POSTER SESSION II

JUNE 12th, 2014

CHAIRPERSONS:

Natalia Vorobets and Grzegorz Zadora

1.

DENDROLIMUS PINI – FIRST RESULTS OF ANALYTICAL AND BEHAVIORAL STUDIES

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Caterpillars of pine-tree lappet moth, *Dendrolimus pini*, are the most dangerous defoliators of pine trees in Poland. Feeding on pine needles, they destroy the assimilation apparatus and weaken the trees which become vulnerable to secondary pests. The straightforward consequence of the damage is death of pine forests. In the post-war Poland, there were 8 gradations of this folivore. The two largest took place in the mid 90-ties and from 2007 to 2008. To prevent the damage, about 105 000 ha of pine forest were sprayed with chemical pesticides in 1993-1995, and 90 000 ha – in 2007-2008. A new large gradation of pine-tree lappet moth started in 2011, so in 2012 more than 56 000 ha of pine forest were preventively sprayed.

The aim of the project is to improve a synthetic analogue of a sexual pheromone of pine lappet moth (*Dendrolimus pini*) and to develop a method for its use in forest protection. Pheromone lures available so far are based on substances discovered in the early 1980s. They were tested in many countries and appeared rather inefficient. Using modern analytical and bioanalytical techniques, such as gas chromatography hyphened to ion trap mass spectrometry, FID detection and electroanthenography, we have started to determine an effective composition of the pheromone mixture, and later to synthesize all its stereocomponents. Then, we intend to determine: a) the optimal doses of the lure components by laboratory and field tests, b) the best type and form of a dispenser, c) the most effective trap type, and d) the optimal height for traps location. Finally, we plan to define: a) how to use the optimal trap-attractant combination for detecting the presence of *D. pini* in pine stands, and b) the methodology of determining the culmination of *D. pini* swarming period that can be used in the forest protection practice.

2.

INSIGHT INTO CHEMISTRY OF ATMOSPHERIC AEROSOL BY LIQUID CHROMATOGRAPHY WITH TANDEM MASS SPECTROMETRIC DETECTION

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Atmospheric aerosol is defined as a complex mixture of solid and liquid particles of minute diameters (d < 10 μm) suspended in the air. –They significantly influence the Earth's climate by scattering or absorbing the sunlight and deteriorate the human health. The adverse effect of aerosol particles results from their inhalation into the respiratory tract and easy deposition therein which causes asthma and cardiovascular diseases. According to data from the World Health Organization, the air pollution reduces by a year or more the life expectancy for people living in European cities [1]. On the other hand, aerosols play an important role in the chemistry of the atmosphere and significantly contribute to the climate change through an array of physicochemical processes the understanding of which is still in its infancy [2] and warrants continuous multidisciplinary research.

One of relevant pathways of the atmospheric aerosol formation is the oxidation of volatile organic compounds~~,~~ emitted by living vegetation~~,~~ with the atmospheric radical oxidants (i.e., ozone, $OH^{\cdot}$, $NO_3^{\cdot}$, $SO_4^{\cdot-}$), followed by further processing of low-volatility products. In the presented study we have evaluated the role of the crotonic acid in the formation of aerosol particles in the laboratory framework. The crotonic acid is one of the unsaturated C_4 plant volatiles playing an important role as an allopathic agent. On the other hand, the crotonic acid bears the C=C–C=O moiety, which increases its chemical reactivity towards radical species. This makes the crotonic acid a likely source of atmospheric aerosol particles, so far unrecognized.

In this work we applied a self-designed simulation chamber to evaluate the fate of crotonic acid in aqueous-phase solutions containing sulphoxy radicals and to follow it by an online monitoring using a mass spectrometric detection. In the poster, we will present the first results of the chemical characterisation of the unknown product from the crotonic acid oxidation obtained using a reversed-phase liquid chromatography/electrospray triple quadruple mass spectrometry, and additionally, MRM modes.

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3.

