (from μs to s) which is called phosphorescence. Phosphorescence in purely organic compounds can be achieved by creating intermolecular interactions that restrict the motion of molecules allowing for the long-living excited triplet state to decay emitting a photon. Other possible methods to achieve phosphorescence includes the use of heavy atom effect [2] or introduction of a carbonyl group in the proximity of an aromatic cycle [3].

Our goal was to design a motif where the carbonyl group is in close proximity to the carbazole moiety. To avoid the lack of intermolecular interaction predictability in the crystal lattice, we designed motif **1**. It could position the carbonyl group near the carbazole moiety in an intramolecular fashion promoting phosphorescence. We envisioned that the linker in **1** could help orient carbazole π -system and carbonyl group in such a way to achieve the desired lone pair- π intramolecular interaction. If the linker in **2** was an aromatic substructure then it would allow for such conformation. To this end we designed **3** and synthesized **3a-i** in which the phenyl or thiophene aromatic rings act as a linker.



Supervisor: Dr. chem. prof. Edgars Sūna, M.S. chem. Kaspars Leduskrasts

References:

- [1] Mukherjee, S., Thilagar, P. *Chem. Commun.*, **2015**, 51, 10988–11003.
- [2] Bolton, O., Lee, K., Kim, H., Lin, K. Y., Kim, J. *Nature Chem.*, **2011**, 3, 205–210.
- [3] Zhao, W., He, Z., Lam, J. W. Y., Peng, Q., Ma, H., Shuai, Z., Bai, G., Hao, J., Tang, B. Z. *Chem.*, **2016**, 1, 592–602.

SYNTHESIS OF α,β -UNSATURATED ARYLSULFONAMIDES

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Carbonic anhydrases (CA) are zinc-containing enzymes which provide pH regulation in cells and control transport of carbon dioxide. There are 15 isoforms of α -CA found in human body. However, only CA IX and XII are highly expressed in tumor cells, and therefore selective inhibition of these isoforms is required [1, 2].

Previously, it was found that 1,2-benzoxathiine 2,2-dioxides (**1**) are selective inhibitors of CA IX and XII [3–6]. 1,2-Benzoxathiine 2,2-dioxides are prodrugs. In the active site of CA they are converted to α,β -unsaturated sulfonic acid derivatives **2** by enzyme mediated hydrolysis [5]. In a search for new inhibitors we designed α,β -unsaturated vinyl sulfonamides **3**, which can be considered as bioisosteres of sulfonic acids **2**.

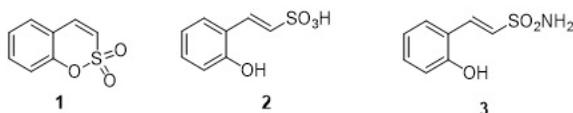
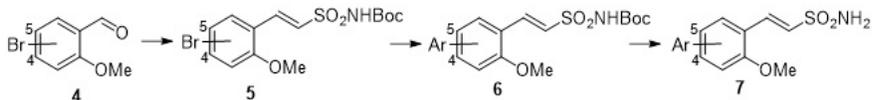


Figure 1. 1,2-Benzoxathiine 2,2-dioxide (**1**), sulfonic acid **2** and α,β -unsaturated arylsulfonamide **3**

The key intermediates α,β -unsaturated sulfonamides **5** were prepared from commercially available benzaldehyde derivatives **4** by Horner-Wadsworth-Emmons reaction. Following Suzuki reaction with aryl boronic acids gave biaryl derivatives **6**. After elimination of Boc-protecting group desired α,β -unsaturated arylsulfonamides were obtained.



Scheme 1. Synthesis of α,β -unsaturated arylsulfonamides

Supervisor: Dr. chem. A. Grandāne¹

References:

- [1] Supuran, C. T. *Curr. Pharm. Des.*, **2010**, *16*, 3233–3245.
- [2] Aterio, V., Fiore, A., D'Ambrosio, K., Supuran, C. T., De Simone, G. *Chem. Rev.*, **2012**, *112*, 4421–4468.
- [3] Tars, K., Vullo, D., Kazaks, A., Leitans, J., Lends, A., Grandane, A., Zalubovskis, R., Scozzafava, A., Supuran, C. T. *J. Med. Chem.*, **2013**, *56*, 293–300.
- [4] Grandane, A., Tanc, M., Zalubovskis, R., Supuran, C. T. *Bioorg. Med. Chem.*, **2014**, *22*, 1522–1528.
- [5] Grandane, A., Tanc, M., Mannelli, L. D. C., Carta, F., Ghelardini, C., Zalubovskis, R., Supuran, C. T. *J. Med. Chem.*, **2015**, *9*, 3975–3983.
- [6] Grandane, A., Tanc, M., Zalubovskis, R., Supuran, C. T. *Bioorg. Med. Chem.*, **2015**, *23*, 1430–1436.
- [7] Reuter, D. C., McIntosh, J. E., Guinn, A. C., Madera, A. M. *Synthesis*, **2003**, *15*, 2321–2324.

SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF SUBSTITUTED PURINE-CARBAZOLE CONJUGATES

Armands Sebris

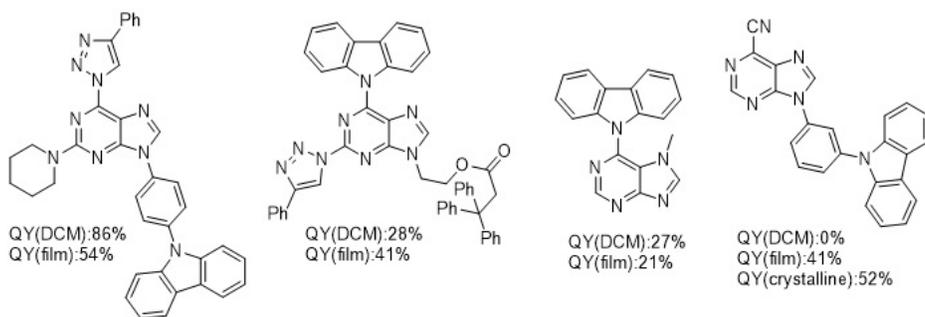
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Earlier we reported the synthesis of fluorescent purine derivatives containing 1,2,3-triazolyl electron withdrawing groups and aliphatic amine electron donating groups at purine C(2) and C(6) positions and their photophysical properties [1]. This work was followed up by modification at purine N(9) position to increase amorphous properties of the fluorescent compounds which was achieved by introducing a trityl moiety there [2].

In this work we investigated the use of carbazole as an electron donating group in electron deficient purine systems and studied photophysical properties of such compounds. The synthetic routes for introduction of carbazole moiety at purine C(6) and N(9) positions and various electron withdrawing groups at purine C(2) and C(6) positions were designed. The photophysical properties were studied in the solutions, in the films and in some cases in the crystalline phase. Quantum yields reached up to 86% in DCM, up to 54% in the films, and up to 52% in the crystalline phase.



This work was supported by ERDF project Nr. 1.1.1.1/16/A/131. Dr. K. Traskovskis and Dr. A. Vembris are acknowledged for the photophysical measurements and calculations.

Supervisors: Dr. chem. M. Turks, Dr. chem. I. Novosjolova

References:

- [1] Šišuljns, A., Bucevičius, J., Tseng, Y.-T., Novosjolova, I., Traskovskis, K., Bizdēna, Ē., Chang, H.- T., Tumkevičius, S., Turks, M. *Beilstein J. Org. Chem.*, **2019**, *15*, 474–489.
- [2] Traskovskis, K., Mihailovs, I., Tokmakovs, A., Kokars, V., Rutkis, M. *Proceedings of SPIE*, **2012**, *8434*: Nonlinear Optics and Applications VI, 1.

FIVE-MEMBERED HETEROCYCLES AS LINKERS FOR CATIONIC AMPHIPHILIC LIPID ANALOUGES

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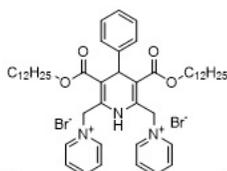
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Liposomes and other types of nanoparticles have been extensively studied as innovative materials for the delivery of DNA, RNA, drugs and as different nanoparticles for transmembrane delivery. The use of lipids and their synthetic analogues in medicine can also significantly improve the effects of well-known drugs and improve bioavailability of the drugs.

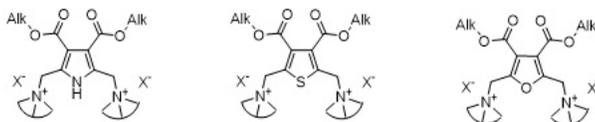
This work is based on previous studies of cationic amphiphilic 1,4-dihydropyridine (1,4DHP) derivatives [1, 2]. According to aforementioned studies, 1,4-DHP derivatives can act as gene delivery agents and could possess higher gene transfection activity compared to well known liposomal and polymer gene delivery agents – DOTAP and PEI 25.