Application of gas chromatography in a lab-scale coal gasification system simulating use of High Temperature Reactor excess heat for synthesis gas production

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Gasification as an alternative to combustion offers increased efficiency, lower negative environmental impact and wider application range of the main product – synthesis gas – in power generation and chemical synthesis. Nuclear energy may also be considered as one of the ways of mitigation of global warming resulting from GHG emission from energy systems. Highly efficient fossil fuel utilization in energy sector may be also combined with an application of excess heat from nuclear reactors within a coal-nuclear synergy concept.
The paper presents the experimental study of application of simulated High Temperature Reactor (HTR) excess heat in allothermal coal gasification to synthesis gas. The heat was applied in pre-heating of gasification agents, such as oxygen, air and steam in a laboratory scale installation of the Laboratory of Advanced Energy Technologies of the Department of Energy Saving and Air Protection, Central Mining Institute. The main element of the test stand is a fixed bed reactor of a volume of approximately 0.8 L heated with a resistance furnace. The installation is also equipped with an additional heating system for gasification agents, simulating the utilization of the excess HTR heat.
Qualitative and quantitative analyses of dry and cooled product gas were performed with application of a two-channel gas chromatograph Agilent 3000A and a flow meter, respectively. In the gas chromatograph a PLOT U column ($8 \cdot 10^{-3}$ x $0.32 \cdot 10^{-3}$ m) with thermal conductivity detector (TCD) for determination of content of carbon dioxide and other compounds of 2÷5 carbon atoms in a molecule and analytical column MS5A PLOT ($10 \times 0.32 \cdot 10^{-3}$ m) with thermal conductivity detector (TCD) for determination of hydrogen, nitrogen, carbon monoxide and methane content in gas analyzed were applied.

4.

Gas chromatography application in steam co-gasification of coal and biowaste

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Waste biomass is a significant element of renewable energy balance in many countries. Research efforts are, however, still required to make its utilization more efficient. This may be achieved for example with an application of gasification technologies of higher efficiency and lower emission of contaminants than combustion technologies, most commonly applied in thermal processing of biomass today. And yet, at present only approximately 0.5% (373 MW_{th}) of synthesis gas production worldwide is based on biomass and waste. This results basically from low energy density of biomass, local shortages in biomass supplies and operating problems inherently combined with biomass utilization in gasifiers designed for fossil fuel processing. The process of co-gasification of coal and biowaste offers solutions to some of the above mentioned problems. It gives the benefits of stable supplies of a primary energy resource – coal and utilization of a zero-emission, waste material (i.e. agriculture waste, sewage sludge, etc.) with higher process efficiency and lower environmental impact than in biomass and coal gasification, respectively.

The study presented concerns co-gasification of coal and biomass to hydrogen-rich gas, as a prospective clean energy carrier. The experiments were performed with an application of a laboratory scale fixed-bed reactor installation of the Laboratory of Advanced Energy Technologies, Department of Energy Saving and Air Protection, Central Mining Institute. Gasification product gas was analyzed with the two-channel gas chromatograph Agilent 3000A. A column PLOT U (8m x 0.32mm), with helium as a carrier gas, was used for separation of CO_2 and C_2-C_5, whereas a backflush injector module with a pre-column PLOT U (3 m x 0.32 mm) and an analytical column MS5A PLOT (10 m x 0.32 mm), with argon as a carrier gas, was used for separation of H_2, N_2, CO and CH_4. The temperature of an inlet, injector and the columns was 60^{o}C. The injection time was $50 \cdot 10^{-3}$ s for both columns and the run time and post run time were 150 s and 10 s for PLOT U and MS5A PLOT, respectively, whereas the backflush time for column PLOT U was 12 s.

5.

Optimization of sample preparation workflow by use of an automated platform – acceleration of clinical proteomic studies

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Clinical proteomics posses a huge potential in understanding pathological processes in human body by identifying the specific proteins that are altered only during the disease. These analyses rely on the extraction of proteins from clinical samples and its subsequent enzymatic digestion in peptides prior to mass spectrometric analysis. This process is mostly hand-made and time consuming, making parallel processing of clinical samples prone to errors and thus compromising the reproducibility needed for confident comparative analyses.

Here, the new Agilent's Bravo Automated Liquid Handling Platform (AssayMAP Bravo) is introduced. Bravo is intended for high-throughput sample preparation proteomic workflows. This allows the analysis of multiple samples in parallel and reduces the experiment time considerably which is the intention of nowadays clinical research.

Herein, the optimization of digestion protocol owing to trypsin-containing cartridges and clean-up workflow by using C18 solid-phase extraction/desalting cartridges was performed for test samples. The digestion parameters (e.g. protein concentration, buffer composition, temperature, washing cycles and flow rates) were adjusted by using both bovine serum albumin and a six protein mixture sample. Resulting peptides were analyzed by LC-MS/MS employing a LTQ Orbitrap Velos mass spectrometer.

Using the AssayMAP Bravo system, the time for protein digestion completion was significantly decreased to 40 minutes when compared to the standard 16 hours in-solution digestion. Sequence coverage of test samples ranged from 14% for lysozyme to 65% for myoglobin which is similar to those obtained by standard procedures.

Based on the above optimized protocol, further processing of archival clinical tumor samples will be carried out. In this case, protein extraction from formaldehyde fixed-paraffin embedded tissues will be carried out following a previously published protocol, using 6M guanidine hydrochloride.

Presented, automated platform evaluated here will contribute to establishing robust and sensitive proteomic strategies that enable high-throughput analyses in clinical environments, especially in the field of cancer.

6.

THIN-LAYER CHROMATOGRAPHY - BIOASSAYS

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Bioassays (biological activity tests) are based on a measurement of an effect emerging in a given biological system as a result of biological action of the substances under investigation. They are often hyphenated with chromatographic methods, preferably with thin layer chromatography (TLC), which enables separation of many samples in the same run and, what is very important, evaporation of a mobile phase. The situation is ideal when TLC-bioassay are followed by spectroscopic methods giving full information about targeted analytes [1]. Thin-layer chromatography–direct bioautography (TLC-DB) usually gives information on antimicrobial properties of separated compounds [2]. The developed and dried HP(TLC) plate is immersed in a suspension of bacteria in a nutrient broth, incubated and sprayed with a reagent (usually tetrazolium salt MTT). Around spots of antibacterials, inhibition zones are formed as pale areas on a purple background. The information about antimicrobial properties of analyzed substances can be complemented with other bioassays as antioxidant activity, enzymatic or estrogenic tests. TLC-DB can be treated as a screening or even semi-quantitative method. The relationship between the diameter or area of inhibition zone plotted against the logarithm of the concentration of the antimicrobial applied is linear or exponential depending on the range of concentrations. Because of the lack of commercially available TLC-DB tests, two direct bioautography assays were developed in our laboratory to be used after TLC separation: one based on Gram (-) bacteria, *Escherichia coli*, and another one based on Gram (+) bacteria, Bacillus *subtilis* [3,4]. These tests were used with success to determine antibiotics at their MRL (maximum residue level) in milk as well as to establish antimicrobial properties of plant extracts and pharmaceuticals.

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7.

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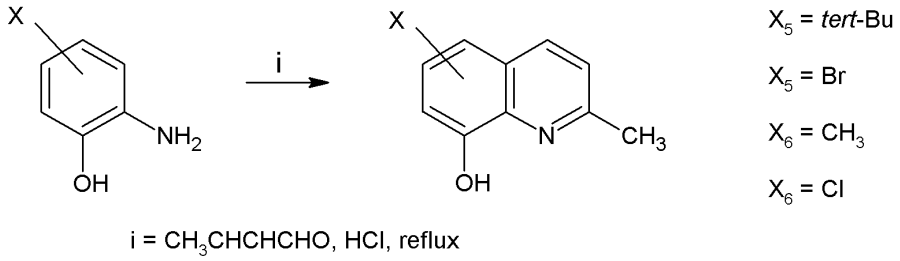
Quinoline was first isolated by F.F. Runge in 1834 during extraction of coal tar [1]. They are widely seen in a number of natural products and have attracted considerable attention due to their biological activities such as anti-malarial, anti-fungal, anti-bacterial, anti-asthmatic, anti-hypertensive, anti-inflammatory, and trichomonal [2, 3]. They received many synthetic protocols and applications both in academia and industry.

Many of them are ligands in coordination chemistry as a N and/or O atom donors for chelating with metals, such as ruthenium metalloantimalarials and are used for the identification of metals. Additionally quinolines have been used in components for molecular electronic devices such as OLED displays (Organic Light-Emitting Diodes) [4].

We reported GC/MS spectra of new aforementioned compounds. Our studies were carried out to compare selected quinolines [5, 6]. On our poster presentation, we will present the GC chromatograms and MS spectra with some discussion.



Scheme: Synthesis of derivatives 8-hydroxy-2-methylquinoline.

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8.