Our focus is on the use of other heterocyclic systems as linkers between hydrophilic and lipophilic parts. Our research is to design five-membered heterocycle derivatives – pyrrole, thiophene and furan, which are well known for their biological activities. To prepare and characterize properties of liposomes formed by original synthetic and natural lipids and their compositions; to estimate the relationships between lipid-membrane interaction.

Bringing biologically active fragment to the transport molecules could result not only in improvement of transport function but also in the protection of the organism.



1,4-DHP amphiphile with higher gene transfection activity compare to DOTAP and PEI 25



Targeting compounds

Supervisor: Dr. chem. Kārlis Pajuste²

References:

- [1] Hyvönen, Z., Plotniece, A., Reine, I., Chekavichus, B., Duburs, G., Urtti, A. *Biochim. Biophys. Acta, Biomembr.*, **2000**, 1509, 451–466.
- [2] Pajuste, K., Hyvönen, Z., Petrichenko, O., Kaldre, D., Rucins, M., Cekavicus, B., Ose, V., Skrivele, B., Gosteva, M., Morin-Picardat, E., Plotniece, M., Sobolev, A., Duburs, G., Ruponen, M., Plotniece, A. *New J. Chem.*, **2013**, 37, 3062–3075.

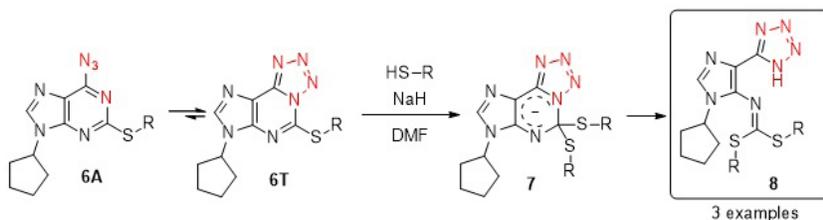
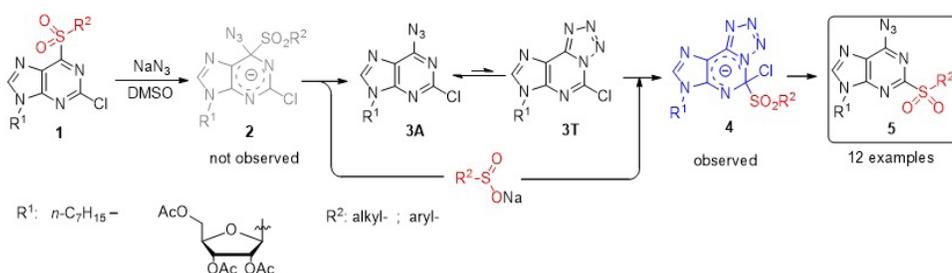
MEISENHEIMER COMPLEXES IN SYNTHESIS AND TRANSFORMATIONS OF AZIDOPURINE DERIVATIVES

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Purine derivatives are widely studied due to their biological properties. They are already being used in treatment of cancer and other malignancies [1, 2].

We have observed a sulfonyl group dance when substrate **1** was treated with NaN_3 . The transformation which lead to product **5** can be explained by azido-tetrazolo tautomerism. The latter activates purine cycle towards $\text{S}_{\text{N}}\text{Ar}$ reaction at C2. Reaction mechanism and kinetics were investigated using NMR experiments, ^{15}N labelling and FTIR analysis.



Current research now focuses on investigation and optimization of purine ring opening reaction. The reaction can be explained by the azido-tetrazolo tautomerism. It appears that the tetrazole is a better leaving group from the Meisenheimer complex **7**.

Supervisors: Dr. chem. M. Turks, Dr. chem. I. Novosjolova

This work was supported by the Latvian Council of Science grant No LZP-2018/2-003.

References:

- [1] Sahasranaman, S., Howard D., Roy S. *Eur. J. Clin. Pharmacol.*, **2008**, 64, 753–767.
- [2] Gruzdev, D. A., Musiyak, V. V., Levit, G. L., Krasnov, V. P., Charushin, V. N. *Russ. Chem. Rev.*, **2018**, 87(6), 604–618.

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