Solid Phase Microextraction as an efficient method for determination of organochlorine pesticides in soil samples

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One of the major soil contaminants are organochlorine pesticides (OCPs), which could cause serious problems for crops, soil organisms and humans. They were widely used worldwide in last century and large amounts of these OCPs were piled up in various storage facilities which nowaday are more or less damage. Today OCPs are banned according to the Stockholm Convention due to their very persistent and bioaccumulating nature.

Recent trends in samples preparation have focused on a development of simpler, faster, more reliable and cost-efficient methods by reducing analysis time and solvent consumption. Solid phase microextraction (SPME) is a technique which combines extraction and concentration processes into one step without using solvent. SPME is a simple, selective and efficient method, based on the redistribution of analytes between microextraction fiber and sample matrix i.e. on the selective sorption of target analytes in the active layer of the fiber and direct thermal desorption in the chromatograph injector (GC).

The aim of the present study is to investigate the applicability of SPME to the determination of organochlorine pesticide in soil samples. The variables involves fiber selection, temperature effect and absorption time. The fibre used (Supelco) were 100 μm and 7 μm polydimethylsiloxane (PDMS). The soil were air dried and sieved (2 mm) before using. The analyses carried out on a gas chromatograph (Agilent 7890A) equipped with electron capture detector (ECD) and headspace automatic injector (Agilent 1888), using an HP-5MS UI (30 m × 0,32 mm × 0,25 μm) capillary column.

The proposed method can be employed in the field for quick turnaround methods. This method is convenient, and reliable for the purity control soil samples. The results obtained confirm that the SPME is high precision and accurate it is also effective in formal quantitative analyses.

9.

5,10,15,20-Tetra(4-hydroxyphenyl)porphyrin as a surrogate for the recovery study of porphyrins in Parma ham

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Porphyrins are compounds which are naturally occurring in prosthetic groups of eukaryotic cells such as hemoglobins, myoglobins and cytochromes. All compounds which belong to this group contain porphin, an organic compound consisting of four pyrrole rings joined together by four methine (=CH—) groups to form a larger macrocycle ring[1]. Due to that, all these molecules are flat, stable, strongly coloured, and prompt to form complexes with metal ions. Porphyrins absorb light and have characteristic absorption spectra both in the visible and ultraviolet wavelength range[2]. In meat tissue, porphyrins play an important role in metabolism of living organisms and can also be found in intermediates of the heme synthesis. Protoporphyrin IX plays a specific role among all tetrapyrroles, as it is a kind of a template for a wide variety of naturally occurring compounds, e.g., for the investigated Zn-protoporphyrin IX and hemin. All these compounds affect the colour properties of meat, and moreover, Zn-protoporphyrin IX contributes to the formation of a characteristic stable red colour of Parma ham[3].

In this study a high-performance liquid chromatography (HPLC) method was developed for the determination and quantification of three porphyrins, i.e., protoporphyrin IX, Zn-protoporphyrin IX, and hemin in Parma ham. Because all compounds are naturally present in meat, no appropriate blank material is available for the recovery study. Therefore, the in-house synthesized porphyrin 5,10,15,20-tetra(4-hydroxyphenyl)porphyrin, which is not present in meat, was used as a surrogate in the recovery study.

Prior to HPLC analyses, the porphyrins of interest were extracted from Parma ham samples according the method of Wakamatsu[3], with some minor modifications. High-performance liquid chromatographic analysis was performed with use of the C18 type stationary phase, in the isocratic mode with use of the following mobile phase: A + B, 9:1 (*v*/*v*). A: MeOH + DCM, 9:1 (*v*/*v*); B: H_2O + CH_3COOH, 97:3 (*v*/*v*). A mobile phase flow rate of 0.8 mL min^{-1} was used. The retention times (t_R) for hemin, 5,10,15,20-tetra(4-hydroxyphenyl)porphyrin, Zn-protoporphyrin IX, and protoporphyrin IX were 2.6, 2.8, 5.5 and 8.2 min, respectively. All analytes were detected by diode array detector (DAD) at a wavelength (λ) of 414 nm, while the surrogate analyte was detected at λ = 444 nm to avoid interference with hemin.

The recovery study with the metal-free surrogate, 5,10,15,20-tetra(4-hydroxyphenyl)porphyrin showed practically total recovery (above 94%) at all spiked levels (10.0, 20.0 and 30.0 μg g^{-1}). As a consequence the standard calibration curves of hemin, Zn-protoporphyrin IX, and protoporphyrin IX can be used for the quantification of these target analytes in meat samples of Parma ham.

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10.

Determination of trans-resveratrol in wine and the extracts from grape vine (*Vitis vinifera*) by means of TLC

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Extracts from grape vine (*Vitis vinifera*) are widely used in pharmaceutical and cosmetic industry. They characterize with anti-oxidative, anti-inflammatory, anti-cancer, detoxifying, antibacterial, antifungal and other properties. In fact, the trans-resveratrol isomer (trans-3,5,4'-trihydroxystilbene) and the stilbene derivatives which are present in vine, exert a wide range of therapeutic activities. Clinical studies have shown that trans-resveratrol can lower lipid level in human blood serum and is effective in anti-cancer prophylaxis. It has been experimentally proved that adding trans-resveratrol to the diet of yeasts, nematodes, fish and mice results in prolongation of medium life expectancy for these organisms[1].

Nowadays, application of wine and the grape vine extracts in cosmetics and cosmetology attracts a lot of interest. In the anti-ageing cosmetic creams, extracts from the grape seeds, grape skin, vine shots, vine leaves, and even wine itself is applied. In cosmetology, therapeutic rites like "wine therapy" or "wine SPA" are becoming increasingly more popular, with wine applied in place of water.

The contents of the phenolics (resveratrol included) are not constant, but they change depending on the part of the grape vine which has been extracted. Also the wines characterize with different contents of resveratrol, depending on their origin, colour, or sweetness (the taste). In this study, samples of wine and the aqueous or aqueous ethanolic extracts from the grape vine underwent the procedure of solid phase extraction (SPE). Then the trapped polyphenols were eluted from the adsorbent with ethyl acetate. Further, extracts containing trans-resveratrol were analyzed by means of high-performance liquid chromatography (HPLC) and thin-layer chromatography (TLC). Quantification of resveratrol was performed with use of an inner standard, IS [2,3,4].

Trans-resveratrol was quantified In the French red and white dry wines, and in the home-made fruit wines (made of white and red grapes, pomegranates, and raisins). Moreover, resveratrol was quantified in the extracts from wine, grape seeds and grape skin, which are used for manufacturing of cosmetics.

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11.

DETERMINATION OF HEXACHLOROCYCLOHEXANE (HCH) ISOMERS IN WATER SAMPLES BY GAS CHROMATOGRAPHY

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An extensive use of pesticides to improve agricultural productivity played an important role in the last century. These compounds have been applied for decades in preventing, repelling or mitigating the effects of pests. Although most of organochlorine pesticides (OCPs) including hexachlorocyclohexane (HCH) isomers, have been banned in many countries because of mutagenic and carcinogenic effects [1,2], they and their metabolites are still present in the environment, especially in soil, water and sediment, owing to their persistence and lipophilic properties [3,4]. Most of these organic compounds have a tendency to bioaccumulate and present low rates of biodegradation and consequently they could represent a risk to environmental and human health. The European Environmental Agency (Directive 76/464/EEC and its daughter Directives) has drawn up a list of pollutants for priority monitoring, which need to be analysed with sensitive instrumental methods. Therefore, a rapid, convenient, accurate, and sensitive method is required to monitor pesticide residue concentrations in water, soil sediments and biotic samples.

Chromatographic techniques have been considered as the best methods to determine OCPs in varied sample matrices. At present, more than 60% of registered pesticides and/or their metabolites can be analyzed by using gas chromatography (GC) [5]. In our research, as determination technique we also used GC equipped with different detectors. Chromatographic analysis usually follows the tedious sample preparation to extract the pollutants from environmental matrices (i.e. soil, water, sediment, plant material). For the isolation of target compounds from matrices various extraction and clean-up procedures can be proposed. In our studies we used traditional method as liquid–liquid extraction (LLE). This conventional extraction method gave us efficient and precise results.

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12.

Self-assembled peptide nanofibers (L-proline and L-phenylalanine)

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In our earlier studies, we have proved that the low molecular weight chiral compounds (e.g., amino acids), can undergo spontaneous oscillatory condensation. This kind of reactions is characteristic of single compounds, or the mixtures of compounds in aqueous or non-aqueous solvents. In our previous research on the pair of amino acids (L-Pro– L-Phe), it was shown that the investigated amino acids characterize with an oscillatory instability, which consists in spontaneous oscillatory oligopeptidization, i.e., in sequential formation and decay of homo- and heterooligopeptides as the products of spontaneous peptidization process [1].

In this study on the same mixture of amino acids (L-Pro and L-Phe), it was found out that the amino acids not only undergo a spontaneous peptidization reaction, but also self-assemble to form nanostructures. To prove that the obtained structures have nanostructure or microstructure characteristics, we used LC-MS, scanning electron microscope (SEM), optical microscope, and IR spectroscopy.

The obtained results confirm the presence of both, nano- and microfiber structures in the solution. In that way, it was additionally confirmed that amino acids in 70% acetonitrile can undergo oscillatory peptidization, forming particles of considerable molar masses, and have an ability to self assemble in nanostructures without an addition of any catalyst.

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13.

Anti-oxidative properties of different thyme species checked by means of different analytical techniques involving reduction of DPPH radical

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Botanical raw materials are rich sources of bioactive substances, which exert positive effects on human health. Scientific investigations reveal a significant preventive influence of phytochemicals as protection against the civilization health problems. Nowadays, pharmaceutical and cosmetic companies turn toward phytochemicals with growing interest and on the basis thereof produce multi-active preparations. Currently, anti-oxidants attract their greatest attention and polyphenols belong to this particular group.[1-3]

Phenolic acids belong to the herbal secondary metabolites, which characterize with diverse structures and properties. They exert a number of biological activities such, as anti-oxidant, anti-allergic, anti-inflammatory, or anti-bacterial. Phenolic acids include in their structures an aromatic ring, which is connected with one or more hydroxyl groups. Number and placement of these groups determine anti-oxidant performance of phenolic acids. Phenolics of plant origin include phenolic acids, flavonoids, lignins, stilbenes, etc.[4-6]

Anti-oxidants are the compounds able to neutralize the oxygen and nitrogen free radicals present in a given system. Participating in numerous metabolic processes, they exert positive effect on various different physiological functions. Owing to that, anti-oxidants exert prophylactic, or even curative effect and they mainly appear in edible parts of the plants.[7]

Common thyme (*Thymus vulgaris* L.) originates from the Mediterranean zone, with characteristic morphology of leaves and purple flowers. It is widely utilized in medicine, cosmetics, and cuisine. Common thyme contains up to 2.5% essential oils, up to 3% tannins, moreover flavonoids, phenolic acids, triterpenes, aluminium salts and carbohydrates.[8]

Phytochemical analysis was performed for the eighteen thyme (Thymus L.) species originating from Botanical Garden of the Maria Curie-Skłodowska University in Lublin. Specially derived thyme extracts were analyzed with use of thin-layer chromatography (TLC), electron paramagnetic resonance spectroscopy (EPR), and UV-Vis spectrophotometry. In order to assess anti-oxidative properties, the characteristic reagent DPPH (2,2-diphenyl-1-picrylhydrazyl) was used. As a result, a differentiated total anti-oxidant potential of different thyme species was shown.

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14.

Chromatographic investigation of spontaneous reactions of sulphur amino acids

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Oscillatory reactions are among the most fascinating ones. They are the non-equilibrium processes in which intermediates undergo periodic changes. Oscillatory reactions are commonly encountered in chemical and physical, biotic and abiotic, systems. *L*-Methionine and *L*-cysteine are essential for normal development of the organisms' functions. Firstly, these compounds play a significant role due to the presence of the sulphur atom in a side chain. *L*-Met is needed for translation of proteins and it is an important reagent in the synthesis of taurine and glutathione. The other amino acid (*L*-Cys) exerts an influence on cardiovascular system. *L*-Met and *L*-Cys possess therapeutic properties as well, so they can be used as components of numerous pharmaceuticals and cosmetics.

Low molecular weight chiral compounds (like profen drugs, amino acids and hydroxyacids) can undergo spontaneous oscillatory chiral inversion and oscillatory peptidization [1]. Present research contributes to the search for the new compounds which can undergo spontaneous chiral inversion and peptidization. The main tool for studying this phenomenon was high performance liquid chromatography with diode array detection (HPLC-DAD), evaporative light scattering detector (HPLC-ELSD) or liquid chromatography with mass spectrometric detection (LC-MS).

The obtained results demonstrate the oscillatory instability of *L*-Met and *L*-Cys, which consists in spontaneous oscillatory chiral inversion and oligopeptidization.

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